Oxidation behaviour of particle reinforced MoSi2 composites at temperatures up to 1700 °C, Part I: Literature Review

Oxidation behaviour of particle reinforced $MoSi_2$ composites at temperatures up to 1700 °C Part I: Literature review

S. Lohfeld and M. Schütze
Karl-Winnacker-Institut der DECHEMA e.V.,
Theodor-Heuss-Allee 25, D-60486 Frankfurt am Main (Germany)

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 $MoSi_2$ and $MoSi_2$ 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 $MoSi_2$ composites (containing 15 vol.-% Al_2O_3, Y_2O_3, ZrO_2, HfO_2, SiC, TiB_2, ZrB_2, or HfB_2, 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 $MoSi_2$ 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_2 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.

$MoSi_2$ 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 $MoSi_2$ composites with 15 vol.-% particle reinforcements was investigated. From a choice of ZrO_2, HfO_2, Al_2O_3, Y_2O_3, SiC, TiB_2, ZrB_2, and HfB_2 as reinforcement particles those combinations with $MoSi_2$ 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 $MoSi_2$ and its composites gained from a literature review is given.

2 Properties of $MoSi_2$ and $MoSi_2$ composites

2.1 $MoSi_2$

According to *Massalski's* phase diagram of Mo-Si the intermetallic phase $MoSi_2$ is a Si rich line compound with a high melting point of 2020 °C and two temperature determined modifications. Tetragonal α-$MoSi_2$ has a $C11_b$ structure and is stable up to 1900 °C, whereas hexagonal β-$MoSi_2$ with its C40 structure is stable between 1900 and 2020 °C [1]. *Boettinger* et al. stated that the $C11_b$ structure of pure $MoSi_2$ 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 $MoSi_2$, denying that it is a line compound.
The melting point of Mo rich Mo_5Si_3 (T_M = 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 $MoSi_2$ the preference for high temperature processes.
High oxidation rates between 400 and 600 °C restrict the usage of $MoSi_2$ as well as the brittleness at room temperature and low creep resistance above 1200 °C.

2.2 Oxidation of $MoSi_2$

The excellent oxidation resistance of $MoSi_2$ is due to the formation of a dense SiO_2 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_2 scale.
Melsheimer [8] and *Liu* et al. [9] gave detailed overviews on the oxidation behaviour of $MoSi_2$. As a general rule it is divided into three temperature regions.

2.2.1 Low temperature range (400– 600 °C)

Up to 750 °C $MoSi_2$ is oxidised by O_2 following the reaction

$$2\ MoSi_{2(s)} + 7\ O_{2(g)} \rightarrow MoO_{3(s)} + 4\ SiO_{2(s)} \qquad (1)$$

This simultaneous oxidation of Mo and Si leads to disintegration of the material. Solid MoO_3 impedes the formation of a dense protective SiO_2 scale. The molar volume increases by 250% [10]. MoO_3 crystals grow chiefly at inhomogeneities like pores and microcracks. High stresses induced by growth of the MoO_3 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_3 rises and it starts to evaporate at 500 °C. At 770 °C formation and evaporation of MoO_3 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_3 [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_3 with poor adhesion after oxidation of $MoSi_2$ at 600 °C. At 900 °C only a black film remained without any MoO_3.

Glushko et al. [15] observed increasing occurrence of pores in the scale when raising the oxidation temperature and time resulting from evaporation of MoO_3.
In this temperature range the formation of a completely dense protective SiO_2 scale is still suppressed.

2.2.3 High temperature range (above 1000 °C)

A dense protective SiO_2 scale forms at temperatures above 1000 °C. The low oxygen partial pressure at the interface between oxide scale and $MoSi_2$ practically prevents further MoO_3 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

$$5\ MoSi_{2(s)} + 7\ O_{2(g)} \rightarrow Mo_5Si_{3(s)} + 7\ SiO_{2(s)} \tag{2}$$

According to equation (2) an area of Mo_5Si_3 should occur below the oxide scale. The diffusion rate of silicon in Mo_5Si_3 exceeds that of oxygen in SiO_2 by several decades at temperatures of 1200 °C and higher, therefore further dissociation of Mo_5Si_3 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_2 scale at high temperatures [17]. At temperatures of 1200 °C and higher the subsurface depleted in Mo_5Si_3. Coincidentally the SiO_2 modification switched from tridymite to cristobalite. It was concluded that MoO_3 diffuses at higher rates in cristobalite than in tridymite. Moreover, the depletion of Mo_5Si_3 showed that formation and evaporation of MoO_3 is faster than the formation of SiO_2. For this reason no Mo_5Si_3 could be found in the subsurface zone after oxidation at temperatures above 1400 °C [17].

