Microstructure and Mechanical Properties of Mo-Si-Al Alloy and Mo-Si-Al/SiC Composite

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SYNOPSIS

Mo-Si-Al alloy and Mo-Si-Al/SiC composite were fabricated by the powder metallurgical process from a novel Mo-Si-Al prealloyed powder, and their microstructure and mechanical properties were evaluated. The Mo-Si-Al and Mo-Si-Al/15 vol%SiC mixed powders were hot-pressed in an argon atmosphere. XRD analyses revealed that Mo-Si-Al/SiC composites were composed of MoSi_2 (tetragonal, C11_b structure), $\text{Mo}(\text{Si},\text{Al})_2$ (hexagonal, C40 structure), $\alpha\text{-Al}_2\text{O}_3$, $\text{Mo}_{55}\text{Si}_3\text{C}_{51}$ and $\beta\text{-SiC}$. Almost no glassy SiO_2 phase was found in Mo-Si-Al and Mo-Si-Al/SiC systems contrary to MoSi_2 and MoSi_2/SiC . The formation of $\alpha\text{-Al}_2\text{O}_3$ was attributed to the predominant oxidation of aluminum at the surface of the Mo-Si-Al prealloyed powder. Mo-Si-Al based systems showed the better high-temperature strength mainly due to the elimination of glassy SiO_2 and the crystallographical change from $t\text{-MoSi}_2$ to $h\text{-Mo}(\text{Si},\text{Al})_2$. Incorporation of fine SiC particles enabled to control microstructure and then to enhance mechanical properties.

KEY WORDS

MoSi_2 , $\text{Mo}(\text{Si},\text{Al})_2$, Mo-Si-Al/SiC composite, mechanical properties, Al_2O_3 formation

1 Introduction

Molybdenum disilicide (MoSi_2) is a promising material for various applications such as aerospace exposed to temperatures more than 1500 °C, mainly because of its high melting point (2030°C) and fairly good oxidation resistance. However, its fracture toughness and strength are not high enough for high-temperature structural applications. Furthermore, glassy SiO_2 which is present in the metallurgically produced MoSi_2 powder strongly degrades the high-temperature mechanical properties¹⁾. Thus, main efforts have focused on improving mechanical properties of this material. Especially, "second phase dispersion"²⁻⁸⁾ and " SiO_2 elimination"⁹⁻¹⁴⁾ have been widely investigated.

Recently "alloying" has been also adapted to improve various properties of MoSi_2 .¹⁵⁻¹⁶⁾ Mo-Si-Al is one of the most fascinating system because of its good cyclic oxidation resistance¹⁶⁻¹⁷⁾ and of crystallographical modification from tetragonal C11_b structure of MoSi_2 to hexagonal C40 of $\text{Mo}(\text{Si},\text{Al})_2$.¹⁸⁻¹⁹⁾ Silva et al.²⁰⁻²²⁾ reported that elemental Al addition enabled to convert SiO_2 to Al_2O_3

in powder processed MoSi_2 . This "in-situ displacement reaction" technique controls Al content easily. However, using fine Al metal powder is sometimes disadvantageous; fine Al metal is flammable and it has relatively high vapor pressure during heating.

In this investigation, a novel Mo-Si-Al prealloyed powder was used to fabricate Mo-Si-Al alloys. In order to control microstructure and to improve mechanical properties, fine SiC particles reinforced alloys were also fabricated. High temperature strength as well as room temperature mechanical properties was evaluated for Mo-Si-Al and Mo-Si-Al/SiC composites.

