Phase Formation and Solidification Routes Near Mo-Mo$_5$SiB$_2$ Eutectic Point in Mo-Si-B System

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The phase formation behavior during solidification in the Mo-Si-B system was experimentally examined around the triple junction point ($T$) of the Mo solid solution (Mo$_ss$), Mo$_5$SiB$_2$ ($T_2$) and Mo$_5$B primary phases in the Mo-Si-B liquidus projection suggested by Yang and Chang through thermodynamic calculations, and the solidification routes of the Mo-Si-B alloys were reconsidered based on the obtained results. Alloys of four different compositions around the $T$ point were produced by arc-melting. The primary phases observed in these alloys were in excellent agreement with the liquidus projection proposed by Yang and Chang. The solidification routes were basically Mo$_ss$ (primary) $\rightarrow$ Mo$_ss$ + Mo$_5$B $\rightarrow$ Mo$_ss$ + T$_2$ eutectic $\rightarrow$ Mo$_ss$ + T$_2$ + Mo$_5$Si (A15), T$_2$ (primary) $\rightarrow$ Mo$_ss$ + T$_2$ eutectic $\rightarrow$ Mo$_ss$ + T$_2$ + A15, or Mo$_5$B (primary) $\rightarrow$ Mo$_ss$ + T$_2$ eutectic $\rightarrow$ Mo$_ss$ + T$_2$ + A15, depending on the composition. However, a quantitative EPMA analysis indicated the compositions of the Mo$_ss$-T$_2$ eutectic and Mo$_ss$ + T$_2$ + A15 phases differed from the reported liquidus projection. This is due to the difficulties interpreting the unusual solidification routes in the Mo-Si-B system and their as-cast microstructures.


(Received April 30, 2010; Accepted July 6, 2010; Published August 19, 2010)

Keywords: molybdenum-silicon-boron system, liquidus projection, eutectic, quantitative analysis, calibration

1. Introduction

Recently, there has been interest in ultra-high temperature structural materials due to their potential as alternatives to Ni-based superalloys in turbine blade applications for energy-efficiency improvement.$^{11}$ Various materials, most notably Nb-based alloys,$^{2,3}$ platinum-group super-alloys,$^{4,5}$ eutectic ceramic oxides,$^{6,7}$ and Mo-TiC, ZrC or HfC eutectic alloys,$^{8-10}$ have been put forward as new ultra-high temperature materials. Among them, Mo-Si-B alloys have attracted a considerable amount of attention quite recently. In particular Mo$_5$SiB$_2$ ($T_2$), the only ternary compound in the Mo-Si-B system, has excellent ultra high temperature yield and creep strengths,$^{11}$ good oxidation resistance$^{12}$ and relatively low density comparable to Ni-base superalloys.$^{13}$ However, the drawback of the phase is its poor fracture toughness, comparable to that of ceramics.$^{14}$ Fortunately, since Mo$_5$SiB$_2$ coexists with a ductile Mo$_ss$ phase in the Mo-Si-B ternary system,$^{15,16}$ its fracture toughness is significantly improved.$^{17}$

Several efforts have been dedicated to understanding the phase formation, stability and solidification pathways of Mo-Si-B ternary alloys.$^{15,16,18-21}$ Liquidus projection charts have played an important role in understanding the sequence of phase formation from liquidus phases to the final alloy product. A number of liquidus projections obtained experimentally and thermodynamically for the Mo-Si-B system have been reported. Nunes et al.$^{18,19}$ were the first to show the solidification pathways for each primary phase region with their corresponding microstructures. Katrych et al. also published the melting diagram of the Mo-Si-B system.$^{20}$ These two studies were followed by a thermodynamic analysis by Yang and Chang.$^{21}$ There are, however, some minor discrepancies between them, particularly with regard to as-cast microstructures and their phase developments during heat treatment.

In this study, the formation of the Mo-T$_2$ eutectic phase was experimentally studied around the triple junction point ($T$) of the Mo$_ss$, T$_2$ and Mo$_5$B primary phases in the Mo-Si-B ternary liquidus projection, the same point of focus by Yang and Chang.$^{21}$ The solidification pathways of the ternary alloy system were reconsidered around the $T$ point from a microstructural evolution perspective.

