Microstructural Evolution of Mo-Si-B Ternary Alloys Through Heat Treatment at 1800°C

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Abstract. First of all, the as-cast microstructures of Mo-rich Mo-Si-B ternary alloys were investigated around the triple junction point of the primary Mo solid solution, Mo₅SiB₂ and Mo₂B in this work, based on the liquidus projections of the Mo-Si-B system which have been reported in earlier studies. Subsequently, their microstructural evolution through heat treatment was investigated. Since Mo₂B crystallizes out during solidification into a primary or secondary phase even though the alloy composition lies in the triangle of Mo-Mo₅SiB₂-Mo₃Si in the Mo-Si-B equilibrium phase diagram, the as-cast microstructures include the non-equilibrated Mo₂B in wide compositional ranges. However, Mo₂B was completely decomposed during heat treatment at 1800 °C for 24 h and this contributed to the development of homogeneous, fine microstructures. On the other hand, since Mo₂B was not decomposed perfectly during 24 h of 1600 °C heat treatment, as-cast microstructures largely remained. Therefore, it is realized that the heat treatment at 1800 °C is necessary to obtain well-developed microstructures of Mo-Si-B alloys.

Introduction

Mo-Si-B ternary alloys containing Mo solid solution (Moₚ), Mo₃Si and Mo₅SiB₂ (T₂) are one of greatly promising candidates as ultra-high temperature structural materials beyond Ni-base superalloys. Several efforts have been dedicated to understand the phase formation and stability and the solidification pathways of Mo-Si-B ternary alloys [1–6]. Liquidus projection charts play an important role in understanding the sequences of phase formation from liquid to a final microstructure of an alloy. A number of the liquidus projections obtained either experimentally or thermodynamically calculated have been reported for the Mo-Si-B system. Nunes et al. [2,3] were the first to publish their projection in 1997, showing the solidification pathways for each primary phase region with their corresponding microstructures. Katrych et al. also published their melting diagram of the Mo-Si-B system [4]. After those, Yang and Chang reconsidered the system using a thermodynamic modeling approach [5]. Despite the attention this system has been getting, some minor discrepancies remain between the studies, particularly with regard to as-cast microstructures and their phase developments during heat treatment.

Some equilibrium ternary phase diagrams have been also proposed for the Mo-Si-B system. Nowotny et al. presented a Mo-Si-B phase diagram at 1600 °C in 1957 [1]. Nunes et al. redrew it 40 years later (1997) [2], and Kim and Perepezko modified it recently (2006) [6]. Microstructural studies have been extensively conducted for the Mo-Si-B system based on the equilibrium ternary phase diagram at 1600 °C [e.g. 7–12]. However, studies concerning the microstructural evolution by heat treatment correlated with as-cast microstructure are few and far between.
Table 1 Weighed and chemically analyzed compositions of Alloys 1 – 4 [at.%].

| Alloy No. | Weighed composition | Chemically analyzed composition |
|-----------|---------------------|--------------------------------|
|           | Si  | B  | Si  | B  |
| 1         | 9.5 | 14.2 | 9.28 | 14.05 |
| 2         | 6.6 | 13.2 | 6.52 | 13.03 |
| 3         | 10.5 | 14.2 | 10.76 | 14.46 |
| 4         | 8.7 | 17.4 | 8.47 | 17.21 |

In this study, the as-cast microstructures were investigated around the triple junction point of primary Mo solid solution (Mo₉₆₃), Mo₅SiB₂ (T₂) and Mo₂B, based on the liquidus projections of the Mo-Si-B system reported by Yang and Chang [5]. This was followed by an investigation into their microstructural change due to heat treatment at 1600 °C or 1800°C. The microstructure evolution will be discussed by comparing the microstructures before and after heat treatment.

