Effect of additional elements on fracture toughness of $(\text{Mo}_{0.85}\text{Nb}_{0.15})\text{Si}_2$ C40/C11_b lamellar-structured crystals

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Abstract

Variations in the fracture toughness of lamellar-structured C40/C11_b silicides as a function of the microstructure were examined by using Cr-, Zr-, and Ir-added $(\text{Mo}_{0.85}\text{Nb}_{0.15})\text{Si}_2$ crystals. Fracture toughness variation showed strong orientation dependence, governed by the occurrence frequency of delamination and crack deflection. The refinement of the lamellar microstructure by Ir-addition led to an increase in fracture toughness when the lamella boundary was laid perpendicular to the loading axis, although it decreased at other orientations. The variation in fracture toughness when the alloyed crystal was loaded parallel to the lamellar boundary qualitatively showed good agreement with the predictions by first-principles calculations on the cohesive energy of the C40/C11_b interface.

Keywords: *transition-metal silicides; fracture toughness; bending test; first-principles calculations; lamellar microstructure*

1. Introduction

As a new class of ultra-high-temperature (UHT) structural materials that can tolerate temperatures above 1200 °C, many researchers have studied duplex disilicide crystals combined with C40 and C11_b phases [1-13]. Among them, Nakano et al. reported that as a result of the heat treatment of the $(\text{Mo}_{0.85}\text{Nb}_{0.15})\text{Si}_2$ C40 single-phase single crystals, C11_b phases with composition of $\sim(\text{Mo}_{0.94}\text{Nb}_{0.06})\text{Si}_2$ were precipitated in the $\sim(\text{Mo}_{0.79}\text{Nb}_{0.21})\text{Si}_2$ C40-phase matrix phase with distinct crystallographic orientation relationships of $(0001)_{\text{C40}}//\{110\}_{\text{C11b}}$ and $\langle \bar{1}2\bar{1}0 \rangle_{\text{C40}}//\langle 1\bar{1}0 \rangle_{\text{C11b}}$, called variant orientation relationships, resulting in the development of an oriented lamellar microstructure [4,6]. To apply this material as a UHT structural material, optimization

of the stability of the microstructure, room temperature (RT) fracture toughness, and high-temperature strength is necessary.

It was recently clarified that the addition of alloying elements such as Cr and Zr effectively increased the thermal stability of the lamellar microstructure and that the addition of Ir refined the lamellar microstructure [11]. In terms of the fracture toughness of the duplex crystal, the development of a lamellar microstructure was found to increase the toughness as compared to that of a C40 single crystal [10]. However, the toughness was still low for practical application. To further increase the toughness, in this study, variations in the toughness of duplex crystals with the addition of Cr, Zr, and Ir were examined. From the results, the influence of microstructure on the fracture toughness of the disilicide duplex crystal is discussed.

2. Experimental procedure

Master ingots of ternary $(\text{Mo}_{0.85}\text{Nb}_{0.15})\text{Si}_2$ and quaternary $(\text{Mo}_{0.85}\text{Nb}_{0.15})_{0.97}\text{X}_{0.03}\text{Si}_2$ where $\text{X} = \text{Cr}, \text{Zr}, \text{or Ir}$, were prepared by melting high-purity raw materials in an Ar plasma arc furnace. Hereafter, we denote these quaternary $(\text{Mo}_{0.85}\text{Nb}_{0.15})_{0.97}\text{X}_{0.03}\text{Si}_2$ crystals as X-added crystals. Single crystals composed of C40-single-phase were grown using the floating zone melting method at a growth rate of 2.5 mm/h. The single crystals obtained were then annealed at 1400 °C for 168 h to develop aligned lamellar microstructures comprising C40/C11_b phases. For non-added $(\text{Mo}_{0.85}\text{Nb}_{0.15})\text{Si}_2$, specimens annealed for 336 h were also prepared, in which the lamellar microstructure was largely degraded by the long-term annealing [11]. Using the crystals, rectangular specimens with dimensions of $\sim 2 \text{ mm} \times 1 \text{ mm} \times 10 \text{ mm}$ were prepared for three-point bending tests, and then notches were introduced using a diamond wire cutter. Specimens with three different crystal geometries were prepared for the tests to examine the orientation dependence of the fracture behavior. Details regarding the crystal orientation and shape of the specimens are shown later.

