Helium and fission gas behaviour in magnesium aluminate spinel and zirconia for actinide transmutation
The research described in this thesis was performed in the department of Materials Science, European Commission, Joint Research Centre, Institute for Transuranium Elements, Postfach 2340, 76125 Karlsruhe, Germany and in the department of Defects in Materials of the Interfacultair Reactor Instituut, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands.

The author would like to thank the European Commission for supporting this work with a Marie Curie fellowship.
Helium and fission gas behaviour
in magnesium aluminate spinel and zirconia
for actinide transmutation

PROEFSCHRIFT

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus prof. dr. ir. J.T. Fokkema,
voorzitter van het College voor Promoties,
in het openbaar te verdedigen

op dinsdag 9 december 2003 om 13.00 uur

door

Patricia Maria Gerardina DAMEN

natuurkundig ingenieur
geboren te Breda
Dit proefschrift is goedgekeurd door de promotor:
Prof. dr. A. van Veen

Samenstelling promotiecommissie:
Rector Magnificus voorzitter
Prof. dr. A. van Veen Rijksuniversiteit Groningen, promotor
Prof. dr. ir. H. van Dam Technische Universiteit Delft
Prof. dr. ir. A.H.M. Verkooijen Technische Universiteit Delft
Prof. dr. T. Hibma Rijksuniversiteit Groningen
Prof. dr. M. Leroy Université Louis Pasteur, Strasbourg
Dr. C. Ronchi Institut für Transurane, Karlsruhe
Dr. R.J.M. Konings Institut für Transurane, Karlsruhe

Published and distributed by: DUP Science
DUP Science is an imprint of
Delft University Press
P.O. Box 98
2600 MG Delft
The Netherlands
Telephone: +31 15 27 85 678
Fax: +31 15 27 85 706
E-mail: info@Library.TUDelft.nl

ISBN 90-407-2446-6

Keywords: actinide transmutation, fission gases, helium

Copyright ©2003 by P.M.G. Damen

All rights reserved. No part of the material protected by this copyright notice may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying, recording or by any information storage and retrieval system, without permission from the publisher: Delft University Press.

Printed in the Netherlands
## Contents

1 Introduction .......................... 1
   1.1 Strategies and scenarios for radioactive waste management ............... 2
   1.2 Transmutation and inert matrix materials .................................. 4
   1.3 Radiation damage in solids .................................................. 5
   1.4 Objectives of the thesis ...................................................... 8
   1.5 Outline of the thesis .......................................................... 9

2 Experimental set-up ..................... 11
   2.1 Knudsen cell ................................................................. 11
      2.1.1 The Knudsen cell set-up ............................................. 12
      2.1.2 Temperature measurements with a thermocouple ..................... 14
      2.1.3 Calibration of temperature ramps .................................... 16
      2.1.4 Calibration of the amount of helium .................................. 17
   2.2 Thermal helium desorption .................................................. 21
      2.2.1 Apparatus and helium calibration system ........................... 21
      2.2.2 Calibration of temperature ............................................ 23
      2.2.3 Modelling of temperature delay ....................................... 25
   2.3 Neutron depth profiling ..................................................... 28
   2.4 Positron beam analysis ...................................................... 29
      2.4.1 S-W mapping and typical values for S and W in a ceramic .......... 30
   2.5 Microscopical investigation methods ...................................... 32
      2.5.1 Scanning electron microscopy ......................................... 32
      2.5.2 Transmission electron microscopy .................................... 32

3 Theoretical background ................. 35
   3.1 Definition and structure of ceramics ...................................... 35
      3.1.1 Microstructure of spinel MgAl$_2$O$_4$ ................................. 36
      3.1.2 Microstructure of fully stabilized zirconia .......................... 37
   3.2 Defects in ceramics ........................................................... 38
      3.2.1 Lattice defects in magnesium aluminate spinel ...................... 39
      3.2.2 Lattice defects in fully stabilized zirconia ........................ 39
      3.2.3 Location of oxygen vacancies in fully stabilized zirconia ....... 40
   3.3 Simulation of $\alpha$-decay and ion implantation effects ................. 42
      3.3.1 An introduction to $\alpha$-decay ....................................... 42
      3.3.2 Simulation of damage caused by $\alpha$-decay ......................... 43
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3.3</td>
<td>An introduction to the theory of ion implantation</td>
<td>45</td>
</tr>
<tr>
<td>3.3.4</td>
<td>Damage introduced by ion implantation</td>
<td>47</td>
</tr>
<tr>
<td>3.4</td>
<td>Defect behaviour under thermal annealing</td>
<td>48</td>
</tr>
<tr>
<td>3.4.1</td>
<td>Diffusion of defects</td>
<td>48</td>
</tr>
<tr>
<td>3.4.2</td>
<td>Diffusion of matrix components</td>
<td>49</td>
</tr>
<tr>
<td>3.4.3</td>
<td>Recrystallisation of an amorphous specimen</td>
<td>50</td>
</tr>
<tr>
<td>3.5</td>
<td>Gas behaviour in ceramics under thermal annealing</td>
<td>51</td>
</tr>
<tr>
<td>3.5.1</td>
<td>Diffusion in single crystals</td>
<td>51</td>
</tr>
<tr>
<td>3.5.2</td>
<td>Grain boundary effects</td>
<td>53</td>
</tr>
<tr>
<td>3.5.3</td>
<td>Bubbles and bubble formation</td>
<td>55</td>
</tr>
<tr>
<td>3.5.4</td>
<td>Coarsening: migration, coalescence and Ostwald ripening</td>
<td>57</td>
</tr>
<tr>
<td>3.5.5</td>
<td>Helium release from bubbles</td>
<td>57</td>
</tr>
<tr>
<td>3.6</td>
<td>Analysis of helium desorption spectra</td>
<td>58</td>
</tr>
<tr>
<td>3.6.1</td>
<td>Ramp annealing and stepwise annealing</td>
<td>59</td>
</tr>
<tr>
<td>3.6.2</td>
<td>Partial annealing</td>
<td>59</td>
</tr>
<tr>
<td>4</td>
<td>Implantation experiments performed on spinel</td>
<td>63</td>
</tr>
<tr>
<td>4.1</td>
<td>Experience with regard to irradiation damage in spinel, based on former research</td>
<td>63</td>
</tr>
<tr>
<td>4.1.1</td>
<td>Fission product damage</td>
<td>63</td>
</tr>
<tr>
<td>4.1.2</td>
<td>$\alpha$-Decay damage</td>
<td>64</td>
</tr>
<tr>
<td>4.1.3</td>
<td>Helium release mechanisms in spinel</td>
<td>65</td>
</tr>
<tr>
<td>4.1.4</td>
<td>Conclusions of former research</td>
<td>66</td>
</tr>
<tr>
<td>4.2</td>
<td>Helium release experiments on implanted polycrystalline spinel</td>
<td>67</td>
</tr>
<tr>
<td>4.2.1</td>
<td>Sample preparation and implantation characteristics</td>
<td>67</td>
</tr>
<tr>
<td>4.2.2</td>
<td>Experimental results</td>
<td>68</td>
</tr>
<tr>
<td>4.2.3</td>
<td>Discussion</td>
<td>68</td>
</tr>
<tr>
<td>4.2.4</td>
<td>Conclusion</td>
<td>70</td>
</tr>
<tr>
<td>4.3</td>
<td>Helium in amorphous spinel</td>
<td>70</td>
</tr>
<tr>
<td>4.3.1</td>
<td>Introduction</td>
<td>70</td>
</tr>
<tr>
<td>4.3.2</td>
<td>Experimental procedure</td>
<td>71</td>
</tr>
<tr>
<td>4.3.3</td>
<td>Results and discussion</td>
<td>75</td>
</tr>
<tr>
<td>4.3.4</td>
<td>Comparison with helium and xenon behaviour in crystalline spinel</td>
<td>83</td>
</tr>
<tr>
<td>4.3.5</td>
<td>Summary, conclusions and final remarks</td>
<td>85</td>
</tr>
<tr>
<td>5</td>
<td>Helium in reactor irradiated spinel</td>
<td>87</td>
</tr>
<tr>
<td>5.1</td>
<td>The EFTTRA experiments, an introduction</td>
<td>87</td>
</tr>
<tr>
<td>5.2</td>
<td>Destructive analysis</td>
<td>95</td>
</tr>
<tr>
<td>5.2.1</td>
<td>Results of destructive analysis presented in the literature</td>
<td>95</td>
</tr>
<tr>
<td>5.2.2</td>
<td>Destructive analysis performed at ITU</td>
<td>96</td>
</tr>
<tr>
<td>5.2.3</td>
<td>Stability of spinel under thermal annealing</td>
<td>96</td>
</tr>
<tr>
<td>5.2.4</td>
<td>Results of Knudsen cell experiments</td>
<td>98</td>
</tr>
<tr>
<td>5.2.5</td>
<td>Microstructural investigations</td>
<td>102</td>
</tr>
</tbody>
</table>
CONTENTS  

5.2.6 Helium and xenon release from the EFTTRA-T4 specimen . 107
5.3 Summary and conclusions .......................... 112

6 Helium in Zirconia ........................................ 115
6.1 Yttria-stabilized zirconia ............................ 115
  6.1.1 Properties of the zirconia samples used ............ 115
  6.1.2 Helium mobility in fully stabilized zirconia ......... 116
6.2 Investigations on specimens implanted with 30 keV helium-ions .... 117
  6.2.1 Sample specification ............................ 117
  6.2.2 Thermal helium desorption measurements ............ 118
  6.2.3 Neutron depth profiling and positron beam analysis .... 124
  6.2.4 Microscopical investigations ..................... 134
  6.2.5 Discussion .................................. 135
  6.2.6 Summary and conclusions ..................... 136
6.3 200 keV and 1 MeV helium investigations .................. 137
  6.3.1 TRIM calculations ............................ 137
  6.3.2 Knudsen cell measurements .................. 139
  6.3.3 Thermal helium desorption measurements ............ 144
  6.3.4 Neutron depth profiling ........................ 145
  6.3.5 Discussion .................................. 148
6.4 Conclusions and recommendations ..................... 149
  6.4.1 Temperature effects .......................... 150
  6.4.2 Discussion ................................ 151

7 Results, conclusions, predictions and final remarks .......... 153
  7.1 Results on spinel .................................. 153
    7.1.1 Recommendations and conclusions concerning spinel .. 154
  7.2 Results on zirconia ................................ 155
    7.2.1 Recommendations and conclusions concerning zirconia .. 155

Bibliography ................................................. 157

A Conversion of the measured NDP data into a depth profile .... 165

Nomenclature ............................................... 171

Summary ...................................................... 177

Samenvatting ................................................ 181

Acknowledgements .......................................... 185

Curriculum Vitae ........................................... 189
Chapter 1

Introduction

The International Energy Agency forecasts that the demand for total world energy will rise by two-thirds between now and 2030 and that energy-related carbon emissions will rise by 70% over the same period [1]. If this increasing demand is to be met and at the same time the CO₂-emission is to be limited, the use of nuclear power seems inevitable. It has the advantage of being a very clean source of energy from the point of view of CO₂-emission, but the public opinion towards nuclear power remains nonetheless distrustful. On the one hand there is the fear of accidents, on the other hand there is the problem of the nuclear waste. The former objection can be countered by improving the safety of the nuclear power plants by so-called inherent safety design. In such third-generation reactor designs passive safety measures are used, i.e. measures that rely fully on natural processes to prevent radiation release incidents and do not require human interaction. It is envisaged that in the near future these reactor types will come into operation on an industrial scale. The latter objection of the public is more difficult to counter: although the amount of nuclear waste in terms of mass or volume produced per year is low compared to that of coal or oil, part of the waste is highly radioactive and remains radiotoxic for millions of years. The concept of safe storage over such a period is difficult to grasp and worrisome for many. As the decay time of a nuclide itself cannot be altered, the present solutions to the waste problem therefore concentrate on transmuting long-lived radioactive nuclides to short-lived ones in order to shorten the waste storage period and thereby increasing the safety of storage. The present thesis will present a study which intends to improve the transmutation cycle for radioactive waste. This cycle will be explained in the next section.
1.1 Strategies and scenarios for radioactive waste management

Currently, storage in a geological repository of either conditioned spent fuel assem-
blies or vitrified high-level waste (HLW), arising from reprocessing of spent fuel to
recover uranium and plutonium, is the most common strategy for the management of
nuclear waste from electric power generation. Because the waste remains highly active
for many years, the repositories must be equipped with man-made isolation to prevent
radionuclides dispersing into the ground water and the environment.

It would therefore be a major advance in nuclear waste management if the radioac-
tive half-life of the waste could be reduced from millions to thousands of years or even
less. This objective can be met by partitioning (separating) the long-lived radionuclides
from the used fuel elements. The short-lived radioactive nuclides, which form the bulk
of the nuclear waste, are stored in the afore-mentioned repository, while the long-lived
nuclides are fed back into the reactor in order to convert them into short-lived nuclides
by fission or transmutation. The long-lived nuclides in the waste are mainly isotopes
of uranium, plutonium and heavier elements (so-called minor actinides) formed dur-
ing reactor operation by neutron capture and possible subsequent decay. Some of the
fission products (like $^{99}\text{Tc}$, $^{126}\text{Sn}$, $^{135}\text{Cs}$ and $^{129}\text{I}$) also have very long half-lives.

![Figure 1.1: An overview of a possible nuclear fuel cycle.](image)

In Figure 1.1 a schematic overview is given of the nuclear fuel cycle in which the
long-lived radioactive nuclides are fed back into the reactor.
- At the beginning of the cycle, after mining the uranium ore, uranium is extracted and if necessary enriched (increased in $^{235}$U concentration) in special plants. The depleted uranium is stored or used for other purposes.
- The next step in the cycle is the fabrication of the fuel, which normally consists of the enriched uranium in the form of an oxide, UO$_2$. The fuel, in the form of fuel elements, is then loaded into a conventional reactor, e.g. a Light Water Reactor (LWR). During reactor operation this fuel element will suffer damage due to fission of part of the fuel, but also from $\alpha$-decay and neutrons and to a lesser extent from $\beta$- and $\gamma$-radiation. Fission products will also cause damage in the material. After discharge from the reactor core when the fuel is spent, the material is stored in a temporary repository to cool down. During this storage, more damage in the material will accumulate mostly due to $\alpha$-radiation and neutrons from spontaneous fission and to a lesser extent due to $\beta$- and $\gamma$-radiation.
- After the decay of the very short-lived fission products, the fuel is transported to a reprocessing plant or directly to a final repository (as e.g. planned in Sweden). In reprocessing plants such as Sellafield and La Hague, uranium and plutonium are isolated and re-used to fabricate new fuel, at present either in the form of the original UO$_2$ fuel or in the form of MOX fuels. MOX is an acronym for Mixed Oxides, indicating a fuel consisting of a mixture of UO$_2$ and PuO$_2$.
- As a part of the partitioning, the reprocessing step can also involve the partitioning of the Minor Actinides (MA), such as americium, curium or neptunium, and Long Lived Fission Products (LLFP) from the spent fuel. The minor actinides contain isotopes that by fission or neutron capture processes can be transmuted into shorter-lived nuclides. Some of the LLFP can be de-stabilized by neutron capture and decay in a shorter time. Therefore, targets are fabricated in which the MA and LLFP are embedded in a material which is inert under neutron irradiation, a so-called transmutation matrix. The MA and LLFP can then either be fissioned or transmuted in an ordinary LWR, in an Accelerator Driven System (ADS) or in a Fast Breeder Reactor (FBR). After the transmutation step, the process of partitioning and transmutation can be repeated in order to achieve a higher transmutation yield.

Another option, which is currently more often used, as the target production and its inclusion into the fuel cycle can be complicated, is to pack the MA and LLFP in a special material, a so-called storage matrix in analogy to the fuel matrix, and directly store it in a special repository for radioactive waste. Although the quantity and volume of these MA and LLFP are small (for a 1 GW$_e$ LWR per year 1180 kg and 3 to 4 m$^3$ in vitrified state), they remain radioactive for millions of years, which imposes high demands on the quality of packing and storage. Furthermore, these actinides are mostly very toxic, from the chemical as well as from the radioactive point of view. The storage matrix should be stable with respect to the radioactive decay of the isotopes (e.g. $\alpha$-, $\beta$- and $\gamma$-radiation), but also with respect to processes such as spontaneous fission where neutrons are emitted. In addition, a storage matrix should be stable with respect to the ingress of ground water in case this infiltrates the repository.
• The Short Lived Fission Products (SLFP) are stored directly in a repository. In France, for example, SLFP with half-lives of less than 30 years are stored in repositories of this type for 300 years. Like the MA and LLFP, the SLFP are embedded in a storage matrix for this final storage.
• Finally, the radioactive waste will be transferred from the repository to a geological depository, where the most important damage caused to the storage matrix material originates from the $\alpha$-decay from long living actinides.

It becomes already apparent from the general analysis of the fuel cycle that a crucial step in fuel production, transmutation and storage will be the choice of a suitable inert matrix material in order to contain the radioactive nuclides. This could be one and the same inert matrix material for all three applications, but normally it will be optimized according to its purpose.

The present thesis will focus on the inert matrix material used for transmutation. The following section will discuss in more detail the considerations leading to a suitable transmutation matrix material.

1.2 Transmutation and inert matrix materials

The enriched uranium fuels currently used consist mainly of $^{238}\text{U}$. This uranium isotope is not fissile but it reacts with thermal neutrons and breeds plutonium according to

$$\text{^{238}U} + \text{neutron} \rightarrow \text{^{239}U} \xrightarrow{\beta^-} \text{^{239}Np} \xrightarrow{\beta^-} \text{^{239}Pu}.$$  \hfill (1.1)

The two $\beta^-$-decay steps have a very short half-life of 23 minutes and 2.4 days, respectively. In this case, the initial isotope is not fissioned but transmuted by neutron capture into another, fissile, isotope. In the case of a MA, like $^{241}\text{Am}$, the transmutation process looks as follows:

$$\text{^{241}Am} + \text{neutron} \rightarrow \text{^{242}Am} \xrightarrow{83\%} \text{^{242}Cm} \xrightarrow{\alpha} \text{^{238}Pu},$$  \hfill (1.2)

which is a typical transmutation process.

The inert matrix material, which contains the affected nuclides, should fulfill the following requirements:
• With regard to the radiation stability, the matrix should:
  - have a low total neutron capture cross-section,
  - not transmute into a material with a large neutron capture cross-section, or into a material which is radioactive with a long half-life, if a neutron is captured. Preferentially, the matrix atoms should not be transmuted into radioactive isotopes as the decay of these isotopes damages the matrix,
  - be stable against $\alpha$, $\beta$- and $\gamma$-radiation [2] and nuclear fission fragments,
• be stable under neutron irradiation,
• be able to accommodate fission products and large quantities of fission gas and helium without cracking or becoming brittle.

• With regard to metallurgical properties, the matrix should:
  - have a sufficiently high melting point,
  - have a sufficiently high thermal conductivity,
  - not undergo any phase changes during irradiation,
  - not dissociate at higher temperatures,
  - not react with the cladding material,
  - be soluble in acid or molten salt in order to facilitate partitioning, in case a reprocessing scenario is selected,
  - have suitable elastic constants, hardness etc. to provide mechanical stability during irradiation,
  - have a sufficient plasticity to cope with swelling caused by fission gases.

1.3 Radiation damage in solids

As follows from the discussion of the fuel cycle of Figure 1.1, knowledge about the development of radiation damage in an inert matrix during transmutation and storage is very important.

A large number of radiation sources is present during the transmutation process. Damage could occur due to neutron interactions and fission products, amongst others. Furthermore, most of the fission products decay by emitting $\beta$- and/or $\gamma$-particles, while most actinides are $\alpha$-emitters. These energetic particles will lose their energy in the matrix material by collisions, which cause damage to the lattice by e.g. displacing matrix atoms. Table 1.1 is an overview of the most important sources of damage in a nuclear fuel. The table shows the typical energy for the particle (MeV) and its range in a spinel (MgAl$_2$O$_4$) matrix [3]. This matrix will be discussed in Chapters 4 and 5. In the table it can be seen that the fission products have a high mass and energy, the dissipation of which will cause a large number of defects in the material. Fission gases

<table>
<thead>
<tr>
<th></th>
<th>Energy (MeV)</th>
<th>Range ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light fission product$^b$</td>
<td>95</td>
<td>10</td>
</tr>
<tr>
<td>Heavy fission product$^c$</td>
<td>67</td>
<td>8.5</td>
</tr>
<tr>
<td>$\alpha$-Particle</td>
<td>6</td>
<td>20</td>
</tr>
<tr>
<td>Recoil atom from $\alpha$-decay</td>
<td>0.1</td>
<td>0.030</td>
</tr>
</tbody>
</table>

$^a$ projected ranges; $^b$ The calculations has been performed for $^{84}$Kr; $^c$ The calculation has been performed for $^{132}$Xe
products are only produced during reactor operation (neglecting spontaneous fission of actinides), and the quantity of fission products produced therefore depends on the burn-up (=measure of the fuel exploitation). The range travelled by the fission products in the material is limited due to their high stopping power; therefore the damage occurs in a zone close to the original position of the fissioned nuclide.

$\alpha$-Particles are produced in the transmutation matrices due to the decay of the actinides to be transmuted (e.g. $^{241}\text{Am}$) or due to the ones newly formed by neutron capture and subsequent decay (e.g. $^{242}\text{Cm}$ and $^{244}\text{Cm}$). $\alpha$-Decay is a continuous process in the matrix material, which occurs before, during and after irradiation!

The $\alpha$-particle will slow down by colliding with matrix atoms and thus causing damage to the matrix. After slowing down to energies far below 1 keV, electrons from the matrix fill the vacant electron levels of the $\alpha$-particle (helium-ion) and form a helium-atom. At very low energies the helium will be trapped in the matrix and occupy a site in the matrix or in a matrix defect, e.g. a bubble. When bubbles are formed, the pressure in the matrix will increase significantly. The range of the $\alpha$-particle is large compared to the range of fission products and especially of the recoil atoms, see Table 1.1.

Because the particles given in Table 1.1 have different energies and different ranges, the distance from the site of formation to the region where they cause damage is different. Thus, the size of the fissile kernels itself (also called inclusions) embedded in the inert matrix material becomes an important factor in determining the regions of damage in a material. To this end a distinction is made between a microdispersed and a macrodispersed fuel. A fuel is called microdispersed if the size of the fissile inclusions is less than 10 $\mu$m, and otherwise is called macrodispersed. Microdispersed fuels can be produced either by infiltration or by compression of a mixture of matrix grains and fissile grains, while macrodispersed fuels can be produced by compression only. The damage effects in microdispersed fuels will approach those in a solid solution, while the radiation effects in macrodispersed fuels will mainly occur in the inclusions themselves and in a thin matrix layer around the inclusion, predominantly due to neutron damage [5]. A schematic example of the range of damage due to a fissile inclusion in a micro- and a macrodispersed inert matrix is shown in Figure 1.2. In the microdispersed fuel, a very small fuel kernel (1) is damaged by fission products, neutrons, $\alpha$-particles and recoil atoms. A small matrix layer surrounding the particle (2) is damaged by fission products, neutrons, $\alpha$-particles and recoil atoms. The range of the recoil atoms from the $\alpha$-decay is so small that the recoil atoms come to rest in this layer. The second matrix zone (3) surrounding the fissile inclusion (1) is subject to damage by fission products, neutrons, and $\alpha$-particles. Because of their range, most fission products will come to rest in this layer. The third matrix layer (4) is subject to damage by $\alpha$-particles and neutrons. Finally, there is a part of the matrix (5) which is subject to neutrons only. In Figure 1.2 it can be clearly seen that in the case of a microdispersed fuel there is an overlap between the different damage zones. In practice, owing to the small size of the inclusions and their homogeneous distribution throughout the matrix, a homogeneous distribution of the damage in a microdispersed fuel can be expected.

In the case of a macrodispersed fuel, the damage will be limited to a thin matrix layer
Figure 1.2: Range of damage due to fissile inclusion in an inert matrix.

around the inclusion due to the large size of the inclusions. The inclusion (1) itself will be heavily damaged by neutrons, fission products, $\alpha$-particles and recoil atoms. There is a small matrix layer (2) surrounding the inclusion which receives a large irradiation dose of recoil atoms, fission products and $\alpha$-particles. Fission gases accumulate in this layer as well as in the second matrix layer (3), which is damaged by neutrons, $\alpha$-particles and fission products. Finally, a matrix zone (4) at a distance of about 20 $\mu$m from the particle is subject to neutron damage and damage caused by the end-of-range interactions of the $\alpha$-particle. The remainder of the matrix is not affected by fission fragments but only by high-energy neutrons. The location of the damage thus depends on the fabrication method of the fuel and the size of the inclusions.

Determining a suitable inert matrix material is complicated. Different applications (e.g. transmutation in an ADS system or in an LWR) impose different requirements on a material. As for the transmutation in LWRs, where the most advanced stage of development has been reached, two types of inert matrix materials are considered: CerCer and CerMet materials. In a CerCer matrix, the inclusions consist of an actinide bonded to a ceramic lattice. These ceramic beads are embedded in a ceramic matrix, which is not necessarily the same as that used for the inclusions. In order to improve the low thermal conductivity of the matrix while preserving the good resistance to radiation damage in the regions of high radiation exposure, a balance is struck with the CerMet matrix. This matrix still contains the fuel in a ceramic kernel, but embeds the kernels in metals in order to increase thermal conductivity. Increasing the conductivity is very important as it reduces peak temperatures in the fuel, thereby increasing fuel integrity and safety.

As seen in Figure 1.2, the inclusion phase and the matrix phase are both subject to damage caused by $\alpha$-decay. As stated before, the $\alpha$-particle will interact with the material, causing damage, and finally stay in the material as helium. Because reactor fuels are operated at high temperatures where fission product mobility in the matrix
increases, the effects of this gas in the material have to be studied in detail from the point of view of safety. In order to obtain information about the processes and mechanisms according to which the helium moves through the material, one must make sure to look only at the effects of $\alpha$-damage in a material. For this reason, i.e. to study solely the effects of helium, experiments using reactor irradiation are not very suitable as the state of the specimen after irradiation is affected by neutrons, fission and decay processes. The damage caused by these processes may have a large effect on the behaviour of helium under heat treatment as the material may e.g. contain more vacant lattice sites which facilitate the movement of the helium atoms. However, with simple accelerators, helium-ions of various energies can be implanted in a material so that the extent of the damage and the amount of helium can be chosen freely. By ion implantation, the exact amount of helium implanted is known, and the damage and helium distribution (when mono-energetic ions are implanted this distribution can be approximated by a Gaussian profile) can be easily calculated with SRIM-2000 [4]. Thus, because the starting conditions are well-known, helium implantations in potential inert matrix materials can be a useful tool for forecasting the helium behaviour during the transmutation of actinides in inert matrices.

It is important to understand the helium behaviour in candidate inert matrix materials in order to anticipate possible swelling and/or cracking of fuel elements due to pressure build-up.

1.4 Objectives of the thesis

This thesis presents a study with regard to the effects of $\alpha$-decay damage and the build-up of helium in two candidate ceramic matrix materials, spinel and zirconia. Spinel (magnesium aluminate spinel, MgAl$_2$O$_4$) has been studied extensively during the past decade. Ref. [3] gives an overview of the work done on spinel. To simulate fission product damage, investigations have been performed by implanting the fission gases krypton [6, 7, 8, 9, 10, 11, 12, 13] and xenon [6, 7, 8, 9, 10, 12, 13, 14], fission products like iodine [8, 9, 10, 12, 13] and antimony [8, 9, 10]. $\alpha$-Decay and helium build-up in spinel have been studied by several authors [14, 15, 16, 17, 18, 19, 20, 21]. Under the impact of fission products, a transformation to amorphization of the spinel matrix has been observed. The behaviour of helium and fission gases in a spinel matrix under this condition has not been studied so far. In oxides like UO$_2$, it is known that helium and fission gases are swept out during recrystallization. It is important to answer the question whether this is also true for spinel.

As a part of the EFTTRA collaboration (Experimental Feasibility of Targets for Transmutation) also a true irradiation experiment on a microdispersed spinel matrix with americium has been performed in the High Flux Reactor (HFR) at Petten. The swelling of this material under neutron irradiation and during the transmutation process turned out to be extremely large. So far, the behaviour of fission gases in a reactor-irradiated
spinel matrix coupled to its microstructure has not been studied. It is very important to gain insight into this process that causes the swelling in the matrix under irradiation. Because of the cost of an irradiation experiment as well as the time necessary to perform a complete test of a new material, prediction of results can prevent inadequate approaches.

Owing to the unstable behaviour of the spinel matrix found in the EFTTRA-T4 experiment, new ceramics were investigated. At present, zirconia (ZrO$_2$), stabilized in the Fm$ar{3}$m spacegroup with the aid of e.g. Y$_2$O$_3$, is a candidate inert matrix material on which many studies are currently being performed. Thermal properties have been studied in detail, e.g. [22], as well as effects of fission products such as xenon [15, 22, 23, 24, 25, 26, 27, 28], iodine [23, 29, 30, 31, 32], cesium [30, 32, 33, 34] and strontium [32]. The material shows good stability under implantation with these nuclides. Effects of neutron irradiation on the material have been presented in Ref. [35]. The effects of $\alpha$-decay on the other hand have not been studied in much detail [15] and almost no data are available in the literature. This topic is of extreme importance if zirconia is to be used as a transmutation matrix since the fractional concentration of helium formed can be very high.

Presently, tests are continued with the irradiation of a zirconia matrix in the Halden Reactor. Moreover, the EFTTRA-T5 experiments foresee the irradiation of zirconia-based fuels. However, these experiments are still in the sample fabrication stage.

### 1.5 Outline of the thesis

The behaviour of helium and fission gases has been studied for two different selected materials for which different techniques of investigation have been used.

Chapter 2 presents the experimental techniques applied. Helium desorption experiments were performed in two different set-ups. One system is the lead shielded Knudsen cell of the Institute for Transuranium Elements (ITU), especially designed to work with irradiated reactor fuels. The second system is the thermal desorption facility of the Interfaculty Reactor Institute (IRI), which has the ability of detecting very small quantities of helium. For both systems some improvements, developed as a part of this thesis, will be described. The spatial helium distribution was studied with neutron depth profiling while the evolution of defects was investigated with positron beam analysis. For some specimens, the surface structure was investigated with scanning electron microscopy (SEM) and the damage inside the material with transmission electron microscopy (TEM).
Chapter 3 presents the theoretical background of helium behaviour in ceramics. Problems like damage introduced by ion implantation, self-diffusivity of matrix components, helium diffusion models, bubble formation and helium release models will be discussed.

Chapter 4 presents results for spinel, MgAl$_2$O$_4$. First, a short introduction is given about helium implantation experiments in single- and polycrystalline spinel performed by others. Then, some newly performed implantation experiments on polycrystalline spinel will be discussed. However, this chapter is mostly devoted to helium behaviour in amorphous spinel as irradiation experiments have shown that the spinel matrix becomes amorphous under neutron irradiation.

Chapter 5 presents the results of gas release investigations coupled to microstructural investigations on the EFTTRA-T4 specimens. The EFTTRA-T4 experiment was initially set up to investigate the possibility of americium transmutation in spinel. After irradiation of the specimen, many non-destructive analyses were performed. In the work described in Chapter 5, the sample was finally vaporized in the Knudsen cell to achieve full gas release. The chapter will be concluded with a comparison between the implantation experiments and the experiments on reactor-irradiated fuels.

Chapter 6 presents the results of the helium implantation experiments on fully stabilized zirconia. This material has been implanted with helium at different energies and with different fluences. Various investigation techniques were applied on these specimens.

Chapter 7 presents some future prospectives. One of the questions discussed is how to continue the investigation on the behaviour of helium in fully stabilized zirconia.
Chapter 2

Experimental set-up

For the experiments in this thesis Knudsen cell measurements and Thermal Helium Desorption Spectrometry (THDS) were utilized in order to measure the temperature dependent helium and fission gas release from candidate inert matrix materials. The temperature dependent helium release profile gives information on release mechanisms. A high gas pressure might cause cracking of pellets and cladding, which has a detrimental effect on safety. Neutron Depth Profiling (NDP) was used to measure the distribution profile of implanted helium as a function of depth below the sample surface. Damage introduced by the implanted helium was assessed by Positron Beam Analysis (PBA) and by SEM and TEM microscopic analysis.

In this chapter, first a description will be given of the Knudsen cell used in the Institute for Transuranium Elements (ITU). The measurement facility will be described together with the method to calibrate the temperature in the cell and the calibration of the amount of helium detected in the mass spectrometer. Secondly, the facility for THDS at the Interfaculty Reactor Institute (IRI) will be described. Finally, the NDP, PBA, SEM and TEM techniques will be discussed in the last sections.

2.1 Knudsen cell

In 1909 Martin Knudsen developed an experimental cell with a tiny opening suitable for determining the mass rate of a flow of vapour into a vacuum. This enabled him to measure equilibrium vapour pressures [36] under the conditions of steady-state which define the so called Knudsen regime. These conditions are that the mean free path of the molecules (about 25 cm, depending on the vacuum conditions) is much larger than the dimensions of the cell. The ITU Knudsen cell was originally built and designed to vaporize highly radioactive targets taken from reactor irradiated fuels in order to obtain insight into their high-temperature behaviour [19, 37, 38, 39]. The theoretical background of determining the equilibrium vapour pressure and calibrated quantity of
isotopes vaporizing from a nuclear sample at high temperature will not be treated in this thesis, as the main interest is to gain insight into fission gas and helium behaviour in candidate inert matrix materials. In the application described in this thesis, the flow of gas from a Knudsen cell is submitted to a different regime than that of condensable vapour and it is used to measure the release rate of gas from a reactor-irradiated or gas-implanted specimen.

The Knudsen cell facility has been mounted inside a lead shielded glove box in order to reduce the exposure to radiation. In this thesis helium implanted matrix specimens as well as a spinel matrix doped with 11% americium irradiated in the HFR at Petten were analysed in this cell. The system, the improvements in the temperature measurements and the calibration of the amount of helium measured will be described in the next subsections.

2.1.1 The Knudsen cell set-up

Figure 2.1 shows a general overview of the Knudsen cell facility.

Figure 2.1: A schematic overview of the Knudsen cell facility. The different numbered parts are described in the text.
The cell (1) used in the experiments is made from tungsten. The cell has a height of 2 cm and a diameter of 1.1 cm. The sample is placed inside the cell. There is a tiny hole in the top of the cell through which the vapour and gas can leave the cell. Normally, when analysing a vapour, there is an equilibrium between the vapour in the cell and the solid fuel target. The calibration of the amount of vapour detected can then be easily performed by adding a known quantity of a material to the cell with a known vapour pressure. However, the situation is different if a gas is released as there is no equilibrium between the gas in the cell and the fuel. This results in the mass spectrometer (7) measuring an unknown fraction of the emitted gas atoms, for which a correction factor has to be determined (see Subsection 2.1.4.)

In Figure 2.2 Knudsen cells used at the ITU are shown which differ in size or material. The cells in the figure are made of tungsten or alumina. For the experiments described in this thesis, a cell made of tungsten with a top hole diameter of 0.5 mm was used.

The bottom of the cell contains three holes. In one of the holes a thermocouple (15) can be mounted for temperature measurements, the other two holes are used to support the cell. The heat loss through these three connections is significant and cannot be neglected. The cell can be moved vertically by a lift inside the furnace (4). The cell is heated by a tungsten resistance coil (2) shown on the left of Figure 2.3. The tungsten resistance coil drawn in Figure 2.1 is not in use anymore as the new type of coil shown in Figure 2.3 is more durable. Seven thermal shields (8) are placed over the cell for insulation, shown on the right of Figure 2.3, and three thermal shields are placed under the cell.

For measurements at higher temperatures, a linear pyrometer (11) has been installed. To prevent pollution of the pyrometer window, a disc with revolving protection windows (9) is mounted in front of the pyrometer.

The vapour and gas coming from the cell first pass the shutter (3) which can temporarily block the vapour stream in order to perform background measurements. If the shutter is closed but the mass spectrometer signal remains high, it is an indication that the signal contains a high fraction of background. A liquid nitrogen cold trap (5) has been installed in the system to reduce the background by condensing all condensable
atoms present in the oven. Especially heavy hydrocarbons which are present in the system, can introduce large background vapour pressure signals in the mass spectrometer signal. The vapour and gas stream effusing from the Knudsen cell is not led through the cold trap but is directly measured in the quadrupole Balzers QMA 420 mass spectrometer (7). The detection mechanism is either a Faraday cup or an electron multiplier (in the present experiments only the electron multiplier was used). The ionization energy of the electrons can be varied between 0 and 70 eV. Masses between 0 and 500 amu can be detected. A CCD camera (6) has been installed in order to align the system by visual inspection. To obtain an ultra-high vacuum in the system it is equipped with a turbomolecular pumping system (14). The pumping speed of the upper pump is 210 dm$^3$s$^{-1}$, that of the lower pump is 340 dm$^3$s$^{-1}$. However, in order to simulate certain conditions, measurements can also be performed in a gaseous atmosphere. For this purpose a gas capillary inlet (10) is present. Finally, not only mass spectrometer measurements can be performed, but the gas evacuated from the oven by the vacuum pumps can also be led through a $\beta$- (13) and a $\gamma$-counter (12) in order to determine the amount of a specific radioactive isotope released.

### 2.1.2 Temperature measurements with a thermocouple

While measurements were being performed, it was noticed that a large discrepancy existed between the temperature indicated by the thermocouple and the pyrometer, although both systems should measure essentially the same cell temperature, which can only have a small gradient over the cell. Both systems were calibrated before installation into the Knudsen cell glove box system. An investigation was carried out to gain insight into the cause of these discrepancies and to quantify the effect. The results are explained by making use of Figure 2.4.

The value indicated by the thermocouple is the temperature at the position of the

---

**Figure 2.3:** *Tungsten resistance coil and thermal shields.*
junction of the thermocouple. It was found that the junction of the thermocouple was located 4 mm under the top of the thermocouple (configuration 1). As the depth of the hole in the cell was only 2 mm, evidently the temperature outside the cell was measured. After drilling a deeper hole (configuration 2), the difference in the temperatures determined with thermocouple and pyrometer was smaller. In order to really solve the problem, it was decided to use a thermocouple with the junction at the top of the thermocouple (configuration 3) in order to measure the temperature of the cell as closely as possible to the sample. In all situations the thermocouple was a tungsten-rhenium thermocouple. The maximum temperature of this type of thermocouple is 2400 K. Because the thermocouple provides at the same time the support for the cell, its top part has to be stiff, which complicates manufacturing.

For all configurations (1 to 3), the melting point of silver was measured by monitoring the temperature of the crucible and the mass spectrometer signal at the same time. During the phase transition from solid to liquid the temperatures of the silver and the crucible did not change. At the same time, the vapour pressure of the material remained constant which also gave a plateau in the mass spectrometer signal. The plateau in the mass spectrometer signal indicates the melting of silver (a well defined temperature, 1234 K). From the value of the thermocouple temperature at this plateau the difference between the theoretical and the measured temperature could be assessed. Table 2.1 shows the melting temperatures measured in the different situations.

### Table 2.1: Measured melting temperature of silver. The melting point of silver is 1234 K.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>measured melting temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1151.5</td>
</tr>
<tr>
<td>2</td>
<td>1165.5</td>
</tr>
<tr>
<td>3</td>
<td>1208.9</td>
</tr>
</tbody>
</table>
From the table it can be seen that the temperature measurement has been improved by almost 60 K. At 1234 K, in the third case, the underestimation of the temperature has been reduced to only 25 K.

**Calibration of the thermocouple**

A thermocouple generates a voltage between its two legs which depends on the temperature difference between the junction and the temperature of the connection to the current leads of the measuring instrument. The voltage per unit of temperature difference is tabulated in handbooks for a variety of thermocouples. The correct functioning of the thermocouple can be checked, for example, by calibrations with ice and boiling water. While measuring the temperature in the Knudsen cell, it should be realized that the temperature indicated by the thermocouple is not the actual temperature of the sample, owing to a temperature gradient over the cell and owing to temperature losses through the thermocouple and the two supporting pins. Furthermore, owing to transparency of the sample material for infrared radiation, a delay in temperature may occur between sample and crucible. This will be described in Subsection 2.2.2. Apart from calibrating the thermocouple itself, the temperature measured by the thermocouple should be corrected for the distance between the thermocouple junction and sample in order to obtain the correct sample temperature. This is not straightforward as the temperature measured by the thermocouple depends on the heating schedule and the optical properties of the sample materials used. However, it is possible, by repeating the same heating schedule several times and determining the melting points of silver and other materials, to improve the accuracy of the temperature measurement.

Two ramps (constant rates of heating) were applied, one ramp with a slope of about 10 K min$^{-1}$, and one with a slope of about 30 K min$^{-1}$. It should be noted that in practice the heating rate is not completely linear with time, as will be shown in Figure 2.5. The calibration of these ramps is described in the next subsection.

<table>
<thead>
<tr>
<th>material</th>
<th>ramp $10$ K min$^{-1}$</th>
<th>ramp $30$ K min$^{-1}$</th>
<th>real melting temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>zinc</td>
<td>685</td>
<td>692.7</td>
<td></td>
</tr>
<tr>
<td>silver</td>
<td>1208</td>
<td>1234.9</td>
<td></td>
</tr>
<tr>
<td>beryllium</td>
<td>1514</td>
<td>1547</td>
<td>1560</td>
</tr>
<tr>
<td>platinum</td>
<td>1969</td>
<td>2037</td>
<td>2041.4</td>
</tr>
</tbody>
</table>

**2.1.3 Calibration of temperature ramps**

Several materials were melted, making use of one of the two ramps to calibrate the system. With these points, the temperature ramps could be calibrated. The materials
used were zinc, beryllium, silver and platinum. Table 2.2 gives the results of these calibration measurements. Not only can the data in the table be used to calibrate the ramps, but one also sees that the error in the temperature indicated is larger for a lower ramp rate, which is counter to expectation. Probably, owing to the lower heating rate greater energy losses occur, which could be a reason for the lower temperature.

Figure 2.5 shows the measured and corrected temperature profiles for both ramps. The data points indicate the real temperatures, the heavy curves are the data recorded by the thermocouple. It can be seen that the temperature of the crucible does not increase completely linearly with time. On the secondary ordinate, the power fed into the spiral is indicated. The voltage over the spiral (and thus the power) is a fixed function of time.

![Temperature and furnace power plots](image)

**Figure 2.5:** Calibration of temperature ramps. The temperature and furnace power are plotted versus time. Figure a: the calibration of the ramp with a heating rate of 10 K min$^{-1}$. Figure b: the calibration of the ramp with a heating rate of 30 K min$^{-1}$.

### 2.1.4 Calibration of the amount of helium

Especially for reactor irradiated-samples, it is of crucial importance to determine the absolute amount of helium measured, i.e. to find a calibration factor for the system. Only a very small fraction of the helium released from the sample is finally measured in the quadrupole mass spectrometer. Gas effusing through a tiny hole has a cosine-shaped distribution. Thus, only the fraction of gas which leaves the crucible in the direction of the mass spectrometer and enters within the acceptance angle will reach the mass spectrometer and might be detected with certain efficiency. The rest of the gas is scattered at the walls of the oven and must be pumped away. From the gas
which enters the mass spectrometer a certain fraction gets ionized and reaches after mass-selection the electron multiplier and gives rise to an output pulse, consisting of a certain electrical charge. The time-integrated mass spectrometer signal for a certain mass is a measure for the original quantity of gas present in the cell.

