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Thermochemical modelling of interfacial reactions in molybdenum disilicide matrix composites

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The thermal and environmental stabilities of molybdenum disilicide have been evaluated using thermochemical modelling. The chemical reactivity of molybdenum disilicide with oxygen indicates that various molybdenum compounds and silica are formed, depending on oxygen pressures. The structure and properties of the silica films play an important role in the oxidation reaction and the reactions of water vapour (moisture) with molybdenum disilicide at high temperatures. The thermodynamic stabilities of various potential reinforcements, e.g. carbon, silicon carbide, silicon nitride, alumina, and some refractory compounds (borides, carbides, and oxides of titanium, zirconium and hafnium) in molybdenum disilicide matrix have been evaluated. Based on the results of thermochemical computations, SiC, Si_3N_4, TiC, ZrC, HfC, TiB, TiB_2, ZrB_2, HfB_2, ZrO_2 and HfO_2 were found to be stable, but carbon and TiO_2 were found to be unstable in $MoSi_2$. The $Al_2O_3/MoSi_2$ system was found to be stable below 1800 K. At temperatures above 1800 K, significant mass losses could occur due to the high vapour pressures of gaseous species (Al_2O, SiO). These thermodynamic predictions are in agreement with available experimental data.

1. Introduction

Intermetallic compounds based on silicides have interesting properties at elevated temperatures. Among these silicides, molybdenum disilicide is quite attractive owing to its high melting point (2283 K), low density, and good oxidation resistance. Berkowitz-Mattuk *et al.* [1–3] and Chang [4] have investigated the oxidation behaviour of molybdenum disilicide. At lower temperatures this material exhibits oxidative degradation called the "pest degradation". This phenomenon is affected by porosity and does not occur for dense materials. At higher temperatures, a self-healing protective silica layer is formed. This film yields usable lifetimes in excess of 2000 h at 1923 K. The stability of the protective layer also depends on the volatilization of the simultaneously formed molybdenum trioxide. It has been observed that the oxidation without the molybdenum trioxide volatilization causes fast intergranular oxidation with severe material damage. The extreme brittleness of molybdenum disilicide at room temperature has prevented its use as an elevated temperature structural material. Schlichting [5] reviewed the available data on the molybdenum silicides and reported some of the problems and their prospects for use as high-temperature structural materials. Umakoshi *et al.* [6] reported that in $MoSi_2$ single crystals, a brittle to ductile transition occurs around 1273 K.

It has been pointed out by various authors [7–12] that molybdenum disilicide matrix composites, reinforced with fibres or whiskers, have great potential for high-temperature and aerospace applications. In addition, toughening and strengthening of molybdenum disilicide have been achieved by silicon carbide, alumina, zirconia and titanium carbide reinforcements. Molybdenum disilicide matrix can also be alloyed with other refractory silicides to improve mechanical properties and oxidation resistance. But interfacial reactions between different constituents occurring under processing and/or operating conditions are of major concern in these composites.

In the present work, thermodynamic stabilities of some ceramic reinforcements, e.g. refractory metal (titanium, zirconium and hafnium) borides, carbides, and oxides, carbon, silicon carbide, silicon nitride, and alumina in molybdenum disilicide ($MoSi_2$) matrix have been evaluated. The environmental stability of molybdenum disilicide under different processing and application conditions is discussed. A detailed analysis of the chemical stabilities and interfacial reactions is required for the selection of thermodynamically stable and chemically compatible reinforcement/matrix combinations.

2. Alloying and reinforcement materials

Suitable reinforcements for molybdenum disilicide are required to improve its low-temperature toughness and high-temperature strength and creep resistance. In addition, some alloying elements/compounds are also desirable to improve the mechanical properties

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TABLE I Relevant physicochemical properties of some refractory silicides

Material	Melting point (K)	Density ($g cm^{-3}$)	CTE[a] ($10^6 °C^{-1}$)	Crystal structure
$MoSi_2$	2303	6.24	8.25	Tetragonal
WSi_2	2433	9.86	7.90	Tetragonal
$NbSi_2$	2203	5.66	11.7	Hexagonal
$TaSi_2$	2473	9.1	8.9	Hexagonal
Mo_5Si_3	2450	8.24	6.7	Tetragonal
W_5Si_3	2643	14.5	—	Tetragonal
Nb_5Si_3	2753	7.16	7.3 (along *a*) 4.6 (along *c*)	Tetragonal
Ta_5Si_3	2773	13.4	6.3 (along *a*) 6.6 (along *c*)	Tetragonal
Ti_5Si_3	2403	4.32	11.0	Hexagonal

[a] Coefficient of thermal expansion.

