

Rathod, H.J., Ouisse, T., Radovic, M. and Srivastava, A., 2021. Room temperature crack-healing in an atomically layered ternary carbide. *Science Advances*, 7(33), p.eabg2549.

Room temperature crack-healing in an atomically layered ternary carbide

Hemant J. Rathod¹, Thierry Ouisse², Miladin Radovic^{1,*}, Ankit Srivastava^{1,*}

¹Department of Materials Science and Engineering, Texas A&M University, College Station, TX, 77843, USA

²Université Grenoble Alpes, CNRS, Grenoble INP, LMGP, F-38000 Grenoble, France

*Corresponding authors: mradovic@tamu.edu (M. Radovic), ankit.sri@tamu.edu (A. Srivastava)

Abstract:

Ceramic materials provide outstanding chemical and structural stability at high temperatures and in hostile environments but are susceptible to catastrophic fracture that severely limits their applicability. Traditional approaches to partially overcome this limitation rely on activating toughening mechanisms during crack growth to postpone fracture. Herein, we demonstrate a more potent toughening mechanism that involves an intriguing possibility of healing the cracks as they form, even at room temperature, in an atomically layered ternary carbide. Crystals of this class of ceramic materials readily fracture along weakly bonded crystallographic planes. However, onset of an abstruse mode of deformation referred to as kinking in these materials induces large crystallographic rotations and plastic deformation that physically heal the cracks. This implies that the toughness of numerous other layered ceramic materials whose broader applications have been limited by their susceptibility to catastrophic fracture can also be enhanced by microstructural engineering to promote kinking and crack-healing.

Introduction

The lack of materials capable of withstanding extreme environments, more often than not, imposes the greatest technological barrier to the development and deployment of a host of next-generation technologies, such as efficient jet engines, hypersonic flights, safer nuclear reactors (1-4). While ceramic materials provide outstanding chemical and structural stability at high temperatures and in hostile environments, their insufficient plastic deformability and damage tolerance compared to metallic materials severely limits their applicability (5, 6). In particular, at room temperature ceramic materials readily undergo catastrophic fracture by cohesive bond breaking at the crack tip. Traditional approaches to partially overcome this issue in ceramic materials rely on microstructure-specific toughening mechanisms such as crack-deflection, crack-bridging, microcracking and stress-induced phase transformations (5, 6). The quest to enhance damage tolerance also includes development of nature inspired ceramic-based (hybrid) materials with hierarchical structures that can trigger a combination of toughening mechanisms (7-12). Although activating toughening mechanisms during crack growth can postpone catastrophic fracture; a more potent toughening mechanism is to heal the cracks as they form.

Crack-healing requires local flow of material to close and heal the cracks by physical or chemical interactions (13). In principle, this can be realized intrinsically (without healing agents) or extrinsically (with healing agents), autonomously (without external triggers) or non-autonomously (with external triggers) and is not limited to a single class of materials (13). Nonetheless, polymers and polymer composites (14-16), and cementitious materials (17, 18) are by far the biggest beneficiaries of crack-healing mechanisms, while only limited successes have been reported for ceramic (19-23) and metallic (24) materials. In ceramic materials, except for few, crack-healing has been mainly realized extrinsically by incorporating healing agents and/or non-autonomously (postmortem) by applying high pressure at high temperatures. In very few cases, autonomous crack-healing in ceramic materials is achieved by high temperature oxidation of the cracks that form during loading (20-23). Crack-healing by high temperature oxidation, however, has several limitations. For example, it at least requires the presence of an oxidative phase, accessibility of the crack surfaces to the oxidizing environment, and good adhesion of the oxide scale to the crack surfaces. Also, selective oxidation of some microstructural features (e.g., grain boundaries) can lead to stress concentration sites while thermal expansion mismatch between the material and the crack-healing oxide can lead to crack initiation during thermal cycling.

Herein, we demonstrate that intrinsic and autonomous crack-healing is possible even at room temperature in crystalline atomically layered ceramic materials such as MAX phases (25-27) by kinking-induced crystallographic rotation and plastic deformation. MAX phases are a family of ternary carbides/nitrides with general formula $M_{n+1}AX_n$, where M is an early transitional metal, A is mostly an element from groups 13-16, X is carbon or nitrogen and n varies from 1-3; and comprise alternating $M_{n+1}X_n$ and A atomic layers within a hexagonal crystal structure (25-27). Numerous studies have shown that several individual grains in polycrystalline MAX phases can readily kink under a variety of external loading conditions, such as tensile, compressive, creep, fatigue, and impact (28-33). Kinking leads to localized plastic deformation in bands referred to as ‘kink-bands’ wherein the material is microstructurally or crystallographically misoriented from the unkinked region. Kinking is not unique to MAX phases and has been observed in a variety of natural (34-37) and engineered (38-46) materials. While in engineering composites kinking results in failure (40-42), in polycrystalline MAX phases it has been postulated that kinking restricts the rapid crack growth along the weakly bonded planes by crack-bridging (28, 29) and is solely responsible for their unconventional damage tolerance (25, 26, 30). However, our discovery that kinking in MAX phases heals the cracks as they form, reveals that it is an even more potent toughening mechanism than previously envisaged.

Specifically, we report on the evolution of kinking and its role in crack-healing during room temperature *in-situ* indentation of carefully grown single crystals of the Cr_2AlC MAX phase (Supplementary Fig. S1) (47) in a scanning electron microscope (SEM). The *in-situ* indentation is carried out using an in-house designed and build fixture that allows us to load single crystal specimens with a punch along predetermined directions, with and without lateral deformation constraint. The lateral deformation constraint considered here mimics the presence of neighboring grains that affect the deformation and damage evolution in individual grains of a polycrystalline aggregate. Until we utilized this fixture, it was extremely difficult to study the effect of local deformation constraint on kinking and the implications of kinking on toughening in MAX phases from mechanical testing of their polycrystalline aggregates (25, 26, 28-32) or micropillars milled from individual grains (48-50).

Results

In-situ indentation of freestanding single crystals

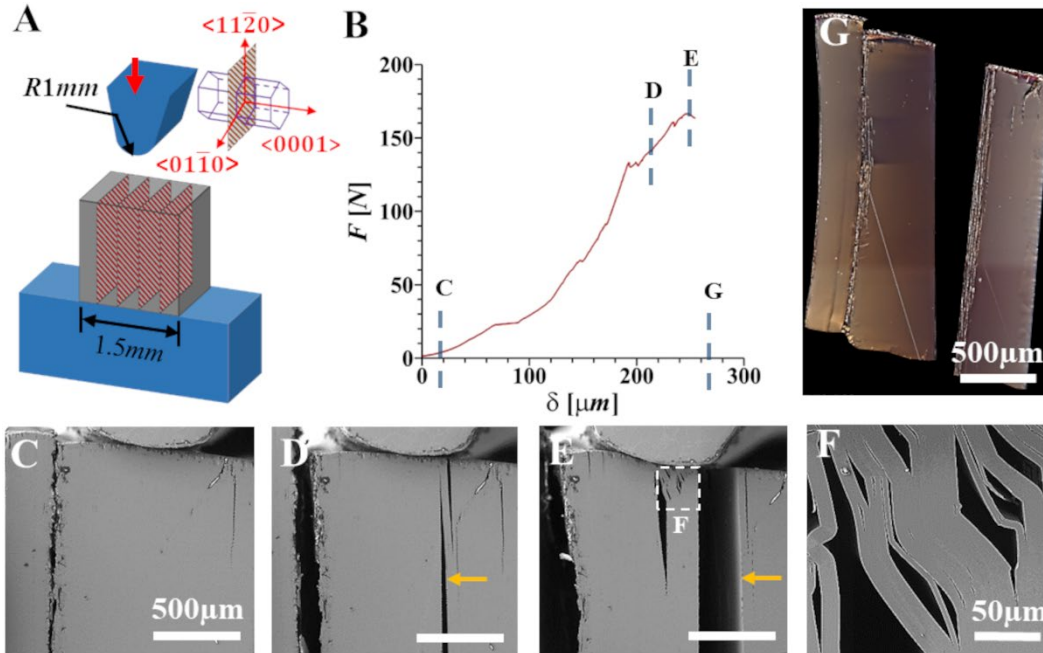


Fig. 1. *In-situ* indentation of a freestanding single crystal specimen of Cr_2AlC . (A) Schematic of the experimental set-up in which a freestanding single crystal specimen of Cr_2AlC is indented along the $\langle 11\bar{2}0 \rangle$ crystallographic direction using a punch with a cylindrical tip. (B) Indentation force (F) – depth (δ) response. (C-E) SEM images showing the initiation and propagation of cleavage cracks along the basal planes i.e., $\{0001\}$ planes and buckling of the ligaments between the cracks underneath the indenter. A dominant cleavage crack is marked with an arrow in (D) and (E). (F) High magnification SEM image of the region marked with a dashed box labeled f in e showing buckling and rotation of the ligaments between the cleavage cracks. (G) Post-deformation polarized light optical microscopy image showing cleavage of the entire specimen parallel to the indentation direction and absence of any local changes in the crystallographic orientation. The scale bars in (C-E) are the same. The indentation depth corresponding to SEM images in (C-E) is marked in (B).

