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Phase Transformation of MoSi₂ Phase in MoSi₂/Mo₅Si₃ Eutectic Alloy Containing Nb[†]

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Role of ternary solute element Nb on the C40→C11b phase transformation of the MoSi₂ phase in MoSi₂/Mo₅Si₃ eutectic alloys which occurs during heat treatment is discussed in this paper. In the case of stoichiometric MoSi₂ a mixture of C40 and C11b phases can be prepared by low-pressure plasma spraying method, in which phase transformation from the metastable C40 to stable C11b is recognized during heating at around 800°C. It is found that the MoSi₂ phase in an as-cast eutectic MoSi₂/Mo₅Si₃ alloy with 8.5 at%Nb consist only of metastable C40 phase. The transformation from C40 to C11b in this alloy does not occur by heating up to 1200°C but a portion transforms into C11b by heating at 1400°C. It is shown that the Nb concentration in C40 phase is higher than that in C11b phase in this alloy, which must be relevant to the observed transformation behavior.

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Keywords: niobium, MoSi₂, C40 phase, C11b phase, Mo₅Si₃, transformation

I. Introduction

Since an intermetallic compound MoSi₂ has a very high melting point (2020°C) and exhibits excellent oxidation resistance at elevated temperatures (1000–1700°C), the compound has been expected for such a high temperature structural application as substitution for the Ni-base superalloy. However the major drawback for the MoSi₂-based materials is the brittleness at temperatures lower than 1000°C^{(1)–(3)}.

For improvement of toughness of MoSi₂, additions of such ternary elements as C, Ti etc. have been attempted⁽⁴⁾, and MoSi₂/SiC composite is an example of a success to impart some toughness to the compound⁽⁵⁾. Furthermore, in this system, the microstructure could be controlled through melting process by plasma spraying⁽⁶⁾ and by cold-hearth melt spinning⁽⁷⁾ methods.

Many investigations for improvement of toughness have been carried out by making the compound multi-phase⁽⁸⁾⁽⁹⁾, and Mishima *et al.* have suggested that a remarkable improvement in room temperature ductility have been obtained by controlling the microstructures of multi-phase intermetallic alloys based on B2 CoAl⁽¹⁰⁾.

In this paper, the possibility to control the microstructures is pursued in a MoSi₂/Mo₅Si₃ eutectic alloy with an ternary addition of Nb. Phase transformation from C40 to C11b phase of the MoSi₂ is expected to occur by heat treatment in the alloy. By comparing the

result for the stoichiometric Nb-free MoSi₂, the role of solute Nb on the phase transformation is discussed.

II. Experimental

The alloys of the Mo–Si–Nb system were prepared by button arc melting method with high purity Mo, Si and Nb bulk mixtures. As a multi-phases alloy based on MoSi₂, MoSi₂/Mo₅Si₃ eutectic alloys are chosen with ternary additions of Nb which would substitute for Mo site of the constituent phases. Since the atomic radius of Nb is very close to that of Mo, it is assumed to substitute for the Mo site. The amount of Nb addition were selected as 4, 8.5, 11.5, 15 and 23 at%. The stoichiometric MoSi₂ consisted of α-(C11b phase) and β-MoSi₂ (C40 phase) was prepared by low-pressure plasma spraying (LPPS) method. The experimental conditions for LPPS are as follows: 1) starting material; α-MoSi₂ (Japan New Metals Co. Ltd., 99% purity), 2) chamber pressure; 4000 Pa, 3) power; 28 kW, and 4) substrate; stainless steel. The MoSi₂ sprayed film was peeled from the substrate and then crushed in agate mortar for powder X-ray diffraction measurement. The heat treatment was carried out in a vacuum (about 10^{−3} Pa) at temperatures ranging from 500 to 1400°C for 30 min or 24 h. Powder X-ray diffraction measurement for Rietveld analysis are conducted with 2θ range (°) being 20 to 100, step scan increment (2θ°) being 0.03, and counting time (s/step) being 3. Identification of the phases for as-cast samples and powder samples, which were crushed in agate mortar, were examined by X-ray diffraction method. Observation of microstructure and analysis of the composition

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of constituent phases were performed by EPMA.

