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► **To cite this version:**

Julien Gu  no  , Vincent Taupin, Maxime Vallet, Wenbo Yu, Antoine Guitton. Features of a nano-twist phase in the nanolayered  $\text{Ti}_3\text{AlC}_2$ . 2021. hal-03207521v2

**HAL Id: hal-03207521**

**<https://hal.univ-lorraine.fr/hal-03207521v2>**

Preprint submitted on 17 Aug 2021 (v2), last revised 8 Nov 2021 (v3)

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# Features of a nano-twist phase in the nanolayered $\text{Ti}_3\text{AlC}_2$

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## Abstract

Complex intermetallic materials known as MAX phases exhibit exceptional properties from both metals and ceramics, largely thanks to their nanolayered structure. With high-resolution scanning transmission electron microscopy supported by atomistic modelling, we reveal atomic features of a nano-twist phase in the nanolayered  $\text{Ti}_3\text{AlC}_2$ . The rotated hexagonal single-crystal is encompassed within basal symmetric twist interfaces similar to grain boundaries. In particular, we show that air-oxidation at 1000 °C can form a twisted phase that leads to the formation of interfacial dislocation networks with screw characters or to severe interfacial reconstructions. Additionally, we explore the contribution of disclinations to the representation by continuum models of the stress field generated by such nano-twist defect in the  $\text{Ti}_3\text{AlC}_2$  bulk phase. The occurrence of this unexpected defect is expected to impact the physical response of this nanolayered-based material as such supports property-by-design approaches.

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## 1. Introduction

$\text{Ti}_3\text{AlC}_2$  belongs to the wide family of MAX phases [1]. These ternary compounds arise a keen interest, because they are stiff, lightweight, machinable, made from relatively inexpensive raw materials, resistant to oxidation and thermal shock, and capable of remaining strong up to temperatures above 1,300°C in air [2]. More than fifty compounds are thermodynamically stable and all of them exhibit the same range of promising properties. Because of their composition, they were called  $\text{M}_{n+1}\text{AX}_n$  phases ( $n = 1$  to 3, M is a transition metal, A is an A-group element and X is nitrogen and/or carbon) [3].

As typical MAX phase,  $\text{Ti}_3\text{AlC}_2$  has a nanolayered structure with an hexagonal lattice, whose the space group is  $P6_3/mmc$  [2, 4]. The primitive cell can be described as a stacking of two  $\text{Ti}_6\text{C}$  octahedron layers with one layer of Al [1]. Furthermore, measurements of lattice parameters with numerous methods reveal that  $\text{Ti}_3\text{AlC}_2$  exhibits elevated high crystalline anisotropy. The  $c/a$  ratio is slightly higher than 6 [5].

It is established, that MAX phases experience plastic deformation by the glide on basal planes of  $a$ -dislocations confined between the  $\text{M}_6\text{X}$  and Al layers, thus forming pile-ups and walls [6, 5, 7]. The latter can form local disorientation areas, known as kink bands [8, 9]. Furthermore, numerous dislocation interactions forming networks (dipoles, reactions) and high lattice friction have been observed [10, 11]. Note, that out-of-basal plane dislocations have been observed as well, but they do not play a role at room temperature in standard deformation conditions [12, 13]. At high temperature, it has been revealed, that out-of-basal plane  $\langle a \rangle$ -dislocations are common events and

hence cross-slip (from basal planes to prismatic or pyramidal planes) plays a key role in the deformation [14, 15]. This increase of available glide systems is likely to originate the brittle-to-ductile transition of MAX phases [14]. Note also that Frank partial  $\langle c \rangle$ -dislocations correlated with a diffusion mechanism were recently reported [16]. Moreover, observations of stacking faults is another major microstructural feature, but their role in deformation both at room and high temperatures remains unclear [6, 13, 15].

Of all MAX phases, those containing Al, such as  $\text{Ti}_3\text{AlC}_2$ , are the most resistant to oxidation [2]. During exposure of Ti–Al–C MAX phases to oxidizing environment at high temperatures, the outward diffusion of the weakly bonded Al atoms is much faster compared to the more covalently bonded Ti atoms [2, 17, 18, 19]. Therefore, it results in a regime, where a superficial protective layer of  $\text{Al}_2\text{O}_3$  is formed. However,  $\text{TiO}_2$  can be formed as well, leading, this time, to a catastrophic regime. Both mechanisms are strongly depend on the oxidation conditions and the initial microstructure [18, 19]. Despite the description of these oxides, operating oxidation mechanisms of  $\text{Ti}_3\text{AlC}_2$  and more generally of MAX phases remain poorly documented, especially on how the crystallographic structure is evolving.

Such is the background of the current letter. This work is motivated by the analysis of original phases that were observed after oxidation in a  $\text{Ti}_3\text{AlC}_2$  matrix by high-resolution scanning transmission electron microscopy (HR-STEM). Such nanolamellar phases appear to be twisted with respect to the surrounding matrix and also associated with diffusion mechanisms in its neighborhood. Hence, by interpreting our HR-STEM observations using molecular dynamics simulations of model nano-twist phases, we study their atomic scale features

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including interfacial crystal defects, excess energy, and mechanical fields. Concerning the latter, a continuous description of the twist phase using a disclination based mechanical framework is conducted complementary to atomistic simulations to further evidence the complexity of such phases.

## 2. Experiments

The specimen was prepared by hot isotropic pressing (HIP). Briefly, powders of Ti, Al and TiC were mixed in stoichiometric proportions  $2\text{Ti}:1.05\text{Al}:0.85\text{C}$  and then cold-compacted into cylindrical steel dies using an uniaxial pressure. Powder compacts were encapsulated into pyrex containers under high vacuum for reactive sintering in the HIP machine. Afterwards, the specimen were oxidized at  $1000^\circ\text{C}$  for 25 h in a flowing air atmosphere. More details are given in [20, 19]. Cross-sectional TEM samples were prepared by focused ion beam (FIB) on a FEI Helios dual beam Nanolab 600i. Atomically-resolved high-angle annular dark field scanning TEM (HAADF-STEM) was performed on an Titan<sup>3</sup> G2 S/TEM fitted with a double aberration corrector for probe and image corrections and operating at 300 kV.

