Kinetics of self-healing reaction in TBC with MoSi2 based sacrificial particles

Weichen (William) MAO
8/20/2013
MSc Materials Science and Engineering

Supervised by Dr. Ir. W. G. Sloof

Department of Materials Science and Engineering
Faculty of Mechanical, Maritime and Materials Engineering
Delft University of Technology
Abstract

The isothermal kinetics is investigated of a self-healing reaction in thermal barrier coatings (TBC) with MoSi$_2$ based sacrificial healing particles. Tablets cold pressed from yttria stabilized zirconia (YSZ) and MoSi$_2$ (with and without Boron) powder mixtures were annealed at 1100 and 1200 °C in open air. MoSi$_2$ is first oxidized to form amorphous SiO$_2$. Then, the amorphous SiO$_2$ wets the surface of YSZ particles. Finally, ZrSiO$_4$ is formed from the reaction between SiO$_2$ and YSZ. The amount of ZrSiO$_4$ and unreacted ZrO$_2$ after annealing was determined using X-ray diffraction (XRD), and is plotted against annealing time as a measure for the kinetics of this healing reaction. The reaction between SiO$_2$ and YSZ was finished within 5 hours at 1200 °C. Both of the reactants (i.e. YSZ and MoSi$_2$) are not fully consumed, and the amount of remnant ZrO$_2$ decreases with annealing temperature.

The kinetics of the zircon formation is dominated by the chemical reaction rather than the diffusion of the reacting species. This kinetics of zircon formation and ZrO$_2$ consumption can be described by a first-order reaction model and geometrical contraction model, respectively. The reaction rate at 1200 °C is about three times higher than that at 1100 °C. At 1100 °C the addition of Boron in the MoSi$_2$ particles effectively promotes the formation of amorphous SiO$_2$ and thereby accelerating the reaction rate by a factor of two. Particles of MoSi$_2$ with Boron are more promising as the healing agent in zirconia ceramics.
Table of Contents

Abstract ........................................................................................................................ II
1 Introduction ............................................................................................................... 1
2 Background ............................................................................................................. 3
  2.1 Principle properties of ZrSiO₄, Yttria-stabilized ZrO₂ and SiO₂ ...................... 3
  2.2 Oxidation behaviour of MoSi₂ powder ............................................................... 5
  2.3 Volume effect of ZrO₂-SiO₂ reaction and MoSi₂ oxidation ......................... 5
  2.4 Formation of zircon from ZrO₂ and SiO₂ ......................................................... 6
  2.5 Kinetic study of solid-state reaction through thermal analysis ....................... 9
  2.6 One-dimensional diffusion controlled reaction kinetics .................................. 12
  2.7 Reaction kinetics of the contracting sphere model ........................................... 14
3 Experimental aspects ............................................................................................. 15
  3.1 Sample preparation .......................................................................................... 15
  3.2 Isothermal annealing experiments .................................................................. 15
  3.3 Methods of Investigation ................................................................................ 15
    3.3.1 Particle size analysis .................................................................................. 15
    3.3.2 X-ray diffractometry .................................................................................. 16
    3.3.3 Scanning electron microscopy (SEM) and X-ray microanalysis (XMA) ...... 17
    3.3.4 Thermal analysis ....................................................................................... 18
4 Results and discussion ........................................................................................... 20
  4.1 Characterization of raw materials ................................................................... 20
  4.2 ZrSiO₄ formation from YSZ-SiO₂ mixture ....................................................... 22
  4.3 ZrSiO₄ formation from YSZ-MoSi₂ mixtures .................................................... 24
    4.3.1 Isothermal kinetics of ZrSiO₄ formation at 1200 °C .................................. 24
    4.3.2 Isothermal kinetics of ZrSiO₄ formation at 1100 °C ................................. 32
    4.3.3 Estimation of the rate of zircon formation ................................................ 34
    4.3.4 Discussion on the kinetics of self-healing reaction of MoSi₂ and MoSi₂B healing particles. ................................................................. 35
  4.4 Thermal analysis ............................................................................................... 37
    4.4.1 Thermal behaviour of MoSi₂ and MoSi₂B powder annealed in synthetic air .... 37
    4.4.2 Determination of the activation energy of MoSi₂ and MoSi₂B oxidation ...... 39
    4.4.3 Thermal analysis on YSZ-MoSi₂ and YSZ-MoSi₂B powder mixture ........... 40
  4.5 Discussion on the mechanism of ZrO₂-SiO₂ reaction ...................................... 43
5 Conclusion ............................................................................................................ 49
6 Recommendations ................................................................................................... 50
  6.1 Isothermal kinetics ......................................................................................... 50
  6.2 Thermal analysis .............................................................................................. 50
6.3 Mechanism of zircon formation from YSZ-MoSi$_2$ system ........................................ 50
Acknowledgement .................................................................................................................. 52
Reference: .................................................................................................................................. 53
1 Introduction

To meet the demand for higher efficiency of gas turbine engine, thereby saving fuel and reducing emission of CO$_2$, higher operating temperatures are desired. Then the materials of turbine blades, vanes and combustion chamber are required to withstand ever higher temperatures. Nowadays, the operating temperature in combustion chamber of engines is higher than the limit of Ni-based superalloy, advanced inner cooling technology as well as coatings are therefore applied. In a modern high temperature coating system as shown in Figure 1.1, an aluminide diffusion or MCrAlY overlay coating, often referred to as bond coat, is applied to the Ni-based superalloy substrate to provide protection against high temperature oxidation. A thermal barrier coating (TBC) which is commonly made of partially yttria stabilized zirconia (PYSZ) is applied to the bond coat as the top coating to further protect the blades against the high temperature environment. A thermally grown oxide (TGO) layer is formed between the BC and TBC during high temperature operation, which acts as a diffusion barrier for oxygen.

![Figure 1.1: Modern high temperature coating system](image)

However, due to the difference of thermal expansion between the TBC and the substrate, compressive stresses are developed in the TBC upon cooling from the operation temperature. Thus, small delamination cracks will be generated in TBC and TGO layer. These cracks may grow and ultimately coalescence into longer cracks. Cracks perpendicular to TGO layer are not detrimental, while cracks along the TGO will result in spallation of TBC. Such spallation of the TBC will reduce the lifetime of the coated components in turbine engines. Unlike BCs, current TBCs do not exhibit self-healing properties. So, to prolong the life span of TBCs, the study and development of self-healing TBC is attractive. A self-healing concept for TBCs was proposed by Sloof [1], in which MoSi$_2$ particles as healing agents encapsulated by an alumina scale are distributed at the bottom part of TBC. MoSi$_2$ is a stable compound at high temperature and not oxidized if fully covered by alumina outer scale. When cracks in the TBC propagate and break the alumina shell of the healing particles, MoSi$_2$ is exposed to the oxidizing environment. Then, SiO$_2$ is formed at high temperature that fills the cracks. Simultaneously, volatile MoO$_3$ is formed that may escape through the existing pores and cracks in TBC. Some preliminary experiments have been done, in which MoSi$_2$ particles and PYSZ powders are mixed and oxidized in air at 1200 °C. The results show that all the cavities and gaps in the mixture are fully filled by SiO$_2$, demonstrating that SiO$_2$ formed from MoSi$_2$ is capable to fill cracks in TBCs [2].
The chemical reaction between SiO$_2$ and YSZ to form ZrSiO$_4$ (zircon) is a vital step in the whole self-healing process. The final healing product ZrSiO$_4$ restores the mechanical integrity of TBC. Therefore, the isothermal kinetics of ZrSiO$_4$ formation from the reaction between YSZ and MoSi$_2$ is of great importance to the healing behaviour. Nevertheless, detailed kinetic study of this self-healing reaction has not yet been done. Therefore, the kinetics of ZrSiO$_4$ formation from the YSZ-MoSi$_2$ mixtures at high temperature is studied, and the mechanism of the reaction between SiO$_2$ and YSZ is discussed.

The thesis is structured as follows. Chapter 2 “Background” describes the fundamental knowledge that is necessary for the study on the kinetics of self-healing process in TBCs with MoSi$_2$ based sacrificial particles. A literature review on the kinetics of zircon formation from ZrO$_2$ and SiO$_2$ is also given. Chapter 3 “Experimental aspects” gives details about the sample preparation and oxidation and annealing experiments. The methods of investigation and the equipment used, are briefly explained. Chapter 4 “Results and discussion” describes and discusses all experimental results with a detailed analysis. This includes the kinetic behaviour of zircon formation and the reaction mechanism. The conclusion are presented in Chapter 5. Finally, some recommendations for further research are given in Chapter 6.
2 Background

2.1 Principle properties of ZrSiO₄, Yttria-stabilized ZrO₂ and SiO₂

Zircon (zirconium silicate) is one of the natural minerals that can be found in earth crust. Zircon is known as an oxide ceramic and refractory material that find its application as construction material or protective coating in glass and steel production industry due to its excellent thermal properties such as low thermal conductivity and low thermal expansion [3]. Zircon crystals have a body-centered tetragonal structure (space group I4₁/amd, Pearson symbol tI24) and consist of chains of alternating edge-linked oxygen tetrahedral and triangular dodecahedra with Si and Zr atoms at the center parallel to the c-direction, respectively. The chains are laterally connected through edge-sharing ZrO₈ dodecahedra [4], as shown in Figure 2.1. Since the cracks in YSZ will be healed by ZrSiO₄, the thermal conductivity and thermal expansion of ZrSiO₄ and ZrO₂ are compared in Table 2.1.

![Figure 2.1: Crystal structure of zircon (ICSD 71945)](image)

<table>
<thead>
<tr>
<th></th>
<th>ZrSiO₄</th>
<th>YSZ (8 wt% Y₂O₃)</th>
<th>Baddeleyite¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal conductivity (Wm⁻¹K⁻¹)</td>
<td>2.6[6]</td>
<td>2.2[5]</td>
<td></td>
</tr>
</tbody>
</table>

Zirconia (ZrO₂) is one of the most studied ceramic materials. Pure zirconia undergoes two phase transformations when cooling from high temperatures, namely: cubic to tetragonal at about 2340 °C and tetragonal to monoclinic at about 1170 °C. No high temperature phases can be retained by quenching to room temperature [7]. The transformation from the tetragonal crystal structure to the monoclinic crystal structure is accompanied by 8% volume expansion that leads ZrO₂ to crack upon cooling. Hence, for practical use, ZrO₂ is doped with oxides such that tetragonal and/or cubic phases can be stabilized at room temperature. Yttria (Y₂O₃) is often used as dopant for ZrO₂. Then, the cubic/tetragonal fluorite structure of ZrO₂ is retained with some of the Zr⁴⁺ ions in the ZrO₂ lattice replaced by Y³⁺ ions. Thus oxygen vacancies are generated which facilitates the diffusion of O²⁻ ions in stabilized ZrO₂. Scott [7] studied the phase relationships of the ZrO₂-Y₂O₃ system and proposed the phase diagram as shown in Figure 2.3. Different non-equilibrium ZrO₂ phases can be retained at room temperature depending on the amount of Y₂O₃ added. Metastable tetragonal structure can be

¹ Monoclinic phase of ZrO₂
obtained at room temperature with 3 to 6 mol% Y$_2$O$_3$ by quenching from the melting point. The phase composition of the ZrO$_2$ - Y$_2$O$_3$ mixture at room temperature depends on the heating temperature and holding time as well as the cooling rate. For example, ZrO$_2$ with 6-11 mol% YO$_{1.5}$, if holding time at 1200 °C is long enough, tetragonal and cubic phase are in equilibrium. The amount of Y$_2$O$_3$ in each phase can be determined from the solvus line in the phase diagram. After quenching to room temperature, monoclinic phase will be formed and both tetragonal and cubic phases are retained.

Figure 2.2: Defect fluorite structure of yttria-stabilized zirconia (Pearson database 1520514, occupation factor for O lattice site is 0.991)

In addition to the amorphous structure, silica (SiO$_2$) has several different crystalline forms, such as: quartz, tridymite and cristobalite. All these crystalline forms are composed by the same basic unit of tetrahedral SiO$_4$ but in different arrangement. At room temperature rhombohedral $\alpha$-quartz is the most stable phase, and it transforms to $\beta$-quartz (hexagonal) at 574 °C. At 870 °C it converts into tridymite. Cristobalite (cubic) is only stable at 1470 °C, but still can exist metastably at lower temperatures. Cupid and Seifert [8] studied the phase stabilities of the SiO$_2$-Y$_2$O$_3$ system and gave the calculated phase diagram as shown in Figure 2.4. It can be predicted that at around 1200 °C reaction between SiO$_2$ and Y$_2$O$_3$ may happen, thereby forming Y$_2$Si$_2$O$_7$. 