2 Experimental procedure

The novel Mo-Si-Al powder was supplied by Japan New Metals Co., Ltd. It was fabricated from elemental powders of molybdenum (>99.9 wt.%), silicon (>99.75 wt.%) and aluminum (99.65 wt.%). The elemental powders (nominal composition; $\text{MoSi}_{1.72}\text{Al}_{0.28}$) were mixed, heated for solid state reaction, crushed and then sieved. The result of chemical analysis of the powder is shown in

Table 1. Since aluminum and silicon have high vapor pressure, the obtained powder became Mo-rich compared with the stoichiometric composition. From the standpoint of mechanical properties, however, such deviation is rather favorable; if elemental Al and Si were remained in the materials, mechanical properties, especially high-temperature strength, will drop down. Spectrochemical analysis revealed that the major impurities were 0.82 wt.% oxygen, 0.09 wt.% carbon and 0.08 wt.% iron. For the composite, a commercial β -SiC powder (Mitsui Toatsu Chemical Co., Ltd.) was added 15 % by volume. The SiC starting powder contained less impurities than the Mo-Si-Al powder as indicated in Table 1. Mean particle sizes of the Mo-Si-Al powder and the β -SiC powder were 1.61 and 0.15 μm , respectively.

Table 1 Chemical analyses of Mo-Si-Al (left) and SiC (right) powders.

	Content			Content
	(wt.%)	(at.%)		
Mo	63.39	33.15	SiC	>99 (wt.%)
Si	31.15	55.64	SiO ₂	0.15 (wt.%)
Al	4.41	8.20	free-C	0.10 (wt.%)
O	0.82	2.57	Fe	120 (ppm)
C	0.09	0.38	Al	48 (ppm)
Fe	0.08	0.07	Ca	40 (ppm)
			Mg	10 (ppm)
			Cr	30 (ppm)
			Ni	20 (ppm)

They were mixed by wet ball-milling in 1-butanol with ZrO₂ balls for 24 h, and then the dried mixture was dry-ball-milled to crush the agglomerations. Mo-Si-Al with/without SiC powders were packed into carbon dies which were coated with BN and then hot-pressed at 1500°C for Mo-Si-Al and at 1600°C for the composite under an applied pressure of 30 MPa for 1 h in an argon atmosphere. The sintered disks were 44 mm in diameter and 5.0 mm in thickness. The hot-pressed bodies were cut, grounded and polished into rectangular bars with 4 × 3 × 36 mm in size.

Phase identification was carried out by the X-ray diffraction (XRD) analysis, and bulk densities were measured by the Archimedes method in toluene. Microstructure was characterized by scanning electron microscopy (SEM, HITACHI S-5000) with an energy dispersive X-ray spectrometer (EDS,

HORIBA EMAX-5770). Samples for SEM observations were pre-coated with Au. More than five specimens were subjected to three-point bending tests (span: 30 mm) to determine the fracture strength. Bending load was applied parallel to hot-press axis with a crosshead speed of 0.5 mm/min. The hardness (H) was evaluated by Vickers indentation under a condition of 98 N load and loading duration of 15 s, and the fracture toughness (K_{IC}) was determined simultaneously by the indentation fracture (IF) method. K_{IC} values were calculated by using the following empirical equation for a median crack²³⁾.

$$K_{IC} = 0.203(c/a)^{-3/2}H \cdot a^{1/2} \quad (1)$$

where c and a are the lengths of a median crack and half of a diagonal of a indentation, respectively.