We first carried out *in-situ* indentation experiments on freestanding single crystal specimens of Cr_2AlC (Fig. 1A). The free-standing crystals were indented along the $\langle 11\bar{2}0 \rangle$ crystallographic direction and the indentation force-depth response (Fig. 1B) was recorded together with secondary electron (SE)-SEM images of the specimen surface (Figs. 1C-E). It is well established by now that the basal slip systems, $\{0001\}\langle 11\bar{2}0 \rangle$, are the only active slip systems for crystallographic slip in MAX phases at room temperature (25). Thus, loading a crystal of MAX phase along the $\langle 11\bar{2}0 \rangle$ crystallographic direction leads to zero resolved shear stress on the basal slip systems and no plastic deformation due to slip is expected under these circumstances. On the other hand, compressing the crystal along the $\langle 11\bar{2}0 \rangle$ crystallographic direction leads to Poisson expansion of the crystal along $\langle 01\bar{1}0 \rangle$ and $\langle 0001 \rangle$ (normal to the basal plane) crystallographic directions. The expansion of the MAX phase crystal, in particular, normal to the basal planes facilitates initiation of cleavage cracks between the weakly bonded A and $M_{n+1}X_n$ layers (25). With progressive indentation, some of these cracks propagate rapidly through the entire specimen (Figs. 1D-E). Note

that the expansion of the material underneath the indenter in these experiments is limited because the specimen surface in direct contact with the indenter undergoes slight frictional adhesion. As a result, the cracks that form directly under the indenter do not grow rapidly, and the ligaments between these cracks buckle and rotate (Fig. 1F). The buckling and rotation of the ligaments in turn arrests the growth of the cracks during loading. However, upon unloading these buckled ligaments snap back to their original configuration and the specimen fractures only in few pieces (Fig. 1G). Additional postmortem observation of the fractured pieces of the specimen using polarized light shows no color contrast suggesting a lack of local changes in the crystallographic orientation of the initial single crystal specimen.

In-situ indentation of constrained single crystals

Next, we carried out *in-situ* indentation experiments on single crystal specimens of Cr_2AlC that were placed in our in-house fixture and subjected to a deformation constraint along the $\langle 0001 \rangle$ crystallographic directions i.e., normal to the basal planes (Fig. 2A). To ensure that the deformation constraint imposed by the fixture is not entirely rigid, a thin layer of epoxy was introduced between the specimen and the fixture. Note that prior to the onset of indentation, the specimen inside the fixture is stress free. Here as well, the specimens were indented along the $\langle 11\bar{2}0 \rangle$ crystallographic direction and the indentation response (Fig. 2B) was recorded together with the SE-SEM images of the specimen surface (Figs. 2C-H).

As in the case of the unconstrained indentation, here as well, first multiple cleavage cracks initiate along the basal planes in the specimens during loading (Fig. 2 and Supplementary Fig. S2). Although, due to the deformation constraint normal to the basal planes, in this case the cracks do not propagate rapidly through the entire specimen. Furthermore, and somewhat surprisingly, despite increasing the load, the cracks are seemingly arrested by the onset of plastic deformation in bands inclined to the indentation axis (indicated by the broken lines in Figs. 2D-E). With further increase in the loading, more cracks and plastic deformation bands (Figs. 2F-H) appear in the specimens. While even more surprisingly, the cleavage cracks that previously initiated, instead of propagating along the basal planes first slightly open in a direction normal to the basal plane before beginning to close (an arrow follows one such crack in Figs. 2D-H). This chain of events continues with the progressive loading and unlike in the case of unconstrained specimens (Fig. 1), it allows for the indentation of the specimen to continue to a greater depth with increasing force (Fig. 2B), without the specimen being fractured into pieces (Fig. 2I). Moreover, after complete unloading, the post-deformation optical images of Cr_2AlC single crystal specimens under polarized light show extensive color contrast throughout the deformed specimen suggesting significant permanent changes in the local crystallographic orientation that resembles a polycrystalline microstructure (Fig. 2I and Supplementary Fig. S3). The apparent polycrystallization (Figs. 3-4) occurs because the localized plastic deformation bands that form in the constrained single crystal specimens are actually kink-bands that cause progressive crystallographic reorientation of the material (Fig. 5). The grain structure in the poly-crystallized specimens also varies through the depth of the specimen. As shown in Fig. 2I (and in Supplementary Fig. S3), underneath the indenter the grains are relatively thinner and the grain boundaries are almost normal to the indentation axis as compared to the regions far away from the indent, where the grains are thicker, and the grain boundaries are inclined at relatively larger angles to the indentation axis.

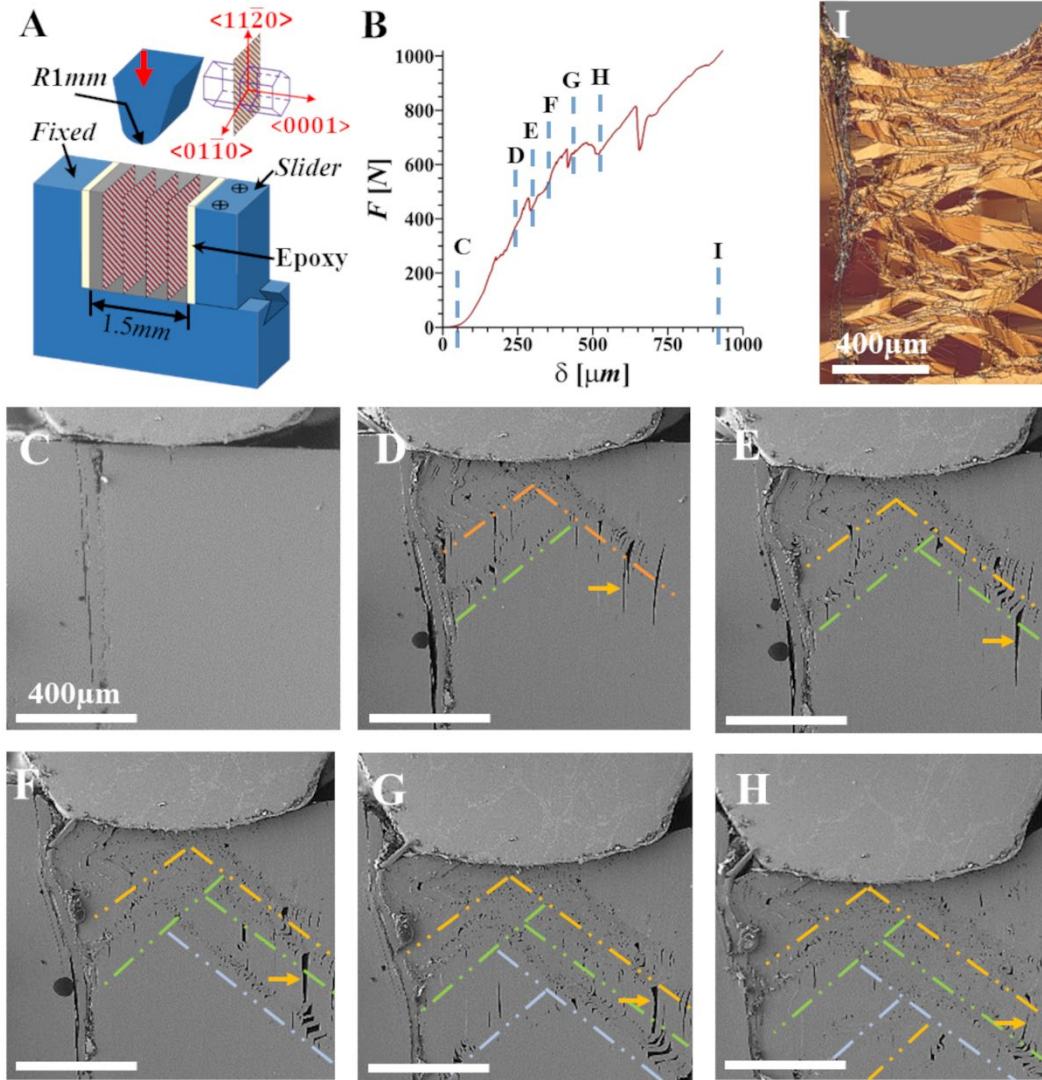


Fig. 2. In-situ indentation of a constrained single crystal specimen of Cr_2AlC . (A) Schematic of the experimental set-up in which a single crystal specimen of Cr_2AlC is indented along the $\langle 11\bar{2}0 \rangle$ crystallographic direction using a punch with a cylindrical tip while being constrained along the $\langle 0001 \rangle$ direction i.e., normal to the basal planes. (B) Indentation force (F) – depth (δ) response. (C–H) SEM images showing progressive initiation of cleavage cracks, kinking of the ligaments between the cracks, and localized plastic deformation in bands (traced with dashed double dotted lines) that are inclined to the indentation axis. An Arrow follows the growth, opening and finally healing of one of the basal plane cleavage cracks in (D–H). (I) Post-deformation polarized light optical microscopy image showing irreversible poly-crystallization of the initial single crystal specimen. The scale bars in (C–H) are the same. The indentation depth corresponding to SEM images in (C–H) is marked in (B).

