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# Oxidation behaviour of particle reinforced MoSi<sub>2</sub> composites at temperatures up to 1700 °C

## Part I: Literature review

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### Abstract

In the first part of this paper the results of a literature review are presented. An overview of the oxidation behaviour in air and in combustion environments of both pure MoSi<sub>2</sub> and MoSi<sub>2</sub> composites in the temperature range from 400 to 1650 °C is given. The second part of this paper reports about our results from oxidation tests with selected MoSi<sub>2</sub> composites (containing 15 vol.-% Al<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, HfO<sub>2</sub>, SiC, TiB<sub>2</sub>, ZrB<sub>2</sub>, or HfB<sub>2</sub>, respectively) from different development stages at temperatures in the pest region as well as up to 1700 °C. The third part describes the oxidation behaviour of the optimised MoSi<sub>2</sub> composites developed on the basis of the results from part II.

### 1 Introduction

Today's materials used in high temperature processes are often burdened up to their limit. New materials are essential when a rise in efficiency of high temperature processes is to be targeted with higher temperatures. Silicides of refractory metals show high potential to be used in turbine technology, because of their melting temperatures above 2000 °C and the formation of thin self-curing SiO<sub>2</sub> films up to 1700 °C in oxidising atmospheres. On the other hand, silicides suffer from insufficient mechanical properties, i.e. brittleness at ambient temperatures and low creep strength at high temperatures. These problems may be faced with reinforcements with other phases, but this naturally affects the oxidation behaviour as well. Especially reactions and formation of eutectics between the matrix material and the reinforcements or their oxidation products may necessitate a decrease of the service temperature, counteracting the original goal. Therefore, the reinforcement material has to be chosen carefully.

MoSi<sub>2</sub> is a silicide which has been well investigated concerning the oxidation behaviour of pure material at temperatures at least up to 1500 °C. In the present work the oxidation behaviour of several MoSi<sub>2</sub> composites with 15 vol.-% particle reinforcements was investigated. From a choice of ZrO<sub>2</sub>, HfO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, SiC, TiB<sub>2</sub>, ZrB<sub>2</sub>, and HfB<sub>2</sub> as reinforcement particles those combinations with MoSi<sub>2</sub> which offered the best oxidation properties after an initial test at 1600 °C were considered for further

tests between 400 and 1700 °C. In the present first part of the paper basic information and data on the oxidation behaviour of MoSi<sub>2</sub> and its composites gained from a literature review is given.

## 2 Properties of MoSi<sub>2</sub> and MoSi<sub>2</sub> composites

### 2.1 MoSi<sub>2</sub>

According to *Massalski's* phase diagram of Mo-Si the intermetallic phase MoSi<sub>2</sub> is a Si rich line compound with a high melting point of 2020 °C and two temperature determined modifications. Tetragonal α-MoSi<sub>2</sub> has a C11<sub>b</sub> structure and is stable up to 1900 °C, whereas hexagonal β-MoSi<sub>2</sub> with its C40 structure is stable between 1900 and 2020 °C [1]. *Boettinger* et al. stated that the C11<sub>b</sub> structure of pure MoSi<sub>2</sub> is stable up to the melting point and the C40 structure occurs only through stabilisation by impurities [2]. The phase diagrams of *Schlichting* [3] and *Brewer* et al. [4] differ from *Massalski's* by giving a small region of homogeneity of MoSi<sub>2</sub>, denying that it is a line compound.

The melting point of Mo rich Mo<sub>5</sub>Si<sub>3</sub> (T<sub>M</sub> = 2180 °C) is higher than that of the disilicide and it offers a better creep resistance at 1200 °C [5], however, its oxidation resistance is lower [6, 7]. Since oxygen is present in most service environments, the oxidation resistance is considered to be the most important criterion, giving MoSi<sub>2</sub> the preference for high temperature processes.

High oxidation rates between 400 and 600 °C restrict the usage of MoSi<sub>2</sub> as well as the brittleness at room temperature and low creep resistance above 1200 °C.

### 2.2 Oxidation of MoSi<sub>2</sub>

The excellent oxidation resistance of MoSi<sub>2</sub> is due to the formation of a dense SiO<sub>2</sub> scale in oxidising atmospheres at temperatures above 1000 °C. However, between 400 and 600 °C no protective layer can form and oxidation rates are high. This may result in disintegration of the material. Moreover, the oxygen partial pressure of the ambient medium is important, since too low partial pressures at high temperatures lead to formation of volatile SiO instead of a protective SiO<sub>2</sub> scale.