3 Results and discussion

3.1 Chemistry and phase identification

Fig.1 shows XRD patterns for (a) Mo-Si-Al pre-alloyed powder, (b) Mo-Si-Al hot-pressed at 1500°C and (c) Mo-Si-Al/15vol%SiC composite hot-pressed at 1600°C, respectively. XRD revealed that Mo-Si-Al alloy was composed of MoSi₂ (tetragonal, C11_b structure), Mo(Si,Al)₂ (hexagonal, C40 structure), α -Al₂O₃ and Mo₅Si₃C₅₁. For the composite, β -SiC was identified in addition to above mentioned phases. The formation of α -Al₂O₃ was attributed to predominant oxidation of aluminum¹⁷⁾ at surfaces of the Mo-Si-Al precursor powder. Mo₅Si₃C₅₁ is the only stable Mo-Si-C ternary phase; called the Nowotny phase²⁴⁾. The formation of Mo₅Si₃C₅₁ phase was ascribed to (1) the deviation from the stoichiometric composition of the Mo-Si-Al powder and (2) the presence of carbon arising from the impurity of powders as well as that from ball milling and hot-pressing processes. From Table 1, the composition of the Mo-Si-Al powder was calculated (Table 2). The calculation was made assuming that phases in the powder were C11_b, C40, Mo₅Si₃, α -Al₂O₃, free carbon and Fe₂O₃. C11_b and C40 were not distinguished in the calculation because C11_b/C40 ratio is subject to change; MoSi₂ dissolves Al up to about 3 at.% and the range of Al composition in Mo(Si,Al)₂ is about 10 to 35 at.%.^{15,17)} Some carbon may dissolve in Mo₅Si₃ to form Mo₅Si₃C₅₁. After hot-pressing, it

is considered that the content of MoSi_2 and $\text{Mo}_{5/3}\text{Si}_3\text{C}_{5/1}$ should increase and that of $\text{Mo}(\text{Si},\text{Al})_2$ should decrease because of the high vapor pressure of Al at high temperatures. Hence, the change of the phase ratio was clearly observed from (100) of $\text{Mo}(\text{Si},\text{Al})_2$ at $2\theta \doteq 22.1^\circ$, (002) of MoSi_2 at $2\theta \doteq 22.6^\circ$ and (200) of $\text{Mo}_{5/3}\text{Si}_3\text{C}_{5/1}$ at $2\theta \doteq 28.2^\circ$ in Fig. 1.

Fig.1 X-ray diffraction patterns for (a)Mo-Si-Al powder, (b)Mo-Si-Al (c)Mo-Si-Al/15 vol% SiC composite.

Table 2 Calculated composition of the Mo-Si-Al powder.

	Matrices (C11 _b +C40)	Mo_5Si_3	Al_2O_3	free-C	Fe_2O_3
Content (mol%)	94.32	1.83	2.56	1.17	0.11

3.2 Microstructure

Figs.2(a) and 2(b) show backscattered electron images taken by SEM for the Mo-Si-Al and the Mo-Si-Al/SiC composite, respectively. As seen from Fig.2 (a), four phases were identified in the Mo-Si-Al alloy; EDS analysis revealed that phases which appear dark (α), relatively dark (M), relatively bright (M') and bright (N) were $\alpha\text{-Al}_2\text{O}_3$, MoSi_2 , $\text{Mo}(\text{Si},\text{Al})_2$ and $\text{Mo}_{5/3}\text{Si}_3\text{C}_{5/1}$, respectively. In combination with polarized optical microscopy observations, it was revealed that the smaller $\alpha\text{-Al}_2\text{O}_3$ phase ($\sim 1\ \mu\text{m}$) had a nearly round shape

and located within matrix grains and at grain boundaries, especially at triple points. This microstructure formation may be explained as follows; The Mo-Si-Al powder had the oxidized layer (i.e. $\alpha\text{-Al}_2\text{O}_3$) on the surfaces and a thin Mo_5Si_3 region below the $\alpha\text{-Al}_2\text{O}_3$ layer.^{17,25)} During hot-pressing, $\alpha\text{-Al}_2\text{O}_3$ was concentrated mainly at triple points, and carbon impurity dissolved in Mo_5Si_3 to form $\text{Mo}_{5/3}\text{Si}_3\text{C}_{5/1}$. In the Mo-Si-Al/SiC system, on the other hand, four domains were observed as shown in Fig.2(b); domains appearing dark (α'), relatively dark (M), relatively bright (M') and bright (N) were $\alpha\text{-Al}_2\text{O}_3/\text{SiC}$, MoSi_2 , $\text{Mo}(\text{Si},\text{Al})_2$ and $\text{Mo}_{5/3}\text{Si}_3\text{C}_{5/1}$, respectively. It is considered that a large portion of SiC particles was trapped by Al_2O_3 during hot-pressing. Table 3 summarizes appeared phases in MoSi_2 -based materials in the presence of carbon.^{14,26)} Grain sizes of matrices were $6.5\ \mu\text{m}$ for Mo-Si-Al and $2.2\ \mu\text{m}$ for Mo-Si-Al/SiC composite. This suggests that added SiC particles effectively inhibit matrix grain growth.

