On the in situ encapsulation of MoSi$_2$B healing particles in YSZ TBCs

Self-healing of thermal barrier coating (TBC)

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Materials Science and Engineering
Mechanical, Maritime and Materials Engineering (3ME)
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Self-healing of thermal barrier coatings (TBCs)

By

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in partial fulfilment of the requirements for the degree of

Master of Science
in Materials Science and Engineering

at the Delft University of Technology,
to be defended publicly on September 29th, 2016

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Abstract

A novel method to encapsulate MoSi$_2$B healing particles was explored via in situ shell formation in yttria-stabilised zirconia thermal barrier coatings (YSZ-BCs). The shell formation was analysed for MoSi$_2$B healing particles alloyed with 2, 6 and 12 wt% Al. According to oxidation kinetics study at 1100°C using thermogravimetry, MoSi$_2$B-12 wt% Al particles formed exclusive alumina formation via selective oxidation of Al due to the more homogeneous distribution of Mo(Si$_{1-x}$Al$_x$)$_2$ among the particles. A more exclusive alumina formation was also favoured by oxidation in lower pO$_2$ using CO/CO$_2$ (ratio of 4.2, pO$_2$ of 9.1x10$^{-14}$ atm) compared to oxidation in pure Argon. The shell formation of the Al-alloyed MoSi$_2$B particles inside YSZ matrix composite was also studied. However, oxidation of composite containing MoSi$_2$B-12 wt% Al in the CO/CO$_2$ resulted in simultaneous oxidation of Al and Si with mixed silica-alumina was formed. This suggests zirconia matrix may play a role in oxidising the particles by partial reduction of YSZ. Nevertheless, shell showed protection for particles even after microcapsule stability test at 1100°C in laboratory air for 100 hours. Crack-gap filling experiment was conducted for composites containing pre-encapsulated and in situ encapsulated MoSi$_2$B-6 wt% Al particles. Healing treatment was done with exposing the composites at 1100 °C for 1, 4 and 16 hours in laboratory air. However, the crack-gap was filled with silica without any significant difference.

Keywords: Self-healing, yttria stabilised zirconia, thermal barrier coatings, selective oxidation, in situ encapsulation, Mo(Si$_{1-x}$Al$_x$)$_2$ hexagonal C40, alumina
During the wonderful 2 years of my study at TU Delft, I have met many amazing people surrounding my life at TU Delft. I have been working on my thesis for the last 10 months and the beauty of experimental research is that it opens the opportunity to work directly or indirectly with others. I would like to send my biggest gratitude to Wim Sloof for letting me be involved in the project in the first place. The things I learnt from oxidation, self-healing, until on how being critical on my analysis have helped me becoming a better person and most importantly challenged my knowledge on materials science. Many thanks also to Alexandra Carabat who has been always a great help since the first day I started my thesis, as well as helping me with all the experiments and analysis. There are no words on how I much appreciate all the times spent for the favours and the countless discussion. Thank you also to Mario Ruiz and Toshio Osada for the many discussions. Working in a team definitely has helped me in to see a problem from different perspectives.

Without less respect, I would also like to express my gratitude to: Hans Brouwer who helped me with all the tools and equipment: SPS, furnace, TAG, and also for all the small-countless things. Kees Kwakernaak for training me to operate SEM and also the tons of analysis with EPMA. Richard Huizenga for the discussion of XRD analysis. To Lu Shen, Linda Boatemaa and Ann-Sophie Farle who helped me with the discussion of mass-gain analysis, crack-healing experiment as well as self-healing. To Guoping Bei who taught me Rietveld refinement using MAUD. To William Mao for lending us the controlled atmosphere furnace and the discussion. Last but not least to the amazing people of MSE/MEA class of 2014, who helped me get through hard and fun times together.

Finally, I would like to thank the members of examination who have invested their time evaluating my thesis.

Irsandi Kurniadi Isnu
Delft, September 2016
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Introduction

1.1 General introduction

Thermal Barrier Coating (TBC) is employed on metal or superalloy surface for its high-temperature resistance. Among many other, Yttria-stabilised Zirconia/YSZ (Y₂O₃-Stabilised ZrO₂) as Top Coat (TC) of the TBC is superior to other materials because it inherits low thermal conductivity, high CTE (\(\sim 11 \times 10^{-6}/°C\)) and resistant to hot corrosion⁴. However, high temperature and prolong thermal cycling of TBC may induce crack. Cracks may be generated by the stress exerted by Thermal Growth Oxide (TGO) formation e.g. Al₂O₃, Cr₂O₃, and also by the thermal expansion mismatch with the layers underneath the TC. The initiation and propagation of this crack ultimately leads to failure of the coating.

In the structural application, self-healing of crack offers an interesting solution to prolong the lifetime of the coating. Autonomous healing in ceramic matrix composite has been observed before⁵, ⁶. Self-crack healing capability with 10-20 vol% SiC particles in ceramic composite has been found in alumina (Al₂O₃)⁵, mullite (3Al₂O₃.2SiO₂)⁶, silicon nitride (Si₃N₄)⁷ and zirconia (ZrO₂)⁸ ceramic matrix. The crack exposes the particles to air and eventually leads to oxidation. The oxidation product SiO₂ has almost two times larger molar volume compared to the initial particle. This newly provided bonded-material on the crack wake administers the autonomous strength recovery of the matrix.

Among any other silicon containing intermetallic materials, WSi₂ and MoSi₂ (CTE of around 8.5x10^{-6}/°C⁹) has comparable thermal expansion with ZrO₂ (CTE of 9 x 10^{-6} /°C¹⁰). Meeting this requirement, these materials thus are applicable as healing particles in YSZ-TBC system¹¹. Upon oxidation, amorphous silica (a-SiO₂, Vm of 27.3 cm³) is formed, and may react with tetragonal ZrO₂ matrix (t-ZrO₂, Vm of 20.4 cm³)¹² by the dissolution of Si⁴⁺ in ZrO₂ forming zircon (ZrSiO₄, Vm of 38.7 cm³)¹³. It has been observed crack healing in YSZ with B-doped MoSi₂ formed B-doped a-SiO₂ oxide (borosilicate) and crack far from the healing particles was filled¹⁴. Third element such as B offers low viscosity SiO₂/B₂O₃ glassy oxide¹⁵,
C/SiC composite containing multilayer of boron-species (BN, B₄C, or SiBC) formed low-viscosity B₂O₃ oxide glass at low temperature oxidation (650 °C<T<900 °C) filling the porous of the composite. Whereas at higher temperature (T > 900 °C), oxide glass of borosilicate heals the crack. Both glassy oxides have a low viscosity and therefore are vitreous to fill the crack/porous present in the matrix; see Figure 1.1 for the self-healing schematic of YSZ-TBC. Due to the oxygen transparency in zirconia-based materials as the matrix (D = 10⁻⁹ – 10⁻¹⁰ m²/s at 1423 K and activation energy of ~1.0 eV), MoSi₂ is easily oxidised even in the absence of crack. This premature oxidation without the presence of crack generates stress by the volume expansion and eventually the failure of TBC system. A protecting shell of the healing particles with low oxygen permeability is thus necessary.

![Figure 1.1](image_url)

Figure 1.1: Schematic of self-healing mechanism in YSZ-TBC with alumina-encapsulated MoSi₂ healing particles.

The importance of microcapsule to prevent premature release of reactive agent has been underlined in self-healing system of polymer. However, a polymer microcapsule is not stable in high-temperature application. At operating temperatures of TBCs, ceramic oxide such as Al₂O₃ is an interesting protection shell due to its low oxygen diffusivity (D = 2 x 10⁻²⁴ m²/s at T = 1423 K). There are several methodologies of alumina coating on particles: pure route, atomization, and wet route. Moreover, MoSi₂B healing particles has also been studied before. Carabat et al. encapsulated MoSi₂ by 150 nm thickness of α-Al₂O₃ by the transformation from γ → δ → Θ → α phase with two step annealing process of boehmite (AlOOH) sol-gel. The Al₂O₃-encapsulated MoSi₂ showed much more oxidation resistant than the non-encapsulated particles. In some of sacrificial particles, a more oxygen-protective shell of aluminosilicate phases such as mullite (3Al₂O₃.2SiO₂, D = 10⁻²⁰ m²/s at 1500 - 1725 °C) is necessary.
K) was also formed. Encapsulation of MoSi$_2$ with Al$_2$O$_3$ via Atomic Layer Deposition (ALD) was also conducted even though the alumina phase transformation was different with those in sol-gel method$^{24}$. In ALD, liquid trimethylaluminium (TMA) was used as the aluminium precursor. However, both sol-gel and ALD method promotes a thin alumina shell (150 nm). These pre-encapsulated MoSi$_2$ particles are then to be incorporated to YSZ matrix. A new method to encapsulate MoSi$_2$ with thicker shell is thus required.

In this thesis, a novel encapsulating method of MoSi$_2$B healing particles with alumina shell is proposed. Instead of pre-encapsulating the particles, alumina shell growth is induced in situ inside the YSZ matrix through the selective oxidation of Al that is alloyed to MoSi$_2$B particles. To this end, the composite of YSZ matrix with Al-alloyed MoSi$_2$B particles was made by Spark Plasma Sintering (SPS). The growth of alumina shell is promoted by careful low pO$_2$ annealing to selectively oxidise Al. In situ encapsulation by using Al-alloyed MoSi$_2$B particles showed successful alumina shell formation protecting the particles from premature oxidation.

1.2 Outline of the thesis

In this thesis, new approach to promote a protective shell around MoSi$_2$B with protective shell is proposed. Chapter 1 addresses the necessity and the importance to develop new encapsulation method for MoSi$_2$B healing particles. In chapter 2, the theoretical background of YSZ as well as oxidation of MoSi$_2$, B-alloyed MoSi$_2$ and Al-alloyed MoSi$_2$ are described as they underline the fundamental of Al depletion during oxidation. Details of the materials, experimental methods and characterisation techniques are presented in chapter 3. Three main studies were performed: oxidation kinetics of Al-alloyed MoSi$_2$B powders, in situ Al$_2$O$_3$-encapsulation of Al-alloyed MoSi$_2$B particles inside YSZ matrix, and crack-gap filling experiment. Oxidation kinetics of self-healing particles is designated to study the oxide growth in low pO$_2$ atmosphere. The oxide formation was then studied for composite containing YSZ matrix and Al-alloyed MoSi$_2$B healing particles. After the in situ encapsulation of MoSi$_2$B healing particles, the composite undergoes microcapsule stability test by exposing it at 1100 °C air for 100 hours in laboratory air. Cracks are also introduced with indentation and then healed through oxidation in air to study the crack-gap filling. Chapter 4 and 5 address the results and discussion, respectively. Finally, the conclusions and proposed recommendations for future work will be presented in chapter 6.
Theoretical Background

2.1 MoSi₂

Due to its high melting temperature (2030 °C), molybdenum disilicide (MoSi₂) intermetallic is beneficial for high temperature application. Figure 2.1 illustrates the binary phase diagram of Mo-Si system. At lower temperature (T < 800 °C), Si self-diffusion is very slow thus Mo and Si are oxidised simultaneously as shown in reaction (2.2). Cracks are generated due to the molar volume is increased by 250% upon the formation of needle like MoO₃ and MoO₃·2SiO₂. The disintegration caused by this MoO₃ formation is called pest oxidation.

\[
\frac{5}{7}MoSi₂ + O₂ \rightarrow \frac{1}{7}Mo₅Si₃ + SiO₂ \quad (2.1)
\]

\[
\frac{2}{7}MoSi₂ + O₂ \rightarrow\frac{2}{7}MoO₃ + \frac{4}{7}SiO₂ \quad (2.2)
\]

At high temperature (T ≥ 1000 °C), oxidation reaction (2.1) is more favourable as it has higher absolute value of Gibbs free energy per 1 mole of O₂. As Si is consumed, a
Si-depleted zone of Mo$_5$Si$_3$ (D8m crystal structure) is formed, i.e. between the bulk MoSi$_2$ and silica layer. It is important to note as well that Mo$_5$Si$_3$ was not always present in all studies which might be due to the volatilisation of Mo oxidation product$^{30,31}$. If the silica film is thick and continuous, the low pO$_2$ between the silica film and bulk Mo-Si prevent MoO$_3$ formation, therefore oxidation of Si becomes selective. Also, at these temperatures the Si self-diffusion in MoSi$_2$ is higher compare to Mo. After the protective silica is formed, the rate-limiting step of oxide formation is the diffusion of O$_2$ molecules through the silica layer. The drawback of silica protective oxide scale is that it is crystallized to tridymite at 1000-1200 °C and to β-cristobalite at 1300-1400 °C$^{27}$ and then to α-cristobalite during cooling to T=540 K accompanied with volume change$^{31}$. This volume change could result in crack and spallation. Sharif et al. measured that the high order of crystal silica also lowered the activation energy of oxygen diffusion and thus rapid oxidation was occurred$^{32}$. SiO$_2$ suffers also from volatilisation of SiO$_{(g)}$ and SiO$_2{(g)}$ during oxidation at very high temperature (1600-2000 K) or at very low pO$_2$ ($<10^{-8}$ atm).

