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# Annealing response of point defects in off-stoichiometric $Mo_5SiB_2$ phase

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**Abstract**

Dislocations and planar faults are found to develop in the $Mo_5SiB_2$ phase during elevated temperature annealing. The dislocations formed in $Mo_5SiB_2$ of annealed alloys are mostly edge dislocations with the Burgers vectors of ⟨100], 1/2⟨111], and ⟨110]. For the Mo-rich $Mo_5SiB_2$ phase that formed in a Mo–10Si–20B alloy, a significant amount of constitutional vacancies is introduced during solidification, and the excess vacancies aggregate and collapse into dislocations. At the same time, these dislocations can act as the heterogeneous nucleation sites for the subsequent Mo precipitation. For the Mo-lean $Mo_5SiB_2$ phase that formed in a Mo–13Si–28B alloy, the constitutional defects are not significant for the development of dislocations.


*Keywords:* A. Molybdenum silicides; B. Precipitates; D. Defects: constitutional vacancies; D. Microstructure; F. Electron microscopy, transmission

## 1. Introduction

The performance improvement of aircraft engines will necessitate the development of new heat resistant materials with superior properties to the Ni-based superalloys. Over the past decades refractory metal silicides and aluminides have been considered as candidate materials because of their high melting temperatures and good oxidation resistance at high temperatures [1,2]. Above about 1400 °C, silicides seem to be more attractive since the parabolic rate constant for oxidation in $SiO_2$ is lower than that in $Al_2O_3$ [3]. This selection is supported by the excellent oxidation resistance of $MoSi_2$ that forms a $SiO_2$ protective layer stable up to about 1700 °C. However, a number of studies have revealed that there seems to be no feasible way to provide $MoSi_2$ based alloys with sufficient creep, fracture and oxidation resistances for structural design [4,5].

Following the discovery of significant improvement in the oxidation resistance of $Mo_5Si_3$ by small boron additions [6–8], Mo–Si–B alloys with Mo-rich compositions have attracted considerable interest for potential high temperature applications. The multiphase alloys that develop in the Mo–Si–B system have been found to exhibit excellent high temperature strength [9–13], moderate fracture toughness [12–17], and favorable oxidation resistance at elevated temperatures [12,18–24]. A focal point of the microstructural designs is the ternary intermetallic $Mo_5SiB_2$ ($T_2$) phase which has a body centered tetragonal structure (*tI*32, *I*4/*mcm*: $D8_l$). Systematic investigations have revealed that the $T_2$ phase develops through a peritectic reaction upon solidification, and exhibits a range of homogeneity around the stoichiometric composition [25–30]. Moreover, the $T_2$ phase exhibits temperature dependent solubility, which is manifested by the formation of Mo precipitates in the $T_2$ matrix upon annealing of as-cast alloys [26,31]. This solubility behavior is one of the characteristic features of the $T_2$ phase, since many silicides with complex crystal structures exhibit limited range of homogeneity that hardly changes with temperature. The constitutional vacancy has been proposed as a defect mechanism to explain the

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development of the non-stoichiometry of the $T_2$ phase [26,32]. It is well known, for example in some B2 type intermetallic compounds, that significant amounts of thermal and constitutional vacancies exist for non-stoichiometric compositions. The vacancy concentrations of some B2 compounds reach several percent near the melting temperature [33–35]. These vacancies are easily retained upon solidification since the activation energy of vacancy migration is higher than that of vacancy formation [36]. This tendency, which is quite the reverse to pure metals, is believed to be one of the reasons for the peculiar point defect behavior of intermetallics [36]. Thus, the elucidation of the constitutional defect mechanism in the $T_2$ phase, as well as the lattice defects that develop from the annealing response of constitutional defects are critical to understand the stability of the $T_2$ phase and to guide microstructural designs based on the $T_2$ phase.

In the present study, the change in the $T_2$ phase substructure upon annealing was observed in alloys with multiphase microstructures. For the alloys that were examined, an off-stoichiometric $T_2$ phase with different terminal compositions is in equilibrium with other phases. The annealing response of constitutional point defects was investigated, so that the lattice defects that developed during annealing could be identified and related to the precipitation behavior of Mo within the $T_2$ matrix.