III. Results and Discussion

1. Constitution of the Mo–Nb–Si ternary system

In the Si–Mo binary phase diagram, the stoichiometric MoSi_2 is indicated as a line compound. It has the C11b crystal structure known as α -phase at temperatures below 1900°C , while it has the C40 crystal structure known as β -phase at between 1900 and 2020°C . The phase transformation from C11b to C40 in pure MoSi_2 occur at about 1900°C ⁽¹¹⁾. On the other hand, in the Nb–Si phase diagram, NbSi_2 is only stable with exists C40 structure up to the melting point⁽¹²⁾. **Figure 1** shows an isothermal section of the Mo–Nb–Si ternary phase diagram at 800°C ⁽¹³⁾. In this diagram, the region indicated as A is the two-phase consisting of MoSi_2 and Mo_5Si_3 . The region marked B is the three-phase region where NbSi_2 (C40), MoSi_2 (C11b) and $(\text{Mo}, \text{Nb})_5\text{Si}_3$ coexist. The region marked C is the two-phase consisting of NbSi_2 (C40) and $(\text{Mo}, \text{Nb})_5\text{Si}_3$ coexist. The alloys with 0 at%Nb and 4 at%Nb fall into the region A, an 8.5 at%Nb alloy into region B, and 11.5, 15 and 23 at%Nb alloys into region C.

2. Identification of the phases in the alloys

All of the as-cast bulk samples were crushed into powder to analyze quantitatively the constituent phases by powder X-ray diffraction method. **Table 1** summarizes the results before and after the heat treatment with different Nb concentrations. The heat treatment condition in this case was at 1400°C for 24 h in a vacuum. In this table, open circle, open triangle and solid circle denote C11b, C40 and Mo_5Si_3 phases, respectively. The alloys with 0 and 4 at%Nb are found to consist of C11b

Table 1 Identified phases before and after heat treatment at 1400°C for 24 h. Open circle, open triangle and solid circle denote C11b, C40 and Mo_5Si_3 phases, respectively.

Added Nb/(at%)	0	4	8.5	11.5	15	23
Before treatment	○ ●	○ ●	△ ●	△ ●	△ ●	△ ●
After treatment	○ ●	○ ●	○ ●	○ △ ●	△ ●	△ ●

and Mo_5Si_3 both before and after the heat treatment, which indicates that the alloy with 4 at%Nb lies within the region A even at 1400°C . Before heat treatment, the alloy with 8.5 at%Nb is found to consist of C40 and Mo_5Si_3 phases. The C40 phase found in this alloy before heat treatment may be a metastable phase because, after heat treatment, the C11b but the C40 phase exists with Mo_5Si_3 . In case for the alloy with 11.5 at%Nb, it is shown that a portion of C40 transforms into C11b by the heat treatment because it, as a result, consists of C40, C11b and Mo_5Si_3 phases in spite of having been two-phase of C40 and Mo_5Si_3 before. Both the alloys with 15 and 23 at%Nb consist of C40 and Mo_5Si_3 phases before and after the heat treatment, which means that the alloys are within the same two-phase region both at 1400°C and at 800°C .

It is suggested by the above results that the C40 phase found in the alloys 8.5 at% and 11.5 at%Nb in as-cast condition is not a stable phase at 1400°C and therefore the constitution of the two alloys could be controlled by a suitable heat treatment.

3. The C40 to C11b transformation in MoSi_2

The stoichiometric MoSi_2 consisting of the metastable C40 phase and the stable C11b phase was successfully prepared by LPPS method in the present work. It has been shown that, in the LPPS process, when molten MoSi_2 powder was quenched into room temperature, the metastable C40 phase being stable at above 1900°C is obtained as a second phase in the C11b matrix which is stable at below 1900°C ⁽¹⁴⁾. By using the two-phase alloy, the transformation from C40 to C11b by the heat treatment at various temperatures is examined.

Figure 2 shows the powder X-ray diffraction patterns of the stoichiometric MoSi_2 with the two-phase structure after heat treatment at between 500 and 1000°C for 30 min. In this figure, open circle and triangle denote C11b and C40 phase, respectively. The peaks for C40 phase, which is marked by a triangle, gradually decreases in intensity with increasing temperature and diminished at 900°C , showing all of the C40 phase transformed to C11b phase by the heat treatment.