2.2.4 $MoSi_2$ in combustion environments

A literature review revealed that predominantly the behaviour of SiO_2 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 $MoSi_2$ to some extent.
Mutated corrosion mechanisms of $MoSi_2$ are possible in environments with $CO_{2(g)}$ and $H_2O_{(g)}$. At low oxygen partial pressure the formation of a protective SiO_2 scale may be prevented by evaporation of $SiO_{(g)}$. Additionally, when oxygen supply is not sufficient for combustion a reducing atmosphere containing CO and H_2 will develop. Hydrogen reduces SiO_2 to normally gaseous suboxides [18].
The degradation mechanism of SiO_2 scale forming SiC in combustion environments was investigates by *Opila* et al. [19]. The primary oxidant in these atmospheres is water vapour, which reacts with the SiO_2 to form silicon hydroxides. In a fuel lean environment formation of $Si(OH)_{4(g)}$ was the main degradation mechanismen, whereas the reducing gases CO and H_2 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 $MoSi_2$ based composites

Overcoming the mechanical inadequateness is essential to enable taking advantage of the good oxidation behaviour of $MoSi_2$ 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 $MoSi_2$ 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 $MoSi_2$ 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 $MoSi_2$ 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 SiO_2 scale or by conducting oxygen themselves quickly, e.g. zirconia. This would increase the oxidation rate even without a reaction of SiO_2 and the reinforcement particles.

Fig. 1 shows pseudo binary phase diagrams of SiO_2 (as this is the oxidation product of $MoSi_2$) in combination with possible particle phases. With the exception of the system SiO_2-SiC, in each diagram eutectics exist with liquidus temperatures below the melting points of the pure substances. For the system TiO_2-SiO_2 the eutectic temperature lies at 1550 °C. The highest eutectic temperatures are found for the systems ZrO_2-SiO_2 (1687 °C) and HfO_2-SiO_2 (1680 ± 15 °C). The maximum service temperature of the system $MoSi_2$/SiC is not influenced by any eutectics since SiO_2 is the oxidation product of both phases.

In the temperature range of 400 to 600 °C, where $MoSi_2$ is liable to "pest", $MoSi_2$ 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.

$MoSi_2$ has a good chemical stability in contact with second phases. *Meschter* identified by calculations and experiments the $MoSi_2$ systems with SiC, TiB_2, and TiC being stable at 1600 °C whereas the system $MoSi_2$-Al_2O_3 is not [24]. At temperatures between 400 and 500 °C the oxidation resistance of the composites $MoSi_2/TiB_2$ and $MoSi_2/Al_2O_3$ was superior to that of pure $MoSi_2$. However, at high temperatures, when a 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, Si_3N_4, TiC, ZrC, HfC, TiB, TiB_2, ZrB_2, HfB_2, ZrO_2, and HfO_2 are stable in a $MoSi_2$ matrix between 1300 and 1900 K [26]. The $MoSi_2/Al_2O_3$ composite is stable up to 1800 K, however, high vapour pressures of Al_2O and SiO cause significant mass losses above 1800 K.

The thermal properties of $MoSi_2$ are said to be comparable to those of SiC and Si_3N_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, Y_2O_3 is stable in a $MoSi_2$ matrix. Cyclic oxidation at 1200 °C of $MoSi_2/TiB_2$ revealed higher oxidation rates than those of other intermetallics and superalloys, however, mass gains of $MoSi_2$ and $MoSi_2$/SiC under the same conditions were much lower [27].

Though oxidation decelerates after formation of a glassy scale on $MoSi_2$ with 20 mass-% TiB_2, the amount of B_2O_3 in this scale results in faster growth compared to the SiO_2 scale on pure $MoSi_2$, 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 $MoSi_2$ with 20 vol.-% Al_2O_3, HfO_2 or SiC, respectively, at 1500 °C by Kurokawa et al. [29], although dissolution of Al_2O_3 in SiO_2 lead to a liquid oxide at 1500 °C. A major degradation of the oxidation resistence was observed when the composite contained 20 vol.-% ZrO_2 due to formation of $ZrSiO_4$.

The pest phenomenon can be prevented when using composites with high density. $MoSi_2$/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 MoO_3 crystals, but a thin SiO_2 scale was found on 100% dense in-situ synthesised $MoSi_2$/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 SiO_2 or Mo_5Si_3 were present in the $MoSi_2$ matrix [32].