Figure 2.3: Phase diagram of the zirconia rich portion of ZrO$_2$-YO$_{1.5}$ system [3].

In addition to the amorphous structure, silica (SiO$_2$) has several different crystalline forms, such as: quartz, tridymite and cristobalite. All these crystalline forms are composed by the same basic unit of tetrahedral SiO$_4$ but in different arrangement. At room temperature rhombohedral $\alpha$-quartz is the most stable phase, and it transforms to $\beta$-quartz (hexagonal) at 574 °C. At 870 °C it converts into tridymite. Cristobalite (cubic) is only stable at 1470 °C, but still can exist metastably at lower temperatures. Cupid and Seifert [8] studied the phase stabilities of the SiO$_2$-Y$_2$O$_3$ system and gave the calculated phase diagram as shown in Figure 2.4. It can be predicted that at around 1200 °C reaction between SiO$_2$ and Y$_2$O$_3$ may happen, thereby forming Y$_2$Si$_2$O$_7$. 

4
2.2 Oxidation behaviour of MoSi$_2$ powder

Numerous studies on the oxidation of MoSi$_2$ material in air has been reported before. The oxidation process of MoSi$_2$ is a relatively complex process. Starting from 500 °C MoSi$_2$ can be oxidized and both MoO$_3$ and SiO$_2$ are formed below 800 °C, expressed as

$$\text{MoSi}_2(s) + 3.5\text{O}_2(g) = \text{MoO}_3(s) + 2\text{SiO}_2(s) \quad (<800 \degree C)$$

Above 800 °C oxidation of MoSi$_2$ consists of two steps. MoSi$_2$ is first oxidized to Mo$_5$Si$_3$ whose reaction formula can be expressed as

$$5\text{MoSi}_2(s) + 7\text{O}_2(g) = \text{Mo}_5\text{Si}_3(s) + 7\text{SiO}_2(s) \quad (>800 \degree C)$$

Formation of Mo$_5$Si$_3$ is thermodynamically more favourable than the formation of MoO$_3$ directly from MoSi$_2$ when the temperature is above 800 °C [9]. Mo$_5$Si$_3$ can be further oxidized to form MoO$_3$ following the reaction formula

$$\text{Mo}_5\text{Si}_3(s) + 10.5\text{O}_2(g) = 5\text{MoO}_3(g) + 3\text{SiO}_2(s) \quad (>800 \degree C)$$

The melting point of MoO$_3$ is 801 °C, and the MoO$_3$ formed at high temperature will evaporate and condense on surfaces colder than 800 °C. The solid SiO$_2$ formed is reported to be in amorphous structure when oxidation is at 1100 °C [10]. The oxidation of MoSi$_2$ will be suppressed if a continuous SiO$_2$ passive scale is formed.

2.3 Volume effect of ZrO$_2$-SiO$_2$ reaction and MoSi$_2$ oxidation

Since ZrO$_2$, SiO$_2$ and ZrSiO$_4$ have different crystal structure, the molar volume of the three materials are different. As a result there is a volume change in the system after the reaction between ZrO$_2$ and SiO$_2$. The molar volume of a material can be calculated through equation:

$$V_m = \frac{N_A}{Z} V_{cell} \quad (2.1)$$

Figure 2.4: Calculated SiO$_2$-Y$_2$O$_3$ phase diagram, given in ref[4]
where \( N_A \) is the Avogadro’s constant, \( V_{\text{cell}} \) is the volume of one unit cell, \( M \) is molar mass and \( \rho \) is density. So the molar volume of tetragonal ZrO\(_2\) can be calculated as 20.2 cm\(^3\) (data selected from Pearson database 1520514, \( V_{\text{cell}} = 67.15 \text{ Å}^3, Z = 2 \)). The molar volume of ZrSiO\(_4\) is obtained as 40.2 cm\(^3\) (ICSD 71945, \( V_{\text{cell}} = 267 \text{ Å}^3, Z = 4 \)). The molar volume of amorphous SiO\(_2\) is estimated as 28.9 cm\(^3\) (\( \rho = 2.08 \text{ g/cm}^3, M = 60.08 \text{ g/mol} \)). Thus it is expected that there is a volume shrinkage of ZrO\(_2\)-SiO\(_2\) reaction.

Similarly, the volume effect of the oxidation of MoSi\(_2\) can also be predicted. Molar volume of MoSi\(_2\) is calculated as 24.3 cm\(^3\) (PDF 00-041-0612, \( V_{\text{cell}} = 80.57 \text{ Å}^3, Z = 2 \)). Since the MoO\(_3\) is volatile at temperature higher than 800 °C, the only oxidation product remaining in the system is SiO\(_2\). Compared with the molar volume of amorphous SiO\(_2\), a 138 % volume expansion of the oxidation of MoSi\(_2\) is expected. The volume effect of the chemical reactions that take place in self-healing process is very important. The volume expansion of oxidation of healing particle MoSi\(_2\) is necessary for crack healing, because cracks can only be filled with SiO\(_2\) formed when the volume of oxidation product is larger than the original healing particles. The volume effect of ZrO\(_2\)-SiO\(_2\) reaction is also beneficial for crack healing, since volume shrinkage of the formation of zircon will tend to close the crack gap.

### 2.4 Formation of zircon from ZrO\(_2\) and SiO\(_2\)

Study of zircon formation from reaction between silica and zirconia dated back to several decades ago. The thermodynamics and kinetics of formation and decomposition of zircon have been investigated. Butterman and Foster [11] have proposed an early version of ZrO\(_2\)-SiO\(_2\) quasi-binary phase diagram (see Figure 2.5), which shows that ZrSiO\(_4\) is a stable phase until its decomposition temperature at about 1676 °C. No other compound will be formed by the reaction between ZrO\(_2\) and SiO\(_2\) below the decomposition temperature. Kaiser et al. [12] reviewed recently the thermal stability of zircon using the results published earlier. They studied the effects of particle size and impurity on the temperature of zircon formation and decomposition using high temperature X-ray diffraction. Their experimental results showed, that ZrSiO\(_4\) powder can decompose as low as 1450 °C when the material is not 100 % pure. The formation of zircon from stoichiometric blends of ZrO\(_2\) (stabilized) and SiO\(_2\) (fused silica and cristobalite) powders was also studied and it was shown that ZrSiO\(_4\) forms rapidly above 1300 °C and decompose above 1500 °C into tetragonal ZrO\(_2\) and amorphous SiO\(_2\); see Figure 2.6. Unstabilized zirconia can react to form zircon at 1200 °C after four hours while for yttria-stabilized zirconia zircon can only be observed above 1300 °C. However, this is not consistent with experimental result from Du et al. [13]. According to their XRD analysis, large amount of zircon is formed from silica and yttria-stabilized zirconia at temperatures as low as 1100 °C. However, it seems that the type of silica (fumed silica or cristobalite) has no effect on the zircon formation starting temperature [12].
The kinetics of isothermal zircon formation from ZrO$_2$ and SiO$_2$ between 1200 to 1400 °C has been investigated by many researchers [14-17]. It has been found that there is a large difference in the reaction rate between amorphous and crystalline SiO$_2$. The formation rate of zircon from equimolar mixtures of amorphous silica and amorphous zirconia at 1300 °C is studied by Itoh [14]. The kinetic curve is shown in Figure 2.7. It can be observed that formation of zircon starts rapidly after about 10 minutes and after about 30 minutes about 80% is completed. Next, the yield rate of ZrSiO$_4$ becomes practically zero. Itoh suggested that the reaction between amorphous silica and zirconia predominate the transformation of amorphous silica to cristobalite at 1300 °C. The transformation of amorphous SiO$_2$ into crystalline SiO$_2$ is not detected during the zircon formation period (see Figure 2.7). Then, it is that zircon is formed exclusively by the reaction between amorphous SiO$_2$ and tetragonal ZrO$_2$. Similar S-shaped yield rate curves are reported by Mori et al. [15], and Spearing [16] who synthesized zircon via milled SiO$_2$ and ZrO$_2$. It was proposed that the reaction mechanism is the same within the temperature range of 1200 to 1400 °C. The reaction rate increases with temperature, as shown in Figure 2.8.
Figure 2.7: Fraction of species in mixture of ZrO$_2$ and SiO$_2$ heated at 1300 °C as a function of time: (1) ZrSiO$_4$; (2) t-ZrO$_2$; (3) m-ZrO$_2$; (4) cristobolite. Data were obtained from XRD analysis of quenched samples[14].

Figure 2.8: Zircon yield rate curve as function of time (left) and reduced time (right) at: 1200 °C, 1250°C, 1300°C, 1400°C[15].

Ramani et al. [18] investigated the kinetics of zircon synthesis from crystalline SiO$_2$ (quartz and cristobalite) at temperature range from 1250 to 1400 °C. It is found that quartz does not react with zirconia to form zircon in this temperature range. Cristobalite reacts with ZrO$_2$ only above 1350 °C, but with a very low reaction rate. However, an amorphous transitional phase of SiO$_2$ is formed during the quartz-cristobalite transformation, and zircon is primarily formed from the reaction between ZrO$_2$ and this transitional phase. The fact that cristobalite reacts much slower than amorphous SiO$_2$ is also reported in the study of Kaiser et al. [12].

A mechanism for zircon formation from zirconia and silica have been proposed by Eppler [19, 20] and Veytizou et al. [17]. It is suggested that Si$^{4+}$ are the only mobile cation species and diffuse through the zircon layer to react with ZrO$_2$ at the zircon-unreacted ZrO$_2$ interface. Marker experiment was performed by Eppler to prove this mechanism; see Figure 2.9. Pt wires which are inert to the reaction are used as markers and placed between ZrO$_2$ and SiO$_2$ layer before reaction. The reaction product was found to be confined at the ZrO$_2$ side. It was also observed that the square of the thickness of the product layer varies linearly with time, which indicates that diffusion of species are the rate-limiting step; see Figure 2.10. Veytizou et al. further illustrate the mechanism with hypotheses that the zircon product layer is non-stoichiometric and contains Si$^{4+}$ interstitials and O$^{2-}$ vacancies. SiO$_2$ first dissociate into Si$^{4+}$ interstitials and Si vacancies. Then the Si$^{4+}$ moves through zircon layer via interstitial sites and dissolves into the tetragonal ZrO$_2$ crystallites. The oxygen vacancies move in the opposite direction, from ZrO$_2$ across the zircon product layer into SiO$_2$; see Figure 2.11. The zircon phase starts to precipitate at the interface between ZrO$_2$ and zircon layers when the solubility limit of silicon in ZrO$_2$ crystal is reached.
In summary, a detailed study on thermodynamics and kinetics of zircon formation from yttria-stabilized zirconia and silica is lacking. A ternary phase diagram of ZrO$_2$-SiO$_2$-Y$_2$O$_3$ system is not available yet. A discrepancy exists about the temperature at which zircon starts to form from zirconia doped with yttria. Whether or not the YSZ-SiO$_2$ reaction can take place below 1200 °C is uncertain. Probably the starting temperature for zircon formation depends on the condition of raw materials, and no research has been done on zircon formation from YSZ-MoSi$_2$ mixture. A full quantitative description of the reaction kinetics of zirconia and silica to form zircon, including the activation energy, is not available yet. Although mechanism of reaction between ZrO$_2$ and SiO$_2$ has already been proposed, the experimental proof of such mechanism is not completed yet. Experiments such as determining the over-stoichiometry and element concentration profile across both the zircon and ZrO$_2$ layer are not reported yet. Moreover, explanation is also not given yet for the large difference in the reaction rate between crystalline and amorphous SiO$_2$ with ZrO$_2$.

2.5 Kinetic study of solid-state reaction through thermal analysis

The rate of a solid-state reaction at a constant temperature can be expressed as:
\[
\frac{d\alpha}{dt} = kf(\alpha) \tag{2.3}
\]

or its integral form:

\[
g(\alpha) = kt \tag{2.4}
\]

where \(f(\alpha)\) and \(g(\alpha)\) are known as the conversion functions or rate expressions and \(\alpha\) is the conversion fraction, defined by:

\[
\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \tag{2.5}
\]

Here, \(m_0\) is initial weight, \(m_t\) is weight at time \(t\), and \(m_\infty\) is final weight. Since a thermally activated process is considered, the Arrhenius relation is usually adopted for the rate coefficient \(k\), hence:

\[
k = A \exp(-E/RT) \tag{2.6}
\]

in which \(A\) is the pre-exponential or frequency factor and \(E\) is the activation energy.