There are several ways of calibrating the amount of gas:

1. A sample with an exactly known quantity of helium can be used. However, certified samples are not commercially available. The quantity of helium implanted with a Van de Graaff accelerator has an error of about 10%. The amount of helium implanted can be determined with neutron depth profiling (see Section 2.3). However, this method is suitable only for $^3$He, and during heating the $^3$He-signal is difficult to distinguish due to interference from the H$_2$-signal. The data obtained with neutron depth profiling also contain certain errors, as will be discussed later.

2. A sample doped with a known quantity of an $\alpha$-emitter can be used. If the storage time is known, the number of $\alpha$-decays in the sample is known and thus the amount of helium. However, a thorough analysis of the $\alpha$-emitting compound will be necessary. Secondly, due to diffusion processes, some of the helium formed during storage may be released, in particular the helium formed near the surface. This is only a small fraction of the total amount of helium formed in the sample. Usually, the amount of gas that can be accumulated in such a sample is small.

3. The third possibility is to fill the cell with a known quantity of gas. If volume, pressure and temperature are known, the number of atoms in the cell is known. Several attempts were made, but the system had many disadvantages:
   - After filling the cell, it had to be closed without leaking, which proved to be very difficult;
   - The hole in the top of the cell had to be closed with a material with a low melting temperature and a low vapour pressure. From several materials the best results were obtained with paraffin, which however had the disadvantage of contaminating the entire furnace and mass spectrometer.

4. A small tube with a known volume acting as a gas reservoir for calibration gas can be filled with helium at a known pressure. This tube is be connected to the temporary gas inlet indicated by number (10) in Figure 2.1. The gas release from the small tube into the cell can be controlled by a microvalve, which allows the mass spectrometer to remain in its linear range. However, the disadvantage of this system is that the microvalve became the limiting factor in the system, as the opening of the microvalve had been chosen smaller than the opening of the cell.

The third and fourth methods were selected to calibrate the Knudsen cell system. With respect to the fourth method, experiments were performed at different pressures, i.e., different numbers of helium atoms. The measurement of the calibration curve was repeated three times as shown in Figure 2.6. The differences in the results between the measurements originate from the fact that the special Knudsen cell necessary to perform the calibration measurements was removed from the oven in order to perform other experiments and was then re-mounted. The variation in temperature of the helium gas may be assumed to be less than 1 °C. The only change as a result of the
re-mounting was expected to be a geometrical change since the opening of the microvalve was kept constant in the period between the measurements, as could be seen from the slope of the helium release curves, that are not displayed here. During the measurements care had to be taken to keep satisfying Knudsen conditions for the effusing gas.

![Helium calibration curve, electron energy = 70 eV. The integrated mass spectrometer signal is plotted versus the number of helium atoms in the calibrated volume. The numbers 1 to 3 refer to the measurement series performed.](image)

The calibration factor can be determined from the slope of the curves as shown in Figure 2.6 by fitting the curves according to the formula:

\[
y = \frac{1}{C_F} x_{\text{He}}
\]  

(2.1)

where \(y\) is the integrated mass spectrometer signal in Coulomb (C), \(C_F\) is the calibration factor (C\(^{-1}\)) and \(x_{\text{He}}\) is the number of helium atoms that has been sampled in the calibration procedure. For the three different measurement sessions, these fitting data are presented in Table 2.3.

<table>
<thead>
<tr>
<th>Series</th>
<th>Fit</th>
<th>(C_F) (C(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(y = 1.8683 \times 10^{-24} x_{\text{He}})</td>
<td>5.35 \times 10^{23}</td>
</tr>
<tr>
<td>2</td>
<td>(y = 2.4677 \times 10^{-24} x_{\text{He}})</td>
<td>4.05 \times 10^{23}</td>
</tr>
<tr>
<td>3</td>
<td>(y = 2.9127 \times 10^{-24} x_{\text{He}})</td>
<td>3.43 \times 10^{23}</td>
</tr>
</tbody>
</table>

In Table 2.4 some results of the third calibration method (a cell which the hole in the top is closed with a material that can melt and has a low vapour pressure) are shown.
The table shows the calibration factors obtained from the measurements. In Figure 2.7

**Table 2.4:** Calibration factors obtained from seven measurements with a cell sealed with paraffin.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>( C_F ) ((\text{C}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( 5.9 \times 10^{23} )</td>
</tr>
<tr>
<td>2</td>
<td>( 6.5 \times 10^{23} )</td>
</tr>
<tr>
<td>3</td>
<td>( 7.0 \times 10^{23} )</td>
</tr>
<tr>
<td>4</td>
<td>( 4.7 \times 10^{23} )</td>
</tr>
<tr>
<td>5</td>
<td>( 5.0 \times 10^{23} )</td>
</tr>
<tr>
<td>6</td>
<td>( 5.4 \times 10^{23} )</td>
</tr>
<tr>
<td>7</td>
<td>( 7.6 \times 10^{23} )</td>
</tr>
</tbody>
</table>

a bar diagram is shown of all the calibration factors determined. 'Cell' refers to the measurements where the top of the cell was closed with paraffin while 'Tube' refers to the system where a small tube was filled with gas at a known pressure. The calibration factors shown in 'Cell' are the result of one single measurement, the calibration factor 'Tube' has been determined from the data points shown in Figure 2.6.

![Bar diagram of the calibration factors determined with two different systems.](image)

**Figure 2.7:** Bar diagram of the calibration factors determined with two different systems.

The calibration factor determined with 'Tube' is: \( (4.3 \pm 1.0) \times 10^{23} \) \((\text{C}^{-1})\), the one determined with 'Cell' is: \( (6.1 \pm 1.1) \times 10^{23} \) \((\text{C}^{-1})\) and the averaged calibration factor calculated from all the measurements is \( (5.5 \pm 1.3) \times 10^{23} \) \((\text{C}^{-1})\). Although this calibration factor is not perfect it will be used in the analysis of the helium release experiments presented in Chapter 6. Unfortunately, at the time of the measurements the calibration system had not yet been installed and it was therefore not possible to
perform a calibration before and after the measurements. The amplification of the quadrupole signal is about 4600 times, thus the sensitivity for the detection of helium in the Knudsen cell is about $4.1 \times 10^8$ helium-atoms per unit of charge detected by the mass spectrometer.

The calibration system described above can be used for the calibration of the amount of helium in the Knudsen cell. However, some remarks regarding improvement of the system can be made:

- The calibration should be performed immediately before and after the experiment.
- The influence of temperature on the calibration factor has not been investigated extensively. However, maybe the influence is limited: one of the curves was reproduced at about 800 and 1100 K and did not yield a different calibration factor.

## 2.2 Thermal helium desorption

### 2.2.1 Apparatus and helium calibration system

The Thermal Helium Desorption Spectrometry (THDS) system of the Interfaculty Reactor Institute consists of an ultra-high vacuum sample chamber (the furnace), an ion gun, a quadrupole mass spectrometer, a sample holder with an electron gun for heating, and a calibration system [40, 41]. The data acquisition used for the THDS-system is described in detail in Ref. [42]. A picture of the THDS facility is shown in Figure 2.8.

![Figure 2.8: Overview of the THDS facility.](image)
The system can be used in two different ways: A specimen can be mounted inside the oven and can be implanted by the ion gun and thermally desorbed in the same system. The second application, used in this thesis, is the desorption of specimens that have been implanted elsewhere. For this application the pre-implanted sample is inserted into a crucible, which is positioned in the vacuum chamber (furnace). The crucible, used for the experiments described in this thesis, is shown in Figure 2.9. Comparing this crucible with the one used in the Knudsen cell (see Figure 2.2), it can be seen that the THDS crucible is much smaller. The crucible is heated up by ion bombardment and its temperature is monitored with the aid of a thermocouple inserted in the bottom of the crucible. As a result of the temperature increase of the crucible the sample temperature will increase as well, although for specimens transparent to infrared there will be a delay in the sample temperature compared to the crucible temperature. This will be discussed in the next subsection. Due to thermal activation the helium will be mobilized, which enables it to migrate through the specimen. If the gas travels towards the surface, it will be released in the vacuum chamber and detected in the mass spectrometer. In this way, the release rate is recorded versus time and temperature, resulting in a thermal desorption spectrum. With the THDS technique, temperatures can be determined at which the damage complexes, caused by the helium, dissociate, which gives information on the dissociation energy of the different complexes. More information about the process itself can be obtained. Among other things, diffusion coefficients can be derived from the shape of the release peaks.

![Figure 2.9: Crucible used for the experiments performed with the THDS system.](image)

The THDS-system is equipped with a gas calibration system. In this system, a calibration volume of $1 \, \text{cm}^3$ is filled at a known pressure. The known quantity of, in this case, helium gas is led through the oven and detected by the mass spectrometer. In the THDS-system there is no direct pumping of the oven; all helium is pumped away through the mass spectrometer, which makes the system more sensitive than the Knudsen cell system. Typical calibration factors measured in the THDS-system are about $5-7 \times 10^7$ atoms per count. The THDS system is about ten times more sensitive than the Knudsen cell of ITU and thus very suitable for detecting small quantities of helium.
2.2.2 Calibration of temperature

In many desorption experiments with THDS, in which the crucible is heated directly by ion bombardment but the specimen inside the crucible is heated by the crucible only, it was noted that the helium release continued even after the temperature dropped. As the release of helium is a temperature activated process, it should stop immediately when the temperature decreases. Therefore, it was concluded that a temperature delay existed between the temperature of the crucible (the measured temperature) and the actual temperature of the sample, especially for materials which are transparent for infrared radiation. The heating of the sample takes place partly by conduction at the place where the sample is in contact with the cell, and partly through thermal radiation from cell to sample. If the sample material has a low thermal conductivity and is transparent for infrared radiation, it is expected that the temperature of the sample will be lower than the temperature of the crucible, especially in the low temperature range. As a test it was decided to equip a spinel sample with a thermocouple by attaching the thermocouple with a ceramic glue to the specimen. The sample was then put in the crucible and both the temperatures of the sample and the crucible (the latter by a thermocouple inserted in the bottom of the crucible) were monitored during heating and cooling. Experiments were performed at a heating rate of $1 \text{ K s}^{-1}$ and $3 \text{ K s}^{-1}$. In Figure 2.10, one of the measurements performed with the double thermocouple system is shown. It can be observed that, in addition to the delay between the maximum temperature of the sample and the crucible, there is a sharp drop in crucible temperature the moment

![Figure 2.10: Example of a measurement with a two-thermocouple system. The measured sample and crucible temperature are plotted versus time. The heating rate applied was 3 K s^{-1}.](image-url)
the heating is stopped (indicated by the oval). As the crucible is heated by means of electron bombardment, not only the electric ground pole of the crucible, but also the wires of the thermocouple inserted in the crucible may be hit by electrons and conduct these electrons. For this reason, more electrons may go through the thermocouple wires than would be the case for a leak-free system. The temperature indicated by the thermocouple might thus be higher than the actual crucible temperature. The moment the electron bombardment is switched off, this current will disappear and the thermocouple will indicate the exact temperature of the crucible. In the rest of this discussion, the data have been corrected for this leak current. In Figure 2.11 the results of in total

![Figure 2.11: Measurement of temperature delay between (spinel)-sample and crucible. The measured sample temperature is plotted versus the measured crucible temperature for two different heating rates. The line without markers has been drawn to guide the eye and represents the curve where the sample temperature equals the crucible temperature.](image)

29 measurements are shown, with the temperature of the crucible on the abscissa and the temperature of the sample on the ordinate. In the figure the ideal situation, $T_c = T_s$, is shown as the line without markers.

For low temperatures, there are large differences between the temperatures of the samples and the crucible. The higher the temperature of the crucible, the smaller the difference between sample and crucible temperature, but the temperature of the sample remains well below the crucible temperature. It can be seen that for a heating rate of 1 K s$^{-1}$ when the crucible temperature is about 1100 K, the temperature of the sample is about 70 K lower. This difference increases for a faster heating rate: for a heating rate of 3 K s$^{-1}$, at 1100 K, the difference is 90 K.
2.2.3 Modelling of temperature delay

In order to determine the specimen temperature from the measured crucible temperature for the experiments described in this thesis, a model was derived in order to perform this correction. The unknown parameters in the model were determined from the measurements described in the previous subsection.

When a sample is placed inside a crucible which is heated from the outside in vacuum, the sample inside the crucible will heat up due to conduction and radiation. It is assumed that the temperature profile over the crucible as well as over the specimen is uniform.

As a first assumption, only radiation will be considered. A part of the radiation emitted by the crucible is reflected by the sample, a part is transmitted and the rest is absorbed by the sample.

When heating a body inside another non-black body in vacuum the heat flow from the crucible to the specimen ($\phi_q$) can be approached by [43]:

$$\phi_q(t) = A_s \frac{\sigma (T_c^4(t) - T_s^4(t))}{\frac{1}{\varepsilon_s} + \frac{A_s}{A_c} \left(\frac{1}{\varepsilon_c} - 1\right)},$$

which is known as Christiansen’s equation. In this equation $A_s$ is the total surface of the sample, $A_c$ the surface of the crucible, $\varepsilon_s$ the emissivity of the sample and $\varepsilon_c$ the emissivity of the crucible, $\sigma$ is the Stefan-Boltzmann constant and $T_c$ and $T_s$ are the crucible and sample temperature, respectively.

As the sample is partly transparent for infrared radiation, the absorbed heat flow $\phi_{abs}$ is given by:

$$\phi_{abs}(t) = f_{abs} \times \phi_q(t),$$

where $f_{abs}$ is the fraction of heat absorbed by the sample. The parameters $\varepsilon_c$, $\varepsilon_s$ and $f_{abs}$ are temperature dependent.

The change in the temperature of the specimen can be described by:

$$\frac{dQ_s(t)}{dt} = \phi_{abs}(t) = m_s c_p \frac{dT_s}{dt},$$

where $m_s$ is the mass of the specimen, $c_p$ the specific heat of the specimen material and $Q_s$ the heat contained by the specimen.

The change in sample temperature can thus be expressed as:

$$\frac{dT_s}{dt} = \frac{\phi_{abs}(t)}{m_s c_p} = C_1(T_c) \left( T_c^4(t) - T_s^4(t) \right),$$
with
\[ C_1(T_c) = \frac{\phi_{\text{abs}}}{m_s c_p (T_c^4(t) - T_s^4(t))} = \frac{A_s \sigma f_{\text{abs}}}{m_s c_p} \left( \frac{1}{\varepsilon_s} + \frac{A_s}{A_c} \left( \frac{1}{\varepsilon_c} - 1 \right) \right)^{-1} [K^{-3} s^{-1}] . \] 

In total 29 measurements were performed with the double thermocouple system. In these measurements, the heating rate and the maximum annealing temperature were varied. The temperature of the crucible \( T_c \) as well as of the sample \( T_s \) were monitored. From the results of these measurements the value for \( C_1 \) can be derived from:
\[ C_1 = \frac{dT_s(t)}{dt} (T_c^4(t) - T_s^4(t))^{-1} . \] 

It was found that \( C_1 \) does not depend on the heating rate. The best fitted curve of \( C_1 \) is shown as a function of the crucible temperature \( T_c \) in Figure 2.12.

**Figure 2.12**: The best fitted curve for \( C_1 \) from Eq. 2.7 as a function of the crucible temperature.

The following fitted relationship was found for \( C_1 \):
\[ C_1 (T_c) = 6.654 \times 10^{-13} + 3.1519 \times 10^{-10} \exp \left( \frac{-T_c}{258.332} \right) \left[ K^{-3} s^{-1} \right] . \]

It can be seen that \( C_1 \) depends on the temperature, in particular for low temperatures. At high temperature this might be due to the temperature dependence of the emissivities. At low temperatures this effect can be explained by the fact that radiation is not the only process responsible for the heating of the sample, but conduction plays a role as well. Since in experiments where the sample is annealed in steps (i.e. the sample is cooled down between different heating stages and the maximum temperature of the
heating is increased for every annealing step), the helium is mostly released at the end of the heating stage, it is especially interesting to gain insight into the error made at the maximum temperature of each annealing step. In Figure 2.13 the results of the sample temperature as calculated from Eq. 2.5 are compared to the measured temperatures of 29 experiments, where for $C_1$ Eq. 2.8 was used. Two parameters are compared. Firstly, the maximum sample temperature measured is compared to the maximum sample temperature determined with the calibration function, by calculating the following error:

$$
\Delta T_s = \frac{T_{s\text{max meas}} - T_{s\text{max fit}}}{T_{s\text{max meas}}},
$$

(2.9)

where $\Delta T_s$ is the error in the maximum of the sample temperature, $T_{s\text{max meas}}$ is the maximum sample temperature measured and $T_{s\text{max fit}}$ is the maximum sample temperature calculated with the calibration function. The error in the time in which these maximum temperatures were reached can be calculated in the same way. It can be seen from Figure 2.13 that the maximum temperature according to the calibration is generally overestimated, while the time in which this maximum temperature is reached is slightly underestimated by the calibration. Most of the errors calculated lie within a range of $\pm 3\%$.

In Figure 2.14 the results of the measured crucible temperature, the measured sample temperature and the calibrated sample temperature are shown for two different tests. Figure 2.14a shows the results for an experiment with a low maximum temperature. Large differences between the temperature of the crucible and the specimen are ob-
erved. For the test presented in Figure 2.14b and most of the other experiments, the temperature data of the sample were not monitored correctly during heating and could not be corrected due to a leak current through the sample thermocouple caused by the ion bombardment. In Figure 2.14b, only the measured sample temperature data during cooling are therefore shown. Because these results are satisfactory with respect to the

![Graph](image)

**Figure 2.14:** Results of a fitted temperature as a function of heating time compared to the measured temperature. For the fitting of the sample temperature only heating through radiation was taken into account. Figure a: heating to a low maximum temperature. Figure b: the results of a test up to 1117 K.

error in the temperature during the heating of the sample, taking heating through conduction and convection into account via $C_1$, the model described above has been used to correct the THDS measurements on the spinel samples described in Chapter 4. The correction has also been applied for the zirconia specimens described in Chapter 6.

### 2.3 Neutron depth profiling

Neutron depth profiling (NDP) is a near-surface analysis technique to measure nondestructively the concentration as a function of the depth distribution of certain isotopes, e.g. $^3$He, $^6$Li and $^{10}$B. The NDP technique was originally developed by Ziegler et al. [44] and some years later thoroughly investigated by Biersack et al. [45]. The basis of NDP is the irradiation of a sample with thermal neutrons and the subsequent release of charged particles due to the neutron-induced exoergic charged particle re-
action. In case of (implanted) $^3$He particles this means that according to the nuclear reaction $^3$He(n,p)$^3$H, energetic $^3$H and $^1$H with primary kinetic energies of 191 keV and 573 keV, respectively, are emitted. If the system is calibrated with a well-known reference sample, the absolute amount of retained $^3$He in the sample can be determined from the number of detected protons. The energy loss of the protons is related to the distance of the emitting $^3$H atom to the sample surface and is therefore a measure for the depth distribution of $^3$He in the sample. The cross-section for this reaction for the flux used (the experiments were performed in the Hoger Onderwijs Reactor of IRI with a neutron flux in the order of $10^7$ cm$^{-2}$s$^{-1}$) is 5333 barn [45] which has the effect that per hour of measuring a fraction of about $1 \times 10^{-9}$ of the total $^3$He-inventory is transmuted into $^3$H. The NDP technique has thus no influence on the total quantity of $^3$He in a specimen.

A description of the transformation from the measured number of counts per channel as a function of proton energy into a density-depth profile is given in Appendix A.

### 2.4 Positron beam analysis

With Positron Beam Analysis (PBA) the generation and evolution of lattice defects can be monitored. A mono-energetic positron beam is used, for which the positron energies can be varied from 0.1 to 25 keV. With increasing positron energy the depth at which a positron is thermalized and annihilates increases. In this way, depth-dependent defect information can be obtained [46]. Once it has lost most of its energy, the implanted positron will annihilate with an electron present in the material, and in most cases two photons (γ-quanta) will be emitted. In the centre-of-mass system of the annihilating particles, the γ-quanta are emitted in exactly opposite directions and the available energy will be divided equally over the two γ-quanta. The available energy is equal to $2m_0c^2 - E_b$ where $E_b$ is the binding energy of the two particles in the solid, $m_0$ is the rest mass of the electron and $c$ the velocity of light in vacuum. In the laboratory coordinate system, the momentum $p$ of the two particles (mostly determined by the electron as the positron has been thermalized) causes the energy of the γ-quanta to increase or decrease with respect to $m_0c^2$ (= 511 keV). In the pulse height spectrum, this energy distribution is seen as a broadening of the 511 keV annihilation peak, a typical Doppler effect. Two parts of the Doppler broadening profile are of interest: Firstly, the low-momentum central part of the peak and secondly the high-momentum tails. Because the positron is positively charged, it is repelled by the atomic nuclei. It therefore samples mainly the interstitial region where it annihilates predominantly with the low-momentum valence electrons and thus contributes to the centre of the profile. The wings of the profile have a much lower intensity compared to the central part. This is due to the small overlap of the positron wavefunction with the core electron wavefunctions. A missing atom (i.e. a vacancy) forms an attractive potential well for positron trapping. The absence of the atom with its high-momentum core electrons manifests itself as a decrease of the high-momentum content and thus as a sharpen-
ing of the profile, compared to the profile of an undamaged specimen. The shape of the Doppler broadening profile can be characterized by two parameters: \( S \) and \( W \), as shown in Figure 2.15. The \( S \)-parameter represents the area under the central part of the profile, divided by the total area under the curve. As positrons implanted in an open volume have a lower probability of annihilating with core electrons the \( S \)-parameter will be higher compared to that of a defect-free reference sample [46]. The second parameter (\( W \)) gives the ratio between the areas under the wings and the total area of the Doppler broadening profile and will be lower compared to the defect-free reference sample.

![Figure 2.15: An example of a Doppler broadened 511 keV peak with the defining intervals for the \( S \)- and \( W \)-parameter.](image)

### 2.4.1 \( S-W \) mapping and typical values for \( S \) and \( W \) in a ceramic

Most of the annihilations between positrons and electrons occur between particles of opposite spin under emission of two \( \gamma \)-quanta. A positron that annihilates with an electron with parallel spin can only decay under the emission of three \( \gamma \)-quanta. If the electron density is sufficiently low, as is the case at surfaces, in voids or in the bulk of insulators, a positron and an electron may form a bound state called (quasi-) positro-nium or Ps. Ps decays under emission of two \( \gamma \)-quanta (para-Ps) or three \( \gamma \)-quanta (ortho-Ps), depending on the spins of the two particles. For Ps in vacuum the ratio of \( 3\gamma \) to \( 2\gamma \) annihilation is 3:1; in matter this ratio is reduced by other processes such as pick-off annihilation, where the positron annihilates with an electron of opposite spin from one of the surrounding atoms. In implantation experiments with positrons there is a certain possibility that positrons return towards the outer surface and form Ps-states. This probability depends on the implantation depth. Positrons arriving at the surface of the sample by diffusion have, apart from the transition to the bound surface state, two other possibilities to escape from the bulk:
1. The positron can be re-emitted as a positron;
2. The positron joins with an electron which is released from the valence band and forms positronium.

In helium-implanted fully stabilized zirconia, vacancies and cavities will be present. In a single vacancy, the positron will annihilate with an electron and two $\gamma$-quanta will be emitted. The $S$-parameter for this mode of annihilation is higher than the $S$ of an undamaged reference sample while its $W$-parameter is lower. In a cavity, the positron will form (para-)Ps. For this case the $S$-parameter will be higher than the $S$ of pick-off annihilation in a cavity while its $W$-parameter will be lower.

Since there are several possible modes of positron annihilation in a material (e.g. cavities and vacancies) with probability $f_i$ and corresponding $S$-parameter $S_i$, the measured $S$-parameter is the result of the weighted average:

$$ S = \frac{\sum_i f_i S_i}{\sum_i f_i} $$

and, similarly,

$$ W = \frac{\sum_i f_i W_i}{\sum_i f_i} $$

These relationships can be used by plotting the $S$-parameter of a profile against the corresponding $W$-parameter. In cases where there is a mixture of annihilations from defects and from the bulk they will be represented by points on a straight line connecting these two special points. An example of such an $S$-$W$-plot is shown in Figure 2.16.

![Figure 2.16](image_url)

**Figure 2.16:** An example of an $S$-$W$-plot for an undamaged crystal, annihilation in a vacancy and annihilation in a cavity.
2.5 Microscopical investigation methods

2.5.1 Scanning electron microscopy

In the case of samples implanted with helium (Chapters 4 and 6), it is interesting to investigate the surface of the specimen after implantation, or after annealing up to a certain pre-defined temperature with a scanning electron microscope (SEM). In the case of irradiated reactor fuels (Chapter 5), it is necessary to study the sample by SEM to obtain a better insight into the microstructure after irradiation, or after annealing up to a pre-defined temperature. The SEM was mounted inside a glove-box. This also facilitated the investigation of samples which had become contaminated in the Knudsen cell glovebox. Especially in the case of irradiated fuels, investigations with backscattered electrons (BSE) are an interesting technique to gain a better insight into the position of the elements with a high atom number. The SEM was coupled to an EDX (energy dispersive X-ray) system in order to determine the local distribution of the single elements. In the case of implanted and irradiated samples, the samples were coated with a layer of graphite and subsequently analysed in the SEM.

2.5.2 Transmission electron microscopy

Transmission electron microscopy (TEM) is a powerful technique for investigating the microstructure of a material. The TEM used in this study was a HITACHI STEM H700HST modified to allow the handling of radioactive materials. TEM investigations were applied to both helium implanted specimens and neutron irradiated materials. For the latter purpose, electron-transparent specimens were prepared from small fragments of the material. After crushing the specimen in ethanol a droplet of the resulting suspension was deposited on a copper TEM grid coated with graphite for a better electron conductivity.

In the case of ion implanted samples, the region of interest is typically within one micron below the surface, and the microstructure usually exhibits a strong depth dependence. For the TEM investigations on helium implanted specimens described in this thesis two different techniques for sample preparation were used:

1. Cross-sectional TEM
   - First, the ion-implanted specimen (eventually pre-annealed) is glued face-to-face to another polished specimen (either implanted or virgin).
   - From the glued specimen a thin slice is cut. (≈ 250 µm)
   - This slice is centered and dimpled to a minimum thickness of ≈ 25 µm.
   - The slice is then mounted on a support ring and ion-milled until perforation occurs near the interface.
   - The sample is mounted on a copper grid and analysed in the TEM [47].
2. Plan-view TEM
   • An unimplanted sample is thinned and dimpled to \( \approx 25 \, \mu\text{m} \).
   • The sample is then implanted at an appropriate energy to let the ions come to rest in the sample.
   • Hereafter, the sample is mounted on a support ring and ion-milled until perforation occurs near the interface.
   • Finally, the sample is analysed in the TEM.
Chapter 3

Theoretical background

This chapter covers the theoretical background necessary to explain the experimental results to be described in Chapters 4 to 6. First, the definition of a ceramic is given and the types of defects to be expected in the ceramics studied in this thesis are discussed. Then, the theory of ion implantation, the simulation of $\alpha$-decay by means of ion implantation and the possible additional defects introduced by ion bombardment are discussed. After this, a section is devoted to the behaviour of the implanted ions under thermal annealing. Possible mechanisms for helium release are described and, whenever possible, simple models are given to evaluate the measurements described in Chapters 4 and 6. The description of the behaviour of implanted ions is coupled to the description of the behaviour of the ceramic itself and of the defects in the ceramic.

3.1 Definition and structure of ceramics

Ceramics can be defined as solid compounds formed by the application of heat, and sometimes heat and pressure, and comprise at least one metal and a nonmetallic elemental solid (like e.g. B and Si) or a nonmetal (like O). It follows that, amongst others, the oxides, nitrides and carbides of all metals and nonmetallic elemental solids are ceramics [48]. The materials investigated in this thesis are:

- $\text{MgAl}_2\text{O}_4$, which is the oxide of a combination of two metals;
- $\text{ZrO}_2$ stabilized in the cubic lattice structure with $\text{Y}_2\text{O}_3$, which are both oxides of a metallic element.

In a crystalline ceramic, atoms are arranged in a three-dimensional periodic lattice. This lattice can be described by defining a unit cell which is the smallest region in space that, when repeated, completely describes the three-dimensional pattern of the atoms in a crystal. There are seven different unit cell shapes. Both materials described in this thesis have the cubic lattice structure. In the cubic structure, the lengths of the edges of the unit cell are the same in all directions and the angle between the edges
is 90°. If the periodic and repeated arrangement of atoms in a material is perfect and extends throughout the entire specimen without interruption, the material is called a single crystal. A polycrystalline solid is composed of a collection of many randomly orientated single crystals, called grains, separated from one another by areas of disorder known as grain boundaries. The shape and size of the grains, together with the presence of porosity, other phases etc., and their individual distribution, describe what is termed microstructure. Many properties of a ceramic depend on its microstructure.

### 3.1.1 Microstructure of spinel MgAl$_2$O$_4$

Spinel has a cubic crystal structure (space group Fd$ar{3}$m), with a lattice parameter of 8.0831 Å at room temperature. In Figure 3.1 the atomic arrangement for the atoms in spinel is shown. A unit cell consists of 56 atoms. The chemical formula of the crystal is $(\text{Mg}^{2+}_{1-i}\text{Al}^{3+}_i)(\text{A})[\text{Mg}^{2+}_i\text{Al}^{3+}_{2-i}](\text{B})\text{O}_4$ with $i$ the so-called inversion parameter. This parameter gives the number of Mg$^{2+}$ and Al$^{3+}$ cations to be found at an A- or B-position, that is, surrounded by four or six O$^{2-}$ anions, respectively. An A-position is then said to have coordination number CN=4, a B-position CN=6. For natural spinel, $i = 0$, the 32 O$^{2-}$ ions form a face-centered cubic structure in which the 8 Mg$^{2+}$ ions are positioned at the A-positions and the 16 Al$^{3+}$ at the B-positions. This equilibrium structure has been observed in geological samples. The state in which $i = 1$ is called inverse spinel, with the 8 Mg$^{2+}$ ions occupying half of the B positions and the 16 Al$^{3+}$ ions occupying the A positions and the remaining half of the B positions. In synthetic spinel, $i = 2/3$, and the Mg$^{2+}$ and Al$^{3+}$ ions are randomly distributed over the A and B positions.

![Figure 3.1](image-url)  
**Figure 3.1:** The atomic arrangement of the atoms in spinel in the synthetic structure.

The ionic radii of the individual components of spinel, which depend on the coordination number (CN), are given in Table 3.1. The data were taken from Ref. [49].
Table 3.1: Ionic radii of the individual atoms present in spinel as a function of their coordination number (CN) in Å.

<table>
<thead>
<tr>
<th>Ion</th>
<th>CN=4</th>
<th>CN=6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$^{2+}$</td>
<td>0.57</td>
<td>0.72</td>
</tr>
<tr>
<td>Al$^{3+}$</td>
<td>0.39</td>
<td>0.535</td>
</tr>
<tr>
<td>O$^{2-}$</td>
<td>1.38</td>
<td>1.40</td>
</tr>
</tbody>
</table>

3.1.2 Microstructure of fully stabilized zirconia

Pure zirconia (zirconium dioxide, ZrO$_2$) occurs in three variations. At room temperature, it has the monoclinic form with a density of 5.6 g cm$^{-3}$, occurring in nature as baddeleyite (zirconia). Between 1273 K and 1443 K a phase transformation to the tetragonal phase with a density of 6.1 g cm$^{-3}$ occurs and this phase remains stable up to the transition to the cubic structure at 2643 K. The cubic structure is stable up to the melting point of 2953 K and has a theoretical density of 6.27 g cm$^{-3}$. Zirconia can be stabilized in the cubic structure via the addition of CaO, MgO or Y$_2$O$_3$, which form cubic solid solutions with ZrO$_2$. If smaller amounts of stabilizers are added, the new compound is referred to as partly stabilized zirconia (PSZ), which is characterized by both cubic and tetragonal (and sometimes monoclinic) forms of zirconia. For the use as an inert matrix material fully stabilized zirconia (FSZ) is interesting because:

- Compounds such as UO$_2$, PuO$_2$ and ThO$_2$, which are fissile phases, are isostructural with the cubic structure of FSZ.
- Rare-earth sesquioxides (like Er$_2$O$_3$ and Gd$_2$O$_3$) are soluble in zirconia [50]. This opens the possibility of doping an actinide-bearing zirconia waste or fuel form with rare earth atoms, which can serve as depletable neutron absorbers [31], useful to enhance reactor safety.
- The material does not undergo a phase transition during heating and cooling. A phase transition may cause sweeping out of fission products.
- The zirconia matrix is stable under thermal annealing up to very high temperatures. As will be discussed in Chapter 5, a spinel matrix on the other hand dissociates at temperatures as low as 1600 K, which has a serious impact on the safety.

The phase diagram for the system ZrO$_2$-Y$_2$O$_3$ is shown in Figure 3.2. In FSZ, the ions are arranged in the cubic structure, which is shown in Figure 3.3. In the cubic structure, the cations are arranged in a face-centered lattice (the fluorite structure) with the anions occupying all the tetrahedral sites. Each metal cation is surrounded by eight oxygen anions, each oxygen anion is tetrahedrally coordinated with four metal cations. The oxygen ions form a cubic sublattice of half the lattice parameter of the fcc cell. Every alternate cube of oxygen ions has a zirconium ion in its centre and one cube has only one edge in common with another.
3.2 Defects in ceramics

Crystals contain imperfections which are classified according to their geometry and shape into point, line, planar and three-dimensional defects. These defects are described in many handbooks like e.g. [48, 52, 53].
3.2.1 Lattice defects in magnesium aluminate spinel

In MgAl$_2$O$_4$ the following defects (in Kröger-Vink notation) should be considered:

- **Vacancies:** In spinel V$_{\text{Mg}}$, V$_{\text{Al}}$ and V$_{\text{O}}$ can be distinguished as single vacancies, which are vacant magnesium, aluminium and oxygen sites.
- **Interstitial atoms:** Mg$^{i+}$, Al$^{i+}$ and O$^{i-}$ are magnesium, aluminium and oxygen ions at an interstitial site.
- **Extrinsic defects:** These defects are created as a result of the presence of impurities, mostly introduced into the material by the fabrication or sintering.
- Other defects such as Frenkel pairs, dislocation loops and extended defects, which will be discussed in the next subsection for fully stabilized zirconia.
- **Stoichiometry:** The ideal spinel crystal has an atomic structure which is defined by MgAl$_2$O$_4$, which is called stoichiometric spinel. However, it may happen that the spinel is non-stoichiometric (defined by e.g. MgAl$_2$O$_{4+x}$). Depending on the sign of $x$, there are excess oxygen ions (which will then be located in interstitial sites) or too few, yielding extrinsic oxygen vacancies. The deviation from stoichiometry can also occur in the magnesium or aluminium sublattice. The stoichiometry of most of the spinel specimens used in this thesis has not been investigated before fabrication or implantation.

3.2.2 Lattice defects in fully stabilized zirconia

In fully stabilized zirconia, the following defects have to be considered: stoichiometric defects and non-stoichiometric defects.

- **Oxygen vacancies:** The substitution of three-valent yttrium for four-valent zirconium creates anion vacancies in the crystal structure. Doping with yttria (Y$_2$O$_3$) can be expressed by the following defect formula:

  $$ \text{Y}_2\text{O}_3 \text{ in } \text{ZrO}_2 \rightarrow 2\text{Y}^{3+}_{\text{Zr}} + \text{V}_{\text{O}} + 3\text{O}_0. $$

  In this equation O$_0$ represents an oxygen ion in an anion lattice site. Y$^{3+}_{\text{Zr}}$ is an Y$^{3+}$ ion on an Zr$^{4+}$ ion lattice site. V$_{\text{O}}$ represents an oxygen vacancy. The ionic radius of Y$^{3+}$ is larger than the ionic radius of Zr$^{4+}$, so the average unit cell parameter of stabilized zirconia increases with increasing yttria fraction. The composition of the material is represented by the formula: (ZrO$_2$)$_{1-x}$(YO$_{1.5}$)$_x$(V$_{\text{O}}$)$_{0.5x}$. The oxygen vacancy concentration can thus be expressed as (0.5x)/(2-0.5x) which yields for the material used in this work an oxygen vacancy concentration of 2.5 at%.

- **Zirconium and yttrium vacancies:** V$^{i+}_{\text{Zr}}$ and V$^{i+}_{\text{Y}}$ are vacant lattice sites which are normally occupied by a zirconium or yttrium ion. These vacant sites can be created during helium ion implantation and may be a trap for the implanted helium ions.

- **Interstitial atoms:** Zr$^{i+}$, Y$^{i+}$ and O$^{i-}$ are a zirconium, yttrium and oxygen ion at an interstitial site, respectively. By ion implantation, an ion can move from its original lattice position and come to rest at an interstitial site, leaving a vacancy behind. This
is called a Frenkel pair. Such defects can occur both on the cation- (Frenkel defects) and anion-sublattice (anti-Frenkel defects).

- **Extrinsic defects:** Defects can also be created as a result of the presence of impurities in the host crystal. It is very difficult to avoid impurities in a material. Firstly, ceramics are often fabricated from different base materials (yttria-stabilized zirconia, ZrO$_2$ + Y$_2$O$_3$ can be fabricated from ZrOCl$_2$ + YCl$_3$). Then, during sintering of the powders, dirt present in the sintering oven may diffuse into the material as impurities. It is very difficult to predict if an impurity will occupy an interstitial site. Secondly, atoms introduced in the material during implantation can also be treated as impurities. An interstitial or a substitutional impurity is an impurity at an interstitial site or at a site where normally another atom is present, respectively.

- **F-centres:** These are oxygen vacancies at which additional electrons have been trapped.

- **Dislocation loops:** These can be introduced into the material during plastic deformation. Dislocations are, like most defects, thermodynamically unstable.

- **Schottky trio:** In this case, a complete ZrO$_2$ molecule is absent, introducing a vacancy complex.

- **Planar defects:** Planar defects are surface imperfections in solids that separate grains or domains of different orientation and include grain boundaries.

- **Three-dimensional defects:** In fully stabilized zirconia, three-dimensional defects in the bulk are formed by pores, cracks and inclusions. The density of a polycrystalline material will always be lower than the theoretical density of the material. For the FSZ investigated in the scope of this work, the density is about 96% of the theoretical density. This is caused by porosity between (open porosity) and inside (closed porosity) the grains. These porosities might be a trap for fission products, but also for fission gases.

- **Stoichiometry:** A material is called non-stoichiometric, when the ratio between cations and anions is different from that of the ideal chemical formula. Zirconia (ZrO$_2$) tends to be slightly sub-stoichiometric [53].

### 3.2.3 Location of oxygen vacancies in fully stabilized zirconia

A single charge-compensating oxygen vacancy is created for every two substitutional yttrium atoms (see Eq. 3.1). As shown in Figure 3.4 there are three possibilities for the position of this vacancy:

1. Both yttrium atoms are nearest neighbours to the oxygen vacancy.
2. Only one yttrium atom is a nearest neighbour to the oxygen vacancy.
3. Neither yttrium atom is a nearest neighbour to the oxygen vacancy.

Assuming oxygen has a fourfold coordination the fraction of ZrO$_8$ (a zirconium ion surrounded by 8 oxygen ions), ZrO$_7$ (a zirconium ion surrounded by 7 oxygen ions and an oxygen vacancy), YO$_8$ (an yttrium ion surrounded by 8 oxygen ions) and YO$_7$ (an yttrium ion surrounded by 7 oxygen ions and an oxygen vacancy) can be calculated as
Figure 3.4: Schematic illustration of three models for cation oxygen vacancy ($V_O$) association.

Figure 3.4: Schematic illustration of three models for cation oxygen vacancy ($V_O$) association.

a function of the $Y_2O_3$ fraction for all three possibilities. This has been done by Li et al. [54]; their data are tabulated in Table 3.2.

Table 3.2: Calculated fraction of four types of oxygen polyhedra around Zr and Y for different models of cation-vacancy association and a composition with a molecular fraction of $Y_2O_3$ of 10%.

<table>
<thead>
<tr>
<th>Model</th>
<th>fraction for each polyhedral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model 1</td>
<td>YO$_7$ ZrO$_8$ ZrO$_7$</td>
</tr>
<tr>
<td>Y-Vo-Y</td>
<td>18.2 63.6 18.2</td>
</tr>
<tr>
<td>Model 2</td>
<td>YO$_8$ YO$_7$ ZrO$_8$ ZrO$_7$</td>
</tr>
<tr>
<td>Y-Vo-Zr</td>
<td>9.1   9.1 54.5 27.3</td>
</tr>
<tr>
<td>Model 3</td>
<td>YO$_8$ ZrO$_8$ ZrO$_7$</td>
</tr>
<tr>
<td>Zr-Vo-Zr</td>
<td>18.2 45.5 36.4</td>
</tr>
</tbody>
</table>

In their work, Li et al. [54] show with measurements and models that, independent of the yttria-fraction, model 3 is probably the only applicable model for yttria-stabilized zirconia. This means that yttria is always 8-fold coordinated. This is also reported by Zacate et al. [55], who observed that large cations favour second-neighbour vacancies. Li et al. [54] have also investigated the Y-O distance in their specimens (with a molecular fraction of $Y_2O_3$ varying between 3 and 20 %). They found that the Y-O distance was 2.33 Å in all the investigated samples.
The following atomic radii for the atoms of FSZ can be used:

Table 3.3: Atomic radii for the individual atoms in yttria-stabilized zirconia.

<table>
<thead>
<tr>
<th>Atom</th>
<th>coordination</th>
<th>atomic radius (pm) [49]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>8</td>
<td>84</td>
</tr>
<tr>
<td>Y</td>
<td>8</td>
<td>102</td>
</tr>
<tr>
<td>O</td>
<td>4</td>
<td>138</td>
</tr>
<tr>
<td>VO</td>
<td></td>
<td>160-172</td>
</tr>
</tbody>
</table>

With a lattice parameter of 5.14842 Å, determined by XRD for the specimens used in this thesis, and the atomic radii given above, the yttrium atom is not expected to fit into the lattice. Zacate et al. [55] describe this problem in their work. They report that the zirconia atoms remain at the correct lattice positions, but that the oxygen atoms shift slightly from their positions to create extra space for the oversized dopant. For oversized cations, the only significant movement is the relaxation of the nearest neighbour oxygen ions along the \(<111>\) directions.

3.3 Simulation of \(\alpha\)-decay and ion implantation effects

Since an \(\alpha\)-particle comes never alone but always together with a recoil atom, the decay process in the lattice should somehow be simulated if one wishes to study only the effects of \(\alpha\)-decay and helium build-up in a solid. This can be done by implantation of helium ions. In this section, first an introduction to the \(\alpha\)-decay process and its damaging effects is given. Subsequently, an introduction is given to the technique of ion implantation and its impact on the material.