Poly-crystallization and crack-healing

More importantly, careful postmortem examination of the deformed specimens upon complete unloading and its removal from the fixture revealed absence of any large cracks (Fig. 3). Even at high resolution (Figs. 3C-D and Supplementary Fig. S3) we do not see any large cracks inside the kinking-induced misoriented regions or along the kink-band (i.e., misorientation) boundaries. This is remarkable, since any compressive stress that builds up normal to the basal planes during loading due to the deformation constraint imposed by the fixture is relieved once the specimen is removed from the fixture. This suggests that the crack closure is not elastic, but the cracks are physically healed during loading otherwise, relaxation of the compressive stress that built up normal to the basal planes would have caused further crack opening upon unloading. Note that the occasional inclined hairline-like features inside the kink-bands in Figs. 3A-B are likely surface marks from physically healed cracks.

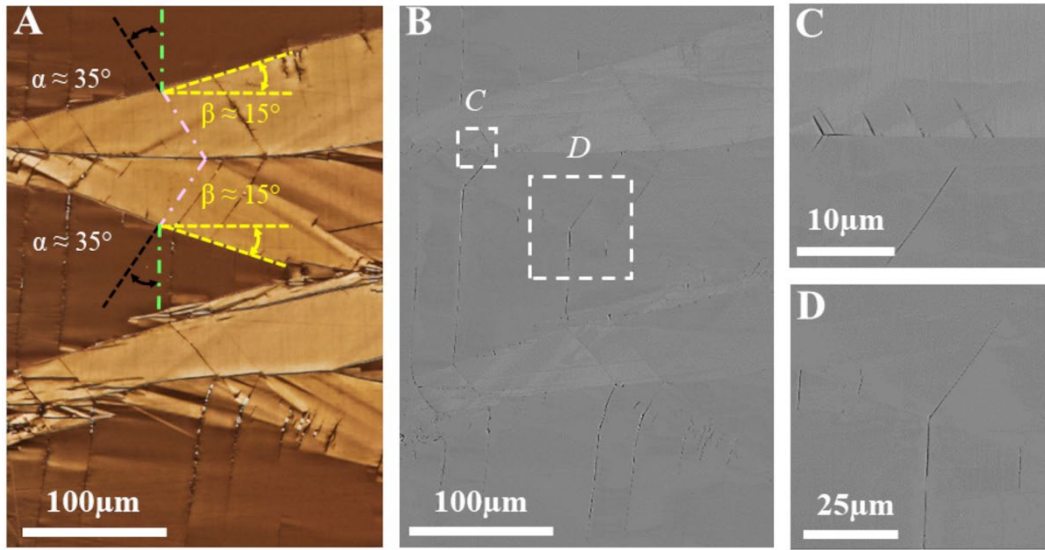


Fig. 3. Poly-crystallization and crack-healing in a constrained single crystal specimen of Cr_2AlC post *in-situ* indentation. (A) Post-deformation high magnification polarized light optical microscopy image showing kinking-induced irreversible poly-crystallization of the initial single crystal specimen at a location (roughly 600 μm) below the remnant impression of the indenter. The average in-plane rotation (α) of the material in select kink-bands together with the inclination (β) of the boundaries of these kink-bands are also marked in (A). (B) SEM image of the same region in (A) showing physically healed cracks inside the kink-bands. (C-D) Even higher magnification SEM images of the regions marked with dashed boxes labeled c and d in (B), respectively, showing healed cracks inside the kink-bands and absence of cracks along the kink-band boundaries.

The local crystal orientation in the kink-bands was examined using electron backscatter diffraction (EBSD) in a SEM. The EBSD inverse-pole figure (IPF) maps of the kink-bands show that the material in the kink-bands within initially single crystal Cr_2AlC specimens not only undergoes in-plane (in the x - y plane) but also out-of-plane (in the x - z and y - z planes) rotations as shown in Fig. 4 and Supplementary Fig. S4. That is the crystal rotation in the kink-bands does not only lead to tilting but also twisting of the basal planes. This is in direct contrast with kinking in layered composite materials where the material in the kink-bands predominantly undergoes in-plane rotation (41). Also, the extent of the material rotation in the kink-bands in Cr_2AlC varies drastically

through the specimen. For instance, in the region shown in Fig. 3A, the material in the two kink-bands that morphologically resemble corners of an eye have undergone an average rotation (θ) of approximately 35° in opposite directions, compared to the initial orientation of the specimen (Figs. 4A-B); while in relatively more deformed regions the average rotation of the material in (rather thin) kink-bands can be greater than 75° (Figs. 4D-E). The rotation of the material in the kink-bands is such that it increases the Schmid factor for the basal slip system that in turn increases the resolved shear stress required to initiate plastic deformation by crystallographic slip in the rotated regions (Figs. 4C, F). Note that the inclination (α) of the occasional hairline-like residual markings of the physically healed cracks (Fig. 3A) is roughly the same as the misorientation angle (θ) of the material in the kink-bands (Fig. 4A-B).

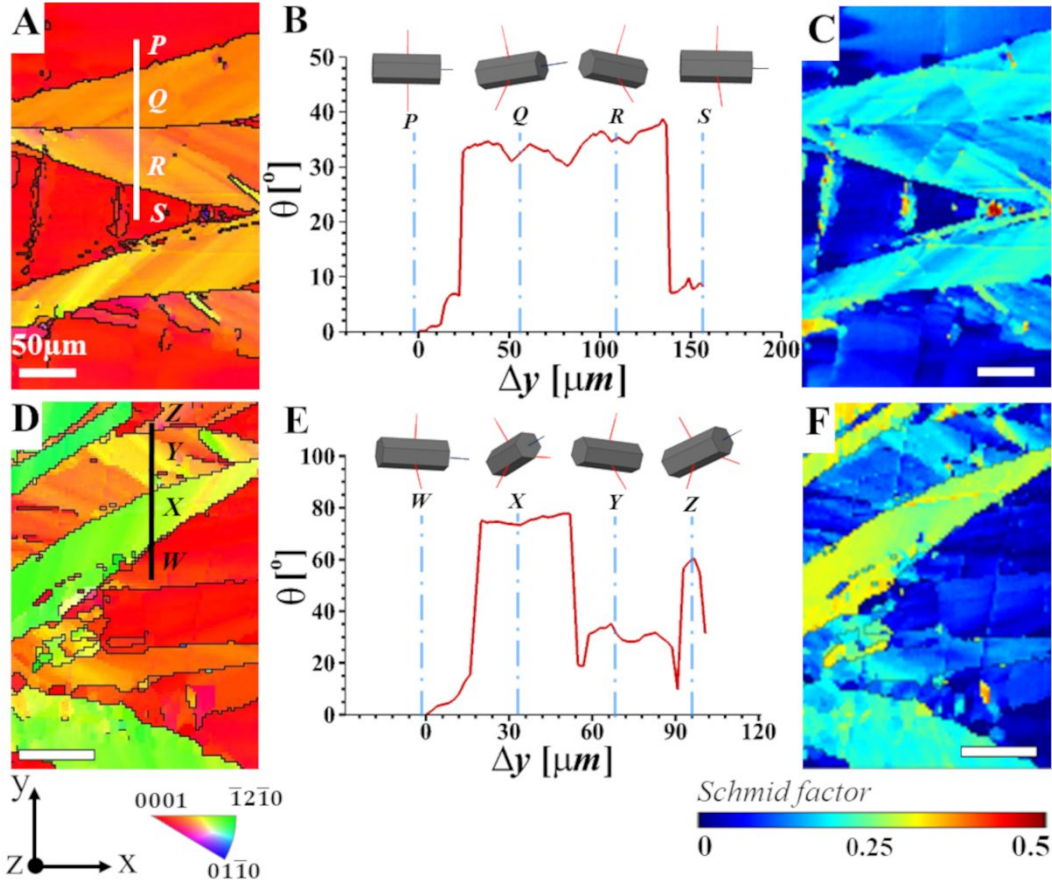


Fig. 4. Kinking-induced crystal reorientation in a constrained single crystal specimen of Cr_2AlC post *in-situ* indentation. (A) EBSD x -IPF map quantifying the local crystal orientation in the kink-bands shown in Fig. 3(A). (B) Crystal misorientation angle (θ) along the P - S line in (A) together with the local orientation of the hcp unit cell at four locations. (C) Contour plot of the classical maximum Schmid factor for the basal slip systems with loading axis along the $\langle 11\bar{2}0 \rangle$ in the region shown in (A). (D) EBSD x -IPF map of a relatively more deformed region. (E) Crystal misorientation angle (θ) along the W - Z line in (D) together with the local orientation of the hcp unit cell at four locations. (F) Contour plot of the classical maximum Schmid factor for the basal slip systems with loading axis along the $\langle 11\bar{2}0 \rangle$ in the region shown in (D). Note that $\langle 11\bar{2}0 \rangle$ and $\langle 0001 \rangle$ crystallographic orientations of the initial single crystal specimen were along y - and x -axes, respectively. The scale bars in (A), (C), (D) and (F) are the same.