The conversion functions, \(f(\alpha)\) and \(g(\alpha)\), are derived based on a model adopted to describe the reaction mechanism. Generally, the reaction models are divided into nucleation, geometrical contraction, diffusion and reaction-order. Each model has its own unique form of the conversion function; see Table 2.2. By fitting the experimental data, in terms of conversion fraction versus reaction time, to the conversion functions, may hint to the mechanism of a specific solid-state reaction. However, to obtain a full kinetic description of a reaction, also the rate coefficient (i.e. the activation energy together with the frequency factor) must be determined.

<table>
<thead>
<tr>
<th>model</th>
<th>(g(\alpha) = kt)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nucleation models</strong></td>
<td><strong>(\alpha^{1/n})</strong></td>
</tr>
<tr>
<td>Power law</td>
<td>([-\ln(1-\alpha)]^{1/n})</td>
</tr>
<tr>
<td>Avrami-Erofeev (An)</td>
<td>(\ln[\alpha / (1-\alpha)] + c^a)</td>
</tr>
<tr>
<td>Prout-Tompkins (B1)</td>
<td></td>
</tr>
<tr>
<td><strong>Geometrical contraction models</strong></td>
<td></td>
</tr>
<tr>
<td>Contracting area (R2)</td>
<td>(1-(1-\alpha)^{1/2})</td>
</tr>
<tr>
<td>Contracting volume (R3)</td>
<td>(1-(1-\alpha)^{1/3})</td>
</tr>
<tr>
<td><strong>Diffusion models</strong></td>
<td></td>
</tr>
<tr>
<td>1-D diffusion</td>
<td>(\alpha^2)</td>
</tr>
<tr>
<td>2-D diffusion</td>
<td>([(1-\alpha)\ln(1-\alpha)] + \alpha)</td>
</tr>
<tr>
<td>3-D diffusion</td>
<td>([1-(1-\alpha)^{1/3}]^2)</td>
</tr>
<tr>
<td>Ginstling-Brounshtein</td>
<td>(1-(2/3)\alpha - (1-\alpha)^{2/3})</td>
</tr>
</tbody>
</table>
The conventional method to determine the rate constant through isothermal analysis (from series of conversion data as a function of time at different but constant temperatures) may be time consuming. Alternatively, the parameters for the rate constant (i.e. the activation energy together with the frequency factor) may be obtained from non-isothermal calorimetric experiments, such as: differential scanning calorimetry (DSC) or differential thermal analysis (DTA). Take DTA for example, the difference in temperature between the sample and reference material is recorded while both are under the same heating programme. When a thermal event such as chemical reaction occurs, the sample temperature will deviate much from reference material temperature and thus a peak will show in the curve, as shown schematically in Figure 2.12.

Kissinger [22] proposed a relation between the peak temperature in the DTA/DSC curve, heating rate and the activation energy of the thermal event that corresponds to the peak. By combining Equation (2.3), (2.6) and the conversion function for reaction-order models, the following equation can be obtained:

\[
\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) \times (1-\alpha)^n
\]  

(2.7)

When the maximum of reaction rate is reached, it holds that:

\[
\frac{d}{dt} \left(\frac{d\alpha}{dt}\right) = 0
\]

(2.8)

Since both the temperature \( T \) and the conversion fraction \( \alpha \) is a function of time, on differentiating (2.7) the result is:

\[
\frac{d}{dt} \left(\frac{d\alpha}{dt}\right) = A \exp\left(-\frac{E_a}{RT}\right)(1-\alpha)^n \left[ \frac{E_a}{RT^2} \frac{dT}{dt} - n(1-\alpha)^{-1} \left(\frac{d\alpha}{dt}\right) \right]
\]

(2.9)
Thus, from (2.8) and (2.9) it is obtained that:

\[
\frac{E}{RT^2} \frac{dT}{dt} = nA(1-\alpha)^{n-1} \exp\left(-\frac{E_a}{RT}\right) \tag{2.10}
\]

By assuming that the reaction rate reaches maximum at the temperature where the DSC/DTA curves show a peak \(T_p\), the following relation can be written:

\[
\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E_a}{RT_p} + \ln\left(\frac{nAR}{E_a}\right) + (n - 1)\ln(1 - \alpha) \tag{2.11}
\]

, or be expressed in differential form as:

\[
\frac{d\ln \left(\frac{\beta}{T_p^2}\right)}{d\left(\frac{1}{T_p}\right)} = -\frac{E_a}{R} \tag{2.12}
\]

, where \(\beta\) is the heating rate \((dT/dt)\), \(R\) is gas constant, and \(E_a\) is the activation energy. Thus, by plotting \(\ln(\beta T_p^2)\) against \(1/T_p\) for a series of experiment data, then the slope of a straight line through the experimental data corresponds to \(E_a/R\). Similarly, based on the assumption that the degree of reaction at the peak temperature of DSC/DTA curve is a constant value and independent of heating rate, Ozawa [23] reached another equation, namely:

\[
\log(\beta) = \text{const} - \frac{0.4567E_a}{RT_p} \tag{2.13}
\]

Then from a plot of \(\log(\beta)\) versus \(1/T_p\), the activation energy \(E_a\) can also be obtained. Both the Kissinger and Ozawa treatment are valid under the condition that the reaction rate at a constant degree of reaction \(\alpha\) is a function of temperature only [24], and that one reaction mechanism occurs in the temperature range considered.

### 2.6 One-dimensional diffusion controlled reaction kinetics

In many cases the overall rate of a solid-state chemical reaction process is determined by the transportation of a reactant. In these diffusion controlled reactions the product is generated at contact region between two reactants, and this product remains there if it is immobile [25]. As a result, the two reacting solids are in separate crystal lattices with the product layer as a barrier in between the reactants. If the reaction is to continue, one reactant species must diffuse across the barrier of product whose thickness increases as reaction proceeds. The one-dimensional model of such reaction mechanism is depicted in Figure 2.13, in which A and B represents two different reactants, AB is reaction product, \(x\) is the distance from AB/B interface into AB, \(l\) is the thickness of product layer.
If the rate of chemical reaction between A and B is sufficiently fast, the rate of total reaction process will mainly depend on the diffusion of species across the product layer. The formation of AB decreases with the increase of the thickness of AB layer. According to Fick’s first law, the rate of increase of AB layer thickness can be expressed as:

\[ \frac{dl}{dt} = -D \frac{M_{AB}}{M_B \rho} \left. \frac{dC}{dx} \right|_{x=l} \]  

(2.14)

where \( M_{AB} \) and \( M_B \) are the molar weights of AB and B respectively, \( D \) is the diffusion coefficient, \( \rho \) is the density of product AB and \( C \) is the concentration of B in AB. Assuming that the concentration profile of B in AB is linear, then:

\[ \left. \frac{dC}{dx} \right|_{x=l} = -\frac{C_2 - C_1}{l} \]  

(2.15)

In which \( C_2 \) and \( C_1 \) are the concentration of reactant B at AB/B and AB/A interface respectively. Thus combining these two formula it is obtained:

\[ \frac{dl}{dt} = D \frac{M_{AB}}{M_B \rho} \frac{(C_2 - C_1)}{l} \]  

(2.16)

Integration of Equation (2.16) gives:

\[ l^2 = 2D \frac{M_{AB}}{M_B \rho} (C_2 - C_1) t \]  

(2.17)

\[ l^2 = kt \]  

(2.18)

Equation (2.18) is known as the parabolic growth rate law, which describes the reaction kinetics in case of an infinite flat plane without considering a shape factor. Therefore, such parabolic growth rate law can often be used to explain the growth of oxides scale formed at metal surfaces. Since the thickness of the product layer is linearly proportional to the conversion fraction \( \alpha \), Equation (2.18) can also be expressed as:

\[ \alpha^2 = k't \]  

(2.19)
which is exactly the same as the conversion function for 1-D diffusion model given in Table 2.2.

It is worth noting that the parabolic growth rate law is only valid when [26]:
1. Transportation of ions across the layer of reaction product is the rate-controlling process.
2. The product layer is a compact and adherent, i.e. short-circuit diffusion such as diffusion along grain boundaries can be neglected.
3. Thermodynamic equilibrium is established at both product-reactant interfaces, i.e. the concentration of certain species at interface remains constant.

2.7 Reaction kinetics of the contracting sphere model
When a solid particle has spherical shape and the reaction occurs homogeneously at the particle surface, the reaction front will progress towards the centre of the particle, then following equation holds:

\[ r = r_0 - k_G t \]  \hspace{1cm} (2.20)

where \( r \) is the radius at time \( t \), \( r_0 \) is the original particle radius, and \( k_G \) is the reaction rate constant that describes the progressing speed of the reaction interface. The unreacted volume of the particle is

\[ \text{volume} = \frac{4}{3} \pi r^3 \]  \hspace{1cm} (2.21)

Therefore, the conversion fraction \( \alpha \) can be expressed as

\[ \alpha = \frac{4}{3} \pi r_0^3 - \frac{4}{3} \pi r^3 = 1 - \frac{r^3}{r_0^3} \]  \hspace{1cm} (2.22)

Substitution into Equation (2.20), it follows that:

\[ 1 - (1 - \alpha)^{1/3} = \frac{k_G}{r_0} t \]  \hspace{1cm} (2.23)

which is the conversion function R3 of the geometrical contraction model.

Equation (2.23) can be applied under the condition that the diffusion of reacting species across the product layer is much faster than the rate of the chemical reaction that occur at the spherical particle interface.
3 Experimental aspects

3.1 Sample preparation

The raw powders of SiO₂, MoSi₂ and yttria stabilized ZrO₂ used in this study, are listed in Table 3.1.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Brand</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yttria-stabilized ZrO₂ (YSZ)</td>
<td>Sulzer NS204, 8 wt% Y₂O₃</td>
</tr>
<tr>
<td>MoSi₂ with 2 wt% Boron</td>
<td>ChemPur</td>
</tr>
<tr>
<td>MoSi₂</td>
<td>ChemPur</td>
</tr>
<tr>
<td>Quartz SiO₂</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Amorphous SiO₂</td>
<td>ABC Nanotech</td>
</tr>
</tbody>
</table>

Four different powder mixtures with YSZ were prepared, namely: with the two types of MoSi₂ powder (with and without the addition of Boron) and with the two types of SiO₂ powder (quartz and amorphous SiO₂). In each mixture, the molar ratio of element Zr over Si equals to one. Before mixing the powders, both two types of MoSi₂ powder were dried in autoclave (TAMSON) at 80 °C for 1 hour to prevent agglomeration of particles. A homogeneous powder mixture was obtained by using a polyethylene bottle (250 ml) filled with 15 g powder putting in a tubular mixer (Turbula T2c) for 3 hours. Next, the powder mixture was cold pressed into circular tablets using a 12 mm-diameter die and a uniaxial pressing machine (Carver M3853). In order to dense tablets, the load was slowly applied until it reached 9500 pounds (4.3 tons) and then kept for 5 minutes at this pressure. The mass of each tablet prepared from YSZ-MoSi₂-B and YSZ-MoSi₂ mixture was 0.8 and 0.9 g, respectively, corresponding with a height of about 1.9 and 2.2 mm. The mass of a YSZ-SiO₂ tablet is about 0.7 g corresponding with a height of about 2.7 mm.

To enhance the integrity of the tables, 4 wt% polyvinyl alchol (PVA) solution was applied as a binder. The PVA solution was added only to the YSZ-SiO₂ powder mixture.

3.2 Isothermal annealing experiments

Annealing of the green-body tablets at 1100 and 1200 °C, was executed in a horizontal tube furnace (Lenton LTF 14/25/180) with an 25 mm inner diameter alumina tube open to air. The tablets were placed in a boat-shape alumina crucible (DEGUSSIT AL23, FRIATEC). After the target temperature inside the furnace reached stably, the crucible with tablet was slide directly into the center furnace hot-zone with an Inconel rod. After annealing the crucible with the sample was removed quickly from the furnace hot-zone and cooled down instantly in ambient air. No breakage of tablets due to instantly heating and cooling was observed.

