Oxidation of MoSi$_2$ and MoSi$_2$-based materials

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Abstract. Oxidation experiments, at 500CC, of MoSi$_z$ and MoSi2-based compounds such as Mo(A1,Si)$_2$ and MoSi$_z$ + I wt% C compacts have been carried out. These compacts were prepared by in situ synthesis and a compaction method, starting from the elemental powders. For comparison, commercial MoSi$_z$ and Mo(AI,Si)$_2$ ¡nfiltrated into SiC preform were also studied under similar conditions. It was found that the synthesized high density MoSi$_2$ and Mo(AI,Si)$_2$ infiltrated into SiC preform did not show any oxidation even after 100 h of heating in air. The colour of the polished surfaces of commercial MoSi$_2$, Mo(AI,Si)$_2$ and MoSi$_z$ + 1 wt% C had changed. The SEM of Mo(At,Si)$_2$ showed open blisters with rods of MoO$_3$ in them whereas MoSi$_z$ + I wt% C surface had MoO3 rods but no blisters and the oxidation was superficial with no penetration into the compact. It is suggested that in compounds, the presence of small amounts of impurities is not as detrimental to pesting as presence of defects like open pores or cracks. Hence, high density of the compact is essential for the prevention of complete disintegration of the compact.

Keywords. Molybdenum disilicide; oxidation; "PEST"ing; defects; hardness.

1. Introduction

MoSi$_2$ intermetallic compound is one of the candidate materials for high temperature applications because of its moderate density (6·3 g/cc), high melting point of 2030 C, and its excellent oxidation resistance at high temperatures. However, the low temperature brittleness and low creep strength at high temperatures are hindering the use of MoSi$_2$ as a high temperature structural material. In order to improve these properties, MoSi$_2$ composites are being developed since MoSi$_2$ forms thermodynamically stable composites with many other intermetallic materials. Thus, composites of MoSi$_2$ with SiC, TiB$_2$, Si$_3$N$_4$, ZrB$_2$, etc have been prepared and studied (Aikin Jr 1991; Bhattacharya and Petrovic 1991; Henager Jr et al 1992; Tiwari 1992).

MoSi$_2$ has a high resistance to oxidation at high temperatures. Oxidation in MoSi$_2$ proceeds according to the reactions (Cook et al 1992),

$$2MoSi_2 + 7O_2 \rightarrow 2MoO_3 + 4SiO_2, \qquad (1)$$

$$5MoSi_2 + 7O_2 \rightarrow Mo_5Si_3 + 7SiO_2. \qquad (2)$$
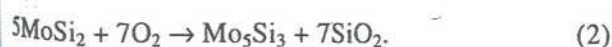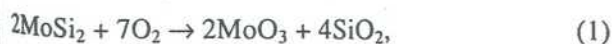
In air, the reaction, (1), occurs at temperatures lower than 500°C, and the reaction, (2), prevails at higher temperatures. At temperatures higher than 750°C, MoO$_3$

volatilizes leaving behind a layer of SiO$_2$ on the surface of MoSi$_2$ which effectively prevents diffusion of oxygen to attack the MoSi$_2$ underneath. However, at low temperatures below 700°C MoO$_3$ does not volatilize and the oxide layer is highly porous, providing an easy passage for oxygen diffusion. In more severe cases, oxidation results in complete disintegration of a compact into powdery products, which is termed as "PEST"ing.

Controlling pesting has been the topic of many investigations (Berztiss 1992; Cook et al 1992; Meschter 1992; Chou and Nieh 1993, 1994; Hebsur 1994). The pesting is reportedly most prominent at 500°C in air. It is found also that controlling defects like pores, microcracks and intergranular boundaries reduced pesting to a large extent as pesting has been attributed to the accelerated formation of voluminous MoO$_3$ in microcracks. Hence pesting should not occur in a dense compact of MoSi$_2$. However, there are reports to the contrary (Chou and Nieh 1994). Chou and Nieh (1993), from their experiments on MoSi$_2$–AlN and MoSi$_2$–Al$_2$O$_3$ composites have found that foreign additives have an effect on the kinetics of the pest disintegration. On the other hand, MoSi$_2$ + 20 vol% SiC compacts prepared by hot pressing and with high density do not show disintegration even after heating for 250 h at 500°C, though the regions close to interfaces and grain boundaries are oxidized preferentially. Also, the oxidation properties of Mo$_5$Si$_3$ were found to improve with the addition of boron. Yanagihara et al (1996) studied effects of ternary elements on pesting, and showed that the third elements with higher affinity to oxygen than silicon