2. Experimental Procedures

The compositions of four kinds of alloys investigated in this study are given in Table 1. Button ingots of Mo-Si-B alloys approx. 20 g in weight were produced by an arc-melting technique from pure Mo (99.9 mass%), Si (99.9999 mass%) and B (99.95 mass%) with a water-cooled copper crucible under an Ar atmosphere. Each of the alloy ingots was flipped and re-melted more than 5 times to obtain maximal compositional homogeneity. Prior to each melting cycle, the furnace was evacuated and filled with high-purity Ar gas several times. A pure Ti ingot was melted before every melting cycle to remove residual O$_2$ and N$_2$ gases. Specimens were taken from the center of the ingots and prepared for chemical analysis and microstructure observation. The atomic ratios of Mo, Si and B in the as-cast alloys were analyzed by inductively coupled plasma (ICP)—the optical emission spectrometry (OES) method.$^{22}$ The impurity levels were calculated by ICP-OES for Ti, Cu, W, by the combustion—irradiation absorption method for C, by the He carrier fusion—thermal conductivity method for N and O by the Ar carrier fusion—thermal conductivity method for H. The microstructures of the samples were characterized by scanning electron microscopy (JEOL JSM-6500F) with back scattered electron images (BSE) and X-ray diffractometry (XRD) (Bruker D-8 Advance). A quantitative compositional
analysis was performed by electron probe micro-analysis (EPMA/WDX) (JEOL JXA-8621MX). It was operated at 15 kV and 2 × 10^-8 A. Thallium acid phthalate (TAP), Pentaerythriol (PET) and Lead Strearate (NSTE) were utilized as dispersive crystals. The microstructure of each of the four alloys was observed and a qualitative composition analysis was done by transmission electron microscopy (TEM) (JEOL JEM3010), operated at 300 kV and equipped with an energy dispersive X-ray spectroscope (EDX) (EDAX Genesis).

3. Results and Discussion

The chemical compositions of all of the alloys employed in this work (Table 1) are plotted in the Mo-Si-B ternary phase diagram at 1873 K reported by Kim and Perepezko in Fig. 1.16) The liquidus projection reported by Yang and Chang is also indicated in this figure, overlapping the phase diagram.21) The triple junction of Mo9s, MoB and T2 primary phase regions, denoted by the letter “T” in Fig. 1, lies near the border but obviously in the Mo9s-Mo3Si-T2 three phase region of the Mo-Si-B ternary phase diagram. As shown in Fig. 1, the composition of Alloy 1 (Mo-9.5 at%Si-14.2 at%B) was almost at the T point, and Alloy 2 (Mo-8.3 at%Si-13.2 at%B), 3 (Mo-10.5 at%Si-14.2 at%B) and 4 (Mo-8.7 at%Si-17.4 at%B) lie in the Mo9s, T2 and Mo3B primary phase region, respectively. (All of the alloy compositions are described in atomic percent hereafter.)

The as-cast microstructure of Alloy 1 is shown in Fig. 2(a). Except for a small amount of primary Mo solid solution (Mo9s), there were two predominant microstructures: a majority two-phase eutectic microstructure (superfine) and a three-phase fine microstructure between the eutectic areas. The distribution of these two areas was uniform at least in the middle of the specimen. Basically, quantitative analysis of light elements such as B is not easy because of low fluorescence yield, preferential absorption of light element x-rays in the sample and so on. Consequently, the microstructural homogeneity of Alloy 1 was used to conduct a compositional calibration on EPMA for quantitative analysis. The electron probe size adopted for the calibration was 30 μm in diameter for each analysis, and the Mo-Si-B compositions of 200 points (400 points in an area of approx. 0.6 x 0.6 mm² in four regions) were quantitatively analyzed, as shown in Fig. 2(b). The basis of these calibrations was the ZAF correction, using the standards of commercially pure Mo, Si and NdB6. The average compositions of the four regions were Mo-(9.6 ± 1.1)Si-(18.8 ± 1.8)B, Mo-(9.6 ± 1.4)Si-(18.7 ± 2.4)B, Mo-(9.5 ± 1.0)Si-(17.1 ± 1.9)B and Mo-(9.7 ± 1.4)Si-(17.4 ± 2.3)B, indicating the alloy was compositionally homogeneous. The relatively large standard deviations can be explained by the existence of two two-phase eutectic and three-phase microstructures. The similarities in the standard deviations strongly suggests both the composition and microstructure

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Table 1 Chemical compositions of Mo-Si-B alloys examined in this study.