The powder X-ray diffraction data in Fig. 2 shows no peak from other phases than C40 and C11b. Then a quantitative analysis of relative volume fraction between two phases becomes possible by the Rietveld analysis on each data in the figure by computer program RIETAN⁽¹⁵⁾⁽¹⁶⁾. The calculated profiles are in good agree-

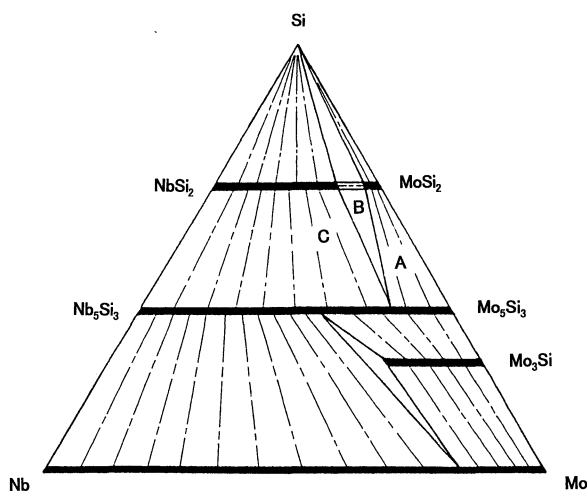


Fig. 1 An isothermal cross section of the Mo–Si–Nb ternary phase diagram at 800°C [4]. The region as indicated A is two-phase consisting MoSi_2 and Mo_5Si_3 . The region marked B is tree-phase where NbSi_2 (C40 structure), MoSi_2 (C11b structure) and $(\text{Mo}, \text{Nb})_5\text{Si}_3$ coexist. The region marked C is two-phase consisting NbSi_2 (C40 structure) and $(\text{Mo}, \text{Nb})_5\text{Si}_3$.

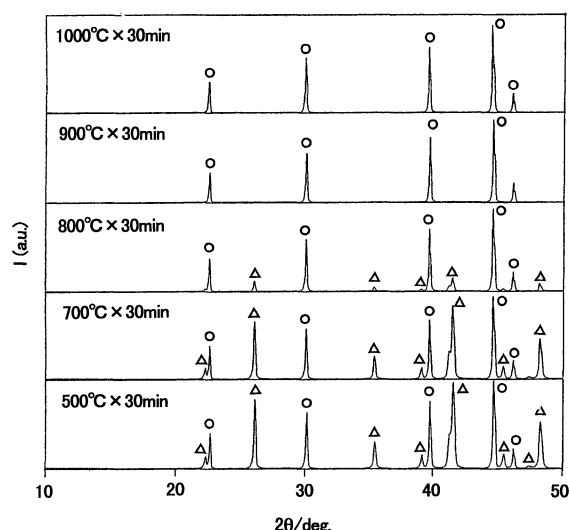


Fig. 2 Powder X-ray diffraction patterns of the stoichiometric MoSi_2 , heat treated at different temperatures between 500–1000°C for 30 min. Circle and triangle denote C11b and C40 phase, respectively.

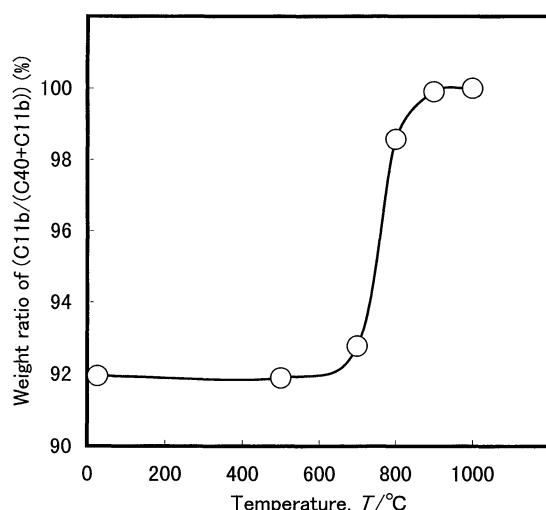


Fig. 3 Calculated weight ratio of $(\text{C11b}/(\text{C11b}+\text{C40}))/\%$ as a function of heat treatment temperature.

ment with the observed profile and the reliable factors RWP are below 10% for all the cases. From the scale factors of C40 and C11b phases obtained by calculation, the relative quantities of C40 and C11b phases are derived according to Ref. (17). **Figure 3** shows the calculated weight ratio of $(\text{C11b})/(\text{C11b}+\text{C40})$ in percent with heat treatment temperature. The weight ratio of C40 phase which is metastable at below 1900°C is found to be drastically reduced by the heat treatment at around 800°C.

