Microstructure and fracture toughness in boron added NbSi₂(C40)/MoSi₂(C11_b) duplex crystals

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Abstract

The effect of B-addition on the microstructure and fracture toughness of (Mo_{0.85}Nb_{0.15})Si₂ 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 varied lamellar microstructure exhibited a value more than 4.0 MPa m^{1/2}, that was significantly higher than that of the ternary crystal. (77 words)

Keywords: Transition metal silicides; Lamellar structure; Toughness; Microstructure

Manuscript

Transition metal disilicides, such as MoSi₂ with C11_b structure and NbSi₂ 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 the 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 NbSi₂(C40)/MoSi₂(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})Si₂ 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 $(\text{Mo}_{0.85}\text{Nb}_{0.15})\text{Si}_2$ - 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 $(\text{Mo}_{0.85}\text{Nb}_{0.15})\text{Si}_2$ 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 data collection was obtained 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 made on the (10T0) 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:

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

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) show 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 show in Fig. 1(f) and (i).

Figs. 2(a)-(f) exhibit 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 $[83\bar{1}0]_{C40}$, 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 Figs. 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 variant 3 (V3) were observed between the C40 phase and C11_b phases as follows:

$$V1: (0001)_{C40} // (110)_{C11b}, [\bar{1}2\bar{1}0]_{C40} // [1\bar{1}0]_{C11b}, [10\bar{1}0]_{C40} // [001]_{C11b} \quad (2)$$

$$V2: (0001)_{C40} // (110)_{C11b}, [2\bar{1}\bar{1}0]_{C40} // [1\bar{1}0]_{C11b}, [0\bar{1}10]_{C40} // [001]_{C11b} \quad (3)$$

$$V3: (0001)_{C40} // (110)_{C11b}, [\bar{1}\bar{1}20]_{C40} // [1\bar{1}0]_{C11b}, [\bar{1}100]_{C40} // [001]_{C11b} \quad (4)$$

As increasing in the annealing period, however, the volume fraction of fine C11_b lamellae showing the above strict-lamellar-variant orientation relationships was decreased from 40.4% to 36.5%, owing to the rapid growth of the non-fine-lamellar-shaped C11_b grains as shown in Figs. 2(d) and (d').

As described in Fig. 1, B-addition was found to drastically reduce the volume fraction of the fine lamellar microstructure, and instead the amount of non-fine-lamellar-shaped C11_b grains was increased, although the sizes were kept to be smaller than those in ternary crystal. SEM-EBSD analysis revealed that the non-fine-lamellar-shaped C11_b grains were not randomly oriented, but exhibited a certain crystal orientation relationship with respect to the C40 matrix phase. This relationship differs from the above-mentioned strict-lamellar-variant orientation

relationship and is given as follows;

$$(0001) \langle 10\bar{1}0 \rangle_{C40} // \{001\} \langle 010 \rangle_{C11b} \quad (5)$$

$$(0001) \langle 10\bar{1}0 \rangle_{C40} // \{001\} \langle 110 \rangle_{C11b} \quad (6)$$

$$(0001) \langle 10\bar{1}0 \rangle_{C40} // \{001\} \langle 210 \rangle_{C11b} \quad (7)$$

$$(0001) \langle 10\bar{1}0 \rangle_{C40} // \{111\} \langle 1\bar{1}0 \rangle_{C11b} \quad (8)$$

$$(0001) \langle 10\bar{1}0 \rangle_{C40} // \{12X\} \langle 2\bar{1}0 \rangle_{C11b} \quad (9)$$

These orientation relationships are similar to those observed in the non-fine-lamellar-shaped C11_b grains in the ternary crystal [11,17]. Hereafter, we refer to these orientation relationships as the secondary-variant orientation relationships. The composition of those constituent phases were examined by energy dispersive X-ray spectroscopy in the SEM (SEM-EDS), and it was confirmed that there is no significant variation in phase composition between the strict-variant C11_b and secondary-variant C11_b phases.