Three-point bending tests were conducted on an Instron-type testing machine with a strain rate of $4.2 \times 10^{-5} \text{ s}^{-1}$ at RT. The fracture toughness values, K_{Q} , were estimated from the fracture load measured on the load–displacement line according to ASTM E399-90 [14]. The fracture surfaces were examined by optical microscopy (OM) and scanning electron microscopy (SEM). In addition, for estimating the variations in the interface strength of the lamellae as a function of the addition of alloying element, first-principles calculations were conducted based on the model previously reported by Yuge et al. [15].

3. Results and discussion

Figs. 1(a–e) show the microstructures of the crystals investigated in this study. The detailed features on the variations in microstructure by the addition of alloying elements were clarified in a previous paper [11]. In a $(\text{Mo}_{0.85}\text{Nb}_{0.15})\text{Si}_2$ crystal annealed at 1400 °C for 168 h [Fig. 1(a)], a fine lamellar microstructure composed of C40/C11_b

phases was developed. However, in addition, some coarse C11_b-phase grains also existed. The anomalous coarsening of those C11_b phase grains was derived from the driving force to reduce the residual strain on lamellar interfaces [6]. Thus, with increasing annealing period to 336 h, the lamellar microstructure was further largely degraded [Fig. 1(e)]. Such thermal instability of the lamellar microstructure could be significantly improved by the addition of Cr and Zr, which would reduce the misfit strain on the lamellar interfaces [11]. The specimen was wholly covered by the finely aligned lamellar microstructure in Cr- and Zr-added crystals [Figs. 1(b,c)]. By the addition of Ir, on the other hand, the microstructure was found to be extremely refined, although the volume fraction of non-lamellar C11_b phases that did not show the variant orientation relationship was not significantly reduced as compared to that in non-added crystal [Fig. 1(d)]. In this study, the variations in toughness with such microstructures were the focus.

Fig. 2 shows the evaluated fracture toughness of the specimens. Three-point bending tests were conducted with three kinds of specimens, denoted as types A, B, and C. The lamella interface was parallel to the loading axis, perpendicular to the loading axis, and parallel to the notch plane in types A, B, and C, respectively. In the bending tests, all the specimens were fractured in the region where the load–displacement lines showed a linear relationship, as similarly to the results obtained in the non-added crystals [10]. Thus, the toughness was evaluated from the fractured stress according to [14]. It was found as the general tendency that the toughness increases along the loading direction perpendicular to the lamella interface but decreases parallel to the lamella interface by the addition of elements.

In addition, the detailed features of the variations in fracture toughness were found to be significantly different according to the element added. Figs. 3(a, b) show the side-view and top-view images, respectively, of the fracture surfaces of the specimens. The fracture surfaces show marked differences depending on loading orientation and added element, indicating that different mechanisms govern the fracture behavior in each sample. Based on the fracture mechanisms previously discussed in (Mo_{0.85}Nb_{0.15})Si₂ non-added crystals [10], the variations in fracture behavior as a function of the added element are hereafter discussed.

At B-orientation, the fracture toughness tended to increase by the addition of alloying elements; an increase of ~20% in particular was confirmed for the Ir-added crystal; ~2.8 MPam^{1/2} in ternary crystal and ~3.3 MPam^{1/2} in Ir-added crystal, respectively. In the B-type specimen, the lamella interface lay perpendicular to the loading axis. Thus, cracks must propagate upon penetrating the lamellar interfaces. During such propagation, blunting of the crack tip by additional crack propagation along the lamella boundary, so-called delamination, was expected to occur. This was proven by the formation of step-like morphologies on the fracture surfaces, as shown by arrows in Fig. 3(b). The fact that the addition of an alloying element increased the fracture toughness in all cases suggests that the smoothing of the lamella interface by

the additions increased the frequency of delamination. Particularly, in the Ir-added crystal, the refinement of the microstructure was significantly effective for increasing the frequency of delamination, leading to the largest increase in the fracture toughness. This result is in good agreement with some previous reports which suggest that the grain size refinement led to substantial improvements in fracture toughness of MoSi₂ composites [12, 16-18].

