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Features of a nano-twist phase in the nanolayered Ti_3AlC_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 Ti_3AlC_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 Ti_3AlC_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.

1. Introduction

Ti_3AlC_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, Ti_3AlC_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 Ti_6C octahedron layers with one layer of Al [1]. Furthermore, measurements of lattice parameters with numerous methods reveal that Ti_3AlC_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 M_6X 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 Ti_3AlC_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 Al_2O_3 is formed. However, 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 Ti_3AlC_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 Ti_3AlC_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°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 Titan³ 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 Ti_3AlC_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 Ti_3AlC_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 Ti_3C_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 Ti_3AlC_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*

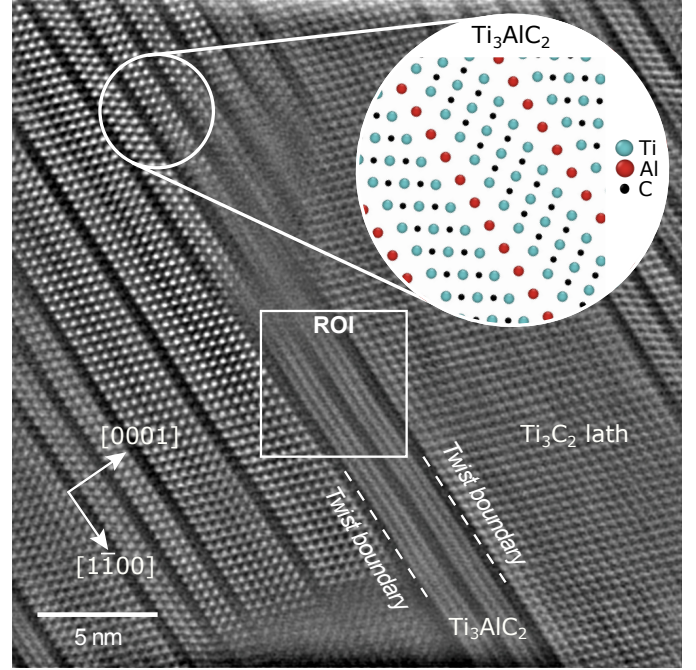


Figure 1: Experimental observation of the nano-twist phase (region of interest, ROI) in the nanolayered Ti_3AlC_2 . Filtered HR-STEM micrograph in HAADF mode with electron direction along $[1\bar{1}\bar{2}0]$. Boundaries of the nano-twist phase are indicated by dashed lines. A model of the Ti_3AlC_2 crystallographic structure is shown in the inset. Some Ti_3C_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 Ti_3AlC_2 phase, a cookie shape region in the center is rotated with an angle Ψ 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 Ψ (Fig. 1).

The as-formed nano-twist phase (NTP) exhibit prismatic and basal interfaces with the Ti_3AlC_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 Ψ . 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 σ_{zz} of the as-relaxed NTB for different Ψ . By showing the dis-

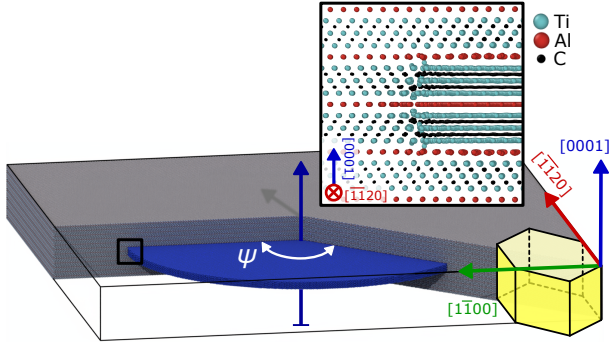


Figure 2: Modeling of the nano-twist phase in the nano-layered Ti_3AlC_2 by means of a cookie-shape rotation region. (a) atomistic simulation setup of the cookie-shape region (in blue) parallel to the basal planes, with $[000 1]$ rotation axis and ψ rotation angle. The black square indicate the location 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.

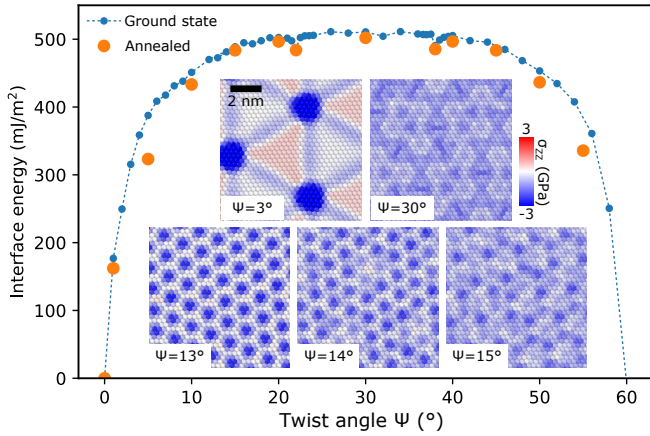


Figure 3: Energy of the basal interface of the nano-twist phase as function of the twist angle ψ . Interfacial energy of the ground state and annealed structure in blue and orange dots, respectively. The dotted line is a guide for the eyes. Insets show magnified views of the stress field σ_{zz} for $\psi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

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 σ_{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 Ti_3AlC_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