TABLE II Relevant physiochemical properties of some potential ceramic reinforcement

Material	Melting point (K)	Density ($g cm^{-3}$)	Crystal structure
C	3925	2.25	Cubic
SiC	3100	3.21	Hexagonal
Si_3N_4	2173	3.19	Cubic
Al_2O_3	2318	3.97	Cubic
TiC	3413	4.9	Cubic
ZrC	3693	6.7	Cubic
HfC	4173	12.6	Cubic
TiB	2453	5.09	Orthorhombic
TiB_2	3253	4.5	Hexagonal
ZrB_2	3373	6.1	Hexagonal
HfB_2	3523	10.5	Hexagonal
TiO_2	2109	4.17	Tetragonal
ZrO_2	2973	6.0	Cubic
HfO_2	3031	10.0	Cubic

and oxidation resistance. Some relevant physicochemical properties of selected refractory silicides, which may be useful for the alloying of molybdenum disilicide matrix, are given in Table I. Some of these silicides (Table I) also have great potential as high-temperature matrices. The corresponding properties of potential ceramic reinforcements are given in Table II.

3. Thermochemical considerations

A critical aspect in the thermochemical modelling is the identification of possible product compounds and the reliability of available thermodynamic data. Owing to the lack of thermodynamic data for ternary and higher order phases of these materials, only binary compounds are considered here. Thermodynamic data for binary compounds have been taken from Barin and Knacke [12] and JANAF [13] tables. The temperature range considered for the environmental stability is 1000–1900 K and for the chemical compatibility computations is 1300–1900 K.

4. Results and discussion

4.1. Thermal and environmental stability

The thermal decomposition of molybdenum disilicide has been investigated by Blair *et al.* [14]. The decomposition and vaporization under vacuum conditions at high temperatures (1800–2500 K) proceeds with formation of the following intermediate phases: $MoSi_2 \rightarrow Mo_5Si_3 \rightarrow Mo_3Si \rightarrow Mo$. The equilibrium vaporization reaction is given by

$$MoSi_2(s) = Mo(s) + 2\,Si(g) \qquad (1)$$

The partial pressures of silicon for Reaction 1 at 1900 and 2100 K are 0.33×10^{-6} and 0.69×10^{-5} atm, respectively. These data indicate that at temperatures around 2100 K and under vacuum conditions, mass losses of molybdenum disilicide can occur as a result of Reaction 1.

In addition, molybdenum disilicide reacts with oxygen and moisture. The oxidation processes of this material may proceed by three different mechanisms, namely, selective oxidation of the metal component, selective oxidation of silicon, and total oxidation. The chemical reactions of molybdenum disilicide with oxygen leading to silicon monoxide and other compounds (Reactions 4–8), the so-called "active" oxidation, considered are as follows:

$$MoSi_2(s) + O_2(g) = MoO_2(s) + 2\,Si(s) \qquad (2)$$

$$MoSi_2(s) + 3/2\,O_2(g) = MoO_3(l,g) + 2Si(s) \qquad (3)$$

$$MoSi_2(s) + O_2(g) = Mo(s) + 2SiO(g) \qquad (4)$$

$$MoSi_2(s) + 5/6\,O_2(g) = 1/3\,Mo_3Si(s) + 5/3\,SiO(g) \qquad (5)$$

$$MoSi_2(s) + 7/10\,O_2(g) = 1/5\,Mo_5Si_3(s) + 7/5\,SiO(g) \qquad (6)$$

$$MoSi_2(s) + 5/2\,O_2(g) = MoO_3(l,g) + 2SiO(g) \qquad (7)$$

$$MoSi_2(s) + 2\,O_2(g) = MoO_2(s) + 2\,SiO(g) \qquad (8)$$

A plot of the silicon monoxide partial pressures, P_{SiO}, versus temperature is given in Fig. 1. From Fig. 1 it is seen that the silicon monoxide pressures of Reactions 7 and 8 leading to the formation of metal oxides are many orders of magnitude higher than those of the other reactions where selective oxidation of silicon takes place (Reactions 4–6). The formation of the molybdenum oxides shifts the equilibrium of Reactions 7 and 8 more towards the products. In all cases, an oxygen partial pressure of 0.2 atm has been used in these computations.