HR-STEM in HAADF mode of the  $\text{Ti}_3\text{AlC}_2$  is shown in Fig. 1. As HAADF detector senses a greater signal from atoms with a higher atomic number  $Z$ , Ti columns appear brighter in the resulting micrograph [21]. The nano-layered structure of  $\text{Ti}_3\text{AlC}_2$  highlighted in the circular inset is consistent with the expected one for a 312-MAX phase projected along  $[\bar{1}\bar{1}20]$  *i.e.* zigzag stacking of three TiC planes followed by one Al plane, the Al plane being the axis of symmetry of the zigzag. Several large  $\text{Ti}_3\text{C}_2$  laths are clearly visible as well. The mechanisms responsible for their formation is out of the scope of this letter. The region of interest shows blurred atomic layers (ROI, white square in Fig. 1). The blur is along the  $[1\bar{1}00]$  direction, localized within the basal plane. This indicates that this part of the lattice has undergone a rotation around the  $[0001]$  direction. The boundaries between this rotated phase and the other phase are marked with dashed white lines. Note, that the upper extremity of the ROI shows a large blurred area and visible inter-diffusion between Al and Ti planes.

## 3. Modelling

To gain more insights on the observed defect and to characterize precisely the structure of the twist boundary, we modeled the nano-twist phase by atomistic simulations. Molecular dynamics (MD) based on interatomic potentials is an excellent modelling method to investigate the atomic-scale configuration of defects, in particular interfaces [22, 23]. It has been widely used over the past decade to investigate grain boundaries [24, 25, 26, 27] and phase boundaries [28, 29, 30, 31]. The only published model suitable to describe  $\text{Ti}_3\text{AlC}_2$  atomic interactions is the bond-order potential (BOP) recently adjusted by Plummer and Tucker [32]. It is based on the formalism initially proposed by Tersoff [33] and described in detail by Albe *et*

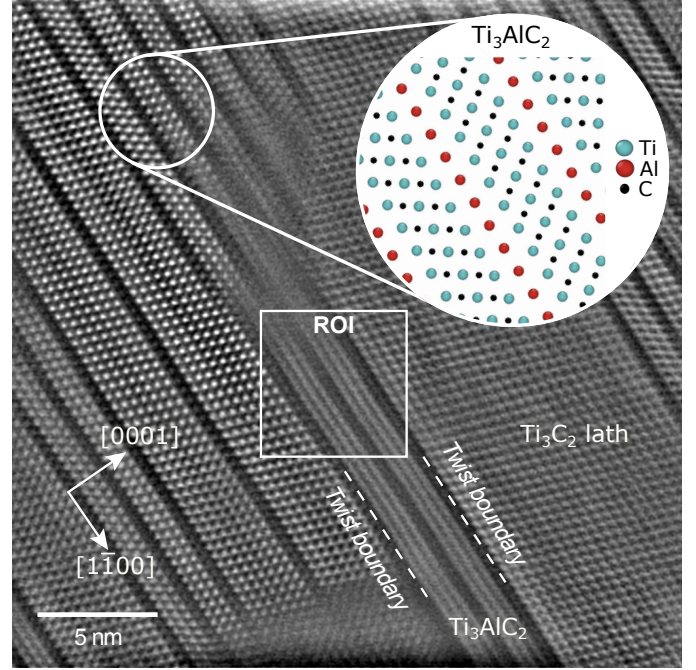


Figure 1: Experimental observation of the nano-twist phase (region of interest, ROI) in the nanolayered  $\text{Ti}_3\text{AlC}_2$ . Filtered HR-STEM micrograph in HAADF mode with electron direction along  $[1\bar{1}\bar{2}0]$ . Boundaries of the nano-twist phase are indicated by dashed lines. A model of the  $\text{Ti}_3\text{AlC}_2$  crystallographic structure is shown in the inset. Some  $\text{Ti}_3\text{C}_2$  laths are also observed.

*al.* [34]. Fig. 2 shows the atomistic simulation setup to compute the energy and the structure of the rotated phase boundaries. Within a fully periodic bulk  $\text{Ti}_3\text{AlC}_2$  phase, a cookie shape region in the center is rotated with an angle  $\Psi$  around an axis normal to the basal plane, as indicated in blue in Fig. 2. The inset shows as an example a rotation of the atomic structure for  $\Psi = 3^\circ$ . Note that structures with similar contrasts to HAADF-STEM ones can be obtained with different values of  $\Psi$  (Fig. 1).

The as-formed nano-twist phase (NTP) exhibit prismatic and basal interfaces with the  $\text{Ti}_3\text{AlC}_2$  phase. The prismatic interface is not clearly define in our experimental observation, whereas the basal interface appear atomically sharp (See Fig. 1). In this work, we thus focus on the characterisation of the NTP basal boundary (NTB). Fig. 3 shows the interfacial energy of the NTB as function of the twist angle  $\Psi$ . The energy is computed by considering a cylindrical region in the center of the NTP, that does not encompass the prismatic boundaries. For each twist angle, the system is statically relaxed by using conjugate gradients and fire [35, 36] methods. The dimensions of the box are adapted to ensure a globally stress-free system. The energy of such as-relaxed NTB is shown with blue small dots in Fig. 3. Selected configurations have been annealed at 600 K for 100 ps. A Nose-Hoover thermostat control the temperature and a Nose-Hoover barostat ensure constant zero pressure. The systems are subsequently quenched and their energies are shown in Fig. 3 with orange large dots.