Experimental Procedures

Four kinds of alloys were prepared by an arc-melting technique from pure Mo (99.9 wt.%), Si (99.9999 wt.%) and B (99.95 wt.%) in an Ar atmosphere. The weighed and chemically analyzed compositions of the four alloys are given in Table 1. Details with regard to sample preparation and chemical analyses are described in our previous paper [13]. Half of one ingot for each alloy was annealed at 1600 or 1800 °C for 24 h in Ar at atmospheric pressure. Their microstructures before and after the heat treatment were observed by scanning electron microscopy (SEM) with back scattered electron images (BSE). Their constituent phases were identified by X-ray diffractometry (XRD). A quantitative composition analysis was performed using an electron probe micro-analyzer (EPMA). The details of how the quantitative composition analysis data were calibrated are also given in our previous paper [13]. Microstructure observation and qualitative composition analysis

![Fig. 1](image-url)  
Fig. 1 Change in concentration of Mo, Si and B by EPMA after the heat treatment at 1800 °C for 24 h in an Ar atmosphere.
Fig. 2 Chemical compositions of the four different alloys examined in this study. Red (thick) lines correspond to the liquidus projection reported by Yang and Chang [5] and black (thin) lines correspond to the ternary phase diagram at 1600 °C reported by Kim et al. [6].

were also conducted using a transmission electron microscope (TEM) operated at 300 kV equipped with an energy dispersive X-ray spectroscope (EDX).

An additional sample was produced by powder-processing in order to check compositional degradation during heat treatment. Mo-Si-B powder with an average composition determined by EPMA as Mo-(12.0 ± 2.0)at.%, Si-(34.7 ± 3.1)at.% B was consolidated using a spark-plasma sintering machine operated at 1600 °C and 65 MPa for 10 min. The compositional degradation from the surface after the heat treatment at 1800 °C for 24 h was quantitatively measured by EPMA.

Fig. 3 BSE images of as-cast microstructures of Alloys 1 – 4. (a) Alloy 1, (b) Alloy 2, (c) Alloy 3 and (d) Alloy 4.
Results and Discussion

During the heat treatment at 1800 °C for 24 h, compositional degradation occurred near the surface. Fig. 1 shows the change in concentration of Mo, Si and B from the surface according to EPMA measurements. The gray zones indicate the standard deviations against the average concentrations of the elements in a non-heat-treated specimen. Si concentration was almost constant from the surface to inside. However, Mo concentration was more than 5 at.% higher and B concentration more than 5 at.% lower near surface than inside and in the non-heat-treated specimen. The enrichment of Mo and the depletion of B resulted mainly from the evaporation of B from the surface during heat treatment even when in an Ar atmospheric pressure. No compositional degradation appears under a depth deeper than 500 µm, as shown in Fig. 1. Considering these results, all of the previously mentioned microstructural observation and phase identification techniques were conducted on the inner parts of the ingot, in regions significantly deeper than 500 µm from the surface.

The chemical compositions of the four different alloys produced by Ar arc-melting are plotted in Fig. 2, which includes the projection of the liquidus surface of the Mo-Si-B system as calculated by Yang and Chang [5] overlapped with the ternary phase diagram at 1600 °C produced by Kim et al. [6]. The composition of Alloy 1 was almost at the triple junction point of the Mo\textsubscript{ss}, T\textsubscript{2} and Mo\textsubscript{2}B primary phases (the so-called “T” point) in the liquidus projection and inside the Mo\textsubscript{ss}-T\textsubscript{2}-Mo\textsubscript{3}Si three-phase region of the ternary phase diagram. The composition of Alloy 2 lay completely in the primary Mo\textsubscript{ss} region of the liquidus projection and in the Mo\textsubscript{ss}-T\textsubscript{2} two-phase region of the ternary phase diagram. In the case of Alloy 3, its composition lay in the primary T\textsubscript{2} region of the liquidus projection and inside the Mo\textsubscript{ss}-T\textsubscript{2}-Mo\textsubscript{3}Si three-phase region of the ternary phase diagram. The composition of Alloy 4 lies in the primary Mo\textsubscript{2}B region in the liquidus projection plot and in the Mo\textsubscript{ss}-T\textsubscript{2} two-phase region of the ternary phase diagram.