Kinking as a crack-healing mechanism

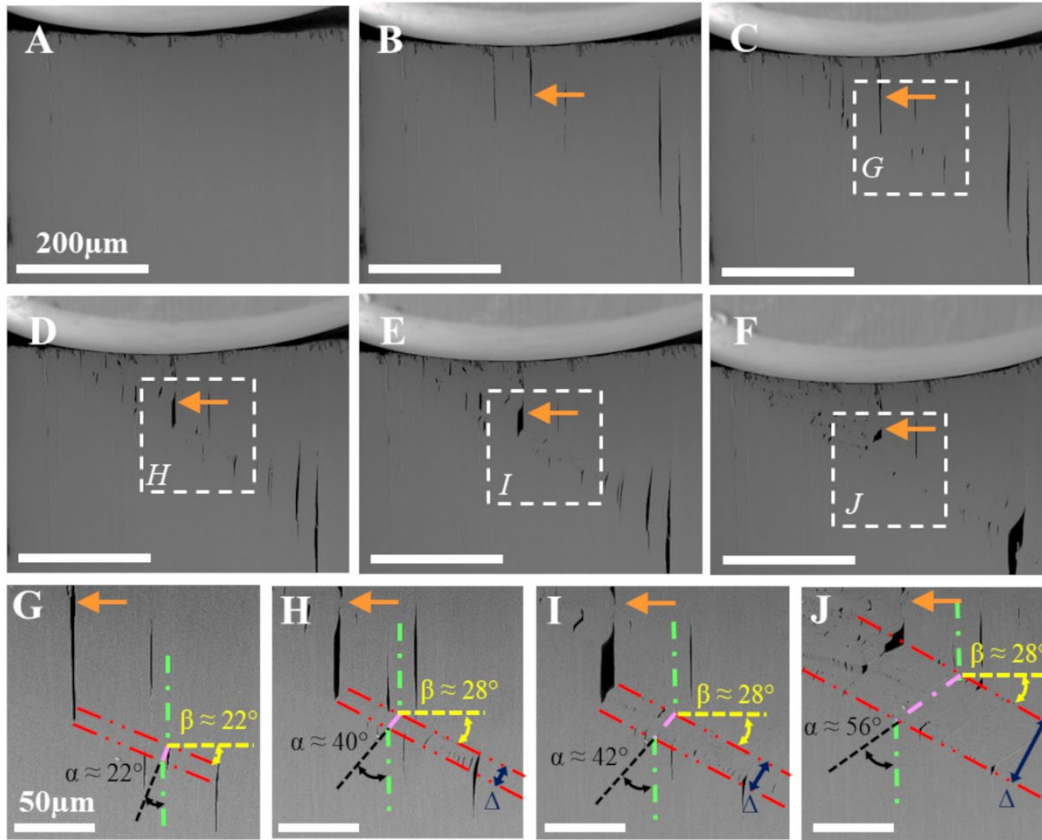


Fig. 5. Evolution of cracking, kinking and crack-healing during *in-situ* indentation of a constrained single crystal specimen of Cr_2AlC . A series of SEM images showing the sequence of events at a fixed location during progressive indentation. (A) Specimen surface at the beginning of indentation. (B) Initiation of multiple parallel cleavage cracks along the basal planes. (C) Growth and opening of the cracks. (D) Buckling and kinking of the ligaments between the basal plane cracks, formation of kink-band, and crack growth arrest. (E-F) Growth and widening of the kink-band and crack-healing. (G-J) High magnification SEM images of the regions marked with dashed boxes labeled (G-J) in (C-F), respectively, showing the sequence of events leading to crack-healing: first, a thin kink-band initiates; next, with increasing deformation the material in the kink-band rotates while the kink-band grows and widens; and finally, heals the cracks. In (B-J) an arrow follows the growth, opening, rotation and finally healing of one of the basal plane cracks. The boundaries of one of the kink-band in (G-J) are traced by dashed double dotted (red) lines and the average in-plane rotation (α) of the material in the kink-band together with the inclination (β) of the kink-band boundaries are also marked. The scale bars in (A-F) and (G-J) are the same.

The chain of events involving cracking, kinking, and crack-healing with increasing indentation load under deformation constraint normal to basal planes was repetitively observed in multiple specimens (Figs. 2, 5 and Supplementary Figs. S2, S5). In all these specimens, with progressive indentation, first multiple parallel cracks initiate and grow along the basal planes. Next, the ligaments between these parallel cracks buckle and kink, arresting the further crack growth, while the kinking-induced local crystallographic rotation of the material in the ligament at least initially increases the driving force for plastic deformation by crystallographic slip in the kink-bands. The

evolution of the in-plane shear strain, γ_{xy} , in the kink-bands (while neglecting out-of-plane rotations and assuming basal planes to be inextensible and incompressible) can be approximated as (51),

$$\gamma_{xy} = \tan(\beta) - \tan(\beta - \alpha) \quad (1)$$

where, α is the in-plane rotation of the crystal inside the kink-bands and β is the inclination of the kink-band boundaries (as described in Fig. 3A). The evolution of α during *in-situ* indentation experiments can be simply determined by following the rotation of the basal plane cracks within the kink-bands, while any change in the inclination of the kink-band boundaries, β , can be directly monitored (Fig. 5). Quantifying the evolution of α and β with increasing loading during *in-situ* SEM experiments shows that both the in-plane rotation of the crystal in the kink-bands as well as, (to an extent and at least initially) the inclination of the kink-band boundaries increases with progressive loading. The increase in the values of α and β with progressive loading is such that the shear strain in the kink-bands continues to increase, for example, from Fig. 5G the value of $\gamma_{xy} \approx 0.4$ while at higher load in Fig. 5J the value of $\gamma_{xy} \approx 1$. This shows that unlike deformation twinning, crystallographic rotation of the material as well as the associated shear deformation during kinking is not crystallographically restricted but it continues to evolve within kink-bands with progressive loading.

However, even though the shear strain in the kink-bands is continuously increasing and the growth of the cracks along the basal planes is arrested, the portion of the cracks within the kink-bands do first partially open before beginning to close (Figs. 5G-J). An approximate analysis of the kink-band geometry, again, by neglecting out-of-plane rotations and assuming basal planes to be inextensible and incompressible shows that the nominal volumetric strain, $\Delta V/V$, in the kink-band follows (51),

$$\frac{\Delta V}{V} = \cos(\beta - \alpha) \sec(\beta) - 1 \quad (2)$$

Thus, as the material inside the kink-band starts to rotate and the plastic deformation evolves, the material volume first tends to dilate before it begins to contract as α approaches (Fig. 5J) or exceeds 2β (Supplementary Fig. S6). The rotation of the material in the kink-bands together with the associated contraction of the material volume leads to permanent tilting, twisting and closure of the portion of the basal plane cracks that lie within the kink-bands. Finally, the growth and widening of multiple adjacent kink-bands leads to permanent distortion and closure or simply physical healing of the entire length of the basal plane cracks (Fig. 5 and Supplementary Fig. S2). This explains why the cracks do not open upon unloading i.e., relaxation of any compressive stresses that built up normal to the basal planes during loading. Also, note that the initial dilation of the material in the kink-bands not only causes the existing cracks to open but can also initiate secondary cracking within the kink-bands (Supplementary Fig. S5). Nevertheless, all these cracks start to heal once $\alpha \rightarrow 2\beta$.