The insets in Fig. 3 present the out-of-plane stress component  $\sigma_{zz}$  of the as-relaxed NTB for different  $\Psi$ . By showing the dis-

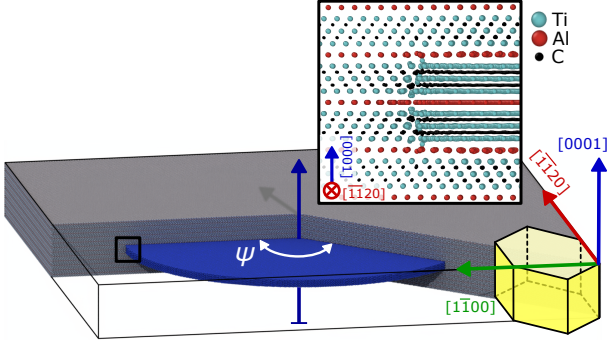


Figure 2: Modeling of the nano-twist phase in the nano-layered  $\text{Ti}_3\text{AlC}_2$  by means of a cookie-shape rotation region. (a) atomistic simulation setup of the cookie-shape region (in blue) parallel to the basal planes, with  $[000 1]$  rotation axis and  $\psi$  rotation angle. The black square indicate the location of the inset. : magnified projected view of a 10 nm thin slice of the side of the cookie-shape nano-twist phase for  $\psi = 3^\circ$ . Ti, Al and C are colored in green, red and black, respectively.

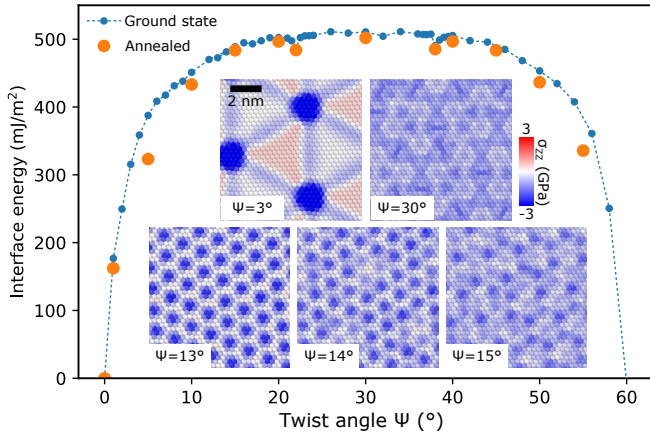


Figure 3: Energy of the basal interface of the nano-twist phase as function of the twist angle  $\psi$ . Interfacial energy of the ground state and annealed structure in blue and orange dots, respectively. The dotted line is a guide for the eyes. Insets show magnified views of the stress field  $\sigma_{zz}$  for  $\psi = 3, 13, 14, 15, 30$ .

tortion of the crystal lattice at the basal boundary, it reveals the structures of the interface. More details are presented in Fig. 4 for  $\psi = 1^\circ$ , the smallest twist angle considered in this work. The distortion of the crystal lattice at the NTB is captured by the out-of-plane stress component  $\sigma_{zz}$  (Fig. 4a,b). This evokes the signature of an interfacial dislocation network, with the three-fold symmetry of the basal plane and the nodes of interacting interfacial dislocations. The atomic positions for different basal interlayers shown in Fig. 4(c)(d) confirm this observation, as the relative displacement of the atoms is characteristic of screw dislocations.

#### 4. Discussion

The NTP we observed experimentally is not a grain on itself, but is located within one  $\text{Ti}_3\text{AlC}_2$  grain. This nano-phase exhibits limited degree of freedom, with its twist axis and at least one interface being precisely defined: the  $\langle c \rangle$  axis and the basal

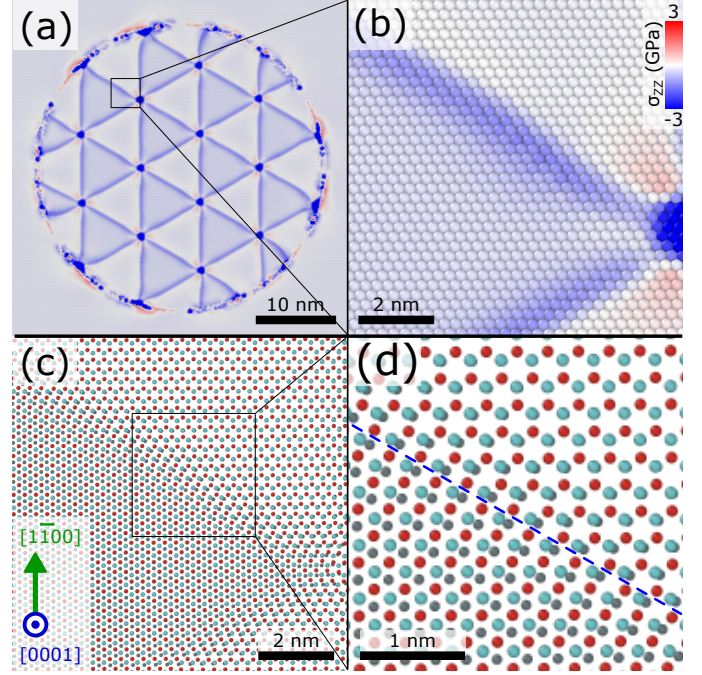


Figure 4: Interfacial structure of the  $\text{Ti}_3\text{AlC}_2$  nano-twist phase for  $\psi = 1^\circ$ . (a) global and (b) magnified views of the local stress field  $\sigma_{zz}$  revealing the typical dislocation network of a low angle grain boundary. (c) identical view as (b) but showing chemical species as in Fig. 2. (d) magnified view of (c) revealing the atomic displacements induced by a screw dislocation. (c) Atomic radius are proportional to the stacking position in the  $[000 1]$  direction: light green, red and dark green, from top to bottom. The screw dislocation line is indicated as a blue dashed line.

planes, respectively. It is clear that the basal interface, we called NTB, shares similarities with pure twist grain boundaries, such as (1) an interfacial energy evolution with a typical bell-shape, (2) an interfacial structure that can be described by a network of screw dislocations lying on basal planes and cross-slipping to 1st-order prismatic planes (consistent with previous experimental observations [14]) for low twist angles, (3) a spacing between interfacial dislocations inversely proportional to low twist angle values and (4) a description of the interface in term of dislocations network that vanished for high twist angles. The transition from a low angle configuration to a high angle configuration is for  $\psi \approx 15^\circ$  (Fig. 3, insets). However, the NTB also exhibits clear differences towards grain boundaries, namely (1) only one macroscopic degree of freedom (DoF) instead of five for grain boundaries and (2) interfacial reconstructions for high twist angle leading to non-monotonous structural patterns.

