

Oxidation of MoSi₂ and MoSi₂-based materials

SHEELA K RAMASESHA* and K SHOBU†

Materials Science Division, National Aerospace Laboratories, Bangalore 560 017, India

†Kyushu National Industrial Research Institute, Tosu, Saga 841, Japan

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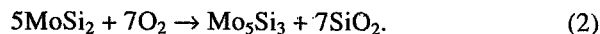
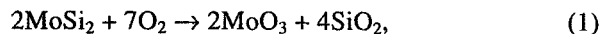
Abstract. Oxidation experiments, at 500°C, of MoSi₂ and MoSi₂-based compounds such as Mo(Al,Si)₂ and MoSi₂ + 1 wt% C compacts have been carried out. These compacts were prepared by *in situ* synthesis and a compaction method, starting from the elemental powders. For comparison, commercial MoSi₂ and Mo(Al,Si)₂ infiltrated into SiC preform were also studied under similar conditions. It was found that the synthesized high density MoSi₂ and Mo(Al,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 MoSi₂, Mo(Al,Si)₂ and MoSi₂ + 1 wt% C had changed. The SEM of Mo(Al,Si)₂ showed open blisters with rods of MoO₃ in them whereas MoSi₂ + 1 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

MoSi₂ 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 MoSi₂ as a high temperature structural material. In order to improve these properties, MoSi₂ composites are being developed since MoSi₂ forms thermodynamically stable composites with many other intermetallic materials. Thus, composites of MoSi₂ with SiC, TiB₂, Si₃N₄, ZrB₂, etc have been prepared and studied (Aikin Jr 1991; Bhattacharya and Petrovic 1991; Henager Jr *et al* 1992; Tiwari 1992).

MoSi₂ has a high resistance to oxidation at high temperatures. Oxidation in MoSi₂ proceeds according to the reactions (Cook *et al* 1992),



In air, the reaction, (1), occurs at temperatures lower than 1000°C, and the reaction, (2), prevails at higher temperatures. At temperatures higher than 750°C, MoO₃

volatilizes leaving behind a layer of SiO₂ on the surface of MoSi₂ which effectively prevents diffusion of oxygen to attack the MoSi₂ underneath. However, at low temperatures below 700°C MoO₃ 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 (Bertziss 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 MoO₃ in microcracks. Hence pesting should not occur in a dense compact of MoSi₂. However, there are reports to the contrary (Chou and Nieh 1994). Chou and Nieh (1993), from their experiments on MoSi₂-AlN and MoSi₂-Al₂O₃ composites have found that foreign additives have an effect on the kinetics of the pest disintegration. On the other hand, MoSi₂ + 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 Mo₅Si₃ 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

*Author for correspondence

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 $1.30\ \mu$ (Japan New Metals, purity 99.94%) and Si powder of less than $44\ \mu$ 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 $2.93\ \mu$ (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).

$\text{MoSi}_{1.5}\text{Al}_{0.5}$ was synthesized *in situ* and compacted from a mixture of elemental Mo, Si and Al ($17.33\ \mu$ average, Toyo Aluminum, Japan, purity 99%) at 1700°C for 15 min. $\text{MoSi}_2 + 1\ \text{wt}\% \text{C}$ was also prepared following the same routine from elemental mixture using carbon powder of $0.02\ \mu$ (carbon black, Mitsubishi Chemical Industries Ltd., Japan). $\text{Mo}(\text{Al},\text{Si})_2$ 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 $1\ \mu$ 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 $1\ \mu$ diamond paste. Samples were heated in air at 500°C for 100 h. The temperature was controlled within $\pm 2^\circ\text{C}$. 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 compacts made from commercial MoSi_2 powder contains many such silica spots. The $\text{Mo}(\text{Al},\text{Si})_2$ has islands of Mo_5Si_3 (lighter colour) distributed uniformly throughout the sample in addition to the silica spots. The $\text{MoSi}_2 + 1\ \text{wt}\% \text{C}$ also contains many dark spots and brighter phase, which could be β -SiC and hexagonal $\text{Mo}_5\text{Si}_3\text{C}$ as found in the XRD pattern of the sample. $\text{Mo}(\text{Al},\text{Si})_2$ infiltrated SiC has α -SiC in hexagonal $\text{Mo}(\text{Al},\text{Si})_2$ 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 $\text{Mo}(\text{Al},\text{Si})_2$ compacts are marginally lower and that of $\text{MoSi}_2 + 1\ \text{wt}\% \text{C}$ higher. $\text{Mo}(\text{Al},\text{Si})_2$ 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 $\text{Mo}(\text{Al},\text{Si})_2$ infiltrated