### 2.2 B-alloyed MoSi$_2$

[Figure 2.2: Phase Diagram of Mo-Si-B system at T=1450 °C $^{33}$.]

A few studies have been conducted to observe the oxidation behaviour of Mo-Si-B alloys usually with rich-Mo alloys. Paswan et al. observed the protective B$_2$O$_3$-SiO$_2$ (B-doped silica) scale formed at 1150 °C. The alloy was fabricated with composition of high Mo (~76 at% Mo) and small amount of Si (~14 at% Si) and B (8-10 at% B). The small amount of B incorporated the silica resulted in glassy-like scale. Supatarawanich et al. studied the Mo-Si-B alloy and found at intermediate temperature oxidation the B-doped silica glass was formed
from the oxidation of Mo$_5$SiB$_2$ with T2 crystal structure\textsuperscript{34}. In the case of B-modified MoSi$_2$ coating, Tian et al. found the viscous B$_2$O$_3$-SiO$_2$ oxide filled porosity of the scale preventing further MoO$_3$ volatilisation.

According to Ingemarsson et al., oxidising Mo(W,Si)$_2$ with boride (10-12 vol% B) at high temperature results in two layer oxide, boron-rich silica on the outer side and boron-poor silica beneath it\textsuperscript{35}. The mixture of B$_2$O$_3$/SiO$_2$ yields a borosilicate phase of glass since B$_2$O$_3$ is known to dissolve into SiO$_2$. Borosilicate glass is a type of glass consisting of SiO$_2$-B$_2$O$_3$-Na$_2$O system which lower viscosity at any temperature compared to silica glass\textsuperscript{36}. B$_2$O$_3$ creates 2D connectivity with SiO$_4$ tetrahedra network that eventually decreases the rigidity of the glass\textsuperscript{37}. Such elements that are able to influence the structure and property of glass/melts are referred as glass-modifying oxides alkali and alkaline earths. Lower viscosity of borosilicate glass was also confirmed by other research as well\textsuperscript{38, 39}.

2.3 Al-alloyed MoSi$_2$

SiO$_2$ may also suffer from pest disintegration and SiO volatilization at low pO$_2$. Metals with higher affinity to oxygen (such as Al, Ta and Ge) are usually alloyed to MoSi$_2$ to overcome the problem that arises from a SiO$_2$ oxide scale\textsuperscript{26, 40}. Due to the large negative Gibbs free energy of formation at high temperatures, Al$_2$O$_3$ is preferentially formed instead of SiO$_2$\textsuperscript{41}. Al$_2$O$_3$ scale offers protection against pest disintegration and it has lower oxide volume expansion compared to SiO$_2$, which are 4.9% and 85.6% respectively\textsuperscript{42, 43}.

The phase diagram of Mo-Al-Si system has been assessed\textsuperscript{44-46} as shown in Figure 2.3. MoSi$_2$ with tetragonal C11$_b$ (space group I4/mmm) crystal structure has a limited Al solubility (<5 mol% Al)\textsuperscript{47}. Mo(Al$_{x}$Si$_{1-x}$)$_2$ with hexagonal with C40 (space group P6$_2$22) crystal structure is formed when more Al is doped exceeding the solubility limit of tetragonal C11$_b$. Dasgupta et al. studied the synthesize of Mo(Al$_{x}$Si$_{1-x}$)$_2$ alloy by arc-melting of the stoichiometric amount of Al-Si eutectic alloy and high-purity Mo powders\textsuperscript{48}. They found that hexagonal C40 phase did not form unless x reached 0.05. The hexagonal C40 phase has the advantage of its higher Al solubility (0.11 < x < 0.55) and wider ratio of Al substitution to Si\textsuperscript{49}. They concluded by adding more Al increases the lattice parameter of tetragonal C11$_b$ since Al has larger atomic radius (143 pm) than Si (117 pm), which consequently increases the d' value and its molar volume\textsuperscript{50}.

The oxidation behaviour of Mo(Al$_{x}$Si$_{1-x}$)$_2$ has been studied for its good oxidation resistance in high temperature application. In the range of 1273-1873 K, the scale consisted mainly of α-Al$_2$O$_3$. However depending on the Al activity and temperature, amorphous silica and aluminosilicate such as mullite (3Al$_2$O$_3$.2SiO$_2$) may be present as well. Stergiou et al.
observed that addition of Al \( x = 0.33 \) and \( x = 0.44 \) increases the resistance against pest oxidation\(^{39}\). An oxide scale consisted of \( \alpha\text{-Al}_2\text{O}_3 \) was found when oxidizing \( \text{Mo(Si}_{1-x}\text{Al}_x\text{)}_2 \) with \( x = 0.33 \) and \( x = 0.44 \) in air at 1623 K. Below this temperature, both of these alloys formed Al-Si mixed oxide instead. Mitra et al. suggested that the oxidation rate was increased for \( \text{Mo(Al}_{0.33}\text{Si}_{1-x})_2 \) compared to \( \text{MoSi}_2 \) due to the rapid depletion of Al\(^{43}\). Similarly, Ramberg et al. investigated the difference of oxide between \( \text{Mo(Al}_{0.01}\text{Si}_{0.99})_2 \) and \( \text{Mo(Al}_{0.1}\text{Si}_{0.9})_2 \) alloys\(^{51}\). At temperature above 1000 °C, the main oxide scale of \( \text{Mo(Al}_{0.01}\text{Si}_{0.99})_2 \) alloy is composed of amorphous silica, mullite, sillimanite \( (\text{Al}_2\text{SiO}_5) \), and even cristobalite after long and high-temperature exposure. On the contrary, \( \text{Mo(Al}_{0.1}\text{Si}_{0.9})_2 \) oxidation consisted mainly of alumina. After oxidation, Al depleted region-Mo\(_2\text{Si}_3\) beneath the scale was found for \( \text{Mo(Al}_{0.01}\text{Si}_{0.99})_2 \) but not for \( \text{Mo(Al}_{0.1}\text{Si}_{0.9})_2 \). Although the Al content of the alloy was unknown, the existence of the Al-depleted Mo\(_2\text{Si}_3\) region was also confirmed by Ingemarsson et al when using \( \text{Mo(Si}_{x}\text{Al})_2 \)-based composite from Kanthal Super ER from Sandvik Heating Technology\(^{31, 52}\). In their study, they found continuous protective alumina oxide scale and the thickness of the scale is two times thicker than the oxide formed on Al-free MoSi\(_2\) material.

![Figure 2.3](image)

**Figure 2.3**: Phase diagram of Mo-Al-Si system at \( T=1200 \) °C \(^{53}\).

## 2.4 Yttria-stabilised zirconia

Zirconia \((\text{ZrO}_2)\) inherits low thermal conductivity, high strength and good chemical resistance properties that make the material beneficial for structural applications in harsh and high-loading condition. Zirconia is polymorph that consists of three phases: room
temperature monoclinic $m$-ZrO$_2$, at higher temperatures tetragonal $t$-ZrO$_2$ (950-1150 °C) and at very high temperatures cubic $c$-ZrO$_2$ (2300±30 °C). Pure zirconia is detrimental due to the martensitic transformation with 8 vol.% changes during $t$-ZrO$_2 \leftrightarrow m$-ZrO$_2$. To prevent this martensitic transformation, stabilisers such as yttria (see Figure 2.4), calcia, magnesia and rare earth oxide are doped to zirconia to stabilise $t$-ZrO$_2$ or $c$-ZrO$_2$ at room temperature$^{54}$.

Doping Yttria ($Y_2O_3$) to zirconia facilitated by substitution of Zr$^{4+}$ with Y$^{3+}$ introduces oxygen vacancies to the lattice to maintain charge neutrality,

$$Y_2O_3 \rightarrow 2Y'_{Zr} + 3O_\circ + V\ddot{o}$$ \hspace{1cm} (2.3)

The incorporation of oxygen vacancies $V\ddot{o}$ (see also Figure 2.5) into the lattice raises the high oxygen conductivity of yttria-stabilised zirconia (YSZ). Depending on the yttria content, the stabilised zirconia phases may be different. With addition of 3 mol% $Y_2O_3$, zirconia is partially stabilised zirconia (PSZ) and it is comprised of $t$-ZrO$_2/c$-ZrO$_2$ and $m$-ZrO$_2$.$^{56}$ About 6-8 wt% (3-5 mol%) addition of $Y_2O_3$, metastable tetragonal $t'$-ZrO$_2$ may be precipitated in a rapid cooled YSZ (e.g. as in plasma sprayed YSZ)$^{57, 58}$. On the other hand, fully stabilised zirconia (FSZ) is comprised only $t$-ZrO$_2/c$-ZrO$_2$ with the addition of 8-10 mol% $Y_2O_3$. 

![Figure 2.4](image1.png) **Figure 2.4:** Phase diagram of ZrO$_2$-Y$_2$O$_3$ system$^{55}$. 

![Figure 2.5](image2.png) **Figure 2.5:** Schematic of $V\ddot{o}$ formation by $Y_2O_3$ doping to ZrO$_2$. 


Materials and Experimental Methods

3.1 Starting materials

3.1.1 Preparation of powders

3 mol% Yttria Stabilised Zirconia (YSZ) powders (Tosoh, Japan) were used as the matrix in the composite. The healing particles, Al-alloyed MoSi$_2$B (2 wt% B-doped MoSi$_2$) powders supplied by Chempur (see Table 3.1). Wind-sifting with an Alpine 100 MRZ laboratory zig-zag classifier was conducted to eliminate fine fraction and to obtain a sharper particle size distribution. The target content of Al doping of MoSi$_2$B was varied from 2, 6 and 12 wt% Al, which from here and onwards will be denoted as MoSi$_2$B-2 wt% Al, MoSi$_2$B-6 wt% Al, MoSi$_2$B-6 wt% Al and MoSi$_2$B-12 wt% Al, respectively. X-Ray Fluorescence (XRF) and X-Ray Diffractometry (XRD) were performed to analyse the composition of the powders. Scanning Electron Microscope (SEM) combined with Energy Dispersive X-Ray Spectroscopy (EDS) and Electron Probe X-Ray Micro Analysis (EPMA) were also employed to analyse the chemical composition. However, MoSi$_2$B-2 wt% Al powders were only investigated with XRD.

**Table 3.1**: Denotations of the composite samples: YSZ matrix with 10 vol% of Al-alloyed MoSi$_2$B particles (YSZ+10MBSA).

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Healing particles</th>
<th>YSZ+10MSBA Composite</th>
</tr>
</thead>
<tbody>
<tr>
<td>3YSZ</td>
<td>MoSi$_2$B-2 wt% Al</td>
<td>YSZ+10MSB2A</td>
</tr>
<tr>
<td></td>
<td>MoSi$_2$B-6 wt% Al</td>
<td>YSZ+10MSB6A</td>
</tr>
<tr>
<td></td>
<td>MoSi$_2$B-12 wt% Al</td>
<td>YSZ+10MSB12A</td>
</tr>
</tbody>
</table>

3.1.2 Oxidation study

Thermogravimetry Analysis (TGA) was performed to study the oxidation of MoSi$_2$B-6 wt% Al and MoSi$_2$B-12 wt% Al particles using a high precision balance and high precision dual furnace (TAG Setaram Instrumentation, France). The mass change with time during isothermal annealing at 1100°C for 48 hours is observed. Alumina crucibles were used for sample powders and also for reference (empty-crucible). A micro-balance (Mettler
Instrumente AG CH-8606, USA) with accuracy of $10^{-6}$ g was used to measure the weight of the mass of the powders used in the TGA experiment. The set of powders and the annealing condition are detailed in Table 3.2. Two different annealing atmospheres were used: pure Argon and CO/CO₂ (ratio of CO/CO₂ is 4.2, $pO_2 = 9.1 \times 10^{-14}$ atm, see Table B.3.1). CO/CO₂ was only flown during the isothermal annealing. Annealing at 200 °C for 30 minutes was designated to evaporate any water vapour and contaminants that may surface on the powders. The annealed powders were then analysed with SEM/EDS to investigate the oxide constituents.

