Control of microstructure and fracture toughness improvement of NbSi₂/MoSi₂ duplex lamellar silicides by TaC particles dispersion

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Abstract

The floating-zone melting method enabled to disperse TaC particles in a C40-(Mo_{0.85}Nb_{0.15})Si₂ single crystal. By the annealing of the C40 crystal, coarse C11_b phases were formed around the TaC particles and the precipitation of the D8₈-(Mo,Nb,Ta)₅Si₃C phase was also induced, in addition to the development of C40/C11_b lamellar microstructure. Such a microstructure containing TaC particles led to a reduction in orientation dependence of the fracture toughness of duplex silicide crystals.

Keywords: Transition-metal silicides; Carbides; Toughness; Microstructure

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Transition metal disilicides such as C11_b-MoSi₂ are promising candidates for use as ultrahigh-temperature structural materials that can potentially replace conventional materials in turbines [1-17]. The use of these materials would help in achieving higher operating temperatures for turbines, and this would improve the thermal efficiency. However, the low-temperature fracture

toughness and high-temperature strength (above 1200 °C) of transition metal disilicides, especially in their monolithic form, are inadequate for practical applications. One of the promising strategies for overcoming these limitations is to combine different disilicides with favorable properties. With this viewpoint, Nakano et al. have recently succeeded in developing NbSi₂/MoSi₂ composite crystals with fine lamellar microstructures [8,9]. A oriented NbSi₂/MoSi₂ duplex lamellar crystal is obtained from a C40-structured (Mo_{0.85}Nb_{0.15})Si₂ single crystal grown by the floating zone (FZ) melting method and subsequent annealing of the C40 crystal at 1400 °C [9]. These duplex crystals showed superior high-temperature mechanical properties [13]. In addition, the development of lamellar microstructure was reported to increase the fracture toughness compared to that of C40 single crystal [12,16]. However, the maximum value is still ~3.2 MPam^{1/2}, and hence further improvement of fracture toughness is strongly desired. As one of the possibilities, the dispersion of carbide particles is expected to increase in the fracture toughness of the crystals by acting as barriers for crack propagation. However, since the superior mechanical properties of the NbSi₂/MoSi₂ duplex lamellar crystals are afforded by the control of the crystal orientation and geometry of the lamellar microstructure [13, 16], the carbide particles must be homogeneously dispersed in the C40 single crystals. In this study, the fabrication of C40 single crystals containing a carbide was attempted by the FZ method, focusing on TaC, WC, and SiC carbides. The microstructure and mechanical properties of the carbide-containing NbSi₂/MoSi₂ duplex lamellar crystals were examined, and the effect of carbide on the microstructure development and the mechanical properties was investigated.

In the experimental procedure, master ingots with a nominal composition of (Mo_{0.85}Nb_{0.15})Si₂ containing 5 at% TaC, WC, or SiC were first prepared by melting high-purity raw materials of Mo, Nb, Si and powdered carbides, with an average size of ~45 μm for TaC, ~150 μm for WC, and ~100 μm for SiC, in a plasma arc furnace. Using the mother alloys, C40 single crystals were grown by the FZ method at a growth rate of 2.5 mm/h under a high-purity argon gas flow. The mother ingots and seed crystals were rotated in the inverse directions each other at 6 rpm during crystal growth in the FZ furnace to prevent the significant clustering of the carbides and to induce a homogeneous

dispersion of them in the melt. Some of the obtained single crystals were subsequently annealed at 1400 °C for 6–168 h to develop a lamellar microstructure. The constituent phases in the crystals were identified by X-ray powder diffraction analysis (XRD, Philips X-pert Pro) and energy-dispersive X-ray spectroscopy using scanning electron microscopy (SEM-EDS, JEOL JEM-6500F). The crystallographic orientation relationships between the constituent phases were examined by electron backscatter diffraction (EBSD) pattern analysis in the SEM. Rectangular specimens with a size of $2 \times 1 \times 10 \text{ mm}^3$ were prepared, and were then subjected to three-point bend tests to evaluate the fracture toughness of annealed specimens at room temperature (RT). The tests were conducted using an Instron-type testing machine with a cross-head speed of 0.005 mm/min. A notch was introduced in each specimen using a diamond wire cutter. Three kinds of specimens having different geometries of the lamellar microstructure with respect to the loading axis and notch direction, called A, B and C, were prepared to examine the orientation dependence of fracture behavior. The details of the crystal geometry of the specimens are shown later in Fig. 4, and are also given in our previous paper [16].