Interestingly, such NTP were already reported by Drouelle *et al.* in  $\text{Ti}_3\text{AlC}_2$  deformed by creep at high temperature. Indeed, they observed by conventional TEM, highly disorganized lenticular defects with a very high density of screw dislocations [15]. Of course, they concluded that such very localized defects may play a role in the plasticity of  $\text{Ti}_3\text{AlC}_2$ .

It is worth noticing that, within the time frame considered by our atomistic simulations, neither the interfacial energy nor the interfacial structure is significantly altered by annealing. The configuration of the NTB predicted by atomistic modelling appears as such stable.

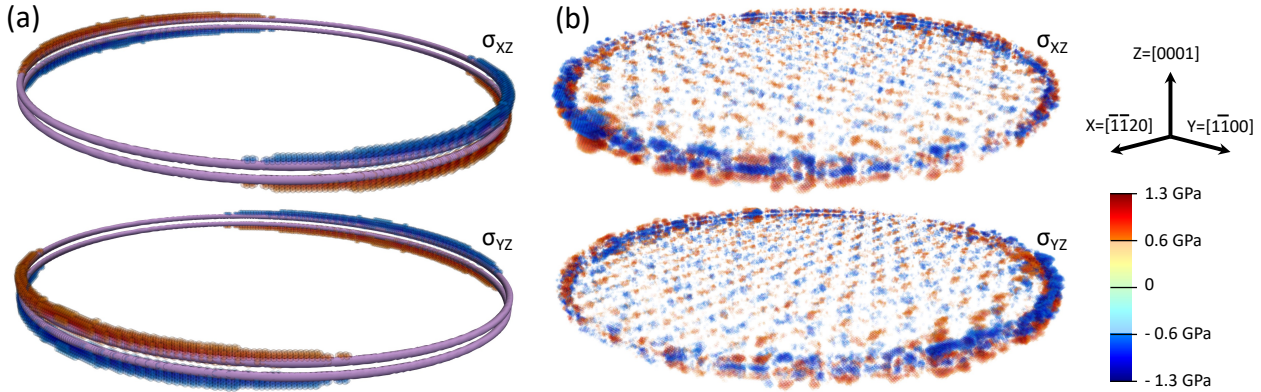


Figure 5: Shear stress fields  $\sigma_{xz}$  and  $\sigma_{yz}$  of a high-angle nano-twist phase represented by (a) a dipole of twist disclination loops and (b) an atomistic cookie-shape region. Only voxels (a) and atoms (b) with stresses with magnitude larger than 600 MPa are shown. In purple (a) is shown the norm of the disclination density tensor.

For high twist angles ( $\Psi > 15^\circ$ ), the interfacial configuration exhibits severe reconstructions. By comparison to configurations with low twist angles, this reconstruction releases localized atomic stresses but does lead to lower interfacial energies. Interfacial energies for tilt and twist boundaries in crystals with cubic structures often show clear drops for particular  $\Psi$  values that correspond to high symmetry misorientations. Yet, such stable high angle configurations are not observed with the NTB investigated in this work. This can be related to the limited DoF accessible to this boundary, as described in the following. Grain boundaries are classically considered within the coincidence site lattice theory (CSL), which predict periodic interfaces for particular misorientation. As such, they are defined by five macroscopic DoF (directions and rotation), among which some lead to particularly stable configurations with low interfacial energy. Additionally, it is known that considering the microscopic DoF (translation) accessible to any grain boundaries is crucial to fully determine the most stable configurations. However, the NTB we observed does not have so many DoF. In particular, the NTB being confined within a well defined bulk  $\text{Ti}_3\text{AlC}_2$  phase, it does not allow the NTB for translation DoF. Allowing the NTB for microscopic DoF might thus lead to lower energy configurations. This is out of the scope of the present work, which is focused on the characterization of the NTB we observed experimentally.

For large angles  $\Psi$ , the NTB cannot be conveniently described by dislocations anymore as discussed above and illustrated in the insets of Fig. 3. We propose that for high-angles of rotation, the NTB can be appropriately represented by disclination loops. As the rotational counterpart of dislocations, disclinations are line defects which introduce a discontinuity of the elastic rotation field, referred to as the Frank vector. The concept of disclinations is appropriate for the description of elastic fields of tilt boundaries with high misorientations [37] and for nanotwin microstructures [38, 39]. Regarding the cookie shape NTB considered in this work, the stress field due to the network of overlapping dislocation arrays can be equivalently and more simply described by using two disclination loops delimiting the NTB. Such representation was successfully applied for

nanolamellar twins with tilt misorientations [39]. Here, we propose to apply this concept to twist interfaces with high misorientations, which has never been attempted so far to our knowledge. More details can be found as Supplementary Material.

As shown in Fig. 5(a), a NTP with misorientation  $30^\circ$  is modelled by a dipole of twist disclination loops with Frank vector magnitude  $30^\circ$  about the Z ([0001]) axis. A recent field disclination mechanics framework is used to build this loop dipole [37, 39]. The two main Cauchy stress tensor components predicted by the model are shear stresses  $\sigma_{xz}$  and  $\sigma_{yz}$ . The latter are characteristic of screw dislocation out of plane shear stresses and clearly arise from the twist rotation discontinuity applied within the NTB.