3.3.1 An introduction to \(\alpha\)-decay

The spontaneous emission of an \(\alpha\)-particle can be represented by the following process:

\[
\overset{\Lambda}{Z}X_n \rightarrow \overset{\Lambda - 4}{Z - 2}X'_n - 2 + \alpha. \quad (3.2)
\]

Rutherford has shown that the \(\alpha\)-particle is a nucleus of \(^4\text{He}\), consisting of two protons and two neutrons. The energy of the emitted \(\alpha\)-particle can be determined from the laws of conservation of mass and energy, linear momentum and angular momentum. In Table 3.4, the energies of the emitted \(\alpha\)-particles are given for the most common actinides in a nuclear fuel, together with the half-life of the parent actinide [56].

It can thus be seen that the energy of an \(\alpha\)-particle is in the order of 4.3 to 6.2 MeV. Typically, about 98% of the total energy released in the decay is released to the \(\alpha\)-particle and only 2% to the recoil atom [57]. If the \(\alpha\)-particle is emitted with an
energy of 5 MeV, the recoil nucleus carries an energy of about 100 keV. Although this energy is a small fraction of the total energy, the damage cascades caused by the recoil cannot be neglected. With respect to the effect of the decay of $^{239}$Pu in FSZ (the material described in Chapter 6), the following remarks can be made. The range of the recoil atom is of the nanometer range while the range of the $\alpha$-particle is in the order of micrometers. Within its very small range the recoil atom causes on the average 800 atomic displacements, while the $\alpha$-particle causes on the average 125 displaced atoms. Thus, the recoil atom causes many displacements over a small range while the $\alpha$-particle causes fewer displacements over a larger range. These displacements are not distributed homogeneously; most defects are formed at the end of the particle range.

### 3.3.2 Simulation of damage caused by $\alpha$-decay

During the $\alpha$-decay process an energetic $\alpha$-particle is emitted into the inert matrix material. From the data shown in Table 3.4 it can be seen that the $\alpha$-decay from most minor actinides is an ongoing and steady process due to the long half-lives of the parent nuclei. The ORIGEN computer code [58] was used to calculate the helium build-up in a typical UO$_2$ and MOX fuel after storage. Table 3.5 gives the composition of the fuels for which the calculations have been performed. A typical PWR neutron spectrum has been used. The irradiation power used was 35.8 MW/tHM (Mega Watt per ton Heavy Metal).
Table 3.5: Composition of fuels as used in ORIGEN [58] calculations. The calculations were performed for a standard PWR neutron spectrum and a power of 35.8 MW/tHM. The table gives the initial isotopic composition as fractions of mass of the actinides.

<table>
<thead>
<tr>
<th></th>
<th>UO₂</th>
<th>MOX</th>
</tr>
</thead>
<tbody>
<tr>
<td>235U</td>
<td>4</td>
<td>0.232</td>
</tr>
<tr>
<td>238U</td>
<td>96</td>
<td>93</td>
</tr>
<tr>
<td>239Pu</td>
<td>0</td>
<td>3.93</td>
</tr>
<tr>
<td>240Pu</td>
<td>0</td>
<td>1.62</td>
</tr>
<tr>
<td>241Pu</td>
<td>0</td>
<td>0.871</td>
</tr>
<tr>
<td>242Pu</td>
<td>0</td>
<td>0.339</td>
</tr>
</tbody>
</table>

The results of the ORIGEN calculations are shown in Figure 3.5 for two different burn-up (BU) values.

For UO₂-fuels, not much helium is built up in the fuel after irradiation. After $10^4$ years of cooling only about 0.04 helium atom will have been formed per initially present uranium atom. This can be explained by the long half-life of $^{238}$U and the small ($\sim 1\%$) quantity of actinides such as plutonium and americium present in the spent fuel. In the case of MOX about 5 times more helium is built up compared to the UO₂-fuel. Here the influence of burn-up can be seen. In the case of fuel containing plutonium, the plutonium will either be fissioned, or neutron capture processes will occur. As a result of neutron capture, higher actinides will be formed, and thus the actinide composition...
will change as a function of burn-up. From Table 3.4 and Figure 3.5 it can be seen that the half-lives of α-emitting actinides are in general relatively large and that it takes a long time to build up a large quantity of α-particles and decay damage in a nuclear fuel. In reality, it is very difficult, if not impossible, to distinguish between the radiation damage caused by α-decay and by other processes like neutrons, β-decay, recoil atoms and fission fragments from investigations performed on reactor irradiated materials. Therefore, in this study on the effect of the helium build-up and the damage caused in the material by α-decay it was decided to use helium-ion implantations. With an accelerator, helium-ions are implanted into the matrix sample in order to simulate the α-decay process. This has the following advantages:

- The damage caused by the helium ions (α-particles) can be studied unperturbed by other effects.
- If longer decay times must be simulated, more helium ions can be implanted. There is virtually no waiting time for helium build-up.
- Due to the absence of actinides, the investigated materials are not radioactive, which facilitates the handling of the samples. Working with non-active samples enables the use of many different methods of investigation.

There are, however, also disadvantages:

- In a real inert matrix material, the actinides will be distributed as small particles over the fuel (either microdispersed or macrodispersed.) Therefore, helium is implanted from the particle into a layer of about 5 µm thickness around the particle. In an implantation experiment where helium with a single energy is implanted, all the ions will end up in a narrow range.
- Damage is only introduced between the surface of the sample and the helium implanted zone.
- There is no damage in the material caused by the recoil atoms; the simulated situation is not realistic from this point of view.

### 3.3.3 An introduction to the theory of ion implantation

This subsection will give a short introduction on ion implantation. Ion implantation involves the bombarding of the surface of a sample with an accelerated beam of ions in a vacuum chamber. For the implantations performed with helium as a part of this thesis, implantation energies of 30, 200, 1000 and 2000 keV were used. The depth is determined by the initial energy and the mass of the ion, and further by the material bombarded. The ions dissipate their kinetic energy by elastic (nuclear) and inelastic (electronic) collisions with the atoms of the target. The energy losses result either in displacement of lattice atoms or in their ionisation or excitation. Both effects lead to the production of radiation damage (e.g. point defects, defect clusters). This damage can be stable or not, depending on parameters such as thermal diffusion in the medium and annihilation of defects by recovery. At present, there are several computer codes which can calculate implantation damage.
Some programs, based on molecular dynamics, can simulate up to $10^6$ interactions simultaneously. In this thesis, calculations with TRIM (version SRIM-2000) [4] have been performed. TRIM is based on the simulation of binary collisions. As most damage is introduced at the end of the range of the implanted helium, the energy of the implanted ions can be much lower than the 5 MeV of the $\alpha$-particle.

Nuclear collisions (elastic collisions)

High-energetic heavy ions (fission products (FP) at the end of their range and recoil atoms of the $\alpha$-decaying atoms), neutrons and $\alpha$-particles (at the end of their range) will produce displacements by direct collisions with the lattice atoms, whenever the energy transferred is higher than the displacement energy ($E_d$). The displacement energies determine the manner in which the energy dissipated by elastic collisions is partitioned among the atoms of the material and thus determine the production of defects. Displacement cascades will occur if the kinetic energy of the ion passing near the lattice nuclei (0.1 nm) is high enough to overcome the screening potential of the atoms (less than $\sim 100$ keV for medium and heavy atoms). If the kinetic energy is lower, electronic repulsion will dominate and the collision can be treated as a hard sphere collision. By elastic collisions, atoms in a sublattice are displaced and may come to rest at lattice sites of a different type. The atoms in the ceramic have different atomic masses and the energy for displacing an atom from its lattice site can be different for each of them [59]. In Table 3.6, the displacement energies $E_d$ for the atoms in fully stabilized zirconia [32] and spinel [19] used in this thesis are shown:

<table>
<thead>
<tr>
<th>Atom</th>
<th>Material</th>
<th>$E_d$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>MgAl$_2$O$_4$</td>
<td>30</td>
</tr>
<tr>
<td>Al</td>
<td>MgAl$_2$O$_4$</td>
<td>30</td>
</tr>
<tr>
<td>O</td>
<td>MgAl$_2$O$_4$</td>
<td>60</td>
</tr>
<tr>
<td>Zr</td>
<td>Zr$<em>x$Y$</em>{1-x}$O$_{1.5+0.5x}$</td>
<td>40</td>
</tr>
<tr>
<td>Y</td>
<td>Zr$<em>x$Y$</em>{1-x}$O$_{1.5+0.5x}$</td>
<td>40</td>
</tr>
<tr>
<td>O</td>
<td>Zr$<em>x$Y$</em>{1-x}$O$_{1.5+0.5x}$</td>
<td>40</td>
</tr>
</tbody>
</table>

Inelastic collisions (excitations)

When a charged particle/ion passes through matter it loses part of its energy via interactions with the electrons of the medium and also via electromagnetic radiation. Electromagnetic radiation produces effects similar to the electron interaction: the main effects are ionisation and excitation of the target atoms. The electronic energy loss is proportional to the energy, the charge of the ion and to the electronic density of the medium and is mostly converted to heat without producing lattice damage.
3.3.4 Damage introduced by ion implantation

The region between the surface and the helium implanted layer will contain point defects, which have been discussed in Section 3.2. During the helium implantations, a preferential forward momentum transfer to interstitials occurs, which might cause an excess of interstitials in the implantation direction and an excess of vacancies in the opposite direction. Damage introduced by implantation recombines easily in yttria-stabilized zirconia, while it is built up in spinel.

Amorphization

A material is called amorphous if the long range periodicity in the position of the individual atoms is missing. However, a degree of short-range order may remain. Disorder in the lattice can be achieved by introducing displacements by ion bombardment. To amorphize a ceramic by means of defect accumulation, a critical defect concentration must be reached. Many models have been developed to predict and describe the amorphization process (e.g. [60]) but it is beyond the scope of this thesis to treat these models in detail. Spinels can be amorphized by irradiating the material at cryogenic temperatures with e.g. xenon up to about 25 displacements per atom (dpa). For this, an implanted xenon fluence of about \(10^{15} \text{ cm}^{-2}\) is required. The dpa-level necessary for a complete amorphization of the material depends on the energy of the xenon ions [61, 62]. Under more realistic conditions, amorphous spinels can be formed by swift heavy ions as shown by Zinkle et al. [13], where amorphization occurred by irradiating spinel with 614 MeV xenon-ions at room temperature at a fluence above \(10^{15} \text{ cm}^{-2}\).

Many attempts have been made to amorphize fully stabilized zirconia. In Table 3.7 an overview is given of ion irradiation damage studies on cubic yttria-stabilized zirconia. The table has been taken from recent work of Afanasyev-Charkin and Sickafus [63]. From the table it can be seen that yttria-stabilized zirconia is a very radiation resistant material. Only Wang [68] has managed to amorphize the material by implantation of high-energy cesium ions at room temperature. However, in this case amorphization is caused by a chemical effect. Due to the high cesium concentration the material can not be defined as fully stabilized zirconia anymore. Amorphization of yttria-stabilized zirconia is caused by the large incompatibility in size and low mobility of cesium ions in the yttria-stabilized zirconia structure, reflecting a relatively low solubility of cesium in yttria-stabilized zirconia. Nevertheless, the cesium concentration at which amorphization of yttria-stabilized zirconia occurred (about 8 at.%) is well above the value that will typically be reached in an inert fuel matrix.
### Table 3.7: Ion irradiation damage studies of cubic yttria-stabilized zirconia.

<table>
<thead>
<tr>
<th>Type of ions and energy</th>
<th>Maximum fluence ion m$^{-2}$</th>
<th>dpa by author</th>
<th>dpa calculated with sputtering</th>
<th>Amorphization</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>240 keV Xe$^{+}$</td>
<td>$1 \times 10^{21}$</td>
<td>-</td>
<td>-</td>
<td>No</td>
<td>[64]</td>
</tr>
<tr>
<td>160 keV Pt$^{+}$</td>
<td>$5 \times 10^{20}$</td>
<td>-</td>
<td>-</td>
<td>No</td>
<td>[65]</td>
</tr>
<tr>
<td>400 keV Xe$^{++}$</td>
<td>$3 \times 10^{20}$</td>
<td>110</td>
<td>-</td>
<td>No</td>
<td>[27]</td>
</tr>
<tr>
<td>60 keV Xe$^{+}$</td>
<td>$1.8 \times 10^{20}$</td>
<td>-</td>
<td>-</td>
<td>No</td>
<td>[66]</td>
</tr>
<tr>
<td>1.5 MeV Xe$^{+}$</td>
<td>$1.8 \times 10^{20}$</td>
<td>-</td>
<td>-</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>72 MeV I$^{+}$</td>
<td>$5 \times 10^{19}$</td>
<td>7.7</td>
<td>-</td>
<td>No</td>
<td>[31]</td>
</tr>
<tr>
<td>400 keV Xe$^{++}$</td>
<td>$3 \times 10^{20}$</td>
<td>-</td>
<td>-</td>
<td>No</td>
<td>[26]</td>
</tr>
<tr>
<td>60 keV Xe$^{++}$</td>
<td>$1.8 \times 10^{20}$</td>
<td>-</td>
<td>-</td>
<td>No</td>
<td>[67]</td>
</tr>
<tr>
<td>340-400 keV Xe$^{++}$</td>
<td>$3 \times 10^{20}$</td>
<td>100</td>
<td>-</td>
<td>No</td>
<td>[23]</td>
</tr>
<tr>
<td>72 MeV I$^{+}$</td>
<td>$5 \times 10^{19}$</td>
<td>7.7</td>
<td>-</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>400 keV Cs$^{+}$</td>
<td>$1 \times 10^{21}$</td>
<td>330</td>
<td>195</td>
<td>Yes</td>
<td>[68]</td>
</tr>
<tr>
<td>70 keV Cs$^{+}$</td>
<td>$1 \times 10^{21}$</td>
<td>177</td>
<td>195</td>
<td>No</td>
<td>[63]</td>
</tr>
<tr>
<td>340 keV Xe$^{++}$</td>
<td>$1 \times 10^{21}$</td>
<td>-</td>
<td>-</td>
<td>No</td>
<td></td>
</tr>
</tbody>
</table>

3.4 **Defect behaviour under thermal annealing**

3.4.1 **Diffusion of defects**

Due to the thermal energy, lattice atoms are continually bumping into each other while vibrating vigorously around their equilibrium positions and exchanging energy with their neighbours and their surroundings. Sometimes, an atom together with its neighbours will gain sufficient energy to leave its position and migrate into an adjacent lattice site. This movement is called diffusion, and the process is essential for the recovery of defects in a ceramic material. For the diffusion of one atom, the neighbouring atoms play an important role, as a configuration has to move to make a jump possible. This should be born in mind in the rest of this section, where for simplicity reasons a single atom is described.

An atom in a ceramic can diffuse due to three different processes:

1. **Vacancy-assisted diffusion:** an atom or ion jumps from a regular site into an adjacent vacant site. In fully stabilized zirconia, due to the addition of yttria, oxygen vacancies are present in the material. An oxygen ion can make a jump from a regular oxygen position into an oxygen vacancy. As a result of the helium implantation also yttrium- and zirconium vacancies will be present.

2. **Interstitial diffusion:** an interstitial atom or ion moves from one interstitial site to the next. In fully stabilized zirconia, an ion in an interstitial site can move through
an oxygen vacancy to another interstitial position. This applies to helium diffusion in zirconia.

3. Interstitial mechanisms: an interstitial atom pushes an atom from a regular site into an interstitial site and moves then to the new vacant position.

For all three cases mentioned above, the atom must overcome an energy or activation barrier to make the jump. The diffusivity $D_{\text{ion}}$ of an atom or ion in a ceramic is a measure of the ease and the frequency with which the atom or ion jumps around in a crystal lattice in the absence of external forces.

The ionic diffusion coefficient $D_{\text{ion}}$ of an atom or ion can be expressed as [48]:

$$D_{\text{ion}} = F_m \exp \left( -\frac{\Delta S_m^*}{k} \right) \exp \left( -\frac{\Delta H_m^*}{kT} \right) = D_0 \exp \left( -\frac{Q}{kT} \right)$$

(3.3)

where $F_m$ is a material dependent constant defined as $\frac{1}{2} \hbar \lambda^2 \nu$, where $\nu$ is the attempt frequency and $\lambda$ is the elementary jump distance which is normally in the order of the atomic spacing, $\Delta S_m^*$ is the change in entropy before and after the jump, $k$ is Boltzmann’s constant, $\Delta H_m^*$ is the change in enthalpy and $T$ the temperature in K. The diffusion coefficient can thus be explained by an activation enthalpy ($Q$) and a pre-factor ($D_0$) which is material dependent.

### 3.4.2 Diffusion of matrix components

**Self-diffusion in fully stabilized zirconia**

In this subsection some data from the literature will be presented for the self-diffusion coefficients of the individual atoms present in yttria-stabilized zirconia with a molecular yttrium fraction of about 10%. The ionic diffusion coefficients as a function of temperature of $Y^{3+}$, $Zr^{4+}$ and $O^{2-}$ are shown in Figure 3.6. In the figure, measurements performed on $O^{2-}$-diffusion in the bulk are labelled (1). These measurements were performed by Fox et al. [69]. Also Perry et al. [70] measured the self-diffusivity of oxygen at 1500 K. They found a value between the markers labelled by (2). These data are higher than the data measured by Fox et al. Diffusivity of zirconium in the bulk was measured by Sakka et al. [71] and is labelled in the figure by number (3), while the curve with number (4) indicates the same data measured by tracer diffusion by Kilo et al. [72]. These data are in quite a good agreement with each other. The self-diffusivity of yttrium in the bulk was measured by tracer diffusion by Kilo et al. [72] as well (5). Grain boundary assisted self-diffusion of yttrium in a fully stabilized zirconia matrix was reported in the same reference and was measured by the same method (6). Finally, a typical diffusion coefficient for helium in a ceramic material is shown ($D_0$ is $4.7 \times 10^{-6}$ m$^2$s$^{-1}$ and $Q$ is 2.1 eV, as presented in Chapter 6 and in Ref. [73]). From the figure it can be seen that oxygen ions become mobile at lower temperatures than the helium atoms. The self-diffusion of yttrium and zirconium is lower than the typical diffusion of helium gas in fully stabilized zirconia. Thus, oxygen vacancies in-
Figure 3.6: Self-diffusion coefficients for the individual atoms of yttria-stabilized zirconia and of helium in yttria-stabilized zirconia with a molecular yttria fraction of about 10%. The numbers indicated in the figure refer to an explanation in the text.

Introduced by the implantation are probably recovered before helium diffusion becomes significant.

**Diffusion of impurities**

Impurities can be introduced in a material by the fabrication procedure, but also implanted ions and fission products can be treated as impurities. The size of the impurity is important for the way an ion can diffuse. Small ions (e.g. helium) can diffuse via interstitial diffusion or via vacancy-assisted diffusion. A larger ion will need a vacancy to be able to jump from one interstitial site to the next and in many cases will remain bound to the vacancy and therefore be substitutional. Diffusion will then only take place when an extra vacancy is arriving on a neighbouring position of the substitutional atom. The fully stabilized zirconia used in this thesis contains small quantities of impurities of which the principal component is hafnium.

**3.4.3 Recrystallisation of an amorphous specimen**

Once a material has been amorphized (See Subsection 3.3.4) it can be recrystallized by annealing to a sufficiently high temperature. Usually, the recrystallization occurs over a small temperature range where the individual atoms have sufficient energy to over-
come the energy barrier and assume the energetically more favourable ordered crystal structure. As fully stabilized zirconia does not amorphize under helium irradiation, effects of recrystallization during annealing have not been taken into account in this study.

### 3.5 Gas behaviour in ceramics under thermal annealing

#### 3.5.1 Diffusion in single crystals

The release of helium from single-crystalline zirconia will be a combination of dissociation of helium from defects and of diffusion. It is likely that the diffusing helium interacts with the intrinsic defects present in the zirconia. As pointed out earlier in Section 3.2 some 2.5% of oxygen vacancies are present which can trap the helium. If the initial helium concentration is high, a considerable fraction of the helium will agglomerate in large clusters, rather than be released, and eventually be retained in bubbles during thermal annealing. In that case the release will be dominated by dissociation from these bubbles. For low implanted helium concentration the release will be dominated by diffusion via the intrinsic traps. Therefore, the release of helium will be described in terms as follows.

The depth and time dependent helium concentration \( C(x,t) \) is given by the diffusion equation:

\[
\frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2},
\]

with the boundary condition

\[
C(x,t)_{x=0} = 0,
\]

where \( x \) is the depth below the sample surface and \( t \) the time. The diffusion coefficient \( D \) is defined as in Section 3.4.1:

\[
D = D_0 \exp \left( \frac{-Q}{kT} \right),
\]

where (see Eq. 3.3) \( D_0 \) is the pre-exponential factor, \( Q \) the activation enthalpy for helium, \( k \) is Boltzmann’s constant and \( T \) the temperature of the specimen. The pre-exponential factor has been described in Section 3.4.1 and is the product of the attempt frequency (\( \nu \)) which is of the order of the Debye-frequency \( \left(10^{12}-10^{13} \text{ s}^{-1}\right)\), and the entropy factor \( \exp(\Delta S^*/k) \). Since \( \Delta S^* \) is the difference between the entropy of the final state and the initial state of the diffusing atom it can turn strongly negative when
a jump is made from a bubble (very high entropy) to a very localized position in a vacancy (low entropy).

If mono-energetic ion implantations are concerned, the initial distribution of the diffusing matter can be described by a Gaussian profile with the maximum concentration at \( x=m \) according to:

\[
C(x,0) = C_0 = \frac{A_{\text{He}}}{\sigma \sqrt{2\pi}} \exp \frac{-(x-m)^2}{2\sigma^2},
\]

where \( \sigma^2 \) is the variance of the initial Gaussian distribution and \( A_{\text{He}} \) the maximum helium concentration in cm\(^{-2}\). The solution of the diffusion equation is given by:

\[
C(x,t) = \int_0^\infty C_0(x') \frac{1}{\sqrt{4\pi Dt}} \left[ \exp \left( \frac{-(x-x')^2}{4Dt} \right) - \exp \left( \frac{-(x+x')^2}{4Dt} \right) \right] x',
\]

where \( x \) and \( x' \) are indicators for the depth below the surface.

This integral has the following solution:

\[
C(x,t) = C_3 \left( \exp \left( \frac{-(x+m)^2}{4Dt + 2\sigma^2} \right) \left[ \text{erf} \left( \frac{-4Dmt + 2\sigma^2x}{C_4} \right) - 1 \right] \right) + C_3 \left( \exp \left( \frac{-(x-m)^2}{4Dt + 2\sigma^2} \right) \left[ \text{erf} \left( \frac{4Dmt + 2\sigma^2x}{C_4} \right) - 1 \right] \right)
\]

where \( C_3 \) and \( C_4 \) are defined as:

\[
C_3 = A_{\text{He}} \sqrt{\frac{1}{4(4Dt + 2\sigma^2)}}
\]

and

\[
C_4 = \sqrt{\frac{4Dt}{\pi}} (4Dt + \sigma^2).
\]

The function \( \text{erf} \) is defined as:

\[
\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp (-t^2) dt.
\]

The helium release rate \( J(t) \) is given by:

\[
J(t) = D \left( \frac{\partial C(x,t)}{\partial x} \right)_{x=0}.
\]
The above expressions can only be used when the temperature is kept constant, i.e. isothermal annealing. If ramp annealing is used, i.e. the temperature increases linearly with time, and the heating rate applied is defined as $\beta$, the temperature of the specimen can be described as:

$$T(t) = T_0 + \beta t,$$

(3.14)

with $T_0$ the starting temperature. It is now convenient to introduce the time integrated diffusion parameter $t'$, which is defined as $t' = \int_0^t D dt$, and rewrite the diffusion equation as follows:

$$\frac{\partial C(x,t)}{\partial t'} = \frac{\partial^2 C(x,t)}{\partial x^2}.$$

(3.15)

The parameter $t'$ indicates the status of the diffusion process irrespective of the heating procedure used. In fact it is proportional to the number of jumps made during the diffusion. The solution of Eq. 3.15 is similar to the solution of Eq. 3.8 with $Dt$ substituted by $t'$.

Results of a model calculation of diffusion of helium implanted into fully stabilized zirconia are shown in Figure 3.7. In Figure 3.7a, the depth dependent helium distribution for different annealing temperatures is shown. It can be noted that the diffusion profile first broadens and later shifts to larger depths. In Figure 3.7b, the theoretical helium fluence released from the sample surface is shown.

### 3.5.2 Grain boundary effects

If diffusion in a polycrystalline material is considered, a fraction of the implanted helium will diffuse into the grain boundaries and it is assumed that from there the helium diffuses easily towards the surface. The total concentration of gas ($C_t(x,t)$) in the material as a function of depth $x$ and time $t$ is defined as:

$$C_t(x,t) = C_g(x,t) + C_{gb}(x,t),$$

(3.16)

where $C_g(x,t)$ is the concentration in the grains and $C_{gb}(x,t)$ the concentration in the grain boundaries. The initial depth dependent concentration ($C_t(x,0)$) is known (e.g. from SRIM-calculations [4]). After implantation, a fraction $a$ ($a \leq 1$) will be implanted in the grains, thus:

$$C_g(x,0) = a C_t(x,0),$$

(3.17)

and

$$C_{gb}(x,0) = (1-a)C_t(x,0).$$

(3.18)
Figure 3.7: Results of calculations with the diffusional model for 200 keV helium implanted in FSZ. The heating rate assumed in the calculations was 10 K min\(^{-1}\). For \(D_0\) a value of \(4.7 \times 10^{-2} \text{ cm}^2\text{s}^{-1}\) was used. The activation enthalpy used was 2.07 eV. Figure a: the depth dependent helium profile for different annealing temperatures; Figure b: the temperature dependent helium release curve.

Now, the diffusion equation can be rewritten as:

\[
\frac{\partial C_g(x, t)}{\partial t} = D_{\text{He,g}}(t) \frac{\partial^2 C_g(x, t)}{\partial x^2} - D_{\text{He,g}} \eta_{gb} C_g(x, t) \tag{3.19}
\]

and

\[
\frac{\partial C_{gb}(x, t)}{\partial t} = D_{\text{He,gb}}(t) \frac{\partial^2 C_{gb}(x, t)}{\partial x^2} + D_{\text{He,g}} \eta_{gb} C_g(x, t), \tag{3.20}
\]

where \(D_{\text{He,g}}\) and \(D_{\text{He,gb}}\) are the diffusion coefficients within the grain or the grain boundaries, respectively. The loss of helium from the grains towards the grain boundaries depends on the areal trapping density \(\eta_{gb}\) in the material. For spherical grains it
can be calculated that \( \eta_{gb} = \frac{3}{r_{gb}^2} \), where \( r_{gb} \) is the grain radius. The trapping rate at the grain boundaries is given by \( \eta_{gb} D_{He,g} \).

Eq. 3.19 can be solved analytically, but the coupled Eq. 3.20 has to be solved numerically. The solution of Eq. 3.19 is similar to Eq. 3.8 but multiplied by a time dependent factor \( f(t) = \exp(-\eta_{gb} t') \):

\[
C_g(x,t) = f(t)C(x,t) \quad (3.21)
\]

In a special case it is not necessary to solve Eq. 3.4. If it is assumed that \( D_{He,gb} \) is much larger than \( D_{He,g} \) all helium arriving at the grain boundaries will directly be released. Then the release rate \( J(t) \) is given by:

\[
J(t) = J_{gb}(t) = \int_0^t \eta_{gb} D_{He,g} C_g(x,t^*) dt^*. \quad (3.22)
\]

The release rate can also be rewritten in terms of a first order desorption process of the total number of helium atoms in the material \( N_{He} \):

\[
\frac{\partial N_{He}}{\partial t} = -J_{gb}(t) = -\eta_{gb} D_{He,g} \int_0^t C_g(x,t^*) dt^* = -\eta_{gb} D_{He,g} N_{He} = -f_1 N_{He}, \quad (3.23)
\]

where \( f_1 = \eta_{gb} D_{He,g} \) is the frequency of the process.

In Figure 3.8 a model calculation is shown for a high grain boundary concentration based on a grain size of about 175 nm. The frequency \( f_1 \) of the first order process corresponds to \( 4.69 \times 10^8 \) s\(^{-1}\). It is observed that the shape of the profile does not broaden during thermal annealing. Helium is released in a narrow temperature interval.

### 3.5.3 Bubbles and bubble formation

In ion implantation, the implanted ions end up in a narrow layer inside the material. If a sufficiently high dose of gas ions is implanted, small bubbles will be created in this layer. If the material is subsequently annealed, several processes will occur. Firstly, the vacancies present in the material, either introduced by the ion bombardment or present in the material, will begin to diffuse as described in Section 3.4.1. Secondly, implanted ions will also begin to diffuse through the host material, as was described in Section 3.5.1. By diffusing, the ions will either reach the surface of the material and be released or they will be re-trapped in the material, possibly forming bubbles. Thirdly, by increasing the temperature the pressure in the bubbles already present in the material increases. At sufficiently high temperatures, the bubbles will attract vacancies until the
bubbles are in equilibrium with the vacancies. The gas pressure \( p_b \) in equilibrium bubbles with radius \( r \) is defined as:

\[
p_b = \frac{2\gamma}{r},
\]

(3.24)

where \( \gamma \) is the surface energy of the bubble. Bubbles can be located within a grain (intragranular bubbles) or at grain boundaries (intergranular bubbles).
3.5.4 Coarsening: migration, coalescence and Ostwald ripening

The growth of bubbles or voids in a material is called coarsening. Two mechanisms can play a role:
1. Migration and coalescence, and
2. Ostwald ripening.

The first mechanism is the migration of bubbles or vacancy clusters, occurring for very small bubbles by a diffusion mechanism. When the bubbles or clusters meet each other they coalesce into a larger bubble or cluster.

The Ostwald ripening process was originally developed to explain the coarsening of precipitates in solids in terms of growth of the larger precipitates at the expense of the smaller ones. Provided there is a sufficient solubility of the precipitated species and a corresponding reflective atomic mobility, a two-phase dispersion will coarsen by transfer of matter from small to large particles. Although the phenomenon was already observed in 1900, the basic theory of particle coarsening was developed almost sixty years later by Lifshitz and Slyozov [74] and Wagner [75]. Migration may occur via diffusion of atoms on the bubble surface.

Large bubbles are energetically more favoured than smaller bubbles. While the formation of many small bubbles is *kinetically* favoured, (i.e. they nucleate more easily), the formation of large bubbles is more favourable in a *thermodynamic* sense. Thus, from the standpoint of kinetics, it is easier to nucleate many small bubbles. However, small bubbles have a higher ratio of surface area to volume than large bubbles. Large bubbles represent a lower energy state than small bubbles. Thus, many small bubbles will attain a lower energy state if transformed into large bubbles. This is called the Ostwald ripening process.

3.5.5 Helium release from bubbles

Helium can be released from a bubble in two ways. Firstly, the surface of the material may vaporize until a bubble layer is reached. In the experiments where helium is implanted in either FSZ or spinel this theory does not have to be taken into account as the material does not vaporize at the investigated temperatures. Secondly, the gas from the bubble can be thermally re-solved in the bulk. This, of course, depends on the solubility of the second phase, in our case helium, in the matrix material. For the time being, the helium solubility in fully stabilized zirconia is not known. A bubble that has released its helium is called a void.
3.6 Analysis of helium desorption spectra

A temperature dependent helium release spectrum is the result of the defect reactions as previously described. The method to analyse a helium desorption spectrum depends on the way of heating. In Figure 3.9, three different methods of heating the specimen are described. In Figure 3.9a, the temperature profile of a ramp annealing is shown, Figure 3.9b shows the temperature profile for partial annealing, where the maximum temperature is increased after every annealing step. Figure 3.9c displays an example of a stepwise heated annealing profile, where the temperature becomes stable before it is increased again.

![Figure 3.9](image)

**Figure 3.9:** Examples of the various ways of heating in the Knudsen cell and in THDS. Figure a: a temperature profile for a constant ramp rate; Figure b: a temperature profile for heating with intermediate cooling; Figure c: a temperature profile for stepwise heating without intermediate cooling.

In the following subsections the analysis of desorption spectra measured with these temperature profiles is described.
3.6.1 Ramp annealing and stepwise annealing

Particularly when high ramp rates are used, a delay between sample and crucible temperature will occur. It is then very important to apply a correction to the temperature data as the diffusion coefficient is a strong function of temperature. If only a diffusion process is expected, the data can be fitted with the model described in Section 3.5.1. If a polycrystalline material is used, the model described in Section 3.5.2 must be used. In this model the areal trapping density \( \eta_{gb} \) can be estimated from microscopic investigations of the samples.

3.6.2 Partial annealing

When the release is a first-order desorption process, the time dependent release can be described as:

\[
\frac{dN}{dt} = -N f,
\]

with \( N(t) \) the number of helium atoms retained in the sample and \( f = f_0 \exp(-Q/kT) \) the temperature dependent release frequency. If we consider only the first part of the release curve, the change in \( N \) is very small so we can assume \( N \) to be constant and equal to \( N_{0,i} \), which is the number of helium atoms at the beginning of the annealing step \( i \). Plotting the logarithm of the release rate versus \( 1/T \) will then show Arrhenius behaviour. From the slopes of the curves the activation enthalpy \( Q \) can be derived. The pre-exponential factors \( f_{0,i} \) of the different partial annealing steps \( (i) \) can be derived by calculating

\[
f_{0,i} = \frac{dN}{dt} \frac{1}{N_{0,i}} \exp\left(\frac{Q}{kT}\right)
\]

(3.26)

The pre-exponential factor is the product of an attempt frequency \( (v) \) and the entropy factor \( \exp(\Delta S/k) \) as described in Eq. (3.3).

It can be shown that a diffusion process can also be approximated by a first order desorption process when the released quantity remains small [76]. When the temperature is changed the first quantity to change in the expression for the release rate (Eq. 3.19) is the diffusion coefficient \( D \) and not the gradient at the surface \( (\partial C/\partial x)_{x=0} \). Therefore, until the concentration profile changes considerably, Arrhenius behaviour will be observed with \( Q \) as the activation energy and \( D_0 \) as the pre-factor. The pre-factor is dependent on the gradient near the surface. When at high temperature most of the helium is released the gradient is smaller, and therefore the pre-factor will be smaller.

Model calculations were performed with the diffusion model described in Subsection 3.5.1, in which a heating and cooling schedule was applied for the temperature profile. The results of these calculations are shown in Figure 3.10. In Figure 3.10a, the time dependent helium release curves are shown. In Figure 3.10b, the temperature depen-
dent helium release is shown, where only helium release during heating is shown. In Figure 3.10c, the Arrhenius plots for the release curves are shown as a function of $1000 \times T^{-1}$. Finally, Figure 3.10d shows the pre-factors and activation enthalpies as calculated from the Arrhenius plots. It can be seen that the activation enthalpies de-

\[ \text{Figure 3.10: Results of a calculation for a partially annealing process for helium in a single crystal of FSZ. The pre-exponential factor was set to } 4.69 \times 10^{-2} \text{ cm}^2 \text{s}^{-1} \text{ and an activation enthalpy of } 2.20 \text{ eV was used. A helium concentration of } 1 \times 10^{15} \text{ cm}^{-2} \text{ was assumed. Figure a: The time dependent helium fluence. Figure b: The temperature dependent helium fluence where only the heating is considered. Figure c: The Arrhenius plot for the data plotted in Figure b and Figure d: The calculated pre-factors and activation enthalpies from the slopes plotted in Figure c.} \]

drived from the figure are in good agreement with the initial 2.20 eV assumed in the model. Small deviations can be explained by the fitting of the curves, in which only a limited number of digits is taken into account. The pre-exponential factor decreases
with increasing annealing temperature. The calculations presented in Figure 3.10 were performed for helium in static zirconia, i.e. the material properties do not change as a function of annealing time, and an ideal crystal is assumed. For smaller quantities of helium and a different helium distribution profile, the change in entropy before and after the jump decreases.

Similar calculations were performed for the diffusion model of a polycrystalline specimen. Results of these calculations are shown in Figure 3.11. On the basis of this figure, the following remarks can be made. Again, the fitted activation enthalpies agree very

**Figure 3.11:** Results of a calculation for a partially annealing process for helium in polycrystalline FSZ. The pre-exponential factor has been set to $4.69 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ and an activation enthalpy of 2.20 eV was used. The initial helium concentration was set to $1 \times 10^{15} \text{ cm}^{-2}$. Helium entering the grain boundaries is released toward the surface very fast. Figure a: The time dependent helium fluence. Figure b: The temperature dependent helium fluence where only the heating is considered. Figure c: The Arrhenius plot for the data plotted in Figure b and Figure d: The calculated pre-factors and activation enthalpies from the slopes plotted in Figure c.
well with the 2.2 eV assumed in the calculation. The pre-exponential factor decreases with increasing annealing temperature. In the model, once helium is released towards the grain boundary it is immediately released towards the surface. It could however also be possible that the grain boundaries form a trap for the helium, and that helium first has to resolve again in the grain before it can diffuse to the surface.
Chapter 4

Implantation experiments performed on spinel

This chapter first presents an overview of irradiation experiments performed on spinel as found in the literature. Subsequently, new results on helium implanted spinel will be discussed. Finally, the behaviour of helium and xenon in an amorphous spinel matrix will be described.

4.1 Experience with regard to irradiation damage in spinel, based on former research

In order to summarize the spinel behaviour under irradiation conditions, a report [3] was recently issued by CEA, ITU, NRG, IE, IRI and JAERI which gives an overview of the results achieved with spinel. This section summarizes the results of experiments performed to investigate the damage by fission products and $\alpha$-decay in spinel.

4.1.1 Fission product damage

During the past decades many investigations on the effects of fission product damage in spinel were carried out. In order to simulate the damage caused by fission products when their kinetic energy is dissipated, spinel targets have been irradiated by krypton [6, 7, 8, 9, 10, 11, 12, 13], xenon [6, 7, 8, 9, 10, 12, 13, 14], iodine [8, 9, 10, 12, 13] and antimony [8, 9, 10] ions. Large accelerators can provide beams of heavy ions with energies of - or even surpassing - fission energy. The key parameter determining the effects of highly energetic ions passing through matter is the energy loss to the lattice as a function of the distance travelled, $(dE/dx)$. These losses arise mainly through excitation and ionization of the target atoms, i.e. they are electronic energy losses (see
Implantation experiments performed on spinel

subsection 3.3.3). The energy fraction of heavy ions at fission energy (or higher), dissipated by collisions with the electrons of the atoms in the crystal, is much higher than the fraction that leads to direct displacements of the atoms in the crystal (nuclear energy loss).

An important macroscopic effect of irradiations with fission products is the swelling of the target (up to 30%) for sintered specimens irradiated at room temperature at a fluence of $10^{16}$ ions cm$^{-2}$. Significant swelling was found already for rather low irradiation fluences ($10^{13}$ ions cm$^{-2}$) [9, 13].

It was shown by SEM examinations that blisters form at the surface of the spinel sample when irradiated with heavy ions with a high dE/dx (larger than 16.5 keV/nm, energies $\gg$ 70 MeV) at fluences above $10^{13}$ ions cm$^{-2}$ [19].

Spinel was shown to turn amorphous when irradiated with typical fission products such as iodine of fission energy (72 MeV) at a fluence of $10^{16}$ ions cm$^{-2}$ [12] or $5 \times 10^{15}$ ions cm$^{-2}$ [10] (70 MeV). The threshold dE/dx for inducing amorphization was determined to be around 6 keV nm$^{-1}$. The swelling decreased from approximately 30% for irradiation at room temperature to approximately 10% for irradiation at 900°C. At 1200°C swelling was essentially absent. The study also showed that ionizing radiation (exposure to the electrons of an electronic microscope beam) induces recrystallization of amorphous spinel.

4.1.2 α-Decay damage

As spinel is being considered as a transmutation matrix, the effects of α-decay damage and helium concentration build-up are important. Therefore, many irradiation experiments with α-particles (helium ions accelerated in a Van de Graaff generator) have been performed in the past years [6, 18, 77]. Channelling properties of spinel, i.e. the possibility for α-particles to penetrate spinel along channels in the interstitial space, were investigated by Turos et al. [6]. Studies were performed on the recoil of the α-emitting nucleus by irradiation of spinel with heavy ions in the 100 keV range [77]. Fromknecht et al. [19] showed that spinel is very resistant against the electronic part of the stopping of the helium-ions. Although very high fluences were used, dechanelling (i.e by blocking of a channel) along the penetration trajectory was small and a damage volume was only seen at the end of the penetration.

Rondinella et al. [38] did not observe damage at the surface nor along the major part of the paths of the helium ions for spinel implanted with $1.2 \times 10^{17}$ and with $5 \times 10^{16}$ ions cm$^{-2}$ at 260 keV. The same was observed using positron beam analysis as described in Ref. [21].
4.1.3 Helium release mechanisms in spinel

The spinel lattice contains two types of interstitial sites which provide sufficient room to accommodate helium ions: tetrahedral sites with a cation occupancy of 12.5%, and octahedral sites which are 50% occupied. After implantation, helium can either be found at such an interstitial position, or in a vacancy initially present in the material or introduced during implantation. Indeed, Rutherford backscattering measurements performed by Allen [17] showed that at 300 K 95% of the helium occupies the empty octahedral sites in spinel.

Helium is preferentially trapped in oxygen vacancies. For polycrystalline materials, also grain boundaries are a favourable location for the helium ions. Implantation induced damage is mainly found at the end of the helium ion penetration path, where most of the helium will be trapped.

Several thermal helium release studies, e.g. [19, 21, 78], have been performed on helium implanted samples. The temperature at which helium is released from the sample during the annealing experiments depends on whether the material is single- or polycrystalline, on the implantation energy, heating rate and the implanted helium fluence. In general it can be said that helium is released between 800 and 1600 K. In Ref. [21] it is concluded that for low implanted helium doses, helium is released from single vacancies with an activation enthalpy of 1.8 eV. For higher implanted fluences, helium is released from vacancy clusters characterized by an activation enthalpy of 2.35 eV.

The concentration of defects at the start of the desorption process is essential for the formation of bubbles and bubble growth during the annealing and therefore for the modelling of the desorption profile. Single crystals can be used to elucidate the release of helium from the bulk of spinel. For the analysis of helium desorption spectra from spinel the following desorption processes should be taken into account:

- In order to start the release process, helium first has to dissociate from its trap, which can be either the octahedral or tetrahedral site, a vacancy or a bubble;
- Helium is released from this trap by adding energy in the form of heat, which will lead to a diffusion process through the material until the surface is reached;
- In the case of a polycrystalline specimen, helium will move along the grain boundaries as soon as it leaves the grain. A much faster diffusion process results, called grain-boundary assisted diffusion;
- In the bulk of the material, helium bubbles may form and grow;
- During thermal annealing, blisters (bubbles just under the surface) can be formed;
- For high helium fluences (larger than $6.4 \times 10^{16}$ cm$^{-2}$ at 2 MeV), flaking may occur. Flaking takes place if the size and density of the bubbles are sufficiently large to cause extensive inter-bubble connection. Cracking or spalling (violent cracking) of the material may result. This is recognizable in the release spectrum as a very sharp release peak;
- Otherwise, helium can resolve from bubbles and pores in the matrix. It is then released via a diffusion process. This can either be interstitial diffusion or vacancy- or grain-boundary assisted diffusion.
In several papers the formation of helium bubbles following $\alpha$-irradiation in spinel has been reported, e.g. at a helium fluence of $1.8 \times 10^{16}$ ions cm$^{-2}$ (60 keV, $^4$He$^+\). These bubbles had a size of 0.9 nm at room temperature and 3.5 nm at 923 K [15]. It was observed that bubble formation occurs at a fluence of $6 \times 10^{15}$ at 35 keV and that the bubble size increases with increasing fluence. Fromknecht et al. [19] observed blistering and a large concentration of $\mu$m-size bubbles when the local helium concentration was larger than 1 at.%. One of the specimens, implanted with 260 keV ions and annealed at 500 °C during approximately 3 hours, showed diffusional release of helium, but most of the release was due to blister formation and subsequent cracking and spalling. Blistering of samples with a high initial helium concentration was also reported by Neeft et al. [78]. Helium concentration profiles recorded by NDP showed that after blistering had occurred a small amount of helium was left in the area of the material just below the blister.