Fig. 1(a) shows a typical microstructure of an as-FZ grown crystal containing TaC carbides. By the X-ray Laue back-reflection method, it was confirmed that the obtained as-grown crystals were mainly composed of the single crystalline C40 matrix phase. In the C40 single crystal, **the dispersion of TaC particles was observed as shown in Fig. 1(a), though a certain extent of particle clustering could not be avoided.** The same experiment was conducted on SiC-containing crystal. However, the SiC particles in a SiC-containing crystal floated and condensed in the upper region of the melt during the FZ process, and hence, the dispersion of SiC carbides in a C40 single crystal was not obtained. These differences are attributed to the difference in the density of carbides. The density of SiC ($\sim 3.2 \text{ g/cm}^3$) is much lower than that of the matrix ($\text{Mo}_{0.85}\text{Nb}_{0.15}\text{Si}_2$ phase ($\sim 6.2 \text{ g/cm}^3$); thus, SiC easily floated in the melt. In contrast, the density of TaC ($\sim 14.6 \text{ g/cm}^3$) is higher than that of the melt. This indicates that the relative density of carbide particles with respect to the C40 matrix phase is an important factor for the fabrication of carbide-dispersed single crystals by the FZ method. From this point of view, WC ($\sim 15.6 \text{ g/cm}^3$) was also considered a suitable carbide. However, WC reacted

significantly with the C40 matrix phase during solidification, and hence, its dispersion could not be obtained.

Figs. 1(b)-(d) show the typical microstructures of a single crystal after annealing at 1400 °C for 6, 24, and 168 h, respectively. Fine C40/C11_b lamellar microstructure was developed by the annealing, and in addition it was found that the TaC particles were gradually covered by coarse C11_b phases as increasing in the annealing period, as can be clearly seen in the higher magnification images in Figs. 1(b) and (c). It should be noted here that many cracks formed in the as-FZ crystals during the mechanical polishing of the surface owing to its brittle nature, as shown in Fig. 1(a). However, the number of cracks clearly reduced with an increase in the annealing period, i.e., with the development of a lamellar microstructure. This demonstrates the effectiveness of the lamellar microstructure for improving the toughness of a silicide crystal. Fig. 1(e) shows the SEM backscatter electron image of a crystal annealed for 168 h at 1400 °C. After long-term annealing of this crystal, another phase was found to be precipitated, as shown by the white contrast. In some parts, the precipitates were observed to be extending from the TaC particles along the C40/C11_b lamellar interface. The change in the constituent phase by annealing was confirmed by XRD analysis. Figs. 2(a) and (b) show the powder X-ray diffraction profile of an FZ-grown crystal before and after heat treatment at 1400 °C for 168 h. The as-grown crystal showed peaks mainly derived from the C40 matrix phase, and peaks from TaC carbides were also observed. In addition, small peaks derived from C11_b precipitates were also observed. This feature was different from those of non-TaC added crystal [9]. Actually the formation of C40/C11_b lamellar microstructure was locally confirmed even in the as-FZ grown TaC-containing crystal in the OM observation. This suggests a possibility that the addition of TaC particles affected the precipitation behavior of C11_b phase, though the detail is not clarified yet. After annealing, on the other hand, the intensity of the peak derived from the C40 phase largely decreased, whereas that of the peaks derived from C11_b precipitates increased. In addition, weak peaks derived from the D8₈-type phase were also observed, as indicated by open rhombuses. The lattice constants of the D8₈-type phase with a hexagonal unit cell were roughly estimated to be $a = 0.747$ and $c =$

