On the small angle twist sub-grain boundaries in Ti$_3$AlC$_2$

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Tilt-dominated grain boundaries have been investigated in depth in the deformation of MAX phases. In stark contrast, another important type of grain boundaries, twist grain boundaries, have long been overlooked. Here, we report on the observation of small angle twist sub-grain boundaries in a typical MAX phase Ti$_3$AlC$_2$ compressed at 1200 °C, which comprise hexagonal screw dislocation networks formed by basal dislocation reactions. By first-principles investigations on atomic-scale deformation and general stacking fault energy landscapes, it is unequivocally demonstrated that the twist sub-grain boundaries are most likely located between Al and Ti$_4$f (Ti located at the 4f Wyckoff sites of P6$_3$/mmc) layers, with breaking of the weakly bonded Al–Ti$_4$f. The twist angle increases with the increase of deformation and is estimated to be around 0.5° for a deformation of 26%. This work may shed light on sub-grain boundaries of MAX phases, and provide fundamental information for future atomic-scale simulations.

Ti$_3$AlC$_2$ is an essentially important member in the family of machinable layered ternary carbides and nitrides$^{1,2}$, whose chemical formula can be generalized as M$_{n+1}$AX$_n$ (referred to as MAX phases; M is an early transition metal element; A is an A group element; X is C or N; n is an integer)$^{1–7}$. Combining the merits of ceramics and metals, MAX phases are of vital technological importance$^{2,4–6}$. Like ceramics, they exhibit high elastic stiffness and strength, good oxidation and corrosion resistance; like metals, they have high electrical and thermal conductivity, excellent machinability and thermal shock resistance$^{1–7}$.

In the deformation of MAX phases, dislocations play a crucial role. The dislocations in uniaxially deformed MAX phases are predominantly confined in the basal plane$^{8–13}$. Out-of-basal-plane dislocations have only been observed in nanoindented Ti$_3$SnC$_2$,$^{14}$ Ti$_2$AlN deformed at 900 °C under gaseous confining pressure$^{15}$ and slowly compressed Ti$_3$AlC$_2$ at 1200 °C$^{11}$. Basal dislocations are prone to be arranged in arrays within the basal plane or walls along [0001]$^9$. The accumulation of dislocation arrays within the basal plane gives rise to the bending of the basal plane, while that of dislocation walls leads to the formation of kinking boundaries.$^{8,9}$

Kinking boundaries in MAX phases are special tilt-dominated grain boundaries with limited twist components$^{8,9}$. Farber et al. interpreted the kinking boundaries as dislocation walls with perfect dislocations threading along [1010]$^8$, wherein the dislocations alternatively have a Burgers vector of 1/3[1120] and 1/3[2110]. An excess of one type of dislocation (e.g. 1/3[1120]) over the other (e.g. 1/3[2110]) contributes to the twist components$^8$. Twist grain boundaries, on the contrary, can be regarded as screw dislocation networks$^{16,17}$. For instance, small angle twist (sub-) grain boundaries (SATGBs) in the typical oxide ceramics Al$_2$O$_3$(0001)/[0001] consist of hexagonal screw dislocation networks (HSDNs) with 1/3<1210> basal dislocations$^{18}$. The SATGBs in face- (with high stacking fault energy) and body-centered cubic metals comprise HSDNs as well$^{16,17,19,20}$. In this letter, the dislocation segments of previously observed hexagonal networks in Ti$_3$AlC$_2$,$^{11}$ are determined to be screw type, and further, the formation and evolution of HSDNs/SATGBs are closely investigated.

Results

Formation of HSDNs. Basal dislocations in MAX phases can react to form complex dislocation networks and dense hexagonal cells$^{12}$. In transmission electron microscopy (TEM) specimens sampled along directions both vertical and parallel to the load, hexagonal dislocation networks were frequently observed near the grain boundaries, wherein the dislocations are prone to be initiated or piled up. Figure 1a shows the typical TEM
morphology. According to the $g \cdot b$ values in Table 1, the Burgers vectors of the dislocation segments out of contrast in Fig. 1b–d are $1/3[12\bar{1}0]$, $1/3[\bar{1}10]$ and $1/3[\bar{1}110]$ (denoted by $a$, $b$ and $c$, Fig. 1c), respectively. For the sake of clarity, the dislocation segments in contrast are illustrated by solid lines and those out of contrast are marked with black dotted lines, as shown in Fig. 1b–d. White arrows represent the Burgers vectors of the dislocation segments out of contrast. (e) Crystallographic directions of the diffraction vectors and Burgers vectors. (f) Illustrations of the formation of HSDNs. $a$- (black) and $b$-type (blue) dislocation arrays encounter (①), and react to form $c$-type (red) dislocation segments (②). Dislocation configurations evolve to be HSDNs (③). Theoretically, the initial $a$- and $b$-type dislocation arrays can be screw, edge or mixed type. Nevertheless, irrespective of the nature of the initial dislocation arrays, the dislocation segments in the final equilibrium dislocation configuration are screw type. For the sake of simplicity, only the case for screw dislocation arrays is considered.