4. The transformation of MoSi_2 phase in an eutectic $\text{MoSi}_2/\text{Mo}_5\text{Si}_3$ alloy

Figure 4 shows the powder X-ray diffraction patterns in an eutectic $\text{MoSi}_2/\text{Mo}_5\text{Si}_3$ alloy with 8.5 at%Nb. In this figure, the peaks with circle and triangle correspond to C11b and C40 phases, respectively, while those with

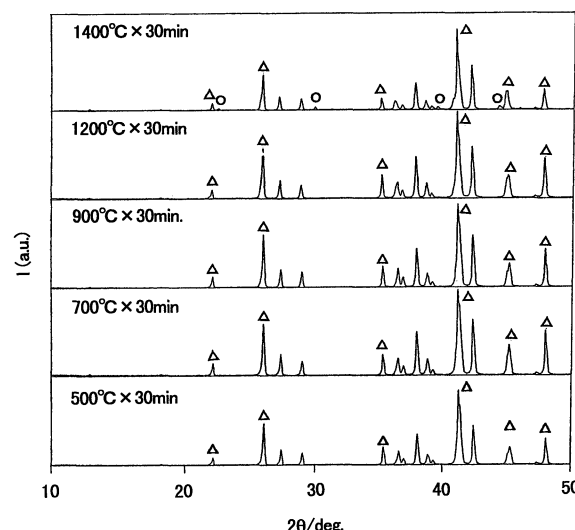


Fig. 4 Powder X-ray diffraction patterns of MoSi_2 with a 8.5 at% Nb. The peaks with circle and triangle denote C11b and C40 phases, respectively. The peaks with no mark denote Mo_5Si_3 phase.

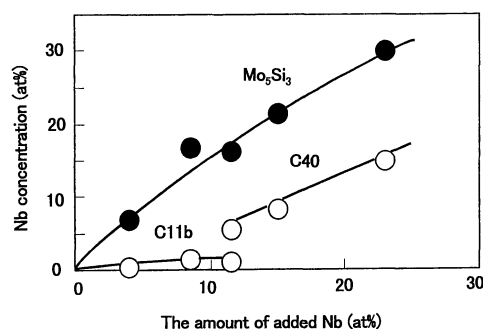


Fig. 5 Nb concentration in each phase for all Nb added samples after heat treatment at 1400°C for 24 h.

no mark to Mo_5Si_3 phase. It is found that the C40 phase does not transform to C11b phase in this alloy by the heat treatment at up to 1200°C, but it does partly by the heat treatment at 1400°C. The time needed for the transformation of all of the C40 phase to C11b phase was for 24 h at the temperature. In view of the results of the previous section, it is now clear that the C40 phase becomes stable against C11b phase by the addition of Nb substituting for Mo.

Figure 5 shows Nb concentration in each phase, identified by EPMA, for all the alloys with Nb additions after heat treatment at 1400°C for 24 h. The concentration of the solute Nb in Mo_5Si_3 is higher than those in C40 and C11b phases. But more importantly, it is clearly found that the Nb concentration in C40 phases is higher than that in C11b in alloys with more than 11.5 at%Nb. It means that the transformation from C40 to C11b should be accompanied by diffusion of Nb out from the C40 phase. Also noted is the difference in Nb concentration becomes larger with increasing Nb content in the alloys. These may interpret the stabilization of C40 phase against C11b phase with increasing Nb additions, but further careful investigation is necessary to confirm the speculation.

IV. Conclusion

The C40 phase of MoSi_2 in eutectic $\text{MoSi}_2/\text{Mo}_5\text{Si}_3$ alloys becomes more stable with increasing ternary Nb additions. This would enable controlling the constitution of phases forming a multi-phase microstructure by a suitable choice of heat treatment condition in this alloy system.

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