Indentation fracture behavior of (Mo_{0.85}Nb_{0.15})Si_{2} crystals with C40 single-phase and MoSi_{2}(C11_{b})/NbSi_{2}(C40) duplex-phase with oriented lamellae

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Abstract

Fracture behavior and toughness of C40-structured (Mo_{0.85}Nb_{0.15})Si_{2} single crystals and MoSi_{2}(C11_{b})/NbSi_{2}(C40) duplex-phase crystals with oriented lamellae were investigated by micro-Vickers hardness tests. The indentation fracture toughness in the C40 single-phase showed low values of about 1.0–1.4 MPa m^{1/2}, while fracture toughness was improved in the duplex-phase crystals. Ductile phase toughening by the C11_{b} phase, deflection of crack-propagation at the lamellar boundary and the effect of residual stress field at the crack tip are considered to be responsible for the increment of fracture toughness of MoSi_{2}(C11_{b})/NbSi_{2}(C40) duplex-phase crystals.

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1. Introduction

There is an increasing demand for high-temperature structural materials superior to the present superalloys to improve gas turbine engine performance and to further accelerate aerospace speed. Refractory transition metal disilicides such as MoSi_{2} with the C11_{b} and NbSi_{2} with the C40 structure are possible candidates for high-temperature structural application because of their high melting points, good oxidation resistance and superior strength at high-temperatures [1]. Those silicides with single crystalline form can deform plastically even at ambient temperature in compression [2–5] and at relatively low-temperatures in tension [6] when they are loaded in the limited orientation area where appropriate slip systems are operative. Moreover, anomalous strengthening behavior appears in single crystals of MoSi_{2} and NbSi_{2} deformed at high-temperatures [2–5], which is very attractive for considering high-temperature application. However, these disilicides have common disadvantages, which should be overcome before industrial application: low-temperature brittleness and poor creep resistance at high-temperatures. Many researchers have devoted a great deal of effort to improve these properties. One promising approach to overcome the problem is to combine some disilicides with favorable properties [7,8]. Recently, we succeeded in making a duplex-phase NbSi_{2}/MoSi_{2} silicide crystal with oriented lamellae [9,10]. It was obtainable by appropriate annealing of the C40-structured (Mo_{0.85}Nb_{0.15})Si_{2} single crystal grown by the floating zone method. It was demonstrated that the high-temperature strength and ductility of the duplex-phase silicide can be controlled by selecting the loading orientation [9,11]. Furthermore, the formation of such a lamellar structure is believed to be effective in improving the fracture toughness of the silicide.

In this study, the indentation fracture toughness (K_{IC}) and the fracture behavior were investigated using the micro-Vickers hardness test. The test was conducted in both the C40 single-phase single crystal and C11_{b}/C40 duplex-phase crystals with a composition of (Mo_{0.85}Nb_{0.15})Si_{2}, and the results were compared to learn the effect of the developed lamellar structure on fracture behavior.
2. Experimental procedure

Master ingots with a composition of (Mo$_{0.85}$Nb$_{0.15}$)Si$_2$ were prepared from high purity raw materials by arc-melting in an Ar atmosphere. Single crystals with the C40 structure were grown by the floating zone method at a rate of 2.5 mm/h. Some single crystals were subsequently annealed at 1673 K for 168 h to develop the oriented lamellae composed of C11$_b$ and C40 phases. Average thickness and volume fraction of each phase were about 2.1 μm and 44% for the C40 phase, and 2.7 μm and 56% for the C11$_b$ phase, respectively. As reported previously [9,10], the lamellar interface satisfied the crystallographic relationship of (0001)$_{C40}$//(110)$_{C11b}$. As a result, the duplex lamellae were composed of the C40 phase with a single orientation and three C11$_b$ variants denoted as Variant 1 (V1), Variant 2 (V2) and Variant 3 (V3). These three C11$_b$ variants obey the following crystallographic relationships on the lamellar plane.

\[
\begin{align*}
\text{V1: } & (\bar{1}2\bar{1}0)_{C40}//(1\bar{1}0)_{C11b} , (10\bar{1}0)_{C40}//(001)_{C11b} \\
\text{V2: } & (2\bar{1}10)_{C40}//(1\bar{1}0)_{C11b} , (0\bar{1}10)_{C40}//(001)_{C11b} \\
\text{V3: } & (1\bar{1}20)_{C40}//(1\bar{1}0)_{C11b} , (1\bar{1}00)_{C40}//(001)_{C11b}
\end{align*}
\]

Detailed information on the lamellar structure can be found in our previous papers [9,10].