**Table 3.2:** Samples and annealing profile for TGA experiment.

<table>
<thead>
<tr>
<th>No</th>
<th>Powders</th>
<th>Gas flow (mL/min)</th>
<th>Cleaning temp (°C)</th>
<th>Time (h)</th>
<th>Annealing temp (°C)</th>
<th>Time (h)</th>
<th>Rate (°C/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MoSi₂B-6 wt% Al</td>
<td>Argon 50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>MoSi₂B-12 wt% Al</td>
<td></td>
<td>200</td>
<td>0.5</td>
<td>1100</td>
<td>48</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>MoSi₂B-6 wt% Al</td>
<td>16.8 CO + 4 CO₂ +</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>29.2 Argon</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(CO/CO₂ = 4.2)*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Only flown during isothermal annealing for 48h

**3.2 MoSi₂-in situ Alumina Encapsulation**

**3.2.1 Mixture of powder and sintering**

The volume ratio of YSZ powders as matrix and Al-alloyed MoSi₂B powders (YSZ+10MSBA) as the healing particles was 9:1 (10 vol% Al-alloyed MoSi₂B). The particles are Al-alloyed MoSi₂B with Al varied from 2, 6 to 12 wt%. With these composition, three composites were prepared: YSZ+10MSB2A, YSZ+10MSB6A and YSZ+10MSB12A (Table 3.1). In a plastic bottle, the powder mixtures were then dispersed in C₃H₇OH (iso-propanol) and mixed using ZrO₂ balls (diameter of 5mm) with a powder to ZrO₂ ball ratio of 1:1 for 16 hours. To this end a tubular mixer (Turbula, Switzerland) was used. Subsequently the powders mixture was dried in an oven (Binder, Germany) at 100 °C overnight. Afterwards, the powders were passed through a sieve of 200 µm to obtain a homogeneous mixture. Afterwards, the sieved-powders were dried again in the oven at 100 °C to ensure no water vapour was stored inside the powder mixture.

The sintering of composites was done with Pulsed Electric Current Sintering or Spark Plasma Sintering/SPS (FCT Systeme GmbH, Germany). The schematic of SPS is shown in Figure 3.1. As zirconia is a highly insulating material, graphite paper (thickness of 0.18 mm)
was placed around the powders, forcing the DC current to go around the powders mixture and allowing joule heating to take place. The operating parameters for the sintering are listed in Table 3.3. The system was flushed with pure Argon and then evacuated repeatedly prior to sintering process to remove the remaining oxygen and water molecules that might reside inside the chamber. The powders were also pre-pressed with force of 5 kN in this stage. After 30 minutes of sintering at 1200 °C, the pistons and punches were released from the sintered sample allowing natural cooling. After the sintering, the graphite around the sample was removed with coarse SiC grinding paper.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Set value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current</td>
<td>5 kA</td>
</tr>
<tr>
<td>Voltage</td>
<td>5 V</td>
</tr>
<tr>
<td>Pre-press</td>
<td>5 kN</td>
</tr>
<tr>
<td>Pressure</td>
<td>16 kN</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Ar</td>
</tr>
<tr>
<td>Power</td>
<td>65% power limit</td>
</tr>
<tr>
<td>5V pulse time</td>
<td>15 μs</td>
</tr>
<tr>
<td>5V pause time</td>
<td>5 μs</td>
</tr>
<tr>
<td>Pre-press</td>
<td>5 kN</td>
</tr>
<tr>
<td>Heating rate</td>
<td>20 °C /min</td>
</tr>
<tr>
<td>Cooling</td>
<td>Natural cooling</td>
</tr>
</tbody>
</table>

**Figure 3.1:** Schematic of Spark Plasma Sintering (SPS).

### 3.2.2 Annealing: aluminium depletion and microcapsule stability test

Two different annealing processes were performed with different objectives (see Table 3.4 for specification of the annealing parameters). Low pO$_2$ annealing inside alumina tube furnace (Carbolite, Sigma-Aldrich, USA) is designated to create α-Al$_2$O$_3$ shell around the particles in the composite. Two different atmosphere of low pO$_2$ was used: pure Argon and CO/CO$_2$(ratio of CO/CO$_2$ is 4.2, pO$_2 = 9.1 \times 10^{-14}$ atm at 1100°C, see Table B.3.1). Argon, CO and CO$_2$ gas was passed through O$_2$, H$_2$O and hydrocarbon filter (Kleinpatrone Aphagaz, air Liquide, Germany) to remove the contaminants from the gas source. For the annealing in pure Argon, the system had been flushed first with Argon gas flow of 500 mL/min for 0.5-1 hour. Afterwards, the sample was exposed directly at 1100 °C for the annealing process. The sample was removed from 1100 °C heating zone and quenched with 500 mL/min Argon.
gas. However, in the case of annealing in CO/CO₂, the samples were heated and cooled down with rate of 10 °C/min.

**Table 3.4:** Annealing parameters of low pO₂ annealing in Argon and CO/CO₂ (with ratio of 4.2) as well as parameters for microcapsule stability test.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Parameters of Annealing</th>
<th>Microcapsule Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al depletion in Argon</td>
<td>Al depletion in CO/CO₂*</td>
</tr>
<tr>
<td>Anning temperature</td>
<td>1100 °C</td>
<td>1100 °C</td>
</tr>
<tr>
<td>Holding annealing time</td>
<td>16 h</td>
<td>16 h</td>
</tr>
<tr>
<td>Gas flow</td>
<td>500 mL/min High-Purity Argon gas</td>
<td>448 Ar + 42 CO + 10 CO₂ (mL/min)</td>
</tr>
<tr>
<td>Heating and Cooling</td>
<td>Quench</td>
<td>Heating and Cooling rate 10 °C/min</td>
</tr>
<tr>
<td>Boat and substrate</td>
<td>Quartz boat and Silicon wafer</td>
<td>Quartz boat and Silicon wafer</td>
</tr>
<tr>
<td>Tube</td>
<td>Alumina tube</td>
<td>Alumina tube</td>
</tr>
</tbody>
</table>

*Experiment was only performed for YSZ+10 MSB6A and YSZ+10 MSB12A composite, not for YSZ+10 MSB2A composite.

Microcapsule stability test was performed in an open alumina tube furnace (Carbolite, Sigma-Aldrich, USA) to check the stability of MoSi₂B particles that had been encapsulated at 1100 °C for 100 hours in laboratory air. In between the total of 100 hours of annealing, the sample was taken out shortly to check the integrity of the sample.

### 3.3 Crack-gap filing

Composite containing YSZ matrix with pre-encapsulated and in situ encapsulated MoSi₂B-6 wt% Al (YSZ+10 MSB6A) healing particles were investigated for crack-gap filling experiment. Details of pre-encapsulation process of the healing particles is discussed somewhere else\textsuperscript{23, 24}. Crack was created with indentation (Zwick Hardness Tester, Germany) using diamond and pyramid-shaped indenter (136° between opposite faces). The load was selected between 200 N and 300 N. Afterwards the healing treatment was done by exposing the composites directly at 1100 °C in laboratory air using an alumina tube furnace and followed by quenched. The healing time was varied from 1, 4 and 16 hours for pre-encapsulated particles and only healed for 4 hours for the in situ encapsulated particles. The parameters for composite fabrication for both composites were the same as discussed in **Section 3.2.1** for SPS and **Section 3.2.2** for low pO₂ annealing.
3.4 Characterisation

A laser diffraction particle size analyser instrument (SDC Microtac S3500, USA) was used to obtain the particle size distribution of Al-alloyed MoSi$_2$B and YSZ powders. X-Ray Diffraction/XRD (Bruker D8 Advance diffractometer, USA) was used for analysing the chemical composition of the sample. Bruker D8 was installed with Bragg-Brentano and Lynxexe position sensitive detector, and monochromatic Cu-Kα radiation. The XRD patterns were analysed using Rietveld refinement with Java program of MAUD (copyright of Luca Lutterorri, University of Trento, Italy). The elemental analysis of the powders was performed using X-Ray Fluoroscence (XRF) spectrometer (Panalytical Axios Max-WD, The Netherlands) and SuperQ5.0i/Omnian for XRF data evaluation.

The surface morphology and local chemical composition analysis was performed with Scanning Electron Microscope (SEM, JEOL 6500FD, Japan) equipped with a ThermoFisher Ultra Dry Energy Dispersive System (EDS). With SEM, two mode of imaging can be used; secondary electrons imaging (SEI) and backscattered electrons imaging (BEI). In case of the cross-section analysis with SEM/EDS, the sample was cut with diamond wafering blade (Isomet diamond blade, USA). A smooth surface was prepared with by grinding down to 2500 grit SiC paper and polishing down to 0.25 μm paste on a polishing cloth. As for investigation of powders, the powders were embedded in a conductive polymer (Technovit 5000, Germany) based on modified methyl methacrylate with dendritic copper particles. Cross-section of the powders was also done with the grinding and polishing of the embedded powders; see above. Prior to SEM/EDS analysis, embedded powders were cleaned with C$_3$H$_7$OH (isopropanol), whereas the composites were cleaned with both (CH$_3$)$_2$CO (acetone) and isopropanol in ultrasonic bath (Branson 2510, Sigma-Aldrich, USA). After the cleaning, the samples were coated with carbon using an Auto-Carbon-Coater (JEOL JEC-530, Japan) with thickness of 10-15 nm. Electron Prove Micro-analyser (EPMA, JEOL JXA 8900R microprobe, Japan) was performed particularly for more accurate chemical composition analysis. In some cases, the samples were coated with carbon and silver to enhance the conductivity prior to EPMA investigation.
Results

4.1 Starting materials
4.1.1 Chemical composition and microstructure

![Particle size distribution of 3 mol% Y₂O₃-ZrO₂ (3YSZ) powders (left, orange line), as well as wind-sifted healing particles: MoSi₂B-6 wt% Al (right, black line) and MoSi₂B-12 wt% Al (right, red line).](image)

Figure 4.1: Particle size distribution of 3 mol% Y₂O₃-ZrO₂ (3YSZ) powders (left, orange line), as well as wind-sifted healing particles: MoSi₂B-6 wt% Al (right, black line) and MoSi₂B-12 wt% Al (right, red line).

Al-alloyed MoSi₂B powders were wind-sifted to eliminate the fine fraction of the powders. However the particle size distribution for both MoSi₂B-6 wt% Al and MoSi₂B-12 wt% Al particles are still bimodal as seen in Figure 4.1. On the contrary, the particle size of YSZ powders is unimodal. The distribution values are tabulated in Table 4.1. Al-alloyed MoSi₂B powders were also characterised with XRD (see Table 4.2) as well as with XRF and SEM/EDS (see Table 4.3, only for MoSi₂B-6 wt% Al and MoSi₂B-12 wt% Al). The XRD shows mainly Mo(AlₓSi₁₋ₓ)₂ hexagonal C40 in MoSi₂B-12 wt% Al with very small fraction of MoSi₂ tetragonal C11_b. However, there is a co-existence with tetragonal C11_b in MoSi₂B-6 wt% Al. Table 4.4 shows the weight fraction of tetragonal C11_b and hexagonal C40 for MoSi₂B-6 wt% Al and MoSi₂B-12 wt% Al powders in the starting condition and after oxidation (oxidation kinetics of MoSi₂B-6 wt% Al and MoSi₂B-12 wt% Al is discussed in Section 4.1.2 using Rietveld refinement in the 2θ range of 0-35.5° (see Table A.2.1 for the complete result). The peak position in the diffractograms for both hexagonal C40 and tetragonal C11_b between MoSi₂B-6 wt% Al and MoSi₂B-12 wt% Al are shifted without peak broadening (see...
Figure 4.2). Beside the dominant peaks of hexagonal C40 and tetragonal C11b, Mo5Si3 and signal corresponding to Al and Si are detected as well. Other considerably high peaks (0.2-7.6 wt%) are corresponded to Mo-B phases: MoB, MoB2 and Mo2B5. The chemical composition of 3YSZ powders was taken from manufacturer data and is shown in Table 4.2.