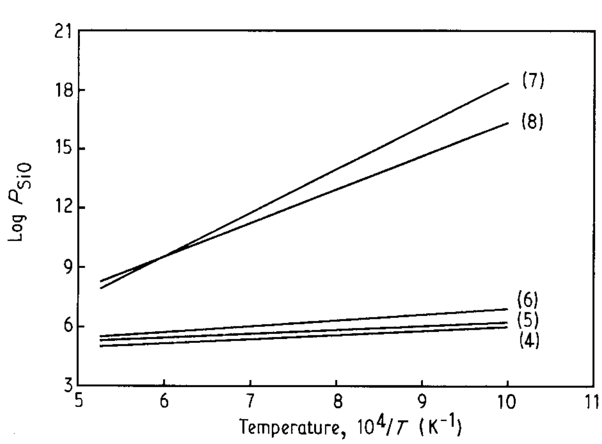

Figure 1 Partial pressures of silicon monoxide due to Reactions 4–8 (P_{O_2} = 0.2 atm) as a function of temperature.

Other oxidation reactions, the so-called "passive" oxidation, in which silica and different molybdenum compounds are formed, are the following:

$$MoSi_2(s) + 2\,O_2(g) = Mo(s) + 2\,SiO_2(s) \qquad (9)$$

$$MoSi_2(s) + 5/3\,O_2(g) = 1/3Mo_3Si(s) + 5/3\,SiO_2(s) \qquad (10)$$

$$MoSi_2(s) + 7/5\,O_2(g) = 1/5\,Mo_5Si_3(s) + 7/5\,SiO_2(s) \qquad (11)$$

$$MoSi_2(s) + 7/2\,O_2(g) = MoO_3(l,g) + 2\,SiO_2(s) \qquad (12)$$

$$MoSi_2(s) + 3O_2(g) = MoO_2(s) + 2\,SiO_2(s) \qquad (13)$$

The equilibrium oxygen pressures for the oxidation of $MoSi_2$ to various molybdenum-containing compounds and SiO_2 are given in Fig. 2. At a given temperature, the dominant reaction is determined by the oxygen partial pressure. Experimental observations by various authors [1–5] indicate that the growth of silica layers in $MoSi_2$ is determined by the rate of diffusion of silicon from the reaction interface through the lower silicide, and by the diffusion of the reacting species through the oxide layers where the formation of new layers of SiO_2 occurs. The state of the SiO_2 layer is decisive for the progress of these reactions. The results in Fig. 2 are consistent with the above observations.

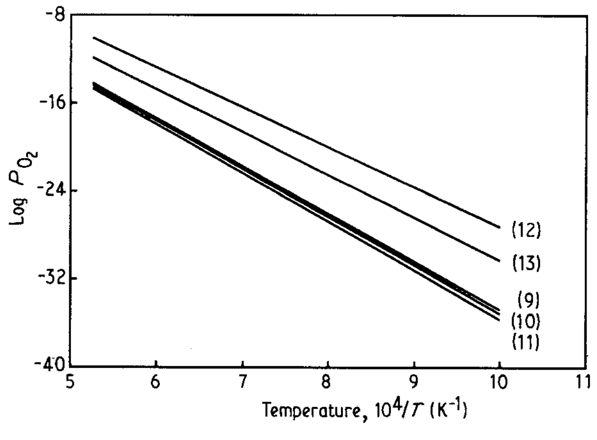

Figure 2 Equilibrium partial pressures of oxygen for Reactions 9–13 as a function of temperature.