3. Results

3.1. Crack-propagation behavior in the C40 single-phase single crystals

The micro-Vickers hardness tests were carried out at room temperature in a load range from 200 to 1000 gf. Indents were made on the (0001), (10\bar{1}0) and (\bar{2}110) plane of the single crystal and on the duplex-phase crystal to examine orientation dependence of the crack-propagation behavior. Before the test, the surface of specimens was polished with SiC paper and finally with 1 μm diamond paste to remove any surface damage. Crack-propagation behavior around the indent was observed with an optical microscope equipped with Nomarski interference contrast.

Fig. 1 shows optical micrographs of indents introduced at 500 gf load in the C40 single-phase single crystals of (Mo$_{0.85}$Nb$_{0.15}$)Si$_2$; the crack-propagation behavior around an indent showed a significant difference depending on the crystal orientation. Fig. 1(a) and (b) show the indents introduced on (0001) Fig. 1(c) and (d) on (10\bar{1}0) and Fig. 1(e) and (f) on (\bar{2}110) (hereafter referred to as specimens A, B, C, D, E and F, respectively). The indents in specimens A, C and E were made with their diagonals
No slip traces were observed around the indents in any of the specimens. Since only the basal slip is known to be dominant in NbSi$_2$ crystals with the C40 structure at ambient temperature [3–5], the slip was not activated clearly under the stress field applied in this study. Many long cracks appeared around the indents; it should be noted that these did not always appear from the four corners of the indents. In specimens C and E, for example, all long cracks were originated not from the corners but from the side of the inverted pyramid, and they propagated parallel to certain preferential directions. Fig. 2 shows the distribution of length and direction of crack-propagation around indents in six different specimens (A–F). Five indents were examined in each specimen. Cracks more than 2 μm in length were monitored and the direction of crack path was defined within the deviation angle of ±5°. Obviously, the length and direction of the crack path were strongly affected by the loading orientation. At the loading orientation parallel to [0001], more than four long cracks generated around the indent. Most of the long cracks propagated along [1210] trace on the specimen surface but some of them which occurred at the corner propagated along (1010). In contrast, just four long cracks were dominantly observed when loaded along [1010] and [2110]; they propagated along the trace parallel to (1213) on (1010) and to (0111) on (2110), respectively. The direction of crack path was irrespective of the rotation of diagonals of the indenter as seen in specimens C and D or E and F. This strongly suggests that the dominant long cracks in the C40 single-phase single crystals preferentially propagated on the specific cleavage planes in each specimen. The exact cleavage plane could not be determined definitely in this study because the trace of a crack could be observed only on the specimen surface. The possible crack plane, however, could be estimated by

Fig. 2. Distribution of length and direction of crack-propagation around indent in six different specimens (A–F). Five indents were examined in each specimen.
the trace on the surface as the zone axis of crack plane. Plausible candidates of the cleavage planes were believed to be \{101\,\bar{1}\} and \{101\,\bar{0}\} etc. belonging to the \{12\bar{1}0\} zone axis.

Although the direction of crack path did not change, the fracture behavior by indentation showed a marked difference depending on the direction of diagonals of the indenter. As seen in Fig. 1, removal of the surface around the indent during the unloading cycle, which is generally called ‘chipping’ [12], occurred frequently in specimens D and F. The chipping may be related to a change in the crack system. An indentation crack system is of two types depending on the geometrical shape of the crack beneath the indent; one is the median crack system and the other is the Palmqvist crack system [13]. They can be determined after polishing away the surface layer. Fig. 3 shows the micrographs near the indent after slightly polishing the original indentation surface. The cracks in specimen C were clearly detached from the inverted pyramid, confirming the presence of a Palmqvist crack system. In contrast, the cracks continued to connect the corners of diagonals in specimen D, indicating the presence of a median crack system. Variation in the crack system may be caused by the difference in geometrical conditions between the applied stress field by indentation and cleavage planes. The formation of median-type cracks in specimens D and F may induce the preferential occurrence of chipping.

The indentation fracture toughness of brittle materials such as intermetallic compounds and ceramics can be estimated by measuring the observed crack length \(l\) and micro-Vickers hardness \(H\) [13]. The equation for estimating indentation fracture toughness differs depending on the type of crack system [13] and it is difficult to compare the absolute value of fracture toughness of different systems. In this study, the value of indentation fracture toughness (customarily designated \(K_{IC}\)) was evaluated by the following equation [14,15] in specimens A, B, D and F in which the median-type crack occurred:

\[
K_{IC} = 0.0168(E/H)^{1/2}(P/c^{3/2})
\]  