Fig.2 Backscattered electron images for (a)Mo-Si-Al and (b)Mo-Si-Al/15 vol%SiC composite; M: MoSi_2 , M': $\text{Mo}(\text{Si},\text{Al})_2$, α : $\alpha\text{-Al}_2\text{O}_3$, α' : $\alpha\text{-Al}_2\text{O}_3/\text{SiC}$ and N: $\text{Mo}_{5/3}\text{Si}_3\text{C}_{5/1}$.

Table 3 Appeared phases in the presence of carbon.

Samples	Microstructure
MoSi ₂ ^{14,26)}	C11 _b + g-SiO ₂ * + Mo ₅ Si ₃ C _{≤1}
MoSi ₂ /SiC ²⁶⁾	C11 _b + g-SiO ₂ * + Mo ₅ Si ₃ C _{≤1} + SiC
Mo-Si-Al	C11 _b + C40 + α-Al ₂ O ₃ + Mo ₅ Si ₃ C _{≤1}
Mo-Si-Al/SiC	C11 _b + C40 + α-Al ₂ O ₃ + Mo ₅ Si ₃ C _{≤1} + SiC

*g-SiO₂: glassy SiO₂

3.3 Room temperature properties

To clarify the effect of the microstructural modification on mechanical properties, hardness, strength and toughness were examined. Table 4 shows average matrix grain size and room temperature mechanical properties for MoSi₂ fabricated from coarse powder²⁷⁾, MoSi₂ from fine powder^{4,14,26)}, MoSi₂/15vol%SiC composite^{4,26)}, Mo-Si-Al alloy and Mo-Si-Al/15vol%SiC composite.

Alloying effect

In order to clarify the alloying effect, the results from finer MoSi₂ and Mo-Si-Al were compared. Although Mo-Si-Al has somewhat larger grain size, its hardness and strength were higher than those of MoSi₂. Harada et. al¹⁵⁾ have briefly described the hardness of Al-alloyed MoSi₂ fabricated by using arc melting; the hardness was decreasing with increasing the Al content in the range of 0-10 at.% (i.e. MoSi₂ to MoSi_{1.7}Al_{0.3}) and then increasing with increasing it in the range of 10-15 at.% (i.e. MoSi_{1.7}Al_{0.3} to MoSi_{1.5}Al_{0.5}). C11_b dissolved Al up to 3 at.% and single phase C40 appeared more than 10 at.% Al. They explained that the decrement of hardness was due to the solid solution "softening" (i.e. Al into Si-site of C11_b) and the increment was due to the crystallographical modification (i.e. C11_b to C40). For powder metallurgically processed systems, however, other phases which are dispersing in alloys affect the hardness in addition to above mentioned mechanisms. Although C11_b phase should be softened by dissolving Al (up to 3at.%)¹⁵⁾, Al₂O₃ and Mo₅Si₃C_{≤1} dispersion should give hardening effect. Combination of these opposite effects, the hardness value of Mo-Si-Al was a little higher than that of MoSi₂. As for strength, the strengthening was mainly due to the Al₂O₃ formation instead of glassy SiO₂. On the contrary to hardness and strength, the toughness value of Mo-Si-Al was

slightly smaller than that of MoSi₂. This was because the intragranular fracture was dominant for Mo-Si-Al in contrast with MoSi₂; both inter- and intragranular fracture was observed for MoSi₂. Furthermore, the change of intrinsic bonding strength may affect the toughness.