3.3 Methods of Investigation

3.3.1 Particle size analysis

The particle size distribution of raw powders is measured by a laser diffraction method. When a laser beam with fixed wavelength passes through a dispersed powder sample, the beam light
will be scattered by the particles at a wide range of angles that directly relate to particle size. Large particles scatter light at small angles relative to the incident beam whereas large angle scattering occurs at small particle size. Moreover, the intensity of scattered light increases with particle size. Thus, by placing a series of detectors at fixed position over a wide range of angles, the angular variation in the intensity of scattered light can then be obtained. Using the Mie theory [27], the size distribution of powder sample can be determined. The size of a particle is expressed as the diameter of a volume equivalent sphere. The equipment used in this study is the Mastersizer X, Malvern Instruments, UK.

3.3.2 X-ray diffractometry

X-ray diffraction (XRD) is a common characterization method used to identify the phases of materials [28]. A diffractogram was recorded in the 20–range from 15° to 90° using Cu Kα radiation of the green sample and after each annealing period. In this study XRD analysis was also a tool to determine quantitatively the reaction kinetics. The rate of the reaction between ZrO₂ and SiO₂ can be derived from the rate of ZrO₂ consumption. To this end, the decrease of the intensity of ZrO₂ peaks was measured after different annealing times. Similarly, the rate of ZrSiO₄ formation was determined from the measured increase of the ZrSiO₄ peak intensity. Here, all the ZrO₂ peaks within the 20–range from 48° to 52°, which includes both monoclinic and tetragonal ZrO₂ phase, were selected to quantify the amount of ZrO₂. The ZrSiO₄-(200) reflection in the 20-range from 26° to 31° is selected to determine the ZrSiO₄ formation.

The XRD measurements were performed with a Bruker D5005 diffractometer equipped with Huber incident-beam monochromator and Braun PSD detector (Cu Kα1). The details of XRD measurements of three diffractograms recorded are listed in Table 3.2. The parameters for recording all diffractograms were kept the same.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>diffractogram 1</th>
<th>diffractogram 2</th>
<th>diffractogram 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 range</td>
<td>15°-90°</td>
<td>48°-52°</td>
<td>26°-31°</td>
</tr>
<tr>
<td>Divergence Slit</td>
<td>1G16</td>
<td>1G16</td>
<td>1G16</td>
</tr>
<tr>
<td>Slit width</td>
<td>Not applied</td>
<td>Not applied</td>
<td>Not applied</td>
</tr>
<tr>
<td>Scatter screen height</td>
<td>5mm</td>
<td>5mm</td>
<td>5mm</td>
</tr>
<tr>
<td>Sample holder</td>
<td>SP52</td>
<td>SP52</td>
<td>SP52</td>
</tr>
<tr>
<td>Step size</td>
<td>0.0387°</td>
<td>0.0387°</td>
<td>0.0387°</td>
</tr>
<tr>
<td>Time/step</td>
<td>0.5s</td>
<td>5s</td>
<td>5s</td>
</tr>
<tr>
<td>Rotation speed of sample</td>
<td>30 rpm</td>
<td>30 rpm</td>
<td>30 rpm</td>
</tr>
</tbody>
</table>

As an illustration of the quantitative analysis, the diffractograms including the selected ZrO₂ and ZrSiO₄ XRD lines are shown in Figures 3.1 and 3.2, respectively. The change in peak area after annealing is evident. The net integrated intensity in the 20–range from 48° to 52° is taken as a measure for the ZrO₂ amount in the sample. It is assumed that throughout the whole annealing process no texture was developed in the sample. Thus, by calculating the ratio between the net integrated intensity before and after annealing, the fraction of unreacted ZrO₂ is obtained. The net integrated area of the ZrSiO₄ (200) peak is taken as the amount of ZrSiO₄ formed. Note that the net integrated intensities were determined using the “integrate” function embedded in “Origin Pro 8” software.
After annealing for 3 hours, several diffraction lines of unidentified phases were observed in 2θ-range from 48° to 52° and overlap with the ZrO₂ peaks. These lines give rise to the peak area of ZrO₂, but were eliminated by curve fitting of the peaks in the diffractogram (using “TopasP3” software).

### 3.3.3 Scanning electron microscopy (SEM) and X-ray microanalysis (XMA)

The morphology and chemical composition of samples was studied with scanning electron microscopy (SEM) [29], using a field-emission gun scanning electron beam microscope (JEOL JSM 6500F), equipped with an energy dispersive spectrometer (EDS, Thermoscientific Ultra dry detector operated with Noran System 7 acquisition software) for X-ray microanalysis (XMA) [29]. The basic principle of SEM is schematically shown in Figure 3.3. A focused primary electron beam interacts with sample and generates different signals that may be used for investigation, such as: backscattered electrons, secondary electrons and characteristic X-rays. The backscattered electrons are primary electrons that deflect after elastic collision with atoms in the sample. The number of collision sites increases with the
number of electrons in an atom. Thus, the yield of backscattered electrons increases with the atomic number (Z). The inelastic collision between primary electrons and sample can ionize a number of sample atoms, and thus secondary electrons are generated. The energy of secondary electrons (0-50 eV) is usually much lower than that of the backscattered electrons. So, only secondary electrons from the region close to sample surface can escape and be detected. The secondary electrons give more information about the topography of sample surface, whereas the backscattered electrons reflect the element distribution in the sample. The characteristic X-rays are generated from the relaxation of ionized atoms and are able to offer quantitative information about chemical composition of materials.

![Figure 3.3: Schematic picture of interaction between primary electron beam and sample](image)

To obtain a more accurate result for the local composition profile, electron probe microanalysis (EPMA) [30] was applied. A qualitative line profile was measured with the JEOL JXA-8900R microprobe employing wave dispersive spectroscopy (WDS) of the elemental X-ray lines of Zr-L\(\alpha\) and Si-K\(\alpha\). For those spectral features the analysing crystals PETJ and TAP were selected, respectively. The electron beam energy used was 5 keV with a beam current of 20 nA. Measurement time for each spot is 5 seconds.

The annealed tablets used for SEM cross-section observation were first cut in half with precision diamond saw (IsoMet low speed saw, Buehler). The half-circular tablets were clamped between two pieces of iron plates with two screws to adjust tightness. Then, the cross-section surface was ground with emery paper starting with 220 grit and finally with 2500 grit. Thereafter, the surface of the cross-sections was polished with 3 \(\mu\)m diamond grains on a soft cloth. Then, the sample was ultrasonic cleaned subsequently in acetone and iso-propanol and dried in an autoclave at 80 °C for 2 hours to evaporate remnant liquid in the pores of the sample. Prior to the SEM observations, the sample surface was coated (JEOL JEC-530 auto carbon coater) with a carbon layer of about 17 nm thickness to enhance the electric conductivity.

### 3.3.4 Thermal analysis

Differential thermal analysis (DTA) was applied to both MoSi\(_2\) and MoSi\(_2\)B powders and both YSZ-MoSi\(_2\) and YSZ-MoSi\(_2\)B powder mixtures to study the thermal behaviour during the annealing process. To this end, a SENTERAM SETSYS Evolution 1750 in DTA-TG configuration (tube diameter of 15 mm) was used, with its schematics shown in Figure 3.4. The mass of each sample is about 20 mg. Reference material is an empty alumina crucible. All the samples were heated from room temperature to 1450 °C with a constant heating rate,
and subsequently cooled down to room temperature with cooling rate of 15 °C/min. A flow of 50 ml/min. ‘synthetic air’ was applied. This gas is composed of dry pure N₂ and O₂ (both better than 5N) with a volume ratio of 4 to 1. Simultaneously, the mass change of the sample during the DTA experiment was recorded, which may offer additional information about the occurring chemical reaction. To determine the activation energy of the oxidation reactions, DTA experiments with different heating rates were executed, namely 2, 5, 10 and 20 °C/min.

![Figure 3.4: Schematic picture of the Setsys Evolution thermal analysis equipment](image)
4 Results and discussion

4.1 Characterization of raw materials
The powders used as reactants to study the formation kinetics of zircon (cf. Table 3.1) were first characterized in terms of phase composition and morphology. XRD measurements, SEM observation and particle size analysis were applied on each type of powders (cf. Section 3.3). The YSZ powder used in the study is the same as used to deposit TBC’s in jet engines. This YSZ powder is not fully stabilized, and is composed by both tetragonal (major phase) and monoclinic ZrO$_2$, as shown in Figure 4.1. SEM images show that most of the YSZ particles have a spherical shape. The particle size analysis shows that the average diameter of YSZ powder ranges from 20 to 80 μm with an average diameter of about 50 μm.

![Figure 4.1: XRD pattern of YSZ powder](image)

![Figure 4.2: Particle size distribution of YSZ powder](image)
Both two types of SiO$_2$ powder, namely crystalline and amorphous SiO$_2$, were analysed by XRD to be sure of their crystallinity; see Figure 4.4. The pattern of the amorphous SiO$_2$ powder reveals only a broad peak at 21 degrees 2θ. The pattern of crystalline SiO$_2$ shows a series of distinct peaks corresponding with pure quartz.

The two types of MoSi$_2$ powder (cf. Section 3.1) have different particle size. The particle size of the MoSi$_2$B powder is larger than the particle size of the MoSi$_2$ powder, with an average diameter of 18 and 5 μm, respectively; as shown in Figure 4.5 and Figure 4.6. The shape of both two MoSi$_2$ powder is irregular. Since the particle size of both two MoSi$_2$ powders is smaller than that of the YSZ powder, the MoSi$_2$ particles will fill the gap between the YSZ particles when a mixture of those particles are pressed into a tablet.
4.2 ZrSiO$_4$ formation from YSZ-SiO$_2$ mixture

Since ZrSiO$_4$ is exclusively formed from the reaction between SiO$_2$ and ZrO$_2$, the kinetics of ZrSiO$_4$ formation from a mixture of YSZ and the two types of SiO$_2$ powder was studied first. Tablets made from YSZ-quartz and YSZ-amorphous SiO$_2$ mixtures were annealed in air at 1200 °C for 15 hours. The XRD pattern of the YSZ-quartz tablet after annealing did not show any diffraction line of ZrSiO$_4$; see Figure 4.8. This result confirms the findings of Ramani [18], namely: ZrO$_2$ does not react with quartz. No difference in the XRD pattern of YSZ before and after annealing was observed, which means that the YSZ powder is stable and no phase transformation happens after 15 hours annealing at 1200 °C. Since a small peak corresponding with cristobalite was identified (see Figure 4.8), some of the quartz may have transformed into cristobalite after annealing.

Also no ZrSiO$_4$ was formed in YSZ-amorphous SiO$_2$ tablet after annealing for 15 hours in air at 1200 °C; see Figure 4.9. XRD analysis shows the amorphous SiO$_2$ transforms into cristobalite instead of reacting with YSZ during annealing. As already have been observed (see above) cristobalite does not react with ZrO$_2$ below 1300 °C [18]. The SEM image of the cross-section of the annealed tablets confirms that no reaction occurred between YSZ and cristobalite, since the integrity of the spherical YSZ powder is preserved after annealing.
Figure 4.8: XRD pattern of YSZ-quartz tablet, annealed at 1200 °C for 15h

Figure 4.9: XRD pattern of YSZ-amorphous SiO$_2$ tablet, annealed at 1200 °C for 15h

Figure 4.10: SEM image of YSZ-amorphous SiO$_2$ tablet, annealed at 1200 °C for 15h
Results of the previous annealing experiments clearly show that study on the kinetics of zircon formation cannot be accomplished directly using the mixtures of YSZ and SiO$_2$ powders. However, in a self-healing TBC based on MoSi$_2$ sacrificial particles [1] the formation of zircon has been observed [2]. Therefore, the kinetics of zircon formation is studied using YSZ-MoSi$_2$ mixtures, which will be discussed in detail in the next session.

4.3 ZrSiO$_4$ formation from YSZ-MoSi$_2$ mixtures

4.3.1 Isothermal kinetics of ZrSiO$_4$ formation at 1200 °C

The YSZ-MoS$_2$ and YSZ-MoSi$_2$B tablets were first annealed for 15 hours in air at 1200 °C to observe any zircon formation. An evident difference between the XRD pattern of green body and annealed tablets can be seen; see Figure 4.11, 4.12 and 4.13. For both two types of tablets, the peak intensity of the zircon phase is much higher than the other phases, which indicates that zircon is formed and becomes the main phase in the sample after annealing. Other phases such as ZrO$_2$, MoSi$_2$ and Mo$_5$Si$_3$ exist which means that the reactants were not fully consumed. The MoO$_3$ formed after oxidation of MoSi$_2$ is volatile and escapes from the system during the annealing process, consequently no peaks of MoO$_3$ were observed in the XRD pattern. The XRD results also indicate that MoSi$_2$ as a healing agent is capable of healing cracks in YSZ through formation of ZrSiO$_4$.