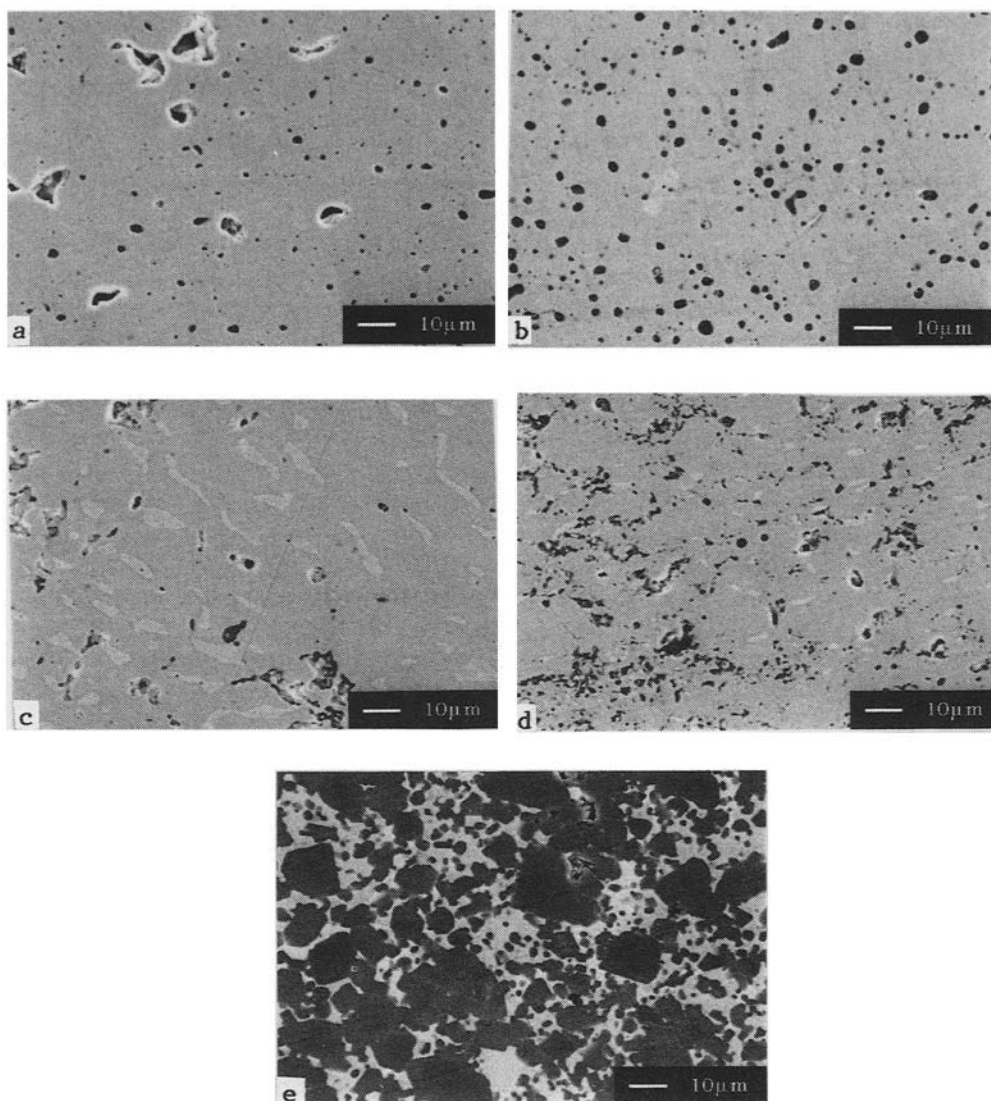


Figure 1. SEM of (a) $\text{Mo} + 2\text{Si}$, the darker spots due to silica, (b) commercial MoSi_2 , more of darker silica spots, (c) $\text{Mo}(\text{Al,Si})_2$, the lighter islands of Mo_5Si_3 and darker silica spots, (d) $\text{MoSi}_2 + 1\text{ wt}\% \text{C}$, the lighter islands are due to $\text{Mo}_5\text{Si}_3\text{C}$ and darker spots of SiC and (e) $\text{Mo}(\text{Al,Si})_2$ infiltrated SiC , the darker phase is SiC while the lighter is $\text{Mo}(\text{Al,Si})_2$.

