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Microstructure and fracture toughness in boron added $NbSi_2(C40)$/$MoSi_2(C11_b)$ duplex crystals

Mitsuharu Todai [a], Koji Hagihara [b], Kyosuke Kishida [c,d], Haruyuki Inui [c,d], Takayoshi Nakano [a,*]

[a] Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, 2-1, Yamadaoka, Suita, Osaka 565-0871, Japan
[b] Department of Adaptive Machine Systems, Graduate School of Engineering, Osaka University, 2-1, Yamadaoka, Suita, Osaka 565-0871, Japan
[c] Department of Materials Science and Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan
[d] Center for Elements Strategy Initiative for Structural Materials (ESISM), Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

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ABSTRACT

The effect of B-addition on the microstructure and fracture toughness of $(Mo_{0.85}Nb_{0.15})Si_2$ crystals with an oriented lamellar microstructure was investigated. B-addition led to an increase in the volume fraction of the $C11_b$ phase, which possesses different orientation relationship from that of the fine lamellae, and a reduction in their precipitation rate. The fracture toughness of the B-added crystal with the varied microstructure exhibited a value more than 4.0 MPa $m^{1/2}$, that was significantly higher than that of the ternary crystal.

Transition metal disilicides, such as $MoSi_2$ with $C11_b$ structure and $NbSi_2$ with C40 structure are regarded as promising candidates for ultra-high-temperature structural materials because they have high melting points and good oxidation resistance. They can be expected to use at temperatures higher than the upper temperature limit of Ni-based superalloys [1–16]. However, these disilicides have some disadvantages which are low temperature brittleness and low creep resistance above 1473 K for industrial applications. To overcome these drawbacks, Nakano et al. developed a $NbSi_2(C40)/MoSi_2(C11_b)$ duplex crystal with an oriented fine lamellar microstructure [11]. This duplex crystal was obtained by the growth of the C40-structured $(Mo_{0.85}Nb_{0.15})Si_2$ single crystal and the following heat treatment at 1673 K. It was reported that this duplex crystal exhibits superior high temperature strength and enhanced low temperature fracture toughness [13,15]. The duplex crystals are comprised primarily of a fine $C40/C11_b$ lamellar microstructure, however, some $C11_b$ grains that do not have flat plate-like shapes are also formed when the C40-crystal is annealed at 1673 K for more than 24 h [11]. Those non-fine-lamellar-shaped $C11_b$ grains were found to rapidly grow and disarrange the oriented fine lamellae during prolonged (≥168 h) annealing. Thus, the control of the microstructure is essential to further improving the mechanical properties of the duplex crystal.

One approach for the microstructure control is the addition of another element to induce the segregation of these elements on the lamellar interface. Hagihara et al. [17,18] reported that the addition of some transition metals such as Cr and Zr led to significant improvement in the thermal stability of the oriented fine lamellar microstructure. However, the effect of adding non-transition elements to the duplex crystal remains unexplored. In the present study, we examine the effect of boron (B) additions on the formation of a lamellar microstructure and fracture toughness of the duplex crystal, because it is well known that the ductility and fracture mode of Ni-based alloys and TiAl are drastically improved by B-addition [19–21].

For our experiments, three master ingots having compositions of $(Mo_{0.85}Nb_{0.15})Si_2 - X$ at.% B ($X = 0$, 0.1 and 1.0) were prepared by arc melting of high-purity raw materials, such as Mo, Nb, Si and Mo_2B powder. Hereafter, the $(Mo_{0.85}Nb_{0.15})Si_2$ crystal is referred to as the ternary crystal and the B-added crystals are referred to by the percentage (X) of B added. Single crystalline rods with a C40 structure were grown by the floating zone (FZ) method at a rate of 2.5 mm/h under a high purity argon flow atmosphere. These rods were subsequently annealed at 1673 K for 24 h and 168 h in order to obtain an oriented lamellar microstructure composed of the C40 and $C11_b$ phases. The microstructures were observed by using an optical microscope and the crystal orientation relationship between the C40 matrix phase and the precipitated $C11_b$ phase was determined by the electron backscatter diffraction (EBSD) pattern analysis; EBSD date collection was conducted at a step size of 0.3 μm by using a scanning electron microscope (SEM, JEOL JEM-6500F).