![Figure 4.11: XRD pattern of YSZ-MoSi$_2$B and YSZ-MoSi$_2$ green body](image1)

![Figure 4.12: XRD pattern of YSZ-MoSi$_2$B tablets annealed at 1200 °C for 15h](image2)
The isothermal transformation of ZrO$_2$ into ZrSiO$_4$ for both two types of samples (with and without Boron) is shown in Figure 4.14 and Figure 4.15. Here the fraction of un-reacted ZrO$_2$ is plotted versus annealing time. The amount of ZrO$_2$ that remains in the sample is quantified using the method illustrated in Section 3.3.2. The net integrated area of ZrSiO$_4$ (200) peak is also recorded as a measure for the amount of ZrSiO$_4$ formed with annealing time. In the YSZ-MoSi$_2$B sample, ZrO$_2$ is consumed rapidly from the start of annealing process. The curve is steep in the early stage and flattens after about 4 hours of annealing. Therefore, it can be concluded that the reaction between ZrO$_2$ and the SiO$_2$ formed from oxidation of MoSi$_2$ is almost accomplished during the first 4 hours. The newly formed zircon does not decompose again during annealing because the dissociation reaction of zircon only occur at above 1450 °C [12]. A similar kinetic curve is also determined for the sample without Boron. The reaction rate becomes almost zero after annealing for 4 hours. However, there is an incubation time of about 0.5 hour before the rapid consumption of ZrO$_2$. No zircon peak is identified at 0.5 hour of annealing and the amount of ZrO$_2$ is practically unchanged. It is worth noting that the solid line for ZrO$_2$ consumption in all the figures is only to guide the eye.

The error bar due to the counting statistics of the X-ray pulse (the 2σ of total counts $N$ equals to $2\sqrt{N}$ ) is also plotted in Figures 4.14 and 4.15. The size of the error bar is smaller than the symbol of each data point and thus can be neglected. The actual error is larger than the counting error of X-ray intensity.
The microstructure of the annealed tablets was analysed with SEM using cross-section of the tablets (cf. Section 3.3.3). The BSE images as shown in Figure 4.16 and Figure 4.17 provide a view on the typical microstructure of YSZ-MoSi₂ tablet annealed at 1200 °C in air for 15 hours. Four main phases with different element composition can be distinguished in the cross-section. Combined with X-ray microanalysis (cf. Section 3.3.3), all the phases were identified. As Si and O are the lightest element in the system, the darkest region in images is SiO₂. Since SiO₂ is exclusively formed by oxidation of MoSi₂, the bright “pebble-shaped” particles surrounded by SiO₂ are confirmed to be the remnant MoSi₂. At the edge of the MoSi₂ particles the Mo₅Si₃ phase is observed, which indicates that Mo₅Si₃ is formed first before further oxidation into MoO₃. The remnant ZrO₂ phase is represented by the whitish area in the BSE images. The greyish region that separates SiO₂ and ZrO₂ is the reaction product of these two reactants, namely ZrSiO₄.
Figure 4.16: BSE image of YSZ-MoSi$_2$ tablet cross-section annealed at 1200 °C in air for 15h

Table 4.1: Results of XMA on the phases as shown in Figure 4.16

<table>
<thead>
<tr>
<th>Location</th>
<th>Atom %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O</td>
</tr>
<tr>
<td>1</td>
<td>64</td>
</tr>
<tr>
<td>2</td>
<td>67</td>
</tr>
<tr>
<td>3</td>
<td>70</td>
</tr>
<tr>
<td>4</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>22</td>
</tr>
</tbody>
</table>

Figure 4.17: Microstructure of YSZ-MoSi$_2$ tablet, annealed at 1200 °C for 15h. (a) BSE image; (b) Zr distribution map; (c) Si distribution map; (d) Mo distribution map

The microstructure of the tablet added with Boron after annealing at 1200 °C in air is similar to the non-Boron case, as shown in Figure 4.18. The phases identified in the sample are the same as the YSZ-MoSi$_2$ sample. However, difference in the microstructure of MoSi$_2$ and SiO$_2$
can be clearly noticed between the two types of tablets. The size of remnant MoSi$_2$ particles in YSZ-MoSi$_2$B sample is generally larger, and the amount of SiO$_2$ that lies in between ZrSiO$_4$ phase and MoSi$_2$ particles is much smaller.

![Figure 4.18: Microstructure of YSZ-MoSi$_2$(B) tablet, annealed at 1200 °C in air for 8h. (1) ZrO$_2$; (2) ZrSiO$_4$; (3) MoSi$_2$; (4) SiO$_2$; (5) Mo$_5$Si$_3$](image)

After identifying all the phases in the SEM images, change in the microstructure and the amount of zircon formed with annealing time can then be studied. Figure 4.19 gives a qualitative comparison of the microstructure between the samples after 8 and 15 hours annealing. No significant change in the microstructure can be seen, suggesting that no further reaction between ZrO$_2$ and SiO$_2$ occurs between 8 to 15 hours. To confirm this observation, the amount of zircon needs to be determined quantitatively with the help of image analysis using the software “Image J”. The volume ratio of ZrSiO$_4$ with respect to ZrO$_2$ in the bulk sample is the same as the ratio between the area of ZrSiO$_4$ phase and ZrO$_2$ phase in the SEM image. By counting the number of pixels corresponding to each phase, the amount of ZrO$_2$ reacted is known.
It is easy to distinguish ZrO$_2$ and ZrSiO$_4$ from the BSE images because the contrast in the grey factor between the two phases is relatively large. However, the difference of grey factor between ZrO$_2$ and MoSi$_2$ is small because of the similar average molecular weight of these two phases. Thus, to avoid including MoSi$_2$ phase when counting the pixels of ZrO$_2$, all the regions of MoSi$_2$ particles in the image were cut off and turned into black. Figure 4.20a shows an example of a BSE image modified in such way. Then the distribution of the number of pixels over the grey value in the modified image is given represented; see Figure 4.21.
The image in Figure 4.20a can be further modified in a way that the pixels with grey level above a certain value are all turned into green colour while those below a certain value are changed into blue, as shown in Figure 4.20b. With this method the upper and lower grey value threshold for ZrSiO₄ phase in the modified BSE image can be determined manually. In this case, the grey value of zircon phase ranges roughly from 86 till 206, and the grey value for remnant ZrO₂ can be determined in the same way and ranges from 234 to 255. Then, from the histogram shown in Figure 4.21, the total number of pixels that represents ZrSiO₄ and ZrO₂ are calculated, and are 859257 and 136952, respectively. Hence, the ratio of the number of pixels of ZrO₂ over ZrSiO₄ equals 0.16, which is regarded as the same value of the volume ratio between the two phases. The volume ratio can be transformed into molar ratio by the formula:

\[
\frac{m_{ZrO_2}}{m_{ZrSiO_4}} = \frac{V_{ZrO_2}}{V_{ZrSiO_4}} \times \frac{V_{m(ZrSiO_4)}}{V_{m(ZrO_2)}}
\]

, where \( m \) is the number of moles, \( V \) is the real volume and \( V_m \) is the molar volume. Thus, the fraction of the ZrO₂ that is not transformed to ZrSiO₄ can be calculated as 23%. It is worth noting that the error in the determination of unreacted ZrO₂ fraction through “Image J” analysis comes from the selection of the boundary threshold of the grey level of each phase. Besides, the magnification of the SEM images and location in the sample where the image is taken may also result in certain error. Thus, by tuning the threshold grey level of ZrO₂ and ZrSiO₄ phases and analysing more than 1 image, the error of the unreacted ZrO₂ fraction is estimated to be +3% and -4%. Same method of analysis through “Image J” software is applied on the other 3 samples, with the results listed in Table 4.2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fraction of unreacted ZrO₂</th>
<th>Range of error</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ+MoSi₂B, 1200 °C, 8h</td>
<td>24%</td>
<td>± 4%</td>
</tr>
<tr>
<td>YSZ+MoSi₂, 1200 °C, 8h</td>
<td>30%</td>
<td>± 2%</td>
</tr>
<tr>
<td>YSZ+MoSi₂, 1200 °C, 15h</td>
<td>27%</td>
<td>± 3%</td>
</tr>
</tbody>
</table>

The similar value for the fraction of remnant ZrO₂ determined by “Image J” analysis between 8 and 15 hours of annealing indicates that for both two samples the reaction between ZrO₂ and SiO₂ has been completed before 8 hours.

The microstructure evolution of the YSZ-MoSi₂B and YSZ-MoS₂ tablets during the early phase of annealing at 1200 °C in air for less than 2 hours was studied with SEM. Comparing Figure 4.22 and Figure 4.23, a significant change in microstructure can be witnessed in the YSZ-MoS₂B samples. Most of the ZrO₂ particles are intact and remains their spherical shape after 0.5 hours of annealing. The ZrSiO₄ phase is observed only at very few ZrO₂ particles near the surface of the tablet. While after annealing for 2 hours, the zircon phase can be detected throughout the whole sample and no unreacted ZrO₂ particles were observed. This is consistent with the rapid consumption of ZrO₂ as follows from the kinetic curve determined by XRD during the first 2 hours of annealing; see Figure 4.14. SiO₂ is formed due to the oxidation of MoSi₂ and can fully wet the surface of ZrO₂ particles after 0.5 hours of annealing. Thus, ZrO₂ is in good contact with SiO₂ from the beginning of annealing process. This indicates that rate of zircon formation only depends on the rate of reaction between ZrO₂ and SiO₂ instead of MoSi₂B oxidation.
A significant change of the microstructure of YSZ-MoS$_2$ tablet between 1 and 2 hours of annealing is observed in the SEM images; see Figures 4.24 and 4.25. The shape of the ZrO$_2$ particles in the sample remains intact after annealing for 1 hour. No evident oxidation of MoSi$_2$ occurs yet since the original morphology of the MoSi$_2$ particles can still be recognized and little amount of SiO$_2$ can be observed. The difference in the grey level in the BSE image between the interior and the surface of ZrO$_2$ particles indicates that Si atoms have already diffused into ZrO$_2$. The ZrSiO$_4$ phase can hardly be identified except at the surface of some certain ZrO$_2$ particles; see Figure 4.24. However, after two hours of annealing, large amount of SiO$_2$ is formed and fill the space between particles. ZrSiO$_4$ is identified clearly at the interface between SiO$_2$ and ZrO$_2$; see Figure 4.25. The rapid loss of ZrO$_2$ during the annealing from 1 to 2 hours determined by XRD is substantiated by the SEM analysis.
4.3.2 Isothermal kinetics of ZrSiO$_4$ formation at 1100 °C

The XRD results proved that ZrSiO$_4$ can be formed by annealing of both two types of YSZ-MoSi$_2$ mixtures at 1100 °C in air; see Figure 4.26 and 4.27. The kinetics of the ZrSiO$_4$ formation at 1100 °C in air is determined; see Figures 4.28 and 4.29. For both two types of YSZ-MoSi$_2$ mixtures, the reaction between YSZ and SiO$_2$ stops before 15 hours. The amount of remnant ZrO$_2$ in the system is much higher than that when annealing at 1200 °C, as can be seen also from the relative peak intensity between ZrSiO$_4$ phase and ZrO$_2$ phase in the XRD patterns; see Figures 4.26, 4.27, Figure 4.12 and Figure 4.13. When Boron is added, ZrO$_2$ reacts with SiO$_2$ rapidly from the start of annealing, as proved by the significant loss in ZrO$_2$ after annealing for 1 hour. The reaction rate slows down after 1 hour and becomes almost zero after 8 hours. For the mixture without Boron, no rapid consumption of ZrO$_2$ is observed during the early stages of annealing. The reaction proceeds slowly and almost finishes after 10 hours. Judged from the initial kinetic behaviour of the YSZ-MoSi$_2$ mixture annealed at 1200 °C, an incubation period for the ZrO$_2$-SiO$_2$ reaction is also expected at 1100 °C when Boron is absent. At the lower temperature, it is reasonable to assume that the incubation time is longer.
Figure 4.27: XRD pattern of YSZ-MoSi$_2$ tablets annealed at 1100 °C for 15h

Figure 4.28: Kinetic curve of zircon formation from YSZ + MoSi$_2$B mixture, annealed at 1100 °C (red curve: zircon formation; black curve: ZrO$_2$ consumption)

Figure 4.29: Kinetic curve of zircon formation from YSZ + MoSi$_2$ mixture, annealed at 1100 °C (red curve: zircon formation; black curve: ZrO$_2$ consumption)
The microstructure of the YSZ-MoSi$_2$B tablet after annealing at 1100 °C for 15 hours is similar to the one annealed at 1200 °C for 2 hours; see Figure 4.23 and 4.30. The SiO$_2$ formed from the oxidation of MoSi$_2$ can fill the space between particles and wet the surface of ZrO$_2$ particles very well. ZrSiO$_4$ is formed at the peripheral of ZrO$_2$ particles and can be identified clearly in the BSE images. Other phases, such as Mo$_5$Si$_3$ and remnant MoSi$_2$, are also detected, which confirms the XRD results.