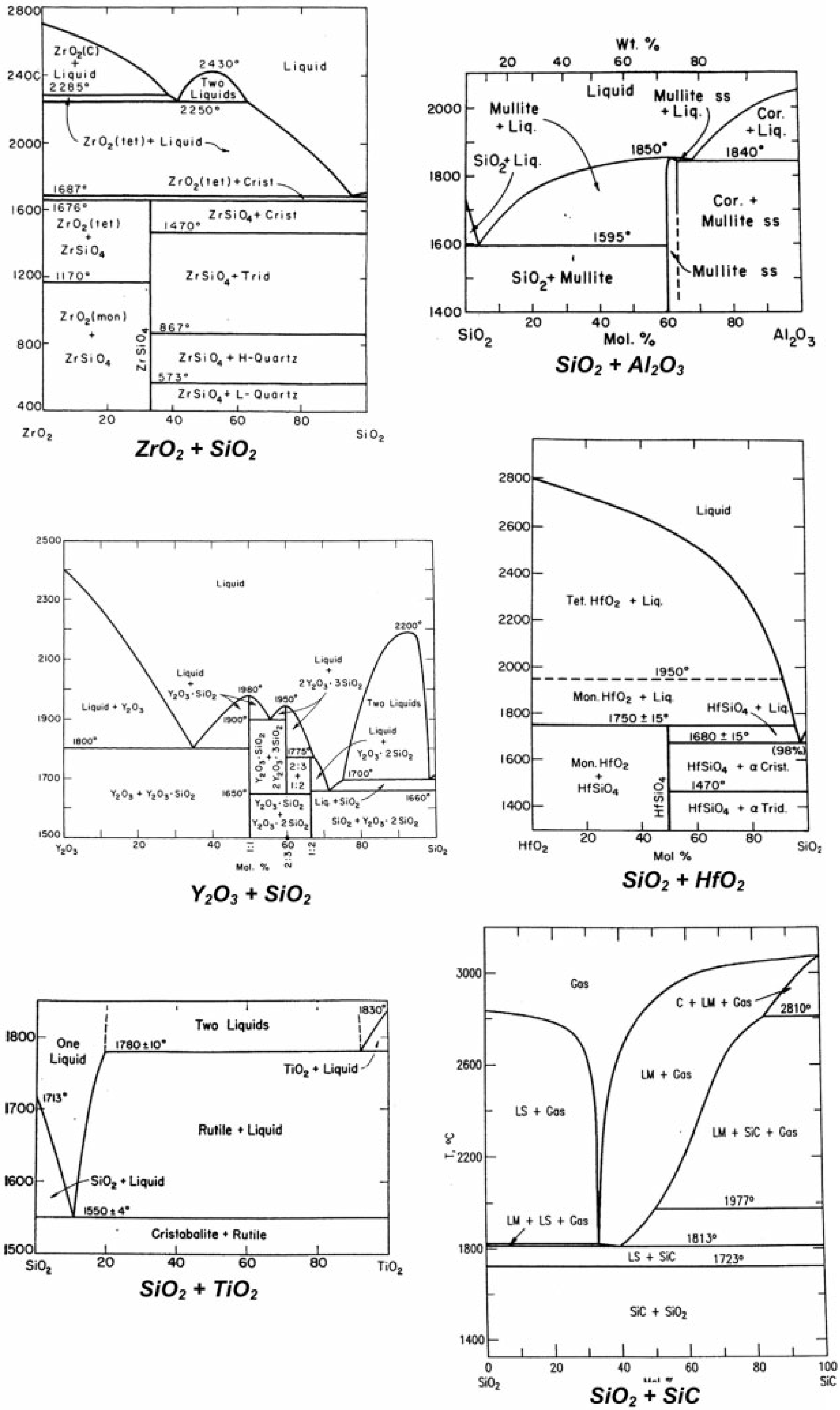

Fig. 1. Pseudo binary phase diagrams of silica and ZrO2, Al2O3, Y2O3, HfO2, TiO2, and SiC, respectively [23]

3 Conclusions of the literature survey

The literature review showed that data about the oxidation behaviour of $MoSi_2$ composites especially in the high temperature region are limited. Most data are available for the system $MoSi_2$/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_2 and the particle phases often decrease the maximum service temperature. Concluding from oxidation data in the literature the systems with SiC and HfO_2 appear to be most suitable for exposure at temperatures above 1500 °C. Concluding from the phase diagrams also $MoSi_2$-ZrO_2 could be an interesting system.
In the investigations reported here, along with these three composites those with 15 vol.-% Al_2O_3, Y_2O_3, TiB_2, ZrB_2, and HfO_2 were oxidised in air up to 1700 °C. The results are presented in the second part of this paper.

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