Meanwhile, the smoothing of the lamella interface was expected to reduce the fracture toughness at C-orientation because the lamella interface was aligned parallel to the notch plane in this specimen. This was actually confirmed in the experiment. The toughness at C-orientation increased in a non-added (Mo_{0.85}Nb_{0.15})Si₂ crystal annealed for 336 h, in which a significant collapse of the lamellae microstructure occurred, whereas it was comparable or slightly lower in crystals with added alloying elements as compared to that in non-added crystals annealed for 168 h. It must be noted here, however, that the extent of the decrease was different depending on the added element; almost no change was measured with the Cr addition, whereas the largest reduction occurred with the Ir addition. This result suggests that we should consider not only the effect of the morphology of the lamellar interface but also the change in interface cohesion by the segregation of additional elements on the interface [11,15,19].

Our previous first-principles study [15] revealed the most energetically stable interface between C11_b and C40. Based on the results, in the present study, we constructed four interface slabs to see the effect of additional elements on interface cohesion: One was the most stable interface slab without additional elements; the other three were interface slabs in which a single Mo atom at the interface region was replaced by Cr, Zr, or Ir, in order to assume their segregation on the interface. Then, we estimated the interface cohesive energy (E_{coh}) of the four slabs through a first-principles calculation, which is defined by

$$E_{\text{coh}} = (E_{\text{C11b}} + E_{\text{C40}}) - E_{\text{int}} \quad (1)$$

where E_{int} represents the total energy of the constructed C11_b/C40 interface slab and E_{C11b} (E_{C40}) denotes the total energy of the constituent C11_b (C40) region, where the rest of the interface slab, i.e., the C40 (C11_b) region, is replaced by vacuum. Details of the conditions of the first-principles calculations are described in our previous paper [15]. With this definition, a larger positive value of interface cohesive energy corresponds to stronger interface cohesion. The interface cohesive energies estimated in this study were listed in Table 1. The calculated result indicates that all the additional elements tend to decrease the interface cohesion of the pure C11_b/C40 interface, but among them the Cr has the highest interface cohesion and Ir the lowest. Note here that for the sake of accomplishing the calculations as described in the previous paper [15], the present calculations were conducted for MoSi₂ as the matrix phase, which is different from the current composition of (Mo_{0.85}Nb_{0.15})Si₂. Thus, more consideration may be required to calculate the precise values of the cohesive energies. However, the obtained variations in cohesive energy with added elements qualitatively explains well the variations in the

measured fracture toughness by the addition of alloying elements shown in Fig. 2. These facts certainly imply that along C-orientation, variations in interface cohesion with additional elements also play a significant role in fracture toughness.

In contrast to the results for B-orientation, the fracture toughness tended to decrease upon adding the elements at A-orientation. As a characteristic feature of the fracture surface observed in the $(\text{Mo}_{0.85}\text{Nb}_{0.15})\text{Si}_2$ non-added crystal at A-orientation, crack propagation was largely deflected along the plane, inclined almost 30° to the loading axis, as shown in Fig. 3(a) [non(168 h)-A]. From the geometrical point of view, the crack-deflected planes corresponded to the $\{10\bar{1}0\}$ cleavage plane in the C40 matrix phase [10]. This crack deflection required additional energy for fracture, because the (001) and $\{1\bar{1}2\}$ planes in the C11_b variants, being parallel to $\{10\bar{1}0\}_{\text{C40}}$ in the duplex lamellar crystal, did not correspond to the easiest cleavage plane upon fracture. This was concluded to be the origin of the increase in fracture toughness at A-orientation [10]. Here, the side views of the fracture surfaces of the Zr- and Ir-added crystals, which exhibited significant decreases in fracture toughness, show that the extent of crack deflection was significantly reduced, as shown in Figs. 3(a) [Zr-A, Ir-A]. This proves the effectiveness of crack deflection for increasing the toughness of duplex lamellar crystals. The disappearance of crack deflection in the Zr and Ir-added crystals may not be due to the microstructural effect but rather to the change in the intrinsic properties of the constituent phases; the sensitivity of cleavage on $\{10\bar{1}0\}_{\text{C40}}$ may vary by the addition of these elements. Because the Cr-added crystal, which shows an aligned lamellar microstructure similar to that of the Zr-added crystal, showed large crack deflection [Fig. 3(a) [Cr-A]], and it did not show a marked decrease in fracture toughness compared to that of non-added crystal. Thus, the variations in cleavage behavior as a function of alloying elements must be further studied to control the fracture toughness of duplex lamellar crystals.