0.517 nm from the XRD profile. It has been previously reported that interstitial C atoms stabilize the M_5Si_3 phase (M is a transition metal such as Mo and Nb) as a $D8_8$ -type M_5Si_3C phase [18]. Thus, it is considered that small amounts of the TaC phase were dissolved in the C40 matrix phase and saturated (Nb, Mo, Ta) atoms and C atoms promoted the precipitation of $D8_8$ - M_5Si_3C . By the SEM-EDS analysis, the composition of the $D8_8$ -type phase was roughly estimated to be $(Mo_{0.29}Nb_{0.33}Ta_{0.38})_5Si_3C$, though the amount of C could not be precisely determined by this method. $D8_8$ phases were dominantly precipitated around and inside the coarse $C11_b$ phases, but some of them were precipitated at the lamellar interface, as shown in Fig. 1(e), suggesting that they precipitated with a distinct crystal orientation relationship with respect to the C40 matrix phase. This was confirmed by the SEM-EBSD pattern analysis. Fig. 3(a) shows the SEM image of an annealed crystal viewed along $[10\bar{1}0]_{C40}$, and Figs. 3(b) and (c) show the corresponding orientation maps analyzed along $[0001]_{C40}$ for $C11_b$ and $D8_8$ phases, respectively. In addition, Figs. 3(d) and (e) show the orientation maps analyzed along $[8\ 3\ \bar{1}\bar{1}\ 0]_{C40}$, which is 15° rotated from $[10\bar{1}0]$ to $[11\bar{2}0]$ in a $[0001]$ zone axis. The crystal orientation of TaC carbides could not be determined since a clear EBSD pattern could not be obtained for them. When the crystal orientations were analyzed along $[0001]_{C40}$, most of the $C11_b$ phases with a lamellar microstructure were colored only by blue. This is because the $C11_b$ phases precipitated with respect to the C40 matrix phase as their close-packed plane of $(110)_{C11_b}$ and $(0001)_{C40}$ became parallel to each other [9]. In contrast, the coarse $C11_b$ phases formed around TaC particles showed various different colors, indicating that they did not have a distinct orientation relationship with respect to the C40 matrix, different from the case of lamellar shaped $C11_b$ phases. When the crystal orientation was analyzed along $[8\ 3\ \bar{1}\bar{1}\ 0]_{C40}$, on the other hand, the $C11_b$ lamellae showed three colors of red, pink, or purple. This is because they had three orientation relationships with respect to the matrix with maintaining the relationship of $(110)_{C11_b} // (0001)_{C40}$. These relationships are denoted as variants 1, 2, 3 as follows [9]:

$$\text{Variant 1: } (0001)_{C40} // (110)_{C11_b}, [\bar{1}2\bar{1}0]_{C40} // [1\bar{1}0]_{C11_b}, [10\bar{1}0]_{C40} // [001]_{C11_b} \quad (1)$$

$$\text{Variant 2: } (0001)_{C40} // (110)_{C11_b}, [2\bar{1}\bar{1}0]_{C40} // [1\bar{1}0]_{C11_b}, [0\bar{1}10]_{C40} // [001]_{C11_b} \quad (2)$$

$$\text{Variant 3: } (0001)_{C40} // (110)_{C11_b}, [\bar{1}\bar{1}20]_{C40} // [1\bar{1}0]_{C11_b}, [\bar{1}100]_{C40} // [001]_{C11_b} \quad (3)$$

The crystallographic features of the lamellar microstructure were identical to those observed for the non-added ($\text{Mo}_{0.85}\text{Nb}_{0.15}\text{Si}_2$) crystal.

On the D8_8 phases, those precipitated nearby the coarse C11_b phases were showed various different orientation colors as shown in Fig. 3(b, d). While, the D8_8 phases precipitated on the $\text{C40}/\text{C11}_b$ lamellar interfaces were often colored red and blue in the orientation map analyzed along $[0001]_{C40}$, as indicated by arrows in Fig. 3(c). This suggests the existence of orientation relationships with respect to the C40 matrix phase. By detailed analyses, following two crystal orientation relationships were confirmed to be shown in many of the D8_8 phases formed on the lamellar interface with respect to the C40 matrix phase:

$$(0001)_{C40} // (0001)_{D88}, [2\bar{1}\bar{1}0]_{C40} // [10\bar{1}0]_{D88} \quad (4)$$

$$(0001)_{C40} // (10\bar{1}0)_{D88}, [2\bar{1}\bar{1}0]_{C40} // [0001]_{D88} \quad (5)$$

The crystal orientation relationship (4) has previously been reported by Geng et al. in a Nb-Mo-Si system [19], but relationship (5) has been found for the first time in this study.