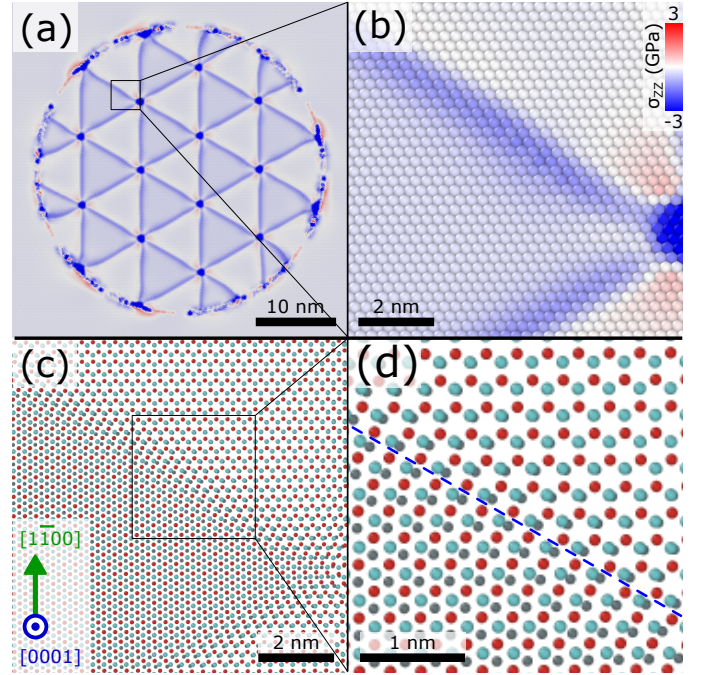


Figure 4: Interfacial structure of the Ti_3AlC_2 nano-twist phase for $\psi = 1^\circ$. (a) global and (b) magnified views of the local stress field σ_{zz} revealing the typical dislocation network of a low angle grain boundary. (c) identical view as (b) but showing chemical species as in Fig. 2. (d) 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 Ti_3AlC_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 Ti_3AlC_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.

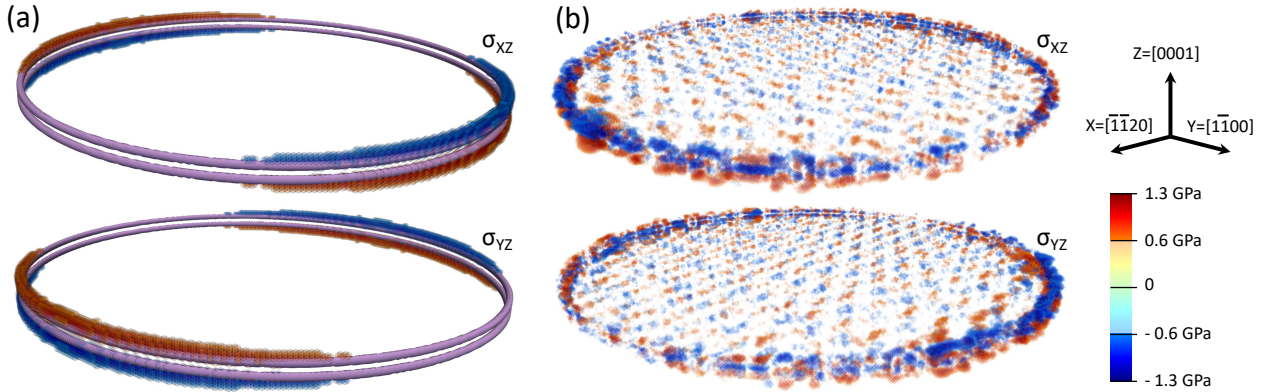


Figure 5: Shear stress fields σ_{xz} and σ_{yz} of a high-angle nano-twist phase represented by (a) a dipole of twist disclination loops and (b) an atomistic cookie-shape region. Only voxels (a) and atoms (b) with stresses with magnitude larger than 600 MPa are shown. In purple (a) is shown the norm 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 Ψ 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 Ti_3AlC_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 Ψ , 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° is modelled by a dipole of twist disclination loops with Frank vector magnitude 30° 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 σ_{xz} and σ_{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 σ_{xz} and σ_{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 ± 1 GPa. This match between atomistic and continuum representation is however partial. The differences are (1) the direction of stress maxima rotated by 90° , 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 ϵ_{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 Ti_3AlC_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 Ti_3AlC_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.

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Features of a nano-twist phase in the nanolayered Ti_3AlC_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 Ω_i about \mathbf{e}_i per unit resolution surface ΔS , 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 ΔS , 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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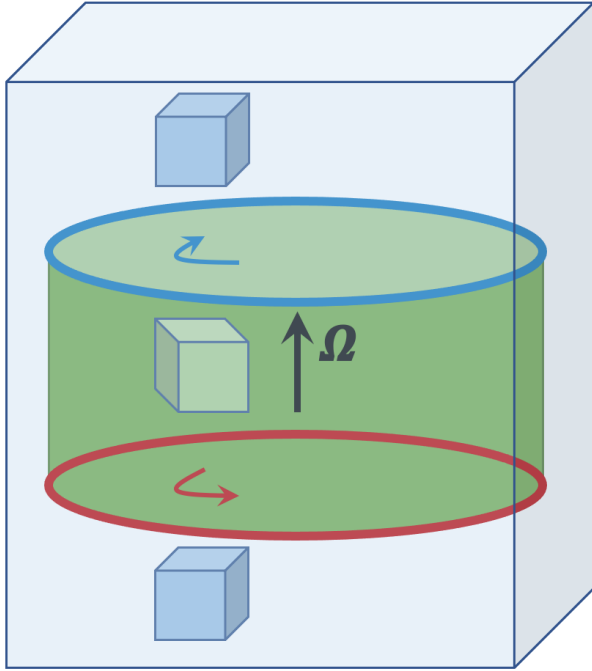


Figure 1: Illustration of the use of the disclination model to build a nano-twist phase. See the text for details.

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 θ_{zx} and θ_{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