Combination of alloying and dispersion

It has been reported that SiC dispersion is fairly effective to enhance mechanical properties of MoSi₂.^{2-4,26)} Alloying and composite techniques were simultaneously adapted to obtain better mechanical properties. The Mo-Si-Al/15vol%SiC system possessed relatively fine grain size and fairly high mechanical properties, especially for hardness. The hardening was due to the hard phases (i.e. Al₂O₃, Mo₅Si₃C_{≤1} and SiC) dispersion, the grain growth inhibition and the decrease of solid solution softening effect with decreasing total Al content. The strengthening was mainly attributed to the grain growth inhibition, and the toughening was caused by residual stress induced by thermal expansion mismatch.^{4,26)}

Table 4 Room temperature mechanical properties of Mo-Si based materials.

	<i>T</i> (°C)	<i>d</i> (μm)	<i>H_v</i> (GPa)	<i>σ_f</i> (MPa)	<i>K_{IC}</i> * (MPa√m)
MoSi ₂ (coarse) ²⁷⁾	1700	10-20	8-10	~250	2-3
MoSi ₂ (fine) ^{4,14,26)}	1500	5.2	10.38	687	2.29
MoSi ₂ /15%SiC ^{4,26)}	1500	2.1	12.44	1216	3.09
Mo-Si-Al	1500	6.5	10.98	764	1.92
Mo-Si-Al/15%SiC	1600	2.2	14.21	1107	3.00

**T*: hot-pressing temperature, *d*: average matrix grain size, *H_v*: hardness, *σ_f*: fracture strength, *K_{IC}*: fracture toughness

3.4 High temperature strength

High temperature strength was evaluated in order to examine the alloying and SiC dispersion effects and to confirm the usefulness of Mo-Si-Al. Fig.3 shows the variation of strength with temperature for MoSi₂ from coarse powder²⁸⁾, MoSi₂ from fine powder²⁶⁾, MoSi₂/SiC composite²⁶⁾, Mo-Si-Al and Mo-Si-Al/ SiC composite. Although the strength values of fine MoSi₂ and MoSi₂/SiC composite were fall down more than 1000° C, Mo-Si-Al and Mo-Si-Al/SiC composite kept high strength values up to 1100° C. The strength values at 1100° C were 833 MPa for Mo-Si-Al and 954 MPa for Mo-Si-Al/SiC

composite. The improvement on high-temperature strength was mainly due to the glassy SiO_2 elimination. It is concluded that alloying with Al was fairly effective to enhance mechanical properties not only at room temperature but also at high temperatures.

It is worthy of note that alloying with aluminum enables us to control microstructure, i.e. elimination of glassy SiO_2 and crystallographical modification from C11₆ to C40. This approach may be available to other silicides.

Fig.3 Variation of strength with temperature for MoSi_2 -based materials.

4 Conclusions

The present work reveals microstructure and mechanical properties of the Mo-Si-Al alloy and the Mo-Si-Al/SiC composite. The results are summarized as follows;

1. Mo-Si-Al alloy and Mo-Si-Al/SiC composite were fabricated by the powder metallurgical process from a novel prealloyed powder. The alloy was composed of MoSi_2 , $\text{Mo}(\text{Si}, \text{Al})_2$, $\alpha\text{-Al}_2\text{O}_3$ and $\text{Mo}_{5/3}\text{Si}_3\text{C}_{5/3}$. The composite was composed of these four phases and $\beta\text{-SiC}$. The intergranular glassy SiO_2 phase could be changed into thermodynamically stable $\alpha\text{-Al}_2\text{O}_3$ by the alloying.
2. Mechanical properties such as hardness and strength were enhanced by alloying. Combination of alloying and composite techniques, hardness, strength, toughness and high-temperature strength were simultaneously improved.

3. These results indicate that the combination of alloying and composite techniques has great advantages to fabricate MoSi_2 -based materials with well-balanced mechanical properties. Further optimization of fabrication conditions will enable to improve the mechanical properties of MoSi_2 -based system.

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