*Melsheimer* [8] and *Liu* et al. [9] gave detailed overviews on the oxidation behaviour of MoSi<sub>2</sub>. As a general rule it is divided into three temperature regions.

#### 2.2.1 Low temperature range (400– 600 °C)

Up to 750 °C MoSi<sub>2</sub> is oxidised by O<sub>2</sub> following the reaction



This simultaneous oxidation of Mo and Si leads to disintegration of the material. Solid MoO<sub>3</sub> impedes the formation of a dense protective SiO<sub>2</sub> scale. The molar volume increases by 250% [10]. MoO<sub>3</sub> crystals grow chiefly at inhomogeneities like pores and microcracks. High stresses induced by growth of the MoO<sub>3</sub> crystals cause crack propagation and provoke together with the consumption of the material the disintegration.

Specimens with a theoretical density of at least 95% [8, 10, 11] do not show this phenomenon, which was originally described and named "pest" by *Fitzer* in 1955 [12].

#### 2.2.2 Medium temperature range (600– 1000 °C)

In this temperature region no disintegration occurs [13]. With the temperature, the vapour pressure of MoO<sub>3</sub> rises and it starts to evaporate at 500 °C. At 770 °C formation and evaporation of MoO<sub>3</sub> are balanced [14], preventing growth of volume and stresses and therefore the disintegration. *Fitzer* observed a high mass loss at 750 °C due to evaporation of MoO<sub>3</sub> [12].

*Samsonow* et al. [14] discovered a thin film consisting of a black phase with good adhesion, which was thought to be molybdenum suboxide, and yellowish MoO<sub>3</sub> with poor adhesion after oxidation of MoSi<sub>2</sub> at 600 °C. At 900 °C only a black film remained without any MoO<sub>3</sub>.

Glushko et al. [15] observed increasing occurrence of pores in the scale when raising the oxidation temperature and time resulting from evaporation of MoO<sub>3</sub>. In this temperature range the formation of a completely dense protective SiO<sub>2</sub> scale is still suppressed.

### 2.2.3 High temperature range (above 1000 °C)

A dense protective SiO<sub>2</sub> scale forms at temperatures above 1000 °C. The low oxygen partial pressure at the interface between oxide scale and MoSi<sub>2</sub> practically prevents further MoO<sub>3</sub> formation. In this temperature region the largest amount of the total mass gain develops during the first 10 minutes of oxidation [16]. The predominant reaction is



According to equation (2) an area of Mo<sub>5</sub>Si<sub>3</sub> should occur below the oxide scale. The diffusion rate of silicon in Mo<sub>5</sub>Si<sub>3</sub> exceeds that of oxygen in SiO<sub>2</sub> by several decades at temperatures of 1200 °C and higher, therefore further dissociation of Mo<sub>5</sub>Si<sub>3</sub> is not necessary to maintain the silica scale [6]. Contrary to these observations *Melsheimer* et al. discovered diffusion of molybdenum from the Mo rich phase through the SiO<sub>2</sub> scale at high temperatures [17]. At temperatures of 1200 °C and higher the subsurface depleted in Mo<sub>5</sub>Si<sub>3</sub>. Coincidentally the SiO<sub>2</sub> modification switched from tridymite to cristobalite. It was concluded that MoO<sub>3</sub> diffuses at higher rates in cristobalite than in tridymite. Moreover, the depletion of Mo<sub>5</sub>Si<sub>3</sub> showed that formation and evaporation of MoO<sub>3</sub> is faster than the formation of SiO<sub>2</sub>. For this reason no Mo<sub>5</sub>Si<sub>3</sub> could be found in the subsurface zone after oxidation at temperatures above 1400 °C [17].

### 2.2.4 MoSi<sub>2</sub> in combustion environments

A literature review revealed that predominantly the behaviour of SiO<sub>2</sub> scale forming SiC was investigated in combustion environments. As failure of this material is mainly due to degradation of the silica scale, the results can be transferred to MoSi<sub>2</sub> to some extent.