Pychlau [18] derived the swelling of helium versus the concentration using the bubble density and the size of the bubbles observed by TEM. Only swelling to a value of 3.4% was observed for implantation at 473 K with a helium concentration at the implantation depth of about 10 at.%. At similar doses but at a temperature of 1073 K no swelling of spinel was observed. This is consistent with the earlier observation that helium, unlike the heavy fission ions, does not heavily damage the spinel lattice. At higher temperatures, the swelling disappears as the lattice recovers.

In addition to simulations, in-situ experiments have been performed in the framework of the EFTTRA collaboration (Experimental Feasibility of Targets for Transmutation). A microdispersed spinel matrix with americium was irradiated in the HFR at Petten. The swelling of this material under neutron irradiation and during the transmutation process turned out to be very large. An explanation of the behaviour of the helium originating from the $\alpha$-decaying actinides in the spinel matrix was provided by the helium and fission gases produced in the EFTTRA-T4 experiment. The helium production in EFTTRA-T4 was approximately $5.1 \times 10^{20}$ He cm$^{-3}$, which corresponds to an atomic concentration of 0.50 at.% in spinel. The EFTTRA experiment and the possible causes for the swelling of the target will be described in detail in Chapter 5 of this thesis.

### 4.1.4 Conclusions of former research

From the large number of spinel irradiations (both fission gases and $\alpha$-decay damage), performed in the past years as single effect studies in order to understand the response of spinel to the different causes of damage, one can draw the following general conclusions: a) spinel has shown to be very stable against neutron and $\alpha$-particle irradiation, b) the heavy recoil atoms of the $\alpha$-decay produce significant disorder and damage but do not amorphize spinel, and c) a large swelling and amorphization is observed when spinel is irradiated with fission products of fission energy, with the energy loss $dE/dx$ as important parameter and d) during thermal annealing, helium is released between 800 and 1600 K.
4.2 Helium release experiments on implanted polycrystalline spinel

4.2.1 Sample preparation and implantation characteristics

Three additional experiments on spinel were performed as a part of this thesis in order to obtain more insight into release mechanisms of helium in polycrystalline spinel and in order to show the applicability of the Knudsen cell method for this type of analysis. Polycrystalline spinel specimens, of which the grain size is unknown, were polished down to a surface roughness less than 1 $\mu$m. The samples were implanted in the Van de Graaff accelerator of the IFP/FZK with $^4$He at 2 MeV. An overview of the sample irradiation conditions and thermal treatment in the Knudsen cell is given in Table 4.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>He-fluence (cm$^{-2}$)</th>
<th>Heating</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$4.3 \times 10^{16}$</td>
<td>Stepwise</td>
</tr>
<tr>
<td>B</td>
<td>$8.6 \times 10^{16}$</td>
<td>Ramp: 10 K min$^{-1}$</td>
</tr>
<tr>
<td>C</td>
<td>$1.7 \times 10^{17}$</td>
<td>Stepwise</td>
</tr>
</tbody>
</table>

TRIM-calculations (version SRIM-2000 [4]) were performed to predict the implantation profile and the displacements produced in the spinel by the helium. The results of these calculations are shown in Figure 4.1.

Figure 4.1: Results of TRIM calculations for 2 MeV $^4$He-ions in spinel. On the vertical axis the helium concentration in cm$^{-3}$ is shown (thin line) and on the vertical axis on the right (bold curve) the displacements per atom (dpa). The data refer to sample C, implanted with $1.7 \times 10^{17}$ He cm$^{-2}$. The displacement energies used are 30/30/60 eV for Mg/Al/O, respectively.
The data in the figure were calculated for sample C, i.e. an implanted dose of $1.7 \times 10^{17}$ He cm$^{-2}$. According to the TRIM calculations, helium is implanted at a depth of about 4.4 $\mu$m and the implanted region is quite narrow. It should be noted that in the region just below the surface, the displacements per matrix atom are negligible compared to those in the helium implanted region. This was also discussed in the previous subsection where reference was made to the work of Rondinella et al. [38] who observed hardly any damage between the surface and the helium implanted layer. For sample C, the calculated maximum helium concentration is about 6.7 at% and the maximum in the displacements is predicted to be about 4.3 dpa. The possibility of blistering should therefore be taken into account when analysing the helium desorption spectra.

### 4.2.2 Experimental results

Owing to the slow heating rate of sample B, the data recorded with the mass spectrometer are difficult to analyse as the signal exceeds the background only slightly. For this reason, the following discussion will focus on samples A and C. In Figure 4.2a, the release profile for sample C ($1.7 \times 10^{17}$ cm$^{-2}$) is shown as a function of annealing time. The sample temperature as a function of time is indicated by the 'staircase' line. In Figure 4.2b, these data are shown for sample A ($4.3 \times 10^{16}$ cm$^{-2}$). The signal of the mass spectrometer is given in Ampere, as the calibration factor determined in Chapter 2 only applies for an ionisation energy of 70 eV. In the measurements shown in Figures 4.2a and 4.2b an ionisation energy of 40 eV has been used. Figures 4.2c and 4.2d show the fractional release for both samples as a function of temperature.

The helium release begins at a temperature of about 800 K and is almost complete at 1800 K. For the low-dose sample A, a larger fraction of the helium is retained up to higher temperatures than for sample C.

### 4.2.3 Discussion

As described previously, for helium concentrations larger than 1 at% the possibility of blistering should be taken into account. Although the helium concentration is larger than 1 at% in samples A and C, no effects of blistering could be observed from the helium release profile and from SEM investigations.

It is expected that after implantation helium will be trapped in single vacancies and interstitials at the end of the implantation range. In order to describe the helium release we assumed two stages. The release mechanism for the low-dose sample begins with a small amount of helium release via the grain boundaries at low temperature (stage 1), and then continues with a major release that can be attributed to the resolution of helium from bubbles and subsequent release by a diffusion process (stage 2). For the higher dose a different release mechanism has been assumed, i.e. a larger fraction of helium is released at lower temperatures as can be seen in Figure 4.2c. A possible ex-
Figure 4.2: The release rate of helium in spinel as a function of time for the high-dose sample (figure a) and the low-dose sample (figure b). The fractional release rate during laboratory thermal annealing in the ITU-Knudsen cell together with the fit of the data for the high-dose sample is plotted in figure c and for the low-dose sample in figure d. An ionisation energy of 40 eV has been used in the mass spectrometer.

Explantation for this is the presence of very small high pressure bubbles, which pressure is likely to be of the order of magnitude larger than 1000 bar. Already at low temperatures, over-pressurized helium bubbles might release helium at low temperature or inter-bubble fracture might occur which induces blistering and flaking with as a consequence early release of helium. The remaining helium might be trapped in bubbles and be released at higher temperature (stage 2).

The activation enthalpies and pre-factors for the different stages were obtained by fitting the diffusional model described in Section 3.5.1 to the experimental data from samples A and C. The presence of grain boundaries was neglected in this analysis as the grain size is unknown. Bubble formation was also left out of consideration. The results of the fits and the calculations are indicated in Figures 4.2c and 4.2d and in Table 4.2. Notwithstanding the simplicity of the model, the results of the fit seem to be good.

The activation enthalpies with their error margins are in agreement with the data presented in Ref. [21], where an activation energy of 1.8 eV is given for interstitial diffusion of helium in spinel. Neeft et al. [21] have shown by numerical simulations that the dominant process in the helium release is interstitial diffusion and not the dissociation from vacancies.
Table 4.2: Activation enthalpies ($Q$) and pre-factors ($D_0$) for the two stages of diffusion of helium implanted with an energy of 2 MeV in polycrystalline spinel, calculated with the diffusion model described in Section 3.5.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$Q_1$ (eV)</th>
<th>$Q_2$ (eV)</th>
<th>$D_{01}$ (cm$^2$ s$^{-1}$)</th>
<th>$D_{02}$ (cm$^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.33±0.31</td>
<td>1.73±0.37</td>
<td>0.93±0.11</td>
<td>0.26±0.18</td>
</tr>
<tr>
<td>C</td>
<td>1.36±0.42</td>
<td>1.77±0.47</td>
<td>0.84±0.19</td>
<td>0.45±0.21</td>
</tr>
</tbody>
</table>

4.2.4 Conclusion

Three Knudsen cell experiments were performed on polycrystalline spinel implanted with 2 MeV $^4$He-ions. Helium is released in two stages with activation enthalpies of 1.4 and 1.7 eV and pre-factors for diffusion of about 0.9 and 0.35 cm$^2$ s$^{-1}$. The results of these experiments are in good agreement with the data presented in the literature and lead to the conclusion that helium release can be investigated successfully in the Knudsen cell of ITU.

4.3 Helium in amorphous spinel

4.3.1 Introduction

Spinel has received considerable attention as a potential inert matrix material because of its relatively high thermal conductivity and its fairly good stability against neutron and $\alpha$-particle damage [79]. However, spinel has been shown to succumb to an amorphization transformation under the impact of fission fragments associated with a large swelling [9]. Following the EFTTRA experiments [80] described in Chapter 5, where americium was transmuted in a spinel matrix, interest began to grow in the interaction between helium gas build-up in the fuel and helium mobility in a spinel matrix which becomes increasingly amorphous due to fission product damage. In many oxides, such as Al$_2$O$_3$, TiO$_2$, U$_3$O$_8$, SiO$_2$ etc., that turn amorphous under the impact of energetic heavy rare gas ions such as xenon and krypton, gas is swept out and released during recrystallization, i.e. at much lower temperatures than in the crystalline oxides [81]. It is an open question whether this is also true for helium, which is expected to be released at lower temperatures from the crystalline oxides than krypton and xenon. The behaviour of helium and xenon in an initially amorphous spinel matrix has not been studied so far, and therefore the following processes will be investigated:
• Helium release from amorphous spinel, compared with results for crystalline spinel;
• Xenon release from amorphous spinel, compared with results for crystalline spinel;
• Helium and xenon release during recrystallization;
• Defect formation and annealing in the presence of helium and xenon.

4.3.2 Experimental procedure

Sample preparation

Spinel single crystals of Union Carbide with (111) orientation were implanted at the Los Alamos Ion-Beam Materials Laboratory with 450 keV Xe$^{3+}$-ions at a cryogenic temperature (100 K). This procedure is known to yield an amorphous layer on the spinel specimen [62]. The temperature is not critical, as an amorphous layer in spinel can also be produced under more realistic reactor conditions, e.g. by irradiating spinel with 614 MeV Xe-ions at room temperature at a fluence above $10^{15}$ cm$^{-2}$.

The samples of Union Carbide were tilted 7° relative to normal beam incidence in order to decrease channelling. The implantation was performed with a flux of $8 \times 10^{11}$ Xe cm$^{-2}$ s$^{-1}$ up to a total fluence of $1 \times 10^{16}$ Xe cm$^{-2}$. A second irradiation on the same surface was performed with 14 keV He$^+$-ions at cryogenic temperatures where the sample was tilted 61° relative to normal beam incidence in an attempt to deposit helium approximately at the centre of the xenon layer. The implantation flux used was $7 \times 10^{12}$ He cm$^{-2}$ s$^{-1}$ up to a total implanted fluence of $1 \times 10^{15}$ He cm$^{-2}$.

Damage Distribution and Implantation Profile

Calculations with TRIM version SRIM-2000.10 [4] were performed with threshold displacement energies of 30/30/60 eV for Mg/Al/O [19], respectively, in order to simulate the damage distribution and the implantation profile of helium and xenon in the target material. The results are shown in Figure 4.3. The calculations show a maximum in the displacements caused by xenon for a fluence of $10^{16}$ Xe cm$^{-2}$ of about 25 displacements per atom (dpa). The dpa-level caused by the helium implantation is too small (less than 0.1 dpa) to be depicted in the figure. According to TRIM, helium is implanted in the centre of the damaged layer produced by the xenon implantation. As for the position of the amorphous layer produced, Yu et al. [62] have compared TRIM calculations for 400 keV xenon, tilted over 10°, with RBS and TEM measurements. According to Yu’s TRIM calculations, the projected range of 400 keV Xe-ions is 90 nm. The thickness of the amorphous layer measured by cross-sectional TEM is 165 nm at a fluence of $10^{16}$ Xe cm$^{-2}$.

In Ref. [82], TEM observations give a thickness of 155 nm for an amorphous spinel layer created by the implantation of 340 keV Xe$^{2+}$-ions. This is according to their TRIM calculations at the end of both the xenon ion and damage range. From these
Implantation experiments performed on spinel

Figure 4.3: Results of a TRIM calculation for xenon ($10^{16}$ Xe cm$^{-2}$) and helium ($10^{15}$ He cm$^{-2}$) in spinel. The displacements caused by helium ions are negligible compared to those caused by the xenon ions. Displacement energies of 30/30/60 eV for Mg/Al/O were used, respectively.

measurements presented in Refs. [62, 82], it may be concluded that the amorphous layer ends at the end of the range of the displacements calculated by TRIM.

The sample used for the current investigations can be compared with the sample described in Ref. [62], though the xenon implantation energy is slightly higher (450 keV vs. 400 keV). One therefore expects to find an amorphous layer slightly thicker than 165 nm. Although the sample was tilted during implantation, the possibility of channeling of the xenon ions should be taken into account; part of them might be implanted deeper than predicted by TRIM. The calculations for helium were performed for spinel without xenon. TRIM calculations with an addition of 1.5% xenon showed negligible differences. In reality, the presence of xenon and the amorphous structure influences the helium path, the damage blocks channeling, and xenon ions scatter the helium. A larger volume (31%) for amorphous spinel (i.e. a lower density), compared to crystalline spinel has been reported [83]. The lower density may influence the depth distribution of the helium. As a final remark with regard to the calculations it can be said that sputtering was also not taken into consideration. For this process, in which the xenon ions damage the sample surface, it is assumed that each impact of a xenon ion sputters nine atoms of the spinel-matrix off the surface, resulting in the removal of a layer of 8.5 nm of the sample at the end of the implantation. Due to sputtering the implantation profile will slightly flatten, and the maximum of this profile is shifted a little towards the surface.

In order to check if the sample has reached an amorphous state, Rutherford backscattering measurements (RBS) for the present sample were performed at Los Alamos National Laboratories (LANL) and are shown in Figure 4.4. The RBS spectra for spinel
Figure 4.4: RBS measurements for spinel: A) random pristine spinel, B) xenon implanted spinel; (111) channelling direction, C) xenon and helium implanted spinel; (111) channelling direction, D) pristine spinel; (111) channelling direction.

with only xenon and for spinel with xenon and helium are almost identical, showing that the damage caused by helium is negligible compared to the damage caused by xenon (see also Figure 4.3). The magnesium and aluminium signal for the amorphous spinel reach the random level, suggesting that the material might be amorphous. The oxygen shoulder remains below the random level even if the oxygen sublattice becomes entirely disordered (amorphous). This is because the helium ion beam channels below the damaged layer, which reduces the RBS yield for backscattered energies between the low end of the magnesium peak and the surface position of the oxygen peak. The oxygen damage peak is then superimposed on this low channelling background. In the case of the random spectrum the yield is high at all backscattered energies.

Desorption experiments

Desorption experiments were performed in the Knudsen cell (KC) [19, 37] of ITU and in the desorption-apparatus (THDS) of IRI described in Chapter 2. Several samples were investigated in one of the two systems, as described in Table 4.3. Anticipating Subsection 4.3.3, the samples investigated with positron beam analysis (PBA) are also included in the table. The data for the peak content as presented in the most right column will be used in Subsection 4.3.3.

The sample sizes and the corresponding helium content are also given in the table. In the THDS, samples were annealed in vacuum with a ramp rate of either 60 K min$^{-1}$ (sample VII) or 180 K min$^{-1}$ (sample VIII) up to 1300 K, or in several annealing steps,
Table 4.3: Overview of investigated samples and applied analyses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type*</th>
<th>Experiment</th>
<th>Heating rate $K_{\min^{-1}}$</th>
<th>Number of He-ions $\times 10^{13}$</th>
<th>Sample surface (mm$^2$)</th>
<th>$T_{\text{max}}$ (K) of peak</th>
<th>$T_{\text{max}}$ (K) of peak</th>
<th>Peak content $\text{He}_A/\text{He}_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1</td>
<td>PBA</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-/1066</td>
<td>-/1249</td>
<td>-/24</td>
</tr>
<tr>
<td>II</td>
<td>2</td>
<td>PBA</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-/1066</td>
<td>-/1249</td>
<td>-/24</td>
</tr>
<tr>
<td>III</td>
<td>2</td>
<td>KC</td>
<td>30</td>
<td>3.16</td>
<td>690/1066</td>
<td>758/1249</td>
<td>44/56/0</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>3</td>
<td>KC</td>
<td>30</td>
<td>2.6</td>
<td>690/1066</td>
<td>758/1249</td>
<td>32/54/14</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>3</td>
<td>KC</td>
<td>30</td>
<td>2.1</td>
<td>690/1066</td>
<td>758/1249</td>
<td>32/54/14</td>
<td></td>
</tr>
<tr>
<td>VI</td>
<td>3</td>
<td>KC</td>
<td>30</td>
<td>3.4</td>
<td>690/1066</td>
<td>758/1249</td>
<td>42/50/8</td>
<td></td>
</tr>
<tr>
<td>VII</td>
<td>3</td>
<td>THDS</td>
<td>60</td>
<td>3.1</td>
<td>627/-</td>
<td>741/-</td>
<td>44/56/0</td>
<td></td>
</tr>
<tr>
<td>VIII</td>
<td>3</td>
<td>THDS</td>
<td>180</td>
<td>3.9</td>
<td>615/-</td>
<td>745/-</td>
<td>44/56/0</td>
<td></td>
</tr>
<tr>
<td>IX</td>
<td>3</td>
<td>THDS</td>
<td>Stepwise</td>
<td>4.6</td>
<td>642/-</td>
<td>741/-</td>
<td>44/56/0</td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>3</td>
<td>PBA</td>
<td>See Fig. 4.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Sample type: Virgin spinel (1); Spinel amorphized with xenon (2); Amorphous spinel implanted with helium (3)

in which the maximum temperature was increased by 50 K for each measurement (i.e. 300-500 K, 300-550 K etc.), from now on referred to as partial annealing (sample IX). Immediately after reaching the maximum temperature, the sample was cooled down (sample IX). In the Knudsen cell experiments the release of both helium and xenon (samples IV, V, VI) and only xenon (sample III) was monitored. The samples were annealed under vacuum with a heating rate of 30 K min$^{-1}$. The helium release curves obtained with both systems will be compared.

**Positron beam analysis (PBA)**

The PBA technique, which gives insight into the damage and the amount and type of open volume in a material, was applied to:

- a virgin single-crystalline sample (sample I);
- spinel with an amorphous layer (spinel with xenon, sample II);
- amorphous spinel implanted with helium (sample X).

For two specimens the investigations were performed at room temperature. For the third sample (X), the defect evolution during thermal annealing was also studied. The sample was annealed in vacuum for 10 minutes at a constant temperature and then cooled down to room temperature before starting the measurement. The annealing of the samples was performed in vacuum.
4.3.3 Results and discussion

Helium and xenon desorption

The results of the continuous heating (ramp annealing) helium and xenon desorption experiments are shown in Figure 4.5, where the THDS results (only helium release, samples VII and VIII) are displayed in figure a and the Knudsen cell results (both helium and xenon release, sample IV) in figure b.

![Graph showing helium and xenon desorption](image)

**Figure 4.5:** Results of helium and xenon release experiments. Figure a: the helium release measured with THDS (samples VII and VIII); figure b: the results of the Knudsen cell experiments (sample IV).

The data in the figure have been plotted as a function of temperature in order to facilitate the comparison between the different heating rates applied. Note that the Knudsen cell results are given in Ampere. Since until now the calibration factor of xenon in the Knudsen cell system has not been determined, the direct output signal of the mass-spectrometer was used, which is linear with the number of ions. For both methods of investigation most of the helium is released between 600 and 800 K, while most of the xenon is released between 1050 and 1500 K.
It is clear that helium is released in two stages (He_A and He_B), which is also observed for the xenon release (figure b). For sample VIII, a further third stage releasing a minor amount of helium is observed (He_C), although this is not observed for sample VII and also not in the Knudsen cell. In these cases, the height of the helium signal cannot be distinguished from the background due to the low annealing rate. The release stages He_A and He_B may be explained by helium release from the zone where no xenon is implanted (close to the surface, He_A) and from the zone where a xenon concentration exists (He_B). This agrees approximately with the amount of helium trapped in both zones. The fractions of helium released in each peak (He_A, He_B and He_C) are also given in Table 4.3. The xenon release begins very suddenly at 1050 K; this might be an effect of sweeping out during recrystallization. During this process, part of the xenon is retrapped and released at higher temperatures by a diffusion process. The release of He_C occurs in the same temperature range as the first part of the xenon release, which makes the hypothesis of gas sweeping during recrystallization stronger. The possibility that the release of the helium in He_C is caused by burst release due to thermally induced flaking [78] has been considered; however, SEM investigations of several samples after annealing have shown that this is not the case. Temperatures at which peak release occur are given in Table 4.3.

The results of the partial annealing experiment, performed with THDS at a heating rate of 3 K s\(^{-1}\) (sample IX), are shown in Figure 4.6. In this figure, the spectra have been labelled with characters A to L, corresponding to the data given in Table 4.4.

**Figure 4.6:** Partial helium desorption for sample IX. The desorption rate is plotted versus the annealing temperature. The heating rate applied was 3 K s\(^{-1}\).

The release rates during both heating and cooling are shown. Again, three release stages can be distinguished, indicated by He_A, He_B and He_C. The maximum release is observed at a temperature of about 850 K. In contrast, in the ramp annealing experi-
Table 4.4: Results of the partial annealing THDS experiments of sample IX shown in Figures 4.6 and 4.7.

<table>
<thead>
<tr>
<th>Annealing step</th>
<th>$T_{\text{max}}$ (K)</th>
<th>Helium content (%)</th>
<th>$Q$ (eV)</th>
<th>$\delta Q$ (eV)</th>
<th>attempt frequency $f_{0,1}$ ($s^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>656</td>
<td>100.0</td>
<td>2.04</td>
<td>0.19</td>
<td>$1.66 \times 10^{14}$</td>
</tr>
<tr>
<td>B</td>
<td>707</td>
<td>97.4</td>
<td>2.05</td>
<td>0.08</td>
<td>$2.24 \times 10^{13}$</td>
</tr>
<tr>
<td>C</td>
<td>760</td>
<td>84.1</td>
<td>1.71</td>
<td>0.07</td>
<td>$1.70 \times 10^9$</td>
</tr>
<tr>
<td>D</td>
<td>811</td>
<td>58.4</td>
<td>2.94</td>
<td>0.18</td>
<td>$2.88 \times 10^{15}$</td>
</tr>
<tr>
<td>E</td>
<td>863</td>
<td>51.9</td>
<td>2.65</td>
<td>0.14</td>
<td>$5.62 \times 10^{13}$</td>
</tr>
<tr>
<td>F</td>
<td>915</td>
<td>44.8</td>
<td>2.73</td>
<td>0.10</td>
<td>$1.74 \times 10^{13}$</td>
</tr>
<tr>
<td>G</td>
<td>963</td>
<td>19.7</td>
<td>2.52</td>
<td>0.09</td>
<td>$1.05 \times 10^{11}$</td>
</tr>
<tr>
<td>H</td>
<td>1012</td>
<td>8.3</td>
<td>2.82</td>
<td>0.16</td>
<td>$1.15 \times 10^{12}$</td>
</tr>
<tr>
<td>J</td>
<td>1063</td>
<td>3.6</td>
<td>1.80</td>
<td>0.14</td>
<td>$1.35 \times 10^{6}$</td>
</tr>
<tr>
<td>K</td>
<td>1111</td>
<td>1.2</td>
<td>2.02</td>
<td>0.17</td>
<td>$6.76 \times 10^{6}$</td>
</tr>
<tr>
<td>L</td>
<td>1183</td>
<td>0.2</td>
<td>1.58</td>
<td>0.14</td>
<td>$5.75 \times 10^{4}$</td>
</tr>
</tbody>
</table>

During most of the helium has been released at this temperature. The helium release in the partial annealing begins at about 600 K, which corresponds to the first release peak observed in the ramp annealing experiments. For successive temperature steps, the

Figure 4.7: Arrhenius plot for the THDS results shown in Figure 4.6. The squares in the figure indicate the parts of the curves that have been used for the calculation of the activation enthalpy.
temperature at which the helium release begins is somewhat lower than the maximum temperature of the previous annealing step. In the case of partial annealing, helium is retained up to the same temperatures as observed for sample VIII, annealed at 3 K s\(^{-1}\). The fact that at the lower ramping rate no release at this temperature is seen, can be attributed to the signal/background ratio, which becomes too low as the helium release per unit of time is reduced.

From the experiments in which the sample was annealed stepwise, information on the release mechanisms can be obtained by looking at the first part of the release curves \cite{76}, as described in Section 3.6.2. The Arrhenius behaviour (release rate versus \(T^{-1}\)) is shown in Figure 4.7. In each curve, the part used for determining the activation energy has been indicated. In Table 4.4, the following data are given for each of the annealing steps: The maximum annealing temperature (\(T_{\text{max}}\)) for the step (these data are already corrected for the delay in temperature between sample and crucible), the fraction of initially implanted helium (4.64\(\times\)10\(^{13}\) ions) still present at the beginning of the annealing step, the activation enthalpy (\(Q\)) determined from the part of the slope indicated in Figure 4.7, the error (\(\delta Q\)) in the activation enthalpy due only to the fitting, and the value of the calculated frequency pre-factors \(f_{0,i}\) (Eq. 3.26). The calculated

**Figure 4.8:** The values for the frequency pre-factor \(f_{0,i}\) (figure a) and the activation enthalpy \(Q\) (figure b) as a function of temperature, calculated from the data presented in Figures 4.6 and 4.7. The horizontal lines indicate the average value per helium release peak.
values for the activation enthalpy and the frequency pre-factor are shown in Figure 4.8. In this figure, one can clearly distinguish the three different regions denoted by HeA, HeB and HeC. The frequencies found for the two stages of desorption (HeA and HeB) are close to what is expected for first-order desorption, namely of the order of the jump frequencies for solids [84]. The HeC-desorption has a very low pre-factor which might indicate a multi-step activated process such as diffusion or desorption from helium bubbles. Three different activation enthalpies are derived from the slopes of the curves: (1.9±0.2) eV for HeA, (2.7±0.3) eV for HeB and (1.8±0.3) eV for HeC. The errors in the activation enthalpy presented above are due only to the uncertainty in the fitting. In this calculation, the uncertainty in the background subtraction was included; however, the real error in the activation enthalpy is caused by more parameters. Although the measured temperature data were corrected for the temperature delay between crucible and sample, some uncertainty in temperature will remain (± 10 K). The real errors in the activation enthalpy will thus be larger than the values given above.

**Positron beam analysis (PBA)**

PBA-experiments were performed at room temperature on a virgin spinel single crystal (sample I) and a spinel crystal with an amorphous layer without helium (sample II). The helium implanted amorphous layer (sample X) was investigated by PBA at room temperature and after annealing at a number of temperatures. The applied heating schedule is shown in Figure 4.9. For each annealing step, the sample was heated to the desired temperature within several minutes. After the temperature was kept constant for about 10 minutes, the sample was cooled down to room temperature before the positron measurement was started.

![Figure 4.9: The applied heating schedule for the PBA measurements. For each annealing step, the sample is heated to the desired temperature within several minutes. After the temperature is kept constant for about 10 minutes, the sample is allowed to cool down to room temperature (R.T.) (no forced cooling) before the positron measurement is started.](image-url)
The PBA measurements on the unannealed helium irradiated amorphous spinel (sample X) reveal a somewhat lower $S$-value compared to the amorphous sample without helium (sample II). The $S$-value is an indicator for the amount of open volume in a material. It is assumed that helium fills up part of the open volume in the amorphous structure. In Figure 4.10, the measured $S$-parameter as a function of the depth in the material is shown for virgin (unimplanted) spinel (sample I) and for amorphous spinel with helium after various annealing stages. In the top part of the figure, the xenon displacements and the xenon ion distribution calculated with TRIM are shown in arbitrary units.

It can be seen that the $S$-parameter increases in the xenon and helium implanted area after annealing up to temperatures of 1470 K. Above 1600 K, the $S$-parameter profile reaches the curve for pristine spinel.

Figure 4.11 shows the fitting results obtained with the program VEPFIT [85, 86] where a three-layer model has been used to describe the amorphous region (layers 1 and 2) on top of the bulk material (layer 3). The reason to split the xenon and helium implanted region into two layers is based on the observation that with increasing positron implantation depth the $S$-parameter first drops, then increases to a maximum after which
it gradually decreases to the $S$-value of the bulk. In the model the $S$-parameters and the upper boundaries of the layers 1 and 2 and the $S$-parameter of the bulk are the fitting parameters. Fitting has been performed on the data obtained after xenon and helium implantation and after annealing at 895 K and 1470 K. The results in this graph are presented numerically in Table 4.5 where the boundary of each zone is given, not its thickness. After implantation, it can be seen that the boundaries of the damaged layer are 41 and 183 nm. Comparing these data with the TRIM calculations as shown in Figure 4.10 it can be seen that the thickness and position are in good agreement with the calculated xenon displacement profile. From this it can be concluded that the TRIM calculations agree well with the real implantation data and that channelling effects can be neglected in our case.

**Table 4.5**: Fitted layer boundary and $S$-parameter per layer with a three-layer model using VEPFIT for sample X annealed at the indicated temperatures.

<table>
<thead>
<tr>
<th>Annealing Temp. (K)</th>
<th>Upper boundary layer 1 (nm)</th>
<th>Upper boundary layer 2 (nm)</th>
<th>$S$ layer 1</th>
<th>$S$ layer 2</th>
<th>$S$ bulk (layer 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>40.5</td>
<td>182.9</td>
<td>0.5097</td>
<td>0.5828</td>
<td>0.4748</td>
</tr>
<tr>
<td>895</td>
<td>14.8</td>
<td>168.0</td>
<td>0.6166</td>
<td>0.5476</td>
<td>0.4748</td>
</tr>
<tr>
<td>1470</td>
<td>48.3</td>
<td>109.0</td>
<td>0.5430</td>
<td>0.5743</td>
<td>0.4748</td>
</tr>
</tbody>
</table>

From the fits with the VEPFIT-program, the following can be observed (see Figure 4.11 and Table 4.5):
- At room temperature the first layer has a width of about 41 nm, which according to TRIM calculations is the region where only helium has been implanted. This layer has a low $S$-parameter. The second layer has a high $S$-parameter, and its depth
location agrees very well with the xenon displacement profile, which is a measure for the thickness of the amorphous layer, as reported in Ref. [62].

- After annealing at 895 K it can be seen that the first layer has become much thinner and its $S$-parameter has increased significantly; this corresponds to a thin layer under the surface with large open volumes. The end position of the second layer has not changed much compared to the room temperature sample; for this layer, there has been a drop in $S$-parameter compared to the second layer at room temperature. From THDS it follows that helium release has occurred, but that xenon is still immobile.

- After annealing at 1470 K it can be seen that the first layer has approximately the same width as the first layer at room temperature. The $S$-parameter of this layer is about the same as the $S$-parameter of the second layer after annealing at 895 K; the second layer at this temperature has a high $S$-parameter comparable to the second layer at room temperature: xenon release has occurred leaving open volumes behind.

In Figure 4.12 the measured $S$-parameter has been plotted vs. the annealing temperature for three different depths in the material. From Figure 4.10 it can be seen that at a depth of 8.5 nm, which is very close to the surface, a large increase in $S$-value at 895 K occurs compared to room temperature. A depth of 24 nm is the regime where only helium is present. A depth of 95 nm is the region where most of the displacements caused by xenon are found. Up to 600 K, no large changes in the $S$-parameter at any of
the selected depths are observed. From the helium desorption experiments it is known that there has been no helium release at these temperatures. Five different stages can be distinguished in the change in $S$-parameter vs. temperature for temperatures beyond 600 K; these changes have been numbered in the figure.

1. In stage 1, between 700 and 950 K, the $S$-parameters at 8.5 nm and 23.8 nm increase while the $S$-parameter at 95 nm remains more or less constant. The increase in $S$-parameter for the lower two depths can be explained by the release of helium and the clustering of defects.

2. In stage 2, between 920 K and 1200 K, the near-surface $S$-parameter remains more or less constant while the $S$-parameters in the deeper regions increase. In this temperature interval, helium has been released; this is the temperature interval where the first release of xenon can be observed. Recrystallization has occurred leaving large defect clusters behind. TEM observations show [82] that recrystallization of the amorphous surface layer takes place in the temperature interval between 883 and 1128 K.

3. In stage 3, between 1200 and 1350 K, there is a large drop in $S$-value for both the near-surface region (8.5 nm) and the deeper regions. It is expected that this is due to defect recovery after recrystallization.

4. In stage 4, between 1350 and 1480 K, an increase in $S$-value in the two regions closest to the surface is observed, while the $S$-value of the deepest layer decreases. According to the literature, the xenon remains immobile up to 1370 K [82] which, however, is not confirmed by Knudsen cell measurements. In this stage, it is expected that xenon is released and a damage recovery process has started in the deeper region.

5. Finally, in stage 5, after annealing to more than 1600 K it can be seen that the $S$-values reach the level of pristine spinel, and that all implantation defects have been removed from the sample.

### 4.3.4 Comparison with helium and xenon behaviour in crystalline spinel

#### Helium release

For the helium in amorphous spinel, three release stages were observed:
- $\text{He}_A$ at about 620 K with an activation enthalpy of 1.9 eV;
- $\text{He}_B$ at about 740 K with an activation enthalpy of 2.7 eV;
- $\text{He}_C$ at about 1000 K with an activation enthalpy of 1.8 eV, probably caused by sweeping out during recrystallization.

No helium implantation experiments could be found in the literature, where helium was implanted in spinel at the same depth and with the same fluence. The present results will therefore be compared with release curves found in the literature based on approximately the same implanted dose. Neeft et al. [78] implanted 900 keV $^3\text{He}$-ions
Implantation experiments performed on spinel

in both single- and polycrystalline spinel with different doses. It was observed that the helium release took place in at least two stages over a wide temperature interval ranging from 600 to 1600 K, where the release temperature range depended on the implanted fluence and on whether the spinel was single- or polycrystalline. It was concluded that for a higher dose of helium, the helium is released at a lower temperature. If the release temperature decreases for a higher implanted dose (more damage), then this would agree with the current experiments where much more damage was introduced than in the cases presented in Ref. [78]. In Ref. [21], single crystals of spinel were implanted with 30 keV $^3$He-ions with four different fluences, varying between $6.2 \times 10^{15}$ and $53 \times 10^{15}$ He cm$^{-2}$. Helium release was observed in three stages; between 550 and 700 K, between 750 and 1100 K and between 1100 and 1400 K. As a second experiment, spinel single crystals were irradiated with $\alpha$-particles of 4.5 MeV originating from a $^{241}$Am-source. Two activation enthalpies were quoted: 1.8 eV for helium interstitial diffusion and 2.4 eV for helium release from vacancy clusters. However, these release processes were assumed; no experimental evidence was given. The temperatures for the THDS experiments on the amorphous spinel specimens described in this section were calibrated with a thermocouple mounted on the sample. On the other hand, the temperature data for the experiments described in Refs. [21, 78] were not corrected for the delay in temperature between sample and crucible (normally the crucible temperature is monitored). Therefore it could be that the measured activation energies were somewhat overestimated.

If the helium release data from the amorphous spinel are compared to the data for crystalline spinel it can be seen that in general helium is released from crystalline spinel with a somewhat higher activation enthalpy than from amorphous spinel. Most of the helium is released before the recrystallization temperature is reached. It is likely that crystalline spinel contains deeper traps for helium than amorphized spinel. Also, one may expect that xenon atoms embedded in the amorphous spinel generate sufficient open space to trap helium better than in amorphous spinel without xenon.

Xenon release

In the literature no information on annealing experiments for xenon-implanted spinel could be found. However, Matzke [87] observed that xenon release in air begins at 1800 K, i.e. at a much higher temperature than in the current experiments. This can be explained by a trapping mechanism of xenon in crystalline spinel. In Ref. [7], Turos et al. investigated the damage caused by xenon and krypton implantations. With RBS, for an implanted fluence of $1 \times 10^{15}$ Kr cm$^{-2}$, it was observed that already after annealing at 775 K a reduction of the number of defects resulted in a decrease of almost 50% of the Al- and O-damage peaks. For crystalline spinel, an important recovery of defects was observed at this temperature for this implanted dose, although for an implanted dose of $7 \times 10^{15}$ Kr cm$^{-2}$ this effect was not observed. For the present samples, RBS measurements were only performed for non-annealed specimens. PBA did not show defect recovery at these temperatures. The xenon release begins most likely at the
recrystallization temperature. Then a part of the xenon is swept out, which can be seen as a very sharp rise in the xenon release signal. The rest of the xenon is at first trapped, probably in bubbles, and later released by diffusion processes, as would be the case in crystalline spinel.

4.3.5 Summary, conclusions and final remarks

Spinel was amorphized by the implantation of $1 \times 10^{16} \text{Xe cm}^{-2}$ of 450 keV at 100 K. After amorphization, 14 keV He$^+$-ions were implanted in the sample up to a total implanted dose of $1 \times 10^{15} \text{He cm}^{-2}$. The helium was implanted in the centre of the amorphous zone. The maximum helium concentration, amounting to 0.07 at.%, could be found at a depth of 77 nm. The release profile of helium under thermal annealing was monitored by two different desorption systems. The major part of the helium was found to be released in two stages, with the maxima of the peaks lying at about 615 and 720 K. A small fraction of helium was released in a third stage. From the measured partial desorption spectra, the activation enthalpies for the different release stages were determined to be 1.9, 2.7 and 1.8 eV for stage 1 (He$_A$), 2 (He$_B$) and 3 (He$_C$), respectively, with frequency factors of $6 \times 10^{13}$, $6 \times 10^{14}$ and $3 \times 10^6 \text{s}^{-1}$. The order of magnitude of the last value can be explained by a restructuring process. Xenon release was found to begin very suddenly at 1050 K. This could be an effect of sweeping out during recrystallization. A second xenon release peak was observed with a maximum at about 1280 K, a temperature at which all helium had been released. PBA experiments were performed at room temperature and after various annealing steps. The PBA data were analysed using the VEPFIT code, where a three-layer model was used. At room temperature, these three layers, which correspond to amorphized spinel without xenon, amorphized spinel with xenon and the substrate, were in good agreement with TRIM calculations.

Placing the results in the broader framework of the application of spinel in a nuclear reactor, it will now be assumed that a pin of spinel with an actinide to be transmuted is irradiated in a light water reactor. One expects that under neutron irradiation the matrix will transfer into an amorphous state due to the impact of fission products. On the basis of the results presented in this chapter it is expected that helium and fission gases (xenon) will become mobile at much lower temperatures than would be the case in a crystalline spinel matrix. At the beginning of the irradiation cycle the temperature in the fuel is high but little helium and few fission gases are present. The spinel matrix will still be crystalline. At the end of the transmutation cycle, the power in the pin will be lower, but more helium and fission gases are present in the fuel and the material will be amorphous or contain amorphous regions. From the implantation experiments presented in this chapter it is found that helium is released between 600 and 800 K. The fuel temperature in a reactor is generally higher than this, so in the case of an amorphized spinel matrix a large fraction of helium can be expected to be released towards the fuel-cladding gap already during reactor operation. In this chapter, the effects of recrystallization on the helium release in an amorphous
Implantation experiments performed on spinel matrix have been presented. It was concluded that helium release occurs below the recrystallization temperature (1050 K).
Chapter 5

Helium in reactor irradiated spinel

5.1 The EFTTRA experiments, an introduction

In Chapter 4, helium, fission product and fission gas implantation experiments in magnesium aluminate spinel were described. These experiments were performed as single-effect studies to understand the response of spinel to different sources of damage. However, in a nuclear reactor, the inert matrix is subject to a combination of these, in addition to other single effects (e.g. damage by neutrons). Even if all single effects are understood in detail, it is extremely difficult to predict the behaviour of a material under neutron irradiation in which actinides are transmuted or fissioned. Not all single effects have a constant importance over an irradiation cycle. Some of them are only important at high temperature (e.g. diffusion of fission gases), or only at the end of burn-up when e.g. large quantities of fission gas are present. During neutron irradiation, damage accumulation occurs in the spinel matrix and the number of impurities in the form of fission products gradually increases. Prediction of the behaviour of helium in the matrix is of great importance since the balance between gas release and precipitation processes with the formation of bubbles defines the swelling rate of the material and the eventual strength of the fuel/cladding mechanical interactions. These parameters are key indicators for the suitability of a given matrix to host americium during transmutation, especially in a "once-through" scenario which entails long irradiation times and high transmutation yields. In practice, two inert matrix fuel (IMF) design options can be implemented, based on whether or not the inert gas is mainly retained in the matrix or released in the smeared porosity of the fuel rod, including the fuel-cladding gap and the plenum. Therefore, fuel fabrication and rod design can be optimized if information on helium and fission gas release as a function of burn-up and irradiation temperature is available. To obtain a better insight into the gas behaviour in inert matrix materials, an irradiation project (EFTTRA) was initiated.

The EFTTRA (Experimental Feasibility of Targets for TRAnsmutation) project was started in 1992. The project was initiated to analyse the behaviour of materials with
regard to the possibility of transmuting long-lived radionuclides [88]. The EFTTRA group is a collaboration between EDF and CEA-Cadarache in France, JRC-ITU and FZK in Germany and JRC-IE and NRG in the Netherlands. The last experiments performed in this collaboration so far are the EFTTRA-T4 and T4bis experiment, where a uranium-free target was investigated. This target consisted of americium in a spinel matrix. In this chapter only the EFTTRA-T4 experiment will be discussed.

The work was divided into five stages shown in Figure 5.1 together with the most important observations made.

The five stages, from fabrication (black in Figure 5.1), irradiation (dark gray in Figure 5.1), non-destructive post irradiation analysis, intermediate storage and destructive post irradiation analysis (light gray to white in Figure 5.1) will be discussed in this chapter. Part of the data or phenomena mentioned in the figure have been estimated or calculated (e.g. the maximum fuel temperature and the amorphization of the matrix), other data have been measured (e.g. porosity). The phenomena mentioned will be discussed in more detail in the remainder of the chapter.