TEM observation of B-added crystals revealed that the growth of non-fine-lamellar-shaped C11_b grains (secondary-variant C11_b phase grains) frequently occurred accompanied by the absorption of the C40/C11_b and C11_b/C11_b lamellar boundaries. This feature is very similar to that previously reported in non-B-added crystal [11]. This suggests that a driving force for nucleation and grain growth of the secondary-variant C11_b phase grain is the reduction in accumulated internal crystal strain on the lamellar boundaries, although the detailed nucleation mechanism of the secondary-variant C11_b phase is not well clarified yet.

The variations in the microstructure indicate that the B-addition altered the precipitation rate of the C11_b phase. In fact, the total amount of precipitated C11_b phase decreased with increasing amount of B in the 24 h annealed crystals as shown in Figs.

2(a')-(c'). Meanwhile, the amount of the C11_b phase was about 60% in all specimens after annealing for 168 h as shown in Figs. 2(d')-(f'). This suggests that the B-addition led to an increase in the incubation time for precipitation of the C11_b phase and a decrease in the volume fraction of the C11_b phases with strict-lamellar-variant orientation relationships.

Fig. 3 shows the variation in the average thickness of the fine-lamellar-shaped C11_b grains with strict-lamellar-variant orientation relationships and the C11_b grains with secondary-variant orientation relationships, measured along the [0001]_{C40} direction on the (10 $\bar{1}$ 0)_{C40} in specimens annealed for 24 h and 168 h, respectively. The error bars in this figure correspond to the standard deviation of the thickness. As the figure shows, the average thickness of the C11_b grains with the strict-lamellar-variant orientation relationships was almost the same independent of B-addition whereas the average thickness of the secondary-variant C11_b grains change significantly. The secondary-variant C11_b grains in ternary crystals had average thickness of 3.4 and 6.7 μm after annealing for 24 h and 168 h, respectively. While those in the 0.1% and 1% B-added crystals were 3.2 and 4.1 μm after annealing for 24 h, and were as small as 3.7 and 4.5 μm after annealing for 168 h, respectively. These results demonstrate that the B-addition effectively suppresses the growth of the secondary-variant C11_b grains.

It has been considered that the formation behavior of the lamellar microstructure is affected by the lattice misfit [17] and the interfacial energy [23] of the lamellar interface. According to Hagihara et al. [17], the thermal stability of the fine lamellar microstructure was improved and secondary-variant C11_b grains almost disappeared by the reduced lattice misfit by Cr and Zr additions. On the other hand, phase-field simulations performed by Koizumi et al. revealed that a fine lamellar microstructure

with flat interfaces on the (0001)_{C40} does not form under conditions of isotropic interfacial energy [23]. In the present study, the B-addition led to a simultaneous increase in the volume fraction of the secondary-variant C11_b grains and a decrease in the fraction of the fine-lamellar-shaped C11_b grains. The B-addition may, therefore, lead to change in the interfacial energy rather than in the lattice misfit of the duplex crystals, although further studied are essentially required to validate this.

It is expected that significant refinement of the secondary-variant C11_b grains has the potential to improve fracture toughness. In fact, grain size refinement led to substantial improvements in the room temperature fracture toughness of a MoSi₂ composite [24-26]. To confirm this, the indentation fracture toughness was first examined by using micro-Vickers hardness tests. This toughness, which is typically referred to K_{IC} was estimated by measuring the crack length (c) and micro-Vickers hardness (H) on the (10 $\bar{1}$ 0)_{C40} of the ternary, 0.1% and 1% B-added crystals [27]. The equation for estimating the K_{IC} classified for different crack systems. In this study, median-type cracks occurred in these crystals [13] and hence the value of K_{IC} was evaluated by the following equation [28,29],