Kink-boundary rotation and secondary kinking

Interestingly enough, continued indentation of the constrained specimens to sufficiently higher load levels, results in the rotation of the kink-band boundaries away from the indentation axis, so that their angle of inclination, β , now starts to decrease (Supplementary Fig. S7). Furthermore, continued loading of the specimens to sufficiently higher load levels also triggers secondary kinking (Supplementary Figs. S2, S6). These secondary kink-bands mostly initiate from the primary kink-band boundaries or from partially healed cracks. These observations can be rationalized based on our recent findings that the crystallographic slip in MAX phases does not follow classical Schmid law, and in this material system slip not only depends on the resolved shear stress but also on the stress normal to the slip planes (50). Thus, the crystallographic rotation of the material in the kink-bands in particular that of the basal planes away from the loading axis first increases the resolved shear stress (driving force for slip), but with continued rotation the compressive stress normal to the basal planes also increases that resists further slip. The decrease in the extent of plastic deformation due to increased resistance to slip past sufficient rotation of the material in the kink-bands is then compensated by the activation of deformation mechanisms such as, the rotation of the kink-band boundaries and secondary kinking. The rotation of the kink-band boundaries and the formation of secondary kink-bands at higher load levels also rationalize the observed variation in the grain structure through the depth in the deformed specimens (Supplementary Fig. S3).

In-situ uniaxial compression of as-grown single crystals and kinking-healed specimens

The results presented thus far clearly show that the onset of kinking during the indentation of constrained single crystals of Cr_2AlC at room temperature leads to physical healing of the cracks as they form. Nevertheless, a question arises to what extent the strength of the material is restored by kinking-induced crack-healing. To answer this question, we carried out *in-situ* uniaxial compression tests on (freestanding) as-grown single crystals and kinking-healed specimens. Both the as-grown single crystals and kinking-healed specimens were compressed along the same direction as in the indentation experiments and the force-displacement response was recorded together with SE-SEM images of the specimen surface.

A comparison of the engineering compressive stress-strain (normalized force-displacement) response of the as-grown single crystals and kinking-healed specimens shows that the kinking-healed specimens exhibit significantly higher compressive strength than the as-grown single crystals (Fig. 6). The as-grown single crystals undergo cleavage cracking along the weak basal planes at a very early stage of deformation (Supplementary Fig. S8). While some of these early-stage cracks that form directly under the punch do not grow rapidly due to slight frictional adhesion between the specimen surface and the punch, with progressive deformation, more cracks initiate and several of them propagate rapidly that fractures the specimen into pieces. On the contrary, in the kinking-healed specimens cleavage cracks initiate at higher load levels that too at locations with relatively large pockets of unkinked regions (Supplementary Fig. S9). Moreover, the cracks in the kinking-healed specimens do not propagate rapidly through the specimen resulting in a rather graceful failure without the specimen fracturing into pieces.

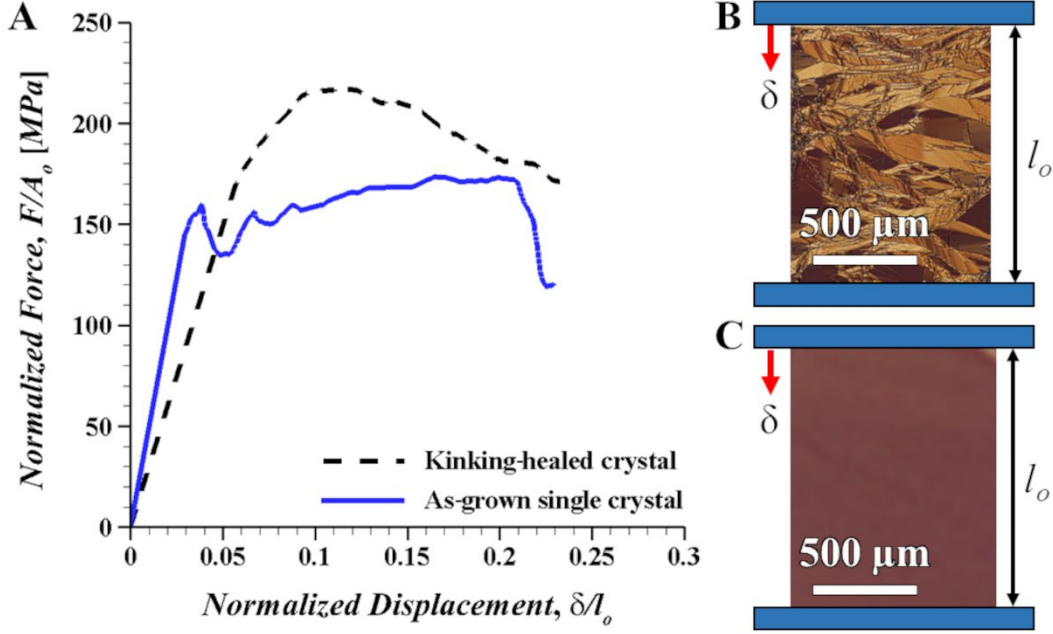


Fig. 6. Comparing the engineering compressive stress-strain response of an as-grown single crystal and kinking-healed specimen of Cr_2AlC . The kinking-healed specimen considered here is taken from the single crystal specimen that was subjected to *in-situ* indentation under deformation constraint normal to the basal planes, as shown in Fig. 2. **(A)** Comparison of the engineering stress-strain (normalized force (F/A_0) – displacement (δ/l_0), where A_0 and l_0 are the initial cross-sectional area and length of the specimen, respectively) response of an as-grown single crystal and kinking-healed specimen showing improved mechanical performance of the kinking-healed specimen. **(B-C)** Schematic of the experimental set-up in which the kinking-healed and as-grown single crystal specimens are subjected to uniaxial compression together with the polarized light optical microscopy images showing the kinking-induced poly-crystallized and initial single crystal microstructures of the respective specimens.

We also analyzed the reopening resistance of several physically healed cracks in the kinking-healed specimens during *in-situ* uniaxial compression tests (Fig. 7 and Supplementary Fig. S10). To this end, we first identified several cracks that are physically healed (i.e., underwent permanent tilting, twisting and closure) by the onset of kinking during *in-situ* indentation experiments under deformation constraint normal to the basal planes (Figs. 7A-D). These same cracks are then tracked during *in-situ* uniaxial compression tests (Figs. 7E-H). Our results show that the physically healed cracks (even with length greater than hundreds of microns) do not easily reopen up to imposed load levels comparable to the compressive strength of the kinking-healed material. This is noteworthy, since the compressive strength of the kinking-healed material is significantly higher than that of the as-grown single crystals.

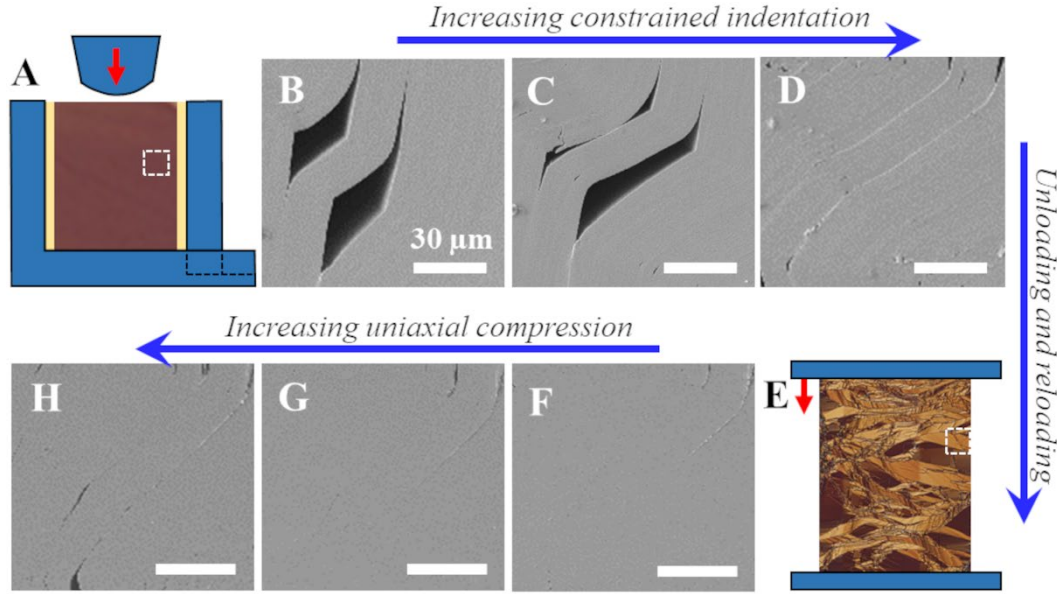


Fig. 7. Kinking-induced crack-healing in a constrained single crystal specimen of Cr_2AlC during *in-situ* indentation and reopening resistance of the same healed cracks during *in-situ* uniaxial compression. (A) Schematic of the experimental set-up in which an as-grown single crystal specimen is subjected to indentation under deformation constraint normal to the basal planes. (B-D) SEM images showing kinking-induced crack-healing with increasing constrained indentation. (E) Schematic of the experimental set-up in which the kinking-healed specimen is subjected to uniaxial compression. (F-H) SEM images of the same region in (B-D) showing negligible opening of the healed cracks during uniaxial compression. The scale bars in (B-D) and (F-H) are the same.