The chemical stability and the oxidation behaviour of molybdenum disilicide in water vapour has been investigated by Nechiporenko *et al.* [15] in the temperature range 1273–1873 K. According to these authors the rate of oxidation follows a parabolic law and silica is the reaction product. The following reactions are considered:

$$MoSi_2(s) + 5\,H_2O(g) = MoO_3(l,g) + 2\,SiO(g) + 5\,H_2(g) \qquad (14)$$

$$MoSi_2(s) + 7/5\,H_2O(g) = 1/5\,Mo_5Si_3(s) + 7/5\,SiO(g) + 7/5\,H_2(g) \qquad (15)$$

$$MoSi_2(s) + 7\,H_2O(g) = MoO_3(l,g) + 2\,SiO_2(s) + 7\,H_2(g) \qquad (16)$$

$$MoSi_2(s) + 14/5\,H_2O(g) = 1/5\,Mo_5Si_3(s) + 7/5\,SiO_2(s) + 14/5\,H_2(g) \qquad (17)$$

A plot of the total pressures of the product gaseous species of the above reactions versus temperature at P_{H_2O} = 10 atm, is given in Fig. 3. The hydrogen partial pressures for the reactions leading to the formation of SiO_2 (Reactions 16 and 17) are a few orders of magnitude higher than the total product pressures for Reactions 14 and 15. These two sets of reactions have opposite trends. In Reactions 14 and 15 the sum of the partial pressures of the product species increases with increasing temperature. On the other hand, for Reactions 16 and 17, the sum of the partial pressures decrease with increasing temperature which is due to the reverse reaction of the solid oxide products with hydrogen at higher temperatures. Experimental investigations [15] suggest that the formation of an oxide film is mainly due to Reaction 16. The MoO_3 has a very high vapour pressure at 1100 K and vaporizes leaving behind an SiO_2 film. In addition, other reactions also take place by diffusion of reacting species through the silica layer and with formation of lower silicides. The properties of the oxide films play an important role in the reaction of molybdenum disilicide with water vapour.

As discussed earlier, in a number of oxidation reactions of $MoSi_2$, silica and lower molybdenum silicides are formed. These molybdenum silicides react with

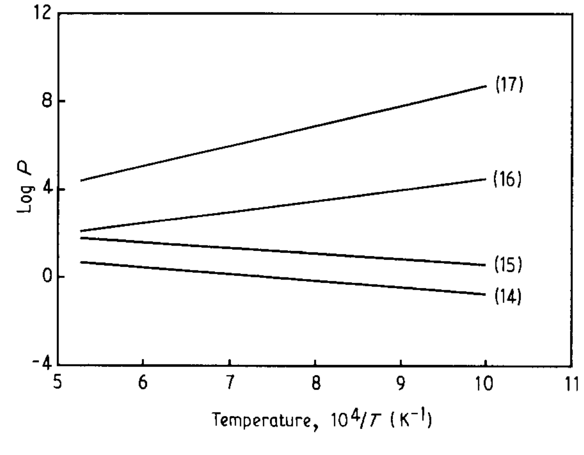

Figure 3 The sum of the equilibrium partial pressures of the product gaseous species at P_{H_2O} = 10 atm of Reactions 14–17 as a function of temperature.

silica at higher temperatures according to the following reactions:

$$Mo_3Si(s) + SiO_2(s) = 3\,Mo(s) + 2\,SiO(g) \quad (18)$$

$$Mo_5Si_3(s) + 4/3\,SiO_2(s) = 5/3\,Mo_3Si(s) + 8/3\,SiO(g) \quad (19)$$

$$MoSi_2(s) + 7/5\,SiO_2(s) = 1/5\,Mo_5Si_3(s) + 14/5\,SiO(g) \quad (20)$$

A plot of the silicon monoxide partial pressures versus temperature is given in Fig. 4. The silicon monoxide partial pressure increases as the metal to silicon ratio of the reactant Mo_xSi_y component decreases. The results in Fig. 4 indicate that at higher temperatures considerable mass losses via SiO(g) vaporization may occur for the above reactions.

4.2. Chemical compatibility

One of the requirements for the use of reinforcing phases for high-temperature composites is that, ideally, they should coexist with the matrices. The protective coatings on the reactive reinforcements may not be very useful at higher temperatures. Thermochemical computations of the compatibility of various reinforcements in molybdenum disilicide are presented in the following sections.