Table 4.1: Particle size distribution for starting powders.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Wind-sifted MoSi2B-6 wt% Al (μm)</th>
<th>Wind-sifted MoSi2B-12 wt% Al (μm)</th>
<th>3YSZ Tosoh (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D[10]</td>
<td>13.4</td>
<td>16.7</td>
<td>0.2</td>
</tr>
<tr>
<td>D[50]</td>
<td>29.9</td>
<td>34.6</td>
<td>0.2</td>
</tr>
<tr>
<td>D[90]</td>
<td>52.8</td>
<td>56.3</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Figure 4.2: X-Ray Diffraction (XRD) of starting MoSi2B-2 wt% Al, MoSi2B-6 wt% Al and MoSi2B-12 wt% Al powders.

Table 4.2: Main and impurities chemical composition of 3YSZ Tosoh powders (taken from manufacturer data).

<table>
<thead>
<tr>
<th>3YSZ Tosoh</th>
<th>Y2O3</th>
<th>HfO2</th>
<th>Al2O3</th>
<th>SiO2</th>
<th>Fe2O3</th>
<th>Na2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>5.2±0.5</td>
<td>&lt;5.0</td>
<td>0.1-0.4</td>
<td>≤0.02</td>
<td>≤0.01</td>
<td>≤0.04</td>
</tr>
</tbody>
</table>
4. Results

Table 4.3: Elemental analysis using XRF and EPMA of the starting MoSi$_2$B-6 wt% Al and MoSi$_2$B-12 wt% Al.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Compound</th>
<th>MoSi$_2$B-6 wt% Al (at%)</th>
<th>MoSi$_2$B-12 wt% Al (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XRF</td>
<td>Mo</td>
<td>43.9</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>41.8</td>
<td>34.4</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>14.1</td>
<td>26.4</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>0.13</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>Ca</td>
<td>0.07</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>Cr</td>
<td>0.02</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>EPMA</td>
<td>Al</td>
<td>$4.7^{+2.7}_{-3.5}$</td>
<td>$8.2^{+8.0}_{-3.0}$</td>
</tr>
</tbody>
</table>

MoSi$_2$B-6 wt% Al and MoSi$_2$B-12 wt% Al powders embedded in a conductive polymer were examined with SEM (See Figure 4.3 for cross-section of MoSi$_2$B-6 wt% Al). According to SEM/EDX analysis, MoSi$_2$B-6 wt% Al and MoSi$_2$B-12 wt% Al particles consist of Mo(Al$_x$Si$_{1-x}$)$_2$, MoSi$_2$ and Mo$_5$Si$_3$ (with dissolved ~0.41 wt% Al in average inside Mo$_5$Si$_3$). Dark-spots of Al$_2$O$_3$ and SiO$_2$ impurities are also found in the starting Al-alloyed MoSi$_2$B powders. It can be seen that the shape of particles is irregular. Statistical analysis using EPMA (Table 4.3) for many particles shows that the average Al content is $4.7^{+2.7}_{-3.5}$ at% Al and $8.2^{+8.0}_{-3.0}$ at% Al for MoSi$_2$B-6 wt% Al and MoSi$_2$B-12 wt% Al, respectively (1 Al atomic fraction/at% in Mo(Al$_x$Si$_{1-x}$)$_2$ is approximately equivalent to 2 Al in weight fraction/wt%). This suggests that the distribution of phases among particles is not homogeneous.

Figure 4.3: Cross-section of wind-sifted MoSi$_2$B-6 wt% Al powders.

4.1.2 Oxidation kinetics and microstructure

The mass gain ($\Delta m/m_o$) of MoSi$_2$B-6 wt% Al and MoSi$_2$B-12 wt% Al particles versus exposure time $t$ of isothermal annealing at 1100 °C for 48 hours in Argon and CO/CO$_2$ is
Results shown in Figure 4.4. The mass-gain difference measured between TGA and the microbalance was of the order of $10^4$-$10^5$ gr, which is reasonable. The oxidation of MoSi$_2$B-6 wt% Al and MoSi$_2$B-12 wt% Al powders in pure Argon and CO/CO$_2$ have different mass-gain behaviour (See Figure 4.4). For oxidation in pure Argon, there are 3 runs for each Al-alloyed MoSi$_2$B powders and the mass-gain is represented in area according to the vertical lines. In this environment, MoSi$_2$B-6 wt% Al has more mass-gain compared to MoSi$_2$B-12 wt% Al. Both of the particles inherit quite constant slope. Oxidation of Al-alloyed MoSi$_2$B particles in CO/CO$_2$ results in more mass-gain compared to the oxidation in pure Argon. Contrary to oxidation in pure Argon, MoSi$_2$B-12 wt% Al has more mass-gain compared to MoSi$_2$B-6 wt% Al in CO/CO$_2$. Here, a steep mass-gain in the first few hours of oxidation clearly revealing the fast-initial oxidation stage which then followed by steady-state oxidation stage.

![Figure 4.4: Mass gain curve $\Delta m/m_o$ as a function of annealing time (h) at 1100 °C for 48 hours for MoSi$_2$B-6 wt% Al and MoSi$_2$B-12 wt% Al powders in Argon and CO/CO$_2$ with ratio of 4.2.](image_url)

During the annealing at T=200 °C (not shown), there was small mass loss (~0.1 mg) probably due to the evaporation of water vapour. From 200 °C to 1100 °C with 10 °C/min, there was only mass gain detected. No MoO$_3$ or other volatilised species were present in the furnace when cleaning after oxidation. Same experiment using empty crucible showed maximum mass loss of 0.3 mg and thus the effect of crucible to the mass-gain of particles during oxidation is neglected.

$\alpha$-Al$_2$O$_3$ is formed as the main oxide accompanied with small amount of aluminium borate (Al$_{4.5}$BO$_{7.33}$ or Al$_5$BO$_3$) and Mo$_5$Si$_3$ for both particles (see XRD results in Figure 4.5 for
Results

oxidation in Ar and Figure 4.6 for oxidation in CO/CO$_2$. Some peaks of Mo-B phase, as well as all Al and Si also disappeared after oxidation. Other than the intensity, the difference between oxidation in Ar and in CO/CO$_2$ is also on the carbide formation. Based on Rietveld refinement (see Table A.2.1 for the result), the carbides are comprised with average of 1.8 wt% Molybdenum carbide ($\zeta$-Mo$_2$C) and 2.6 wt% Molybdenum silicide carbide (Mo$_{4.8}$Si$_3$C$_{0.6}$).

**Figure 4.5**: XRD for MoSi$_2$B-6 wt% Al and MoSi$_2$B-12 wt% Al powders after annealed for 48 hours at 1100 °C in Argon atmosphere.

**Figure 4.6**: XRD for MoSi$_2$B-6 wt% Al and MoSi$_2$B-12 wt% Al powders after annealed for 48 hours at 1100 °C in CO/CO$_2$ (ratio of 4.2).
**Table 4.4:** Semi-quantitative analysis of weight fraction of MoSi$_2$ tetragonal C11$_b$ and Mo(Si$_{1-x}$Al$_x$)$_2$ hexagonal C40 between starting and after oxidation MoSi$_2$B-6 wt% Al and MoSi$_2$B-12 wt% Al powders with Rietveld refinement. See Table A.2.1 for more detailed information.

<table>
<thead>
<tr>
<th>Crystal Structure</th>
<th>Starting powders</th>
<th>Oxidation at 1100 °C for 48h in Ar</th>
<th>Oxidation at 1100 °C for 48h in CO/CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MoSi$_2$B-6 wt% Al</td>
<td>MoSi$_2$B-12 wt% Al</td>
<td>MoSi$_2$B-6 wt% Al</td>
</tr>
<tr>
<td>Tetragonal C11$_b$</td>
<td>18.9 wt%</td>
<td>3.0 wt%</td>
<td>48.0 wt%</td>
</tr>
<tr>
<td>Hexagonal C40</td>
<td>68.2 wt%</td>
<td>86.9 wt%</td>
<td>22.6 wt%</td>
</tr>
</tbody>
</table>

**Table 4.5:** Summary of chemical composition analysed with SEM/EDS of the oxide formed after oxidising at 1100 °C for 48 hours in Ar and CO/CO$_2$ with TGA for MoSi$_2$B-6 wt% Al and MoSi$_2$B-12 wt% Al powders.

<table>
<thead>
<tr>
<th>Oxidation atmosphere</th>
<th>Powders</th>
<th>Morphology</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Argon</td>
<td>MoSi$_2$B-6 wt% Al</td>
<td>Whisker/bumps</td>
<td>SiO$_2$ (+Al), and Al$_2$O$_3$, B$<em>2$O$<em>3$, Al$</em>{4.5}$BO$</em>{7.33}$/AlBO$_9$</td>
</tr>
<tr>
<td></td>
<td>MoSi$_2$B-12 wt% Al</td>
<td>Columnar oxide</td>
<td>Al$_2$O$_3$</td>
</tr>
<tr>
<td>CO/CO$_2$ (4.2)</td>
<td>MoSi$_2$B-6 wt% Al</td>
<td>Columnar oxide</td>
<td>Al$<em>2$O$<em>3$, Al$</em>{4.5}$BO$</em>{7.33}$/AlBO$_9$</td>
</tr>
<tr>
<td></td>
<td>MoSi$_2$B-12 wt% Al</td>
<td>Whisker/bumps</td>
<td>Al$_2$O$_3$, SiO$_2$, Al$<em>4$BO$</em>{7.33}$/AlBO$_9$</td>
</tr>
</tbody>
</table>

**Figure 4.7:** Oxide scale of MoSi$_2$B-6 wt% Al after oxidation treatment for 48 hours at 1100 °C in Ar.
Semi-quantitative analysis using Rietveld refinement between tetragonal C11\textsubscript{b} and hexagonal C40 was also done and it is shown in Table 4.4. The amount of hexagonal C40 phase in MoSi\textsubscript{2}B-12 wt\% Al particles after the oxidation in Argon is not significantly reduced and almost no new tetragonal C11\textsubscript{b} phase is formed. On the other hand, the peak of tetragonal C11\textsubscript{b} in MoSi\textsubscript{2}B-6 wt\% Al after oxidation is higher. On the contrary, oxidation in CO/CO\textsubscript{2} resulted in higher tetragonal C11\textsubscript{b} fraction in both powders.

The morphology and chemical composition of MoSi\textsubscript{2}B-6 wt\% Al and MoSi\textsubscript{2}B-12 wt\% Al particles after oxidation at 1100 °C is summarised in Table 4.5. The oxide of MoSi\textsubscript{2}B-6 wt\% Al particles analysed with SEM after oxidation in pure Argon can be seen in Figure 4.7. The oxide constituent after oxidation consists mainly of Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2} and mixture of Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} oxide as shown in Figure 4.7(a-b). Partially oxidised MoSi\textsubscript{2}B particles are also found; see Figure 4.7(c-d) where BEI image clearly shows the contrast of oxide and Al-alloyed MoSi\textsubscript{2}B particle. Mixed Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} oxide can consist of rich SiO\textsubscript{2} with a few incorporated Al and rich Al\textsubscript{2}O\textsubscript{3} with a few incorporated Si. Both of these oxides inherit whiskers or bumps morphology. On the contrary, there are mainly scale of alumina and no rich SiO\textsubscript{2} found in the case of oxidation of MoSi\textsubscript{2}B-12 wt\% Al in pure Argon (see Figure 4.8). In Figure 4.8(c-d), the morphology of columnar alumina can be clearly seen. The whiskers are rich in Al\textsubscript{2}O\textsubscript{3} with few Si incorporated in the compound. This compound inherits the morphology of...
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bumps/whisker similar with the case in MoSi$_2$B-6 wt% Al particles. Oxide of Aluminium borate cannot be detected due to the inaccuracy in detecting B element with EDS.

**Figure 4.9**: Oxide scale of MoSi$_2$B-6 wt% Al after oxidation treatment for 48 hours at 1100 °C in CO/CO$_2$.

**Figure 4.10**: Oxide scale of MoSi$_2$B-12 wt% Al after oxidation treatment for 48 hours at 1100 °C in CO/CO$_2$.
According to Figure 4.9, oxidation of MoSi₂B-6 wt% Al and MoSi₂B-12 wt% Al in CO/CO₂ forms mainly of Al₂O₃ with a few incorporated Si. In the case of MoSi₂B-6 wt% Al, the main oxide is rich Al₂O₃ with a few incorporated Si inheriting the morphology of bumps and short-whiskers as seen in Figure 4.9(c-d). Rich-SiO₂ film instead of whisker is also formed (Figure 4.9(d)). In the case of MoSi₂B-12 wt% Al oxidation in CO/CO₂, oxide rich in Al₂O₃ with a few incorporated Si is the only oxide forming (see Figure 4.10(b-d)). No columnar alumina is formed anymore as in the case oxidation of MoSi₂B-12 wt% Al in Argon.