Fig. 5(b) shows  $\sigma_{xz}$  and  $\sigma_{yz}$  as predicted by atomistic simulations and evidenced a fair match with what is predicted by the disclination model in Fig. 5(a). The similarities are (1) the morphology of the surrounding stress field maxima with two inverse dipoles in a particular crystallographic direction, and (2) the magnitude of these stress dipoles around  $\pm 1$  GPa. This match between atomistic and continuum representation is however partial. The differences are (1) the direction of stress maxima rotated by  $90^\circ$ , and (2) stresses within the NTB predicted by MD but not by the disclinations. These differences clearly originate from characteristics not considered by the disclination based model. Typically, dislocation cores effects are only considered by atomistic modelling and leads to  $\epsilon_{zz}$  eigenstrains. Additionally, the reconstruction of the NTB for high twist angles we observed by MD, appears to play a crucial role in the distribution of the stress field. Disclination based models will have to be enriched to consider such atomistic mechanisms, but they are yet much promising to model general interfaces in complex materials at the continuum scale.

Regarding the formation mechanism of the NTB, our preliminary observations suggest a strong influence of the Ti-Al diffusion in the basal planes at the onset of the NTB. The diffusion could be favoured by the interfacial dislocation network that locally induce a variation of free volume within basal planes.

The exact impact of a nano-twist phase on the properties of the  $\text{Ti}_3\text{AlC}_2$  nanolayered structure is yet unclear. But it seems

that they are not anecdotal events, as reported in [18]. Similarly to what has been observed with the formation of Frank partial dislocations [16], the interfacial dislocation network could limit the propagation of  $\langle a \rangle$  dislocations and thus participate to the strengthening of  $\text{Ti}_3\text{AlC}_2$  phases. The prismatic interfaces of the NTP would require more investigations as they should play an important role by hindering the propagation of basal dislocation more efficiently than the basal interfaces. From a more general perspective, nano-twist crystals have been shown to exhibit peculiar optical properties [40].

Additional investigations are ongoing to gain a comprehensive understanding on the formation mechanisms of this nano-twist phase, in order to open up new possibilities for tailored properties MAX phases.

## 5. Acknowledgments

This project has received financial supports from the CNRS through the MITI interdisciplinary programs and from the National Natural Science Foundation of China (no. 51701010). This work was performed using HPC resources from GENCI-TGCC (grant 2020-A0080911390 and 2021-A0100911390) and from the EXPLOR center of the Université de Lorraine.