<table>
<thead>
<tr>
<th>Alloy No.</th>
<th>Nominal composition (at%)</th>
<th>Analyzed Composition (at%)</th>
</tr>
</thead>
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<tr>
<td></td>
<td>Si</td>
<td>B</td>
</tr>
<tr>
<td>1</td>
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</tr>
<tr>
<td>2</td>
<td>6.6</td>
<td>13.2</td>
</tr>
<tr>
<td>3</td>
<td>10.5</td>
<td>14.2</td>
</tr>
<tr>
<td>4</td>
<td>8.7</td>
<td>17.4</td>
</tr>
</tbody>
</table>

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Fig. 1 Chemical compositions of the alloys plotted in the Mo-Si-B ternary phase diagram at 1873 K by Kim and Perepezko overlapped with the liquidus projection reported by Yang and Chang.21)

Fig. 2 (a) As-cast microstructure and (b) the data points used for quantitative analysis by EPMA for Alloy 1.
of the alloys were homogenous. The average composition of the 1600 points in total was Mo-9.6Si-18.0B, and assuming that the average value corresponded to the composition of Alloy 1 (Mo-9.5Si-14.2B) shown in Table 1, the compositions were determined for Mo, Si and B by EPMA. Subsequently, the compositions in the two-phase eutectic and three-phase areas in Alloy 1 were selectively analyzed by the calibrated EPMA, and were Mo-8.7Si-15.7B and Mo-13.7Si-11.7B, respectively. The X-ray diffraction pattern for Alloy 1 (Fig. 3(a)) indicated that the constituent phases were Mo, T2 and Mo3Si (A15). Figure 4 shows the TEM-EDX results of the three-phase area. The crystal structure determination according to the diffraction patterns shown in Figs. 4(b)–(c) confirmed the existence of Mo, T2 and A15 in the observed area, as shown in Fig. 4(a). The intensity profiles for the phases were analyzed by EDX; there was a moderate B-Kα peak but slight Si-Kα peak for Mo (e), a strong B-Kα peak compared to the Mo-Kα peak and a moderate Si peak for T2 (f), and moderate B-Kα and Si-Kα peaks for A15 (g). These results indicate that the three-phase areas were composed of Mo, T2 and A15 (the grey phase). The two-phase eutectic areas were also characterized by TEM-EDX, and the results are shown in Fig. 5. The characteristic X-ray intensity profiles of Figs. 5(b) and (c) indicate that the matrix is T2 and the dispersions are Mo3Si, which is in good agreement with the eutectic microstructures reported in the literature.8,19 Therefore, the solidification steps of Alloy 1 were confirmed to be Mo3Si (primary) → Mo3Si + T2 eutectic → Mo3Si + T2 + A15.