4.2 MoSi₂ in situ encapsulation

4.2.1 Sintering of YSZ + Al-alloyed MoSi₂B composite via spark plasma sintering (SPS)

![Figure 4.11: Piston displacement curve in SPS during the sintering of YSZ+10MSBA composite.](image)

After mixing YSZ and Al-alloyed MoSi₂B powders (cf. Section 3.2.1), composites were made with Spark Plasma Sintering (SPS). There were three YSZ+10MSBA composites prepared: YSZ+10MSB2A, YSZ+10MSB6A and YSZ+10MSB12A (see Table 3.1). The colour of the composite was dark-grey after sintering process even though the dominant of the mixture was 90 vol% white 3YSZ Tosoh powders. From the piston displacement curve in SPS of all composites (Figure 4.11), it is shown that the sintering/densification is started around ~T=1000 °C due to the piston movement towards the sample. The microstructure of cross-section of YSZ+10MSBA composites was investigated with SEM and can be seen in Figure 4.12). It is observed that the composite shows a dense material and no YSZ grains are seen.
Figure 4.12: Cross-section microscopic view of YSZ + Al-alloyed MoSi$_2$B (YSZ+10MSBA) composite after sintering with SPS by Scanning Electron Microscope (SEM) for particles in YSZ+10MSB2A composite ((a) and (b)), in YSZ+10MSB6A composite ((c) and (d)), and in YSZ+10MSB12A composite in ((e) and (f)).

In order to obtain the variation of the composition of the particle in the composites, 20-50 particles were analysed using SEM/EDX (see Figure 4.12 for the cross-section microscopic view) and EPMA (see Table 4.6 for the result). It is found that the particles are mainly composed of Mo$_5$Al$_3$Si$_3$, MoSi$_2$, Mo$_2$Si$_3$, SiO$_2$ (oxidized MoSi$_2$) and Mo-B phase. Mo$_5$Al$_3$Si$_3$ is usually present with lighter grey region compared to the darker grey MoSi$_2$.
(see Figure 4.12(c)) which having a maximum of ~1.2 wt% Al. From the EPMA, MoSi$_2$B-6 wt% Al has an average of $1.3 \pm 0.1$ wt% Al and MoSi$_2$B-12 wt% Al an average of $1.9 \pm 0.9$ wt% Al. Underneath the alumina shell, Mo$_2$Si$_3$ is formed. The average thickness of Mo$_2$Si$_3$ is also different for the three composites. Very thin and rarely Mo$_2$Si$_3$ is formed in YSZ+10MSB2A composite, whereas thicker Mo$_2$Si$_3$ was formed in YSZ+10MSB6A and YSZ+10MSB12A, respectively. The particles are surrounded with oxide shell. The particles in YSZ+10MSB6A (Figure 4.12(c-d)) and YSZ+10MSB12A (Figure 4.12(e-f)) are encapsulated with alumina shell. However not all particles in YSZ+MoSi$_2$B-2 wt% Al (Figure 4.12(a-b)) are encapsulated. In this case, the shell is composed of thin SiO$_2$ and Al$_2$O$_3$+SiO$_2$. Slightly more particles are also heavily or fully oxidised to silica in the YSZ+10MSB2A composite. It is also important to note also that the shell around particles is not homogeneous.

**Figure 4.13:** EPMA Elemental mapping of a Al-alloyed MoSi$_2$B particles for Mo, Si, B, Al and O element in YSZ + Al-Alloyed MoSi$_2$B-6 wt% Al (YSZ+10MSB6A) composite after sintering process.

Element mapping with EPMA is shown in Figure 4.13. In the Mo-B region, it is shown the complex composition with the presence of Mo, B and Si. MoB, MoB$_2$ and Mo$_2$B$_5$ indeed were detected however often accompanied with varying Si and O as well. However, from the mapping it can be proven that the low amount of Si and O are found in Mo-B region.
4.2.2 Aluminium depletion in low pO$_2$ annealing

Figure 4.14: Cross-section microscopic view of YSZ + Al-alloyed MoSi$_2$B (YSZ+10MSBA) composite after low pO$_2$ annealing in pure Argon with Scanning Electron Microscope (SEM). The particles (a) and (b) in YSZ+10MSB2A composite, (c) and (d) in YSZ+10MSB6A composite, (e) and (f) YSZ+10MSB12A composite.

In order to thicken the alumina shell, all YSZ+10MSBA composites were annealed at 1100 °C for 16 hours in low pO$_2$ atmosphere. Two different atmospheres were used: pure Argon and CO/CO$_2$ with ratio of 4.2; cf. Section 3.2.2. Statistical analysis of the Al content in the MoSi$_2$B particles as well as shell composition and thickness was also done and the results are presented in Table 4.6. Overall, a thicker shell is formed for all composites after low pO$_2$ annealing, even though the shell constituent is different (see Figure 4.14). Zircon (ZrSiO$_4$), SiO$_2$, and mixture of SiO$_2$+Al$_2$O$_3$ shell are formed around the particles in
YSZ+10MSB2A composite (Figure 4.14(a-b)) and YSZ+10MSB6A composite (Figure 4.14(c-d)). On the contrary, zircon and silica are not formed around the particles in the case of YSZ+10MSB12A composite in Figure 4.14(e-f). The comparison of shell composition and thickness after SPS and low pO\textsubscript{2} annealing process in pure Argon is shown in Figure 4.15. EDX linescan in one of the shell around MoSi\textsubscript{2}B-6 wt% Al particles shows the presence of SiO\textsubscript{2} with few Al\textsubscript{2}O\textsubscript{3} (Al\textsubscript{2}O\textsubscript{3}+SiO\textsubscript{2} shell) underneath Al\textsubscript{2}O\textsubscript{3} and ZrSiO\textsubscript{4} shell (Figure 4.15(g)). On the contrary, the shell of particles in YSZ+10MSB12A composite consists only of alumina.

**Figure 4.15:** Shell composition and the thickness evolution for YSZ + Al-Alloyed MoSi\textsubscript{2}B (YSZ+10MSB6A) composite after (a), (c), (e) SPS and (b), (d), (f) low pO\textsubscript{2} annealing in pure Argon. (g) shows the linescan of shell around particle in YSZ+ MoSi\textsubscript{2}B-6 wt% Al (YSZ+10MSB6A) composite

According to the SEM/EDS analysis in Figure 4.14, the phases present inside and around the particles of all composites after low pO\textsubscript{2} annealing are the same after sintering in SPS: Mo(Al\textsubscript{x}Si\textsubscript{1-x})\textsubscript{2}, MoSi\textsubscript{2}, Mo\textsubscript{5}Si\textsubscript{3}, and Mo-B. Al is mainly depleted from the particles for all composites. However, in the case of YSZ+10MSB6A and YSZ+10MSB12A composite, few particles still contain lighter-grey Mo(Al\textsubscript{x}Si\textsubscript{1-x})\textsubscript{2}. The continuous Mo\textsubscript{5}Si\textsubscript{3} underneath the shell of the particles are also thicker in YSZ+10MSB6A and YSZ+10MSB12A composite. Faint Mo\textsubscript{5}Si\textsubscript{3} starts to form as well for particles in YSZ+10MSB2A composite. Most particles in all
composite are mainly still protected from oxidation, only a few are heavily/fully oxidised to silica and more can be found in the case of particles in YSZ+10MSB2A composite.

Figure 4.16: Particles in YSZ + MoSi2B-6 and 12 wt% Al (YSZ+10MSB6A and YSZ+10MSB12A) composite after annealing in CO/CO₂ for 16 hours. (a) and (c) show the BEI image of one particle, (b) and (d) show the magnification of the shell.

Low pO₂ annealing in CO/CO₂ (with ratio of 4.2) atmosphere was also conducted for YSZ+10MSB6A and YSZ+10MSB12A composite. SEM images can be seen in Figure 4.16. No particular difference between YSZ+10MSB6A composite annealed in pure Argon and CO/CO₂. In both cases zircon was found as a sign of silica presence in the shell around the particles. However, annealing in low pO₂ in CO/CO₂ for YSZ+10MSB12A composite formed silica and zircon in the shell as well, unlike in the case of oxidation in pure Argon.

4.2.3 Microcapsule stability test

After the encapsulation of MoSi₂B particles, the sample was exposed directly at 1100 °C in air for total of 100 hours to check the stability of the encapsulated particle. After the exposure, the samples turned their colour to light and eventually to ivory/yellow. Regardless,
all composites were still intact. Visually the composite shows two different colours of the composite: yellow region at the outer and dark-grey region at the inner side (Figure 4.17). Crack appears between those two regions. For all composites, cracks and pores are found and more particles are oxidised in the outer side.

**Figure 4.17:** Cross-section microscopic view of YSZ + Al-alloyed MoSi,B (YSZ+10MSBA) composites after microcapsule stability test at 1100 °C in air for 100 hours. (a) shows the outer side (yellow region) and inner side (dark-grey region). The particles are shown in (b) for YSZ+10MSB2A, (c) for YSZ+10MSB6A, (d) for YSZ+10MSB12A composite.

For the particles in the inner side, the shell of the particles is comprised of Al₂O₃, SiO₂, mixed Al₂O₃ and SiO₂, and ZrSiO₄ in the case of all composites. The SEM images for the particles in all of the composites are shown in Figure 4.18. Shell becomes thicker with previously formed alumina or with newly formed silica and zircon. More alumina is now found with mixed silica. Shell composition for a particle in YSZ+10MSB12A was analysed with EDS linescan and it is shown in Figure 4.18(e). The shell composition from inside the particle towards the matrix is mixed SiO₂-Al₂O₃, Al₂O₃ and ZrSiO₄ oxide. Mo₂Si₂ the shell for all composites are now also thicker.
Figure 4.18: Cross-section microscopic view of YSZ + Al-alloyed MoSi$_2$B (YSZ+10MSBA) composites after microcapsule stability test at 1100 °C in air for 100 hours. (a) shows the low magnification showing the trend of particles in YSZ+10MSB6A composite. (b) shows the particles in YSZ+10MSB2A composite, (c) in YSZ+10MSB6A composite, (d) in YSZ+10MSB12A composite. (e) (See arrow in (d)) linescan of the shell.
Table 4.6: Statistical data on YSZ + Al-alloyed MoSi₂ (YSZ+10MSBA) composites after SPS, low pO₂ annealing and microcapsule stability test. Al content was analysed from 50 particles using EPMA.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shell composition</th>
<th>Fully oxidized particles</th>
<th>Remaining Al (wt%)</th>
<th>Shell thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al₂O₃</td>
<td>SiO₂</td>
<td>Al₂O₃+SiO₂</td>
<td>ZrSiO₄</td>
</tr>
<tr>
<td><strong>After Spark Plasma Sintering (SPS)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YSZ+10MSB2A</td>
<td>✓</td>
<td>✓</td>
<td>1%</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YSZ+10MSB6A</td>
<td>✓</td>
<td>✓</td>
<td>0.5%</td>
<td>1.9 ± 7.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YSZ+10MSB12A</td>
<td>✓</td>
<td>✓</td>
<td>0.5%</td>
<td>1.9 ± 7.9</td>
</tr>
<tr>
<td><strong>After low pO₂ annealing in pure Argon</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YSZ+10MSB2A</td>
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<td>✓</td>
<td>2%</td>
<td>0</td>
</tr>
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<td></td>
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<td>2%</td>
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<td>✓</td>
<td>1%</td>
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<td><strong>After low pO₂ annealing in CO/CO₂ of 4.2</strong></td>
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</tr>
<tr>
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<td>✓</td>
<td>✓</td>
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<td></td>
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</tr>
<tr>
<td>YSZ+10MSB12A</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td><strong>After Microcapsule Stability Test</strong></td>
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</tbody>
</table>

*Taken out from 50 particles with SEM/EDX and EPMA
†With EPMA and Including Mo(AlₓSi₁₋ₓ)₂ → MoSi₂

4.3 Crack-gap filling

The width of the crack-gap after the indentation with Vickers Indenter of 200-300 N was in the range of 0.1-1 μm for both YSZ+10MSB6A composite with pre-encapsulated and in situ encapsulated particles. Figure 4.19(a) shows an example of the indentation with cracks going through the particles for pre-encapsulated YSZ+10MSB6A composite. Figure 4.19(c-d) shows the crack-gap before and after filled crack with oxide. Figure 4.19(e-f) shows also the filled crack however unfilled crack denoted with zirconia matrix underneath the crack is also observed. Figure 4.20(a) shows the crack going straight through the particles. However the cracks are more occasionally going through the interface of particle (i.e. MoSi₂ or Mo₅Si₃) and shell (i.e. Al₂O₃ or mixed Al₂O₃-SiO₂) as shown in Figure 4.20(b). After the heating treatment at 1100 °C, the crack-gap became smaller. Thus polishing was done to investigate oxidation product deeper into the crack gap. Figure 4.20(c-h) shows the surface condition with SEI/BEI images of YSZ+10MSB6A pre-encapsulated after the heating treatment (1, 4 and 16 hours) and after polishing. Zircon may form around the crack as seen in Figure 4.20(c-d). Figure 4.20(e-f) and Figure 4.20(g-h) show the filled crack-gap with oxide. Analysis with EDS for the filling shows signal up to 30 at% Si. However, most of the time the signal of Si is very low (1-5 at%) not corresponding with SiO₂ or ZrSiO₄.
healing product. Overall, the successful rate of crack-gap filling is about 50% and the trend is similar regardless of the healing time.