4. Conclusion

- (1) The fracture toughness of the C40/C11_b duplex-crystal was found to be significantly affected by the occurrence frequency of delamination and crack deflection. As a result, the variations in fracture toughness strongly varied depending on the loading orientation with respect to the lamellar interface and the species of the added element.
- (2) It was clarified both by the experimental results and by first-principles calculations that the changes in interface cohesion with additional elements play a significant role in the fracture toughness when loaded parallel to the lamellar boundary.

Acknowledgements

This work was supported by the projects of “Advanced Low Carbon Technology Research and Development Program (ALCA)” of the Japan Science and Technology Agency, and also partly supported by Cross-Ministerial Strategic Innovation Promotion Program (SIP) from the NEDO, Japan. The authors wish to express their appreciation to

Prof. H. Inui, Prof. K. Kishida of Kyoto University, Japan, and Prof. Y. Koizumi of Tohoku University, Japan, for their valuable comments on this research.

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Figure captions

Fig. 1 OM images showing the C40/C11_b duplex microstructures developed by annealing a C40-single-phase single crystal (a-d) at 1400 °C for 168 h. (a) (Mo_{0.85}Nb_{0.15})Si₂ and (b) Cr-, (c) Zr-, and (d) Ir-added crystals. (e) (Mo_{0.85}Nb_{0.15})Si₂ annealed at 1400 °C for 336 h.

Fig. 2 Fracture toughness of five (Mo_{0.85}Nb_{0.15})Si₂-based duplex crystals measured at three different orientations.

Fig. 3 (a) Side views observed by OM and (b) top views observed by SEM, of fractured specimens prepared from the non-added (Mo_{0.85}Nb_{0.15})Si₂ crystal, and the Cr-, Zr-, Ir-added crystals annealed at 1400 °C for 168 h, and the non-added (Mo_{0.85}Nb_{0.15})Si₂ crystal annealed at 1400 °C for 336 h. In the images showing the fractured specimens at B-orientation in Fig. 3(b), the arrows indicate the formation of step-like fracture morphology owing to the occurrence of delamination. At the lower left corner of the figures, the higher magnification images of the step-like fracture morphology are also inserted.

Table 1

C40/C11_b interface cohesive energy [defined by Eq. (1)] obtained through first-principles calculations.

Figure1

Fig. 1 OM images showing the C40/C11_b duplex microstructures developed by annealing a C40-single-phase single crystal (a-d) at 1400 °C for 168 h. (a) (Mo_{0.85}Nb_{0.15})Si₂ and (b) Cr-, (c) Zr-, and (d) Ir-added crystals. (e) (Mo_{0.85}Nb_{0.15})Si₂ annealed at 1400 °C for 336 h.

Figure2

Fig. 2 Fracture toughness of five $(\text{Mo}_{0.85}\text{Nb}_{0.15})\text{Si}_2$ -based duplex crystals measured at three different orientations.

Fig. 3 (a) Side views observed by OM and (b) top views observed by SEM, of fractured specimens prepared from the non-added ($\text{Mo}_{0.85}\text{Nb}_{0.15}\text{Si}_2$) crystal, and the Cr-, Zr-, Ir-added crystals annealed at 1400 °C for 168 h, and the non-added ($\text{Mo}_{0.85}\text{Nb}_{0.15}\text{Si}_2$) crystal annealed at 1400 °C for 336 h. In the images showing the fractured specimens at B-orientation in Fig. 3(b), the arrows indicate the formation of step-like fracture morphology owing to the occurrence of delamination. At the lower left corner of the figures, the higher magnification images of the step-like fracture morphology are also inserted.

Table 1: C40/C11_b interface cohesive energy [defined by Eq. (1)] obtained through first-principles calculations.

Interface	No addition	Cr-added	Zr-added	Ir-added
E_{coh} (eV/Å ²)	0.264	0.261	0.244	0.223