4.3.3 Estimation of the rate of zircon formation

The rate of ZrSiO$_4$ formation at the start of ZrO$_2$-SiO$_2$ reaction is quantified. As shown in Figure 4.15, Figure 4.28 and Figure 4.29 (red curve), the kinetics of zircon formation can be represented by the formula [25]:

$$ y = a[1 - \exp(-kt)] $$

(4.1)

where $k$ is the reaction constant, and $a$ is the maximum vertical value of the fitted curve (in this case $a$ represents the integrated zircon peak area). The value of $k$ and $a$ can be directly obtained from the software “Origin” by fitting Equation (4.1) to the experimental data. The reaction rate decreases with annealing time. By differentiating equation (4.1), the initial reaction rate can be expressed as:

$$ \frac{dy}{dt} \bigg|_{t=0} = ak $$

(4.2)

From the data in Table 4.2, the amount of ZrSiO$_4$ in the sample (i.e. YSZ+MoSi$_2$ tablet annealed at 1200 °C) can be related to the integrate area of ZrSiO$_2$ peak in XRD pattern (i.e. the value of $a$). Thus, the reaction rate can be expressed in the unit of mol/hour per tablet. Since the parameters of all the XRD measurement are the same, and by assuming that all the samples have the same density with ZrSiO$_4$ phase homogeneously distributed, the value of the initial reaction rate of the samples annealed at 1100 °C can also be estimated and compared. The results are listed in Table 4.3.

The data that corresponds with ZrSiO$_4$ formation for the YSZ-MoSi$_2$B sample annealed at 1200 °C is not considered due to an instrumental defect. As a result, the rate of ZrSiO$_4$ formation of this sample is determined from the consumption rate of ZrO$_2$. The rate constant $k_C$ in this case represents the rate of the shrinkage of the YSZ particle diameter (cf. Section 2.7), and its value can be acquired from the slope of the line that fit the conversion function of volume contraction model to the experimental data; cf. Figure 4.45 and Section 4.5. The total surface area of all the YSZ particles is needed to determine the initial rate of zircon formation.
It is assumed that all the YSZ particles in the sample have the same average diameter of 50 μm.

Table 4.3: Comparison of the initial reaction rate in different samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Annealing temperature (°C)</th>
<th>(a) (degree×counts)</th>
<th>(k) (h(^{−1}))</th>
<th>(k_G) (μm/h) (^2)</th>
<th>Reaction rate (mol/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ+MoSi(_2)B</td>
<td>1200</td>
<td>-</td>
<td>-</td>
<td>2.75</td>
<td>0.0014</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>4479</td>
<td>0.37</td>
<td>-</td>
<td>0.00081</td>
</tr>
<tr>
<td>YSZ+MoSi(_2)</td>
<td>1200</td>
<td>6121</td>
<td>0.47</td>
<td>-</td>
<td>0.0015</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>2197</td>
<td>0.34</td>
<td>-</td>
<td>0.00037</td>
</tr>
</tbody>
</table>

4.3.4 Discussion on the kinetics of self-healing reaction of MoSi\(_2\) and MoSi\(_2\)B healing particles

The experimental results given in Session 4.3 has proven that the envisioned principle of the self-healing process in thermal barrier coatings can be accomplished by using MoSi\(_2\) and MoSi\(_2\)B as sacrificial healing particles; cf. Chapter 1. In view of this application, the isothermal kinetics of ZrSiO\(_4\) formation from the YSZ-MoSi\(_2\) and YSZ-MoSi\(_2\)B mixtures annealed at 1200 and 1100 °C in air will be discussed.

Difference in the kinetic behaviour of YSZ-MoSi\(_2\) system between 1200 and 1100 °C is first compared. At both temperatures an incubation time exists because of the relatively low oxidation rate of MoSi\(_2\) during the initial period. The amount of SiO\(_2\) formed is too low to make full contact or react with ZrO\(_2\) at early stage, as indicated from the SEM image in Figure 4.24. The reaction between ZrO\(_2\) and SiO\(_2\) below 1676 °C is thermodynamically favourable, and the molar ratio between Zr and Si in the system is one. Thus it is expected that the ZrO\(_2\) will be fully consumed after reaction. However, the amount of remnant ZrO\(_2\) in the system after 15 hours of annealing at 1200 °C reaches about 30 %. This may be explained as follows. Firstly, the reaction product, namely zircon, which separates the ZrO\(_2\) and SiO\(_2\), becomes a barrier for the diffusion of reactant species (e.g. oxygen vacancies, Si ions, electrons) when its thickness is large. Secondly, the YSZ raw powder is composed by both tetragonal and monoclinic phase, and the reaction rate for tetragonal ZrO\(_2\) is likely to be much faster than that of monoclinic ZrO\(_2\) as indicated by the change in the ratio of peak intensity between tetragonal and monoclinic ZrO\(_2\) in the XRD pattern before and after annealing (see Figure 4.11 and Figure 4.13). Thirdly, part of the amorphous SiO\(_2\) transforms into cristoballite during annealing (see Figure 4.13), and crystalline SiO\(_2\) does not react with ZrO\(_2\). When the annealing temperature is 1100 °C, the rate of ZrO\(_2\)-SiO\(_2\) reaction drops significantly. There is a large increase in the amount of remnant ZrO\(_2\) when lowering the annealing temperature. This can be explained by the large transformation of amorphous SiO\(_2\) into cristoballite, which is proved by the high peak intensity of cristoballite phase shown in Figure 4.27.

The addition of Boron in the MoSi\(_2\) powder effectively influences the kinetics of zircon formation. For both annealing temperatures of 1200 and 1100 °C, no incubation time is observed in the kinetics curve in YSZ-MoSi\(_2\)B system. The reaction between ZrO\(_2\) and SiO\(_2\) starts rapidly from the beginning of annealing. The formation of SiO\(_2\) from the oxidation of MoSi\(_2\) is faster when Boron is added, which can be clearly seen from the comparison between the SEM images of the two tablets at early phase of annealing (see Figure 4.22 and Figure 2)

\(^2\) Since no data are available for ZrSiO\(_4\) peak intensities (see text for details), the reaction rate is estimated on the basis of the volume contraction model (see Section 2.7)
It is interesting to find that at 1100 °C the initial rate of ZrSiO$_4$ formation in YSZ-MoSi$_2$B sample is almost twice as that in the YSZ-MoSi$_2$ sample. This indicates the better capability of MoSi$_2$B particles in rapid healing than that of MoSi$_2$ particles at lower temperature. The effect of Boron on the crystallinity of the SiO$_2$ formed is proved. The addition of Boron promotes the formation of amorphous SiO$_2$ and postpones the transition of SiO$_2$ from amorphous state to cristobalite. This can be clearly determined from the peak intensity of cristobalite in the XRD patterns of YSZ-MoSi$_2$ and YSZ-MoSi$_2$B system after 15 hours annealing at both 1100 and 1200 °C; cf. Figure 4.12, Figure 4.13, Figure 4.26 and Figure 4.27. The crystallization of SiO$_2$ does not occur before the completion of its reaction with ZrO$_2$ at 1200 °C when boron is added. This can also explain the result that the fraction of remnant ZrO$_2$ is lower when Boron is added, especially at 1100 °C.

The effect of Boron and annealing temperature can also be revealed considering the initial rate of the chemical reaction between YSZ and amorphous SiO$_2$; see Table 4.3. As expected, the reaction rate constant $k$ increases with temperature. The reaction rate constant $k$ in the YSZ-MoSi$_2$B tablet is close to that of YSZ-MoSi$_2$ tablet at 1100 °C, whereas there is a large difference in the formation rate of zircon between the two samples. This suggests that the rate of chemical reaction between YSZ and amorphous SiO$_2$ itself is not influenced by Boron. However, the addition of Boron increases the amount of amorphous SiO$_2$ (cf. Section 4.3.2) so that the contact area between YSZ and amorphous SiO$_2$ is higher, and this leads to the higher formation rate of zircon.

The images of the microstructure of the YSZ-MoSi$_2$B tablet annealed for 0.5 hours at 1200 °C provide qualitative information on the self-healing capability of MoSi$_2$B healing particles. The amorphous SiO$_2$ formed from the oxidation of MoSi$_2$B has good wettability. As shown in Figure 4.31a, the SiO$_2$ fills the crack inside one ZrO$_2$ particle, and zircon is formed at the interface of SiO$_2$ and ZrO$_2$. At some region all the SiO$_2$ that fills the crack is consumed and ZrSiO$_4$ connects the two neighbouring ZrO$_2$ particles. Similarly, Figure 4.31b shows another example of the connection between two ZrO$_2$ particles by the formation of ZrSiO$_4$. The minimum size of the gap between the two particles is estimated to be 0.8 µm from the SEM image. The interface between ZrO$_2$ and ZrSiO$_4$ shows good bonding between the two phases, and no sign of delamination was observed. Therefore it is anticipated that a good mechanical integrity of TBC after crack healing can be achieved.

![Figure 4.31: BSE images of YSZ-MoSi$_2$B annealed for 0.5 hours at 1200 °C](image)

Since the reactions in YSZ-MoSi$_2$ (with and without Boron) mixtures is rather complex, chemical reactions that is not self-healing related also occur during annealing process and some by-products are formed. As shown in Figure 4.32, a phase with grey level between ZrO$_2$ and ZrSiO$_4$ can be found near the remnant ZrO$_2$. This reaction by-product is identified as a Y-
Mo-O compound from the X-ray microanalysis. However, such Y-Mo-O phase cannot be seen in the XRD patterns. From the LPF database [31] of Y-Mo-O compound, it is found that diffraction peaks of Y$_2$Mo$_2$O$_7$ and Y$_{0.44}$Mo$_{0.56}$O$_{1.78}$ overlap with those of tetragonal ZrO$_2$, and their crystal structure and lattice parameter are similar to ZrO$_2$. Further, Y$_2$Si$_2$O$_7$ is found only in YSZ-MoSi$_2$ sample at 1200 °C annealing; see Figure 4.13. The amount of these by-product phases formed is relatively small, and thus they are not supposed to have a large influence on the ZrSiO$_4$ formation.

![Figure 4.32: BSE image of YSZ-MoSi$_2$B (left) and YSZ-MoSi$_2$ (right) annealed at 1200 °C for 15 hours. (1) ZrO$_2$; (2) ZrSiO$_4$; (3) MoSi$_2$; (4) SiO$_2$; (5) Y-Mo-O compound](image)

### 4.4 Thermal analysis

#### 4.4.1 Thermal behaviour of MoSi$_2$ and MoSi$_2$B powder annealed in synthetic air

The result of thermal analysis on the MoSi$_2$ powder is shown in Figure 4.33. DTA and TG curves are plotted against sample temperature for a constant heating rate of 5 °C/min. The thermal behaviour of MoSi$_2$ oxidized in air can be interpreted as follows. Oxidation of MoSi$_2$ starts at about 400 °C and ends before 600 °C, as proved by the significant exothermic peak together with a dramatic increase in the weight of sample. At around 800 °C the mass of the sample suddenly drops. This can be explained by the evaporation of the volatile MoO$_3$ above 800 °C. The heat effect of such evaporation is relatively small, since only a slight peak is shown in DTA curve at 800 °C. No significant reaction or phase transformation in the sample happened at high temperature region (i.e. above 900 °C), because no evident deviation from the baseline of DTA and TG curve is observed.