Figure 4.19: (a) Example of Vickers indentation and indentation crack YSZ + pre-encapsulated MoSiB-6 wt% Al (YSZ+10MSB6A) composite. (b) and (c) show the crack indentation before healing, (d) and (e) show the filled and partially filled crack by silica.

The composite of in situ encapsulated YSZ+10MSB6A composite was only healed for 4 hours at 1100 °C in air. Figure 4.21 shows the SEI/BEI images of this sample after healing and polishing treatment. Similar to the case of pre-encapsulated YSZ+10MSB6A composite, there is oxide filling the crack-gap. According to Figure 4.21(a-d), it is found that the oxide filling is silica. Zircon is also observed in Figure 4.21(e-h) along the crack or at few sports along the crack-gap. However, with EDS observation it is only found up to 10 at% Si and
also sometimes with a very few Al. Same as before, cracks are filled with about 50% successful rate.

**Figure 4.20**: Surface observation YSZ + pre-encapsulated MoSi$_2$B-6 wt% Al (YSZ+10MSB6A) composite (a) and (b) after indentation. (c) and (d) show the condition after healing for 1 hour, (e) and (f) show the condition after healing for 4 hours, (g) and (h) show the condition after healing for 16 hours (images of healing was taken after polished). (c),(e),(g) show the SEI images and (d),(f),(g) show the BEI images.
Figure 4.20: (continued).

Figure 4.21: Surface observation of different cracks of YSZ + in situ encapsulated MoSi$_2$B-6 wt% Al (YSZ+10MSB6A) composite healed at 1100 °C in air for 4 hours. (a),(c),(e),(g) show the SEI images. (b),(d),(f),(h) show the BEI images.
Figure 4.21: (continued).
5

Discussion

5.1 Powders

5.1.1 Oxide growth kinetics

The plot of normalised mass gain $\Delta m / m_o$ in function of isothermal annealing time $t$ for MoSi$_2$B-6 wt% Al and MoSi$_2$B-12 wt% Al is shown in Figure 4.4. The complex surface area inherited by the irregular (e.g. Figure 4.3) and quite inhomogeneous size (e.g. Figure 4.1) of powders sample caused the different results between 3 experiments for each Al-alloyed MoSi$_2$B (the 3 different results ware represented with vertical line along the mass-gain curve). The power law of oxidation is expressed as$^{59, 60}$:

$$\Delta m = k t^n$$  \hspace{1cm} (5.1)

Where $\Delta m$ is the weight change, $k$ is the oxidation rate constant and $n$ is the growth rate exponent. With the derivation from (5.1) the growth rate exponent $n$ can be calculated by,

$$n = \frac{\delta (\log (\Delta m))}{\delta (\log (t))}$$  \hspace{1cm} (5.2)

To obtain the growth rate exponent $n$, Equation (5.2) can be rewritten as:

$$n = \frac{\partial (\Delta m) \Delta m}{\partial (t) \cdot t}$$  \hspace{1cm} (5.3)

With the equation above, the growth rate exponent $n$ versus the isothermal annealing time $t$ can be plotted as shown in Figure 5.1(a). Oxidation in pure Argon resulted in growth rate exponent $n$ of 1.3-2.2 for MoSi$_2$B-6 wt% Al and 1.1-1.5 for MoSi$_2$B-12 wt% Al. Therefore, both powders showed parabolic-like rate law kinetics. This suggests that the oxygen anion or metal cation diffusion through oxide as the rate-limiting step$^{61}$. Plotting the growth rate exponent $n$ with the same equation for oxidation in CO/CO$_2$ resulted in inconstant $n$ (Figure
5.1(a)) showing that it does not satisfy power law. However, the oxide growth in CO/CO$_2$ can be described with a logarithmic rate law as can be seen in Figure 5.1(b) showing the good fit of $R^2$. Logarithmic rate law denotes more protective shell against oxidation.

![Figure 5.1](image)

**Figure 5.1**: (a) Plot of growth rate exponent $n$ versus isothermal annealing time $t$ for oxidation of MoSi$_2$B-6 wt% Al and MoSi$_2$B-12 wt% Al in pure Argon (black axis, vertical line for $n$ of oxidation in Argon represents the 3 different experiments) and CO/CO$_2$ (blue axis, bold-solid line). (b) Logarithmic plot of mass gain for 48h TG/m$_o$ for MoSi$_2$B-6 wt% Al and MoSi$_2$B-12 wt% Al oxidation in CO/CO$_2$. (c) Initial stage (0-1 hour) for MoSi$_2$B-6 wt% Al and MoSi$_2$B-12 wt% Al oxidation in pure argon and CO/CO$_2$.

In the initial oxidation stage, an oxide scale is not present and thus the surface reaction between particles/gas controls the oxide growth rate. This is denoted by linear growth kinetics for oxidation in both Argon and CO/CO$_2$ (see Figure 5.1(c)). The goodness of fit $R^2$ of logarithmic plot at the initial stage is slightly smaller than the following oxidation stage. This suggests that the initial oxidation stage in CO/CO$_2$ is described with the combination of linear and logarithmic rate law. According to mass-gain curve in Figure 4.4, oxidation in Argon leads to a higher mass gain for MoSi$_2$B-6 wt% Al compared to MoSi$_2$B-12 wt% Al due to simultaneous oxidation of Al and Si in the initial oxidation stage. Oxidation with CO/CO$_2$ shows more mass-gain than in pure Argon due to more alumina formation.
Therefore, oxidation in low pO$_2$ favours the selective Al oxidation and prevents simultaneous oxidation of Al and Si. This suggests higher mass gain of MoSi$_2$B-12 wt% Al than in MoSi$_2$B-6 wt% Al caused by the higher fraction of Mo(Al$_{x}$Si$_{1-x}$)$_2$ hexagonal C40 constituting the particles.

5.1.2 Composition and phases of the healing particles

Based on real Al content analysed with EPMA of many particles (see Table 4.3), the composition for starting MoSi$_2$B-6 wt% Al and MoSi$_2$B-12 wt% Al particles is much lower than the nominal composition. There is 4.1 $^{+4.0}_{-1.5}$ wt% Al for MoSi$_2$B-12 wt% Al and the composition lies in a three-phases region of Mo(Al$_{x}$Si$_{1-x}$)$_2$ hexagonal C40 + MoSi$_2$ tetragonal C11$_b$ + Mo$_5$Si$_3$ D8m (see Figure 5.2). On the contrary, MoSi$_2$B-6 wt% Al with 2.7 $^{+13.7}_{-1.6}$ wt% Al, is in a two-phases region of MoSi$_2$ tetragonal C11$_b$ + Mo$_5$Si$_3$ D8m. This analysis is in good agreement with XRD results of the starting powders (Figure 4.2).

According to the EPMA analysis of Mo-B region inside the particles (see Mo-B region in Figure 4.13), the Mo-B phases are found but also accompanied with varying Si and O. Mole fraction of Mo:Si:B in MoSi$_2$B (MoSi$_2$ + 2 wt% B) alloy is 32.7 : 9.0 : 58.3. In Mo(Al$_{x}$Si$_{1-x}$)$_2$ system, Al substitutes Si thus mole fraction of Si is lower than 58.3. This composition lies between two three-phases regions (MoSi$_2$-MoB-Mo$_5$Si$_3$ and MoSi$_2$-MoB-Mo$_5$B$_5$) as shown in phase diagram of Mo-Si-B system (Figure 2.2). This suggests the phases present in Mo-B region are constituted with complex co-existence of all these phases. In addition, trapped oxygen during embedding the particles in copper polymer might be the reason of observed O during EPMA investigation.

Figure 5.2: Plotting of composition in Mo-Si-Al phase diagram for MoSi$_2$B-6 and 12 wt% Al. Phase diagram was calculated with ThermoCalc based on the study by Turchi et al.53.
There are shifting of diffraction lines for hexagonal C40 and tetragonal C11b between starting MoSi2B-6 wt% Al and MoSi2B-12 wt% Al powders (see Figure 4.2 for the XRD results). In addition, the diffraction lines of these phases are also shifted between starting powders and after oxidation treatment; see Figure 5.3. This denotes the change of lattice parameters of hexagonal C40 and tetragonal C11b due to the variation of Al content as confirmed by Tabaru et al.\(^\text{49}\). Besides this diffraction lines shifting, growth of MoSi\(_2\) tetragonal C11b and loss of Mo(Al\(_{x}\)Si\(_{1-x}\))\(_2\) hexagonal C40 (see Table 4.4) also suggest that Al is depleted from these phases during the oxidation. This is in agreement with observation by SEM (Figure 4.9 and Figure 4.10) where rich Al\(_2\)O\(_3\) is the main forming oxide.

![Figure 5.3: XRD results showing the shifting between Mo(Si\(_{1-x}\)Al\(_x\))\(_2\) C40 and MoSi\(_2\) tetragonal C11b between starting powders and after oxidation in TGA for MoSi2B-6 wt% Al (top) and MoSi2B-12 wt% Al (bottom).](image-url)
5.1.3 Oxide formation

As mentioned before, more alumina was formed after oxidation in CO/CO\(_2\) compared to after oxidation in pure Argon. However, measurement with Rietveld refinement shows slightly lower amount of alumina (see Table A.2.1) after oxidation in CO/CO\(_2\). This might be caused by reaction between the alumina and B\(_2\)O\(_3\) forming Aluminium borate during the initial oxidation stage. According to measurement with Rietveld refinement, carburisation of the particles resulted in carbide formation with 1.83-2.78 wt\% of Mo\(_2\)C (\(\rho = 8.9 \text{ gr/cm}^3\)) and 1.36-3.89 wt\% of Mo\(_{1.8}\)Si\(_{3.6}\)C (\(\rho = 8.2 \text{ gr/cm}^3\)). Beside these carbides, Mo (\(\rho = 10.28 \text{ gr/cm}^3\), see Figure 4.6 for the XRD result) and excess of B\(_2\)O\(_3\) might also form as the by-product of the carburisation of the particles. The disappearance as well as change of intensity of few diffraction lines corresponding to the Mo-B peaks i.e. MoB\(_2\) and Mo\(_2\)B\(_5\) after oxidation (Figure 4.5 and Figure 4.6) suggests the formation of B\(_2\)O\(_3\) and this oxide together with alumina forms Aluminium borate. Therefore, in addition to more exclusive alumina formation via selective oxidation of Al, the formation of high-mass density of carbides might be also the cause of higher mass gain in CO/CO\(_2\) compared to oxidation in pure Argon.