Fig. 3 shows the as-cast microstructures of Alloys 1 – 4. As reported in our previous paper [13],

![Microstructures of Alloys 1 to 4](image-url)

Fig. 4 BSE images of Alloys 1 – 4 microstructures after heat treatment at 1800 °C for 24 h. (a) Alloy 1, (b) Alloy 2, (c) Alloy 3 and (d) Alloy 4.
composition dependence on primary phase formation was in excellent agreement with the liquidus projection by Yang and Chang [5]. Alloy 1 had a slight amount of very small primary Mo₅S₆ areas, superfine Mo₅S₆-T₂ two-phase eutectic and fine Mo₅S₆-T₂-Mo₃Si three-phase areas. Alloy 2 had large primary Mo₅S₆ areas, largely-elongated secondary Mo₂B areas containing Mo₅S₆ grains, superfine Mo₅S₆-T₂ two-phase eutectic and fine Mo₅S₆-T₂-Mo₃Si three-phase areas. As described above, the composition of Alloy 2 was in the Mo₅S₆-T₂ two-phase region of the ternary phase diagram. Thus, the Mo₂B contained in Alloy 2 was not equilibrated at 1600 °C. Alloy 3 had large angular shapes of primary T₂, superfine Mo₅S₆-T₂ two-phase eutectic and fine Mo₅S₆-T₂-Mo₃Si three-phase areas. Alloy 4 had elongated primary Mo₂B areas, superfine Mo₅S₆-T₂ two-phase eutectic and fine Mo₅S₆-T₂-Mo₃Si three-phase areas. The composition of Alloy 4 was also in the Mo₅S₆-T₂ two-phase region of the ternary phase diagram, and thus Alloy 4 also contained Mo₂B non-equilibrated at 1600 °C.

Fig. 4 shows the microstructures of Alloys 1 – 4 after heat treatment at 1800 °C for 24 h. The microstructures of all of the alloys drastically changed during heat treatment. Alloy 1 had a homogeneous microstructure consisting of Mo₅S₆, T₂ networks and a small amount of Mo₃Si grains, which corresponds well to the ternary phase diagram. From the microstructure observation of Alloy 1, it is clear that heat treatment at a temperature of 1800 °C is sufficient to enhance the microstructural evolution of the Mo-Si-B alloys. Alloys 2 and 4 had non-equilibrated Mo₂B in their as-cast microstructures, but it disappeared completely during heat treatment. In Alloy 2, the matrix was T₂. Some primary Mo₅S₆ areas are assumed to have merged together and small Mo₅S₆ grains distributed homogeneously between primary Mo₅S₆ areas. Alloy 4 had a simple microstructure, that is, small Mo₅S₆ grains were distributed homogeneously in the matrix of T₂. The Mo₅S₆ and T₂ two-phase microstructures in Alloys 2 and 4 also correspond to the ternary phase diagram. Mo₃Si was occasionally observed in Alloys 2 and 4, suggesting that the compositions of Alloys 2 and 4 stand on the phase boundary between Mo₅S₆-T₂ and Mo₅S₆-T₂-Mo₃Si regions in the ternary phase diagram at 1800 °C. In Alloy 3, primary angular T₂ areas remained after heat treatment, with a homogeneous microstructure consisting of Mo₅S₆, T₂ and Mo₃Si grains developed between the T₂ areas.

On the other hand, microstructural evolution was not sufficiently achieved during heat treatment at 1600 °C for 24 h for the Mo-Si-B alloys. Fig. 5 shows an example of the microstructure observed of Alloy 4 heat-treated at 1600 °C for 24 h. Not only did a significant amount of primary Mo₂B areas remained, but the microstructure development between the primary areas was insufficient in the entire specimen. Consequently, it is clear that the heat treatment at 1600 °C for 24 h is inadequate and that a temperature of 1800 °C is necessary to obtain a well-developed microstructure from as-cast Mo-Si-B alloys, which should be stable at ultra-high temperatures.
Conclusions

In this work, the microstructural evolution from as-cast states was investigated for the Mo-Si-B alloys after heat treatment at 1600 or 1800 °C for 24 h. Microstructures after heat treatment at 1800 °C for 24 h were strongly influenced by their as-cast microstructures. Primary phases of Mo₆S₃ and T₂ remained, but primary or secondary Mo₂B was completely decomposed, contributing to the development of homogeneous, fine Mo₆S₃-T₂ or Mo₆S₃-T₂-Mo₃Si microstructures since the compositions of the alloys lie in the two or three phase region and Mo₂B is not in equilibrium at that temperature. On the other hand, Mo₂B was not decomposed perfectly during heat treatment at 1600 °C for 24 h, and thus microstructure development was not sufficient after the treatment. Therefore, it is realized that heat treatment needs to be carried out at 1800 °C in order to obtain well-developed microstructures of the Mo-Si-B alloys.

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