SiC samples did not show any change whereas the commercial MoSi_2 sample had a layer of slightly off-white coloured powder on the surface. $\text{MoSi}_2 + 1\text{ wt}\% \text{C}$ and $\text{Mo}(\text{Al,Si})_2$ specimens were covered with a deeper bluish green layer.

The SEM micrographs of the oxidized samples are shown in figure 2. The SEM micrograph of the $\text{Mo} + 2\text{Si}$ sample taken at the edge of the polished surface also shows the fractured surface. There is no indication of MoO_3 or more silica spots than before the oxidation experiment. The commercial MoSi_2 had a layer of oxide loosely covering the surface (which could be dusted), the SEM micrograph showed long needle like MoO_3 on the wiped surface. However, $\text{Mo}(\text{Al,Si})_2$ had many opened

blisters and SiO_2 on the surface. $\text{MoSi}_2 + 1\text{ wt}\% \text{C}$ had only MoO_3 whiskers and no blisters on the surface.

Bertziss *et al* (1992) reported that the arc-melted MoSi_2 disintegrated to powder at 500°C in 43 h whereas in the HIPed MoSi_2 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 MoSi_2 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 MoSi_2 used by Chou and Nieh (1993, 1994) contained Mo_5Si_3 and SiO_2 as impurity. The $\text{Mo} + 2\text{Si}$ and

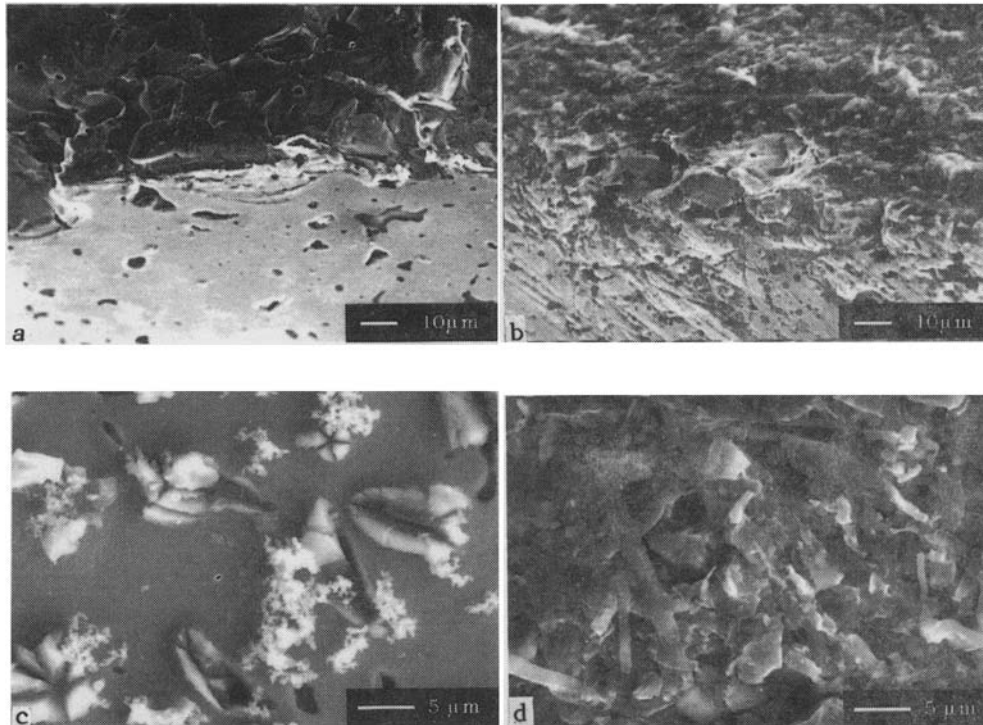


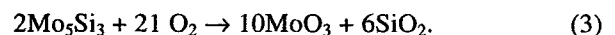
Figure 2. SEM of oxidized samples (a) Mo + 2 Si showing the polished as well as the fractured surfaces, (b) commercial MoSi₂, (c) Mo(Al,Si)₂ showing the open blisters and MoO₃ rods in them and (d) MoSi₂ + 1 wt% C displaying MoO₃ rods.