Discussion

In summary, it is evident from our results that catastrophic fracture of atomically layered ceramic materials, such as Cr_2AlC , can be effectively overcome by not only suppressing the crack growth along the weakly bonded planes but, more importantly, by healing them as they form. For instance, by indenting unconstrained specimens we showed that even a small Poisson's expansion of the crystal normal to the weakly bonded basal planes is enough to cause initiation and rapid growth of cracks along these planes. However, indentation of these materials while under slight deformation constraint normal to the weakly bonded basal planes enables buckling and kinking of the ligaments between multiple parallel cracks, and formation of kink-bands. Once a kink-band forms, the faces of the portion of the crack that lie within the kink-band undergo permanent tilting, twisting and closure leading to physical healing. Furthermore, the growth and widening of multiple adjacent kink-bands leads to physical healing of the entire crack with length greater than hundreds of microns.

The importance of this finding cannot be overstated as this explains the puzzling observation that the MAX phases, instead of undergoing catastrophic fracture demonstrate unconventional damage tolerance (25, 26). The unconventional damage tolerance of polycrystalline MAX phases is not only limited to monotonic compressive loading but has also been observed under a variety of loading conditions (28-32). From our results it can be concluded that in polycrystalline MAX phase aggregates even the grains that are oriented for easy cleavage along weakly bonded planes can undergo kinking due to the deformation constraint imposed by the neighboring grains and

consequently heal the cracks. Thus, the kinking-induced crack-healing mechanism endows these otherwise brittle materials with exceptional resistance to catastrophic fracture. This also implies that the toughness of this class of atomically layered ceramic materials can be further enhanced by carefully designing microstructures to promote extensive kinking and crack-healing.

In ceramic materials limited autonomous crack-healing i.e., healing of the cracks as they form during loading has been previously realized by high temperature oxidation of the cracks (21-23). However, we are not aware of any realization of intrinsic and autonomous crack-healing at room temperature in a monolithic ceramic material. Although we have demonstrated room temperature kinking-induced crack-healing in a particular class of atomically layered ceramic material i.e. MAX phases, it should be noted that MAX phases are an extremely diverse class of material with approximately 155 MAX phase compositions discovered till date (27). Moreover, kinking is not unique to MAX phases and has also been observed in a variety of other atomically layered ceramic materials, and thus it is reasonable to assume that kinking-induced crack-healing can be achieved in these materials as well. These other atomically layered ceramic materials include graphite (37), micas (34), hexagonal carbides (43), boron-nitride (44) and layered borides (46), among others whose broader applications have been limited by their poor damage tolerance and propensity to cleave along weakly bonded planes.

Materials and Methods

Material synthesis

Single crystals of the Cr_2AlC MAX phase were synthesized using a flux growth method in an induction heated Al_2O_3 crucible based in part on a previous work (47). Flux composition (in atomic fraction) was $X_{\text{Cr}} = 0.354$, $X_{\text{Al}} = 0.566$ and $X_{\text{C}} = 0.08$. Carbon was introduced at 1650°C by dipping a rotating graphite rod into the flux. This allowed for precise control of the carbon content; and prevented the formation of unwanted Al_4C_3 and subsequent breaking of the crucible during temperature ramping. After 30 minutes, the temperature was decreased to 1600°C in 20 minutes. Next, nucleation and crystal growth were achieved by slow cooling to 1100°C over 5 days. Finally, the single crystals were extracted from the solidified flux by HCl etching.

Sample preparation for in-situ indentation testing

As-grown single crystals of Cr_2AlC were first coated with epoxy to avoid fracture in the single crystal by cleavage cracking along the weakly bonded Al and Cr_2C planes during machining and polishing. The epoxy coated as-grown single crystals were carefully machined into small cuboids of dimensions $2 \times 2 \times 1.5 \text{ mm}^3$ using a diamond wire saw. Next, the four faces of the cuboids that are normal to the basal planes (i.e., the $\langle 01\bar{1}0 \rangle$ and $\langle 11\bar{2}0 \rangle$ faces) of the crystal were mechanically polished up to $0.1 \mu\text{m}$ diamond suspension and fine polished with $0.05 \mu\text{m}$ colloidal silica. The final cuboidal shaped specimens also contained thin ($\sim 150 \mu\text{m}$ thick) layers of epoxy on the faces of the cuboids that are parallel to the basal planes of the crystal.

In-situ indentation tests

The *in-situ* indentation tests were carried out inside a Tescan FERA-3 SEM using a miniature tension-compression module by Kammrath & Weiss and an in-house designed and build fixture. The in-house *in-situ* indentation fixture was machined from a solid block of A2 (air hardened, 60 RC) tool steel. As shown in Fig. 2A, the fixture comprises a fixed wall and a sliding wall equipped

with two tightening screws. The cuboidal specimen is first placed between the fixed and the sliding wall with the basal planes being parallel to the walls, and then the sliding wall is moved towards the specimen and fixed using the tightening screws. Although the specimen is confined between the two walls, prior to the onset of any deformation the specimen inside the fixture is stress free. Note that for the unconstrained tests (Fig. 1A), the specimen is not confined between the walls. Next, a punch with a cylindrical tip of 1 mm radius also machined from A2 (air hardened, 60 RC) tool steel is used to indent the specimen along a direction parallel to the basal planes at a crosshead speed of 0.5 $\mu\text{m/s}$. During the indentation, the indentation force-depth response was continuously recorded while the test was interrupted at regular indentation depth to capture the SE-SEM images of one of the specimen surfaces.

Sample preparation for in-situ uniaxial compression testing

As-grown single crystal and kinking-healed specimens (i.e., single crystal specimens that were subjected to *in-situ* indentation under deformation constraint normal to the basal planes, Fig. 2) of Cr_2AlC were carefully machined into small cuboids of dimensions $1 \times 1.2 \times 1.5 \text{ mm}^3$ using a diamond wire saw. Next, all the faces (except the two faces parallel to the basal planes of the initial single crystal) of the cuboids were mechanically polished up to 0.1 μm diamond suspension and fine polished with 0.05 μm colloidal silica.

In-situ uniaxial compression tests

The *in-situ* uniaxial compression tests were carried out inside a Tescan FERA-3 SEM using a miniature tension-compression module by Kammrath & Weiss and a simple compression test fixture. The compression test fixture consists of two tungsten carbide plates between which the cuboidal specimens were subjected to uniaxial compression at a crosshead speed of 0.5 $\mu\text{m/s}$, as shown schematically in Figs. 6B-C. During the uniaxial compression, the force-displacement response was continuously recorded while the test was interrupted at regular displacements to capture the SE-SEM images of one of the specimen surfaces.

Microstructural characterization

The microstructural characterization of the as-grown and deformed single crystal specimens of Cr_2AlC were carried out by SE-SEM imaging, Electron Back Scattered Diffraction (EBSD) and polarized light optical microscopy. The SE-SEM imaging and EBSD were carried out using a Tescan FERA-3 SEM equipped with a NordlysNano EBSD detector by Oxford instruments, and optical microscopy was carried out using an Olympus DSX500 digital microscope equipped with polarized light and live panorama options. The EBSD scan was carried out at an operating voltage of 10 kV and with a step size of 2 μm . The EBSD pattern was indexed using the Cr_2AlC phase and post-processing was carried out using HKL Channel 5 software by Oxford instruments.

Supplementary Materials

Fig. S1. Crystallographic orientation of as-grown single crystals of Cr_2AlC .

Fig. S2. *In-situ* indentation of a constrained single crystal specimen of Cr_2AlC showing the evolution of cracking, kinking and crack-healing.

Fig. S3. Irreversible poly-crystallization in a constrained single crystal specimen of Cr₂AlC post *in-situ* indentation.

Fig. S4. Kinking-induced crystal reorientation in a constrained single crystal specimen of Cr₂AlC post *in-situ* indentation.

Fig. S5. Evolution of cracking, kinking and crack-healing in a constrained single crystal specimen of Cr₂AlC during *in-situ* indentation.

Fig. S6. Initiation of secondary kink-bands within a primary kink-band at higher indentation depths in a constrained single crystal specimen of Cr₂AlC during *in-situ* indentation.

Fig. S7. Rotation of the kink-band boundaries away from the indentation axis and secondary kinking at higher indentation depths in a constrained single crystal specimen of Cr₂AlC during *in-situ* indentation.

Fig. S8. *In-situ* uniaxial compression of an as-grown single crystal of Cr₂AlC.