$$K_{IC} = 0.016(E/H)^{1/2}(P/c^{3/2}) \quad (10)$$

where c is the median-type crack length, which is calculated from the observed crack length on the surface and half the diagonal of the indent. E is Young's modulus of the material along the indentation direction and P is the applied load (1000 gf in the case of this study). The E of the binary NbSi₂ single crystal [30] was used during the calculation of the K_{IC} , as rough estimations. Fig. 4(a) shows the variation in the estimated K_{IC} with annealing period. All the as-FZ-grown C40-structured single crystals exhibit a low K_{IC} of about 0.8-1.2 MPa m^{1/2}. The value of K_{IC} for ternary crystal increased upon annealing

for 24 h, but decreased again by annealing for 168 h. This indicates that the development of a fine lamellar microstructure increases the fracture toughness K_{IC} , but the development of coarse secondary-variant C11_b grains decreases the K_{IC} . Furthermore, B-added crystals had lower K_{IC} than that in the ternary crystal in 24 h annealed crystals. This must be owing to the decreases in volume fraction of the precipitated C11_b phase in the B-added crystals compared to that in the ternary crystal by the reduction in the precipitation rate as described in Fig. 2. This highlights the importance of the C11_b phase as a ductile phase. However, when the annealing period was extended to 168 h, B-added crystals have higher K_{IC} than the ternary crystal. This suggests that the suppression of the grain growth of secondary-variant C11_b grains induced the suitable microstructure for increasing the fracture toughness.

We examined the variations in fracture toughness more precisely by performing three-point bending tests for 168 h annealed crystals, as the results are shown in Fig. 4(b). The 0.1% and 1% B-added crystals have average fracture toughness values of ~4.1 MPa m^{1/2} and ~3.9 MPa m^{1/2}, respectively. These values are much higher than that (~2.8 MPa m^{1/2}) of the ternary crystal. This obviously demonstrates the validity of increase in fracture toughness by the suitable control of microstructure in duplex crystals.

In summary, we successfully controlled the microstructure of a NbSi₂/MoSi₂ duplex crystal by the B-addition. B-addition led to an increasing in the volume fraction of the C11_b phase having secondary-variant orientation relationship, accompanied by the reduction in their growth rate. As a result, a microstructure composed of the C40 matrix phase, finer secondary-variant C11_b grains, and strict C40/C11_b fine lamellae was developed in the B-added crystal. It was found that this varied microstructure drastically improved the fracture toughness of the duplex crystal, exhibiting the highest value of

~4.5 MPa m^{1/2} in the three-point bending test.

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Figure captions

Figure 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 Fig. 1(b) show the non-fine-lamellar-shaped C11_b phase.

Figure 2

Crystal orientation maps of the precipitated C11_b phases in the C40 matrix examined by SEM-EBSD analysis, of specimens annealed at 1673 K for (a-c) 24 h and (d-f) 168 h, in the (a,d) ternary, (b, e) 0.1% and (c, f) 1% B-added crystals. The direction of observation in the microstructures was approximately parallel to the $[10\bar{1}0]_{C40}$, but the corresponding crystal orientation maps were colored along a direction rotated by 15° from the $[10\bar{1}0]_{C40}$ toward the $[11\bar{2}0]_{C40}$ to divide color of the three strict-lamellar-variants [17]. Pie charts (a')-(f') show the volume fractions of the C40 and C11_b phases with strict-lamellar-variant orientation and secondary-variant orientation relationships in (a)-(f), respectively.

Figure 3

Variation in the average lamellae thickness of the C11_b grains with (a) strict-lamellar-variant and (b) secondary-variant orientation relationships in specimens annealed at 1673 K for 24 h and 168 h.

Figure 4

(a) Indentation fracture toughness (K_{IC}) of the ternary, 0.1% and 1% B-added crystals with the C40 single-phase and C40/C11_b duplex microstructures. (b) The fracture toughness values of the ternary, 0.1% and 1% B-added crystals annealed at 1673 K for 168 h evaluated by three-point bending tests.

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Figure 1 7.5x5 100words

Figure 2 15x4 160words

Figure 3 7.5x4 80words

Figure 4 7.5x4 80words

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Figure_1

Figure 1

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Figure_2

Figure 2

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Graphical Abstract