## References

- [1] X. Wang, Y. Zhou, Solid-liquid reaction synthesis of layered machinable  $\text{Ti}_3\text{AlC}_2$  ceramic, *Journal of Materials Chemistry* 12 (3) (2002) 455–460. doi:10.1039/b108685e.
- [2] M. Barsoum, T. El-Raghy, The MAX Phases: Unique New Carbide and Nitride Materials, *American Scientist* 89 (4) (2001) 334. doi:10.1511/2001.4.334.
- [3] M. W. Barsoum, MAX Phases, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2013. doi:10.1002/9783527654581. URL <http://doi.wiley.com/10.1002/9783527654581>
- [4] M. W. Barsoum, The MN+1AX<sub>n</sub> phases: A new class of solids, *Progress in Solid State Chemistry* 28 (1-4) (2000) 201–281. doi:10.1016/S0079-6786(00)00006-6.
- [5] M. W. Barsoum, M. Radovic, Elastic and Mechanical Properties of the MAX Phases, *Annual Review of Materials Research* 41 (1) (2011) 195–227. doi:10.1146/annurev-matsci-062910-100448.
- [6] L. Farber, M. W. Barsoum, A. Zavaliangos, T. El-Raghy, I. Levin, Dislocations and Stacking Faults in  $\text{Ti}_3\text{SiC}_2$ , *Journal of the American Ceramic Society* 81 (6) (2005) 1677–1681. doi:10.1111/j.1151-2916.1998.tb02532.x.
- [7] K. Gourié, P. Carrez, P. Cormier, A. Guitton, A. Joulain, L. Thilly, C. Tromas, Dislocation modelling in  $\text{Ti}_2\text{AlN}$  MAX phase based on the Peierls–Nabarro model, *Philosophical Magazine* 95 (23) (2015) 2539–2552. doi:10.1080/14786435.2015.1066938.
- [8] M. W. Barsoum, L. Farber, T. El-Raghy, Dislocations, kink bands, and room-temperature plasticity of  $\text{Ti}_3\text{SiC}_2$ , *Metallurgical and Materials Transactions A* 30 (7) (1999) 1727–1738. doi:10.1007/s11661-999-0172-z.
- [9] A. Guitton, S. Van Petegem, C. Tromas, A. Joulain, H. Van Swygenhoven, L. Thilly, Effect of microstructure anisotropy on the deformation of MAX polycrystals studied by in-situ compression combined with neutron diffraction, *Applied Physics Letters* 104 (24) (2014) 241910. doi:10.1063/1.4884601.
- [10] A. Guitton, A. Joulain, L. Thilly, C. Tromas, Dislocation analysis of  $\text{Ti}_2\text{AlN}$  deformed at room temperature under confining pressure, *Philosophical Magazine* 92 (36) (2012) 4536–4546. doi:10.1080/14786435.2012.715250.
- [11] G.-P. Bei, A. Guitton, A. Joulain, V. Brunet, S. Dubois, L. Thilly, C. Tromas, Pressure-enforced plasticity in MAX phases: from single grain to polycrystal investigation, *Philosophical Magazine* 93 (15) (2013) 1784–1801. doi:10.1080/14786435.2012.755272.
- [12] C. Tromas, P. Villechaise, V. Gauthier-Brunet, S. Dubois, Slip line analysis around nanoindentation imprints in  $\text{Ti}_3\text{SnC}_2$ : a new insight into plasticity of MAX-phase materials, *Philosophical Magazine* 91 (7-9) (2011) 1265–1275. doi:10.1080/14786435.2010.494584.
- [13] A. Joulain, L. Thilly, J. Rabier, Revisiting the defect structure of MAX phases: the case of  $\text{Ti}_4\text{AlN}_3$ , *Philos. Mag.* 88 (9) (2008) 1307–1320.
- [14] A. Guitton, A. Joulain, L. Thilly, C. Tromas, Evidence of dislocation cross-slip in MAX phase deformed at high temperature, *Scientific Reports* 4 (1) (2015) 6358. doi:10.1038/srep06358.
- [15] E. Drouelle, A. Joulain, J. Cormier, V. Gauthier-Brunet, P. Villechaise, S. Dubois, P. Sallot, Deformation mechanisms during high temperature tensile creep of  $\text{Ti}_3\text{AlC}_2$  MAX phase, *Journal of Alloys and Compounds* 693 (2017) 622–630. doi:10.1016/j.jallcom.2016.09.194.
- [16] W. Yu, J. Guérolé, J. Ghanbaja, M. Vallet, A. Guitton, Frank partial dislocation in  $\text{Ti}_2\text{AlC}$ -MAX phase induced by matrix-Cu diffusion, *Scripta Materialia* 191 (2021) 34–39. doi:10.1016/j.scriptamat.2020.09.007.
- [17] E. Drouelle, V. Brunet, J. Cormier, P. Villechaise, P. Sallot, F. Naimi, F. Bernard, S. Dubois, Oxidation resistance of  $\text{Ti}_3\text{AlC}_2$  and  $\text{Ti}_3\text{Al}_0.8\text{Sn}_0.2\text{C}_2$  MAX phases: A comparison, *Journal of the American Ceramic Society* 103 (2) (2020) 1270–1280. doi:10.1111/jace.16780.
- [18] E. Drouelle, V. Gauthier-Brunet, J. Cormier, P. Villechaise, P. Sallot, F. Naimi, F. Bernard, S. Dubois, Microstructure-oxidation resistance relationship in  $\text{Ti}_3\text{AlC}_2$  MAX phase, *Journal of Alloys and Compounds* 826 (2020) 154062. doi:10.1016/j.jallcom.2020.154062.
- [19] W. Yu, M. Vallet, B. Levraut, V. Gauthier-Brunet, S. Dubois, Oxidation mechanisms in bulk  $\text{Ti}_2\text{AlC}$ : Influence of the grain size, *Journal of the European Ceramic Society* 40 (5) (2020) 1820–1828. doi:10.1016/j.jeurceramsoc.2020.01.042.
- [20] W. Yu, V. Gauthier-Brunet, T. Cabioch, S. Dubois, Synthesis and microstructural characterization of substoichiometric  $\text{Ti}_2\text{Al}(c_xn_y)$  solid solutions and related  $\text{Ti}_2\text{AlC}_x$  and  $\text{Ti}_2\text{AlN}$  end-members, *Journal of the American Ceramic Society* 97 (7) (2014) 2308–2313. doi:https://doi.org/10.1111/jace.12930.
- [21] D. B. Williams, C. B. Carter, *Transmission Electron Microscopy*, Springer US, Boston, MA, 2009. doi:10.1007/978-0-387-76501-3. URL <http://link.springer.com/10.1007/978-0-387-76501-3>
- [22] L. Priester, *Grain Boundaries: From Theory to Engineering*, Springer, 2013.
- [23] C. R. Weinberger, G. J. Tucker (Eds.), *Multiscale Materials Modeling for Nanomechanics*, Vol. 245 of Springer Series in Materials Science, Springer International Publishing, Cham, 2016. doi:10.1007/978-3-319-33480-6. URL <http://link.springer.com/10.1007/978-3-319-33480-6>
- [24] F. Sansoz, J. F. Molinari, Mechanical behavior of  $\Sigma$  tilt grain boundaries in nanoscale Cu and Al: A quasicontinuum study, *Acta Materialia* 53 (7) (2005) 1931–1944. doi:10.1016/j.actamat.2005.01.007.
- [25] T. Frolov, S. V. Divinski, M. Asta, Y. Mishin, Effect of interface phase transformations on diffusion and segregation in high-angle grain boundaries, *Physical Review Letters* 110 (25) (2013) 255502. doi:10.1103/PhysRevLett.110.255502.
- [26] M. A. Tschopp, S. P. Coleman, D. L. McDowell, Symmetric and asymmetric tilt grain boundary structure and energy in Cu and Al (and transferability to other fcc metals), *Integrating Materials and Manufacturing Innovation* 4 (1) (2015) 11. doi:10.1186/s40192-015-0040-1.
- [27] H. Zhao, L. Huber, W. Lu, N. J. Peter, D. An, F. De Geuser, G. Dehm, D. Ponge, J. Neugebauer, B. Gault, D. Raabe, Interplay of Chemistry and Faceting at Grain Boundaries in a Model Al Alloy, *Physical Review Letters* 124 (10) (2020) 106102. doi:10.1103/PhysRevLett.124.106102.
- [28] Y. Mishin, Atomistic modeling of the  $\gamma$  and  $\gamma'$ -phases of the Ni-Al system, *Acta Materialia* 52 (6) (2004) 1451–1467. doi:10.1016/j.actamat.2003.11.026.
- [29] A. Prakash, J. Guérolé, J. Wang, J. Müller, E. Spiecker, M. J. Mills, I. Povstugar, P. Choi, D. Raabe, E. Bitzek, Atom probe informed simulations of dislocation-precipitate interactions reveal the importance of local interface curvature, *Acta Materialia* 92 (2015) 33–45. doi:10.1016/j.actamat.2015.03.050.
- [30] A. Vaid, J. Guérolé, A. Prakash, S. Korte-Kerzel, E. Bitzek, Atomistic simulations of basal dislocations in Mg interacting with  $\text{Mg}_{17}\text{Al}_{12}$  precipitates, *Materialia* 7 (2019) 100355. doi:10.1016/j.mta.2019.100355.