Fig. S9. *In-situ* uniaxial compression of a kinking-healed specimen of Cr₂AlC.

Fig. S10. Reopening resistance of the healed cracks during *in-situ* uniaxial compression of a kinking-healed specimen of Cr₂AlC.

References:

1. J. J. Bertin, R. M. Cummings, Fifty years of hypersonics: where we've been, where we're going. *Progress in Aerospace Sciences* **39**, 511-536 (2003).
2. J. H. Perepezko, The hotter the engine, the better. *Science* **326**, 1068-1069 (2009).
3. N. P. Padture, Advanced structural ceramics in aerospace propulsion. *Nature materials* **15**, 804 (2016).
4. J. Knaster, A. Moeslang, T. Muroga, Materials research for fusion. *Nature Physics* **12**, 424-434 (2016).
5. M. E. Launey, R. O. Ritchie, On the fracture toughness of advanced materials. *Advanced Materials* **21**, 2103-2110 (2009).
6. R. O. Ritchie, The conflicts between strength and toughness. *Nature materials* **10**, 817-822 (2011).
7. E. Munch *et al.*, Tough, bio-inspired hybrid materials. *Science* **322**, 1516-1520 (2008).
8. A. R. Studart, Bioinspired ceramics: Turning brittleness into toughness. *Nature materials* **13**, 433-435 (2014).
9. F. Bouville *et al.*, Strong, tough and stiff bioinspired ceramics from brittle constituents. *Nature materials* **13**, 508-514 (2014).
10. U. G. Wegst, H. Bai, E. Saiz, A. P. Tomsia, R. O. Ritchie, Bioinspired structural materials. *Nature materials* **14**, 23-36 (2015).
11. F. Bouville, A. R. Studart, Geologically-inspired strong bulk ceramics made with water at room temperature. *Nature communications* **8**, 1-8 (2017).

12. Z. Yin, F. Hannard, F. Barthelat, Impact-resistant nacre-like transparent materials. *Science* **364**, 1260-1263 (2019).
13. M. D. Hager, P. Greil, C. Leyens, S. van der Zwaag, U. S. Schubert, Self-Healing Materials. *Advanced Materials* **22**, 5424-5430 (2010).
14. S. R. White *et al.*, Autonomic healing of polymer composites. *Nature* **409**, 794-797 (2001).
15. K. S. Toohey, N. R. Sottos, J. A. Lewis, J. S. Moore, S. R. White, Self-healing materials with microvascular networks. *Nature materials* **6**, 581-585 (2007).
16. H. Guo, Y. Han, W. Zhao, J. Yang, L. Zhang, Universally autonomous self-healing elastomer with high stretchability. *Nature Communications* **11**, 1-9 (2020).
17. K. Van Tittelboom, N. De Belie, Self-healing in cementitious materials—A review. *Materials* **6**, 2182-2217 (2013).
18. N. De Belie *et al.*, A review of self-healing concrete for damage management of structures. *Advanced materials interfaces* **5**, 1800074 (2018).
19. K. Ando *et al.*, Crack healing behaviour and high-temperature strength of mullite/SiC composite ceramics. *Journal of the European Ceramic Society* **22**, 1313-1319 (2002).
20. K. Ando, K. Furusawa, K. Takahashi, S. Sato, Crack-healing ability of structural ceramics and a new methodology to guarantee the structural integrity using the ability and proof-test. *Journal of the European Ceramic Society* **25**, 549-558 (2005).
21. G. Song *et al.*, Oxidation-induced crack healing in Ti₃AlC₂ ceramics. *Scripta Materialia* **58**, 13-16 (2008).
22. W. G. Sloof *et al.*, Repeated crack healing in MAX-phase ceramics revealed by 4D in situ synchrotron X-ray tomographic microscopy. *Scientific reports* **6**, 23040 (2016).
23. T. Osada *et al.*, A novel design approach for self-crack-healing structural ceramics with 3D networks of healing activator. *Scientific reports* **7**, 1-9 (2017).
24. N. van Dijk, S. van der Zwaag, Self-healing phenomena in metals. *Advanced Materials Interfaces* **5**, 1800226 (2018).
25. M. W. Barsoum, M. Radovic, Elastic and mechanical properties of the MAX phases. *Annual review of materials research* **41**, 195-227 (2011).
26. M. Radovic, M. W. Barsoum, MAX phases: bridging the gap between metals and ceramics. *American Ceramics Society Bulletin* **92**, 20-27 (2013).
27. M. Sokol, V. Natsu, S. Kota, M. W. Barsoum, On the chemical diversity of the MAX phases. *Trends in Chemistry* **1**, 210-223 (2019).
28. C. J. Gilbert *et al.*, Fatigue-crack growth and fracture properties of coarse and fine-grained Ti₃SiC₂. *Scripta Materialia* **42**, 761-767 (2000).
29. D. Chen, K. Shirato, M. W. Barsoum, T. El-Raghy, R. O. Ritchie, Cyclic fatigue-crack growth and fracture properties in Ti₃SiC₂ ceramics at elevated temperatures. *Journal of the American Ceramic Society* **84**, 2914-2920 (2001).
30. M. Radovic, M. Barsoum, T. El-Raghy, S. Wiederhorn, Tensile creep of coarse-grained Ti₃SiC₂ in the 1000–1200° C temperature range. *Journal of Alloys and compounds* **361**, 299-312 (2003).
31. R. Bhattacharya, R. Benitez, M. Radovic, N. C. Goulbourne, High strain-rate response and deformation mechanisms in polycrystalline Ti₂AlC. *Materials Science and Engineering: A* **598**, 319-326 (2014).
32. R. Benitez *et al.*, Mechanical properties and microstructure evolution of Ti₂AlC under compression in 25-1100 C temperature range. *Acta Materialia*, (2020).

33. G. Plummer *et al.*, On the origin of kinking in layered crystalline solids. *Materials Today* **43**, 45-52 (2021).
34. F. Hörz, Static and dynamic origin of kink bands in micas. *Journal of Geophysical Research* **75**, 965-977 (1970).
35. M. Manley, E. Schulson, Kinks and cracks in S1 ice under across-column compression. *Philosophical magazine letters* **75**, 83-90 (1997).
36. R. Menig, M. Meyers, M. Meyers, K. Vecchio, Quasi-static and dynamic mechanical response of *Haliotis rufescens* (abalone) shells. *Acta Materialia* **48**, 2383-2398 (2000).
37. M. Barsoum, A. Murugaiah, S. Kalidindi, T. Zhen, Y. Gogotsi, Kink bands, nonlinear elasticity and nanoindentations in graphite. *Carbon* **42**, 1435-1445 (2004).
38. E. Orowan, A type of plastic deformation new in metals. *Nature* **149**, 643-644 (1942).
39. P. Flewitt, A. Crocker, The formation of deformation kinks in body centred cubic crystals. *Philosophical Magazine* **34**, 877-891 (1976).
40. A. G. Evans, W. F. Adler, Kinking as a mode of structural degradation in carbon fiber composites. *Acta Metallurgica* **26**, 725-738 (1978).
41. B. Budiansky, N. A. Fleck, Compressive failure of fibre composites. *Journal of the Mechanics and Physics of Solids* **41**, 183-211 (1993).
42. S. Kyriakides, R. Arseculeratne, E. Perry, K. Liechti, On the compressive failure of fiber reinforced composites. *International Journal of Solids and Structures* **32**, 689-738 (1995).
43. H. Suematsu, T. Suzuki, T. Iseki, T. Mori, Kinking and cracking caused by slip in single crystals of silicon carbide. *Journal of the American Ceramic Society* **74**, 173-178 (1991).
44. S. Turan, K. Knowles, High resolution transmission electron microscopy of the planar defect structure of hexagonal boron nitride. *Physica status solidi (a)* **150**, 227-237 (1995).
45. T. Nizolek, N. A. Mara, I. J. Beyerlein, J. T. Avallone, T. M. Pollock, Enhanced Plasticity via Kinking in Cubic Metallic Nanolaminates. *Advanced Engineering Materials* **17**, 781-785 (2015).
46. Y. Chen, S. Kota, M. W. Barsoum, M. Radovic, Compressive deformation of MoAlB up to 1100° C. *Journal of Alloys and Compounds* **774**, 1216-1222 (2019).
47. T. Ouisse *et al.*, High temperature solution growth and characterization of Cr₂AlC single crystals. *Journal of Crystal Growth* **384**, 88-95 (2013).
48. C. Brüsewitz, I. Knorr, H. Hofsäss, M. W. Barsoum, C. A. Volkert, Single crystal pillar microcompression tests of the MAX phases Ti₂InC and Ti₄AlN₃. *Scripta Materialia* **69**, 303-306 (2013).
49. M. Higashi, S. Momono, K. Kishida, N. L. Okamoto, H. Inui, Anisotropic plastic deformation of single crystals of the MAX phase compound Ti₃SiC₂ investigated by micropillar compression. *Acta Materialia* **161**, 161-170 (2018).
50. Z. Zhan, Y. Chen, M. Radovic, A. Srivastava, Non-classical crystallographic slip in a ternary carbide – Ti₂AlC. *Materials Research Letters* **8**, 275-281 (2020).
51. J. Dewey, Nature and origin of kink-bands. *Tectonophysics* **1**, 459-494 (1965).