Alumina is thermodynamically more favoured to form than silica due to its low Gibbs free energy (see Table B.3.1) i.e. at > 1000 °C. However simultaneous oxidation of Al and Si can occur due to inhomogeneity of Mo(Al\(_{1-x}\)Si\(_{1-x}\))\(_2\) hexagonal C40 distribution among particles. Si is also started to oxidise if the phases with lower Al content e.g. Mo\(_5\)Si\(_3\), Mo-B or MoSi\(_2\) were present instead of Mo(Al\(_{1-x}\)Si\(_{1-x}\))\(_2\). This prevents protective alumina shell to form and thus Si can be easily oxidised. If Al is completely depleted from Mo(Al\(_{1-x}\)Si\(_{1-x}\))\(_2\) e.g. after low pO\(_2\) annealing process, Si is also then oxidised. Low-viscosity a-SiO\(_2\) can also penetrate Al\(_2\)O\(_3\) followed by the dissolution of Al\(_2\)O\(_3\) according to the study of mullite formation from \(\alpha\)-Al\(_2\)O\(_3\)/a-SiO\(_2\) coupling\(^{62, 63}\). Toshio et al. also suggested that the dissolution of alumina into silica occurred at T=1863 K through the substitution of Al\(^{3+}\) ion to Si\(^{4+}\)\(^{64}\). Diffusion of the metal cation Al\(^{3+}\) or Si\(^{4+}\) through the oxide was faster due to the small amount of oxygen and therefore new oxide formed towards oxide/gas interface with whisker morphology (see Figure 4.7-Figure 4.10). Moreover, Aluminium borate\(^{65}\) and mullite\(^{66}\) also inherits whisker morphology. Mullite phase exist in different ratio of Al\(_2\)O\(_3\):SiO\(_2\) ranging from 1:1, 2:1 and 3:1\(^{67}\). According to literature, mullite scale or particles in the oxide was indeed observed when oxidizing bulk Mo(Si,Al)\(_2\) alloys however only after long oxidation in air atmosphere\(^{30, 51, 52, 68}\). In our experiment, mullite was not observed by XRD. This suggests mullite was not formed due to the mild oxidizing conditions in Argon or CO/CO\(_2\).
5.2 In situ encapsulation

5.2.1 Mechanism of in situ encapsulation

Theoretical alumina shell thickness $\delta$ can be calculated by assuming the particle is perfectly spherical and only composed of Mo(Al$_x$Si$_{1-x}$)$_2$ hexagonal C40 according to:

$$\delta = \frac{X \text{ wt.\% } \text{Al} M_r \rho_{\text{alumina}} r_{\text{particle}}}{2 \rho_{\text{alumina}} A r_{\text{Al}}} \left(1 - \frac{1}{3}ight)$$

(5.4)

With $r_{\text{particle}}$ (µm) is taken from D[50] in Table 4.1, $x$ is the wt% Al in the starting alloy and is taken from real Al content in Table 4.3 and assuming $\rho_{\text{particle}} \approx \rho_{\text{MoSi}_2}$. If Al is completely depleted from Mo(Al$_x$Si$_{1-x}$)$_2$, the optimum alumina shell thickness $\delta$ for MoSi$_2$B-6 wt% Al and MoSi$_2$B-12 wt% Al are 0.40 µm and 0.69 µm, respectively. Referring to Al depletion from SEM/EDS and EPMA (see Table 4.5 for the Al content after SPS and after low pO$_2$ annealing), the theoretical alumina shell thickness and the measured thickness from SEM images can be compared as well. After SPS, the theoretical alumina shell thickness is about 0.22 µm for MoSi$_2$B-6 wt% Al and 0.38 µm for MoSi$_2$B-12 wt% Al particle. Whereas after low pO$_2$ annealing for 16 hours at 1100 °C in pure Argon, the thickness for MoSi$_2$B-6 wt% Al is 0.38 µm and for MoSi$_2$B-12 wt% Al is 0.52 µm. The discrepancy between theoretical and measured scale thickness is due to the particle shape irregularity and inhomogeneous distribution of Mo(Al$_x$Si$_{1-x}$)$_2$ hexagonal C40 which eventually resulted in simultaneous oxidation of Al and Si.

Figure 5.4 shows the schematic for shell development around MoSi$_2$B-6 wt% Al particles in the composite. Other than Mo(Al$_x$Si$_{1-x}$)$_2$, phases such as MoSi$_2$, Mo$_5$Si$_3$ and Mo-B phase are also present in the starting particle. The region with Mo(Al$_x$Si$_{1-x}$)$_2$ creates uniform layer of alumina shell. However except MoSi$_2$B-12 wt% Al particles, MoSi$_2$B-2 wt% Al and MoSi$_2$B-6 wt% Al particles contain also a large fraction of MoSi$_2$ tetragonal C11$_b$ with no Al content. Thus the region with this low Al content (e.g. tetragonal C11$_b$, Mo$_5$Si$_3$ and Mo-B phases) forms very limited alumina shell. The formation of Mo$_5$Si$_3$ underneath alumina shell is provided by the rapid oxidation of Al from Mo(Al$_x$Si$_{1-x}$)$_2$ phase. Thicker Mo$_5$Si$_3$ in the case of YSZ+10MSB12A composite is in agreement with the study from Ramberg et al.$^{31}$ Ramberg et al. found that Mo$_5$Si$_3$ formed only for Mo(Al$_{0.1}$Si$_{0.9}$)$_2$ and did not form for Mo(Al$_{0.01}$Si$_{0.99}$)$_2$. The particles with less Al such as MoSi$_2$B-2 wt% Al then formed very thin Mo$_5$Si$_3$ underneath the shell because of the oxidation of slow Si instead of Al at this high temperature.$^{49}$ Mo$_5$Si$_3$ is also formed according to $\frac{5}{2}$MoSi$_2$ + O$_2$→$\frac{1}{2}$Mo$_5$Si$_3$ + SiO$_2$ and may be followed by 2Mo$_5$Si$_3$ +
21O₂→10MoO₃ + 6SiO₂ if Si is also oxidised. Mo₅Si₃ formation is accompanied by volume expansion, creating irregularity between particle/shell interfaces. MoO₃ does not form due to the low pO₂ at oxide/particle interface, which also not formed according to the TGA study of the particles.

After low pO₂ annealing, the shell becomes thicker either with previously alumina growth or newly formed silica. Simultaneous oxidation of Al and Si occurred if there is no alumina shell protection and also if the phases are consisted with no Al i.e. Mo₅Si₃ and Mo-B phase, or if the Al is already depleted. Furthermore, mixed alumina-silica can form when a-SiO₂ dissolve Al₂O₃ or formed via Al³⁺-Si⁴⁺ substitution (cf. Section 5.1.3). Subsequently, Si⁴⁺ diffusion to zirconia initiated the zircon formation. If the shell is not protective, the particles may be fully oxidised to silica.

![Figure 5.4: Schematic of alumina shell formation around MoSib particles in YSZ + MoSib-6 wt% Al (YSZ+10MSB6A) composite.](image)

After in situ encapsulation of the composite via low pO₂ annealing in pure Argon, the shell composition is in agreement with oxide composition of Al-alloyed MoSi₂B particles after TGA in pure Argon: mixed Al₂O₃-SiO₂ for MoSib-6 wt% Al and more exclusive alumina for
MoSi₂B-12 wt% Al. However, the formation of silica and zircon shell for particles in YSZ+10MSB12A composite annealed in CO/CO₂ with pO₂ = 9.1 x 10⁻¹⁴ atm is conflicting with the TGA result. In the same oxidising condition, more exclusive alumina shell was formed around MoSi₂B-12 wt% Al particles. Whereas silica is also formed for the same particles in the presence of YSZ matrix. Therefore exclusive alumina formation in the composite was not achieved as in the case of oxidation of Al-alloyed MoSi₂B powders in lower pO₂ by CO/CO₂.

5.2.2 Oxygen source

The SPS process took place at high temperature (1200 °C) under inert Argon and also reducing atmosphere created by the graphite (mold, punch and paper, see Figure 3.1 for the schematic of SPS). Alumina formation in this atmosphere was thus not expected (see Figure 4.12). Entrapped oxygen may be the cause for this oxidation in inert/reducing atmosphere. Another possibility is also oxidation-reduction reaction of Al-alloyed MoSi₂B particles with zirconia matrix. The oxidation-reduction reaction is not spontaneous since zirconia is a more stable oxide compared to alumina and silica (see Table B.3.1 for the calculation of dissociation pO₂ of oxide). However, Li et al. found oxidation of titanium accompanied with darkening and partially reduced zirconia ZrO₂₋ₓ after joining titanium-containing brazing materials with ceramics in low pO₂ environment (vacuum ∼ pO₂<10⁻⁶ atm)⁷⁰-⁷². The formation of in situ thermally growth oxide (TGO) as aluminium oxide in an inert atmosphere also suggested the partial reduction of YSZ in the case of TBC fabrication with SPS⁷³-⁷⁵. Song et al. also observed the darkening of 7YSZ top-coat post-sintering process as a result from partial reduction of zirconia with formation of alumina from Al foil⁷⁶. Anselmi-Tamburini et al. associated the darkening of YSZ after SPS with the occurrence of oxygen non-stoichiometry via partial reduction of the zirconia⁷⁷. All YSZ+10MSBA composites were dark-grey after the SPS process, which therefore suggests that the partial reduction of zirconia may play a role in oxidising the particles.

According to the Brouwer diagram of pure zirconia (Figure 5.5), types of dominating defects may be changed under the non-equilibrium condition. In low pO₂ atmosphere, the predominant defects are oxygen vacancies which are compensated by electron \( n = 2[V\bar{O}] \). The relationship in equilibrium condition is,

\[
n = (2K_1)^\frac{1}{3}PO_2^{-\frac{1}{6}}
\]  

(5.5)
The evolution of oxygen vacancy $[V\bar{o}]$ according to Equation (5.5) is succeeding the decomposition of oxygen from the lattice $\sigma_o^{78,79}$:

$$O_o^\sigma \leftrightarrow \frac{1}{2}O_2 + V\bar{o} + 2e'$$  \hspace{1cm} (5.6)

According to the study of YSZ membrane with pO$_2$ gradient ranging from 0 to $10^{-9}$ atm between feed and permeate side, the oxygen flux in 1 mm YSZ thickness at high temperature was of the magnitude of $J_{O_2} \approx 10^{-8} \text{mol.cm}^{-2}\text{s}^{-1}$ 80. With thicker YSZ, the oxygen flux is lowered even more. However after low pO$_2$ annealing, the shell of the particles near the surface and towards the centre of the composite did not show any difference. Therefore, zirconia matrix may also play role in alumina formation during this stage. The presence of mixed alumina-silica shell in YSZ+10MSB12A composite also indicated the role of zirconia in oxidising the particles after annealing in lower pO$_2$ using CO/CO$_2$.

Figure 5.5: Brouwer diagram for pure zirconia\textsuperscript{81}. $[V\bar{o}]$ and $[O_{i}^{\prime}]$ denote the Kröger-Vink notation for oxygen vacancies and interstitial oxygen, respectively.

5.2.3 Zirconia matrix decomposition

Observed cracks at outer side/yellow region of the composite (see Figure 4.17) after 100 hours annealing in open air are probably caused by the zirconia decomposition via martensitic transformation from t-ZrO$_2$ to m-ZrO$_2$. The surface of the sample was not perfectly free of micro-cracks from the surface preparation. These micro-cracks acted as high-diffusivity paths for oxygen and in the end it resulted in accelerated oxidation of
particles near the surface. The oxide formation was accompanied with stress to the surrounding and cracks eventually appeared. In addition, other than the stable phases of zirconia, metastable t'-ZrO₂ may be formed as well e.g. after rapid cooling⁵⁷. This phase can decompose to high (c-ZrO₂) and low yttria (m-ZrO₂ and t-ZrO₂) domain due to Yttria segregation⁵⁸, ⁷⁹. The martensitic transformation via t-ZrO₂ ↔ m-ZrO₂ exerted volume change and eventually cracks may be initiated in the outer side. The difference of oxygen and temperature exposure between the inner side (dark-grey) and outer side (yellow) region of the composite resulted in different stable phase between the two. According to Ho et al., the colour change to ivory/yellow due denotes the stoichiometry recovery of ZrO₂-x⁷⁷, ⁷⁹. During the cooling, the volume expansion between the two regions resulted in crack between them the inner side (dark-grey region) and outer side (yellow region). Nevertheless, even after severe oxidation in the yellow region, few particles were still intact showing the protection by alumina shell.

