Deformation Microstructure Developed by Nanoindentation of a MAX Phase Ti$_2$AlC

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Deformation microstructure that developed during nanoindentation of a MAX phase Ti$_2$AlC was characterized by the scanning probe microscopy and the transmission electron microscopy. To investigate the plastic anisotropy, nanoindentation measurements were made on grains of Ti$_2$AlC exhibited some metallic properties. For Ti$_2$AlC, the Ti$_2$C layer and the Al layer are alternatively stacking up along the c-axis. It has been reported that the crystal structure of Ti$_2$AlC is $hP8$ (P6$_3$/mmc; Cr$_2$A-type) with the lattice parameters of $a = 0.3056$ nm and $c = 1.3623$ nm. It has been documented that the basal slip is predominant as the deformation mechanism in MAX phase compounds, while the other slip systems, i.e., non-basal slip, are hardly operative at room temperature. Thus, MAX phase alloys in a polycrystalline form are brittle because the number of operative slip systems is quite limited. However, it has been demonstrated that ductility and toughness can be improved by texture developments through thermo-mechanical treatments, and slip casting in a strong magnetic field.

Besides the basal slip, kink-band formation is known as another deformation mechanism that can operate in MAX phase compounds at room temperature. Kink-band formation is also observed in some hexagonal metals such as Cd and mica. Although several models have been proposed to explain the formation of kink-bands, the detail of the mechanism still remain unclear. It is well accepted that kink-band formation occurs when the basal slip was suppressed under a load applied parallel to the basal plane. On the other hand, Tomlin et al. reported that, based on the slip lines observed by the atomic force microscopy (AFM), a non-basal slip was indicated to have occurred upon nanoindentation of a MAX phase Ti$_2$SnC$_2$ at room temperature, although they did not identify its slip system. To take advantage of the plastic anisotropy, the knowledge on the kink formation mechanism and non-basal slip is inevitably necessary.

Recently, nanoindentation has become a common methodology to characterize the mechanical behavior of small volumes. One advantage of this method is versatility to investigate the orientation dependence of plastic deformation behavior without preparing a single crystal. Therefore in this study, the anisotropy in the deformation behavior was investigated by nanoindentation of a polycrystalline Ti$_2$AlC alloy. The grain orientation was preliminarily investigated by the electron backscatter diffraction (EBSD). The detailed deformation behavior was examined by surface observation with the scanning probe microscopy (SPM), and by deformation microstructure observation with the transmission electron microscopy (TEM).

2. Experimental Procedure

Polycrystalline Ti$_2$AlC alloys were prepared by sintering pure elemental powders with the nominal composition of Ti–25Al–25C (at%). Ti powder (99.9%, <45 µm), Al powder (99.9%, <3 µm) and C powder (99.7%, <5 µm) were mixed with a rocking mill, followed by spark plasma sintering (SPS) at 1400°C for 20 min under the pressure of 30 MPa under vacuum (<10$^{-3}$ Pa). The sintered compacts were wrapped with Ta foil, and annealed at 1500°C for 24 h under vacuum.

The sample for nanoindentation was prepared by mechanical polishing with SiC grinding papers, followed...
by finishing with diamond and colloidal silica (40 nm) slurries. Nanoindentation measurements were performed by a Hysitron TI950 equipped with a Berkovich indenter. The measurements were conducted under the load-control condition with the constant loading rate of 50 µN/s to the maximum loads of 3 mN and 10 mN. The grains with the normal parallel to (3362), (0001), and (1120) were found by EBSD for nanoindentation measurements. The sample surface topography was imaged by scanning the indenter tip with the contact load of 1 µN, which is a scanning probe microscopy (SPM) function equipped with the nanoindenter. The surface images were recorded before and after each measurement.

Deformation microstructure developed by nanoindentation was observed by the transmission electron microscopy (TEM) operated at 200 kV. TEM samples for the cross sectional observation of the residual impressions were prepared by a focused ion beam (FIB) system. The original surface was protected by carbon deposition before FIB milling. The foils were lifted out from the sample and fixed on a Cu-grid.