Mutated corrosion mechanisms of MoSi<sub>2</sub> are possible in environments with CO<sub>2(g)</sub> and H<sub>2</sub>O<sub>(g)</sub>. At low oxygen partial pressure the formation of a protective SiO<sub>2</sub> scale may be prevented by evaporation of SiO<sub>(g)</sub>. Additionally, when oxygen supply is not sufficient for combustion a reducing atmosphere containing CO and H<sub>2</sub> will develop. Hydrogen reduces SiO<sub>2</sub> to normally gaseous suboxides [18].

The degradation mechanism of SiO<sub>2</sub> scale forming SiC in combustion environments was investigated by *Opila* et al. [19]. The primary oxidant in these atmospheres is water vapour, which reacts with the SiO<sub>2</sub> to form silicon hydroxides. In a fuel lean environment formation of Si(OH)<sub>4(g)</sub> was the main degradation mechanism, whereas the reducing gases CO and H<sub>2</sub> in combination with water vapour were liable for the degradation in a fuel rich environment.

A detailed report on corrosion of silicon based materials in combustion environments is given in [20].

## 2.3 Oxidation of MoSi<sub>2</sub> based composites

Overcoming the mechanical inadequateness is essential to enable taking advantage of the good oxidation behaviour of MoSi<sub>2</sub> for structural parts. Particle reinforcement is a method to alter mechanical, thermal and electrical properties of a material to meet certain requirements. Though numerous publications report about the mechanical properties of MoSi<sub>2</sub> composites with several second phases, especially with SiC [21, 22], the oxidation behaviour at high temperatures of the same composites is barely investigated. However, the resistance of non-oxide materials in oxidising environments is the most important requirement, since in most high temperature processes air is present in the atmosphere. Undoubtedly pure MoSi<sub>2</sub> has a high oxidation resistance in air, however, the influence of the reinforcement particles may not be limited to mechanical, thermal and electrical properties, but also on the oxidation behaviour. Reactions of MoSi<sub>2</sub> with the particles or formation of eutectics of matrix and particles or their oxidation products, respectively, with melting temperatures

far below those of the composites are surely detrimental. Therefore, knowledge of possible interactions of matrix and particles lowering the maximum service temperature is essential.

Furthermore, desired and undesired second phases, i.e. impurities for the latter, can influence the oxidation resistance by acceleration of diffusion rates of oxygen within the  $\text{SiO}_2$  scale or by conducting oxygen themselves quickly, e.g. zirconia. This would increase the oxidation rate even without a reaction of  $\text{SiO}_2$  and the reinforcement particles.

Fig. 1 shows pseudo binary phase diagrams of  $\text{SiO}_2$  (as this is the oxidation product of  $\text{MoSi}_2$ ) in combination with possible particle phases. With the exception of the system  $\text{SiO}_2$ -SiC, in each diagram eutectics exist with liquidus temperatures below the melting points of the pure substances. For the system  $\text{TiO}_2$ - $\text{SiO}_2$  the eutectic temperature lies at 1550 °C. The highest eutectic temperatures are found for the systems  $\text{ZrO}_2$ - $\text{SiO}_2$  (1687 °C) and  $\text{HfO}_2$ - $\text{SiO}_2$  (1680 ± 15 °C). The maximum service temperature of the system  $\text{MoSi}_2$ /SiC is not influenced by any eutectics since  $\text{SiO}_2$  is the oxidation product of both phases.

In the temperature range of 400 to 600 °C, where  $\text{MoSi}_2$  is liable to “pest”,  $\text{MoSi}_2$  composites are more prone to disintegration especially when the difference between thermal expansion coefficients of matrix and particles is very high and microcracks occur or when adhesion of particles is not strong enough. These sites are additional starting locations for pesting.

$\text{MoSi}_2$  has a good chemical stability in contact with second phases. *Meschter* identified by calculations and experiments the  $\text{MoSi}_2$  systems with SiC,  $\text{TiB}_2$ , and TiC being stable at 1600 °C whereas the system  $\text{MoSi}_2$ - $\text{Al}_2\text{O}_3$  is not [24]. At temperatures between 400 and 500 °C the oxidation resistance of the composites  $\text{MoSi}_2$ / $\text{TiB}_2$  and  $\text{MoSi}_2$ / $\text{Al}_2\text{O}_3$  was superior to that of pure  $\text{MoSi}_2$ . However, at high temperatures, when a  $\text{SiO}_2$  scale can form, the composites had higher oxidation rates due to faster diffusion of oxygen in the oxide scales of the composites. The maximum temperature up to which the oxidation resistance is not harmed by the second phases was quoted to be 1200 °C [25].