The fracture toughness was examined by micro-Vickers hardness tests at room temperature at an applied load of 1000 gf. Indents were

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* Corresponding author.
E-mail address: nakano@mat.eng.osaka-u.ac.jp (T. Nakano).

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made on the $(10\bar{1}0)$ plane of the C40 matrix phase. In addition, three-point bending tests were conducted at a cross-head speed of 0.005 mm min^{-1}, using an Instron-type testing machine. The fracture toughness value, K_Q based on the ASTM E399-90 guideline [22], was estimated by using the following equation:

$$K_Q = \left(F_Q S/BW^{3/2}\right) \times f(a/W) \tag{1}$$

where F_Q is the fracture load measured on the load–displacement line, and S, B, W and a donate the dimensions of the specimen, as shown in Fig. 4(b). The shape factor, indicated by $f(a/W)$, depends on the size of the specimen [22]. The loading axis was set to be parallel to the $[0001]_{C40}$; the lamellar boundary was laid perpendicular to the loading axis of the specimens. The notch being parallel to $(\bar{1}2\bar{1}0)_{C40}$ was introduced by using a diamond wire cutter.

Fig. 1 shows the variations in the microstructure with annealing period in the 0% (ternary), 0.1% and 1% B-added crystals. Fig. 1(a, d, g) shows the successful growth of C40-structured single crystals of each composition using the FZ method. The C40-single-phase microstructure in the ternary crystal evolved to oriented fine lamellae (Fig. 1(b)) with the precipitation of $C11_b$ phases by annealing at 1673 K for 24 h. However, a few $C11_b$ grains (indicated by the arrows) that do not have flat plate-like shapes formed in addition to the C40/$C11_b$ fine lamellae. The non-fine-lamellar-shaped $C11_b$ grains rapidly grew by further annealing to 168 h, resulting in the destruction of fine lamellar microstructure as shown in Fig. 1(c).

In contrast, the amount of $C11_b$ grains with non-flat interfaces increased significantly in the 0.1% and 1% B-added crystals (Fig. 1(e) and (h)) even by the annealing for 24 h. The volume fraction of non-fine-lamellar-shaped $C11_b$ grains were further increased by extending the annealing period to 168 h. It is to be noted that the size of those non-fine-lamellar-shaped $C11_b$ grains was kept to be smaller than that in the ternary crystal as shown in Fig. 1(f) and (i).

Fig. 2(a)–(f) exhibits the crystal orientation maps of the precipitated $C11_b$ phase in the annealed specimens, analyzed by SEM-EBSD method. The analyzed direction is parallel to the $[83\bar{1}\bar{1}0]_{C40}$, which is rotated by 15° from the $[10\bar{1}0]_{C40}$ to $[11\bar{2}0]_{C40}$ along the $[0001]_{C40}$ zone axis. The EBSD analysis and X-ray diffraction (XRD) measurements confirmed that all examined duplex crystals consisted of C40 and $C11_b$ phases; the black regions in Fig. 2(a)–(f) correspond to the C40 phase. In the ternary crystal, a large portion of the $C11_b$ grains exhibited a fine lamellar microstructure after 24 h annealing. Those grains were shown to belong to one of three colors; red, pink or purple, in Fig. 2(a). This is because these $C11_b$ phases had three orientation relationships with respect to the C40 matrix phase while maintaining the crystallographic relationship of $(0001)_{C40}//(110)_{C11b}$. The so-called strict-lamellar-variant orientation relationships denoted as variant 1 (V1), variant 2 (V2) and