### Table 1. Values of $g \cdot b$ for basal dislocations in Ti$_3$AlC$_2$.

Since no stacking faults were observed in the present studies, only the Burgers vectors ($b$) of full dislocations are considered. Imaged with a diffraction vector $g$, dislocations with $g \cdot b = 0$ are out of contrast.
Figure 2. Changes in bond length. (a) Illustration of the unit cell of Ti₃AlC₂. Ti₂a and Ti₄f denote the Ti atoms located at the 2a and 4f Wyckoff sites of P6₃/mmc, respectively. Changes in bond length of Al–Ti₄f, C–Ti₂a and C–Ti₄f under (b) uniaxial tension along [0001], and (c) hydrostatic compression.

\[ \sum b_i \xi_i = 0 \]  

where \( b_i \) is the Burgers vector and \( \xi_i \) is the direction vector of dislocation line.

Since \( a^2 + b^2 > c^2 \), the above-mentioned reaction is energetically favorable. However, not all the crossing \( a \)-and \( b \)-type segments can react to form \( c \)-type segments. As marked by the black arrows in Fig. 1a, a long \( a \)-type segment fails to react with \( b \)-type segments although they intersect at several positions, wherein the intersection angles are approximately 90°. This is more apparent in Supplementary Fig. S1. According to Hirth et al., crossing dislocations that are a few degrees from being orthogonal cannot react. Therefore, orthogons (Supplementary Fig. S1) or pentagons (Fig. 1a) instead of hexagons are formed because of unfavorable dislocation line directions. It is worth noting that, apart from \( a + b \rightarrow c \) (marked by the black circle in Supplementary Fig. S1), the reaction \( a + c \rightarrow b \) (marked by the red circle in Supplementary Fig. S1) contributes to the formation of HSDNs as well.

The plane of twist sub-grain boundaries. With the formation of HSDNs, SATGBs are established on the basal plane where the networks are located. Then, a scientific question naturally arises: which basal atomic plane is the most likely boundary plane? We address this issue via studies on atomic-scale deformation (illustrations are presented in Supplementary Fig. S2) and general stacking fault energy (GSFE) landscapes. The crystal structure of Ti₃AlC₂ comprises edge-sharing Ti₃C octahedron layers bonded by C–Ti₂a and C–Ti₄f, and Ti₆Al triangular prism layers bonded by Al–Ti₄f (Fig. 2a; Ti₂a and Ti₄f denote the Ti atoms located at the 2a and 4f Wyckoff sites of P6₃/mmc, respectively). Figure 2b plots the changes in bond length for Al–Ti₄f, C–Ti₂a and C–Ti₄f against applied tensile strains along [0001]. It can be seen that the changes in C–Ti₂a and C–Ti₄f are negligible, and most of the strains are accommodated by the elongation of Al–Ti₄f. Specifically, the stretches of Al–Ti₄f are 6–10 and 9–66 times those of C–Ti₂a and C–Ti₄f, respectively. Similar features can be identified in the hydrostatic compression (Fig. 2c), where the contractions of Al–Ti₄f are 2–3 times those of C–Ti₂a and C–Ti₄f. Therefore, Al–Ti₄f is the weakest bond in Ti₃AlC₂, and shear is believed to occur most easily therein.

To further quantitatively confirm this from an energetic point view, GSFE was calculated (see the Methods and Supplementary Fig. S3 for details). The GSFE of Al–Ti₄f is significantly lower than those of C–Ti₂a and C–Ti₄a (Fig. 3a), and the local maximum (USF) of Al–Ti₄f is only 18.9% and 12.2% of those of C–Ti₂a and C–Ti₄f, respectively (Table 2). Besides, the ideal shear strength (maximum restoring force, defined as the maximum slope of the GSFE curve) of Al–Ti₄f is only 19.2% and 12.2% of those of C–Ti₂a and C–Ti₄f, respectively (Table 2), indicating that the most probable shear plane is the one between the Al and Ti₄f layers. Schematically, the shear of Ti₆Al triangular prisms is illustrated in Fig. 3b. Therefore, the SATGBs observed in
this study are believed to be there. As a characteristic parameter of the twist boundary, the twist angle, \( \theta \), can be estimated by equation (2)\(^{16,20}\):

\[
\theta = \frac{b}{\sqrt[3]{l_h}}
\]

where \( b \) and \( l_h \) are the lengths of the Burgers vector and hexagon edge, respectively. The calculated twist angle in Fig. 1a is approximately 0.26°. Figure 4a-c present the typical TEM morphologies of the HSDNs in the specimens with various deformations (4%, 14% and 26%). As the deformation proceeds, new dislocations intersect and react with the as-formed hexagonal networks. Consequently, small hexagonal dislocation cells form in large cells, and the average cell size diminishes. Statistical data of \( l_h \) and \( \theta \) are plotted in Fig. 4d against the strain. It can be seen that the twist angle scales with the applied strains. For the sample deformed by 26%, the twist angle is about 0.5°. Notably, the HSDNs can be observed in other slowly deformed MAX phases (like Ti2AlC, Nb4AlC3 and etc., Supplementary Fig. S4). The formation of HSDNs/SATGBs is generic to low-energy dislocation configurations in slowly deformed MAX phases. For MAX phases, the collective behavior of basal dislocations includes not only the previously reported accumulation of dislocations vertical and parallel to the basal plane\(^9\), but also the formation of HSDNs/SATGBs.