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effectively prevented pest disintegration. Additives or the third element, however, would have significant influence not only on the oxidation mechanism but also on densification and pre-existing defects in the material.

Most of the samples which have been used to study the pesting phenomenon have been either prepared by the arc melting or hot pressing of the commercial $MoSi_2$ which have inherent defects and impurities. Also, the oxidation rate of $MoSi_2$ increases with increasing temperature with a maximum at 500°C and decreases again with further increase in temperature (Maruyama and Yanagihara 1997). In this communication, we present the oxidation studies at 500°C on more dense samples of $MoSi_2$ prepared by high temperature *in situ* synthesis and compaction technique, together with some other $MoSi_2$-based composites. Our result implies again that dense compact of $MoSi_2$ does not show a problem of pest disintegration.

2. Experimental

$MoSi_2$ was synthesized by direct reaction between Mo and Si powders. The Mo powder of average particle size 1·30 μ (Japan New Metals, purity 99·94%) and Si powder of less than 44 μ particle size (Toyo Kinzoku Fun, Japan, purity 99·9%) were used. The powders of Mo and Si were mixed in alcohol in the required ratio in a ball mill and dried. The mixture was packed in a graphite die (12 mm i.d.) and hot-pressed in 1 atm. argon under a die pressure of 20 MPa. In the first routine, the mixture was heated to 1500°C, held for 10 min for the completion of the reaction and then pressure was applied before raising the temperature to 1800°C for sintering for 15 min. In the second routine pressure was applied on the mixture at room temperature, heated directly to 1800 C and sintered for 15 min. For comparison commercial $MoSi_2$ powder of average particle size 2·93 μ (Japan New Metals) was also compacted at 1700°C for 15 min (for this material compacting at 1700°C is sufficient to get high density).

$MoSi_{1.5}Al_{0.5}$ was synthesized *in situ* and compacted from a mixture of elemental Mo, Si and Al (17·33 μ average, Toyo Aluminum, Japan, purity 99%) at 1700°C for 15 min. $MoSi_2 + 1$ wt% C was also prepared following the same routine from elemental mixture using carbon powder of 0·02 μ (carbon black, Mitsubishi Chemical Industries Ltd., Japan). $Mo(Al,Si)_2$ infiltrated SiC samples were prepared as described elsewhere (Shobu *et al* 1996).

The pellets obtained were cut into half, and the cut surface was polished with diamond paste of 1 μ and observed by SEM equipped with EDX (JEOL JSM-6400 scanning microscope). Vicker's hardness measurements were made on the polished surface of the compacts using a Shimadzu hardness tester. Loads of 1, 5, 10 and 20 kg and an indentation time of 15 s were used.

Pesting experiments were done on rectangular samples cut from the above compacts, where surfaces were polished with 1 μ diamond paste. Samples were heated in air at 500°C for 100 h. The temperature was controlled within ± 2°C. The oxide surfaces of the samples were then examined with SEM.

3. Results and discussion

The $MoSi_2$ compacts prepared by the first routine invariably broke while polishing and had a large void at the body centre of the pellet. This is due to the volumetric shrinkage upon reaction of as much as 40%, so that the resultant product is highly porous. Application of uniaxial pressure of 20 MPa later while sintering is not enough to eliminate the porosity in the compact. On the other hand samples prepared under a load seem to be compacting to almost full density. During the formation of $MoSi_2$ from Mo and Si, silicon melts and molybdenum dissolves into it followed by $MoSi_2$ precipitation (Jo *et al* 1996). Thus the continuous application of pressure during synthesis helps full compaction.