## 2. Experimental procedures

The Mo–10Si–20B and Mo–13Si–28B alloys (at.%) were prepared by arc melting under an Ar atmosphere. The alloys were wrapped with Ta foil, and annealed at 1400, 1550 and 1600 °C under an Ar atmosphere, followed by furnace cooling. The lattice parameters of the $T_2$ phase were measured by X-ray diffractometry (XRD) using powder specimen. The microstructures were characterized by scanning electron microscopy, and transmission electron microscopy. The foils for TEM observation were mechanically thinned, and perforated by an ion mill with an accelerating voltage of 4 kV. TEM observation was conducted on a JEM200CX-II operated at 200 kV. The Burgers vectors of the dislocations formed in the $T_2$ phase were determined by the weak-beam thickness fringe method [37] and the invisibility criterion. The line vectors of the dislocations were determined by a combination of stereo-observation and trace analysis [38]. The dislocation density is determined by measuring the total length of dislocations per unit area with a typical foil thickness of about 100 nm.

## 3. Results and discussions

### 3.1. Microstructure changes of the $T_2$ phase during annealing

Fig. 1 shows the isothermal section at 1600 °C and the liquidus projection in the Mo–Si–B system previously reported [28,39]. The compositions of the present alloys, Mo–10Si–20B and Mo–13Si–28B (at.%), are in the Mo/$T_2$ two-phase field and the α-MoB/$T_1$/$T_2$ three-phase field, respectively. Considering the liquidus projection shown in Fig. 1b, the primary solidification phase of a Mo–10Si–20B alloy is $T_2$, followed by the co-precipitation of Mo and $T_2$. The final solidification product is a Mo/$T_2$/A15 three-phase microstructure. Since the liquid composition associated with the $T_2$ primary precipitation changes into a Mo-rich composition and reaches the Mo/$T_2$ monovariant eutectic trough, the $T_2$ primary possesses a Mo-rich composition as compared with the $T_2$ stoichiometry. For a Mo–13Si–28B alloy, on the other hand, the primary solidification phase is β-MoB, followed by the co-precipitation of β-MoB and $T_2$. The final solidification product of a Mo–13Si–28B alloy is an A15/$T_1$/$T_2$ three-phase microstructure. Since the liquid composition of the L/β-MoB/$T_2$ tie-triangle shifts to a Si-rich composition along the monovariant line, a Mo-lean $T_2$ forms during solidification in a Mo–13Si–28B alloy. Hereafter the $T_2$ phase

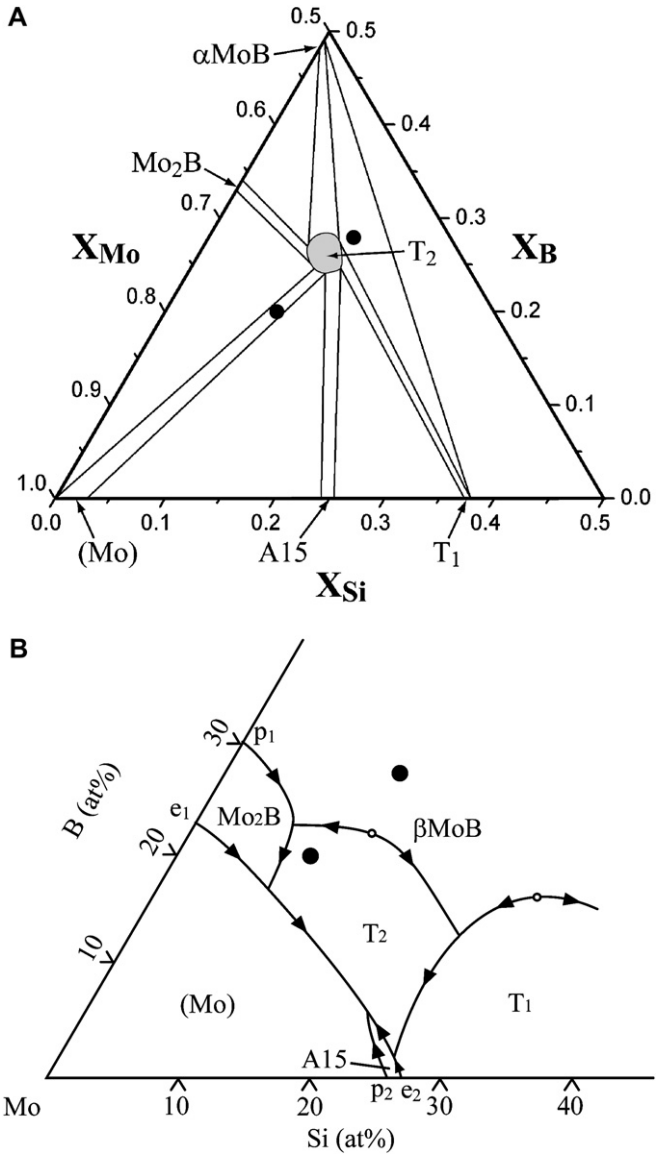


Fig. 1. Isothermal section at 1600 °C and liquidus projection in the Mo–Si–B ternary system.