where \(c\) is the median-type crack length which is the summation of observed crack length on the surface \(l\) and half the diagonal of the indent \((a)\), \(E\) is Young’s modulus of the single crystal along the indentation direction and \(P\) is the applied load of 500 gf. The Young’s modulus of the single crystal used was from the data for binary NbSi\(_2\) single crystals [16]. The Vickers hardness, the observed crack length and the estimated indentation fracture toughness of C40-structured (Mo\(_{0.85}\)Nb\(_{0.15}\))Si\(_2\) single-phase single crystals are shown in Table 1. The crack length was evaluated as the average length of the four longest cracks around the indent. The calculated fracture toughness showed low values of about 1.0–1.4 MPa m\(^{1/2}\) at all orientations. Treatments for improving the fracture toughness are therefore essential for practical application. The value of fracture toughness varied slightly depending on the loading orientation, which was derived from the difference in fracture behavior at each orientation. The value fracture toughness on (0001) was higher than the others. On (0001), more than four cracks were often generated around

![Fig. 3. Optical micrographs of indents after polishing the original indentation surface; (a) specimens C after polishing 7 \(\mu\)m, and (b) specimens D after polishing 15 \(\mu\)m. The formation of Palmqvist-type crack and median-type crack is clearly seen in specimens C and D, respectively.](image)

### Table 1

| Vickers hardness \(H\) | Observed crack length \(l\) (\(\mu\)m) | Indentation fracture toughness \(K_{IC}\) (MPa m\(^{1/2}\)) |
|------------------------|----------------------------------------|---------------------------------|
| (a) 1092               | 37.5                                   | 1.40                            |
| (b) 1100               | 39.6                                   | 1.31                            |
| (c) 1120               | 51.4                                   | 1.04                            |
| (d) 1075               | 45.0                                   | 1.04                            |
| (e) 1120               | 43.8                                   | 1.09                            |
| (f) 1059               | 43.1                                   | 1.09                            |
the indent to aid in accommodating the stress. Therefore, the apparent fracture toughness estimated from the length of the four longest cracks showed a higher value than the others. A more reliable method should be applied to examine the intrinsic orientation dependence of the fracture toughness. Measurement of the toughness by a three-point bending test is now in progress.

3.2. Crack-propagation behavior in MoSi₂ (C11₇)/NbSi₂ (C40) duplex-phase crystals with oriented lamellae

Fig. 4 shows an optical micrograph of an indent introduced at 1000 gf load in the MoSi₂ (C11₇)/NbSi₂ (C40) duplex-phase crystal. The crystal orientation relationship of the C40 matrix phase is the same as that in specimen D. Unlike in the C40 phase, slip traces appeared around the indent in the C11₇ phases, indicating the occurrence of plastic deformation. Several cracks were propagated in the C40 phases, but most of them were stopped at the two-phase interfaces as indicated by arrows. This implies that the duplex lamellar structure has a significant effect on improving the fracture toughness of C40-based silicide crystals.

To evaluate the increment of fracture toughness quantitatively, the length of cracks around the indent was analyzed. Fig. 5 shows the variation in indentation crack length (c) with 2/3 power of the applied load (P) in the C40 single-phase single crystal and the duplex-phase crystal. As shown in Fig. 3, it was confirmed that a median-type crack was formed around the indent in specimen D. Several researchers reported that the length of median-type cracks followed a 2/3 power dependence of applied indentation load [13,14]; that was also confirmed in this study. Linear relationships clearly appeared in both the C40 single crystal and the duplex-phase crystal. Focusing on the slopes of lines for the c–P relationship, the slope for the duplex-phase crystal was much smaller than that for the C40 single-phase single crystal, indicating that a duplex lamellar structure effectively improves the indentation fracture toughness of the latter. The indentation fracture toughness in the duplex-phase crystal calculated by Eq. (1) reached about 3.7 MPa m¹/².

4. Discussion

The fracture toughness measured by the indentation tests in the C40 single-phase showed a low value of about 1.0–1.4 MPa m¹/², while it increased significantly with development of the duplex-phase lamellar structure to about 3.7 MPa m¹/². In this section, three controlling mechanisms to improve fracture toughness resulting from the development of the duplex-phase lamellar are discussed.