The SEM micrographs of these samples are shown in figure 1. The *in situ* synthesized and compacted $MoSi_2$ samples (will be called Mo + 2Si from now on) has dark spots in the microstructure which could be amorphous SiO_2, as EDX revealed Si present in the dark phase while the XRD examination revealed only single-phase tetragonal $MoSi_2$. Even though the elemental Mo and Si were mixed in the required proportion, the commercially available elements would be covered by a thin layer of their oxides. MoO_3 volatilizes during processing whereas silica remains in the product. The SEM of the compact made from commercial $MoSi_2$ powder contains many such silica spots. The $Mo(Al,Si)_2$ has islands of Mo_5Si_3 (lighter colour) distributed uniformly throughout the sample in addition to the silica spots. The $MoSi_2 + 1$ wt% C also contains many dark spots and brighter phase, which could be β-SiC and hexagonal Mo_5Si_3C as found in the XRD pattern of the sample. $Mo(Al,Si)_2$ infiltrated SiC has α SiC in hexagonal $Mo(Al,Si)_2$ matrix. The amount of SiC in the composite is about 70 vol%. For all the samples the relative densities were more than 95%.

The Vicker's hardness is in the range of 9·2–9·9 GPa for Mo + 2Si. The hardnesses of the commercial $MoSi_2$ and $Mo(Al,Si)_2$ compacts are marginally lower and that of $MoSi_2 + 1$ wt% C higher. $Mo(Al,Si)_2$ infiltrated SiC has a rather high hardness, in the range of 17·4–19 GPa. This higher value could be due to the presence of SiC.

The samples after the oxidation test in air were examined under an optical microscope. None of the sample pieces disintegrated and crumbled into smaller bits even after 100 h oxidation at 500°C in accordance with the previous report (Meschter 1992) on high density specimens. The Mo + 2Si and the $Mo(Al,Si)_2$ infiltrate
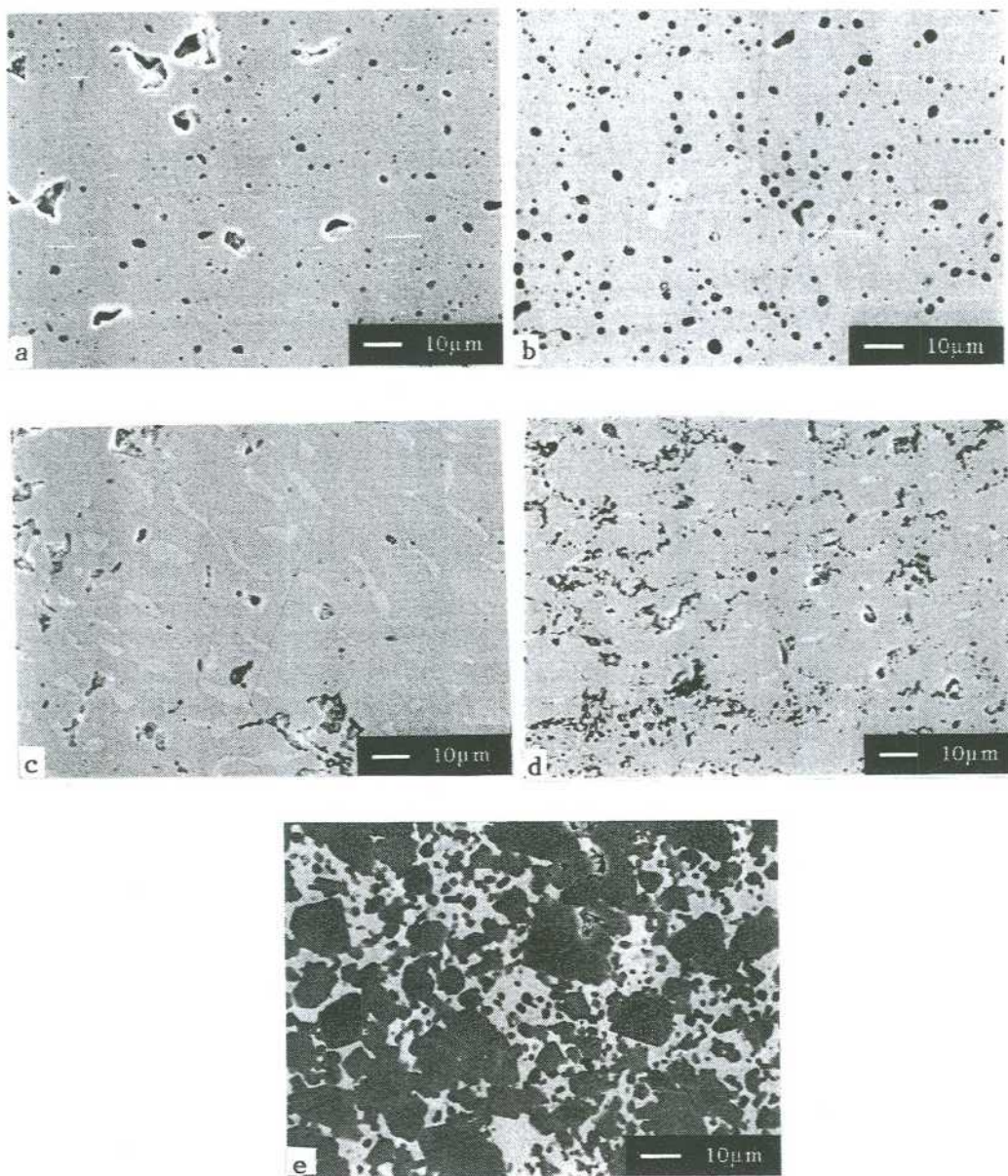
Figure 1. SEM of (**a**) Mo + 2 Si, the darker spots due to silica, (**b**) commercial MoSi₂, more of darker silica spots, (**c**) Mo(Al,Si)₂, the lighter islands of Mo₅Si₃ and darker silica spots, (**d**) MoSi₂ + 1 wt% C, the lighter islands are due to Mo₅Si₃C and darker spots of SiC and (**e**) Mo(Al,Si)₂ infiltrated SiC, the darker phase is SiC while the lighter is Mo(Al,Si)₂.