3. Results

Polycrystalline Ti$_2$AlC alloys were successfully synthesized by SPS of high purity elemental materials, followed by annealing at 1500°C for 24 h. TEM observations revealed that the dislocation density at the grain interior was as low as $2 \times 10^{11}$ (m$^{-2}$). In the MAX phases, the (0001)(1120) basal slip is considered as the dominantly operative deformation mode. In this study, the crystal orientation was measured by EBSD, and nanoindentation measurements were conducted on grains with the normal parallel to (3362), (0001) and (1120). These indentation orientations are indicated on the standard stereographic triangle in Fig. 1. Figure 2 shows typical load-displacement curves by nanoindentation with the maximum load of 3 mN. Several pop-ins, i.e., discontinuous jumps during loading, have been observed for all the indentation directions. It has been documented that pop-in events correspond to the onset of plastic deformation within a dislocation-free small volume. The present study focuses on the indentation plasticity following the pop-in events. The effect of the indentation directions on the plastic deformation behavior will be discussed hereafter in terms of the surface topology and the deformation microstructure.

3.1 Deformation by nanoindentation along (3362)

Figure 3(a) shows an SPM image around the residual impression after a nanoindentation measurement with the maximum load of 10 mN. In this study, the contrast in the SPM images represents the magnitude of the gradient of the surface asperity. The deformation band that consists of a number of slip lines has developed from the impression. The deformation band extends toward [1100], implying that dislocation slip has potentially occurred on (112$n$) planes.
Note that the basal slip is known as the predominant deformation mechanism in the MAX phase compounds, and the trace of the basal plane on the surface coincides with that direction. The depth profiles across the deformation band are shown in Fig. 3(b) and (c). It is well known that the material around the contact area deforms either upward or downward against the original surface, and the pattern of such upward material flow is called “pile-up”, and the other “sink-in”. Figure 3(b) shows a depth profile over the residual impression, and it clearly exhibits the occurrence of “pile-up” by indentation. In contrast, the depth profile across the deformation band shows that the zone is depressed by several nanometers and no pile-up was observed on the edge.

Figure 4 shows bright-field TEM images of the cross section of the impressions with the maximum loads of (a) 3 mN and (b) 10 mN. The bold arrows represent the areas where the indenter was in contact. Numerous dislocations have developed on (0001) in both specimens, suggesting that the basal slip was predominant as the deformation mechanism for nanoindentation along (3362). Therefore, the deformation band developed on the surface would be derived from the glide of a large number of basal dislocations.

Although no cracking was confirmed in the specimen tested with the maximum load of 3 mN, a crack along (0001), i.e., delamination, was observed at the point 200 nm beneath the surface when the maximum load was 10 mN as shown in Fig. 4(b). A selected-area electron diffraction (SAED) pattern taken from the area around the crack indicates the occurrence of several degree of in-plane rotation as shown in Fig. 4(c). This lattice rotation would be caused by the arrangement of a number of basal dislocations, since non-basal dislocations were not observed in this area. It is therefore speculated that the delamination along (0001) is another option to release the accumulated strain in Ti$_2$AlC.

### 3.2 Deformation by nanoindentation along (0001)

Figure 5(a) shows an SPM image around the residual impression with the maximum load of 10 mN. Contrary to indentation along (3362), no slip lines or deformation bands were observed on the surface around the residual impression. The depth profile across the residual impression is shown in Fig. 5(b). The “pile-up” that developed at the edges of the residual impression appears to be more sharply angulated than those of the other indentation directions.

Bright-field TEM images of the cross section of the impression are shown in Fig. 6. The pile-up was not formed by nanoindentation with the maximum load of 3 mN as shown in Fig. 6(a). On the other hand, a large pile-up was formed by nanoindentation with the maximum load of 10 mN, accompanying the delamination along (0001) and buckling, as shown in Fig. 6(b). SAED observations have confirmed that a large lattice rotation has developed near the buckle. Therefore, the large sized pile-up observed in this direction was caused by delamination and kink-band formation near the contact of the indenter. A similar kink-band formation has been observed by indentation of a Ti$_3$SiC$_2$ thin film.

As shown in Fig. 6(b), dislocations were found to develop on (0001). These dislocations are basal dislocations since they were out of contrast under the reflection vector of $g = 0008$ (Fig. 6(c)). On the other hand, there were several dislocations that were not on (0001) right beneath the contact of indenter, as indicated by the white arrows in Fig. 6(c). Since they exhibited a strong contrast under $g = 0008$, the Burgers vector of these non-basal dislocations contains $c$-axis component.