*Wiedemeier* and *Singh* reported that second phase particles of SiC,  $\text{Si}_3\text{N}_4$ , TiC, ZrC, HfC, TiB,  $\text{TiB}_2$ ,  $\text{ZrB}_2$ ,  $\text{HfB}_2$ ,  $\text{ZrO}_2$ , and  $\text{HfO}_2$  are stable in a  $\text{MoSi}_2$  matrix between 1300 and 1900 K [26]. The  $\text{MoSi}_2$ / $\text{Al}_2\text{O}_3$  composite is stable up to 1800 K, however, high vapour pressures of  $\text{Al}_2\text{O}$  and SiO cause significant mass losses above 1800 K.

The thermal properties of  $\text{MoSi}_2$  are said to be comparable to those of SiC and  $\text{Si}_3\text{N}_4$ , i.e. no additional efforts in cooling are essential which is beneficial when using this material in turbines [27]. In addition to the phases mentioned above,  $\text{Y}_2\text{O}_3$  is stable in a  $\text{MoSi}_2$  matrix. Cyclic oxidation at 1200 °C of  $\text{MoSi}_2$ / $\text{TiB}_2$  revealed higher oxidation rates than those of other intermetallics and superalloys, however, mass gains of  $\text{MoSi}_2$  and  $\text{MoSi}_2$ /SiC under the same conditions were much lower [27].

Though oxidation decelerates after formation of a glassy scale on  $\text{MoSi}_2$  with 20 mass-%  $\text{TiB}_2$ , the amount of  $\text{B}_2\text{O}_3$  in this scale results in faster growth compared to the  $\text{SiO}_2$  scale on pure  $\text{MoSi}_2$ , and the scale on the composite can be eight times as thick after 4 hours at 1650 °C [28].

Only minor alterations in the oxidation kinetics were observed for reinforced  $\text{MoSi}_2$  with 20 vol.-%  $\text{Al}_2\text{O}_3$ ,  $\text{HfO}_2$  or SiC, respectively, at 1500 °C by Kurokawa et al. [29], although dissolution of  $\text{Al}_2\text{O}_3$  in  $\text{SiO}_2$  lead to a liquid oxide at 1500 °C. A major degradation of the oxidation resistance was observed when the composite contained 20 vol.-%  $\text{ZrO}_2$  due to formation of  $\text{ZrSiO}_4$ .

The pest phenomenon can be prevented when using composites with high density.  $\text{MoSi}_2$ /SiC composites containing up to 33.9% SiC with a density of 98% and higher show high oxidation resistance at 500 °C [30, 31]. No  $\text{MoO}_3$  crystals, but a thin  $\text{SiO}_2$  scale was found on 100% dense in-situ synthesised  $\text{MoSi}_2$ /SiC composites after oxidation at 500 °C [30].

Like desired second phases also impurities in the composites can impede grain growth during exposure. However, Newman et al. observed that the higher the amount of impurities, the faster was oxidation at 500 °C. Further the oxidation rate was increased when larger amounts of  $\text{SiO}_2$  or  $\text{Mo}_5\text{Si}_3$  were present in the  $\text{MoSi}_2$  matrix [32].