![Figure 4.33: DTA and TG result on MoSi$_2$ powder, heating rate 5 °C/min](image)
The result of XRD analysis of the MoSi$_2$ sample after DTA experiment is given in Figure 4.34. The MoSi$_2$ powder is not fully oxidized, and the major phase still is MoSi$_2$. Mo$_5$Si$_3$ is formed as one of the oxidation products. The cristobalite peak is identified, which means that some of the SiO$_2$ formed from MoSi$_2$ oxidation is crystalized. No MoO$_3$ peaks are identified, which indicates that MoO$_3$ totally escapes the system after evaporation.

The DTA/TG result for the MoSi$_2$B powder is given in Figure 4.35. The thermal behaviour of MoSi$_2$B sample in the low temperature region is similar to that of MoSi$_2$. An exothermal peak due to MoSi$_2$ oxidation is observed between 400 to 600 °C. The mass of the sample increases continuously from 400 °C until 800 °C, followed by a sudden drop due to the evaporation of MoO$_3$. However, in the case of MoSi$_2$B powder, there is a very sharp peak near 800 °C. Normally, such peaks correspond to melting in DTA curve, because it occurs over a narrow temperature interval [24]. Thus it can be falsely believed that this sharp peak at 800 °C is related to the melting and evaporation of MoO$_3$. The melting and evaporation is an endothermic process (i.e. peak should point to negative value in the DTA curve). Therefore, the exothermic peak at 800 °C must be the result of another thermal event in the system (e.g. oxidation and evaporation of Boron), and the nature of this thermal event is unknown yet.
The XRD pattern of MoSi$_2$B powder after DTA measurement shows that the MoSi$_2$ is not fully consumed in the oxidation process; see Figure 4.36. All the MoO$_3$ formed during oxidation has escaped the system. The difference with the XRD pattern of MoSi$_2$ sample is that no Mo$_5$Si$_3$ peaks are identified. Thus it is believed that the oxidation rate of Mo$_5$Si$_3$ is fast. Moreover, Boron is not fully oxidized and still exists in the sample after thermal measurement. Most importantly, no cristobalite is found which indicates that the addition of Boron in the MoSi$_2$ powder promotes the amorphous state of SiO$_2$ effectively.

![XRD pattern of MoSi$_2$B powder after DTA measurement](image)

**Figure 4.36**: XRD pattern of MoSi$_2$B powder after DTA measurement

### 4.4.2 Determination of the activation energy of MoSi$_2$ and MoSi$_2$B oxidation

Since the peak position in DTA curve shifts to higher temperature with increasing heating rate, the activation energy of the MoSi$_2$ oxidation process can be determined by the Kissinger method as illustrated in Section 2.5. To this end, $\ln(\beta/T_p^2)$ is plotted against $1/T_p$ as shown in Figure 4.37. By linear fitting the four data points, the slope of the line is estimated to be -9061. Using Equation (1.12), the activation energy for the oxidation of MoSi$_2$B sample is determined as $75^{+18}_{-10}$ kJ/mol. It is worth noting that the error in determination of $T_p$ leads to the error bar of the data points in horizontal axis in the Kissinger plot, while the vertical error is within 0.3% (i.e. the vertical error bar is the same size as the symbol in the plot) and thus can be neglected. With the Ozawa method, the activation energy calculated is $79^{+7}_{-12}$ kJ/mol.

The activation energy of the oxidation process of MoSi$_2$ sample is determined in the same manner; see Figure 4.38. The activation energy determined by Kissinger and Ozawa method is $64^{+22}_{-14}$ and $68^{+11}_{-19}$ kJ/mol, respectively. Unlike the MoSi$_2$B sample, the result of MoSi$_2$ sample shows that the deviation of two data points from the linear fitted line is larger than experimental error.

The activation energy of the oxidation of MoSi$_2$B and MoSi$_2$ powder are close, which means that the rate of the oxidation of MoSi$_2$B is similar to that of MoSi$_2$. However, this is not consistent with the result observed from SEM images of YSZ-MoSi$_2$B and YSZ-MoSi$_2$ tablets during early period of annealing (see Figure 4.22 and Figure 4.24). The particle size of MoSi$_2$ powder is smaller than that of MoSi$_2$B powder, and thus the frequency factor of the oxidation
of MoSi$_2$ powder is expected to be higher than MoSi$_2$B powder. The experiment procedure on both two systems, namely with and without Boron, is the same in all experiments. Therefore it is speculated that the existence of ZrO$_2$ influence the oxidation kinetics of MoSi$_2$ and MoSi$_2$B.

Figure 4.37: Determination of activation energy of MoSi$_2$ oxidation with Kissinger method for MoSi$_2$B sample

Figure 4.38: Determination of activation energy of MoSi$_2$ sample oxidation with Kissinger method

4.4.3 Thermal analysis on YSZ-MoSi$_2$ and YSZ-MoSi$_2$B powder mixture
The same thermal analysis procedure as used for the oxidation of the MoSi$_2$ based powders is applied on the YSZ-MoSi$_2$B powder mixture. The result of this analysis is shown in Figure 4.39. Both of the DTA and TG curves are different from MoSi$_2$B sample. Exothermic peak of MoSi$_2$ oxidation cannot be clearly recognized from the DTA curve. Nevertheless, it is believed that the oxidation process occurs because the mass of the sample increases continuously until 1100 °C. There is no significant mass loss at 800 °C as MoSi$_2$B sample, which indicates that the oxidation product remains in the sample during heating.

The YSZ powder is again proved to be stable during the annealing process, since no thermal event is observed from the DTA curve of YSZ. Comparison is made between the DTA curves
of YSZ-MoSi$_2$B mixture, YSZ and MoSi$_2$B powder; see Figure 4.40. Superimposing the curve of YSZ on the curve of MoSi$_2$B cannot obtain the curve of the mixture below 1000 °C. Therefore, it can be concluded that the existence of the YSZ powder influences the oxidation behaviour of MoSi$_2$B.

The XRD result of YSZ-MoSi$_2$B mixture after DTA measurement shows that ZrSiO$_4$ is formed during the experiment; see Figure 4.41. Since the reaction between ZrO$_2$ and SiO$_2$ is active above 1000 °C and the enthalpy of this reaction is negative [FACT oxide database/FactSage], an exothermic peak for zircon formation is expected in temperature region above 1000 °C. However, no such peak can be identified clearly in the DTA curve. Besides, no MoO$_3$ peak is found in XRD pattern, which suggests that MoO$_3$ may have escaped mainly during the cooling process.

Figure 4.39: DTA and TG result on YSZ-MoSi$_2$B powder mixture, heating rate 5 °C/min

Figure 4.40: comparison between DTA curves of YSZ, MoSi$_2$B powder and YSZ-MoSi$_2$B mixture, heating rate 5 °C/min
The result of the thermal analysis of YSZ-MoSi₂ mixture is shown in Figure 4.42. Similar to the system added with Boron, ZrO₂ also affects the oxidation behaviour of MoSi₂; see Figure 4.43. But the influence is less effective, since an exothermic peak can be identified between 400 to 500 °C. The mass of the sample keeps increasing during heating without any loss at 800 °C. Judged from the relative peak intensity of ZrSiO₄ phase in the XRD result, only a very small amount of ZrSiO₄ is formed, which indicates that the addition of Boron promotes the formation of ZrSiO₄. Still, the peak that corresponds to zircon formation can hardly be located in the DTA curve.
4.5 Discussion on the mechanism of ZrO$_2$-SiO$_2$ reaction

The kinetic data of ZrO$_2$ consumption upon reaction with SiO$_2$ (i.e. Figure 4.14 and Figure 4.15) can be used to determine the conversion function associated with the reaction forming zircon. All the conversion functions listed in Table 2.2 (see Chapter 2) were tried to fit the experiment results. For the YSZ-MoSi$_2$B sample annealed at 1200 °C in air, the change in the conversion fraction $\alpha$ of ZrO$_2$ during first four hours can be represented by the conversion function of the volume contraction model (R3), as shown in Figure 4.45. The good linearity of the first five data points proves that the mechanism of the reaction is the same during first 2 hours of annealing (e.g. activation energy and frequency factor). The deviation of the data points at 3 and 4 hours annealing from the linear fit may be due to the relative large error in the data. The reaction mechanism changes after annealing for 4 hours, since the data points after 4 hours cannot be fitted with the R3 function. The fitting of the data points of YSZ-MoSi$_2$ sample to R3 function starts from annealing time of 0.5 hours (see Figure 4.46),
because before that the oxidation rate of MoSi$_2$ limits the reaction between ZrO$_2$ and SiO$_2$. The relative lower speed of wetting by amorphous SiO$_2$ when Boron is absent may also influence the linearity of the data fitting result of YSZ-MoSi$_2$ sample.

![Figure 4.45: fitting of conversion function R3 to the experiment results of YSZ-MoSi$_2$B annealed at 1200 °C](image)

![Figure 4.46: fitting of conversion function R3 to the experiment results of YSZ-MoSi$_2$ annealed at 1200 °C](image)

The SEM images of the microstructure of the YSZ-MoSi$_2$B and YSZ-MoSi$_2$ tablets after annealing for 2 hours further substantiate the volume contraction model of the YSZ-SiO$_2$ reaction. As shown in Figure 4.47, zircon is formed at the surface of ZrO$_2$ particles and the diameter of remnant ZrO$_2$ particles shrinks after annealing.

![Figure 4.47: SEM image of tablets annealed at 1200 °C for 2 hours, (a) YSZ-MoSi$_2$B; (b) YSZ-MoSi$_2$](image)
It is worth noting that the kinetics of solid-state reaction mainly depends on the rate of two reaction processes, namely the chemical reaction between reactants and the diffusion of the reacting species. The volume contraction model is derived on the basic assumption that the chemical reaction is the rate-determining step and diffusion of reactants is fast enough to be neglected. The decrease in the consumption rate of ZrO$_2$ with time is only due to the decrease in the surface area of ZrO$_2$ particles as the reaction proceeds.

As proposed by Eppler [20] and Veytizou [17], for the reaction between ZrO$_2$ and SiO$_2$, Si$^{4+}$ is the cation diffusing species instead of Zr$^{4+}$. The SEM images of the microstructure after annealing in this study (e.g. Figure 4.16 and Figure 4.17) can qualitatively confirm their theory. The curvature of the interface between SiO$_2$ and ZrSiO$_4$ is similar to the curvature of the original ZrO$_2$ particles. If Zr$^{4+}$ is the diffusing species and diffuses outwards into the SiO$_2$, the ZrSiO$_4$ will be formed inside the original SiO$_2$ area and the depletion of Zr element will generate Zr$^{4+}$ vacancies at the interface between ZrO$_2$ and SiO$_2$. Such Zr$^{4+}$ vacancies will diffuse to the inner area of ZrO$_2$ particles and finally coalesce to form a number of pores. However, such pores are not observed inside the remnant ZrO$_2$ phase.

The reaction model given by Veytizou et al. [17] is adopted to describe the mechanism of zircon formation in the YSZ-MoSi$_2$ (with and without Boron) sample. Oxygen molecules first enter the YSZ-MoSi$_2$ tablet through the porosity and oxidize the MoSi$_2$ particles. The SiO$_2$ formed is amorphous and it can fill the empty space in the sample and lead to a high contact area with ZrO$_2$ due to the volume expansion after oxidation. The SiO$_2$ dissociates into Si$^{4+}$ interstitial ions and Si vacancies. The difference in the concentration of Si$^{4+}$ ions between SiO$_2$ and YSZ is the driving force for the diffusion of Si$^{4+}$ into YSZ. Since the lattice site in YSZ is not fully occupied due to oxygen vacancies, the Si$^{4+}$ ions can partly dissolve in the tetragonal ZrO$_2$. Simultaneously, the concentration difference in the oxygen vacancy between YSZ and SiO$_2$ results in the diffusion of oxygen vacancies into SiO$_2$. ZrSiO$_4$ is formed at the interface between YSZ and SiO$_2$ and separates the two reactants. To continue the reaction, the diffusing species, namely Si$^{4+}$ ions and O$^{2-}$ vacancies, need to transport across the ZrSiO$_4$ layer. Therefore, a gradient in Si and O concentration as well as the overstoichiometry in ZrSiO$_4$ layer are expected. Based on the result of volume contraction model fitting, the diffusion of species across ZrSiO$_4$ layer is relatively fast compared with the rate of chemical reaction between SiO$_2$ and ZrO$_2$.