samples did not show any change whereas the commercial MoSi₂ sample had a layer of slightly off-white coloured powder on the surface. MoSi₂ + 1 wt% C and Mo(Al,Si)₂ specimens were covered with a deeper ash green layer.

The SEM micrographs of the oxidized samples are shown in figure 2. The SEM micrograph of the Mo + 2Si sample taken at the edge of the polished surface also shows the fractured surface. There is no indication of MoO₃ or more silica spots than before the oxidation experiment. The commercial MoSi₂ had a layer of oxide nearly covering the surface (which could be dusted), the SEM micrograph showed long needle like MoO₃ on the oxidized surface. However, Mo(Al,Si)₂ had many opened

blisters and SiO₂ on the surface. MoSi₂ + 1 wt% C had only MoO₃ whiskers and no blisters on the surface.

Berztiss *et al* (1992) reported that the arc-melted MoSi₂ disintegrated to powder at 500°C in 43 h whereas in the HIPed MoSi₂ cracks started appearing on the surface in 41 h. It was speculated that the initial cracks and pores were the sites of internal oxidation which in turn was responsible for the disintegration. Chou and Nieh (1993) found severe pesting in their hot pressed commercial MoSi₂ with 90% density in 21 h at 500°C. The arc melted samples inherently contain many cracks and pores, which would enhance the pesting process. The hot pressed MoSi₂ used by Chou and Nieh (1993, 1994) contained Mo₅Si₃ and SiO₂ as impurity. The Mo + 2Si and
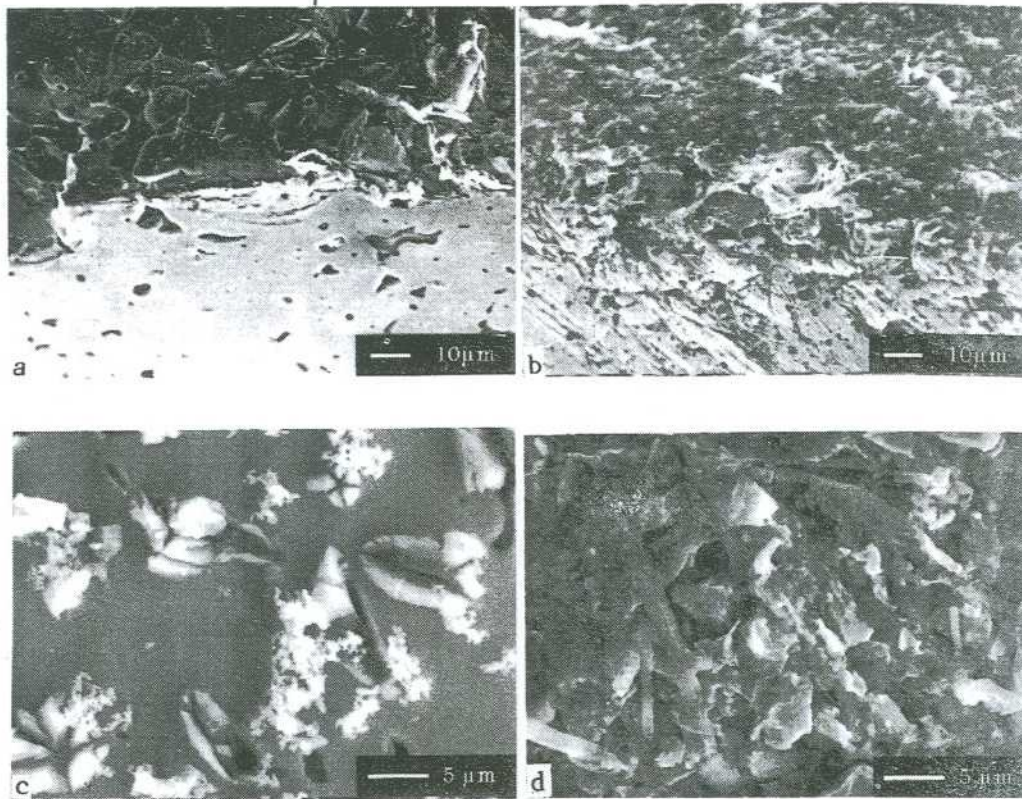
Figure 2. SEM of oxidized samples (a) Mo + 2 Si showing the polished as well as the fractured surfaces, (b) commercial MoSi$_2$, (c) Mo(Al,Si)$_2$ showing the open blisters and MoO$_3$ rods in them and (d) MoSi$_2$ + 1 wt% C displaying MoO$_3$ rods.

Mo(Al,Si)$_2$ infiltrated SiC compacts in the present study are almost fully dense and also do not contain any impurity other than SiO$_2$ (as seen from XRD and SEM). Thus, there is no pesting, cracking or surface oxidation even after 100 h in air at 500°C. The commercial MoSi$_2$ did show surface oxidation but no catastrophic disintegration.

If grain boundaries are the sites for oxide formation that leads to pesting failure, then the disintegration has to be more in hot pressed samples as the area of grain boundaries per unit volume is higher than in arc melted sample. Maruyama and Yanagihara (1997) observed that in the cross-section of the oxidized samples, one grain had much oxide whereas the neighbouring one did not have any at all, which would indicate that the grain boundary is not the site of internal oxidation leading to disintegration. The disintegration would occur due to the oxide formation in the pre-existing defects. The volumetric change associated with the reaction, (1), is more than double, so that the oxide formation opens and extends the cracks. The complete disintegration into powdery products, however, must need sufficient amounts of such defects, or continuous nucleation of them. In this sense, open pores seem to be the most likely sites that are responsible for such disintegration. In order to prevent complete disintegration, then, density must be more than 95% to have pores closed.