1. Fuel fabrication.

The fuel fabrication (shown in black in Figure 5.1) was performed in 1996. Pellets were pressed from a commercial powder (Baikalox S33CR, Baikowski Chemie), which was granulated and compacted at a pressure of 390 MPa using a bi-directional press [80]. According to Konings [89], this was a stoichiometric spinel powder. The pellets were then thermally treated at 925 K to remove zinc stearate used as
a lubricant in the pressing step. The resulting pellets had a diameter of 6.5 mm, a height varying between 8 and 9 mm and a porosity of 49%. Afterwards, the samples were infiltrated with an americium nitrate solution (400 g/l) by the so-called INRAM process [88]. The target is thus of the microdispersed type with inclusions smaller than 2-3 µm.

After infiltration, the samples were dried, and then calcinated at 975 K for four hours in an Ar/H₂ atmosphere before being sintered at 1925 K in the same atmosphere. After these operations, the pellets had a diameter of about 5.4 mm and a density of about 96% of the estimated theoretical density [88]. The average americium content in the fuel pin determined by gravimetric analysis was 11.2%. It was however found that the americium, intended to be present in the form of the oxide AmO₂, formed a compound with the perovskite structure during sintering, probably AmAlO₃. The actual composition of the target was thus MgAl₂O₄ + AmAlO₃. From one of the pellets, the americium distribution was determined by α-radiography. The results of these investigations are shown in Figure 5.2.

Figure 5.2: Optical macrograph (left) and α-autoradiograph (right) of one of the pellets of the EFTTRA-T4 batch. The figures were taken from Ref. [80].

The left-hand part shows the optical macrograph. A rectangular area in the pellet is visible which is slightly lighter than the rest (indicated by arrows and number 1). Cracks can be observed as well (labelled with number 2). The rectangular area can be seen more clearly by the α-autoradiograph in the right-hand part of the figure. There, a more or less cylindrical shell can be seen with a thickness of 200 µm, where the americium content was higher (14 wt.% [88]) than in the remainder of the pellet; this effect is most likely due to a porosity change in this region. In the remainder of the pellet, the americium distribution was approximately homogeneous with a concentration of about 9 wt.% [88].
2. Irradiation in the High-Flux Reactor at Petten.
The EFTTRA-T4 target capsule was placed in the central hole of the sample holder, which had been equipped with thermocouples and monitor sets for neutron metrology. The monitor set consisted of neutron fluence detectors, two tubes for purging the containment with pure helium for an integrity check and four gamma-scanning wires. The irradiation was carried out in one leg of the TRIO irradiation facility, which is a standard in-core device of the HFR at Petten [90].

**EXPECTED PHENOMENA:**
Production of fission products, fission gases, helium and actinides by fission and transmutation
Increasing damage caused by fission products, neutrons and recoil atoms, alpha-, beta-, and gamma-decay
Bubble formation and bubble growth, gas release towards fuel/cladding gap
Swelling
Amorphization

![Graph showing temperature and time in core](image)

**Figure 5.3:** An overview of the irradiation history of the EFTTRA-T4 target. The ordinate shows the average temperature, measured over 12 thermocouples which are closely located around the target caps.

In Figure 5.3 a schematic overview is presented of the irradiation history of the EFTTRA-T4 target in the High-Flux Reactor (HFR). The irradiation in the HFR was performed between September 1996 and January 1998. The irradiation lasted for 14 HFR cycles which are clearly visible in Figure 5.3. In total, the target was irradiated in the HFR for 358.42 effective full power days (EFPD). After 231 EFPD, the irradiation was interrupted for a neutron radiograph, as indicated in the figure. The results showed that the fuel pin and the fuel stack were still intact. According to Ref. [88], there was no indication of significant swelling since the gap between
pellets and cladding could still be observed. However, in Ref. [80] it is reported that the stack length and diameter of the pellet did not change between that moment and the end of the irradiation. In this contradiction on the swelling, the latter observation sounds more logical. It is unlikely that all of the fuel swelling occurs during the last five irradiation cycles. The first 11 cycles were performed in core position C5 after which, for core management reasons, the position in the core was changed to C7. At a different core position there might be a different neutron spectrum, yielding different fission and transmutation rates. This can be seen in the abscissa of Figure 5.3. After the change in position the cladding temperature increased by 20 K as a result of a higher fission rate. It should be mentioned that in the figure only the temperature of the aluminium carrier measured during irradiation is shown. The cladding temperature during the maintenance period is unknown. As can be seen in the figure, the temperature of the fuel and cladding during irradiation was kept at $\sim 670$ K in the outer part, apart from the first irradiation cycle where the temperature was about 720 K. This temperature gave an estimated maximum temperature during irradiation of 1000 K in the central part, assuming virgin stoichiometric spinel.

According to Pijlgroms [91], at the beginning of the irradiation the fission power was 39.1 W cm$^{-3}$ and the total power generation 145 W cm$^{-3}$. At the end of the irradiation the fission power was 399 W cm$^{-3}$ and the total power 450 W cm$^{-3}$. As the irradiation progressed, the fission power increased to its maximum value during the last cycle. The cause of this is that a large fraction of $^{241}$Am first is transmuted and then by decay and neutron capture steps, transforms into fissile $^{239}$Pu.

It was calculated [92] that in the EFTTRA-T4 experiment about 96% of the $^{241}$Am was transmuted; 28% of the americium and actinides formed in the inert matrix were fissioned. In Figure 5.4 the transmutation scheme of $^{241}$Am is shown, together with the transmutation path from $^{241}$Am into $^{239}$Pu.

![Transmutation scheme of $^{241}$Am in a neutron flux.](image)

**Figure 5.4:** Transmutation scheme of $^{241}$Am in a neutron flux.
From the figure the following can be seen: By neutron capture of $^{241}\text{Am}$, 90% $^{242}\text{Am}$ and 10% $^{242m}\text{Am}$ are formed. $^{242}\text{Am}$ decays partly through $\beta^{-}$-emission into $^{242}\text{Cm}$ (83%); the other 17% is $\beta^{+}$-decay into $^{242}\text{Pu}$, which has a very long half-life. Part of the newly formed $^{242}\text{Cm}$ is transformed into $^{243}\text{Cm}$ by neutron capture, but its major part decays by emitting an $\alpha$-particle into $^{238}\text{Pu}$ which has a half-life of 87.74 years.

In Table 5.1 the composition of the principal actinides in the fuel after irradiation is shown. It can be seen that first of all $^{242}\text{Cm}$, but also $^{241}\text{Am}$ and $^{238}\text{Pu}$, are responsible for the helium build-up during the first decades after irradiation because of their half-life. At the end of irradiation, the amount of helium is about 10 times larger than the amount of noble fission gases. From the table it can be seen that the major newly formed actinides ($^{238}\text{Pu}$ and $^{242}\text{Cm}$) have relatively short half lives and from this point the transmutation of $^{241}\text{Am}$ was very successful.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Half life</th>
<th>Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{242}\text{Cm}$</td>
<td>162.8 d</td>
<td>0.156</td>
</tr>
<tr>
<td>$^{241}\text{Am}$</td>
<td>432.6 a</td>
<td>0.037</td>
</tr>
<tr>
<td>$^{243}\text{Am}$</td>
<td>7370 a</td>
<td>0.051</td>
</tr>
<tr>
<td>$^{242}\text{Pu}$</td>
<td>$3.76 \times 10^5$ a</td>
<td>0.074</td>
</tr>
<tr>
<td>$^{238}\text{Pu}$</td>
<td>87.74 a</td>
<td>0.241</td>
</tr>
<tr>
<td>$^{239}\text{Pu}$</td>
<td>$2.14 \times 10^6$ a</td>
<td>0.065</td>
</tr>
</tbody>
</table>

In Figure 5.3 an indication is given of processes occurring in the spinel matrix under neutron irradiation. Processes to be taken into account are:

- The production of fission products, fission gases, helium from $\alpha$-decay and actinides, which are present as impurities in the material. The amount of fission products, fission gases and helium from $\alpha$-decay increases as a function of irradiation time;
- Damage is introduced into the material due to fission products, recoil atoms, neutrons and radioactive decay processes. During irradiation, accumulation of damage in the matrix material will occur;
- Fission gases may diffuse towards the gap between cladding and fuel, bubbles may be formed due to the low solubility of fission gases in the matrix material;
- It is expected that the spinel matrix will undergo a transformation to amorphization under the impact of fission product damage;
- An extremely large swelling of the matrix material has been observed, either caused by fission fragment damage or by the accumulation of helium. A detailed discussion on the swelling will be presented elsewhere in this chapter.

3. Storage.

The helium build-up in the fuel after irradiation and the isotopic composition as a function of storage time were calculated by making use of the Nuclides 2000
computer code [56]. The assumption was made that the capsule is stored directly after irradiation. The calculation yields the average concentration of the isotopes. The original inhomogeneity of the distribution of $^{241}$Am was not taken into account. It was assumed that helium is immobile and thus the possible diffusion of helium towards the gap between cladding and fuel has been neglected. The results of these calculations are shown in Figure 5.5. In Figure 5.5a, the helium concentration and the nuclides with the highest concentrations are shown; these are $^{234}$U, $^{235}$U, $^{238}$U and $^{206}$Pb. In Figure 5.5b, these isotopes are shown in more detail. It can be seen that after 100 years of storage on the average 1 helium atom per 100 matrix atoms (which are either magnesium-, aluminium- or oxygen ions) is present in the material.

![Figure 5.5: Calculated helium build-up in the fuel as a function of storage time after irradiation in the HFR.](image)

From the figure it can also be seen that helium build-up increases dramatically after $10^5$ years of storage. However, most of the radioactive products have decayed by this time. As already discussed, the values in the figure are an overestimate as part of the helium will diffuse towards the gap between cladding and fuel.

In Figures 5.1 and 5.3 it is stated that the spinel matrix is amorphized during reactor irradiation. This assumption is based on implantation experiments with fission products which have shown that fission products may amorphize the material, at the same time inducing an important swelling [9, 10, 12, 13]. In SEM and TEM investigations, described later in this chapter, no amorphous phase was observed, so the material must have recrystallized during storage. The temperature if the irradiated fuel pin will be well above room temperature during storage. The higher temperature, together with the radioactive decay of fission products, may have caused this recrystallization. It was shown that the originally 10 µm sized grains had a size
of 500 nm at the time of the microscopical investigations. An explanation for this aspect is the recrystallization of the material into smaller grains. The recrystallization can be induced by $\beta$-decay of fission products. Yu et al. [93] have shown that amorphous spinel can be recrystallized by electron bombardment.

4. Post-irradiation examinations.

Non-destructive and destructive analyses have been performed on the irradiated EFTTRA-T4 specimen. The following remarks can be made on the basis of the non-destructive analysis: After irradiation, visual inspection of the target pin revealed a minor expansion of the cladding, which indicated that the gap between fuel and cladding was completely closed. Observations made by means of X-ray radiography revealed a swelling of the pellets of $\sim$18%. A swelling of this order of magnitude has a significant impact on the safety as it can cause cracks in the cladding. If the cladding is damaged, an interaction of the fuel with the cooling liquid will occur. The release of highly radioactive fission products and gases into the coolant should be prevented at all time. A target which exhibits a large swelling under reactor irradiation is dangerous to use as a transmutation matrix.

The swelling (together with a large porosity) can be caused by:

- accumulation of helium, produced by $\alpha$-decay of $^{242}$Cm which is a product in the transmutation scheme of $^{241}$Am;
- accumulation of fission gases;
- damage of the spinel matrix by the fission fragments;
- transformation to an amorphous state.

Effects caused by neutrons can be neglected as irradiation experiments of spinel under almost the same conditions as in the HFR did not show any significant effect as far as swelling [94, 95] was concerned. Most likely, the swelling of the spinel matrix is caused by a combination of the above-mentioned processes. The amount of helium in the EFTTRA-T4 experiment after irradiation in the HFR is about 0.5 at.%. The swelling of 18% is caused partly by the swelling of the matrix material as a result of amorphization. Owing to the presence of large quantities of helium and fission gases with a low solubility in the spinel matrix, large pores are formed which are responsible for the major part of the swelling. Gamma tomography of the fission products reflected the original inhomogeneous distribution of the americium in the spinel matrix [80]. Gas puncturing yielded a pressure of 5 bar and a free volume of 1.76 cm$^3$. Mass-spectrometrical measurements of the gas resulted in the following volume fractions: 0.9492 for helium, 0.0303 for xenon and 0.0027 for krypton. The remaining 0.0178 was composed of N$_2$, O$_2$, Ar and CO$_2$. The latter gases are most likely impurities present during the filling of the rod. The results of the gas-puncturing experiments were corrected for the helium present as filling gas; these corrected data are shown in Table 5.2.

Owing to the very small quantity of krypton in the target after irradiation, the errors in the measured data for krypton are large. The measured concentrations of the krypton isotopes were close to the limits of detection of the measuring device. It is expected that for all krypton isotopes the same fraction was released in the gas puncturing tests. The data for xenon release are more reliable for the three
Table 5.2: Results of the gas puncturing of the EFTTRA-T4 target pin. The calculated mass inventory is based on the results of the MCNP-FISPACT calculations. The fraction of gas released is based on the calculated inventory.

<table>
<thead>
<tr>
<th></th>
<th>Mass (mole) Released</th>
<th>Mass (mole) Inventory</th>
<th>fraction released (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4\text{He}$</td>
<td>$2.66 \times 10^{-4}$</td>
<td>$1.37 \times 10^{-3}$</td>
<td>19.5</td>
</tr>
<tr>
<td>Fission gases (total)</td>
<td>$1.19 \times 10^{-5}$</td>
<td>$2.29 \times 10^{-4}$</td>
<td>5.2</td>
</tr>
<tr>
<td>$^{83}\text{Kr}$</td>
<td>$9.92 \times 10^{-8}$</td>
<td>$1.04 \times 10^{-6}$</td>
<td>9.5</td>
</tr>
<tr>
<td>$^{84}\text{Kr}$</td>
<td>$4.13 \times 10^{-7}$</td>
<td>$2.56 \times 10^{-6}$</td>
<td>16.1</td>
</tr>
<tr>
<td>$^{85}\text{Kr}$</td>
<td>$6.74 \times 10^{-8}$</td>
<td>$7.81 \times 10^{-7}$</td>
<td>8.6</td>
</tr>
<tr>
<td>$^{86}\text{Kr}$</td>
<td>$4.86 \times 10^{-7}$</td>
<td>$4.54 \times 10^{-6}$</td>
<td>10.7</td>
</tr>
<tr>
<td>$^{131}\text{Xe}$</td>
<td>$5.57 \times 10^{-7}$</td>
<td>$1.79 \times 10^{-5}$</td>
<td>3.1</td>
</tr>
<tr>
<td>$^{132}\text{Xe}$</td>
<td>$2.51 \times 10^{-6}$</td>
<td>$4.79 \times 10^{-5}$</td>
<td>5.2</td>
</tr>
<tr>
<td>$^{134}\text{Xe}$</td>
<td>$2.66 \times 10^{-6}$</td>
<td>$5.23 \times 10^{-5}$</td>
<td>5.1</td>
</tr>
<tr>
<td>$^{136}\text{Xe}$</td>
<td>$5.12 \times 10^{-6}$</td>
<td>$1.01 \times 10^{-4}$</td>
<td>5.0</td>
</tr>
</tbody>
</table>

xenon-isotopes with the highest concentration in the fuel. The fractions released are in good agreement with each other (5.2, 5.1 and 5.0%, respectively). The release of helium and other fission gases after puncturing can be explained by the cracks present in the material, in combination with diffusion of the gases towards cracks and grain boundaries.

5.2 Destructive analysis

5.2.1 Results of destructive analysis presented in the literature

The results of post-irradiation examinations after irradiation of the EFTTRA-T4 capsule in the HFR reactor in Petten (NL) have been reported in Ref. [80]. The composition of the irradiated material was evaluated from burn-up calculations using the burn-up code OCTOPUS [96] of NRG and from neutron spectrum calculations with the 3D Monte Carlo code MCNP-4B [97] and the depletion calculation code FISFACT-4 [98]. A ceramographic sample was made at the maximum activity position according to the axial gamma scanning. Two principal conclusions were drawn from these analyses [90]:

1. The gap between fuel and cladding was completely closed. A crack healing phenomenon could be seen, which indicated a strong pellet-cladding interaction as a result of the swelling;

2. A 350 $\mu$m shell could be observed, characterized by a significantly higher porosity than the rest of the pellet. This band probably coincides with the 200 $\mu$m zone of higher americium content shown for the un-irradiated samples in Figure 5.2. The difference between the 200 $\mu$m and 350 $\mu$m is explained by the position in the target
where the bandwidth was measured. The high-porosity band did not have the same thickness over the whole specimen.

In the periphery of the sample the pore size was about 1.4 \( \mu \text{m} \) while at the centre and in the high-porosity band, pores with an average diameter of about 4.5 \( \mu \text{m} \) were predominant. Thus, the pore size is related to the initial concentration of actinides in the material and to the temperature during irradiation (which was higher at the centre).

### 5.2.2 Destructive analysis performed at ITU

After four years of cooling a slice was cut of one from the pellets, which was subsequently crushed in one of the hot cells of ITU. Two of these crushed pieces were analysed in the Knudsen cell and in the SEM and TEM of ITU. Fragments of the EFTTRA-T4 material were annealed in the Knudsen cell up to different temperatures. For most of the samples a heating rate of 10 K min\(^{-1}\) was used but one of the samples was annealed stepwise. The release profiles were evaluated and the different samples were investigated with the aid of SEM. The starting material and the material annealed up to 1600 K were studied with the aid of Transmission Electron Microscopy (TEM) to investigate the microstructure. For this purpose, electron-transparent specimens were prepared from the small fragments of the material. This was done by crushing in ethanol after which a droplet of the suspension obtained was deposited on a copper TEM grid coated with a thin graphite layer for better electron conductivity.

The following specimens of the EFTTRA-T4 pellet were investigated:

**Table 5.3: Investigated EFTTRA samples.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass (mg)</th>
<th>Activity (mSv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.3</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>22.3</td>
<td>30</td>
</tr>
</tbody>
</table>

Sample 1 was annealed stepwise until a maximum temperature of 2250 K. The original axial position of this specimen in the irradiated target is unfortunately unknown. This sample was not analysed by electron microscopy. Sample 2 was taken from the border between the americium-rich zone and the zone where the americium was homogeneously distributed, as seen in Figure 5.10a. It was annealed several times to different maximum temperatures with a heating rate of 10 K min\(^{-1}\). After every annealing step, a part of the sample was removed and transferred to the laboratory for electron microscopical investigations. The maximum temperatures and investigatory methods applied are described in Table 5.4.

### 5.2.3 Stability of spinel under thermal annealing

The time and temperature dependent release of magnesium and aluminium from sample I measured in the Knudsen cell are shown in Figure 5.6.
Table 5.4: Experiments performed with EFTTRA sample 2.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Max. annealing temperature (K)</th>
<th>Microscopic technique</th>
<th>Properties of matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>1450</td>
<td>SEM</td>
<td></td>
</tr>
<tr>
<td>2.2</td>
<td>1634</td>
<td>SEM and TEM</td>
<td></td>
</tr>
<tr>
<td>2.3</td>
<td>2020</td>
<td>SEM</td>
<td>dissociation</td>
</tr>
<tr>
<td>2.4</td>
<td>2380</td>
<td>SEM</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>2690</td>
<td>SEM</td>
<td>molten</td>
</tr>
<tr>
<td>2.6</td>
<td>2920</td>
<td>SEM</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.6: Time and temperature dependent release of magnesium and aluminium from the EFTTRA-T4 specimen, annealed in vacuum. Before the production of the pellet, the spinel powder was stoichiometric.

In the figure it can be seen that magnesium is released from the spinel matrix at temperatures as low as 1600 K in vacuum. In the EFTTRA-T4 irradiation experiment, the maximum temperature of the target was calculated to be about 1000 K. During irradiation Mg- and Al-colloids might have been formed which evaporate much earlier than MgO or Al₂O₃.

The thermal properties of spinel are well-known. Although the melting point (2408 ± 20) K is about 600 K lower than that of UO₂, its thermal conductivity is higher (between 5 and 15 W m⁻¹K⁻¹), which leads to a lower peak temperature in the fuel.
As far as the thermal stability of the matrix material is concerned, it seems that spinel has drawbacks as an inert matrix material. However, it might still be suitable as a storage matrix or as a part of a CerCer or CerMet composite inert matrix material.

### 5.2.4 Results of Knudsen cell experiments

From gas puncturing results and inventory calculations [92] the total amount of helium released during irradiation was estimated at $\sim 20\%$; the fission gas release at $\sim 5\%$. These values pertaining to the end of irradiation (EOI) were corrected for four years of storage preceding the reported investigations. In Table 5.5 the calculated concentrations of the principal actinides, helium and the most important fission products in the fuel at the time of measurement are presented. The most important actinide in the

<table>
<thead>
<tr>
<th>Isotope</th>
<th>wt.%</th>
<th>at.%</th>
<th>Isotope</th>
<th>wt.%</th>
<th>at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4\text{He}$</td>
<td>$1.03 \times 10^{-1}$</td>
<td>$5.72 \times 10^{-1}$</td>
<td>$^{133}\text{Cs}$</td>
<td>$8.22 \times 10^{-2}$</td>
<td>$1.37 \times 10^{-2}$</td>
</tr>
<tr>
<td>$^{24}\text{Mg}$</td>
<td>$1.48 \times 10^{+1}$</td>
<td>$1.37 \times 10^{+1}$</td>
<td>$^{137}\text{Cs}$</td>
<td>$1.06 \times 10^{-1}$</td>
<td>$1.72 \times 10^{-2}$</td>
</tr>
<tr>
<td>$^{27}\text{Al}$</td>
<td>$3.34 \times 10^{+1}$</td>
<td>$2.75 \times 10^{+1}$</td>
<td>$^{138}\text{Ba}$</td>
<td>$1.14 \times 10^{-1}$</td>
<td>$1.83 \times 10^{-2}$</td>
</tr>
<tr>
<td>$^{16}\text{O}$</td>
<td>$4.09 \times 10^{+1}$</td>
<td>$5.69 \times 10^{+1}$</td>
<td>$^{139}\text{La}$</td>
<td>$1.06 \times 10^{-1}$</td>
<td>$1.70 \times 10^{-2}$</td>
</tr>
<tr>
<td>$^{95}\text{Zr}$</td>
<td>$4.04 \times 10^{-2}$</td>
<td>$9.55 \times 10^{-3}$</td>
<td>$^{140}\text{Ce}$</td>
<td>$9.47 \times 10^{-2}$</td>
<td>$1.50 \times 10^{-2}$</td>
</tr>
<tr>
<td>$^{94}\text{Zr}$</td>
<td>$4.95 \times 10^{-2}$</td>
<td>$1.15 \times 10^{-2}$</td>
<td>$^{142}\text{Ce}$</td>
<td>$8.56 \times 10^{-2}$</td>
<td>$1.34 \times 10^{-2}$</td>
</tr>
<tr>
<td>$^{95}\text{Mo}$</td>
<td>$4.20 \times 10^{-2}$</td>
<td>$9.84 \times 10^{-3}$</td>
<td>$^{141}\text{Pr}$</td>
<td>$8.55 \times 10^{-2}$</td>
<td>$1.35 \times 10^{-2}$</td>
</tr>
<tr>
<td>$^{97}\text{Mo}$</td>
<td>$5.44 \times 10^{-2}$</td>
<td>$1.25 \times 10^{-2}$</td>
<td>$^{143}\text{Nd}$</td>
<td>$5.07 \times 10^{-2}$</td>
<td>$7.89 \times 10^{-3}$</td>
</tr>
<tr>
<td>$^{98}\text{Mo}$</td>
<td>$6.12 \times 10^{-2}$</td>
<td>$1.39 \times 10^{-2}$</td>
<td>$^{144}\text{Nd}$</td>
<td>$8.43 \times 10^{-2}$</td>
<td>$1.30 \times 10^{-2}$</td>
</tr>
<tr>
<td>$^{100}\text{Mo}$</td>
<td>$7.07 \times 10^{-2}$</td>
<td>$1.57 \times 10^{-2}$</td>
<td>$^{145}\text{Nd}$</td>
<td>$5.06 \times 10^{-2}$</td>
<td>$7.76 \times 10^{-3}$</td>
</tr>
<tr>
<td>$^{99}\text{Tc}$</td>
<td>$5.87 \times 10^{-2}$</td>
<td>$1.32 \times 10^{-2}$</td>
<td>$^{146}\text{Nd}$</td>
<td>$5.51 \times 10^{-2}$</td>
<td>$8.39 \times 10^{-3}$</td>
</tr>
<tr>
<td>$^{101}\text{Ru}$</td>
<td>$7.44 \times 10^{-2}$</td>
<td>$1.64 \times 10^{-2}$</td>
<td>$^{234}\text{U}$</td>
<td>$1.25 \times 10^{-1}$</td>
<td>$1.19 \times 10^{-2}$</td>
</tr>
<tr>
<td>$^{102}\text{Ru}$</td>
<td>$8.89 \times 10^{-2}$</td>
<td>$1.94 \times 10^{-2}$</td>
<td>$^{238}\text{Pu}$</td>
<td>$4.16 \times 10^{+0}$</td>
<td>$3.89 \times 10^{-1}$</td>
</tr>
<tr>
<td>$^{104}\text{Ru}$</td>
<td>$8.97 \times 10^{-2}$</td>
<td>$1.92 \times 10^{-2}$</td>
<td>$^{239}\text{Pu}$</td>
<td>$7.11 \times 10^{-1}$</td>
<td>$6.62 \times 10^{-2}$</td>
</tr>
<tr>
<td>$^{103}\text{Rh}$</td>
<td>$1.19 \times 10^{-2}$</td>
<td>$2.58 \times 10^{-3}$</td>
<td>$^{240}\text{Pu}$</td>
<td>$2.15 \times 10^{-1}$</td>
<td>$1.99 \times 10^{-2}$</td>
</tr>
<tr>
<td>$^{105}\text{Pd}$</td>
<td>$6.28 \times 10^{-2}$</td>
<td>$1.33 \times 10^{-2}$</td>
<td>$^{241}\text{Pu}$</td>
<td>$1.36 \times 10^{-1}$</td>
<td>$1.26 \times 10^{-2}$</td>
</tr>
<tr>
<td>$^{106}\text{Pd}$</td>
<td>$8.47 \times 10^{-2}$</td>
<td>$1.78 \times 10^{-2}$</td>
<td>$^{242}\text{Pu}$</td>
<td>$7.67 \times 10^{-1}$</td>
<td>$7.05 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

Continued on next page
target at the time of measurement in the Knudsen cell is $^{238}\text{Pu}$, and large quantities of the gases helium and xenon are present. The quantities of helium and xenon produced and retained in the matrix (indicated in atomic ppm) and the fraction released during irradiation are represented as charts in Figure 5.7. In the left part of the figure the

<table>
<thead>
<tr>
<th>Isotope</th>
<th>wt.%</th>
<th>at.%</th>
<th>Isotope</th>
<th>wt.%</th>
<th>at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{107}\text{Pd}$</td>
<td>$6.08 \times 10^{-2}$</td>
<td>$1.26 \times 10^{-2}$</td>
<td>$^{241}\text{Am}$</td>
<td>$4.43 \times 10^{-1}$</td>
<td>$4.09 \times 10^{-2}$</td>
</tr>
<tr>
<td>$^{108}\text{Pd}$</td>
<td>$4.63 \times 10^{-2}$</td>
<td>$9.54 \times 10^{-3}$</td>
<td>$^{243}\text{Am}$</td>
<td>$5.71 \times 10^{-1}$</td>
<td>$5.23 \times 10^{-2}$</td>
</tr>
<tr>
<td>$^{131}\text{Xe}$</td>
<td>$3.95 \times 10^{-2}$</td>
<td>$6.70 \times 10^{-3}$</td>
<td>$^{243}\text{Cm}$</td>
<td>$9.33 \times 10^{-2}$</td>
<td>$8.54 \times 10^{-3}$</td>
</tr>
<tr>
<td>$^{132}\text{Xe}$</td>
<td>$9.62 \times 10^{-2}$</td>
<td>$1.62 \times 10^{-2}$</td>
<td>$^{244}\text{Cm}$</td>
<td>$5.35 \times 10^{-1}$</td>
<td>$4.88 \times 10^{-2}$</td>
</tr>
<tr>
<td>$^{134}\text{Xe}$</td>
<td>$1.13 \times 10^{-1}$</td>
<td>$1.88 \times 10^{-2}$</td>
<td>$^{245}\text{Cm}$</td>
<td>$4.69 \times 10^{-2}$</td>
<td>$4.26 \times 10^{-3}$</td>
</tr>
<tr>
<td>$^{136}\text{Xe}$</td>
<td>$2.25 \times 10^{-1}$</td>
<td>$3.67 \times 10^{-2}$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.7: Pie-charts representing the helium and xenon release after puncturing (left side of the figure) and the release temperatures of helium and xenon in the Knudsen cell experiments (right side).
helium and xenon concentrations produced during irradiation and the amount of these gases released during the puncturing tests can be seen. The right part of Figure 5.7 indicates the helium and xenon concentration at the time of the present investigation. It is assumed that all additional helium produced from decaying α-emitters remains in the material. The increase in the helium amount is about 40%. The right part of the figure shows the fraction released for various temperature ranges. The temperature dependent release of helium and xenon from sample 1 is shown in Figure 5.8. The heavy line is the mass spectrometer signal of $^4\text{He}$; the thin line is the signal of $^{132}\text{Xe}$. Helium begins to be released at 600 K but the release is significant only at 1500 K. The release is almost complete at 1750 K. About 99% of the helium is released between 1500 and 1750 K (see Figure 5.7). The picture is different for xenon; the release also starts becoming significant at 1500 K but increases continuously until 1900 K (see Figure 5.8). In the range 1500 - 1750 K only 43% is released, the remainder being released above 1750 K. In the figure different release stages are indicated for helium and xenon. They are summarized in Table 5.6 and will be discussed at the end of this chapter by making use of the observations from the microscopical investigations.

The fractional release of helium and xenon are also indicated in Table 5.6. It should be noted that the data in Figure 5.8 are plotted versus temperature. The released fraction at
Table 5.6: Release stages for helium and xenon.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Temperature range (K)</th>
<th>Released fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heₐ</td>
<td>500-1000</td>
<td>0.28</td>
</tr>
<tr>
<td>Heₐ₂</td>
<td>1100</td>
<td>0.17</td>
</tr>
<tr>
<td>Heₐ₃</td>
<td>1100-1500</td>
<td>0.65</td>
</tr>
<tr>
<td>Heₐ₄</td>
<td>1500</td>
<td>98.9</td>
</tr>
<tr>
<td>Xeₐ</td>
<td>1100</td>
<td>0.23</td>
</tr>
<tr>
<td>Xeₐ₂</td>
<td>1500</td>
<td>37.0</td>
</tr>
<tr>
<td>Xeₐ₃</td>
<td>1500-1900</td>
<td>16.4</td>
</tr>
<tr>
<td>Xeₐ₄</td>
<td>1900-2100</td>
<td>46.4</td>
</tr>
</tbody>
</table>

each stage given in Table 5.6 was determined from the time dependent signal. Sample 2 was annealed in different experiments as shown in Table 5.4. After every annealing, a small piece of the sample was removed for microscopical investigations, the remainder of the sample was annealed again at a higher temperature. The release of helium from the specimens for the various annealing steps is shown in Figure 5.9. From Figure 5.9

Figure 5.9: Helium release from EFTTRA-specimen during successive annealing steps. Every annealing was performed using a ramp rate of 30 K min⁻¹. The maximum annealing temperature is indicated in each of the figures.
the following remarks can be made, where Figure 5.8 is used as a reference for the sample annealed without intermediate cooling. In the first annealing step, the heating of the sample was stopped at the beginning of the large helium release peak (1450 K) and an almost identical release profile as in Figure 5.8 was found. The second heating was performed up to the maximum of the large release peak. However, even for low temperatures an increase in the helium signal can be observed, although the sample had been heated up in this temperature range in the first attempt. Thus, under thermal annealing, helium ions become mobile. However, due to the macroscopic scale of the system, the distances between the original position of the helium atom and the surface may be too large to be overcome within the heating time. The helium-atom may, after this heating step, be located in a position closer to the surface and thus be released at a lower temperature during the next heating step. During the third heating stage the specimen was annealed up to 2020 K. There was not much helium left in the sample; however, again helium was released within the temperature range where the previous heating was performed. During the last three heating steps (up to 2380 K, 2690 K and 2920 K, respectively), hardly any helium release was observed. These experiments where originally performed to prepare specimens for microscopical investigations to gain insight into the microstructure and the behaviour of helium after thermal annealing.

5.2.5 Microstructural investigations

SEM analyses of the samples were performed at different stages of the annealing. The high porosity after irradiation, observed by ceramography (on the average 18% compared to 3% after fabrication) was confirmed by SEM. The porosity can be seen in Figure 5.10a. The pores were probably filled with gas at pressures in the order of 10 MPa. Although the material showed this large porosity, it was still able to retain a large fraction of the gas inventory. It is remarkable that this structure is stable under thermal annealing up to temperatures much above the in-pile conditions. On the left side of the figure, the region with a higher $^{241}$Am content after fabrication is visible. In this 200 $\mu$m shell, the porosity has increased to 40%. It should be noted that a lower porosity is observed in the immediate vicinity of the cladding. This is probably due to an increased stress field caused by the pellet-cladding interaction. The porosity at the side of the high-porosity band facing the centre consists of larger pores than that in the region facing the cladding. This trend of larger and more separated pores towards the centre of the pellet is continued towards the centre and reveals the influence of the central temperature of the sample during irradiation. Metallic fission product precipitates like Ru, Pd, Tc, Rh and Mo (see Figure 5.10b) were distributed all over the specimen as confirmed by EDX analysis. The arrows in Figure 5.10b indicate these precipitates. It seems that the matrix is constituted of small (500 nm) grains embedded in a metamict phase. This is visible in Figures 5.10b and 5.10c. Bright areas surrounding the pores, evenly distributed over the matrix, were also visible. They were rich in plutonium and aluminium as observed by EDX analysis. In Figure 5.10c the inhomogeneous
Figure 5.10: SEM micrograph of the EFTTRA-T4 target after cleavage showing: a) high porosity after irradiation. The region of higher porosity in the left-hand part of this picture corresponds to a 350 µm wide band with a higher initial americium concentration, b) the arrows indicate metallic fission product inclusions of Pd, Mo, Ru, Rh and Tc, c) enlarged details of the porosity with a brighter gray plutonium-containing phase surrounding the pores, d) backscattered electron image where the plutonium-containing phase around the pores is clearly visible.

distribution of the plutonium distributed around the pores in the form of lighter areas is clearly visible. The presence of this 1-2 µm wide plutonium-rich layer sustains the conclusion that the large pores grow inside the original americium inclusions [99]. The distance between the pores is about 5-7 µm, corresponding to the range of the fission products. It is therefore reasonable to state that the large pores contained both helium and fission gases. In the backscattered electron (BSE) mode (Figure 5.10d), a contrast is found depending on the Z-value of the nuclide. The heavier the atom, the lighter the area. In the BSE-mode, grey areas surround the pores. These grey areas will thus mainly consist of $^{238}$Pu, which is the principal plutonium isotope in the target and is produced by neutron capture and subsequent decay of the $^{241}$Am originally present. As the range of the recoil atoms from the $\alpha$-decay of $^{242}$Cm and $^{238}$Pu is about 20 nm, the newly formed actinides will stay in the vicinity of the original $^{241}$Am-inclusions, as long as they do not diffuse thermally. Smaller plutonium-rich inclusions (∼100 nm) dispersed in the matrix were also found by TEM investigations [99] but contained neither cavities nor bubbles.
TEM investigations were performed only for the specimen after irradiation and storage, and for the specimen annealed at 1600 K. Two important aspects became clear as a result of the TEM investigations:

1. As discussed previously, phases containing plutonium surrounding the pores could be observed. These phases were located at the original position of the americium inclusions. Porosity developed inside the inclusions and grew with gas build-up. Figure 5.11 shows such a pore surrounded by a plutonium-rich phase. Furthermore, in the same figure, arrows indicate bubbles associated with fission product inclusions. There is a sharp boundary between the matrix (denoted by Mg Al) and the plutonium-rich zone (denoted by Pu-Al), which indicates that there is no inter-diffusion between the original americium grains and the matrix atoms. The gas bubbles were observed mostly in the plutonium-rich phase surrounding the pores and were often associated with metal precipitates as can be seen for example in Figure 5.11.

![Figure 5.11](image)

*Figure 5.11*: TEM micrograph showing a Pu-Al-rich phase surrounding a large bubble produced by helium precipitation and presumably bubble coalescence. The spinel matrix, denoted by Mg-Al, has been restructured in a nano-crystallized form. The arrows indicate small gas bubbles associated with inclusions of fission products. The inset, upper left, shows a diffraction pattern attributed to the coexistence of several phases.

2. The TEM investigations also revealed that the spinel matrix has recrystallized into nanometre size grains. In Figures 5.12a to 5.12c TEM micrographs representative of the material are shown. Figure 5.12a is a view of the Pu-Al rich phase with some
gas bubbles associated with inclusions of fission products. In Figures 5.12b and 5.12c the nanograin structure of the matrix is shown. The TEM selective area electron diffraction (SAED) patterns shown in Figures 5.12a to 5.12d reveal a complex phase distribution in the EFTTRA-T4 material. From the diffraction rings and the calibrated camera length (the camera was calibrated with an aluminium standard) net peaks were deduced and the corresponding $d$-spacing was calculated by using a special software package. In Figure 5.12d the microstructure and SAED pattern of a single crystal of spinel, amorphized with 70 MeV I-ions, is shown [10]. Comparing Figures 5.12a to 5.12c with 5.12d, the $d$-spacing deduced from the diffraction rings could be assigned to belong partially to a MgAl$_2$O$_4$ structure. The principal differences in the patterns are probably caused by reflections of lower intensity in the different examined areas of the EFTTRA-T4 material. Contributions are probably given by phases segregated from spinel (like MgO and Al$_2$O$_3$) and by compounds

**Figure 5.12**: TEM bright field images and associated SAEDs (shown with the calculated half circles) of a) a Pu-Al rich phase, b) and c) nano-sized spinel grains and d) nanocrystallized grains from an ion-irradiation-induced amorphous spinel. To calibrate the camera length, an aluminium standard was used.
like PuO₂ and PuAlO₃, although the diffraction rings could not be assigned to any known Pu phase with either O or Al. It was checked in particular for the Pu-Al rich phase whether the diffraction patterns gave more detailed information. One has to keep in mind that the electron diffraction as produced in the condition of such a sample (crushed specimen of several possible phase) is not as precise as e.g. XRD. The SAED pattern are qualitatively indicative and cannot be considered the best tool to identify phases as the area investigated is only several hundreds of nanometres wide and the inhomogeneity of the material is rather high at that scale.

The as-irradiated sample (labelled as RT in Figures 5.13a and b) showed clearly two phases; one nano-crystalline phase of spinel with some fission product (FP) inclusions (see Figure 5.13a) and a Pu-Al-rich phase with gas bubbles of a few tens of nanometres often associated with FP inclusions (see Figure 5.13b). In the sample annealed at 1600 K it was observed that the spinel matrix remains nano-crystalline, showing no structural defects (see Figure 5.13c), but that nano-sized gas bubbles could be found in some areas. In the Pu-Al-rich phase the gas bubbles were easily observed and showed the same aspect as in the as-irradiated sample shown in Figure 5.13d. In the Figures 5.13b and 5.13d, metallic precipitates of insoluble metals can be seen in the cavities. The same occurs in the regular UO₂-fuels. It is not clear whether the gas precipitates preferentially at this precipitates or the precipitates were formed in bubbles but they are often found associated. Both mechanism

![Figure 5.13: TEM results for samples after irradiation (RT) and after annealing at 1600 K.](image-url)
need diffusion of the species (insoluble metals or gas atoms). From Figures 5.13b and 5.13d, it seems that the size of bubbles increases after thermal annealing. However, the micrographs were not taken from the same specimen. The difference in bubble size might be an effect of the initial americium distribution in the target as well. To perform a statistic distribution of the bubble size more TEM micrographs as presently available are necessary.

In Figure 5.14 it is shown in a TEM micrograph that in some cases bubbles interconnect and form open paths in the matrix.

![Figure 5.14: Interconnection of bubbles forming open paths in the matrix as observed with TEM.](image)

### 5.2.6 Helium and xenon release from the EFTTRA-T4 specimen

As described earlier, SEM analyses were performed at different annealing stages. In Figure 5.8 it was shown that the release of helium and xenon is congruent only to a certain extent (see e.g. the small peak at 1150 K in the figure). The integrated signals for the helium and xenon releases are shown in Figure 5.15, where the different release stages for helium and xenon are denoted by the symbols given in Table 5.6. The integral of the helium signal is $1.48 \times 10^{-6}$ Coulomb which, making use of the calibration factor presented in Subsection 2.1.4, corresponds to $(8.15 \pm 1.94) \times 10^{17}$ helium ions in sample 1. This yields a helium concentration of $(4.40 \pm 1.05) \times 10^{-2}$ wt.%.
a value of $1.03 \times 10^{-1}$ wt.% was given. Those data, however, are based on ORIGEN calculations and do not take into account the inhomogeneous distribution of the helium ions and the release of helium during the four years of storage. The amount of helium determined from the Knudsen cell measurements can thus be lower than the calculated amount. It was shown that the original grains (10 $\mu$m after fabrication) recrystallize into 500 nm grains from an amorphous state. Below 1450 K no changes were observed in the surface morphology of the specimen, i.e. the large porosity and the matrix consisting of 500 nm grains dispersed in a vitreous phase are visible in the micrographs in Figure 5.16. In Figure 5.8 it could be seen that below 1500 K three release stages for helium and one release stage for xenon are observed. The helium release defined as $\text{He}_A$, $\text{He}_B$ and $\text{He}_C$ and the xenon release denoted as $\text{Xe}_A$ can be ascribed to venting of helium and xenon from near surface grains or grain boundaries towards the surface or to helium and xenon atoms using permeation paths within the grains.