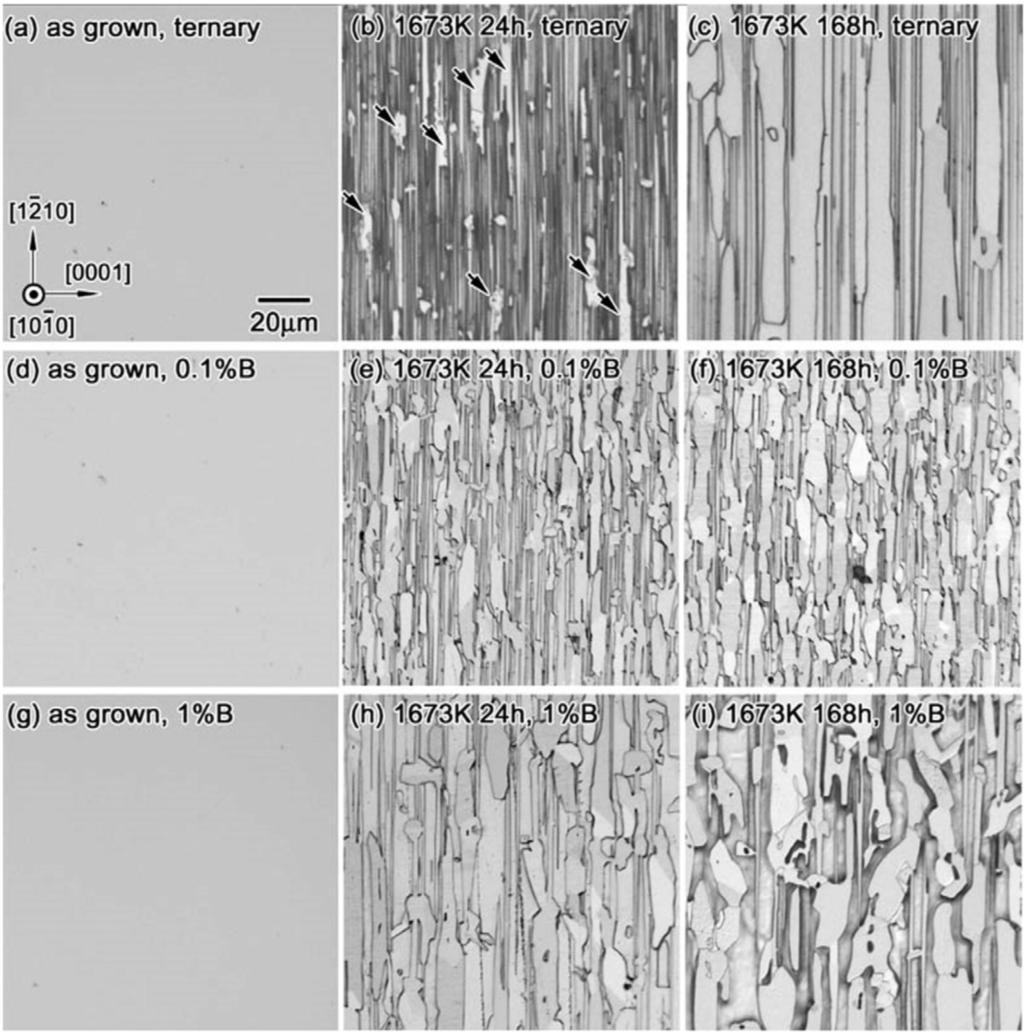

Fig. 1. Variations in the microstructure with annealing period in the (a–c) ternary, (d–f) 0.1% and (g–i) 1% B-added crystals. (a, d, g) as-FZ-grown, (b, e, h) annealed at 1673 K for 24 h, and (c, f, i) annealed at 1673 K for 168 h. The arrows in (b) show the non-fine-lamellar-shaped $C11_b$ phase.