- [31] J. Guérolé, M. Zubair, S. Roy, Z. Xie, M. Lipińska-Chwałek, S. Sandlöbes-Haut, S. Korte-Kerzel, Exploring the transfer of plasticity across Laves phase interfaces in a dual phase magnesium alloy, *Materials & Design* 202 (2021) 109572. doi:10.1016/j.matdes.2021.109572.
- [32] G. Plummer, G. J. Tucker, Bond-order potentials for the Ti<sub>3</sub>AlC<sub>2</sub> and Ti<sub>3</sub>SiC<sub>2</sub> MAX phases, *Physical Review B* 100 (21) (2019) 214114. doi:10.1103/PhysRevB.100.214114.
- [33] J. Tersoff, New empirical approach for the structure and energy of covalent systems, *Physical Review B* 37 (12) (1988) 6991–7000. doi:10.1103/PhysRevB.37.6991.
- [34] K. Albe, K. Nordlund, J. Nord, A. Kuronen, Modeling of compound semiconductors: Analytical bond-order potential for Ga, As, and GaAs, *Physical Review B - Condensed Matter and Materials Physics* 66 (3) (2002) 352051–3520514. doi:10.1103/PhysRevB.66.035205.
- [35] E. Bitzek, P. Koskinen, F. Gähler, M. Moseler, P. Gumbsch, Structural relaxation made simple, *Physical Review Letters* 97 (17) (2006) 1–4. doi:10.1103/PhysRevLett.97.170201.
- [36] J. Guérolé, W. G. Nöhring, A. Vaid, F. Houllé, Z. Xie, A. Prakash, E. Bitzek, Assessment and optimization of the fast inertial relaxation engine (FIRE) for energy minimization in atomistic simulations and its implementation in LAMMPS, *Computational Materials Science* 175 (2020) 109584. doi:10.1016/j.commatsci.2020.109584.
- [37] C. Fressengeas, V. Taupin, L. Capolungo, Continuous modeling of the structure of symmetric tilt boundaries, *International Journal of Solids and Structures* 51 (6) (2014) 1434–1441. doi:https://doi.org/10.1016/j.ijsolstr.2013.12.031.
- [38] B. Reinholz, S. Brinckmann, A. Hartmaier, B. Muntiferer, W. B. Knowlton, P. Müllner, Influence of the twin microstructure on the mechanical properties in magnetic shape memory alloys, *Acta Materialia* 108 (2016) 197–206. doi:https://doi.org/10.1016/j.actamat.2016.02.007.
- [39] L. Capolungo, V. Taupin, Gd<sub>3</sub>: generalized discrete defect dynamics, *Materials Theory* 3 (1) (2019) 2. doi:10.1186/s41313-018-0013-9.
- [40] H. Y. Lee, M. M. A. Ezzi, N. Raghuvanshi, J. Y. Chung, K. Watanabe, T. Taniguchi, S. Garaj, S. Adam, S. Gradečák, Tunable Optical Properties of Thin Films Controlled by the Interface Twist Angle, *Nano Letters* 21 (7) (2021) 2832–2839. doi:10.1021/ACS.NANOLETT.0C04924.

# Features of a nano-twist phase in the nanolayered $\text{Ti}_3\text{AlC}_2$

## Supplementary Material

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### 1. Disclination model of the nano-twist phase

The main aspects of the disclination model is presented here. For more details, the reader is referred to papers mentioned in the main text and references therein. A small deformation framework is chosen. The material displacement vector  $\mathbf{u}$  is a single-valued continuous field. The distortion tensor is the gradient of the displacement  $\mathbf{U} = \mathbf{grad} \mathbf{u}$ . It is a curl-free field:

$$\mathbf{curl} \mathbf{U} = 0. \quad (1)$$

The strain field  $\boldsymbol{\epsilon}$  is the symmetric part of  $\mathbf{U}$ , while the rotation field  $\boldsymbol{\omega}$  is the skew-symmetric part. The rotation vector  $\vec{\omega}$  reads:

$$\vec{\omega} = \frac{1}{2} \mathbf{curl} \mathbf{u}. \quad (2)$$

This rotation field is also a single-valued and continuous quantity. The gradient of the rotation vector is the curvature tensor  $\boldsymbol{\kappa}$ :

$$\boldsymbol{\kappa} = \mathbf{grad} \vec{\omega}. \quad (3)$$

It is also called the bend-twist tensor. Like the material distortion  $\mathbf{U}$ , the material curvature tensor is a curl-free tensor. To introduce disclinations in the body, we use the deWit's disclination density tensor  $\boldsymbol{\theta}$ . It has components  $\theta_{ij} = \Omega_i t_j$  in the cartesian frame  $(\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z)$ . The components correspond to a Frank vector angle  $\Omega_i$  about  $\mathbf{e}_i$  per unit resolution surface  $\Delta S$ , for a line vector component along direction  $\mathbf{e}_j$ ,  $t_j$ . Disclinations are indeed line defects, like dislocations, but they introduce a discontinuity of the elastic (or plastic, up to a sign) rotation that corresponds to the Frank vector. Considering a finite surface  $S$  of unit normal  $\mathbf{n}$ , which is thread by an ensemble of disclination lines corresponding to a non-zero disclination density, the Frank vector reads:

$$\boldsymbol{\Omega} = \int_S \boldsymbol{\theta} \cdot \mathbf{ndS}. \quad (4)$$

Because of the elastic/plastic rotation discontinuity the plastic  $\boldsymbol{\kappa}_p$  and elastic  $\boldsymbol{\kappa}_e$  parts building the total material curvature contain incompatible components that are not curl-free. The incompatibility of elastic and plastic curvatures writes:

$$\mathbf{curl} \boldsymbol{\kappa}_e = -\mathbf{curl} \boldsymbol{\kappa}_p = \boldsymbol{\theta}. \quad (5)$$