The chemical reactions of carbon, silicon carbide and silicon nitride with molybdenum disilicide considered are

$$C(s) + 1/2\,MoSi_2(s) = Mo(s) + SiC(s) \quad (21)$$

$$SiC(s) + 2\,MoSi_2(s) = Mo_2C(s) + 5\,Si(s) \quad (22)$$

$$Si_3N_4(s) + 8\,MoSi_2(s) = 4\,Mo_2N(s) + 19\,Si(s) \quad (23)$$

The Gibbs free energy change, $\Delta G°$, for Reaction 21 is -6.9 kcal mol^{-1} at 1300 K and -11.5 kcal mol^{-1} at 1900 K. These data indicate that the $C/MoSi_2$ system is reactive. On the other hand, the chemical reactions of silicon carbide and silicon nitride with molybdenum disilicide (Reactions 22 and 23) have Gibbs free energy changes, $\Delta G°$, of 64.4 and 326.3 kcal mol^{-1} at 1300 K and 52.1 and 263.1 kcal-mol^{-1} at 1900 K, respectively. These data indicate that silicon carbide and silicon nitride are stable with molybdenum disilicide in the temperature range 1300–1900 K.

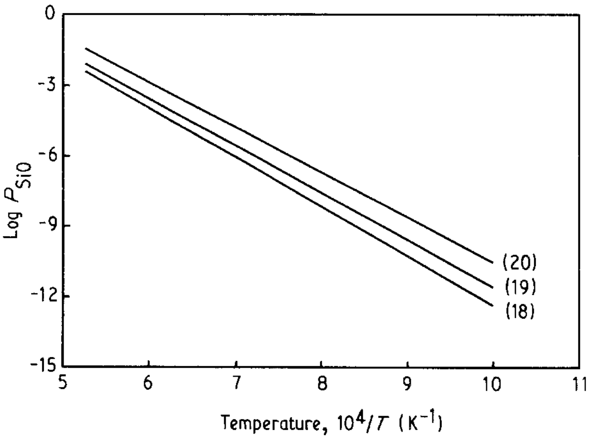

Figure 4 Partial pressures of silicon monoxide of Reactions 18–20 as a function of temperature.

The chemical reaction of alumina with molybdenum disilicide is

$$Al_2O_3(s) + 10/7\,MoSi_2(s) = 2\,SiO(g) + Al_2O(g) + 2/7\,Mo_5Si_3(s) \quad (24)$$

The $\Delta G°$ values for the above reaction are 165.5 kcal mol^{-1} at 1300 and 91.6 kcal mol^{-1} at 1900 K. The partial pressures of gaseous species (Al_2O and SiO), reach critical limits (about 10^{-4} atm) at 1800 K. Thus, the $Al_2O_3/MoSi_2$ system could loose appreciable amounts of silicon and aluminium above 1800 K according to Reaction 24.

Using the same approach, chemical reactivities of other potential reinforcements with molybdenum disilicide have been computed. The thermodynamically stable reinforcements in molybdenum disilicide matrix are TiB, TiB_2, ZrB_2, HfB_2, TiC, ZrC, HfC, ZrO_2 and HfO_2. An unstable reinforcement is TiO_2.

5. Conclusions

Thermochemical data indicate that molybdenum disilicide reacts with oxygen and water vapour at high temperatures. In "active" oxidation processes, silicon monoxide pressures of the reactions including also the formation of metal oxides are many orders of magnitude higher than those of other reactions. The "passive" oxidation reactions are controlled by the state of the silica layer and the oxygen partial pressures. The structure and properties of the silica films play an important role in the reactions of molybdenum disilicide with water vapour. In addition, molybdenum silicides (Mo_3Si, Mo_5Si_3 and $MoSi_2$) also react with silica at higher temperatures. Thermodynamic stabilities of various ceramic reinforcements in molybdenum disilicide matrices have been computed in the temperature range 1300–1900 K. Based on these results, compatible reinforcements are SiC, Si_3N_4, TiC, ZrC, HfC, TiB, TiB_2, ZrB_2, HfB_2, ZrO_2 and HfO_2. On the other hand, carbon and TiO_2 are reactive. The $MoSi_2/Al_2O_3$ system is stable below 1800 K. At temperatures above 1800 K, significant mass losses could occur due to the high vapour pressures of gaseous species.

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