In Figure 5.17 a SEM micrograph of the specimen after annealing up to 1600 K is shown. At 1600 K, etching of the grains occurred in conjunction with the release of helium and the beginning of the release of xenon. The quantity of helium released in peak $\text{He}_D$ is about 98% of the total amount of helium released. The helium was for the largest part trapped in pores formed within the original 2-3 $\mu$m size americium inclusions. From the microstructure of the fuel it was shown that it is highly probable that

**Figure 5.15:** Integrated helium and xenon release profiles as a function of annealing temperature.
the spinel turned amorphous during irradiation and recrystallized during storage due to electronic energy loss from the β- and α-decaying fission products and actinides. This corroborates the observation that intragranular gas bubbles where xenon was probably located during irradiation are rarely found in the matrix. Rather they are formed at
the periphery of the spinel matrix, in the plutonium-rich phase, to which they were punched out during recrystallization of the matrix. It is highly probable that the entire matrix did not fully recrystallize and that the major release peaks denoted HeD and XeB in Figure 5.8 are due to the punch out during thermally activated recrystallization of the matrix. The fact that almost all helium is released in a very narrow temperature interval implies that a massive purging mechanism, controlled by lattice reorganization rather than by helium random diffusion, is responsible for the helium release. A similar example was shown in Chapter 4 where the helium release from a xenon-irradiation-induced amorphous spinel matrix showed similar behaviour, i.e. release of helium and subsequent release of xenon by sweeping during recrystallization. For helium, however, one expects a higher mobility. It is remarkable that, once helium has reached grain boundaries or other extended defects, it is not, like xenon, permanently trapped in coarse intergranular porosity, but rather escapes to free surfaces with low activation enthalpies. When compared to ion-irradiated samples (see Chapter 4), the main release occurs at a higher temperature. It can be assumed, based on the microstructure observations and release profiles, that the trapped helium must first dissolve in the spinel matrix and therefore needs to overcome the barrier of the $\mu$m-sized Pu-Al phase. The apparent release temperature and activation energy is therefore higher than it would be for pure spinel.

At 2020 K grain growth occurs in the material, the spinel matrix grains having sizes between 2 and 5 $\mu$m (Figure 5.18). This is the region where the release stages XeC and XeD are observed. Immediately after irradiation, helium was only found in large pores of the material while xenon was distributed partly in these large pores and partly in bubbles within the matrix. The release parts denoted by XeC and XeD take place only when the matrix begins to evaporate and is not complete until all the PuO$_2$ is released. The latest fact indicates that part of the xenon remains in the pores surrounded by the plutonium-rich phase until spinel grain growth occurs with segregation of the plutonium-rich phase (at 2020 K, see Figure 5.18).

Figure 5.18: SEM-micrographs for sample 2 after annealing at 2020 K.
The phenomenon of grain growth was further observed in a specimen annealed at 2250 K where two phases were detected; the spinel matrix with grains measuring between 5 and 20 $\mu$m and a phase containing plutonium totally segregated from the spinel (Figure 5.19) and forming lenticular precipitates on top of or between the spinel grains (see the arrow in Figure 5.19).

![Figure 5.19: SEM-micrographs for sample 2 after annealing at 2250 K.](image)

When comparing the release temperature of helium in single-effect studies, e.g. in the amorphous spinel specimen described in Chapter 4, it is noticed that in the case of the EFTTRA-T4 material the release temperature is much higher. According to the microstructure characteristics it becomes evident that the helium contained in the pores first must overcome the barrier of the plutonium-rich phase surrounding these pores before diffusing into the spinel matrix. The microstructure of the spinel matrix is also unusual when compared to previous single-effect experiments in the sense that it consists of grains of some tens of nanometres. Therefore, once helium has been released from the pores surrounded by the plutonium-rich phase, the presence of numerous grain boundaries enhance the release.

If solely the pores are considered open volume containing the gases helium and xenon formed during irradiation (krypton can be neglected), the pressure inside the bubbles/pores can be estimated to be about 7 MPa. This pressure was calculated from the total amount of gas and assumed to be present in the large porosity. Although this is an assumption and does not take into account the helium that is dissolved in the lattice. The microstructure examination did not reveal any cracking around the pores attributable to either the amorphous state of the surrounding plutonium-rich phase or of the spinel matrix during irradiation.

As discussed previously, according to the fission power history, the temperature during irradiation in the EFTTRA-T4 experiment was 670 K at the outside of the capsule, which results in a maximum temperature of about 1050 K at the centre of the target. With regard to the laboratory release profiles recorded on the EFTTRA-T4 material it is clear that a complete release of helium would have required higher irradiation temperatures.

In this section remarks have been made on microstructural observations. However, the
overall description given in the chapter does not take into account the greater complexity of the system. The so-called plutonium-rich phase consists of other actinides as well. It appears to contain crystalline components in some cases and is not regular in thickness. It is also postulated that recrystallization has occurred during storage, leading to the conclusion that during in-pile irradiation the amorphous matrix retains the helium better than a crystalline material would. The specific microstructure of the starting material probably played a major role in the observed pore formation, i.e. the pores developed within the original 2-3 µm americium inclusions. The plutonium-rich phase surrounding these pores acts as a barrier for the diffusion and re-solution of the gases in the spinel matrix. The distribution of the americium inclusions and therefore of the pores should also be considered since their mutual distance leads to a high probability for the gaseous fission products to be stopped in the vicinity of trapping sites, the same being true for the α-particles. Small fission products were found to be distributed homogeneously over the spinel matrix. Moreover, small bubbles had formed in the matrix after annealing at 1600 K, confirming that gas was dissolved in the recrystallized spinel matrix. It should be taken into account that a large quantity of helium was formed during storage at room temperature.

5.3 Summary and conclusions

A spinel matrix containing 11.2% ²⁴¹Am was irradiated successfully in the HFR at Petten for about 360 EFPD after which 96% of the ²⁴¹Am had been either transmuted into other actinides or fissioned. This was an excellent result from the point of view of americium transmutation. However, problems occurred during the fabrication of the material. The infiltration method used for producing the pellets gave an inhomogeneous distribution of the americium in the pellet. Secondly, the spinel matrix itself did not behave well under irradiation. Owing to the large quantities of gas build-up in the material, a swelling of the pellets of about 18% occurred, caused by a large porosity and leading to microcracks in the fuel.

A schematic overview of the observations on the microstructure as well as on the helium and xenon behaviour under thermal annealing is shown in Table 5.7.

Scanning electron microscopy showed that the actinides formed by neutron capture and subsequent decay (mainly Pu isotopes) are located around the pores in inclusions of 2-3 µm corresponding to the original Am-inclusions. The spinel matrix material between the pores observed by transmission electron microscopy showed a nano-grain structure containing neither gas bubbles nor large defects. The matrix is assumed to have been turned amorphous before its subsequent recrystallization during storage. Large pores and bubbles were formed in the matrix, mainly by the helium and the fission gases produced during irradiation. The fission products were distributed throughout the matrix and metal precipitates were found in the matrix, often in association with gas bubbles. The original americium-inclusions had transformed into plutonium-rich inclusions. Since the spinel matrix showed a pronounced plastic deformation associated
Table 5.7: A schematic overview of the evolution of the microstructure and the xenon and helium behaviour during irradiation, storage and post-irradiation thermal annealing experiments.

<table>
<thead>
<tr>
<th>Microstructure</th>
<th>He</th>
<th>Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>IRRADIATION</strong></td>
<td>Precipitation in pores surrounded by</td>
<td>Precipitation in pores and in bubbles</td>
</tr>
<tr>
<td>Gas bubble/pore formation.</td>
<td>a Pu-Al phase and in bubbles:</td>
<td>in the matrix:</td>
</tr>
<tr>
<td>18-20% swelling</td>
<td>20% in-pile release</td>
<td>5% in-pile release</td>
</tr>
<tr>
<td><strong>STORAGE</strong></td>
<td>Start recrystallization</td>
<td>Build-up of additional helium</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>800 K</td>
<td>Bulk recrystallization</td>
<td>Sudden total escape of gas from matrix and pores</td>
</tr>
<tr>
<td></td>
<td>Opening of gas percolation paths.</td>
<td>Sudden partial release</td>
</tr>
<tr>
<td></td>
<td>Matrix vaporization</td>
<td></td>
</tr>
<tr>
<td>1600 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2200 K</td>
<td>Mg sublimation</td>
<td>Final release from large pores</td>
</tr>
<tr>
<td></td>
<td>Grain growth</td>
<td></td>
</tr>
</tbody>
</table>

with a large swelling it is no longer to be considered as a candidate microdispersed inert matrix for actinide transmutation. Its unpredictable behaviour is linked to a poor chemical stability when used in conjunction with americium and its transmutation products, and to its property to amorphize under reactor irradiation conditions.

The helium is mostly trapped in pores formed within the original 2-3 \(\mu\)m sized americium inclusions. When compared to ion-irradiated samples, the main release from the EFTTRA-T4 samples occurs at a higher temperature. It can be assumed, based on the microstructure observations and release profiles, that the trapped helium should first dissolve in the spinel matrix and must therefore overcome the barrier of the \(\mu\)m-sized Pu-Al phase. The apparent release temperature and activation energy is therefore higher than it would be for pure spinel. The development of the porosity associated with a large swelling is attributed to the original microstructure (micro-dispersion) which affects its evolution. It was shown that the spinel behaves poorly from the chemical as well as from the mechanical point of view. By considering all these aspects there is no argument anymore to consider its use as an inert matrix. For the development of new targets for transmutation it becomes evident that the gas behaviour and more specifically the helium behaviour should be considered in the design of the fuel pin.
114

Helium in reactor irradiated spinel
Chapter 6

Helium in Zirconia

6.1 Yttria-stabilized zirconia

In this chapter, the results of experimental investigations on helium behaviour in fully stabilized zirconia (FSZ) are presented. Presently, FSZ is studied intensively in connection with its use as an inert matrix material.

6.1.1 Properties of the zirconia samples used

Fully stabilized zirconia samples were obtained from ‘Technische Keramik Metoxit AG’. The molecular fraction of Y₂O₃ in the material was 10%, which gave a chemical composition of Zr₀.₉₂₅Y₀.₁₀₂₅O₁.₉₅. XRD investigations were performed on the samples in order to determine their structure. The most important results of the XRD analysis are:

- At room temperature, the material is stabilized in the Fm̅₃m-spacegroup.
- The material has a lattice parameter of (5.14842 ± 0.00029) Å.

The results of the XRD-analysis are shown in Figure 6.1. On the abscissa, the reflection angle 2θ is given. The solid vertical lines are the typical diffraction angles for the cubic phase.

The density of some of the samples was determined by making use of the method of Archimedes. The experimental density was determined to be 5.74 ± 0.03 g cm⁻³. The grain size, observed by TEM, was several hundreds of nanometers, i.e. much smaller than the 20-30 μm quoted by the manufacturer. No change in grain size exists between unannealed specimens and specimens annealed at 1673 K.

The samples which were finally implanted with helium ions were firstly polished down to a surface roughness less than 1 μm and subsequently annealed in air at 1673 K for two hours. This was done to remove defects in the surface region introduced by the polishing. Afterwards the samples were implanted with helium.
6.1.2 Helium mobility in fully stabilized zirconia

Helium atoms will, after implantation, come to rest in the oxygen vacancies and in interstitial sites. Under thermal treatment, helium will become mobile. The helium can move by vacancy or grain boundary assisted diffusion towards the surface. Grain boundaries can also trap helium, or bubble formation at grain boundaries or within the grains may occur. Self-diffusion of oxygen ions will occur at temperatures below the release temperature of helium (see Figure 3.6). The oxygen vacancies introduced in the material due to the addition of yttria will remain in the matrix. At higher temperatures, the zirconium- and yttrium-ions will be mobilized in the material. In Table 3.3 the radius of an oxygen vacancy has been given as lying between 160 and 172 pm. Thus the size of the oxygen vacancies is sufficiently large for a helium atom to be accommodated. During thermal annealing, helium will be released from the trap, after which it will be either trapped again in e.g. a bubble or a vacancy cluster, or it will move towards the surface by vacancy or grain boundary assisted diffusion. Release processes will be described in more detail in the remainder of this chapter.
6.2 Investigations on specimens implanted with 30 keV helium-ions

6.2.1 Sample specification

In total, eight specimens have been implanted with 30 keV helium ions ($^3$He or $^4$He) at room temperature at IRI. The helium flux was $3 \times 10^{12}$ cm$^{-2}$s$^{-1}$. The total helium ion fluences have been varied between $1.7 \times 10^{15}$ and $5.1 \times 10^{16}$ cm$^{-2}$. An overview of the samples and the analysis applied is given in Table 6.1.

Table 6.1: Overview of the investigated specimens implanted with 30 keV helium ions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gas</th>
<th>He-dose (×10$^{15}$ cm$^{-2}$)</th>
<th>Method of investigation*</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$^3$He</td>
<td>1.7</td>
<td>NDP/PBA</td>
</tr>
<tr>
<td>II</td>
<td>$^3$He</td>
<td>6.3</td>
<td>NDP/PBA</td>
</tr>
<tr>
<td>III</td>
<td>$^3$He</td>
<td>26</td>
<td>NDP/PBA</td>
</tr>
<tr>
<td>IV</td>
<td>$^3$He</td>
<td>51</td>
<td>NDP/PBA</td>
</tr>
<tr>
<td>V</td>
<td>$^4$He</td>
<td>1.7</td>
<td>THDS</td>
</tr>
<tr>
<td>VI</td>
<td>$^4$He</td>
<td>6.3</td>
<td>THDS</td>
</tr>
<tr>
<td>VII</td>
<td>$^4$He</td>
<td>26</td>
<td>THDS</td>
</tr>
<tr>
<td>VIII</td>
<td>$^4$He</td>
<td>51</td>
<td>THDS</td>
</tr>
</tbody>
</table>

* NDP: Neutron Depth Profiling; PBA: Positron Beam Analysis; THDS: Thermal Helium Desorption Spectrometry.

To estimate the defect and helium distribution after implantation, calculations have been performed using the SRIM-2000 code [4], where for FSZ a displacement energy of 40 eV has been used [32]. The results for both $^3$He and $^4$He implantations with the highest fluence (i.e. $5.1 \times 10^{16}$ He cm$^{-2}$) are shown in Figure 6.2. In Figure 6.2a, it can be seen that $^4$He-atoms, which have a larger mass than the $^3$He-atoms, penetrate deeper into the material than $^3$He-atoms with the same energy (heavy lines). This is due to the fact that the isotope with the higher mass loses a smaller fraction of its energy in every collision. The $^4$He-atoms also cause more displacements in the material than the $^3$He-atoms (dashed lines). In Figure 6.2b the vacancies caused by the implantation of the helium ions are shown. The oxygen vacancies introduced into the material due to the addition of yttria are not included in the figure. In Eq. 3.1 it was shown that the addition of one Y$_2$O$_3$ molecule yields one oxygen vacancy. The material used for the investigations described in this thesis can be defined as: Zr$_{0.9}$Y$_{0.1}$O$_{1.95}$V$_{0(0.05)}$, which gives an oxygen vacancy fraction of about 2.5% (the amount of oxygen vacancies divided by the amount of oxygen sites). Thus, by looking at Figure 6.2 most of the vacancies present in the material are oxygen vacancies introduced by the implantation of helium. However, as discussed previously, these vacancies are mobilized below the mobilization temperature of the helium gas and will have disappeared before helium mobility occurs. In the temperature interval in which helium release occurs, the
yttrium- and zirconium-vacancies introduced into the material by the helium implantations are still present. These data are indicated in Figure 6.2b, where the replacement collisions filling up most of these vacancies have not been taken into account. It may be concluded that in the temperature range where the helium release occurs, oxygen vacancies introduced into the material by the addition of yttrium will play a dominant role.

An overview of the calculated data from the TRIM-results is given in Table 6.2. The average helium concentration shown in the table has been calculated over the region with a helium concentration larger than zero.

### 6.2.2 Thermal helium desorption measurements

The samples for THDS were annealed stepwise, the heating rate used was about 1 K s\(^{-1}\) and the maximum temperature was increased for every step. After reaching the maximum temperature the heating was stopped immediately and the sample was left to cool down naturally to room temperature. In Figure 6.3, for samples V to VIII (i.e. the samples implanted with \(^4\)He), the fraction retained after every annealing step is plotted versus the maximum annealing temperature. The temperatures were corrected with the method described in Section 2.2.3. For each implanted dose, the experiments were duplicated. It can be seen that for the lowest dose (sample V), all helium had been released at about 850 K. For sample VI (implanted with \(6.3 \times 10^{15} \text{ cm}^{-2}\)) the first...
Table 6.2: Results of the TRIM calculations for 30 keV implanted FSZ. The maximum of the displacements is given in dpa (displacements per atom). Furthermore, the average helium concentration over the region with a helium concentration larger than zero is given as well as the maximum helium concentration in the peak.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gas</th>
<th>Peak displacements (dpa)</th>
<th>Average He-concentration (cm(^{-3}))</th>
<th>Maximum He-concentration (cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>(^3)He</td>
<td>0.05</td>
<td>5.4(\times)10(^{19})</td>
<td>1.2(\times)10(^{20})</td>
</tr>
<tr>
<td>II</td>
<td>(^3)He</td>
<td>0.18</td>
<td>2.0(\times)10(^{20})</td>
<td>4.3(\times)10(^{20})</td>
</tr>
<tr>
<td>III</td>
<td>(^3)He</td>
<td>0.73</td>
<td>8.3(\times)10(^{20})</td>
<td>1.8(\times)10(^{21})</td>
</tr>
<tr>
<td>IV</td>
<td>(^3)He</td>
<td>1.46</td>
<td>1.6(\times)10(^{21})</td>
<td>3.4(\times)10(^{21})</td>
</tr>
<tr>
<td>V</td>
<td>(^4)He</td>
<td>0.05</td>
<td>5.4(\times)10(^{19})</td>
<td>1.0(\times)10(^{20})</td>
</tr>
<tr>
<td>VI</td>
<td>(^4)He</td>
<td>0.18</td>
<td>1.9(\times)10(^{20})</td>
<td>3.7(\times)10(^{20})</td>
</tr>
<tr>
<td>VII</td>
<td>(^4)He</td>
<td>0.73</td>
<td>8.2(\times)10(^{20})</td>
<td>1.5(\times)10(^{21})</td>
</tr>
<tr>
<td>VIII</td>
<td>(^4)He</td>
<td>1.46</td>
<td>1.6(\times)10(^{21})</td>
<td>3.0(\times)10(^{21})</td>
</tr>
</tbody>
</table>

part of the release had the same shape and temperature as for sample V, but \(~ 30\%\) of the helium was retained up to higher temperatures and the helium release was complete at 1150 K. The results for sample VII (2.6\(\times\)10\(^{16}\) cm\(^{-2}\)) are comparable to those of sample VIII (5.1\(\times\)10\(^{16}\) cm\(^{-2}\)). Helium was released with a more or less constant release rate (no clear changes in slope are visible) and the helium release was complete at 1500 K.

Figure 6.3: Fraction of helium retained measured with THDS for \(^4\)He implanted with four different doses, plotted versus the maximum annealing temperature of each annealing step.

In Figure 6.4, the results of the desorption experiments are shown. Here it can clearly be seen that for the lowest-dose sample (Figure 6.4a), all helium is released in one peak at low temperature. The shape of the release curves agrees well with the model shown
in Figure 3.11a. In Figure 6.3, a change in slope for sample VI is observed, which indicates helium release in two stages. In Figure 6.4b, these two stages can clearly be seen. The first release peak is finished at about 850 K, then the second release peak is visible until about 1150 K. For the samples VII and VIII (Figures 6.4c and 6.4d), a sudden start of the helium release is observed. However, a large portion of the helium is retained up to very high temperatures.

![Figure 6.4](image)

Figure 6.4: Partial desorption spectra from the THDS measurements for samples V to VIII. The helium desorption rate is plotted versus the annealing temperature; both the heating and cooling are shown. The size of the samples used was between 3 and 4 mm².

In Figure 6.5, the Arrhenius plots for samples V to VIII are shown. On the abscissa the value of $1000 \times T^{-1}$ is given, and for clarity the secondary abscissa gives the temperature. In each of the figures the implanted helium fluence is indicated.

The results of the partial annealing experiments performed on specimen V (the lowest-dose specimen, implanted with $1.7 \times 10^{15}$ He cm$^{-2}$) were fitted with the diffusion model for a polycrystalline material. For this, the model described in Section 3.6.2...
Figure 6.5: Arrhenius plot for samples V to VIII. The implantation energy of the helium was 30 keV. The helium desorption rate is plotted vs. $1000 \times T^{-1}$. For clarity, the temperature is given at the secondary abscissa.

was used. An activation energy of 1.9 eV was used with a pre-exponential factor of $10^{10}$ s$^{-1}$. An areal trapping density ($\eta_{gb}$) of $10^{10}$ cm$^{-2}$ was assumed. The Arrhenius plots for both the model and the measurements are shown in Figure 6.6.

To make a fair comparison, on the ordinates, the same number of decades is shown. It can be seen that both Arrhenius plots are in good agreement with each other. Comparing the slopes of the calculated results to the experimental data, it can be concluded that the activation enthalpy of 1.9 eV is slightly overestimated. From the figure, it may be concluded that the model for diffusion in a polycrystalline material applies very well to the measurements performed on such a low-dose implanted specimen.

For the high-dose implanted specimens (specimens VII and VIII) for which the Arrhenius plots are shown in Figures 6.5c and 6.5d, it seems that each curve consists of two
different slopes. More than one process is responsible for the release of helium from the specimen. Firstly, the diffusion theory as applied to the low-dose implanted specimen plays a role, but secondly, bubble formation and release of bubbles occurs, which introduces a second thermal activation process with a different activation enthalpy.

With the method described in Chapter 3, Section 3.6.2, the activation enthalpy $Q$ and the pre-factor $f_{0,1}$ can be calculated from the Arrhenius plots. For the samples V to VIII, these data are shown in Figure 6.7. For the two high-dose specimens, only the first part of the release curve has been used.

From the figures the following remarks can be made:

- For the lowest He-fluence (sample V, $1.7 \times 10^{15}$ cm$^{-2}$, Figure 6.7a) the activation enthalpy is almost the same for all annealing steps. It has an average value of 1.93 eV. The pre-exponential varies between $2.5 \times 10^9$ and $5.0 \times 10^{11}$, and this value is decreasing with increasing temperature.

- For sample VI ($6.3 \times 10^{15}$ cm$^{-2}$, Figure 6.7b) all helium is released at 1200 K as seen in the upper figure for this dose. The activation enthalpy varies between 1.69 eV and 2.27 eV. For the lower temperatures, an increase in activation enthalpy with increasing temperature is observed, until the activation enthalpy stabilizes at about 1000 K. The pre-exponential factor for low temperatures is of the same order of magnitude as the value for sample V ($1.7 \times 10^{15}$ cm$^{-2}$). With increasing temperature, the pre-exponential factor decreases with increasing temperature.

- For sample VII ($2.6 \times 10^{16}$ cm$^{-2}$, Figure 6.7c) the calculated activation enthalpies behave as in sample VI, low for low temperatures, and then increasing towards a
Figure 6.7: Calculated pre-factors $f_{0,i}$ and activation enthalpies $Q$ for samples V to VIII vs. the maximum annealing temperature of the desorption step. Each of the four figures (for the four different doses) shows the following: the fraction of helium retained (top); the activation enthalpies for all annealing steps (middle); the pre-factors $f_{0,i}$, in the form of $10 \log (f_{0,i})$ (bottom).

constant value. For very high temperatures the activation enthalpy drops again. The pre-exponential factor shows the same behaviour as for sample VI. It decreases with increasing annealing temperature.

- For sample VIII ($5.2 \times 10^{16}$ cm$^{-2}$, Figure 6.7d) the same remarks can be made as for sample VII, although the determined values of the activation enthalpy are systematically lower than for sample VII.
The activation enthalpies for all four samples are in agreement with each other, if the errors made in e.g. temperature and fitting are taken into account. There is a difference in the pre-exponential factor depending on the implanted helium dose and the annealing temperature. In general, for higher annealing temperatures, the frequency pre-factor becomes smaller.

### 6.2.3 Neutron depth profiling and positron beam analysis

**Comparison between the THDS and NDP experiments**

Neutron Depth Profiling (NDP) measurements were performed to determine the fraction of helium retained as a function of the maximum temperature reached during partial thermal annealing. The same has been done with the THDS experiments. The samples for THDS and NDP were implanted with identical helium fluences; however, the NDP specimens were implanted with \(^3\)He while the THDS-specimens were implanted with \(^4\)He. This has a slight influence on the depth of implantation and the helium distribution profile, as was shown in Figure 6.2. In the case of \(^3\)He implantation, fewer vacancies are introduced into the material compared to \(^4\)He implantation with an identical helium dose. Most of the vacancies in the material are structural oxygen vacancies introduced by the addition of yttria. Additionally introduced oxygen vacancies are mobilized at lower temperatures than the helium gas and the zirconium and yttrium atoms, as was shown in Figure 3.6. The data presented for helium in this figure, are results of the measurements presented in this chapter. Experiments in the Knudsen cell on samples with an identical dose of either \(^3\)He or \(^4\)He did not reveal different release profiles for the two types of helium. The fractions of \(^3\)He retained in the case of NDP and \(^4\)He in the case of THDS are shown in Figure 6.8.

It is clear that in the NDP experiments for the lower temperature range, helium is released at lower temperatures than in the case of THDS. In THDS, the sample is heated with a heating rate of 1 K \(s^{-1}\) until the maximum annealing temperature (plotted on the abscissa) is reached. The sample is then cooled down immediately; i.e. the sample is less than a few seconds at its maximum temperature. In the annealing of the samples used for NDP, the sample is kept at its maximum temperature for about half an hour, which gives the helium more time to be released from the sample. For samples I and V \((1.7 \times 10^{15} \text{ cm}^{-2})\), a shift of about 100 K is observed between the NDP and THDS experiments. In the NDP experiments, the sample is empty after annealing at 800 K; in the THDS experiments, this state is reached at a temperature of approximately 80 K higher. The partial release curves have been fitted for this low-dose sample with the model described in Subsection 3.6.2. Results are presented in Figure 6.8a for an activation enthalpy of 1.9 eV and a pre-exponential factor of \(10^{10} \text{ s}^{-1}\). It can be seen that the results of the fit show the same shift in temperature. The same shift in temperature was observed for samples II and VI, which were implanted with \(6.3 \times 10^{15} \text{ cm}^{-2}\) (Figure 6.8b). For samples III and IV (and VII and VIII, implanted with \(2.6 \times 10^{16} \text{ cm}^{-2}\) (Figure 6.8c) and \(5.1 \times 10^{16} \text{ cm}^{-2}\) (Figure 6.8d), respectively)
Figure 6.8: Results of NDP (circles) and THDS (squares). The retained fractions of helium vs. the maximum annealing temperature are plotted for four different doses of implanted $^3$He in the case of NDP or $^4$He in the case of THDS. In figure (a) also the results of the fitting to a helium release model are shown.

the difference between THDS and NDP versus temperature can be explained as follows. For the lower temperatures, a shift in release profile between THDS and NDP is observed which can be explained as described for the low-dose samples. In this low-temperature range, helium diffusion will occur. While for the low-dose samples all helium is released towards the surface, for the two higher dose specimens a part of the helium will be trapped in bubbles, as will be discussed in the section on TEM in this chapter. The helium has then to be solved again in the matrix in order to be able to diffuse towards the surface. This process can be seen in the higher temperature range for the high-dose samples, the temperature delay between NDP and THDS becoming smaller. Once the high energy barrier to be solved again in the matrix has been overcome, helium diffuses easily towards the surface. Two different release mechanisms can be identified from the slopes of the curves. One centered around 750 K in a narrow temperature interval and the other around 950 K in a broad temperature interval. These two release stages have been discussed in Subsection 6.2.2. It seems that in order to form bubbles the minimum helium concentration in the specimen should be between $1.2 \times 10^{20}$ cm$^{-3}$ to $4.3 \times 10^{20}$ cm$^{-3}$. 
Figure 6.9: Results of the NDP-measurements for sample II, implanted with $6.3 \times 10^{15}$ He cm$^{-2}$. The data points on the left show the measured numbers of counts, the curves are the results of a Gaussian fit. The figures on the right show the helium distribution versus the depth, where the signal has been corrected for the detector resolution. The curves show Gaussian fits to the measured data.

Results of neutron depth profiling experiments

The results of the NDP-experiments were evaluated with the method described in Appendix A. In Figures 6.9 and 6.10 the results of these evaluations are shown for samples II and IV.

At the left side of each of the figures the measured results are shown versus the detected proton energy. These data are not corrected for the detector resolution. The curves are Gaussian fits to the measured data versus the energy. The maximum annealing temperature, which has an error less than 20 K, the position of the maximum of the Gaussian distribution ($E_m$) and the FWHM of the distribution are given in each figure. The fitted
Figure 6.10: Results of the NDP-measurements for sample IV, implanted with $5.1 \times 10^{16}$ He cm$^{-2}$. The data points on the left show the measured number of counts, the curves are the results of a Gaussian fit. The figures on the right show the helium distribution versus the depth, where the signal has been corrected for the detector resolution. The curves show the Gaussian fits to the measured data.

Gaussian is then deconvoluted to correct the data for the detector function; the result is another Gaussian peak. Subsequently, the proton energy is converted into a depth profile (within the energy range of interest the relation between these two parameters is
a second-order polynomial). The curves in the figures on the right are the deconvoluted Gaussian fits which are converted into a depth profile and a helium concentration by making use of the calibration factor. Because not the original measured data points are converted into a depth profile but rather the deconvoluted Gaussian fits to these data, negative values of the depth may occur. The FWHM of the helium distribution and the position of its maximum ($X_m$) as well as the temperature are given in the figure. It should be noted that the scale on the ordinate is not the same in all figures; the scale has been chosen in such a way that the measured data points are clearly visible. The position of the maximum of the peak and its FWHM are shown in Figure 6.11.

The following remarks can be made with respect to the figures:

- For the unannealed sample implanted with $1.7 \times 10^{15}$ He cm$^{-2}$ and the sample annealed at 600 K, the measured data points can be fitted very well with a Gaussian. The FWHM of the distribution increases with increasing annealing temperature, as can be seen in Figure 6.11. After annealing at 600 and 650 K, a considerable broadening of the helium distribution can be observed. This is a behaviour typical of a diffusion process. After annealing at 700 K, the centre of the peak has shifted considerably towards greater depth and the broadening becomes less, but it should be mentioned, that at this temperature the measured data points cannot be fitted with a Gaussian anymore.

- In Figure 6.9 the results are shown for the sample implanted with $6.3 \times 10^{15}$ He cm$^{-2}$. A broadening of the helium distribution peak is seen in the form of an increase in

---

**Figure 6.11:** Position of the maximum of the peak (upper figure) and the FWHM (lower figure) of the helium distribution for samples I to IV.
the FWHM. This takes place already after annealing up to 600 K, which is typical of a diffusion process. The centre of the peak shifts towards greater depth with increasing annealing temperatures. This can be explained as follows. During annealing helium will diffuse both towards the surface and further into the sample. Once the helium has reached the surface it will be released and cannot diffuse back into the sample. Helium diffusing into the sample will eventually, at a latter stage be released. For this reason the maximum shifts towards greater depth.

- In Figure 6.10 the results are shown for the sample implanted with $5.1 \times 10^{16} \text{He cm}^{-2}$. These results are comparable to those of sample III, for which only the centre and the FWHM of the helium peak are displayed in Figure 6.11. After implantation, the implantation depth and FWHM of the helium distributions agree well with the other implanted doses. If Figure 6.10 is compared to Figure 6.9 it can be observed that the shift of the maximum of the peak is considerably smaller than in the case of samples I and II. Secondly, the FWHM of the peak decreases instead of increasing. These two properties are typical of helium trapping in bubbles.

- According to TRIM [4] (see Section 6.2.1) the maximum of the 30 keV $^3\text{He}$ implantation peak is located at a depth of 151 nm and the peak has a FWHM of 115 nm. NDP experiments at room temperature give a depth of the maximum of the helium peak of about 85 nm and a FWHM of about 72 nm. The same effect has been seen for an implantation experiment at 200 keV (see Section 6.3). Thus, either is helium implanted at a shallower depth and with a narrower distribution than predicted by TRIM, or helium has moved towards the defects in the direction of the sample surface.

**Results of positron beam analysis**

Positron beam analysis (PBA) was performed on the samples I to IV after various annealing steps. The samples used were the same samples as used for the NDP investigations. However, the NDP investigations were stopped when all the helium was released from the sample, whereas the investigations with positrons were continued to see whether open volume defects introduced by the implantation would disappear. In the following discussions, the PBA experiments for samples II and IV will be discussed in more detail. The results for sample I are very similar to those for sample II, while the results for sample III are very similar to those for sample IV.

In Figure 6.12, the measured positron data and the corrected NDP data are shown as a function of depth for the different annealing steps. In the figure for the unannealed specimen (lower left), the heavy curve shows the implantation profile calculated with TRIM. It can be seen that the maximum in the $S$-value is situated between the sample surface and the helium profile. The $S$-parameter gives different information than NDP, which gives a depth distribution of the helium in a specimen. It is possible that helium has moved towards the defects. The $S$-parameter indicates only the open volumes (vacancies or voids) present in the material that are not filled with helium. When vacancies or voids are filled with helium, there $S$-parameter will be close to the value
Figure 6.12: Comparison between the helium depth profile determined with NDP and the damage profile as recorded with PBA for sample IV, implanted with $5.1 \times 10^{16}$ He cm$^{-2}$. The square markers are the measured positron data, the curves along the markers are the results of the program VEPFIT, while the Gaussian shaped lines curves represent the corrected NDP data.

of $S$ of the bulk. Furthermore, positrons are a very sensitive probe for defects, but only in the range of 1 to 100 ppm defect concentration the relation between the $S$-parameter and the defect concentration is linear. Thereafter, saturation occurs which explains the tail observed in the $S$-parameter. In the figure it can also be seen that the maximum of the $S$-profile remains at the same depth in the sample. There is a shift in the maximum of the helium distribution profile which is explained in the section on neutron depth profiling.

In Figure 6.13 the $W$-parameter is plotted versus the $S$-parameter for the as-implanted sample (300 K) and the same sample after various annealing steps indicated in the individual figures. The fraction of helium retained, determined with NDP, is also indicated in the individual figures. The data points are the measured data, the lines through the data points are the fitted results obtained with the program VEPFIT. Finally, the large open circular markers are the results for the $S$- and $W$-parameter for the two layers obtained from VEPFIT.

From the VEPFIT analysis for this sample it follows that the thickness of the damaged layer decreases after every annealing step. Already after annealing at 700 K, it can be seen in the figure that the $S$- and $W$-parameters of the damage layer approach the $S$- and $W$-parameters of the bulk. The NDP experiments showed that the sample was almost empty at these temperatures. In the figure it can be seen that for higher
Figure 6.13: SW-plot for sample II, implanted with $6.3 \times 10^{15}$ He cm$^{-2}$. The small points in the figures are the measured data points. The lines through the points are the results of the VEPFIT analysis. The large open circular markers are the results of VEPFIT where a two-layer model has been used, one for the damaged layer and the other for the bulk of the material. The percentages indicated in the figures are the fraction of helium retained in the specimen.

Annealing temperatures the $S$- and $W$-parameters of the damaged layer and the bulk become identical: all the damage has been annealed out. The helium dose implanted in this specimen is too small to cause damage that is stable up to high temperatures in the material. With the release of the helium, the $S$- and $W$-parameters reach the level of an unimplanted specimen. This can be explained as follows. By implanting
Figure 6.14: SW-plots for sample IV, implanted with $5.1 \times 10^{16}$ He cm$^{-2}$ for various annealing temperatures. The small points in the figures are the measured data points. The lines through the points are the results of the VEPFIT analysis. The large open circular markers are the results of VEPFIT where a three-layer model has been used, layer 1 and 2 for the damaged layer and the layer 3 for the bulk of the material. The percentages indicated in the figures are the fraction of helium retained in the specimen.

A relatively low dose of helium in the specimen, mostly single vacancies are created in the material, while a higher helium dose (more damage) produces vacancy clusters. Single vacancies can easily be annihilated by recombination with highly mobile oxygen ions. Vacancy clusters are not observed at low helium dose because the vacancy concentration is too low to nucleate and let grow vacancy clusters. Only at high dose
this will occur.
In Figure 6.14 the results are shown for the sample implanted with $5.1 \times 10^{16}$ He cm$^{-2}$. For this sample it was not possible to fit the measured data with a two-layer model and thus a three-layer model was used. The same was done for sample III. In the figure, these layers are denoted by the numbers 1, 2 and 3, where the last one represents the bulk of the material. It can be seen that after implantation there is not much difference between the $S$- and $W$-parameters of the near-surface layer (1) and the deeper lying layer (2). From the figures the following can be observed: after each annealing step, the $S$- and $W$-parameters of layer 1 approach more and more those of the bulk. For layer 2 an increase in the $S$-parameter and a decrease in the $W$-parameter can be seen. This process continues up to annealing temperatures of 1000 K, where it reverses. In Figure 6.14j, two additional points have been added. These are data of measurements on FSZ-specimens performed by Popma et al. [100]. The open triangle represents the measured $SW$-data for a fully stabilized zirconia sample prepared by the sol-gel technique and annealed up to 1273 K. The closed square marker gives the $SW$-data for a commercially available single crystal of FSZ. The $SW$-data represented by these two additional markers are in good agreement with the $S$- and $W$-parameters of the samples used for the investigations described in this chapter. The conclusion is that the fabrication method, the presence of grains in the material and the fraction of Y$_2$O$_3$ do not influence the values of $S$ and $W$ of the bulk of fully stabilized zirconia, as long as the sintering temperature has been higher than 800 K.

The results obtained from VEPFIT [85, 86] are shown in Figure 6.15 for all four implanted doses. As explained before, the two lowest-dose samples have been fitted with a two-layer model, the two high-dose samples with a three-layer model, where the last layer is the bulk material, which has a fixed $S$-value. Figure 6.15a shows the $S$-parameter for each layer, while the dashed line represents the $S$-parameter of the bulk material. Figure 6.15b gives the thickness of each layer, where layer 1 is the surface layer. From the lower figure, it can be seen that after implantation (300 K) the damaged layer has a thickness between 110 and 155 nm. From Figure 6.15 the following is observed:

- For the low-dose samples, the $S$-parameter of the layer has a value slightly larger than the $S$-parameter of the bulk material. With increasing annealing temperature, the $S$-parameter decreases towards the bulk value. Already after annealing at 700 K the difference in $S$-value between the damaged layer and the bulk cannot be distinguished by VEPFIT. For both low-dose samples the thickness of the damaged layer becomes narrower after thermal annealing.

- For the high-dose samples not much change is observed in the $S$-parameter and the thickness of layer 1. It is clear, however, that the second layer becomes narrower after each annealing step (which was also observed by NDP), and that its $S$-parameter increases. The release of bubbles leaves behind large open volumes. The specimen must be annealed up to 1000 K before the $S$-parameter starts decreasing again.
Figure 6.15: Results obtained with the program VEPFIT for samples I to IV after various annealing temperatures. Figure a: The S-parameter for each layer is given as a function of the maximum annealing temperature. The dashed curve gives the S-value for the bulk material. Figure b: The thickness of each zone in the material.

6.2.4 Microscopical investigations

SEM investigations on samples after implantation or after annealing up to predefined temperatures, did not reveal any irregularities. It was thus decided to prepare TEM specimens. Specimens identical to the 30 keV implanted THDS specimens were prepared according to the first preparation method described in Section 2.5.2. Unfortunately, in none of the samples, annealed or not, thin areas could be found in the helium implanted region. It was then decided to prepare TEM specimens according to the second method described in Section 2.5.2. In order to deposit the helium in the pre-thinned layer, an implantation energy of 10 keV was selected. Two different ion fluences were implanted: $3 \times 10^{16}$ and $1.5 \times 10^{16}$ He cm$^{-2}$ which yielded an almost identical maximum helium concentration as in the 30 keV implanted samples III and
IV. Specimens were investigated after implantation and after annealing at 650, 750 and 950 K. After annealing at 750 K, some small bubbles were observed. However, their concentration was much lower than reported by Sasajima et al. [15]. This may have been caused by the fact that the specimen was too thin and the implantation energy too high, so that most helium was transmitted through the material. In the annealing stage up to 850 K helium release was observed. This helium may have been released from the thicker areas at the edges of the specimen, as the complete pre-thinned specimen was subject to helium irradiation. It is unclear whether or not helium was really present in the thin areas investigated by electron microscopy.

6.2.5 Discussion

Due to the addition of Y$^{3+}$ into ZrO$_2$, structural oxygen vacancies are present in the matrix. The region between the surface and the helium implantation zone contains point defects like $V_{O}$, $V_{Zr}^{\prime\prime}$ and $V_{Y}^{\prime\prime}$ as well as Frenkel pairs, F-centres and complementary hole centres. The activation enthalpy for self-diffusion of O$^{2-}$ in FSZ has been determined by Fox et al. to be about 1 eV [69] which is much lower than the 1.9 eV on the average (see Figure 6.7) measured for helium. The peak displacements vary between 0.05 dpa (lowest dose) and 1.46 dpa (highest dose) as shown in Table 6.2. After implantation it is expected that helium is trapped in vacancies and vacancy clusters.

- In the case of the lowest-dose samples (sample I and V, $1.7 \times 10^{15}$ He cm$^{-2}$), the peak displacement damage is about 0.05 dpa. The helium will be trapped mostly in oxygen vacancies or interstitial sites. The increase in $S$-parameter after implantation can be explained by an increase in open volume, mostly in the form of single vacancies. The maximum helium concentration for this dose is 0.13 at%. During thermal annealing, helium is released by dissociation from the vacancies and subsequent vacancy-assisted diffusion towards the surface. NDP shows a broadening of the helium peak, typical for diffusion. After annealing at 700 K, the $S$-parameter almost reaches the value of the reference sample. Apparently, the vacancies introduced by this low-dose implantation are very mobile and can be easily removed by thermal annealing.

- For samples II and VI ($6.3 \times 10^{15}$ He cm$^{-2}$) the $S$-profile after implantation does not differ much from those of the lowest-dose samples. Helium is trapped in vacancies and vacancy clusters. NDP measurements show a broadening of the helium distribution typical of a diffusion process. NDP and THDS show that a small fraction of the helium is retained up to higher temperatures, but from NDP it follows that the centre of the broadened peak shifts to a larger depth. A small fraction of the initially implanted helium is trapped in bubbles.

- For samples III and IV ($2.6 \times 10^{16}$ He cm$^{-2}$) and VII and VIII ($5.1 \times 10^{16}$ He cm$^{-2}$) there is hardly any variation in the $S$-profile immediately after implantation compared to the $S$-profiles of the as-implanted samples I and II. Helium filled vacancies do not show an increased $S$-parameter. In THDS it was shown that helium is
retained up to high temperatures. This was also shown by NDP; the helium distribution does not broaden and at high temperatures the maximum of the distribution shifts towards a larger depth. Instead of diffusing towards the surface, helium becomes trapped in a band of bubbles. It is proposed that at the temperatures where for the lowest-dose case the helium diffusion starts, Ostwald ripening occurs in the high-dose specimens. During thermal annealing, small clusters dissociate and larger ones grow at the expense of the smaller ones. This process continues until nano-size bubbles are present. TEM pictures of bubbles in FSZ implanted with 35 keV He-ions to a dose of $10^{17}$ He cm$^{-2}$ after annealing are shown in Ref. [15]. At higher temperatures, between 700 and 800 K, helium starts being released slowly from the bubbles, as seen by NDP, and the $S$-parameter of the damaged layer increases with every annealing step. This can be explained by the open volumes left behind by the bubbles, which yield a high $S$-value. The cavities develop up to a depth of about 120 nm, which is less than the helium implantation depth predicted by TRIM. This is explained by the fact that the helium has to move towards smaller depths in order to combine with vacancies.