Although it is not the case in the present simulations, dislocations can also be introduced in addition to disclinations. Such is done by using the Nye's dislocation density tensor  $\boldsymbol{\alpha}$ . It has components  $\alpha_{ij} = B_i t_j$ , corresponding to a Burgers vector length  $B_i$  along direction  $\mathbf{e}_i$  per unit resolution surface  $\Delta S$ , and to a dislocation line vector component  $t_j$  along direction  $\mathbf{e}_j$ . Due to the elastic/plastic displacement discontinuity, *i.e.* the Burgers vector, the plastic  $\boldsymbol{\epsilon}_p$  and elastic  $\boldsymbol{\epsilon}_e$  strains building the total material strain contain incompatible, non curl-free components, such that:

$$\mathbf{curl} \boldsymbol{\epsilon}_e = +\boldsymbol{\alpha} + \boldsymbol{\kappa}'_e - \text{tr}(\boldsymbol{\kappa}_e)\mathbf{I} \quad (6)$$

$$\mathbf{curl} \boldsymbol{\epsilon}_p = -\boldsymbol{\alpha} + \boldsymbol{\kappa}'_p - \text{tr}(\boldsymbol{\kappa}_p)\mathbf{I}. \quad (7)$$

The above incompatibility equations show how elastic strains are related to the presence of dislocations and disclination-induced elastic curvatures. The elastic strains and curvatures must satisfy the higher-order quasi-static balance equation:

$$\mathbf{div} \boldsymbol{\sigma} + \frac{1}{2} \mathbf{curl} \mathbf{div} \mathbf{M} = 0. \quad (8)$$

In the above equation,  $\boldsymbol{\sigma}$  is the Cauchy stress tensor. The tensor  $\mathbf{M}$  is called couple stress tensor and is the work-conjugate of curvatures, just like the stress tensor is that of strains. Usually, the elastic constitutive relations are taken in the form:

$$\boldsymbol{\sigma} = \mathbf{C} : \boldsymbol{\epsilon}_e + \mathbf{D} : \boldsymbol{\kappa}_e \quad (9)$$

$$\mathbf{M} = \mathbf{A} : \boldsymbol{\kappa}_e + \mathbf{B} : \boldsymbol{\epsilon}_e. \quad (10)$$

In the above  $\mathbf{A}$ ,  $\mathbf{B}$ ,  $\mathbf{C}$  and  $\mathbf{D}$  are elasticity tensors. In the present simulations, only the classical tensor  $\mathbf{C}$  is considered

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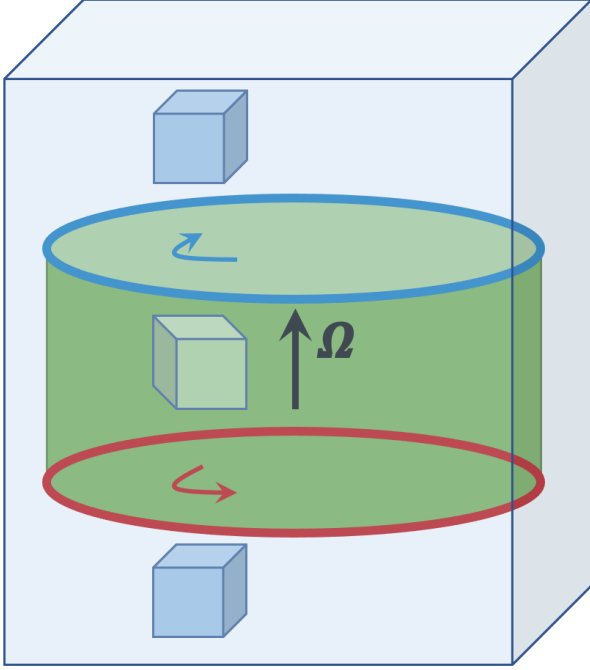


Figure 1: Illustration of the use of the disclination model to build a nano-twist phase. See the text for details.

the middle of the material. The crystal is twisted with respect to the matrix phase. Finally, to finish building the nano-twist phase, we must add a negative disclination loop near the top surface, with the same Frank vector magnitude, such that when crossing the surface delimited by this disclination loop, the crystal rotation encounters an opposite jump and recovers the initial value in the matrix. The two disclination loops are built with appropriate disclination density components  $\theta_{zx}$  and  $\theta_{zy}$  spread on a few voxels and such that the Frank vector magnitude according to equation (4) is 30 degrees. Note that elastic stresses and strains are continuous and not singular close to disclination lines because we use continuous disclination densities.

such that couple stresses are neglected. This choice does not alter the predicted internal stresses due to disclinations. The elasticity moduli are in Voigt notation in the hexagonal crystal frame  $C_{11} = C_{22} = 353$  GPa,  $C_{12} = 75$  GPa,  $C_{13} = 69$  GPa,  $C_{33} = 296$  GPa and  $C_{44} = C_{55} = C_{66} = 119$  GPa. All equations are numerically solved with a spectral code taking advantage of Fast Fourier Transform (FFT) algorithms. The incompatibility equations are solved in the Fourier space with the use of centered difference schemes for the evaluation of spatial derivatives. The stress equilibrium equation is solved by using the accelerated scheme together with the use of the rotated scheme for the evaluation of the modified Green operator. In the simulation shown in the main text, the FFT grid size is  $256 \times 256 \times 32$  voxels in the X, Y and Z directions. The voxel size is 0.4 nm in all directions. Periodic boundary conditions are used in all directions, like in molecular dynamics simulations.

The figure (1) explains how the disclination concept is used to build a nano-twist, penny-shaped, phase. The big cube is the matrix material. In this matrix the crystal is unrotated, as sketched by the two small cube orientations near the bottom and the top surfaces. To start building the nano-twist phase, we first introduce a positive twist disclination loop near the bottom surface. The Frank vector is shown in the figure, it is perpendicular to the surface delimited by the disclination loop. By crossing upwards the surface delimited by the disclination loop, the elastic rotation encounters a jump equal to the Frank vector of the disclination loop. The jump of crystal rotation is shown by the rotating arrow inside the disclination loop, and the new orientation of the crystal is shown by the small cube in