The fracture toughness of TaC-containing duplex lamellar crystals was examined by three-point bending tests, and the results were compared with those for non-added crystals [16]. The bending tests were conducted at three different loading orientations with respect to the lamellar interface, as depicted in Fig. 4(a). At all loading orientations, the fracture toughness increased compared to that of non-added duplex crystal as expected. Figs. 4(b) and (c) show side-view images depicting the crack propagation behavior in the B-oriented specimens of non-added and TaC-containing crystals, in which the lamellar interfaces were perpendicular to the loading orientation. TaC-containing crystals showed considerable crack deflection, whereas non-added crystals showed only little deflection. Crack deflection was frequently induced along the TaC carbides, demonstrating that the carbides effectively acted as barriers to crack propagation. In addition, the coarse C11_b phase that formed

around the TaC particles may have effectively contributed to crack-tip blunting, since the C11_b phase is more ductile than the C40 matrix phase owing to the existence of many slip systems [2,7]. These features contributed to the increase in the fracture toughness. This toughness increase effect was more pronounced at B and C orientations, in which the lamellar interfaces were perpendicular and parallel to the loading orientation, respectively. In particular, at the C orientation, there was a disadvantage on the toughness in the duplex crystal; the value was lower than that of the C40 single-phase crystal since the cracks propagated easily along the lamellar interface [16]. However, such disadvantage of the lamellar crystal also could be improved by the addition of TaC particles.

To conclude, in this study, we successfully fabricated carbide-dispersed oriented NbSi₂/MoSi₂ duplex lamellar crystals by using TaC particles. The density of the carbide particles was found to be an important factor in the fabrication of carbide-dispersed C40 single crystals by the FZ process. The long-term annealing resulted in the TaC particles getting covered by ductile C11_b phases **in addition to the development of fine lamellar microstructure**. The addition of TaC particles **led to an increase in the fracture toughness of the duplex crystal to some extent** by inducing crack propagation deflection, and resulted in the reduction in orientation dependence of the toughness of the crystal. However, the highest value of the fracture toughness was still $\sim 3.9 \text{ MPam}^{1/2}$, thus further effort is continuously required to achieve the practical use of this materials.

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Figure captions

Figure 1

(a-d) Optical microscopy images showing the typical microstructures of (a) as-FZ grown $(\text{Mo}_{0.85}\text{Nb}_{0.15})\text{Si}_2$ crystal containing TaC carbides, and those after annealing at 1400 °C for (b) 6 h, (c) 24 h, and (d) 168 h. In the upper right-hand corner of Fig. 1(a-c), the corresponding higher-magnification SEM image is also inserted. (e) SEM backscatter electron images of the crystal annealed at 1400 °C for 168 h.

Figure 2

Powder X-ray diffraction profiles of TaC-particle-containing $(\text{Mo}_{0.85}\text{Nb}_{0.15})\text{Si}_2$ crystals: (a) as-FZ grown crystal, (b) crystal annealed at 1400 °C for 168 h.

Figure 3

(a) SEM image of a specimen annealed at 1400 °C for 168 h observed along $[10\bar{1}0]_{\text{C40}}$. (b, c) Corresponding orientation maps along $[0001]_{\text{C40}}$ obtained by EBSD pattern analysis for (b) C11_b and (c) D8_8 phases. (d, e) Orientation maps obtained along $[8\ 3\ \bar{1}\ 1\ 0]_{\text{C40}}$ for (d) C11_b and (e) D8_8 phases.

Figure 4

(a) Fracture toughness of TaC-containing $(\text{Mo}_{0.85}\text{Nb}_{0.15})\text{Si}_2$ crystals annealed at 1400 °C for 168 h, compared with those of non-added $(\text{Mo}_{0.85}\text{Nb}_{0.15})\text{Si}_2$ duplex crystals and $(\text{Mo}_{0.85}\text{Nb}_{0.15})\text{Si}_2$ C40-single-phase crystals, examined at RT. (b, c) Side-view images of the fractured surface of B-oriented specimen for (b) non-added duplex crystals and (c) TaC-containing crystals.

Estimated length of manuscript

Text : 2835 words (including the figure caption)

Equation x 5 = 100 words

Figures and tables:

Figure 1 : $7.5 \times 8 = 180$ words

Figure 2 : $7.5 \times 6 = 120$ words

Figure 3 : $7.5 \times 8 = 180$ words

Figure 4 : $7.5 \times 6 = 120$ words

Total length = $2820 + 100 + 600 = 3535$ words: (135 words were reduced.)

Figure1

Figure2

Figure3

Figure 4