The line vectors of the non-basal dislocation were analyzed by trace analysis. The trace analysis was done on the images taken from three zone axes as shown in Fig. 7: (a) [2110], (b) [8441] and, (c) [6331]. Since the dislocation analyzed was curved, we defined the dislocation line vector as the line that...
connects the two ends of the dislocation. Note that, to enhance the reliability for the trace analysis, these images were taken from the exact zone axes (not in two-beam conditions). In addition, the dislocation was nearly edged-on when observed from the \( \frac{1}{2} 15/C226/C2292/C138 \) direction, and this information is included in the following analysis. Figure 7(e) represents the result of the line vector analysis on the standard stereographic [0001] projection. Since the dislocation line vector lies on the slip plane of a glide dislocation, the slip plane can be identified by the intersection of the great circles of the vector parallel to the projected dislocation line on each image. The point of intersection is determined as \( \langle 36320 \rangle \). Considering that the analysis can contain some margin of errors, the \( \langle 1216 \rangle \) plane, which is deviated by 3° from \( \langle 36320 \rangle \), is suggested to be a potential slip plane of the non-basal dislocations.

### 3.3 Deformation by nanoindentation along \( \langle 1120 \rangle \)

Figure 8(a) shows an SPM image around the residual impression with the maximum load of 10 mN. Similar to the indentation along \( \langle 3362 \rangle \), the deformation band that extends toward \( [1100] \) has developed from the residual impression. The occurrence of “pile-up” was confirmed as shown in Fig. 8(b). The deformation band was depressed from the original surface and no protrusion on the edge was observed as shown in Fig. 8(c). Compared to the indentation along \( \langle 3362 \rangle \), the deformation band was sharp and extended in a longer distance.
Several arc-shaped dislocations are observed underneath the kink-band formation. Slip is the predominant deformation mechanism rather than indentation with the maximum load of 10 mN, dislocation while few kink-bands were observed. That is, for nano-

Numerous dislocations were found to develop on (0001), and [0001] were prepared by FIB as shown in Fig. 10(a). Figure 10(b) shows a bright-field TEM image under the reflection vector of \( g = \langle 1120 \rangle \) and \( g = 0006 \), respectively. The dislocations forming the wall exhibit a strong contrast under the reflection vector of \( g = \langle 1120 \rangle \), as shown in Fig. 9(c), while they are out of contrast under \( g = 0006 \) as shown in Fig. 9(d). Therefore, the dislocation wall would be a kink-boundary composed of the basal dislocations. Figure 9(e) shows an HRTEM image showing the (0001) lattice fringes in the deformation band B. The rotation angles of the (0001) basal planes at the boundaries are too large to be explained by dislocation array. Therefore the deformation band B is believed to be deformation twins, although its twinning system could not be identified in this study.

Figure 10 shows bright-field TEM images of the cross section of the residual impression with the maximum load of 3 mN. Two deformation bands denoted by A and B have developed as shown in Fig. 9(a). These deformation bands were fine-scaled; the width of the bands is approximately 200 nm or less. Besides, delamination along (0001) has occurred right adjacent to the deformation bands. As will be discuss in detail later, the deformation band A is a kink-band and B is a deformation twin.

Figure 9(b) shows an SAED pattern from the kink-band and matrix, which indicates that development of the kink-band is accompanied by a lattice rotation of 5.2°. Figures 9(c) and (d) are magnified bright-field TEM images of the kink-band under the reflection vectors of \( g = \langle 1120 \rangle \) and \( g = 0006 \), respectively. The dislocations forming the wall exhibit a strong contrast under the reflection vector of \( g = \langle 1120 \rangle \), as shown in Fig. 9(c), while they are out of contrast under \( g = 0006 \) as shown in Fig. 9(d). Therefore, the dislocation wall would be a kink-boundary composed of the basal dislocations. Figure 9(e) shows an HRTEM image showing the (0001) lattice fringes in the deformation band B. The rotation angles of the (0001) basal planes at the boundaries are too large to be explained by dislocation array. Therefore the deformation band B is believed to be deformation twins, although its twinning system could not be identified in this study.