### 6.2.6 Summary and conclusions

Fully stabilized zirconia was implanted with either $^3$He or $^4$He at 30 keV at four different doses. For the samples implanted with a low He-fluence (in the order of $10^{15}$ cm$^{-2}$), helium is released at low temperatures with an activation enthalpy of about 2 eV. A broadening of the helium distribution was observed with NDP. Positron beam analysis shows that the small defects introduced by the implantation can easily be removed by thermal annealing. From the two-layer model used to model the PBA-results it can be seen that after every annealing step the first layer becomes thinner and its $S$-parameter decreases toward the $S$-parameter of the bulk material. For the samples implanted with doses in the order of $10^{16}$ cm$^{-2}$, it was found that part of the helium is retained up to high temperatures. In NDP investigations no broadening of the helium distribution was seen; instead, the FWHM of the distribution peak remained almost constant. A three-layer model was used for the analysis of the PBA results. After thermal annealing the second layer shrinks slightly and its $S$-parameter increases due to a clustering of defects in the helium-rich zone. For all four investigated doses, a decrease in the pre-exponential jump factor $f_{0,i}$ was observed with increasing temperature. This can be explained by realizing that the pre-exponential factor is the product of an attempt frequency ($\nu$) in the order of the Debye-frequency ($10^{12} - 10^{13}$ s$^{-1}$) and the entropy factor $\exp(\Delta S/k)$ (see Section 3.4.1). Since $\Delta S$ is the difference between the entropy of the final state and the initial state of the helium it can turn strongly negative when helium jumps from a bubble (very high entropy) to a localized position in a vacancy (low entropy) [46]. The activation enthalpy was measured and found to be about 2 eV. Depending on the implanted dose, helium is released between about 600 and 1200 K. In a reactor, irradiation temperatures of 1000 K are not uncommon. Thus, the helium formed in the zirconia-matrix due to $\alpha$-decay of actinides will migrate in
the fuel during irradiation with neutrons in a nuclear reactor. The helium will either migrate to the gap between cladding and fuel or be trapped in bubbles, most likely together with the fission gases krypton and xenon. The migration of helium towards the gap between the cladding and the fuel is not necessarily problematic as long as the fuel pins are designed in such a way that they are able to accommodate the helium produced. In the experiments described in this section, the maximum helium concentration in the sample expressed in helium atoms per matrix atom, was about 4 at%. In the EFTTRA-T4 experiments (see Chapter 5), the helium concentration after irradiation was 0.5 at% (helium atoms per matrix atom). In the case of the high-dose samples, annealing up to high temperatures is necessary to remove the damage caused by the implantation of the helium. During reactor irradiation, apart from the damage caused by $\alpha$-decay, it is also important to take into account the damage caused by neutrons, fission products, recoil atoms and $\beta$-decay. Although the implantation experiments show that FSZ behaves well with respect to damage caused by fission products and $\alpha$-decay, real irradiation experiments have to be performed to study the stability of FSZ in a more realistic situation.

6.3 200 keV and 1 MeV helium investigations

In this section, results of 200 keV and 1 MeV helium implanted fully stabilized zirconia specimens will be discussed. After polishing and thermal treatment, the samples were implanted in the Van de Graaff generator of the 'Institut für Festkörperphysik' (IFP) of the Forschungszentrum Karlsruhe (FZK). The helium release from the samples was studied by the Knudsen cell method as well as by thermal helium desorption spectrometry. Neutron depth profiling measurements were performed in order to gain insight into the depth-dependent helium distribution. Sample surfaces and morphology were studied by SEM and TEM.

6.3.1 TRIM calculations

To estimate the defect and helium distribution after implantation with energies of either 200 keV or 1 MeV, calculations were performed using the SRIM-2000 code [4], in which for FSZ, similar to the case of 30 keV implantations, a displacement energy of 40 eV was used [32]. The results for both 200 keV and 1 MeV implantations for an implanted helium dose of $2.1 \times 10^{16}$ He cm$^{-2}$ are shown in Figure 6.16. In Figure 6.16a, the concentration of additional zirconium-, yttrium- and oxygen-vacancies caused by the implantation of helium are shown. The unit on the ordinate is the number of vacancies per matrix atom, where a matrix atom can be either zirconium, yttrium or oxygen. Replacement collisions have not been taken into account in the calculations and in Chapter 3 it was shown that the oxygen vacancies are more mobile than the implanted helium. Figure 6.16b shows the depth-dependent helium distribution and the number of displacements caused by the helium implantation.
Figure 6.16: Results of TRIM calculations for $2.1 \times 10^{16}$ cm$^{-2}$ 200 keV and 1 MeV $^4$He in FSZ. The displacement energies used are 40/40/40 eV for Zr/Y/O, respectively.

The calculations show that although the range of the 1 MeV helium ions is much larger than that of helium ions implanted at 200 keV, there is not much difference in the number of displacements and vacancies and in the helium concentration profile for the two energies if a similar helium fluence is considered. An implanted helium atom first has to slow down before damage is introduced (see Subsection 3.3.3). It can be seen that the maximum helium concentration for the two implantation profiles is of the same order of magnitude. Implanted helium doses for 200 keV and 1 MeV in FSZ can thus easily be compared. The question whether this is also true for 30 keV implanted helium in FSZ will be discussed on the basis of Table 6.3. In the table, results of TRIM calculations of 30, 200 and 1000 keV helium in FSZ are shown for an implanted helium fluence of $1 \times 10^{16}$ cm$^{-2}$. It can be seen that the maxima in the helium concentration for 200 keV and 1 MeV do not differ much; owing to the different energies the depths at which the maxima occur are different. For the same implanted helium fluence, the maximum helium concentration for 30 keV implanted helium is almost double that for 1 MeV implanted helium. There is an increase of 50% in the maximum number of displacements going from 1000 to 30 keV. When comparing the results of 200 keV and 1 MeV implanted FSZ with the results for 30 keV described in Section 6.2, instead of comparing the implanted doses, a comparison should be made between experiments with similar helium concentrations and displacement profiles.
Table 6.3: A comparison between the results of the TRIM calculations for 30, 200 and 1000 keV helium in Fully Stabilized Zirconia. The displacement energies used are 40/40/40 eV for Zr/Y/O, respectively. The results have been normalized to an implanted helium dose of $1 \times 10^{16}$ cm$^{-2}$. The values for the depth are the positions of the maxima of either the helium concentration or the number of displacements.

<table>
<thead>
<tr>
<th>Energy (keV)</th>
<th>Depth (nm)</th>
<th>Maximum He-concentration (at%)</th>
<th>Depth (nm)</th>
<th>Displacements per atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>180</td>
<td>0.80</td>
<td>135</td>
<td>0.36</td>
</tr>
<tr>
<td>200</td>
<td>702</td>
<td>0.47</td>
<td>639</td>
<td>0.27</td>
</tr>
<tr>
<td>1000</td>
<td>2115</td>
<td>0.40</td>
<td>2050</td>
<td>0.24</td>
</tr>
</tbody>
</table>

6.3.2 Knudsen cell measurements

Correction of the implanted amount of helium

Some of the signals measured with the Knudsen cell were integrated using the calibration factor described in Section 2.1.4 and the amount of helium released from the sample was calculated with this calibration factor. In Table 6.4 these data are compared with the requested implanted quantities. Secondly, data from Section 6.3.4 are given for which the amount of helium implanted in the sample was measured with NDP.

Table 6.4: Ratio between implanted and measured amounts of helium obtained from Knudsen cell measurements (KCM) and neutron depth profiling investigations. The electron energy used in the quadrupole mass spectrometer was set to 70 eV.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Investigation technique</th>
<th>He-ions measured</th>
<th>He-ions implanted</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF</td>
<td>NDP</td>
<td>$1.4 \times 10^{15}$ cm$^{-2}$</td>
<td>$1.0 \times 10^{16}$ cm$^{-2}$</td>
<td>7.14</td>
</tr>
<tr>
<td>AG</td>
<td>NDP</td>
<td>$6.5 \times 10^{15}$ cm$^{-2}$</td>
<td>$5.0 \times 10^{16}$ cm$^{-2}$</td>
<td>7.69</td>
</tr>
<tr>
<td>C</td>
<td>KCM</td>
<td>$2.1 \times 10^{14}$</td>
<td>$2.0 \times 10^{15}$</td>
<td>9.77</td>
</tr>
<tr>
<td>B</td>
<td>KCM</td>
<td>$2.3 \times 10^{14}$</td>
<td>$2.0 \times 10^{15}$</td>
<td>8.71</td>
</tr>
<tr>
<td>F</td>
<td>KCM</td>
<td>$5.1 \times 10^{14}$</td>
<td>$3.5 \times 10^{15}$</td>
<td>6.82</td>
</tr>
<tr>
<td>G</td>
<td>KCM</td>
<td>$5.6 \times 10^{14}$</td>
<td>$3.5 \times 10^{15}$</td>
<td>6.20</td>
</tr>
<tr>
<td>H</td>
<td>KCM</td>
<td>$5.7 \times 10^{14}$</td>
<td>$3.5 \times 10^{15}$</td>
<td>6.10</td>
</tr>
<tr>
<td>K</td>
<td>KCM</td>
<td>$2.6 \times 10^{14}$</td>
<td>$2.0 \times 10^{15}$</td>
<td>7.61</td>
</tr>
<tr>
<td>L</td>
<td>KCM</td>
<td>$2.4 \times 10^{14}$</td>
<td>$2.0 \times 10^{15}$</td>
<td>8.52</td>
</tr>
<tr>
<td>M</td>
<td>KCM</td>
<td>$2.6 \times 10^{14}$</td>
<td>$2.5 \times 10^{15}$</td>
<td>9.57</td>
</tr>
<tr>
<td>N</td>
<td>KCM</td>
<td>$2.8 \times 10^{14}$</td>
<td>$2.5 \times 10^{15}$</td>
<td>8.82</td>
</tr>
<tr>
<td>P</td>
<td>KCM</td>
<td>$3.6 \times 10^{14}$</td>
<td>$2.4 \times 10^{15}$</td>
<td>6.68</td>
</tr>
</tbody>
</table>

It can be concluded that on average about 7.8 times less helium was implanted in the samples than expected and requested. This discrepancy is caused by charging problems of the material. Furthermore, this factor includes the inaccurate calibration factor. In the evaluation of the experiments described in this section the factor 7.8 will be used.
Helium release experiments performed in the Knudsen cell

In Table 6.5, an overview is shown of helium release experiments on FSZ performed in the Knudsen cell. The table shows the corrected implanted helium concentration, the implantation energy and the heating schedule applied.

Table 6.5: Zirconia samples investigated in the Knudsen cell. The implantations were performed at room temperature. The helium fluence was corrected for the charging effects.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Corrected He-fluence (cm$^{-2}$)</th>
<th>He-energy (keV)</th>
<th>Heating</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$1.8 \times 10^{13}$</td>
<td>200</td>
<td>30 K min$^{-1}$</td>
</tr>
<tr>
<td>B</td>
<td>$2.6 \times 10^{14}$</td>
<td>200</td>
<td>10 K min$^{-1}$</td>
</tr>
<tr>
<td>C</td>
<td>$2.6 \times 10^{14}$</td>
<td>200</td>
<td>30 K min$^{-1}$</td>
</tr>
<tr>
<td>D</td>
<td>$1.3 \times 10^{15}$</td>
<td>200</td>
<td>10 K min$^{-1}$</td>
</tr>
<tr>
<td>E</td>
<td>$1.3 \times 10^{15}$</td>
<td>200</td>
<td>10 K min$^{-1}$</td>
</tr>
<tr>
<td>F</td>
<td>$1.8 \times 10^{15}$</td>
<td>200</td>
<td>10 K min$^{-1}$</td>
</tr>
<tr>
<td>G</td>
<td>$1.8 \times 10^{15}$</td>
<td>200</td>
<td>steps + cooling</td>
</tr>
<tr>
<td>H</td>
<td>$1.8 \times 10^{15}$</td>
<td>200</td>
<td>steps + cooling</td>
</tr>
<tr>
<td>J</td>
<td>$1.3 \times 10^{16}$</td>
<td>200</td>
<td>steps + cooling</td>
</tr>
<tr>
<td>K</td>
<td>$2.6 \times 10^{14}$</td>
<td>1000</td>
<td>10 K min$^{-1}$</td>
</tr>
<tr>
<td>L</td>
<td>$2.6 \times 10^{14}$</td>
<td>1000</td>
<td>30 K min$^{-1}$</td>
</tr>
<tr>
<td>M</td>
<td>$1.3 \times 10^{15}$</td>
<td>1000</td>
<td>30 K min$^{-1}$</td>
</tr>
<tr>
<td>N</td>
<td>$1.3 \times 10^{15}$</td>
<td>1000</td>
<td>steps, 11.5 K min$^{-1}$ average</td>
</tr>
<tr>
<td>O</td>
<td>$1.3 \times 10^{16}$</td>
<td>1000</td>
<td>10 K min$^{-1}$</td>
</tr>
<tr>
<td>P</td>
<td>$1.3 \times 10^{16}$</td>
<td>1000</td>
<td>30 K min$^{-1}$</td>
</tr>
<tr>
<td>Q</td>
<td>$1.3 \times 10^{16}$</td>
<td>1000</td>
<td>steps, 15.7 K min$^{-1}$ average</td>
</tr>
<tr>
<td>R</td>
<td>$2.1 \times 10^{16}$</td>
<td>1000</td>
<td>10 K min$^{-1}$</td>
</tr>
<tr>
<td>S</td>
<td>$2.1 \times 10^{16}$</td>
<td>1000</td>
<td>30 K min$^{-1}$</td>
</tr>
<tr>
<td>T</td>
<td>$2.1 \times 10^{16}$</td>
<td>1000</td>
<td>30 K min$^{-1}$</td>
</tr>
<tr>
<td>U</td>
<td>$2.1 \times 10^{16}$</td>
<td>1000</td>
<td>30 K min$^{-1}$</td>
</tr>
</tbody>
</table>

In Figures 6.17 and 6.18 some of the experiments listed in Table 6.5 and implanted with either 200 keV (Figure 6.17) or 1 MeV (Figure 6.18) are depicted. On the abscissa, the corrected temperature is given while the helium release rate is shown in arbitrary units on the ordinate, to make possible a comparison between the various experiments.

The release peaks shown in Figures 6.17 and 6.18 were fitted with the release model described in Section 3.5.2. An areal trapping density of $10^{10}$ cm$^{-2}$ was used, which is representative for a grain size of several hundreds of nanometres. The values for the activation enthalpy $Q$ were varied in order to get a good fit of the measured data. It turned out that the value for $D_0$ could be kept constant at $4.69 \times 10^{-2}$ cm$^2$ s$^{-1}$. The data are presented in Table 6.6. It should be mentioned that this is probably not the best possible fit. For samples P and S, only the first part of the release was fitted (the part where the signal increases very rapidly as a function of temperature); the part where the
Figure 6.17: Results of Knudsen Cell experiments for samples A, B, D and G implanted with 200 keV helium-ions. The heating rate applied was either 10 or 30 K min\(^{-1}\) and is indicated in the figure. The data are plotted versus the annealing temperature.

The helium signal gradually decreases could not be fitted with the grain boundary diffusion model. A possible explanation for this behaviour will be given later in this section.

The activation enthalpies determined with the grain boundary model vary between 1.90 and 2.21 eV. For the samples P and S, implanted with 1 MeV helium up to high fluence, the activation enthalpy is slightly higher than in the other cases. This can be recognized in the figures in the form of a sharper rise in the release spectrum.

The following remarks and comparisons between the different experiments, release profiles and activation enthalpies can be made:

- In Figure 6.17 the results for some of the samples implanted with 200 keV helium are shown. It can be seen that for a slow heating rate the helium is released at temperatures approximately 50 K lower than for the faster heating rate. This can be
modelled with Eqs. 3.19 and 3.20 as described in Section 3.5.2. For lower ramp rates, helium will be released at lower temperatures. The lower the ramp rate, the more time the helium has to become mobile and to move towards the surface.

- Apart from an increase in noise due to a smaller sample surface, there is no difference between the sample implanted with 200 keV $2.6 \times 10^{14}$ He cm$^{-2}$ (sample B) and the sample implanted with 200 keV $1.3 \times 10^{15}$ He cm$^{-2}$ (Sample C). The helium release starts at about 800 K and all the helium is released at 900 K. In both experiments the annealing rate was 10 K min$^{-1}$. Also, the activation enthalpies derived are very similar for both specimens (1.90 vs. 1.92 eV).

**Figure 6.18:** Results of Knudsen Cell experiments for samples K, M, P and S implanted with 1 MeV helium-ions. The heating rate applied was either 10 or 30 K min$^{-1}$ and is indicated in the figure. The data are plotted versus the temperature.
Table 6.6: Fitting results for Knudsen cell measurements performed on 200 keV and 1 MeV implanted FSZ specimens where the grain boundary diffusion model was used. Fast diffusion along the grain boundaries was assumed. The areal trapping density was set to $10^{10}$ cm$^{-2}$ and for $D_0$ a value of $4.69 \times 10^{-2}$ cm$^2$ s$^{-1}$ was used.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Implanted fluence (cm$^{-2}$)</th>
<th>Energy (keV)</th>
<th>ramp rate (K s$^{-1}$)</th>
<th>$Q$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$1.8 \times 10^{13}$</td>
<td>200</td>
<td>30</td>
<td>2.01</td>
</tr>
<tr>
<td>B</td>
<td>$2.6 \times 10^{14}$</td>
<td>200</td>
<td>10</td>
<td>1.90</td>
</tr>
<tr>
<td>D</td>
<td>$1.3 \times 10^{15}$</td>
<td>200</td>
<td>10</td>
<td>1.92</td>
</tr>
<tr>
<td>G</td>
<td>$1.8 \times 10^{15}$</td>
<td>200</td>
<td>30</td>
<td>1.91</td>
</tr>
<tr>
<td>K</td>
<td>$2.6 \times 10^{14}$</td>
<td>1000</td>
<td>10</td>
<td>1.89</td>
</tr>
<tr>
<td>M</td>
<td>$1.3 \times 10^{15}$</td>
<td>1000</td>
<td>30</td>
<td>1.91</td>
</tr>
<tr>
<td>P</td>
<td>$1.3 \times 10^{16}$</td>
<td>1000</td>
<td>30</td>
<td>2.21</td>
</tr>
<tr>
<td>S</td>
<td>$2.1 \times 10^{16}$</td>
<td>1000</td>
<td>30</td>
<td>2.07</td>
</tr>
</tbody>
</table>

- For Sample A, implanted with 200 keV at the lowest dose of $1.8 \times 10^{13}$ He cm$^{-2}$ and a heating rate of 30 K min$^{-1}$, the helium release starts at about 850 K and is almost complete at 950 K. The activation enthalpy is in good agreement with the ones derived for samples B and D. However, for the 200 keV sample with the highest dose (Sample G, implanted with $1.8 \times 10^{15}$ He cm$^{-2}$), a small fraction of the helium is retained up to temperatures of about 1450 K, where suddenly a second release stage starts. The occurrence of this second release peak has been reproduced several times with different samples implanted with a dose of the same order of magnitude as Sample G. Microscopic investigations of the surface of the sample after annealing did not show any irregularities which could indicate e.g. a burst release of the helium from the sample. It is expected that during the annealing of this sample, a small fraction of the helium is trapped in bubbles. The activation enthalpy for the re-solution of the helium from the bubble into the matrix is expected to be very high. Once the helium has been re-solved again, it can then, due to its thermally active state, easily move towards the surface.

- For the two low-dose samples implanted with 1 MeV helium (sample K: $2.6 \times 10^{14}$ and sample M: $1.3 \times 10^{15}$ He cm$^{-2}$), the helium is released mostly in one release peak. Again it can be seen that the temperature shifts due to the different heating rates. The activation enthalpies of 1.89 and 1.91 eV are in good agreement with each other. In the figure it can also be seen that a small fraction of the implanted helium is released at higher temperatures. For the sample annealed at 10 K min$^{-1}$ (sample K), this second release stage occurs between 1200 and 1400 K, for the sample annealed at 30 K min$^{-1}$ (sample M) the release occurs up to 1600 K. As already seen for sample G implanted with 200 keV $1.8 \times 10^{15}$ He cm$^{-2}$, a small fraction of the helium is retained up to higher temperatures. However, for the 200 keV sample, it was shown that the second release stage starts very suddenly. In the 1 MeV samples a more gradual release of the small fraction of helium not released in the large release
peak can be seen. A possible explanation for this is the presence of an undamaged layer between the implanted helium and the sample surface (see Figure 6.16).

- For the two samples (P and S) implanted with 1 MeV helium, a different release profile is observed. The helium release starts very suddenly at about 800 K. After that, the helium is retained up to high temperatures and gradually released. The helium begins to diffuse and then partly diffuses via grain boundary assisted diffusion towards the surface and partly becomes trapped in bubbles. The limiting factor in the release is then the re-solution of the helium from the bubble into the matrix. Once the helium has been re-solved in the matrix it easily diffuses towards the surface.

A more detailed discussion in which Knudsen cell experiments are compared with thermal helium desorption spectrometry, neutron depth profiling and microscopic investigations will be given at the end of this section in Subsection 6.3.5.

### 6.3.3 Thermal helium desorption measurements

Various samples were analysed in the THDS facility of IRI. The implanted number of helium ions and the implantation energy were varied. Secondly, some of the samples were annealed with a single ramp up to high temperatures, other samples stepwise (such as the 30 keV samples used in the THDS described in Section 6.2) while the maximum annealing temperature was increased for every annealing step. An overview of the investigated samples, the implantation energy, the implanted number of helium ions and the heating rate is given in Table 6.7.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Energy (keV)</th>
<th>Corrected He-concentration (cm$^{-3}$)</th>
<th>Heating (K min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>200</td>
<td>$1.8 \times 10^{13}$</td>
<td>60</td>
</tr>
<tr>
<td>W</td>
<td>200</td>
<td>$1.8 \times 10^{13}$</td>
<td>Steps</td>
</tr>
<tr>
<td>X</td>
<td>200</td>
<td>$1.8 \times 10^{13}$</td>
<td>Steps</td>
</tr>
<tr>
<td>Y</td>
<td>200</td>
<td>$2.6 \times 10^{14}$</td>
<td>240</td>
</tr>
<tr>
<td>Z</td>
<td>200</td>
<td>$1.8 \times 10^{15}$</td>
<td>60</td>
</tr>
<tr>
<td>AA</td>
<td>200</td>
<td>$1.8 \times 10^{15}$</td>
<td>60</td>
</tr>
<tr>
<td>AB</td>
<td>200</td>
<td>$1.8 \times 10^{15}$</td>
<td>Steps</td>
</tr>
<tr>
<td>AC</td>
<td>1000</td>
<td>$1.3 \times 10^{13}$</td>
<td>240</td>
</tr>
<tr>
<td>AD</td>
<td>1000</td>
<td>$2.6 \times 10^{14}$</td>
<td>Steps</td>
</tr>
<tr>
<td>AE</td>
<td>1000</td>
<td>$1.3 \times 10^{16}$</td>
<td>240</td>
</tr>
</tbody>
</table>

The measurements performed on samples V, W and X are in good agreement with each other and agree also with the Knudsen cell experiments performed on sample A. The release experiment carried out on sample AE is in very good agreement with the Knudsen cell experiments performed on samples P and Q. The shape of the release
profile for sample Q agrees well with the shape for sample P (sample P is shown in Figure 6.18).

For samples Z and AC, the model described in Section 3.5.2 was used to fit the measured helium release curves. As was done for the Knudsen cell experiments, an areal trapping density of $10^{10} \text{cm}^{-2}$ was used, and the values for the activation enthalpy $Q$ and the pre-exponential factor for diffusion were varied in order to obtain a good fit of the measured data. The data are presented in Table 6.8.

Table 6.8: Fitting results for THDS experiments performed on 200 keV and 1 MeV implanted FSZ specimens for which the grain boundary diffusion model was used. Fast diffusion along the grain boundaries was assumed. The areal trapping density was set to $10^{10} \text{cm}^{-2}$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Implant. fluence (cm$^{-2}$)</th>
<th>Energy (keV)</th>
<th>ramp rate (K s$^{-1}$)</th>
<th>$Q$ (eV)</th>
<th>$D_0$ (cm$^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z</td>
<td>$1.8 \times 10^{15}$</td>
<td>200</td>
<td>60</td>
<td>1.91</td>
<td>$6.29 \times 10^{-2}$</td>
</tr>
<tr>
<td>AC</td>
<td>$1.3 \times 10^{13}$</td>
<td>1000</td>
<td>240</td>
<td>1.64</td>
<td>$4.69 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

For samples AB and AD, which were annealed in steps, the activation enthalpy $Q$ and the pre-factor $f_{0,i}$ were determined from the Arrhenius plots of the measured data. The results are shown in Figure 6.19. The results of one of the 30 keV implanted specimens have also been included in the figure. It is clear that the results of the experiments are in good agreement with each other.

6.3.4 Neutron depth profiling

As a first attempt at NDP investigations, two samples were implanted with 200 keV helium. An overview of these samples is given in Table 6.9.

Table 6.9: Samples investigated with NDP. The helium implantation energy was 200 keV.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount implanted He cm$^{-2}$</th>
<th>Amount measured at RT $^3\text{He}$ cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF</td>
<td>$1 \times 10^{16}$ $^3\text{He}$</td>
<td>$1.4 \times 10^{15}$</td>
</tr>
<tr>
<td>AG</td>
<td>$5 \times 10^{16}$ $^3\text{He} + 5 \times 10^{16}$ $^4\text{He}$</td>
<td>$6.5 \times 10^{15}$</td>
</tr>
</tbody>
</table>

Large discrepancies between the (requested) amount implanted and the actual amount present in the sample are observed. This may be caused by charging effects during the implantations. Because zirconia is an insulator, it is charged during irradiation with ions. Since the implanted number of ions is measured on the basis of an integrated current, an error may be introduced here. As described before, with the aid of the NDP technique one can only measure the profile of $^3\text{He}$. Sample AG was implanted with $5 \times 10^{16}$ $^3\text{He}$ and $5 \times 10^{16}$ $^4\text{He}$. The quantity of $^3\text{He}$ in this sample was measured with NDP and found to be $6.5 \times 10^{16}$ cm$^{-2}$. The assumption is made that the error in the
number of $^3$He implanted is equal to the error in the number of $^4$He. With Knudsen cell measurements it was found that the release of $^3$He is identical to the release of $^4$He so it is assumed that the total amount of helium present in sample AG is twice the amount measured.

The helium profile and the amount of helium for these two samples (AF and AG) were measured after implantation at room temperature, after annealing at 600 K for about half an hour and after annealing at 900 K for about half an hour. The results of these measurements are shown in Figures 6.20 and 6.21.

As in the 30 keV-case, the depth predicted by TRIM is an overestimate of the real implantation depth. From the figures, it can be seen that after annealing at 600 K the amount of helium and its spatial distribution in the sample are effectively unchanged for both high and low fluence. No significant release processes have occurred for the 200 keV implanted specimens. After annealing at 900 K, all the helium was released.

**Figure 6.19**: Pre-factors $f_{0,i}$ and activation enthalpies $Q$ determined from the Arrhenius plots of samples AB and AD. As a reference, the results from a 30 keV implantation are also shown.
for sample AF, while for sample AG about 38% of the $^3$He is retained in the material. (It is assumed that this is 38% of the total amount of implanted helium, since in Knudsen cell experiments it was found that the release profile of $^3$He is identical to the

Figure 6.20: Results of the NDP-measurements for sample AF, implanted with $1.4 \times 10^{15}$ $^3$He cm$^{-2}$. The data points in the figures on the left show the measured data, the curves are the result of a Gaussian fit. The figures on the right show the helium distribution versus depth, where the signal has been corrected for the detector resolution. The curves show the values determined from the Gaussian fit to the measured data.

Figure 6.21: Results of the NDP-measurements for sample AG, implanted with $6.5 \times 10^{15}$ $^3$He cm$^{-2}$ and an equal amount of $^4$He. The data points in the figures on the left show the measured data, the curves are the result of a Gaussian fit. The figures on the right show the helium distribution versus depth, where the signal has been corrected for the detector resolution. The curves show the values determined from Gaussian fits to the measured data. The heavy curve in the figure at the bottom is the result calculated by TRIM.
release profile of $^4$He). In the figure, it can be seen that for sample AG the distribution of the helium peak becomes narrower after thermal annealing.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Annealing temp. (K)</th>
<th>Depth (nm)</th>
<th>FWHM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF</td>
<td>300</td>
<td>511</td>
<td>201</td>
</tr>
<tr>
<td>AF</td>
<td>600</td>
<td>501</td>
<td>184</td>
</tr>
<tr>
<td>AG</td>
<td>300</td>
<td>514</td>
<td>203</td>
</tr>
<tr>
<td>AG</td>
<td>600</td>
<td>493</td>
<td>225</td>
</tr>
<tr>
<td>AG</td>
<td>900</td>
<td>522</td>
<td>155</td>
</tr>
</tbody>
</table>

### Microscopic investigations

Specimens implanted with 200 keV or 1 MeV helium were only analysed by SEM, as, unfortunately, no thin areas could be found in the helium implanted region of the cross-sectional TEM specimens. SEM investigations were performed for specimens after implantation, after annealing up to the beginning of the helium release and after annealing up to the end of the release. No difference was found between virgin specimens (no helium), low-dose ($\approx 10^{15}$ He cm$^{-2}$) and high-dose ($10^{16}$-10$^{17}$ He cm$^{-2}$) implanted specimens, nor could any influence of annealing temperature be detected.

### 6.3.5 Discussion

- After implantation, helium is trapped in vacancies, vacancy clusters or pressurized bubbles [11]. Pressurized bubbles develop only at high fluences. If the helium concentration is sufficiently high, ripening of the bubbles will occur during thermal annealing. It is observed by NDP that for the highest fluence (sample AB) agglomeration of the bubbles leads to shrinkage of the bubble layer thickness. The process of release takes place in two steps: Firstly, helium dissociates from the trap or bubble, and secondly it diffuses (vacancy and grain boundary assisted) to the surface. NDP provides evidence for the fact that the helium remains at the implantation depth and does not spread as it would do in a diffusion process.
- Up to a certain fluence/concentration of helium in FSZ the dominating release mechanism during annealing can be described by a diffusion process although it seems that the helium is retained shorter than predicted by a simple diffusion equation. The desorption spectra show a relatively narrow temperature interval in which release takes place. This could possibly be explained by grain boundary assisted diffusion.
- The high-fluence behaviour corresponds first to bubble formation [76]; then, the high-pressure helium is released from the bubbles at a lower temperature than from vacancy clusters because of the high pressure. When the pressure becomes less the release slows down and continues up to very high temperatures. The cavities
remain and do not shrink easily; instead they coarsen. For bubbles and cavities in helium-implanted silicon a similar process has been modelled by Godey et al. [76].

6.4 Conclusions and recommendations

In the previous two sections various techniques of investigation were applied to specimens implanted with 30, 200 and 1000 keV helium. As discussed in Table 6.3, specimens implanted with 200 keV and 1 MeV helium can be easily compared on the basis of the implanted number of helium ions per surface area. In order to compare these two energies with 30 keV helium implantations, one should not compare the total implanted dose, but rather the helium concentration and the amount of displacements in the material. In general, in order to compare 30 keV with 200 or 1000 keV implanted samples, the helium fluence for the higher dose should be about twice that for the 30 keV specimens. Thus, \(5 \times 10^{16}\) 30 keV He cm\(^{-2}\) can be compared with \(1 \times 10^{17}\) 200 keV or 1 MeV He cm\(^{-2}\). However, it should not be forgotten that this is an approximation.

The results obtained for 30 keV, 200 keV and 1 MeV implanted helium in FSZ and investigated in various experimental set-ups are in good agreement with each other. It is clear from the discussions in the previous sections that there is a difference between low-dose and high-dose helium implantation, where a helium dose of \(\geq 10^{16}\) He cm\(^{-2}\) is considered to be a high dose. Finally, an intermediate dose is considered, for which both aspects of the low-dose and high-dose implanted specimens play a role.

In Table 6.11 an overview is given of the most important processes occurring in the helium implanted material under thermal annealing. These results will be discussed and summarized in the following subsections. In the case of a low implantation dose,

<table>
<thead>
<tr>
<th>Table 6.11: An overview of the different processes occurring in helium-implanted fully stabilized zirconia.</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 K - 500 K</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>no mobility of He. diffusion of (V_O)</td>
</tr>
</tbody>
</table>

helium is released at low temperatures in a narrow release interval. NDP shows a
broadening of the helium distribution peak, typical of a diffusion process. After implantation, helium is trapped mostly in single vacancies or interstitial sites. During thermal annealing, helium is released by dissociation from the vacancy or trap and by subsequent vacancy-assisted diffusion towards the surface. It was shown by PBA that the $S$-parameter, which increases after implantation, decreases towards the reference value of the bulk under thermal treatment. This stage is reached at relatively low temperatures. Vacancies introduced by low-dose implantation are very mobile and can be easily removed by thermal annealing.

For high-dose helium implantations the story is different. After implantation, helium is trapped in vacancies and cavities. Helium is retained up to high temperatures and by NDP it was shown that the helium distribution does not broaden and at high temperatures the maximum of the distribution shifts towards a larger depth. Instead of diffusing towards the surface, the helium becomes trapped in bubbles. Ostwald ripening occurs, at the temperatures at which for the lowest-dose case the helium diffusion starts. During thermal annealing, small clusters dissociate while larger ones grow at the expense of the smaller ones. This process will continue until nano-size bubbles are present, which are visible with TEM. At higher temperatures, starting between 700 and 800 K, NDP shows that helium begins to be released from the bubbles. However, as seen with NDP, helium is released slowly from the bubbles and the $S$-parameter of the damaged layer increases with every annealing step. This can be explained by the open volume left behind by the bubbles, which yields a high $S$-value.

### 6.4.1 Temperature effects

In the Knudsen Cell of ITU several specimens were investigated in which helium was implanted at a relatively high temperature. The release profile of these specimens is very different from the release profiles of specimens implanted at room temperature. Helium release starts always at or above the implantation temperature. Probably, part of the helium is released during implantation. The higher the implantation temperature, the higher the temperature at which the largest fraction of helium is released. The behaviour of helium implanted at different temperatures under thermal annealing in FSZ is not an easy phenomenon to understand. It is, however, a very important aspect of the use of the ceramic as an inert matrix material for the transmutation of actinides. If the inert matrix is used for the transmutation of actinides and not only for final storage of the actinides, helium will build up under the following conditions:

1. After fabrication, helium will build up due to the $\alpha$-decay of the actinides incorporated in the inert matrix. As a result of this decay, the temperature of the material will be slightly above room temperature (stage I).

2. If the inert matrix is inserted in a nuclear reactor the temperature of the fuel will increase significantly. Fuel temperatures of 1000 K are not uncommon. Due to the $\alpha$-decay of the incorporated actinides and of newly formed short living actinides, helium is formed. This helium is formed at very high temperatures, and thus will behave differently from helium implanted at room temperature. However, the helium
formed in stage I will become mobile as well, since it was shown that helium release starts at about 800 K. Another problem is that during reactor irradiation the temperature of the fuel does not remain constant. Recent experiments [101] have shown large fluctuations of the fuel temperature of inert matrix fuels under irradiation.

3. In the third stage, the fuel is removed from the reactor and is cooled down. Helium is formed due to the $\alpha$-decay of the not yet transmuted incorporated actinides and the newly formed actinides. The temperature of the fuel will be higher shortly after irradiation than after some decades of cooling, when short-living fission products have decayed.

### 6.4.2 Discussion

In this Chapter, results of helium implanted in fully stabilized zirconia were discussed. In the past, it has been shown that FSZ is stable against neutron and fission product damage. Although helium release from FSZ occurs at low temperatures compared to e.g. spinel, this does not have to be a disadvantage. If gas is released from a fuel at low temperature, i.e. during reactor operation, less gas will remain in the fuel which decreases the chance of swelling and cracking of the fuel. Some of the investigated helium doses are very high compared to the more realistic situation in a reactor fuel. However, in a reactor fuel, fission gases like krypton and xenon may start bubble formation, after which these bubbles may form a trap for helium as well. The helium solubility in FSZ is not known at present. It would be interesting to study this parameter in order to find out how much helium the perfect zirconia crystal can accommodate. An inert matrix fuel used for reactor irradiation will always be polycrystalline, and during fabrication the formation of some cracks or pores is inevitable. The material studied in this chapter was a high quality polycrystalline material. No cracks could be found by microscopic investigation, and the grains were very tightly packed as observed by TEM and SEM.

During the transmutation of actinides the formation of large quantities of gas is inevitable. In spinel (EFTTRA-T4) this gave rise to a large swelling of the target pin and a large fraction of gas which was released towards the fuel-cladding gap. A large gas release does not have to be a problem as long as the fuel is designed to accommodate the gas somewhere. A major concern in the design of an IMF fuel with zirconia is the low thermal conductivity of the material which leads to very high fuel temperatures. Currently, an FSZ based inert matrix is being irradiated in the Halden reactor [101]. The temperature at the centre of the rod was measured to be about 1500 K. Hopefully, the Halden experiments will give more insight into the gas build-up and helium behaviour in FSZ.
Chapter 7

Results, conclusions, predictions and final remarks

In the perspective of the more efficient exploitation of uranium resources, and of the fact that the spent fuel stays radioactive during millions of years, partitioning and transmutation of actinides appears to be a practical and maybe imperative strategy. In such a scenario, actinides can be embedded in a so-called inert matrix material. In this thesis, two candidate inert matrix materials have been studied with respect to helium and fission gas behaviour.

7.1 Results on spinel

Chapters 4 and 5 of this thesis were devoted to magnesium aluminate spinel. In Chapter 4, helium and xenon implantation experiments in crystalline and amorphous spinel were discussed. In Chapter 5, results on the release of helium, xenon and krypton release from a reactor irradiated spinel target were described. In spite of the work described in these two chapters, it is only a very small fraction of the total research performed on spinel as a candidate inert matrix material [3]. The results presented in Chapter 5 provide a crucial explanation for the puzzling spinel behaviour, and some concluding remarks can now be made concerning its use in an inert matrix fuel.

The information summarized in Chapters 4 and 5, but also in the literature (e.g. [3]), has shown that MgAl$_2$O$_4$ is certainly not the ideal matrix for composite fuels or targets for transmutation. In spite of a number of good thermal and mechanical characteristics the following important drawbacks have been noted:
• Limited stability towards the impact of fission products of fission energy.
• Mixtures of MgAl$_2$O$_4$ and fissile phases like AnO$_{2-x}$ and (Zr,An)O$_{2-x}$, where An stands for actinides, are not in chemical equilibrium.
• It has been shown that spinel exhibits a large swelling under reactor irradiation.
• The material itself is unstable under thermal treatment.

MgAl$_2$O$_4$-based fuels, if no better alternatives are found, must be designed to cope with the limitations arising from these drawbacks. The limited stability of the material under the impact of the fission products must be minimized by design optimization. The main penalty will therefore come from the operating temperature, which must be low in view of eutectic melting which can occur at temperatures well below the melting point of MgAl$_2$O$_4$. This would imply that MgAl$_2$O$_4$-based fuels must certainly be excluded from normal fast reactor applications and should only be considered for low-linear-power applications (low actinide concentrations), as for example the case in the EFTTRA-T4 and -T4bis irradiation experiments. Such low-power applications are typical of targets for once-through transmutation schemes in which a high extent of fission must be realized. The EFFTRA-T4 and -T4bis irradiation experiments have shown that, as a result of its thermomechanical behaviour, MgAl$_2$O$_4$ will satisfactorily retain the helium produced under these circumstances. Whether this is an advantage or disadvantage should follow from the safety analysis. However, an unacceptable swelling at the end of irradiation of the EFFTRA-T4 target was observed.

7.1.1 Recommendations and conclusions concerning spinel

Presently, work is being performed on the modelling of the release data of xenon and helium as presented in Chapter 5. The modelling of these data gives insight in the combination and importance of the release mechanisms which cause the release of helium and the fission gases. A more detailed knowledge of these mechanisms will make it easier to understand the differences between helium and fission gas implantation experiments in spinel and helium and fission gas release from reactor irradiated targets.

Spinel is probably one of the most studied candidate inert matrix materials, and, as a conclusion from the available data it can be said that spinel is not a suitable inert matrix candidate. However, for materials that look more promising, not so many data are available. It is therefore necessary to study other candidate materials in more detail in order to be able to make an equal comparison between spinel and other candidate fuels.
7.2 Results on zirconia

At present, one of the most promising candidate materials is fully stabilized zirconia. In Chapter 6, the helium behaviour in this material has been studied in detail. Firstly, the applicability of FSZ as an inert matrix material depends on the application and on the fuel design. Based on the results presented in Chapter 6, it can be said that the FSZ studied in Chapter 6 is very stable under the impact of $\alpha$-particles. The material did not swell under the impact of the implanted helium, nor did any cracks form. In the experiments described in Chapter 6, it has been shown that for higher helium concentrations bubbles will be formed, and that this is even more likely to occur in the presence of fission gases. Helium in fully stabilized zirconia starts to become mobile at rather low temperatures. In the design of a zirconia-based inert matrix fuel serious attention should be paid to the diffusing gases. A sufficient large fuel-cladding gap should be included in the design in order to accommodate the gas. From the point of view of stability against damage from $\alpha$-decay and the build-up of helium, fully stabilized zirconia behaves very well. Helium is released at low temperatures, even compared with in-core conditions. Furthermore, damage introduced by the decay of actinides is easily recovered. While in an implantation study all damage is accumulated simultaneously, in a transmutation scenario at higher temperatures the low-dose $\alpha$-decay damage may easily recover.

7.2.1 Recommendations and conclusions concerning zirconia

When an inert matrix material is exposed to a neutron flux at the beginning of the transmutation cycle the helium concentration will be low but the fuel temperature will be high. At the end of the transmutation cycle, fuel temperature will be lower, depending on irradiation conditions, but the helium concentration will be high. As there is a large difference between the experiments described in Chapter 6 and a real transmutation scenario more experiments are necessary to predict the helium behaviour under in-core conditions together with a more detailed modelling of the behaviour of helium in fully stabilized zirconia.

The diffusion models presented in Chapter 3 can be used very well to model the behaviour of low doses of helium in polycrystalline fully stabilized zirconia. The model presented in Chapter 3 for diffusion over the grain boundaries can be used to characterize the diffusion mechanisms for low dose implanted helium. For higher implanted doses however, the model becomes more complex as more interacting mechanisms play a role in the release of the helium. Here one should think about the trapping of helium in bubbles and the re-solution of helium from the bubbles or the traps in the matrix. For such a complex analysis, more information about the temperature dependent bubble sizes and densities has to be known. Although, as described in Chapter 6, attempts were made to visualize the bubbles by TEM, so far, unfortunately, no accurate
Information on bubble sizes and densities has been obtained from these analysis. It is recommended that the study on helium bubble formation in fully stabilized zirconia is continued in order to gain better insight in the interacting release mechanisms. This is necessary in order to predict the behaviour of FSZ under neutron irradiation. The behaviour of helium in FSZ depends on its concentration, as well as on the temperature at which the helium was implanted. More laboratory experiments must and can be performed, that reflect the reactor conditions better. Some of these are:
1. A systematical study on implantation experiments at elevated temperatures;
2. Implantation of helium at different energies in order to get a more homogeneous helium distribution;
3. Implantation of inert matrix simulated fuel, where impurities are already present in the form of fission products that are expected after or during burn-up;
4. Implantation of helium in zirconia that has been damaged by neutrons;
5. Combined implantations of helium and fission gases;
6. Investigation of the solubility of helium in FSZ;
7. Investigation of the effect of the yttria fraction in FSZ.