4.1. Ductile phase toughening by an additional C11₇ phase

The value of fracture toughness in binary C11₇ MoSi₂ single crystal was reported by Peralta et al. in micro-Vickers tests [15] and by Inui et al. in three-point bending tests [17]. They reported values of about 2–6 MPa m¹/² depending on the crystal orientation, which are much higher than that in the C40 single crystal investigated in this study. In addition, more slip systems are operative in the C11₇ phase than in the C40 phase because of the moderate high crystal symmetry in the former. Therefore, the C11₇ phase intrinsically has potential to behave as a ductile phase. Since the duplex-phase crystal contained about 56 vol% of the C11₇ phase, ductile phase toughening should be induced. This effect may provide the strongest contribution to improving the fracture toughness of the three mechanisms described here.
4.2. Deflection of crack-propagation by the developed lamellar structure

The lamellar boundary sometimes induces the deflection of crack-propagation, which contributes to toughening of materials. Cracks in the C40 single crystal preferentially propagated on the specific cleavage planes such as \{10\overline{1}0\} and \{10\overline{1}1\} as described in Section 3.1. The fracture behavior in MoSi$_2$ is also known to show strong orientation dependence. The fracture toughness was reported to show low values when cracks were propagated along \{110\} [17] and along \{001\} [15]. Taking the crystal orientation relationship between the phases shown in Section 2 into consideration, it is obvious that the cleavage planes in the C11$_b$ and C40 phases do not always geometrically correspond to each other in duplex-phase crystal. The cracks propagated in the C40 phase may therefore frequently deflect along definite planes when the cracks invade the C11$_b$ phase. This requires extra energy-consumption, resulting in an improvement of fracture toughness. Another deflecting mechanism is the crack-propagation along the lamellar boundary, so-called delamination [18]. This was not macroscopically confirmed in this study, but it might contribute to an increase in the toughness to some extent.

4.3. The effect of residual stress field at the crack tip

As seen in Fig. 5, the crack length (c)–applied load (P) relation extrapolated from high loads passes through the origin for the single crystals but does not for the duplex-phase crystals. At c = 0, the line for the duplex-phase crystals exhibits a positive intercept with the load axis. The threshold indentation load ($P_0$) was estimated to be about 17 gf. Shetty et al. explained that the positive threshold indentation load is related to the residual compressive stress on the surface region [19]. They suggested that the residual stress was brought about by inadequate preparation of the specimen surface. However, the difference in threshold indentation loads found in the duplex-phase crystals is believed to have another derivation. Lawn et al. investigated the behavior of crack-propagation on indentation [12]. They concluded that the lateral crack system mainly operates as the indenter is withdrawn from the specimen surface, and the driving force for propagation of the lateral crack must originate from some residual stress field associated with the irreversible deformation zone introduced by the indentation. In this study, the threshold indentation load $P_0$ showed higher value in the duplex-phase crystals than in the single-phase crystals. This implies that the irreversible plastic deformation zone in the duplex-phase crystals suppresses the crack-propagation more effectively. The mechanism is believed to be as follows. Fig. 6 shows a schematic drawing of distribution of the residual stress introduced by indentation. For simplicity, it was assumed that the applied load by indentation is transmitted perpendicular to the lamellar boundary. Under the applied stress field, the C11$_b$ phases plastically deform by indentation since the slip systems \{01\overline{1}1\} < 1000 \} and \{013\} < 331 \} can be operative even at room temperature [2]. Indeed, some slip traces were observed around the indent in the C11$_b$ phase as shown in Fig. 4; in contrast, none was observed in the C40 phases, indicating that they dominantly deform elastically. The difference of deformation behavior in each phase will induce the residual stress field at the interface when the indenter is withdrawn as shown in Fig. 6. Under this stress condition, the crack tip receives compressive residual stress when the crack invades the C11$_b$ phase. Therefore, the effect of residual stress may effectively prevent the further propagation of cracks in the C11$_b$ phase, thus contributing to the apparent increase in fracture toughness to some extent.

5. Summary

Crack-propagation behavior and toughness in different microstructures of the C40 single-phase crystal and MoSi$_2$(C11$_b$)/NbSi$_2$(C40) duplex-phase crystal with oriented lamellae for the (Mo$_{0.85}$Nb$_{0.15}$)Si$_2$ silicide were investigated by the micro-Vickers hardness test. The indentation fracture toughness in the C40 single-phase showed low values of about 1.0–1.4 MPa m$^{1/2}$. Cracks around the indent preferentially propagated along the preferential planes. The cleavage fracture plane for crack-propagation was estimated to be \{10\overline{1}0\} and \{10\overline{1}1\} belonging to a \{1\overline{2}\overline{1}0\} zone axis. The fracture toughness significantly increased with development of the duplex-phase lamellar structure to about 3.7 MPa m$^{1/2}$. Crack-propagation was frequently suppressed at the lamellar interface. The results suggest that ductile phase toughening by introduction of the C11$_b$ phase, deflection of crack-propagation at the lamellar boundary and the effect of residual stress field at the crack tip
contributed to improving the fracture toughness of MoSi$_2$(C11b)/NbSi$_2$(C40) crystals.

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