Mo(Al,Si)₂ infiltrated SiC compacts in the present study are almost fully dense and also do not contain any impurity other than SiO₂ (as seen from XRD and SEM). Thus, there is no peeling, cracking or surface oxidation even after 100 h in air at 500°C. The commercial MoSi₂ did show surface oxidation but no catastrophic disintegration.

If grain boundaries are the sites for oxide formation that leads to peeling 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 MoSi₂ + 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 MoO₃ 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 Mo₅Si₃ before and no such islands were present after the peeling experiments, it looks as though the Mo₅Si₃ has preferentially reacted with the oxygen (Meyer and Akinc 1996; Mitra *et al* 1997).

Mo₅Si₃ would oxidize according to the following reaction (Meyer and Akinc 1996),



The volumetric change associated is almost triple in this case. When the compacts contain large amounts of Mo₅Si₃, preferential oxidation of Mo₅Si₃ will result in more severe peeling and disintegration as Mo₅Si₃ is known to have a poor oxidation resistance than MoSi₂ (Meyer and Akinc 1996). Similar observation has been

made by Mitra *et al* (1997) in the oxidation experiments on MoSi₂ + 20 vol% SiC. However, as described by Chou and Nieh (1993), vapour pressure of MoO₃ 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 MoSi₂ + 1 wt% C sample even though MoO₃ rods were present is interesting. It is possible that the passage of oxygen through Mo₅Si₃C is more difficult than through Mo₅Si₃. Hence blisters do not form underneath the top surface to burst. Mo₅Si₃C on the surface reacts with oxygen as,



leaving behind MoO₃, 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 MoSi₂ + 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 MoSi₂ containing impurities could be controlled with the full densification of the compact in the absence of external stress.

In conclusion, oxidation tests on MoSi₂, Mo(Al,Si)₂ and MoSi₂ + 1 wt% C samples, prepared by the *in situ* synthesis and compaction technique, are done. The MoSi₂ did not show any visible oxide formation on the surface even after 100 h at 500°C in air. For comparison commercially available MoSi₂ 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 MoO₃ in them and MoSi₂ + 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 MoSi₂ material when the density is sufficiently high (> 95%) and amount of Mo₅Si₃ is sufficiently low.

References

- Aikin Jr R M 1991 *Ceram. Engg. Sci. Proc.* **12** 1643
 Berztiss D A, Cerchiara R R, Gulbransen E A, Pettit F S and Meier G H 1992 *Mater. Sci. Engg.* **A155** 165
 Bhattacharya A K and Petrovic J J 1991 *J. Am. Ceram. Soc.* **74** 2701
 Chou T C and Nieh T G 1993 *J. Mater. Res.* **8** 214
 Chou T C and Nieh T G 1994 *Mater. Res. Soc. Symp. Proc.* **288** 965
 Cook J, Khan A, Lee E and Mahapatra R 1992 *Mater. Sci. & Engg.* **A155** 183
 Hebsur M G 1994 *Mater. Res. Soc. Symp. Proc.* **350** 177
 Henager Jr C H, Brimhall J L and Hirth J P 1992 *Scr. Metall. Mater.* **26** 585
 Herman H and Sampath S 1992 *Mater. Sci. Engg.* **A155** 95
 Jo S, Lee G, Moon J and Kim Y 1996 *Acta Mater.* **44** 4317
 Maruyama T and Yanagihara K 1997 *Mater. Sci. & Engg.* **A239-240** 828
 Meschter P J 1992 *Metall. Trans.* **A23** 1763
 Meyer M K and Akinc M 1996 *J. Am. Ceram. Soc.* **79** 938
 Mitra R, Rama Rao V V and Mahajan Y R 1997 *Mater. Sci. & Techn.* **13** 415
 Shobu K, Tani E, Akiyama M and Watanabe T 1996 *J. Am. Ceram. Soc.* **79** 544
 Tiwari R, Herman H and Sampath S 1992 *Mater. Sci. & Engg.* **A155** 95
 Westbrook J H and Wood D L 1964 *J. Nucl. Mater.* **12** 208
 Yanagihara K, Maruyama T and Nagata K 1996 *Intermetallics* **S4** 133