EPMA was applied to the YSZ-MoSi$_2$ sample annealed for 15 hours at 1200 °C. The region at which a line scan is performed from the ZrO$_2$ area across the ZrSiO$_4$ layer and into SiO$_2$ is displayed in Figure 4.48a. The normalized intensity of the characteristic X-ray signal that corresponds with Zr and Si is plotted versus the distance from the starting point of the scan, as shown in Figure 4.48b. A concentration gradient of Si can be observed at the interface between ZrSiO$_4$ and ZrO$_2$. Such concentration profile is not related to the resolution of experimental techniques. This can be supported by an estimation of the volume of the electron beam-sample interaction. The electron beam radius is over-estimated as 100 nm for an electron beam current (20 nA) used in the EPMA experiment [32]. Using the software “Casino” with the same parameters in the EPMA test (e.g. accelerate voltage 5 kV, beam radius 100 nm), the distribution of the energy of the scattered incident electrons in the sample can be simulated; see Figure 4.49. It is estimated that for both ZrO$_2$ and ZrSiO$_4$, the diameter of the boundary at which the primary electrons lose 95% of energy after scattering in sample is about 0.3 μm. It is worth noting that the real value of the resolution in this EPMA experiment is smaller than 0.3 μm, because only those primary electrons with energy higher than the binding energy of electrons in the sample (i.e. Zr L shell and Si K shell) after
scattering are capable of generating characteristic X-rays. Moreover, the real electron beam radius is lower than 100 nm and the diameter of the interaction volume decreases with electron beam radius. The spacing between two spots along the scanning line as shown in Figure 4.48b is 0.25 μm. Therefore, it can be concluded that Figure 4.48b represents the element concentration profile in the ZrO$_2$ and ZrSiO$_4$ region.

The interface region between ZrO$_2$ and ZrSiO$_4$ is about 1.5 μm. The concentration gradient of Si at ZrO$_2$-ZrSiO$_4$ interface indicates the diffusion of Si from ZrSiO$_4$ into ZrO$_2$ during the reaction process. When the solubility limit for Si in ZrO$_2$ is reached, ZrSiO$_4$ can be formed and the interface moves into ZrO$_2$. A gradient of Si in the ZrSiO$_4$ layer can hardly be observed. However, it is anticipated that a chemical potential gradient of Si$^{4+}$ ions exists and drives the diffusion of Si. A concentration gradient of Zr is also observed at the ZrO$_2$-ZrSiO$_4$ interface. However, it is expected that the flux of Zr is small compared with Si, because the diffusion coefficient of Zr in ZrSiO$_4$ is lower than that of Si [33] due to the high formation energy of Zr vacancies and interstitials [34].

![Figure 4.48: Concentration profile of Si and Zr along the arrow direction, measured by EPMA](image)

![Figure 4.49: Energy distribution of incident electrons in ZrO$_2$ and ZrSiO$_4$ below the sample surface (XZ plane)](image)

During the XRD analysis on the quantification of ZrO$_2$ amount in the sample (cf. Section 3.3.2), it is observed that the XRD peaks of ZrO$_2$ are broadened after annealing, see Figure 4.50. Such peak broadening is not caused by the change in YSZ properties due to annealing. This is supported by a comparison experiment in which the same XRD peaks of YSZ powder are compared before and after 4 hours of annealing; see Figure 4.51. No peak broadening
effect can be observed in YSZ powder after annealing, which indicates that there is no significant change in the structure of YSZ powder after annealing. Therefore, the main reason that causes the peak broadening is the reaction between ZrO$_2$ and SiO$_2$. Generally, small domain size and high concentration of dislocation makes XRD peaks broaden. However, annealing increases the domain size (energy of material tends to be lower by eliminating defects such as grain boundaries), and XRD peaks will become sharper after annealing. Moreover, usually ionic compounds are not expected to contain high density of dislocations [35]. Therefore, it is suggested that the peak broadening results from the ZrO$_2$ lattice distortion caused by the dissolution of Si element. Moreover, the volume effect of zircon formation (cf. Section 2.3) exerts force on the remnant ZrO$_2$, since the unreacted ZrO$_2$ is connected to ZrSiO$_4$ without any delamination found in SEM images. Such force is on a microscopic scale and may also lead to broadening of ZrO$_2$ peaks.

![Figure 4.50: Comparison of XRD peaks of ZrO$_2$ between green body, annealed tablet and YSZ raw powder](image)

![Figure 4.51: Comparison of XRD peaks of YSZ raw powder before and after annealing](image)

The effect of Boron on the kinetics of zircon formation as well as the experiment results from YSZ-SiO$_2$ powder mixture clearly shows that the crystallinity of SiO$_2$ strongly affects the reaction between ZrO$_2$ and SiO$_2$. It is anticipated that the enthalpy for the formation of Frenkel defect in amorphous SiO$_2$ is much lower than that in crystalline SiO$_2$. The concentration of Frenkel defects can be expressed by [36]:

\[ \text{Frenkel defect concentration} = \frac{1}{\text{Density of SiO}_2} \times \frac{1}{\text{Volume of ZrO}_2} \]
\[
\frac{n}{N} = \exp\left(-\frac{\Delta G}{2kT}\right) \approx \exp\left(-\frac{\Delta H}{2kT}\right)
\]
, where \( n/N \) is fractional concentration, \( \Delta G \) and \( \Delta H \) are the change in Gibbs free energy and enthalpy respectively. Therefore, the concentration of Si\(^{4+}\) interstitial ions at the SiO\(_2\)-ZrSiO\(_4\) interface is much higher when SiO\(_2\) is in amorphous state. The higher gradient of Si\(^{4+}\) concentration across the two reactants, namely ZrO\(_2\) and SiO\(_2\), results in a high flux of Si ions into ZrO\(_2\), which facilitates the reaction between SiO\(_2\) and ZrO\(_2\).
5 Conclusions

Crack healing in Yttria Stabilized Zirconia (YSZ) can be realized by reaction between amorphous silica (SiO$_2$) and zirconia (ZrO$_2$) at high temperatures forming stable zircon (ZrSiO$_4$). However, ZrO$_2$ does not react with crystalline SiO$_2$. Hence, zircon cannot be formed directly from a mixture of YSZ and SiO$_2$ powder. But, if instead of SiO$_2$ powder MoSi$_2$ (with and without Boron) is used, then upon high temperature oxidation amorphous SiO$_2$ is formed and the reaction with YSZ forming ZrSiO$_4$ proceeds.

The MoSi$_2$ is first oxidized resulting into MoO$_3$ and amorphous SiO$_2$. The MoO$_3$ is volatile at high temperature and fully escapes from the powder mixture. The amorphous SiO$_2$, due to oxidation of MoSi$_2$, is capable of filling the small gaps between the YSZ particles. The reaction between YSZ and SiO$_2$ is ceased after about 4 and 15 hours of annealing at 1200 and 1100 °C, respectively. At both annealing temperatures, the reactants are not fully consumed and the amount of remnant YSZ decreases with temperature.

The addition of Boron to MoSi$_2$ promotes the formation of amorphous SiO$_2$ and postpones the crystallization of amorphous SiO$_2$, and thus facilitates the formation of ZrSiO$_4$. The activation energy for the oxidation of MoSi$_2$ with boron is similar to that of MoSi$_2$ at temperatures ranging from 400 to 600 °C, viz. $75^{+8}_{-10}$ and $64^{+22}_{-14}$ kJ/mol, respectively.

The kinetics of ZrO$_2$ consumption and ZrSiO$_4$ formation can be represented by the conversion function of geometrical volume contraction model and first-order reaction model, respectively. This suggests that the kinetics of the crack healing reaction depends on the rate of chemical reaction between ZrO$_2$ and SiO$_2$ instead of the diffusion of reactant species. The initial rate of ZrSiO$_4$ formation in the YSZ-MoSi$_2$ powder mixture equals 0.0015 and 0.00037 mol/h at 1200 and 1100 °C, respectively. The addition of Boron increases the reaction rate, viz. 0.0014 and 0.00081 mol/h at 1200 and 1100 °C, respectively.
6 Recommendations

6.1 Isothermal kinetics
In order to quantify the measured X-ray intensities in terms of composition, an XRD measurement with same parameters should be applied with pure zircon crystal (without texture). Data on the evolution of the net area of zircon peak with time for the YSZ-MoSi$_2$B sample annealed at 1200 °C needs to be completed. The rate of zircon formation with higher accuracy is to be determined from its kinetic curve.

Since the isothermal kinetics of the zircon reaction in the YSZ-MoSi$_2$B sample annealed at 1100 °C is rather fast, data on the transformation of ZrO$_2$ and the formation of ZrSiO$_4$ at the early stages are required to determine the reaction rates.

In view of the envisioned application, i.e. crack healing in YSZ TBC, the kinetics of zircon formation at temperatures below 1100 °C will be attractive. The TBC in stationary gas turbine engines often operate at such temperatures.

6.2 Thermal analysis
The activation energy of zircon formation from the reaction between ZrO$_2$ and SiO$_2$ may be determined using a mixture of fine YSZ-MoSi$_2$ (with and without Boron) powders. Then the contact area between the reactants will be larger, because the smaller size of the particles the more dense the powder mixture will be. In this case more ZrSiO$_4$ is expected to be formed during DTA and the associate heat effect may be large enough to be observed.

It is suggested to apply more than four heating rates to obtain an accurate result for the activation energy.

6.3 Mechanism of zircon formation from YSZ-MoSi$_2$ system
The mechanism of ZrSiO$_4$ formation from the YSZ-MoSi$_2$ mixture is not fully understood yet. The result of conversion function fitting (see Figure 4.45) shows that in the tablet of YSZ-MoSi$_2$ powder mixture the rate of zircon formation is mainly subject to the chemical reaction between YSZ and SiO$_2$ instead of the diffusion rate of reacting species. This theory needs to be further substantiated by new experiments. A two-layer structured sample is available now; see Figure 6.1a. YSZ is air-plasma sprayed on top of MoSi$_2$ layer. After annealing, it is expected that a layer of SiO$_2$ is formed first at the interface between MoSi$_2$ and YSZ. Then, layer of ZrSiO$_4$ can be formed at the interface between SiO$_2$ and YSZ, and the front of ZrSiO$_4$ layer will be moving into the YSZ as reaction proceeds; see Figure 6.1b. Therefore, it will be very interesting to investigate the change of the thickness of ZrSiO$_4$ layer with annealing time by observing the cross-section of sample with SEM. If the chemical reaction between ZrO$_2$ and SiO$_2$ is the rate-determining step, then thickness of ZrSiO$_4$ layer will increase linearly with time. If, however, the diffusion of reacting species (e.g. Si$^{4+}$ ions or O vacancies) dominates the kinetics, a parabolic relation between thickness and annealing time is expected.

Also an accurate quantitative analysis of the concentration profile across the SiO$_2$, ZrSiO$_4$ and ZrO$_2$ layers, may help to resolve the mechanism of the zircon formation. The over stoichiometry in ZrSiO$_4$ layer, namely the deficiency of oxygen, may be determined with EPMA.
Further, it was observed that amorphous SiO₂ reacts with ZrO₂ faster than crystalline SiO₂; see Section 4.3. This difference in behaviour of amorphous and crystalline SiO₂ may be due to a higher concentration of Si⁴⁺ interstitial ions in amorphous than in crystalline SiO₂. To further prove this proposition, it is recommended that the enthalpy of the formation of Frenkel defect in amorphous SiO₂, quartz and cristoballite should be computed by ab initio method. It is anticipated that the computation result of enthalpy of Frenkel defect formation in amorphous SiO₂ is much lower than that in crystalline SiO₂.
Acknowledgement

I like to express my gratitude to my mentor Dr. Ir. Wim G. Sloof for his guidance throughout my thesis project. He is the most dedicated supervisor who not only shows great patience in answering my endless questions, but also inspired and offered me opportunities to challenge myself. He also guided me into the real world of materials science. Also I express my special thanks to Ruud Hendriks, Niek van der Pers, Kees Kwakernaak, Hans Brouwer and Alexandra Carabat. Without their sincere help my thesis could never be completed. Finally, I like to thank all my friends and colleagues for both mental and technical support during the past 6 months. It was all you guys who made my thesis project the most joyful time in my Master program.
Reference:


