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Solidification of Bcc/T_1/T_2 three-phase microstructure in Mo–Nb–Si–B alloys

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ABSTRACT

The three-phase, $(Mo,Nb)_{ss}$/$(Mo,Nb)_5Si_3$/$(Mo,Nb)_5SiB_2$, Bcc/T_1/T_2 microstructures that develop in Mo–Nb–Si–B alloys have been examined in arc cast and directionally solidified samples to identify the phase sequencing during solidification. A Mo-32.6Nb-19.5Si-4.7B (at.%) alloy was directionally solidified using an optical floating zone (OFZ) furnace in a flowing Ar gas atmosphere at a constant growth rate of 10 mm/h. The microstructure of the directionally solidified alloy is characterized by an elongated T_2 phase surrounded by bcc and T_1 phases with an interwoven morphology From the evaluation of the microstructures in arc cast ingots of several alloys at a constant 32.6 at%Nb composition, the path of the liquidus valleys with decreasing temperature has been determined to intersect at a common point that establishes the solidification reaction as a eutectic. The incorporation of the experimental results into a computational thermodynamic analysis provides insight on the partitioning of components within each phase during solidification.

1. Introduction

In order to increase the performance and efficiency in jet engines and stationary gas turbines, it is essential to increase the gas inlet temperature. For the commonly used Ni-based superalloys, the highly refined cooling and coating schemes to prevent melting in the current high-pressure turbine can reduce the surface temperature below 1100 °C, but they incur a penalty as a loss of efficiency [1,2]. In order to advance beyond Ni-based systems, alternative materials such as refractory metals are needed to significantly improve the performance of jet engines and gas turbines. The candidate materials are multiphase Mo and Nb based alloys such as Mo–Si–B and Nb–Ti–Hf–Cr–Al–B–Si [2]. In addition to the basic requirements of high melting temperature, phase stability and environmental resistance, high temperature materials must also exhibit microstructural stability for extended periods during service. The satisfaction of this requirement creates a dilemma for processing. Most high temperature processing treatments involve diffusion, but microstructural stability requires a suppression of diffusional processes. To solve this dilemma the focus of processing must be directed towards the initial microstructure synthesis since subsequent modification is undesirable.

For Mo–Si–B alloys many investigations of microstructure development and mechanical properties were conducted on samples produced by PM methods. However, even with careful processing the PM samples contain some inclusions of SiO_2, Fe pick up from ball milling and residual porosity [3–6]. The experience with the solidification processing of Mo–Si–B alloys is limited to mainly test sample ingots with some successful examples of directional solidification [7–9]. Solidification processing is challenged by the high melting temperatures, but scaled up sizes produced by VAR (vacuum arc melting) or other solidification methods are possible and can yield fully dense castings without inclusions.

The most widely studied Mo–Si–B ternary alloys consist of α-Mo, Mo_3Si (A15), and the Mo_5SiB_2 (T_2) phases and are known to have attractive high temperature mechanical properties and some oxidation resistance [3–14]. Since the Mo_3Si phase does not contribute to an effective oxidation resistance [15], alternate alloy

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designs have been examined to modify the microstructure. For example, the addition of Nb into the Mo–Si–B alloys can destabilize the A15 phase, resulting in the formation of a three phase region of bcc + T_2 + Mo_5Si_3 (T_1) with exceptional high temperature strength [16–18]. The solidification microstructure exhibits the organized interwoven morphology [2,7,17], which suggests a three-phase decomposition as a L → bcc + T_1 + T_2 eutectic reaction or as a L + T_2 → bcc + T_1 peritectic reaction in the Mo–Nb–Si–B quaternary system. The character of the final solidification reaction depends on the trajectories of the liquidus valleys that determines the phase sequencing. For a eutectic reaction the trajectories of the three liquidus valleys with decreasing temperature intersect at a common point. In a peritectic type reaction the liquidus paths intersect at a point, but one path continues decreasing in temperature from the intersection point. It is essential to understand the solidification reaction in order to control the multiphase solidification microstructure and to satisfy several application requirements for the Mo–Nb–Si–B alloys.

2. Experimental procedure

In order to define the solidification pathways and the character of the final solidification reaction, a series of nine alloys was examined with compositions given in Table 1 along with the observed primary and secondary phases. Alloy 5 was examined following directional solidification, but the other eight alloy compositions listed in Table 1 were examined as arc-cast ingots. For all compositions listed in Table 1 the Nb level was maintained at 32.6 at%Nb since previous work [7] has identified this Nb level as favorable for the development of the $(Mo,Nb)_{ss}$ +T_1 +T_2 three phase microstructure.