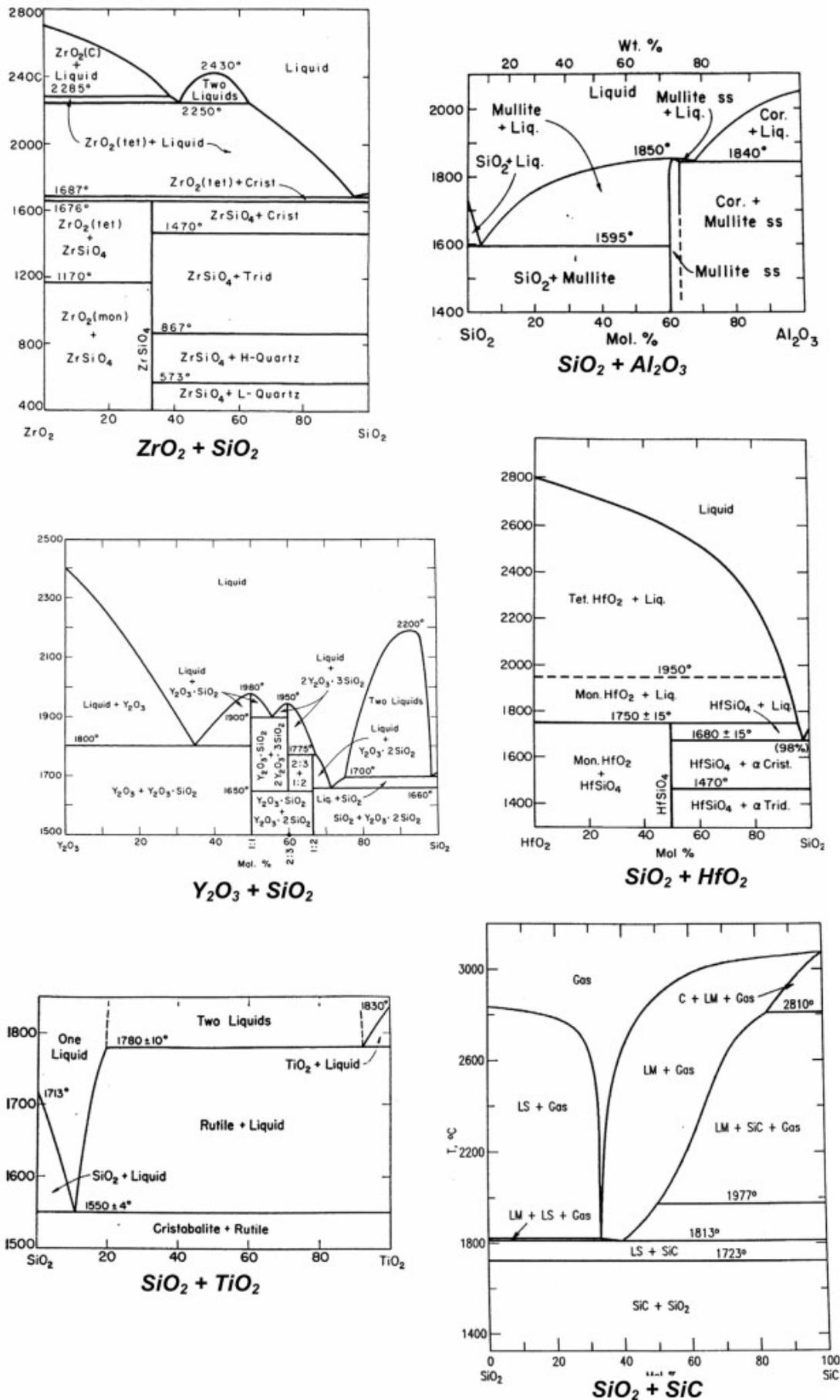


Fig. 1. Pseudo binary phase diagrams of silica and  $ZrO_2$ ,  $Al_2O_3$ ,  $Y_2O_3$ ,  $HfO_2$ ,  $TiO_2$ , and  $SiC$ , respectively [23]

### 3 Conclusions of the literature survey

The literature review showed that data about the oxidation behaviour of MoSi<sub>2</sub> composites especially in the high temperature region are limited. Most data are available for the system MoSi<sub>2</sub>/SiC. Though boride particles enhance the oxidation resistance in the pest region due to formation of a borosilicate scale, at high temperatures this scale does not offer good protection. A detrimental effect of second phase particles at pest temperatures can be prevented when the material is dense. Above 1200 °C second phases lead to accelerated oxidation. Furthermore, eutectics of SiO<sub>2</sub> and the particle phases often decrease the maximum service temperature. Concluding from oxidation data in the literature the systems with SiC and HfO<sub>2</sub> appear to be most suitable for exposure at temperatures above 1500 °C. Concluding from the phase diagrams also MoSi<sub>2</sub>-ZrO<sub>2</sub> could be an interesting system.

In the investigations reported here, along with these three composites those with 15 vol.-% Al<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, TiB<sub>2</sub>, ZrB<sub>2</sub>, and HfO<sub>2</sub> were oxidised in air up to 1700 °C. The results are presented in the second part of this paper.

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