Dislocations are the carriers of plastic deformation. Their mutual interactions and reactions bring about work hardening. The formation of HSDNs contributes to previously identified strain hardening of Ti3AlC2\(^{11}\), giving rise to SATGBs. Since the twist angle is very small (around 0.5°), the contribution of SATGBs to the plastic deformation of Ti3AlC2 is quite limited. Sub-grains have been reported in the tensile and compressive creep of MAX phases\(^{26–28}\). Since the SATGBs are formed in compression with remarkably low strain rates, it is inferred that they likely contribute to the creep at high temperature.

With the formation of low energy dislocation structures, misorientations at grain and sub-grain scale are established. The misorientation angle increases with the strain in metals, linearly\(^{29,30}\) or in a power law (with an exponent of 1/2)\(^{31,32}\). Our work indicates that the twist angle scales with the deformation in a roughly linear manner in the investigated strain and temperature ranges.

In summary, small angle twist sub-grain boundaries (around 0.5°) have been ubiquitously observed in uniaxially compressed Ti3AlC2. The twist sub-grain boundaries predominantly comprise hexagonal screw dislocation networks that result from basal dislocation reactions. The grain boundary plane is believed to be between the relatively weakly bonded Al and Ti4f layers. In addition, it is unambiguously demonstrated that the twist angle scales with the deformation. This work may shed light on the formation of low-energy dislocation configurations and its evolution with the deformation of MAX phases.
Methods

High-temperature deformation. \(\text{Ti}_3\text{AlC}_2\) bulk sample was synthesized using the method reported by Wang and Zhou\(^{33}\). For the compression tests, cylinders about 9 mm in diameter and 12 mm in height were cut from the as-prepared sample by electric discharge machining and then mechanically polished. Subsequently, three cylinders were compressed to a strain of 4%, 14% and 26% at 1200 °C with a strain rate of \(10^{-5}\) s\(^{-1}\) in a universal testing machine (SANS CMT4204, Shenzhen, China).

TEM characterization. Dislocation configurations were analyzed using a transmission electron microscope (FEI Tecnai G2 F20, Oregon, USA) working at 200 kV. For TEM investigations, slices were cut from the deformed sample in two directions, vertical and parallel to the load. Then, the slices were mechanically thinned and ion-milled to be electron transparent. The Burgers vectors of the dislocations were determined by the \(g \cdot b\) method. For each deformation, statistics of hexagonal cell size were determined on seven TEM images obtained from different regions.

First-principles calculations. The deformation at atomic scale was modelled with the CASTEP module\(^{34}\). Electronic exchange-correlation energy was treated under a generalized gradient approximation (GGA–PBE)\(^{35,36}\). Interactions of electrons with ion cores were represented by Vanderbilt-type ultrasoft pseudopotential\(^{37}\). The Broyden–Fletcher–Goldfarb–Shanno minimization method was used for geometry optimization, where the plane-wave cut-off energy and the Brillouin zone sampling were fixed at 450 eV and \(5 \times 5 \times 2\) Monkhorst–Pack-point meshes\(^{38}\), respectively. Differences in total energy, maximum ionic Hellmann–Feynman force, maximum ionic displacement and maximum stress were converged to \(5 \times 10^{-6}\) eV/atom, 0.01 eV/Å, \(5 \times 10^{-4}\) Å and 0.02 GPa, respectively. The fully optimized structure was used for uniaxial tension and hydrostatic compression. The deformation modes are illustrated in Supplementary Fig. S2. To ensure a uniaxial deformation along [0001], the lattice parameters perpendicular to the applied strain, as well as the internal coordinates of atoms, were fully relaxed until the stresses were converged to 0.02 GPa. For the GSFE calculation, a supercell with twenty-five
atomic layers with Al layers at the center and surfaces was constructed using the fully optimized Ti₃AlC₂ unit cell, where a vacuum slab of 15 Å in thickness was symmetrically added (see Supplementary Fig. S3). The disregility on the plane of interest was introduced by rigidly shifting all the atoms above the target plane relative to those below that plane along <2110>. Without relaxing the supercell further, total energies of faulted structures were calculated. Then, the energy difference between the faulted and unfaulted structures gives the GSFE.

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Author Contributions
H.Z. and C.Z. carried out the sample synthesis and microstructure characterization. H.Z. and T.H. conducted the first-principles calculations. X.H.W. conceived and designed the project. H.Z., X.H.W., X.Z. and Y.C.Z. wrote the paper. All authors contributed to data analysis and scientific discussion.

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