To provide a perspective on the relative location of the alloy compositions selected for solidification with respect to the equilibrium phases at 1500 °C the compositions are plotted on the calculated isotherm for a constant 32.6 at%Nb level in Fig. 1. The majority of the alloy compositions lie within the calculated $(Mo,Nb)_{ss}$ +T_1 +T_2 region.

A rod alloy with a composition of Mo–32.2Nb–19.5Si–4.7B (at.%) with a diameter of 8 mm was prepared by arc-melting in an Ar atmosphere. The directional solidification was conducted on the rod alloy using an optical floating zone (OFZ) furnace in a flowing Ar gas atmosphere at a constant growth rate of 10 mm/h. The alloy was directionally solidified to about 6 mm in length and then rapidly cooled by cutting off the lamp source of the OFZ furnace. The button ingots with the compositions of Mo–32.6Nb–xSi–xB (at. %) were prepared by repeated arc melting under a Ti-gettered Ar atmosphere. These compositions plotted on a 32.6% Nb section in a Mo–Nb–Si–B quaternary system are shown in Fig. 1. Table 1 summarizes the compositions of studied alloys. The sample surface for the observation was mechanically polished and then finished using colloidal silica. The microstructures were observed using a scanning electron microscope (SEM).

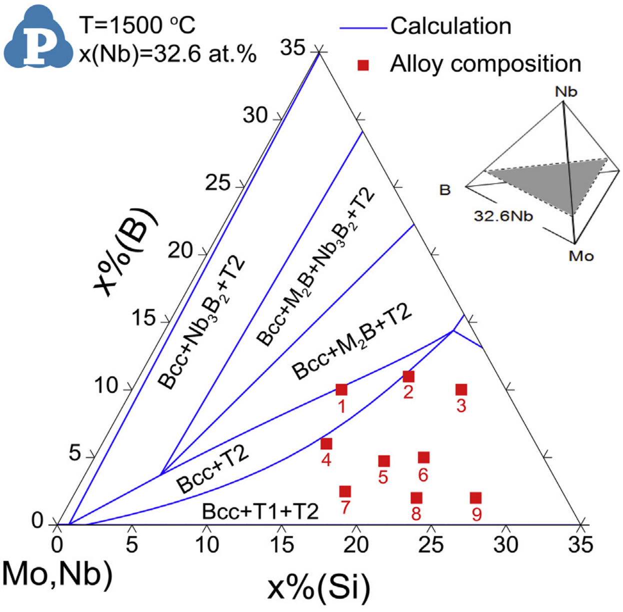

Fig. 1. Chemical compositions of the studied alloys plotted on a 32. 6 at % Nb section in a calculated Mo–Nb–Si–B quaternary phase diagram at 1500 °C.

The chemical compositions of constituent phases in the studied alloys were measured using CAMECA SX50 electron microprobes operated at an accelerating voltage of 6 kV and a current density of 6.3×10^{-9} A. calibration standards consisted of 99.9% pure Mo, Nb,Si and B metals. Mo Lα and Nb Lα peaks were analyzed with a PET crystal, Si Kα with a TAP crystal and B Kα with a PC2 crystal. The B concentration was quantified by separating the intensity of B Kα peak (at 0.182 kV) from Mo Mζ peak (at 0.192 kV) using the analysis software Probe for Windows (Advanced Microbeam Inc) [19]. The probe sizes ranging from the finest available up to 10–20 μm were used to measure the compositions of constituent phases and solidified zones (with a fine-scale solidification microstructure), respectively.

3. Thermodynamic modeling

The thermodynamic modeling work on the Mo–Nb–Si–B quaternary system was carried out using the CALPHAD approach [20], which is a phenomenological methodology to obtain a thermodynamic database for a multicomponent system. The term “thermodynamic database” means that the parameters for the Gibbs energies of all the phases in a system are known. The first step in developing a thermodynamic database for a multicomponent system is to collect thermodynamic and phase equilibrium

Table 1
Chemical compositions of studied Mo–Nb–Si–B alloys and primary and secondary solidified phases in these alloys determined by microstructure observation.

Chemical composition (at.%)	Primary solidified phase	Secondary solidified phase
Alloy 1:Mo-32.6Nb-14Si-10B	T_2	bcc
Alloy 2: Mo-32.6Nb-18Si-11B	T_2	–
Alloy 3: Mo-32.6Nb-22Si-10B	T_2	T_1
Alloy 4: Mo-32.6Nb-15Si-6B	bcc	T_2
Alloy 5: Mo-32.6Nb-19.5Si-4.7B	(T_2)	–
Alloy 6: Mo-32.6Nb-22Si-5B	T_1	T_2
Alloy 7: Mo-32.6Nb-18Si-2.5B	bcc	T_1
Alloy 8: Mo-32.6Nb-23Si-2B	T_1	bcc
Alloy 9: Mo-32.6Nb-27Si-2B	T_1	bcc