An accurate modelling of these laboratory experiments is essential, in order to obtain insight in the interactions of these effects in a reactor irradiation transmutation matrix. The model presented in Chapter 3, forms an important part of the final model, although it can be improved. The model assumes that the defect concentration present after implantation is constant and does not change during the release. Improvements of the model should be made, taking into account the clustering of defects and dissociation of clusters. The final model for helium interaction with inert matrices should include also the build-up of defects during irradiation and the modifications caused by this. In the model, for the temperature profile, the fuel temperature during reactor irradiation should be used. Finally, of course, in-core neutron irradiation experiments are necessary to test the selected materials. As in-core experiments are very time-consuming and expensive, the interaction of systematic implantation experiments together with a detailed modelling of these experiments can accelerate the implementation of transmutation on an industrial scale.
Bibliography


[27] N. Yu, K.E. Sickafus, P. Kodali, and M. Nastasi. In Situ Observation of Defect Growth Beyond the Irradiated Region in Yttria-Stabilized Zirconia Induced by


Appendix A

Conversion of the measured NDP data into a depth profile

If a neutron reacts with $^3$He, protons with an energy of 572 keV are created. If it is assumed that the helium is implanted exactly at the surface, all emitted protons have an energy $E_0$ of 572 keV. However, due to the detector resolution, energies greater, equal or less than $E_0$ are detected. A schematical overview of such a detector system is shown in Figure A.1.

Figure A.1: A schematic overview of the detector system, where $X(E)$ is the released proton spectrum, $H(E)$ is the detector function and $Y(E)$ is the measured proton spectrum.

In the figure $X(E)$ represents the emitted proton spectrum, $H(E)$ the detector function and $Y(E)$ the measured proton spectrum. If all the protons are emitted at the surface, $X(E)$ can be described as follows:

$$X(E) = A_m \delta (E - E_0), \quad (A.1)$$

where $A_m$ is the amplitude of the measured signal and $\delta$ the Dirac-delta function.

The measured signal $Y(E)$ can be described as a Gaussian function:

$$Y(E) = \frac{A_m}{w_d} \sqrt{\frac{2}{\pi}} \exp \left[ -2 \left( \frac{E - E_0}{w_d} \right)^2 \right], \quad (A.2)$$
where \( w_d \) is a measure of the peak width, which is defined as:

\[
  w_d = \frac{1}{2} \frac{\text{FWHM}}{\sqrt{\frac{1}{2} \ln(2)}},
\]

where FWHM is the full width at half maximum of the peak, which is 12.5 keV for the detector used.

The system shown in Figure A.1 can now be described by the following convolution equation:

\[
  Y(E) = X(E) \ast H(E),
\]

or

\[
  Y(\omega) = X(\omega)H(\omega),
\]

where \( Y(\omega), X(\omega) \) and \( H(\omega) \) are the fast Fourier transformation (FFT) of \( Y(E), X(E) \) and \( H(E) \), respectively.

The FFT of \( X(E) \) is defined as:

\[
  X(\omega) = \int_{-\infty}^{\infty} X(E) \exp(-j\omega E)dE = A_s \exp(-j\omega E_0)
\]

and

\[
  Y(\omega) = \int_{-\infty}^{\infty} Y(E) \exp(-j\omega E)dE = A_s \exp\left(-\frac{1}{8} w_d^2 \omega^2 - j\omega E_0\right).
\]

\( H(\omega) \) is defined as:

\[
  H(\omega) = \frac{Y(\omega)}{X(\omega)} = \exp\left(-\frac{1}{8} w_d^2 \omega^2\right).
\]

The detector function can thus be described as:

\[
  H(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} H(\omega) \exp(j\omega E)d\omega = \frac{1}{\sqrt{\frac{1}{2} w_d}} \exp\left(-2 \left(\frac{E}{w_d}\right)^2\right).
\]

The protons measured are not created at the surface of the sample, but somewhere in the bulk. The measured signal has in general a Gaussian distribution and is defined as follows:

\[
  Y_m(E) = \frac{A_m}{\sqrt{\frac{1}{2} w_m}} \exp\left(-2 \left(\frac{E - E_m}{w_m}\right)^2\right),
\]
and

\[ Y_m(\omega) = A_m \exp \left( -\frac{1}{8} w_m^2 \omega^2 - j\omega E_m \right) . \]  

(A.11)

The FFT of the energy distribution of protons being released from the sample can be defined as:

\[ X(\omega) = \frac{Y(\omega)}{H(\omega)} = A_m \exp \left( -\frac{1}{8} \omega^2 (w_m^2 - w_d^2) - j\omega E_m \right) , \]  

(A.12)

and

\[ X(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} X(\omega) \exp (j\omega E) d\omega \]

\[ = \frac{A_m}{\sqrt{\frac{\pi}{2}} \sqrt{w_m^2 - w_d^2}} \exp \left( -\frac{2(E_m - E)^2}{w_m^2 - w_d^2} \right) . \]  

(A.13)

An example of the correction of the fitted energy spectrum is shown in Figure A.2.

![Figure A.2](image)

**Figure A.2:** The correction of the FWHM of the NDP results. The fit of the measured energy profile (open squares) is corrected for the detector resolution by making use of the deconvolution integral (closed circles).

As one is interested in determining the depth at which the reaction took place, the measured energy distribution should be convoluted into a depth profile. In the ideal case,
the information stored in the energy spectrum corrected for the detector resolution can be correlated with a depth profile by the relations:

\[
x = \int_{E(x)}^{E_0} \frac{dE}{s(E)} \quad \text{and} \quad d = x \times \cos(\theta),
\]

(A.14)

where \( E_0 \) is the initial proton energy, \( E(x) \) the detected energy, corrected for the detector resolution, \( S(E) \) is the stopping power of the host material, \( x \) is the pathlength of the particle in the material and \( d \) is the depth at which the parent nuclide was located.

The stopping power for protons in fully stabilized zirconia in the range between 450 and 700 keV has been calculated with SRIM-2000. For this case, the stopping power is defined as:

\[
S(E) = AE^2 + 2BE + C,
\]

(A.15)

with:

\[
A = 1.5807 \times 10^{-11} \text{ A·eV}, \quad B = -1.4902 \times 10^{-5} \frac{1}{\text{A}}, \quad \text{and} \quad C = 2.2874 \times 10^1 \text{ eV}.
\]

The path length \( x \) travelled by the proton can thus be defined as:

\[
x = \frac{1}{\sqrt{AC - B^2}} \left( \arctan \left[ \frac{AE_0 + B}{\sqrt{AC - B^2}} \right] - \arctan \left[ \frac{AE + B}{\sqrt{AC - B^2}} \right] \right),
\]

(A.16)

where \( E \) and \( E_0 \) are the energy values in eV. The results shown in Figure A.2 have been converted to a depth profile by making use of Eq. A.16. These results are shown in Figure A.3.

**Figure A.3**: The correction of the FWHM of the NDP results versus the depth. The fit of the measured energy profile (open squares) is corrected for the detector resolution by making use of the deconvolution integral (closed circles).
The measured data in channel \( x \), \( (N(x)) \), their Gaussian fit and the Gaussian fit corrected for detector resolution can be converted to a helium density \( \rho \) by making use of the cross-section for the \(^3\text{He}(n,p)^3\text{H}\) reaction. The path length which a proton can travel within the channel is used as well and is defined as:

\[
dX(x) = \frac{E(x+1) - E(x)}{S(E_x)},
\]

(A.17)

where \( E(x+1) - E(x) \) is the energy width of the channel and \( S(E_x) \) the stopping power for this energy.

For channel \( x \), \( \rho \) can be calculated from:

\[
\rho(x) = \frac{N(x)}{C_{\text{NDP}}} \frac{1}{\sigma dX},
\]

(A.18)

where the calibration factor \( C_{\text{NDP}} \) was determined with a calibrated sample with a known implantation profile and has the unit count \( s^{-1} \text{ cm}^2 \text{ He}^{-1} \text{ barn}^{-1} \).
Conversion of the measured NDP data into a depth profile
Nomenclature

List of Symbols

\( \beta \)  \quad \text{heating rate} \quad \text{K s}^{-1}

\( \gamma \)  \quad \text{bubble surface energy} \quad \text{N m}^{-1}

\( \Delta t \)  \quad \text{time step} \quad \text{s}

\( \Delta T_s \)  \quad \text{error in sample temperature} \\

\( \Delta S_m^* \)  \quad \text{change in entropy for an ion making a jump in a material} \quad \text{W m}^{-2} \text{K}^{-4}

\( \Delta H_m^* \)  \quad \text{enthalpy change for an ion making a jump} \quad \text{W m}^{-2} \text{K}^{-4}

\( \varepsilon_s \)  \quad \text{specimen emissivity} \\

\( \varepsilon_c \)  \quad \text{crucible emissivity} \\

\( \eta_{gb} \)  \quad \text{areal trapping density} \quad \text{cm}^{-2}

\( \lambda \)  \quad \text{elementary jump distance} \quad \text{m}

\( \nu \)  \quad \text{attempt frequency} \quad \text{s}^{-1}

\( \rho \)  \quad \text{density} \quad \text{g cm}^{-3}

\( \sigma^2 \)  \quad \text{variance of Gaussian distribution} \quad \text{m}^2

\( \phi_q \)  \quad \text{heat flow} \quad \text{W}

\( \phi_{\text{abs}} \)  \quad \text{absorbed heat flow} \quad \text{W}

\( A_c \)  \quad \text{crucible inner surface area} \quad \text{m}^2

\( A_{\text{He}} \)  \quad \text{normalisation constant for helium concentration} \quad \text{cm}^{-2}

\( A_m \)  \quad \text{amplitude of measured proton signal} \\

\( A_s \)  \quad \text{specimen surface area} \quad \text{m}^2

\( a \)  \quad \text{fraction of helium implanted in the grain} \\

\( C \)  \quad \text{concentration of the diffusing substance} \quad \text{g cm}^{-3}

\( C_0(x,t) \)  \quad \text{initial helium distribution} \quad \text{cm}^{-3}

\( C_1 \)  \quad \text{fitting parameter for sample temperature} \quad \text{K}^{-3} \text{s}^{-1}

\( C_3 \)  \quad \text{variable in solution of C(x,t)} \quad \text{m}^{-1}

\( C_4 \)  \quad \text{variable in solution of C(x,t)} \quad \text{m}^2

\( C(x,t) \)  \quad \text{depth and time dependent helium concentration} \quad \text{cm}^{-3}

\( C_F \)  \quad \text{calibration factor for helium} \quad \text{C}^{-1}

\( C_{\text{NDP}} \)  \quad \text{calibration factor for helium in NDP} \quad \text{s}^{-1} \text{cm}^2 \times \text{He}^{-1} \text{barn}^{-1}
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_g(x,t)$</td>
<td>helium concentration within the grain</td>
</tr>
<tr>
<td>$C_{gb}(x,t)$</td>
<td>helium concentration at the grain boundaries</td>
</tr>
<tr>
<td>$C_t(x,t)$</td>
<td>total helium concentration</td>
</tr>
<tr>
<td>$c$</td>
<td>velocity of light</td>
</tr>
<tr>
<td>$c_p$</td>
<td>specific heat of specimen</td>
</tr>
<tr>
<td>$D$</td>
<td>diffusion coefficient</td>
</tr>
<tr>
<td>$D_0$</td>
<td>prefactor for diffusion</td>
</tr>
<tr>
<td>$D_{He,g}$</td>
<td>diffusion coefficient for helium within the grain</td>
</tr>
<tr>
<td>$D_{He,gb}$</td>
<td>diffusion coefficient for helium at the grain boundaries</td>
</tr>
<tr>
<td>$D_{ion}$</td>
<td>ionic self-diffusion</td>
</tr>
<tr>
<td>$D_{O1}$</td>
<td>prefactor stage 1</td>
</tr>
<tr>
<td>$D_{O2}$</td>
<td>prefactor stage 2</td>
</tr>
<tr>
<td>$d$</td>
<td>depth</td>
</tr>
<tr>
<td>$E_0$</td>
<td>energy of emitted proton</td>
</tr>
<tr>
<td>$E_b$</td>
<td>binding energy of $\gamma$-particles</td>
</tr>
<tr>
<td>$E_d$</td>
<td>displacement energy</td>
</tr>
<tr>
<td>$E_m$</td>
<td>energy at which the maximum of the Gaussian distribution occurs</td>
</tr>
<tr>
<td>$F$</td>
<td>rate of transfer of mass per unit area</td>
</tr>
<tr>
<td>$F_m$</td>
<td>material dependent constant for diffusion</td>
</tr>
<tr>
<td>$f$</td>
<td>temperature dependent release frequency</td>
</tr>
<tr>
<td>$f_{abs}$</td>
<td>fraction of heat absorbed</td>
</tr>
<tr>
<td>$f_i$</td>
<td>probability for the $i^{th}$ mode of positron annihilation</td>
</tr>
<tr>
<td>$f_0$</td>
<td>pre-exponential factor</td>
</tr>
<tr>
<td>$H(\omega)$</td>
<td>FFT of H(E)</td>
</tr>
<tr>
<td>$H(E)$</td>
<td>detector function</td>
</tr>
<tr>
<td>$i$</td>
<td>spinel inversion parameter</td>
</tr>
<tr>
<td>$J(t)$</td>
<td>time dependent helium release rate</td>
</tr>
<tr>
<td>$k$</td>
<td>boltzmann constant</td>
</tr>
<tr>
<td>$m$</td>
<td>position of maximum of initial Gaussian distribution</td>
</tr>
<tr>
<td>$m_s$</td>
<td>mass of specimen</td>
</tr>
<tr>
<td>$m_0$</td>
<td>rest mass of the electron</td>
</tr>
<tr>
<td>$N$</td>
<td>number of helium ions retained in the specimen</td>
</tr>
<tr>
<td>$N_{0,i}$</td>
<td>fraction of helium present at the beginning of the $i^{th}$ annealing step</td>
</tr>
<tr>
<td>$p$</td>
<td>momentum of emitted $\gamma$-particles in PBA</td>
</tr>
<tr>
<td>$p_b$</td>
<td>bubble pressure</td>
</tr>
<tr>
<td>$Q$</td>
<td>activation enthalpy for diffusion</td>
</tr>
<tr>
<td>$Q_s$</td>
<td>energy of specimen</td>
</tr>
<tr>
<td>$Q_1$</td>
<td>activation enthalpy stage 1</td>
</tr>
<tr>
<td>$Q_2$</td>
<td>activation enthalpy stage 2</td>
</tr>
<tr>
<td>$r$</td>
<td>bubble radius</td>
</tr>
<tr>
<td>$r_{gb}$</td>
<td>grain radius</td>
</tr>
</tbody>
</table>
$S$ \hspace{1cm} S-parameter

$S(E)$ \hspace{1cm} energy dependent stopping power \hspace{1cm} eV A$^{-1}$

$S_i$ \hspace{1cm} S-parameter which is created with the $i^{th}$ annihilation mode

$T_c$ \hspace{1cm} crucible temperature \hspace{1cm} K

$T_s$ \hspace{1cm} specimen temperature \hspace{1cm} K

$T_{s_{\text{max\ meas}}}$ \hspace{1cm} maximum sample temperature measured \hspace{1cm} K

$T_{s_{\text{max\ fit}}}$ \hspace{1cm} maximum sample temperature fitted \hspace{1cm} K

$T$ \hspace{1cm} temperature \hspace{1cm} K

$t$ \hspace{1cm} time \hspace{1cm} s

$t'$ \hspace{1cm} integrated diffusion parameter \hspace{1cm} cm$^2$

$W$ \hspace{1cm} W-parameter

$W_i$ \hspace{1cm} W-parameter which is created with the $i^{th}$ annihilation mode

$w_d$ \hspace{1cm} peak width of signal

$w_m$ \hspace{1cm} peak width of measured signal \hspace{1cm} m

$X_m$ \hspace{1cm} depth of the center of the Gaussian curve \hspace{1cm} m

$X(\omega)$ \hspace{1cm} FFT of $X(E)$ \hspace{1cm} -

$X(E)$ \hspace{1cm} emitted proton spectrum

$x_{\text{He}}$ \hspace{1cm} initial amount of helium ions \hspace{1cm} -

$x$ \hspace{1cm} space coordinate \hspace{1cm} m

$x'$ \hspace{1cm} space coordinate \hspace{1cm} m

$Y(E)$ \hspace{1cm} detected proton spectrum

$Y(\omega)$ \hspace{1cm} FFT of $Y(E)$ \hspace{1cm} -

$y$ \hspace{1cm} integrated mass spectrometer signal \hspace{1cm} C
## Abbreviations and Acronyms

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADS</td>
<td>Accelerator Driven System</td>
</tr>
<tr>
<td>AMU</td>
<td>Atomic Mass Unit</td>
</tr>
<tr>
<td>appm</td>
<td>Atomic Part Per Million</td>
</tr>
<tr>
<td>BSE</td>
<td>Backscattered Electrons</td>
</tr>
<tr>
<td>BU</td>
<td>Burnup</td>
</tr>
<tr>
<td>CEA</td>
<td>Centre Energy Atomique</td>
</tr>
<tr>
<td>CerCer</td>
<td>Ceramic Ceramic, a mixture of a ceramic matrix with ceramic inclusions</td>
</tr>
<tr>
<td>CerMet</td>
<td>Ceramic Metallic, a mixture of a ceramic matrix with metallic inclusions</td>
</tr>
<tr>
<td>CN</td>
<td>Coordination Number</td>
</tr>
<tr>
<td>dpa</td>
<td>Displacements Per Atom</td>
</tr>
<tr>
<td>EDF</td>
<td>Electricité de France</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray</td>
</tr>
<tr>
<td>EFPD</td>
<td>Effective Full Power Days</td>
</tr>
<tr>
<td>EFTTRA</td>
<td>Experimental Feasibility of Targets for Transmutation</td>
</tr>
<tr>
<td>FBR</td>
<td>Fast Breeder Reactor</td>
</tr>
<tr>
<td>FFT</td>
<td>Fast Fourier Transform</td>
</tr>
<tr>
<td>FP</td>
<td>Fission Product</td>
</tr>
<tr>
<td>FSZ</td>
<td>Fully Stabilized Zirconia</td>
</tr>
<tr>
<td>FZK</td>
<td>Forschungszentrum Karlsruhe</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width Half Maximum</td>
</tr>
<tr>
<td>HFR</td>
<td>High Flux Reactor</td>
</tr>
<tr>
<td>HLW</td>
<td>High Level Waste</td>
</tr>
<tr>
<td>IE</td>
<td>Institute for Energy (Joint Research Centre)</td>
</tr>
<tr>
<td>IFP</td>
<td>Institut für Festkörper Physik</td>
</tr>
<tr>
<td>IMF</td>
<td>Inert Matrix Fuel</td>
</tr>
<tr>
<td>IRI</td>
<td>Interfaculty Reactor Institute</td>
</tr>
<tr>
<td>ITU</td>
<td>Institut für Transurane</td>
</tr>
<tr>
<td>JAERI</td>
<td>Japan Atomic Energy Research Institute</td>
</tr>
<tr>
<td>JRC</td>
<td>Joint Research Centre</td>
</tr>
<tr>
<td>KC</td>
<td>Knudsen Cell</td>
</tr>
<tr>
<td>KCM</td>
<td>Knudsen Cell Measurements</td>
</tr>
<tr>
<td>ITU</td>
<td>Institute for Transuranium Elements</td>
</tr>
<tr>
<td>LANL</td>
<td>Los Alamos National Laboratories</td>
</tr>
<tr>
<td>LLFP</td>
<td>Long Living Fission Product</td>
</tr>
<tr>
<td>LWR</td>
<td>Light Water Reactor</td>
</tr>
<tr>
<td>n</td>
<td>neutron</td>
</tr>
<tr>
<td>NDP</td>
<td>Neutron Depth Profiling</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>NRG</td>
<td>Nuclear Research and Consultancy Group</td>
</tr>
<tr>
<td>MA</td>
<td>Minor Actinide</td>
</tr>
<tr>
<td>MeV</td>
<td>Mega electronvolt</td>
</tr>
<tr>
<td>MOX</td>
<td>Mixed Oxide</td>
</tr>
<tr>
<td>NDP</td>
<td>Neutron Depth Profiling</td>
</tr>
<tr>
<td>p</td>
<td>Proton</td>
</tr>
<tr>
<td>PBA</td>
<td>Positron Beam Analysis</td>
</tr>
<tr>
<td>ppm</td>
<td>part per million</td>
</tr>
<tr>
<td>Ps</td>
<td>Positronium</td>
</tr>
<tr>
<td>PSZ</td>
<td>Partly Stabilized Zirconia</td>
</tr>
<tr>
<td>PWR</td>
<td>Pressurized Water Reactor</td>
</tr>
<tr>
<td>RBS</td>
<td>Rutherford backscattering</td>
</tr>
<tr>
<td>RT</td>
<td>Room Temperature</td>
</tr>
<tr>
<td>SAED</td>
<td>Selective Area Electron Diffraction</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SLFP</td>
<td>Short Living Fission Product</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>THDS</td>
<td>Thermal Helium Desorption Spectrometry</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
</tbody>
</table>
Summary

The demand for total world energy is expected to rise by two-thirds between now and 2030, and energy-related carbon emissions are foreseen to rise by 70% over the same period. If this increasing demand is to be met, and at the same time the CO₂-emission is to be limited, the use of nuclear power seems inevitable. One of the main concerns of nuclear power is the radioactive waste produced during the fission process. The nuclear waste consists of short-lived fission products, the majority of which will decay within several decades after the fuel is removed from the reactor, of long lived fission products, which stay active for a much longer time and of actinides, formed as a product of neutron capture and radioactive decay processes. The most important actinides in the nuclear waste are plutonium, americium, curium and neptunium. Actinides can either be fissioned or transmuted into a less radiotoxic species. In such a transmutation process, the actinide is irradiated in a neutron flux and as a result, the actinide either fissions, yielding two fission products, or it captures a neutron. By decay processes the actinide can then be transmuted into an isotope with a shorter half-life. The transmutation process can be performed in various types of reactors, e.g. a fast reactor, a light water reactor or an accelerator driven system. In order to insert the actinide to be transmuted into a neutron system, the actinide first has to be embedded in a material which is inert under neutron irradiation, a so-called inert matrix material. Depending on the application, the inert matrix material should fullfil several requirements with respect to its thermal and material properties. Most of the actinides are α-emitters and, when they decay large quantities of helium will be formed in the inert matrix materials.

The behaviour of helium in two candidate inert matrix materials was studied with different experimental investigation techniques. The temperature dependent helium desorption rate was measured in the Knudsen cell setup of ITU. In both setups, a specimen is inserted in a tiny cell which is heated through radiation. The vapour and gas stream effusing from a small hole at the top of the cell is analysed by mass spectrometry. As a part of this thesis, extensive experiments aimed at improving the accuracy of temperature measurements were performed and a new system was implemented suitable for measuring the absolute quantity of helium ions effusing from the cell. Helium effusion from inert matrix materials was investigated in the helium desorption facility of IRI. In this setup, a large delay between the temperature of the specimen and the crucible was observed due to the transparency of the sample material to infrared radiation. Calibration experiments were performed where the size of this effect was measured.
By making use of these measured data, a model was derived to convert the measured temperature data into the absolute temperature of the specimen. The depth dependent helium distribution in several specimens was investigated by neutron depth profiling and the temperature dependent evolution of defects was monitored by positron beam analysis. Both SEM and TEM were used to investigate the microstructure of the investigated specimens.

In order to get insight in the processes responsible for the helium release during thermal treatment, two helium release models have been used based on helium dissociation from defects and bubbles, followed by diffusion. The first model can be used for helium diffusion in single crystals, the second model for helium diffusion along the grain boundaries. Partial annealing during desorption has been shown to be a powerful technique to derive the activation energy and the kinetic parameters of the desorption processes.

Polycrystalline spinel (MgAl_2O_4) specimens were implanted with helium ions and subsequently annealed in the Knudsen cell. Helium release occurred between 800 and 1600 K, depending on the implanted dose. A single crystal of spinel was amorphized by the implantation of xenon ions at cryogenic temperatures. Helium was subsequently implanted in the centre of the amorphous layer. The helium release profile under thermal annealing was monitored in both desorption systems. It was found that the major part of the helium is released in two stages, with the maximum of the peaks at about 615 and 720 K, which is at much lower temperatures than in polycrystalline spinel. Xenon release from the amorphous spinel starts very suddenly at 1050 K, caused by sweeping out during recrystallization. A second xenon release peak was observed with a maximum at about 1280 K, attributed to xenon release during restructuring of the matrix.

Experiments with positrons were performed at room temperature and after various annealing steps. The data of these measurements were analysed using the VEPFIT code with a three-layer model. At room temperature, these three layers corresponded to amorphized spinel without xenon, amorphized spinel with xenon and the substrate.

Helium and fission gas behaviour was also studied for a reactor irradiated spinel specimen with an initial americium content of 11%. The specimen was irradiated in the HFR at Petten for about 360 EFPD after which 96% of the 241Am was either transmuted or fissioned. This was an excellent result from the point of view of americium transmutation. However, problems occurred during the fabrication of the material. The infiltration method used for producing the pellets gave an inhomogeneous distribution of the americium in the pellet. Secondly, the spinel matrix itself did not behave too well under neutron irradiation. Due to the large quantities of gas built up in the material, a swelling of the pellets of about 18% occurred, caused by a large porosity and leading to microcracks in the fuel. Scanning electron microscopy showed that the actinides formed by neutron capture and subsequent decay (mainly Pu-isotopes) were located around the pores in inclusions of 2-3 \( \mu \text{m} \) corresponding to the original Am-inclusions. The spinel matrix observed by transmission electron microscopy showed a nano-grain structure containing neither gas bubbles nor large defects. The helium pro-
duced during irradiation and storage was mainly located in the large porosity formed during irradiation. The matrix is assumed to have been turned amorphous before its subsequent recrystallization during storage. Large pores but also bubbles had been formed in the matrix mainly from the helium and from the fission gases produced during irradiation. The fission products were distributed throughout the matrix and metal precipitates, often associated with gas bubbles, were found in the matrix. The original Am-inclusions had been transformed into Pu-rich inclusions. Since the spinel matrix showed a pronounced plastic deformation associated with a large swelling it can no longer be considered as a reliable candidate microdispersed inert matrix for actinide transmutation. Its unpredictable behaviour is linked to a poor chemical stability when used in conjunction with americium and its transmutation products and to its predilection to amorphize under reactor irradiation conditions.

Another candidate inert matrix material is zirconia, stabilized in the cubic structure with the aid of yttria. It was observed that the behaviour of helium under thermal annealing in such a material strongly depends on the quantity of helium implanted in the specimen. For small quantities, helium is released at low temperatures in a narrow release interval. It was shown by neutron depth profiling that a broadening of the helium distribution occurs, typical of a diffusion process. After implantation, helium is trapped mostly in single vacancies or at interstitial sites. During thermal annealing, helium is released by dissociation from the vacancy or trap and by subsequent vacancy assisted diffusion towards the surface. It was shown by positron beam analysis that the $S$-parameter, which increases after implantation, decreases towards the reference value under thermal treatment. This stage is reached at relatively low temperatures. Vacancies introduced by low-dose implantation are very mobile and can easily be removed by thermal annealing. For high-dose helium implantations the story is different. After implantation, helium is trapped in vacancies and cavities. By thermal desorption experiments it was shown that the helium is retained up to high temperatures. This was confirmed by neutron depth profiling; the helium distribution does not broaden and at high temperatures the maximum of the distribution shifts towards a larger depth. Instead of diffusing towards the surface, the helium becomes trapped in bubbles. Ostwald ripening occurs at the temperatures where for the lowest-dose case the helium diffusion starts. During thermal annealing, small clusters dissociate and larger ones grow at the expense of the smaller ones. This process continues until nano-size bubbles are present, which are visible with TEM. At higher temperatures, starting between 700 and 800 K, NDP shows that helium begins to be released from the bubbles. However, as seen with NDP, helium is released slowly from the bubbles and the $S$-parameter of the damaged layer increases with every annealing step. This can be explained by the open volume left behind by the bubbles, which yields a high $S$-value.
Samenvatting

Wetenschappers voorspellen dat tot 2030 de totale vraag naar energie in de wereld met twee-derde, en de energie-gerelateerde CO₂ uitstoot met 70% zal toenemen. Om aan deze stijgende vraag naar energie te voldoen lijkt het gebruik van kernenergie onvermijdelijk, temeer daar de uitstoot van CO₂ gas beperkt moet blijven. Een van de grote nadelen aan het gebruik van kernenergie is het radioactieve afval dat tijdens het splijtingsproces geproduceerd wordt. Het radioactieve afval bestaat uit kortlevende splijtingsprodukten die binnen enkele decennia vervallen nadat de splijtstof uit de reactorkern verwijderd is, en uit langlevende splijtingsprodukten, die over een veel langere periode radioactief blijven. Het langlevende afval uit de kerncentrales bevat tevens actiniden, die in de splijtstof gevormd zijn door neutronenvangst en radioactieve vervalprocessen. De belangrijkste actiniden in de splijtstof en het radioactieve afval zijn americium, curium en neptunium. Actiniden kunnen door thermische neutronen gespleten worden en ze kunnen getransmuteerd worden in een minder radiotoxisch isotoop. Bij transmutatie vangt het actinide een neutron in, en door daaropvolgende radioactieve vervalprocessen transmuteert het actinide in een isotoop met een kortere halfwaardetijd. Transmutatie kan uitgevoerd worden in verschillende reactortypen, zoals snelle reactoren, lichtwaterreactoren of versneller aangestuurd systemen. Om het actinide dat getransmuteerd moet worden aan een neutronenflux te kunnen blootstellen, moet het actinide ingesloten worden in een materiaal dat zich inert gedraagt wanneer dit met neutronen bestraald wordt; dit materiaal wordt een inerte matrix genoemd. Afhankelijk van de gekozen toepassing moet het inerte matrixmateriaal vol doen aan een aantal eisen wat betreft warmte- en materiaaleigenschappen. De meeste actiniden vervallen onder uitzending van α-straling, met als gevolg dat er grote hoeveelheden helium in het inerte matrixmateriaal gevormd worden.

Het gedrag van helium in twee potentiële inerte matrixmaterialen is onderzocht door gebruik te maken van verschillende experimentele technieken. Het temperatuur-afhankelijke gedrag waarmee helium vrijkomt uit de matrix is gemeten in de Knudsen-cel van ITU. In deze opstelling wordt een klein stukje inerte matrixmateriaal dat met helium geimplanteerd is of materiaal dat in een neutronenflux bestraald is, in een kleine cel geplaatst. Deze cel wordt in vacuum verwarmd. De damp en de gassen die uit een klein gaatje in de bovenkant van deze cel komen, worden geanalyseerd in een massaspectrometer. Als een onderdeel van dit promotiewerk zijn er experimenten uitgevoerd om de nauwkeurigheid van de temperatuurmetingen van deze cel te ver-
beteren. Bovendien is er een systeem ontworpen waarmee de absolute hoeveelheid helium bepaald kan worden. Het temperatuurafhankelijke heliumgedrag in verschillende inert matrixmaterialen is ook onderzocht in de heliumdesorptie-opstelling van het IRI. In deze opstelling wordt het te onderzoeken materiaal in een kleine cel in vacuum geplaatst en deze wordt vervolgens opgewarmd door elektronenbombardement. In deze meetopstelling werd een groot verschil waargenomen tussen de temperatuur van het te onderzoeken monster en de temperatuur van de cel, mede veroorzaakt door de transparantie van het monstermateriaal voor infrarode straling. Er zijn experimenten uitgevoerd om de omvang van dit effect te meten, en aan de hand van de meetresultaten is een model ontwikkeld waarmee de gemeten temperatuur naar de echte temperatuur van het monster omgerekend kan worden. De diepte-afhankelijke heliumverdeling is in verschillende monsters onderzocht met neutronendiepteprofileringmetingen en het temperatuurafhankelijke gedrag van defecten in het inert matrixmateriaal is onderzocht met positronen. Er is zowel van SEM als van TEM gebruik gemaakt om inzicht te krijgen in de microstructuur van de onderzochte materialen.

Om de effecten die een rol spelen bij het vrijkomen van helium te karakteriseren, zijn er twee modellen ontwikkeld. De modellen zijn erop gebaseerd dat het helium eerst vrij moet komen uit het defect of de bel waarin het zit, om vervolgens naar het oppervlak van het monster te diffunderen. Het eerste model is geschikt voor helium diffusie vanuit een een-kristal, het tweede model bevat ook de korrelgrenzen waardoor het model voor polykristallijn materialen geschikt is. Er is aangetoond dat het in stappen desorberen van het helium een goede methode is om de activeringsenergien en de kinetische parameters van het desorptieproces te bepalen.

Polykristallijn spinel MgAl$_2$O$_4$ is geïmplanteer met heliumionen en vervolgens verwarmed in de Knudsen-cel. Helium komt vrij uit het materiaal tussen 800 en 1600 K, afhankelijk van de geïmplanteerde dosis. Een spinel een-kristal is amorf gemaakt door het bij 73 K te implanteren met xenonionen. Vervolgens is helium geïmplanteer in het centrum van de amorfe laag. Het temperatuurafhankelijke profiel van het helium dat vrijkomt uit het materiaal is onderzocht in de twee desorptiesystemen. Het grootste deel van het helium komt vrij in twee fasen, met het maximum van de pieken bij 615 en 720 K, wat veel lager is dan voor polykristallijn spinel. Het vrijkomen van xenon begint zeer plotseling bij 1050 K, wat verklaard kan worden door het rekristallisatieproces. Een tweede xenonpiek heeft zijn maximum bij 1280 K, en deze piek kan verklaard worden met het vrijkomen van xenon tijdens de herstructurering van het rooster.

Experimenten met positronen zijn gedaan voor een monster na implantatie, en voor monsters die verwarmed waren tot verschillende maximumtemperaturen. De resultaten van deze experimenten zijn geanalyseerd met een drie-lagen model in VEPFIT. Voor het monster dat niet verwarmed is komen deze drie lagen overeen met amorf spinel zonder xenon, amorf spinel met xenon en het dieper liggende, onbeschadigde deel van het materiaal.

Het gedrag van helium en splijtingsgassen is ook onderzocht voor een in een reactor bestraald spinelmonster waarvan de initiële americiumfractie 11% was. Het monster is ongeveer 360 dagen bestraald in de HFR in Petten, waarna 96% van het $^{241}$Am
getransmuteerd of verspleten was. Uit het oogpunt van americiumtransmutatie is dit een zeer goed resultaat. Helaas traden er problemen op tijdens de fabricage van het monster. Het infiltratieproces dat gebruikt is om het monster te maken, leverde een niet-homogene verdeling van americium in het monster op. Het spinel matrixmateriaal gedroeg zich niet goed onder neutronenbestraling. Door de grote hoeveelheden gas die zich in het materiaal opbouwd, trad een zwelling op van ongeveer 18%. Deze zwelling was het gevolg van holten in het materiaal en veroorzaakte kleine scheurtjes. Met SEM is aangetoond dat de actiniden (voornamelijk plutonium-isotopen) in de buurt van deze porositeit zitten, en wel in insluitingen met een grootte van 2-3 µm. Dit komt overeen met de oorspronkelijke americiumdeeltjes. Met behulp van TEM is aangetoond dat de spinelmatrix opgebouwd is uit een nano-korrel structuur waarin geen gas en ook geen grote defecten zitten. Het helium dat tijdens de bestraling en de periode van opslag geproduceerd is, zit voornamelijk in de grote porositeit die tijdens bestraling gevormd is. Tijdens de bestraling is de matrix amorf geworden en vervolgens is deze tijdens de opslag gerekristalliseerd. Er zijn grote open holten en tevens bellen ontstaan in het matrixmateriaal, voornamelijk door het helium en de splijtingsgassen die tijdens bestraling gevormd zijn. De splijtingsprodukten zijn door de hele matrix heen verdeeld en bovendien zijn er precipitaties van metalen gevonden in de matrix. Deze zijn vaak aanwezig in de vorm van bellen. Zones die rijk zijn aan plutonium worden aangetroffen op de oorspronkelijke posities van de americium deeltjes. Omdat de spinelmatrix een zeer duidelijke plastische deformatie vertoonde in samenhang met een aanzienlijke zwelling kan dit materiaal niet langer gezien worden als een materiaal dat geschikt is voor de transmutatie van actiniden. Het onvoorspelbare gedrag in samenhang met de chemische instabiliteit als het gebruikt wordt met americium en transmutatieprodukten, en het feit dat het materiaal amorf wordt bij bestraling met neutronen zijn de belangrijkste argumenten hiervoor.

Een ander kandidaat voor inert matrixmateriaal is zirconia, gestabiliseerd in de kubische structuur met yttria. Een belangrijke observatie is dat het gedrag van helium tijdens het verwarmen zeer sterk afhangt van de heliumconcentratie in het materiaal. Als helium in lage concentraties aanwezig is, wordt het vrijgemaakt bij lage temperaturen en in een smal temperatuurinterval. Met neutronendiepteprofilering is aangetoond dat de heliumverdeling zich verbrekt, wat typisch is voor een diffusieproces. Na implantatie is helium voornamelijk gelokaliseerd in enkelvoudige vacatures of interstitiële posities. Tijdens het verwarmen wordt het helium vrijgemaakt uit deze posities en diffuseert het naar het oppervlak van het monster via de vacatures en de korrelgrenzen. Met behulp van positronenonderzoek is aangetoond dat de $S$-parameter, die na implantatie groter is dan voor het niet-geimplanteerd materiaal, bij verwarmen daalt naar de referentiewaarde. Dit gebeurt al bij lage temperaturen. Vacatures die bij implantatie met lage dosis in het materiaal ontstaan zijn zeer mobiel en kunnen op eenvoudige wijze uit het materiaal verwijderd worden door dit te verwarmen. Monsters die een hoge dosis helium bevatten laten een ander gedrag zien. Na implantatie zit het helium in vacatures en in holten. Door middel van desorptie-experimenten is het aangetoond dat het helium vastgehouden wordt tot hoge temperaturen. Hetzelfde is bewezen met neutronendiepteprofileringonderzoek. Het heliumdiepteprofiel verbreedt zich niet en
Acknowledgements

In a thesis where many experimental techniques are combined and some of the investigated specimens were highly radioactive, I was lucky to receive the help of so many people.

As my promotor, many thanks go to Tom van Veen, for the trips he made to Karlsruhe to discuss my results with the ITU-colleagues, and for the hospitality to perform part of my work in the laboratories of IRI. Without these experiments, there would be no thesis. I would not have started this thesis without the efforts of Mr. Matzke to get me a contract in ITU. Even after his retirement, he continued showing interest in my work.

Within the ITU, there are many people who have helped me with performing experiments, the theoretical background or the reading of publications and this thesis. Thanks go to Mr. C. Ronchi and JeanPol Hiernaut, for their help in interpreting the experimental results and the development of the models. I would not have done any experiment in the Knudsen Cell without the help of JeanYves Colle and Franco Capone. Thank you for helping me performing the experiments, but more important, thanks to both of you, I have had a great time in the ITU. It was a pleasure to answer the phone for you, JeanYves, and thanks Franco, for the fruitful discussions we had, with or without coffee. The microscopical laboratory would be nothing without the help of Mr. Thielle and Thierry Wiss. Thierry, thank you for your help with writing publications, fruitful discussions, preparing TEM specimens and unpaid lunches ...

During my thesis, many of the samples have been implanted by Mr. Fromknecht of IFP, FZK. Thank you Rainer, for the implantation of the specimens, although it was not always as easy as expected.

During my stays in Delft, I got the help of many people in performing experiments. Alexander Fedorov and Kees Westerduin, thank you for helping me with THDS, Freek Labohm, thank you for performing the NDP experiments, Henk Schut thank you for learning me how to work with VEP, Marijn van Huis, thank you for measuring some of my samples in the VEP. Thanks to Peter Mijnarends, for reading and correcting the entire manuscript twice. Finally, I would like to thank the other people of the Defects in Materials Group, it has been a pleasure to work in your department.
For the work on the amorphous spinel samples, I have to thank Kurt Sickafus and James Valdez, for supplying me with the specimens and for the reading of our JNM-article.

I have had a great time in Germany. This would not have been possible without the many nice people I have met there, who accepted me as one of theirs, and not as the girl with the 'funny Dutch accent'. Many of my Dutch friends took the time to visit me, often on their way to Italy. Thank you all for taking the time to come and see how I lived, I have enjoyed those sight-seeing weekends a lot. Finally, I would like to thank Ewout, for his monthly visit to Karlsruhe, just to bring me a little present from Ikea.
List of Publications

Publications to the subject of the thesis


T.A.G. Wiss, P.M.G. Damen, J.P. Hiernaut and C. Ronchi, "Helium and fission gases behaviour in irradiated Am-containing MgAl2O4 (EFTTRA-T4)" To be submitted to Journal of Nuclear Materials and Chapter 5 of this thesis.

Other publications


J.L. Kloosterman and P.M.G. Damen, "Reactor physics aspects of plutonium burning in inert matrix fuels" Journal of Nuclear Materials 274 (1999) 112-119

O. Köberl, P.M.G. Damen and C. De Saint Jean, "Transmutation of Americium in the Petten High Flux Reactor; A Physical Analysis” Proceedings Global 1999
O. Köberl and P.M.G. Damen, ”Benchmark on the transmutation of americium in the framework of the EFTTRA-T4 experiments” *Proceedings Jahrestagung Kerntechnik* 1999

P.M.G. Damen and B.T. Adams, ”Determination of the axial burnup profile of HOR fuel elements using gamma emission measurements” *Proceedings Jahrestagung Kerntechnik* 1998

Patricia Damen was born on the 6th of June, 1974 in Breda, The Netherlands. After attending grammar school, Gymnasium Beekvliet at St. Michielsgeest, she took up the study of applied physics at the Delft University of Technology in 1992. In 1995, she spent 6 months in the University of Trondheim as part of the Erasmus Exchange Programme. The graduate research for the study of applied physics was performed at the Interfaculty Reactor Institute in Delft in the department of Reactor Physics. This research was concluded with the Masters’s thesis 'Determination of the Axial Burn-up Profile of HOR Fuel Elements using Gamma Emission Tomography'. In 1997 she obtained the degrees of Natuurkundig Ingenieur and Master of Science in Applied Physics. She worked 2.5 years at ECN/NRG at Petten in the department of 'Fuels, Actinides and Isotopes', after which she started the PhD-work in 2000 at the Institute for Transuranium Elements of the European Commission in Karlsruhe, Germany. The study comprised the effects of helium buildup due to \( \alpha \)-decay of actinides in candidate inert matrix materials, which will be used for actinide transmutation, and resulted in this thesis. Since August 2003, she is working as a scientist at the NMI-Van Swinden Laboratorium in the department of Ionising Radiation.