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Figure 10 shows bright-field TEM images of the cross section of the residual impression with the maximum load of 3 mN. Two TEM samples with the foil normal of (1100) and (0001) were prepared by FIB as shown in Fig. 10(a). Figure 10(b) shows a bright-field TEM image under the reflection vector of \( g = \langle 1120 \rangle \) from the [1100] zone axis. Numerous dislocations were found to develop on (0001), while few kink-bands were observed. That is, for nanoindentation with the maximum load of 10 mN, dislocation slip is the predominant deformation mechanism rather than kink-band formation.

Figure 10(c) shows a bright-field TEM image under the reflection vector \( g = \langle 1120 \rangle \) from the [0001] zone axis. Several arc-shaped dislocations are observed underneath the residual impression. Since these dislocations are present on (0001), they were expected to be shear loop dislocations. Besides the shear loop dislocations on (0001), some non-basal dislocations are found to develop as indicated by a circle in Fig. 10(c). The Burgers vector \( \mathbf{b} \) of these dislocations was analyzed by the invisibility criterion. A dislocation is out of contrast when the reflection vector \( g \) and the Burgers vector of a dislocation \( \mathbf{b} \) are perpendicular (i.e., \( g \cdot b = 0 \)). Therefore, if two reflection vectors \( (g_1, g_2) \) that satisfy the invisible condition are found, the Burgers vector \( \mathbf{b} \) can be determined by the following equation.

\[
\mathbf{b} \parallel g_1 \times g_2.
\]

Figures 10(d)–(f) represent bright-field TEM images taken under the reflection vectors of (d) \( g = \langle 1120 \rangle \), (e) \( g = 1010 \) and (f) \( g = 2113 \). The dislocations show a strong contrast when imaged under \( g = \langle 1120 \rangle \) as shown in Fig. 10(d), while they are out of contrast when imaged under \( g = 1010 \) and 2113, as shown in Fig. 10(e) and (f). Therefore, the Burgers vector of the non-basal dislocations was identified to be [1211].
4. Discussion

4.1 Slip system of non-basal dislocation

It has been demonstrated that basal dislocations can easily glide and multiply on (0001) in the MAX phases. However, only few reports are available for the occurrence of non-basal slips at room temperature; i.e., it has been only indicated qualitatively by AFM observations around the residual impression of nanoindentation in Ti₃SnC₂. In this study, non-basal dislocations were observed in the specimens indented along [111] and [111]. It is suggested that the slip plane is \( \langle 12\overline{2}1 \rangle \) from Fig. 7, and the Burgers vector of the dislocations is \( \frac{1}{2} \langle 1\overline{2}2 \rangle \) from Fig. 10. Although slip plane analysis and Burgers vector analysis were performed on different dislocations, the determined Burgers vector of \( \frac{1}{2} \langle 1\overline{2}2 \rangle \) lies on \( \langle 12\overline{2}1 \rangle \). In addition, rough estimation for the slip plane of the dislocation analyzed in Fig. 10 represents a reasonable agreement with the above results. That is, although only rough estimation was possible for the slip plane analysis for these dislocations because the dislocation lines are very short, it is indicated that the trace of the projection line of the dislocations is roughly parallel to \( \langle 1\overline{2}2 \rangle \) when viewed from [0001], and thus the slip plane can be deduced from the cross product between \( \frac{1}{2} \langle 1\overline{2}2 \rangle \) and the Burgers vector of \( \frac{1}{2} \langle 1\overline{2}2 \rangle \) to be \( \langle 1\overline{2}2 \rangle \), which is only deviated by 9° from \( \langle 12\overline{2}1 \rangle \). Therefore, it is reasonable to assume that the slip system of the non-basal dislocations observed is \( \langle 12\overline{2}1 \rangle \frac{1}{2} \langle 1\overline{2}2 \rangle \) in Ti₂AlC.

Figure 11 shows the atomic arrangement of the \( \langle 12\overline{2}1 \rangle \) plane for Ti₂AlC. There are two kinds of atomic layers for \( \langle 12\overline{2}1 \rangle \); (a) Ti–Al mixed layer, and (b) C layer, and these layers are alternately stacked up as shown in Fig. 11(c). The determined Burgers vector of \( \frac{1}{2} \langle 1\overline{2}2 \rangle \) can be expressed by the summation of the fundamental translation vectors to be \(-3a + c\), which is indicated by the arrow in Fig. 11. The magnitude of the Burgers vector is 1.6421 nm, which is about 5 times longer than that of the basal dislocation (0.3056 nm). This means that the non-basal slip hardly occurs particularly at room temperature, because cracking can precede the onset of the non-basal slip for conventional mechanical tests on polycrystalline samples. On the other hand, the present study has confirmed that the non-basal slip occurs at room temperature because cracking is suppressed by the presence of the hydrostatic pressure applied underneath the indenter.