Figure 6 shows the as-cast microstructures of Alloys 2, 3 and 4. The four kinds of microstructural areas identified in Alloy 2 are shown in Fig. 6(a); there were large primary particles, elongated large secondary areas containing bright particles, superfine eutectic and fine three-phase areas. XRD showed the existence of Mo3Si, T2, A15 and Mo2B (Fig. 3(b)). EPMA analysis showed the primary particles were Mo3Si, and the secondary areas consisted of a matrix of Mo2B with Mo3Si particles. Since the compositions and microstructural features of the superfine eutectic and fine three-phase areas correspond well to those in Alloy 1, it is assumed they were Mo3Si-T2 eutectic and Mo3Si-T2-A15 three-phase areas. Consequently, the solidification steps of Alloy 2 were Mo3Si (primary) → Mo3Si + Mo2B → Mo3Si + T2 eutectic → Mo3Si + T2 + A15. The primary phase of Mo3Si in Alloy 2 was consistent with that shown in the liquidus projection of Fig. 1. The three kinds of microstructural areas in Alloy 3 are shown in Fig. 6(b); there were large angular primary areas, and superfine eutectic and fine three-phase areas. XRD confirmed the existence of Mo, T2 and A15 (Fig. 3(c)), and then EPMA analysis indicated the primary angular areas were composed of T2, and the eutectic and three-phase areas were Mo3Si and Mo3Si-T2-A15, respectively. Hence, the solidification steps of Alloy 3 were T2 (primary) → Mo3Si + T2 eutectic → Mo3Si + T2 + A15. The existence of a primary T2 phase in Alloy 3 is also consistent with that in the liquidus projection shown in Fig. 1. In Alloy 4 (Fig. 6(c)), the elongated primary phase co-existed with the superfine two-phase eutectic and fine three-phase areas. XRD showed the existence of Mo3Si, T2, A15 and Mo2B (Fig. 3(d)), and EPMA indicated the primary elongated areas consisted of Mo2B, and the eutectic and three-phase areas were Mo3Si-T2 and Mo3Si-T2-A15, respectively. Thus, the solidification steps of Alloy 4 were Mo2B (primary) → Mo3Si + T2 eutectic → Mo3Si + T2 + A15. The primary phase of Mo2B in Alloy 4 is also consistent with that in the liquidus projection.
Figure 7 shows the compositions of the two-phase eutectic and three phase areas for Alloys 1–4 determined by a quantitative EPMA analysis, and plotted against the overlapped liquidus projections reported by Yang and Chang\textsuperscript{21}) and Nunes \textit{et al.}\textsuperscript{19}). All four data points for the two-phase eutectic and the three-phase areas are plotted at the same point, irrespective of the primary phase. Note that the Mo\textsubscript{2}T\textsubscript{2} eutectic points are inside the Mo\textsubscript{2}B primary area in the liquidus projection by Yang and Chang. This clearly indicates that their solidification steps do not run on the routes indicated in the liquidus projection. The data points come together not on the solidification route lines but between the lines drawn by Yang and Chang\textsuperscript{21}) and Nunes \textit{et al.}\textsuperscript{19)} except for Alloy 4. Since only Alloy 4 has a Mo\textsubscript{2}B primary phase, that is, it has a composition much close to the Mo\textsubscript{2}T\textsubscript{2} eutectic point, the compositions of the two-phase eutectic and three phase areas may fluctuate significantly due to super-cooling during solidification. In this study we were able to clarify that the primary phase regions are in excellent agreement with the liquidus projection by Yang and Chang\textsuperscript{21}) but the subsequent solidification steps do not concur with the solidification routes indicated in the liquidus projection. This conflict in the interpretation of the solidification routes and as-cast microstructures can be attributed to the unusual solidification routes in the Mo-Si-B system. The compositions of the Mo\textsubscript{2}T\textsubscript{2}-A15 areas also lie between the solidification routes indicated by Yang and Chang\textsuperscript{21}) and Nunes \textit{et al.}\textsuperscript{19}) and also near the midpoint between the T point of the primary Mo\textsubscript{2}T\textsubscript{2} and Mo\textsubscript{2}B and the Mo\textsubscript{2}T\textsubscript{2}-A15 three-phase eutectic point. Since solidification is complete in the three-phase area, the composition can be expected to deviate larger between the outer and inner parts of the ingot. The composition may eventually reach the Mo\textsubscript{2}T\textsubscript{2}-A15 three-phase eutectic point. Further research

Fig. 4 (a) Bright field TEM micrograph for a three-phase area. (b)–(d) Diffraction patterns, and (e)–(f) characteristic X-ray intensity profiles by EDX for the three phases, respectively.
needs to be done to confirm the solidification pathways for the Mo-Si-B system.

Through this study, we were able to realize the unreliability of the EPMA quantitative analysis results for B. As mentioned before, the average composition of Alloy 1 by EPMA was Mo-9.6Si-18.0B even if the ZAF correction was adopted with the standards of Mo, Si and NdB₆, while the nominal composition was Mo-9.5Si-14.2B. The MoₙₓT₂ eutectic phase in Alloy 1 was estimated to be Mo-8.7Si-23.0B with Mo, Si and NdB₆ standards in contrast to the calibrated value of Mo-8.7Si-15.7B. The low accuracy of the results of the EPMA quantitative analysis of B in the Mo-Si-

4. Conclusions

In this study, the phase formation behavior of the Mo-Si-B system during solidification was experimentally examined around the triple junction point (T) of primary Moₙₓ, T₂ and Mo₂B phases in the Mo-Si-B liquidus projection proposed by Yang and Chang. Among the alloys employed, the alloy
with a composition closest to the T point (Mo-9.5Si-14.2B) had two microstructural areas, that is, Mo\textsubscript{ss}-T\textsubscript{2} superfine eutectic and Mo\textsubscript{ss}-T\textsubscript{2}-A\textsubscript{15} fine three-phase areas. Utilizing the microstructural and compositional homogeneity of the alloy, the quantitative analysis results obtained by EPMA were well calibrated, with particular interest in the results for B. The calibrated EPMA results indicate that the primary phase regions are in excellent agreement with the liquidus projection by Yang and Chang\textsuperscript{21)} but the subsequent solidification steps do not run on the solidification routes shown in the liquidus projection. Further research needs to be done to ascertain the precise solidification routes and as-cast microstructures of the Mo-Si-B system.

Acknowledgment

I would like to express my gratitude to Mr. Y. Murakami of Institute for Materials Research, Tohoku University for his assistance operating EPMA. This work was supported by Global COE Program “Materials Integration (International Center of Education and Research), Tohoku University”, MEXT, Japan and the Grant-in-Aid for Science Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan, under Contract No. 21360334.

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