5.3 Mechanism of crack-gap filling

![Figure 5.6](image)

**Figure 5.6**: The schematic of healing in YSZ + MoSi₂B-6 wt% Al (YSZ+10MSB6A) composite.

The irregularity of particle/oxide interface caused by Mo₅Si₃ formation result in weak region between particle/oxide where often cracks were deflected to this interface (see Figure 4.19). Nevertheless, the attraction of crack to the particle is beneficial for crack healing. Figure 5.6 shows the mechanism of crack gap filling in YSZ+10MSB6A composite. During healing treatment in air, reaction \(\frac{5}{7}MoSi_2 + O_2 \rightarrow \frac{1}{7}Mo_5Si_3 + SiO_2\) and \(2Mo_5Si_3 + 21O_2 \rightarrow 10MoO_3 + 6SiO_2\) takes place. At high temperature, MoO₃ was volatilised due to the high pO₂ in air. The formed amorphous silica flows through the crack and reacts with zirconia matrix to form zircon ZrSiO₄. Visually, the cracks were filled with 50% success rate. Healing product was consisted of silica, while no zircon inside the crack-gap was formed. Al may be present inside the healing product due to the present Mo(Si₁₋ₓₐₓAlₓ)_₂ phase. Dissolved alumina inside
the amorphous silica may change the viscosity\textsuperscript{82} and ultimately affect the crack-gap filling successful rate.

There are two possible reasons for the unfilled crack-gap: B\textsubscript{2}O\textsubscript{3} volatilisation and small crack-gap. According to other study, B is easily volatilised to B\textsubscript{2}O\textsubscript{3}\textsuperscript{83} which ultimately may reduce the flow ability of amorphous silica. Nevertheless, zircon was sometimes observed around the crack, proving the flow ability of B-doped SiO\textsubscript{2} inside the crack gap. Oxides sometimes did not fill crack also due to small cracks and further the crack narrowing during the healing treatment. Thus the oxide may tend to go to the surface instead of filling the crack-gap. The EDS analysis was not accurate since the oxide usually located inside the crack-gap. In order to observe clearly the chemical composition of the filled crack, larger and more controlled cracks are required.
Conclusions and Recommendations

1.1 Conclusions

Oxidation kinetics:
Two healing particles with different Al composition were analysed with TGA: MoSi$_2$B-6 wt% Al and MoSi$_2$B-12 wt% Al in Argon and also CO/CO$_2$ with ratio of 4.2 at 1100 °C for 48h.

- Mixed Al$_2$O$_3$-SiO$_2$ oxide in MoSi$_2$B-6 wt% Al occurred during oxidation under Argon due to the shape irregularity and inhomogeneity distribution of Mo($\text{Al}_{x}\text{Si}_{1-x}$)$_2$ hexagonal C40 while alumina was formed more exclusively with MoSi$_2$B-12 wt% Al. Oxidation of MoSi$_2$B-6 wt% Al and MoSi$_2$B-12 wt% Al particles in pure Argon at 1100 °C showed linear oxide growth rate kinetics at the initial oxidation stage followed by parabolic oxide growth rate kinetics.

- An alumina shell was exclusively formed after oxidation of MoSi$_2$B-6 wt% Al and MoSi$_2$B-12 wt% Al under CO/CO$_2$ with a ratio of 4.2 due to the lower pO$_2$. Oxidation of MoSi$_2$B-6 wt% Al and MoSi$_2$B-12 wt% Al particles in CO/CO$_2$ of 4.2 showed linear + parabolic oxide growth rate kinetics in the initial oxidation stage followed by logarithmic oxide growth kinetics.

In situ encapsulation of MoSi$_2$B particles:
Three composites were prepared to study the in situ alumina formation around the particles: YSZ+10MSB2A (YSZ matrix + MoSi$_2$B-2 wt% Al particles), YSZ+10MSB6A (YSZ matrix + MoSi$_2$B-6 wt% Al particles), and YSZ+10MSB12A (YSZ matrix + MoSi$_2$B-12 wt% Al particles). Low pO$_2$ annealing in pure Argon and also CO/CO$_2$ with a ratio of 4.2 at 1100 °C for 16 hours was conducted to thicken the shell encapsulation.

- After low pO$_2$ annealing in pure Argon, particles in YSZ+10MSB12A formed alumina more exclusively while in YSZ+10MSB2A and YSZ+10MSB6A composite was composed of...
alumina and silica mixture denoting the lack of Al content inside the particles. Nevertheless all particles showed protection during the exposure of composite in air at 1100 °C for 100 hours.

- Low pO₂ annealing with CO/CO₂ with ratio of 4.2 (pO₂ = 9.1 x 10⁻¹⁴ atm) showed simultaneous oxidation of Al and Si even for the particles in YSZ+10MSB12A composite. This suggested that oxygen source during low pO₂ annealing in Argon or CO/CO₂ came from the zirconia matrix as well. Annealing the composite in inert/reducing atmosphere promoted V'O allowing non-stoichiometry of zirconia ZrO₂ₓ and eventually partially reduced zirconia to establish through oxygen decomposition from zirconia lattice.

 Crack-gap filling:

Two samples were analysed for the crack-gap filling experiment: YSZ+10MSB6A with pre-encapsulated healing particles and in situ encapsulated healing particles. The healing treatment was done by exposing the composite at 1100°C in laboratory air for 1, 4 and 16 hours.

- Silica filled the crack made by Vickers indentation about 50% success rate with no difference between all samples. There are two possible reasons for unfilled crack-gap. First, B₂O₃ may be volatilised reducing the flow ability of amorphous silica. Second, small crack-gap from Vickers indentation and even narrower crack-gap after healing may also prevent silica to fill the crack-gap.

1.2 Recommendations for future work

The following recommendations are proposed in order to get more understanding of the in situ encapsulation of the particles:

- TGA study of MoSi₂B particles to validate the selective oxidation of Al and to validate the kinetics of silica or borosilicate formation in pure Argon and CO/CO₂ with ratio of 4.2.
- Creating particles with more homogeneous Mo(Si₁₋ₓ₋ₓ,Alₓ)₂ hexagonal C40 by alloying Al to the composition of two phases region Mo(Si₁₋ₓ₋ₓ,Alₓ)₂ hexagonal C40 + Mo₅Si₃ D₈m (from 5-30 mol% Al). For this this composition the MoSi₂ tetragonal C11b will be absent and therefore regardless of the shape inhomogeneity, selective oxidation of Al is still favoured.
- Creating larger and more controlled crack-gap to study the crack-gap filling composition and kinetics.
Result of Semi-quantitative Analysis using Rietveld Refinement

The weight-fraction semi-quantitative analysis for powders was conducted with Maud software by Java. The 2θ(°) from 0-35.5 was selected to minimise the fitting error caused by complex diffraction lines around 37-45°. As a result, free Mo (approximately at 41-42°) was not included in the measurement. $R_{wp}$ stands for weighted profile R-factor where $R_{wp} < 10\%$ corresponded to good refinement$^{84,85}$. On the other hand, sigma is the goodness of fit and it is the ratio between $R_{wp}$ and $R_{exp}$ ($R_{exp}$ is the expected or the best possible $R_{wp}$). Value of sigma lower than 2 denotes acceptably good refinement. High $R_{wp}$ for MoSi$_2$B-12 wt% Al (TGA in pure Argon) was due to the few yet unidentified XRD peaks.

**Table A.2.1:** Weight fraction (wt%) of compounds analysed using Rietveld Refinement.

<table>
<thead>
<tr>
<th>Compound (wt%)</th>
<th>Starting Powders</th>
<th>TGA in pure Argon</th>
<th>TGA in CO/CO$_2$ of 4.2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MoSi$_2$B-6 wt% Al</td>
<td>MoSi$_2$B-6 wt% Al</td>
<td>MoSi$_2$B-12 wt% Al</td>
</tr>
<tr>
<td>Tetragonal C11$_b$</td>
<td>18.9 3</td>
<td>48 0.8</td>
<td>62.3 22.1</td>
</tr>
<tr>
<td>Hexagonal C40</td>
<td>68.2 86.9</td>
<td>22.6 85.7</td>
<td>0.71 36.1</td>
</tr>
<tr>
<td>MoB</td>
<td>1.1 1.4</td>
<td>3.8 0.9</td>
<td>13.4 6.9</td>
</tr>
<tr>
<td>MoB$_2$</td>
<td>0.9 0.2</td>
<td>0 0</td>
<td>0 0</td>
</tr>
<tr>
<td>MoB$_{2.5}$</td>
<td>7.6 5.5</td>
<td>8.5 7.9</td>
<td>10.7 20.6</td>
</tr>
<tr>
<td>Al$<em>{13}$BO$</em>{7.33}$/AlBO$_9$</td>
<td></td>
<td>14.5 2.9</td>
<td>7.2 1.1</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td></td>
<td></td>
<td>1.8 2.8</td>
</tr>
<tr>
<td>Mo$_2$C</td>
<td></td>
<td></td>
<td>1.4 3.9</td>
</tr>
<tr>
<td>MoSiC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>3.2 3</td>
<td>2.6 0.002</td>
<td>3.41 5.5</td>
</tr>
<tr>
<td>Mo$_2$Si$_3$</td>
<td></td>
<td>6.5 24.6</td>
<td>10.6 12.6</td>
</tr>
<tr>
<td>Rwp (%)</td>
<td>5.1 6.5</td>
<td>0.6 1.1</td>
<td>0.9 1.1</td>
</tr>
<tr>
<td>Sigma</td>
<td>0.6 0.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Thermodynamic of Oxide Formation

The calculation of dissociation $pO_2$ for oxide (alumina, silica and zirconia) formation was done with assuming pure and immiscible oxide (activity $a_{oxide} \approx 1$). Gibbs free energy was obtained from Richardson-Ellingham diagram (i.e. see the diagram from this reference61). The activity of element $a_{\text{Al}} = y_{\text{Al}} \chi_{\text{Al}}$ and $a_{\text{Si}} = y_{\text{Si}} \chi_{\text{Si}}$ was also taken equal to its mole fraction with the assumption of $y_{\text{Al}} = y_{\text{Si}} = 1$. Yttria-stabilised zirconia was assumed as pure-zirconia and with the mole fraction of Zr according to crystal structure in Figure 2.5. The equilibrium constant $k$ at fixed total pressure is as follows:

$$k = \exp\left(-\frac{\Delta G_f}{RT}\right) \quad (B.3.1)$$

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Reaction</th>
<th>$\Delta G_f$ (kJ/1 mole O$_2$)</th>
<th>Dissociation pO$_2$ (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>$\frac{4}{3} \text{Al} + \frac{1}{3} \text{O}_2 \rightarrow \text{Al}_2\text{O}<em>3$&lt;br&gt;$\chi</em>{\text{Al}} = 11.25$ mol% for MoSi$<em>2$B-6 wt% Al&lt;br&gt;$\chi</em>{\text{Al}} = 22.45$ mol% for MoSi$_2$B-12 wt% Al</td>
<td>- 800 kJ/mole&lt;br&gt;(T = 1473 K)</td>
<td>8.1.10$^{-28}$ for MoSi$_2$B-6 wt% Al&lt;br&gt;3.1.10$^{-28}$ for MoSi$_2$B-12 wt% Al</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>$\text{Si} + \frac{1}{2} \text{O}_2 \rightarrow \text{SiO}<em>2$&lt;br&gt;$\chi</em>{\text{Si}}$ is 61.91 mol% Si in MoSi$_2$B-6 wt% Al</td>
<td>- 640 kJ/mole&lt;br&gt;(T = 1473 K)</td>
<td>3.3 x 10$^{-23}$</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>$\frac{5}{7} \text{MoSi}_2 + \frac{1}{7} \text{O}_2 \rightarrow \frac{3}{5} \text{Mo}_5\text{Si}_3 + \frac{3}{5} \text{Si}_2\text{O}_2$&lt;br&gt;$\Delta G_f(\text{MoSi}_2) \approx -116.5$ kJ 41&lt;br&gt;$\Delta G_f(\text{Mo}_5\text{Si}_3) \approx -333.8$ kJ 41&lt;br&gt;$\Delta G_f(\text{Si}_2\text{O}<em>2) \approx -640$ kJ/mole&lt;br&gt;$\chi</em>{\text{Zr}} = 1.25$ mol% for yttria-stabilised zirconia</td>
<td>- 810 kJ/mole&lt;br&gt;(T = 1473 K)</td>
<td>10$^{-30}$&lt;br&gt;10$^{-29}$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>$2\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$</td>
<td>- 310 kJ/mole&lt;br&gt;(T = 1373 K)</td>
<td>9.1 x 10$^{-14}$</td>
</tr>
</tbody>
</table>
References

References

53. Turchi, P.E.A. and A.I. Landa, THERMODYNAMIC DATABASE, LOWER LENGTH SCALE, PART II.
54. THERMODYNAMIC ASSESSMENT OF AL-MO-Si-U (M3MS-12LL0602092). 2012, Lawrence Livermore National Laboratory.