4.2 Kink formation mechanism underneath the indenter

In this study, a fine-scaled kink-band was found to develop by nanoindentation along [1120]. The kink-boundary was formed approximately 130 nm beneath the surface, as shown in Fig. 9(c). Assuming that the kink-boundary was composed of an array of the basal dislocations, the following relationship is established:\(^{31}\)

\[
\frac{b}{D} = 2 \sin \frac{\theta}{2}.
\]

Here, \( b \) is the magnitude of Burgers vector, \( D \) is the mean distance of dislocations, and \( \theta \) is the lattice rotation angle at the kink-boundary. The mean distance of the dislocations was estimated to be 3.6 nm from Fig. 9(c). Using \( |b| = 0.3056 \) nm,

Fig. 10 (a) An SPM image showing the way of micro-sampling by FIB for TEM foils with the normal parallel to [1110] (solid lines), and [0001] (broken lines). Bright-field TEM images of the cross sections of the impressions after nanoindentation along [1120] under the reflection vectors of \( g = \{1120\} \) taken from zone axes (b) [1110] and (c) [0001]. Bright-field TEM images showing the non-basal dislocations under the reflection vectors of (d) \( g = \{1120\} \), (e) \( g = 1010 \) and (f) \( g = 21\overline{1}3 \). The non-basal dislocations were indicated by black circle.
which is a perfect Burgers vector in Ti$_2$AlC, the rotation angle $\theta$ is calculated to be 4.9°. This value is in good agreement with the value of 5.2° determined experimentally from the SAED pattern in Fig. 9(b). Farber et al. have demonstrated that the kink-boundary in Ti$_3$SiC$_2$ MAX phase was composed of parallel alternating mixed perfect dislocations with two different Burgers vectors lying on the basal plane. However, the present analysis suggests that the kink-boundary is composed of an array of dislocations with the Burgers vector of $b = \frac{1}{3}a + c$. According to the model for the kink formation proposed by Hess and Barrett, kink formation is initiated from elastic buckling of (0001) planes to nucleate a pair of dislocations with the opposite sign of the Burgers vectors, which is followed by the gliding of these two dislocations toward the opposite directions. However, elastic buckling is difficult to occur for nanoindentation, since the zone subjected to high stress is constrained from the surrounding. Therefore, cracking would be necessary for releasing the constraint to produce buckling. In fact, a delamination crack was formed right adjacent to the fine-scaled kink-band as shown in Fig. 9(c). Furthermore, it is indicated from micropillar compression tests in Ti$_3$SiC$_2$ MAX phase that the delamination precedes the formation of kink-bands.

Based on these pieces of knowledge, a kink-band formation mechanism during nanoindentation of Ti$_2$AlC is proposed as shown schematically in Fig. 12. When the applied load reached a critical value, a delamination crack would form underneath the indenter (a). The delamination crack releases the constraint from the surroundings, which leads to elastic buckling (b), and nucleation of the dislocation pairs from the inside and/or the surface (c). These dislocations will glide and stop at the depth of the crack tip, by which the kink-boundary forms (d). This is supported by the experimental fact that the depth of the kink-boundary is almost the same as that of the delamination crack tip as shown in Fig. 9(c). Namely, delamination is an inevitable process for the kink formation, which includes nucleation and glide of the basal dislocations to form the boundary upon nanoindentation.

5. Conclusion

Plastic anisotropy of Ti$_2$AlC was examined by nanoindentation from different orientations. SPM and TEM observations revealed that the basal slip, (0001)(1120), was predominant as the deformation mechanism for all the indentation orientations. It was also indicated that, by indentation along (0001) and (1120), non-basal slips had occurred underneath the residual impressions of nanoindentation. The slip system of the non-basal slip was identified to be (1216)(0001) by analyzing the line vector and the Burgers vector of the dislocations. Furthermore, fine-scaled kink-bands were found to form underneath the residual impression. The formation of the kink-band was accompanied by delamination, i.e., micro-cracking along the basal plane; suggesting that the delamination is the trigger for the kink-band formation during nanoindentation of Ti$_2$AlC.

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