The oxidation in Mo(Al,Si)$_2$ and MoSi$_2$ + 1% C samples is much more than in the other samples. The colour of the polished surface had visibly changed. In Mo(Al,Si)$_2$, the blisters, which were burst open, were surrounded by smooth surface which was not affected by oxidation in Mo(Al,Si)$_2$. The open blisters contained MoO$_3$ rods in them though the surface of the blister was still Mo(Al,Si)$_2$ implying that there is no oxidation of Mo(Al,Si)$_2$. Maruyama and Yanagihara (1997), in their experiments, have also observed that oxidation of the samples is considerably reduced by the addition of aluminium. Since the polished surface of the sample contained islands of Mo$_5$Si$_3$ before and no such islands were present after the pesting experiments, it looks as though the Mo$_5$Si$_3$ has preferentially reacted with the oxygen (Meyer and Akinc 1996; Mitra et al 1997).

Mo$_5$Si$_3$ would oxidize according to the following reaction (Meyer and Akinc 1996),

$$2Mo_5Si_3 + 21\ O_2 \rightarrow 10MoO_3 + 6SiO_2.$$

The volumetric change associated is almost triple in this case. When the compacts contain large amounts Mo$_5$Si$_3$, preferential oxidation of Mo$_5$Si$_3$ will result more severe pesting and disintegration as Mo$_5$Si$_3$ known to have a poor oxidation resistance than Mo (Meyer and Akinc 1996). Similar observation has be

made by Mitra *et al* (1997) in the oxidation experiments on $MoSi_2$ + 20 vol% SiC. However, as described by Chou and Nieh (1993), vapour pressure of MoO_3 is far insufficient to explain the blister formation. They, therefore, suggested that water vapour existing in the furnace may be one of the sources. In the present study, however, blisters were observed only in the case of $Mo(Al,Si)_2$ oxidation, so that water vapour in the furnace seems to have little relevance to the blister formation. Vapourization of oxide of some minor unidentified impurity, which would be in the Al raw powder, may be another possibility.

The absence of blisters on the surface of $MoSi_2$ + 1 wt% C sample even though MoO_3 rods were present is interesting. It is possible that the passage of oxygen through Mo_5Si_3C is more difficult than through Mo_5Si_3. Hence blisters do not form underneath the top surface to burst. Mo_5Si_3C on the surface reacts with oxygen as,

$$2Mo_5Si_3C + 23O_2 \rightarrow 10MoO_3 + 6SiO_2 + 2CO_2, \quad (4)$$

leaving behind MoO_3, which are seen in the SEM.

The SEM of the fractured surface in all the above samples did not show any indication of oxidation inside the body. Even in the severely oxidized $Mo(Al,Si)_2$ and $MoSi_2$ + 1% C samples the oxidation was very superficial indicating that the oxidation has not penetrated deeper into the compact. Hence the high density of the compacts has prevented the oxygen from diffusing into the compact and thereby leading to disintegration of the compact even though there were small amounts of impurities. The pesting requires oxide penetration of pores and cracks and is not predominantly a grain boundary oxidation effect (Westbrook and Wood 1964). Thus, pesting in $MoSi_2$ containing impurities could be controlled with the full densification of the compact in the absence of external stress.

In conclusion, oxidation tests on $MoSi_2$, $Mo(Al,Si)_2$ and $MoSi_2$ + 1 wt% C samples, prepared by the *in situ* synthesis and compaction technique, are done. The $MoSi_2$ did not show any visible oxide formation on the surface even after 100 h at 500°C in air. For comparison commercially available $MoSi_2$ was also hot pressed and oxidation tests were done. A layer of oxide was found on

the surface. $Mo(Al,Si)_2$ surface had many opened blisters containing MoO_3 in them and $MoSi_2$ + 1 wt% C had no blisters on the surface. $Mo(Al,Si)_2$–SiC composite, prepared by the melt infiltration, was also studied and no detectable oxidation of the surface was found. The cut and fractured surfaces did not show any penetration of the oxide into the bulk of the compact and thus providing evidence to the hypothesis that presence of small amounts of impurities is not as detrimental for the catastrophic failure of a compact as presence of defects like cracks and pores. The pesting would not be the critical problem of $MoSi_2$ material when the density is sufficiently high (> 95%) and amount of Mo_5Si_3 is sufficiently low.

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