Acknowledgments

Funding: The financial support provided by the U.S. National Science Foundation grants CMMI – 1729350 and CMMI – 1944496 are gratefully acknowledged.

Author contributions: HR build the experimental setup, prepared samples, and carried out all the *in-situ* SEM experiments as well as EBSD and OM analysis. TO synthesized large single crystals of Cr₂AlC used in this study. MR and AS conceived, planed and supervised the experimental work. All authors contributed to the analysis of the results and discussion. MR and AS wrote the manuscript with input from HR and TO. All authors have reviewed and approved the manuscript.

Competing interests: The authors declare no competing interests.

Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the “Supplementary Materials.”

Supplementary Materials for

Room temperature crack-healing in an atomically layered ternary carbide

Hemant J. Rathod¹, Thierry Ouisse², Miladin Radovic^{1,*}, Ankit Srivastava^{1,*}

¹Department of Materials Science and Engineering, Texas A&M University, College Station, TX, 77843, USA

²Université Grenoble Alpes, CNRS, Grenoble INP, LMGP, F-38000 Grenoble, France

*Corresponding authors: mradovic@tamu.edu (M. Radovic), ankit.sri@tamu.edu (A. Srivastava)

This file includes:

Supplementary Figs. S1 to S10

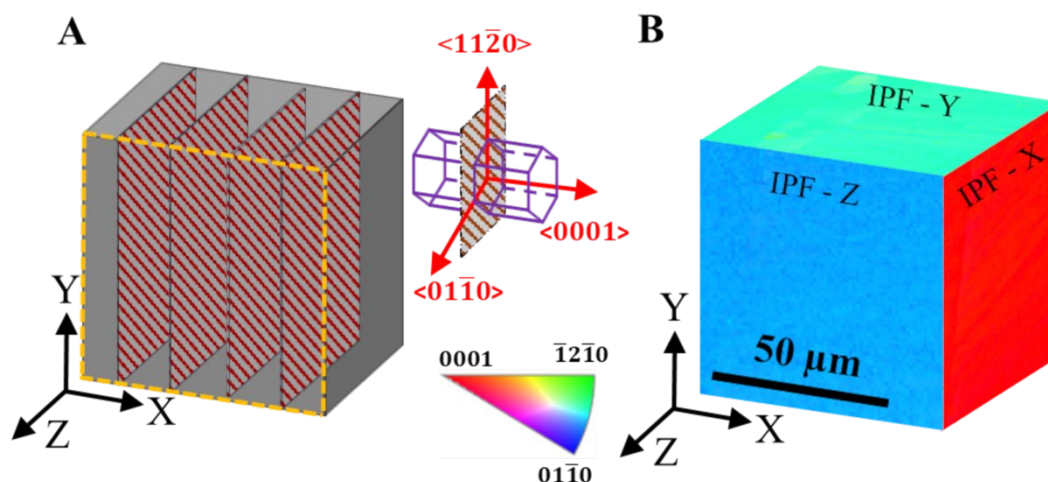


Fig. S1. Crystallographic orientation of as-grown single crystals of Cr_2AlC . (A) Schematic representation of an as-grown single crystal of Cr_2AlC highlighting the basal planes. (B) EBSD X-, Y- and Z-IPF maps of the plane marked by (orange) dashed box in (A).

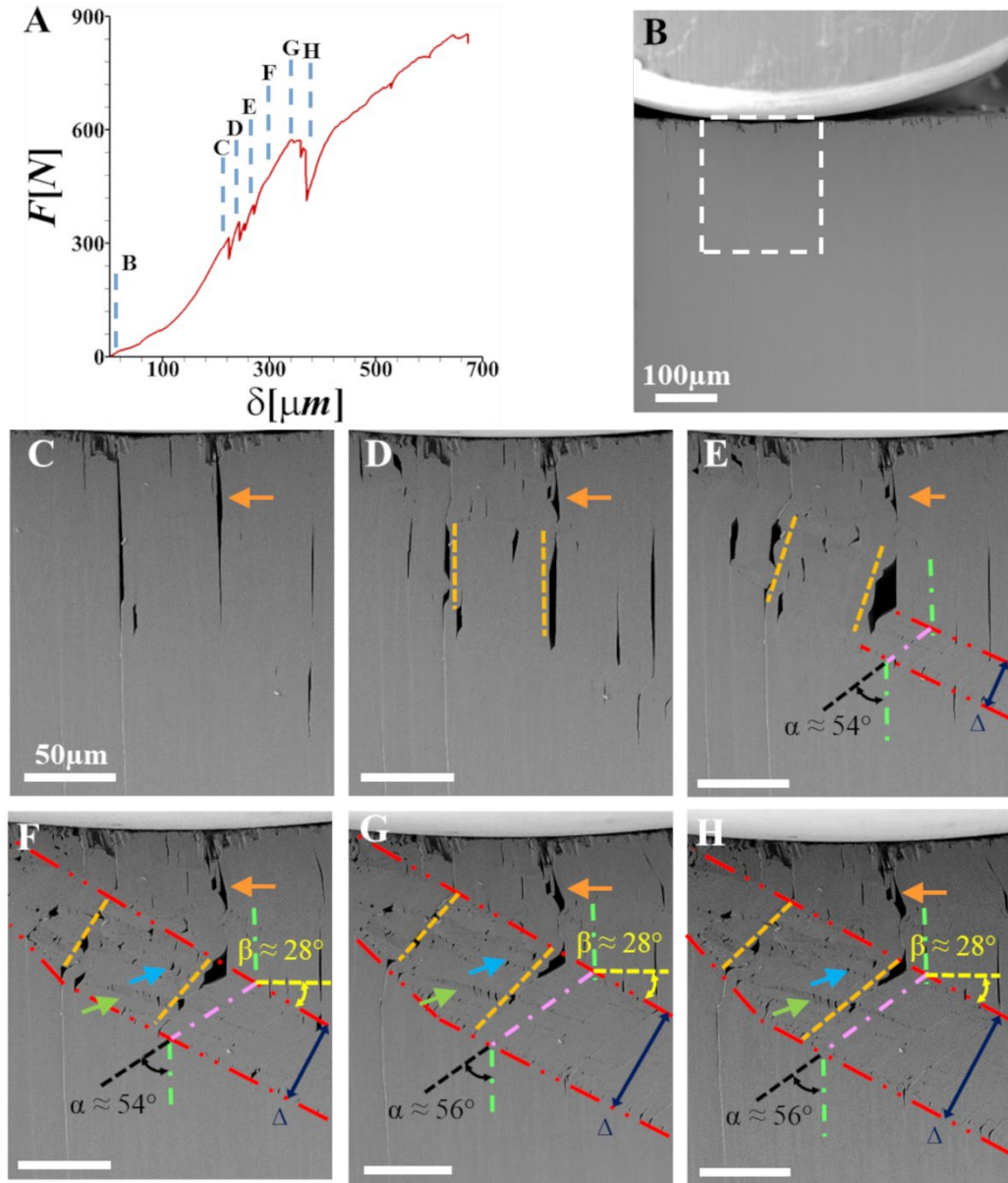


Fig. S2. *In-situ* indentation of a constrained single crystal specimen of Cr_2AlC showing the evolution of cracking, kinking and crack-healing. (A) Indentation force (F) – depth (δ) response. (B) SEM image showing the specimen surface and the indenter at the onset of loading. (C) Initiation and propagation of multiple cleavage cracks along the $\{0001\}$ i.e., basal planes during loading. (D-H) SEM images showing buckling and kinking of the ligaments between parallel cracks and formation of kink-bands leading to crack-healing during loading. An (orange) arrow follows one of the basal plane cleavage cracks through (C-H). This crack physically heals during loading due to the growth and widening of the adjacent kink-bands. The boundaries of one of the kink-bands in (E-H) is traced by dashed double dotted (red) lines and the average in-plane rotation (α) of the material in the kink-band together with the inclination (β) of the kink-band boundaries are also marked. The onset of secondary kinking within the primary kink-band traced by the dashed double dotted (red) lines are marked with (light blue and green) arrows in (F-H). The indentation depth corresponding to SEM images in (B-H) is marked in (A). The scale bars in (C-H) are the same.

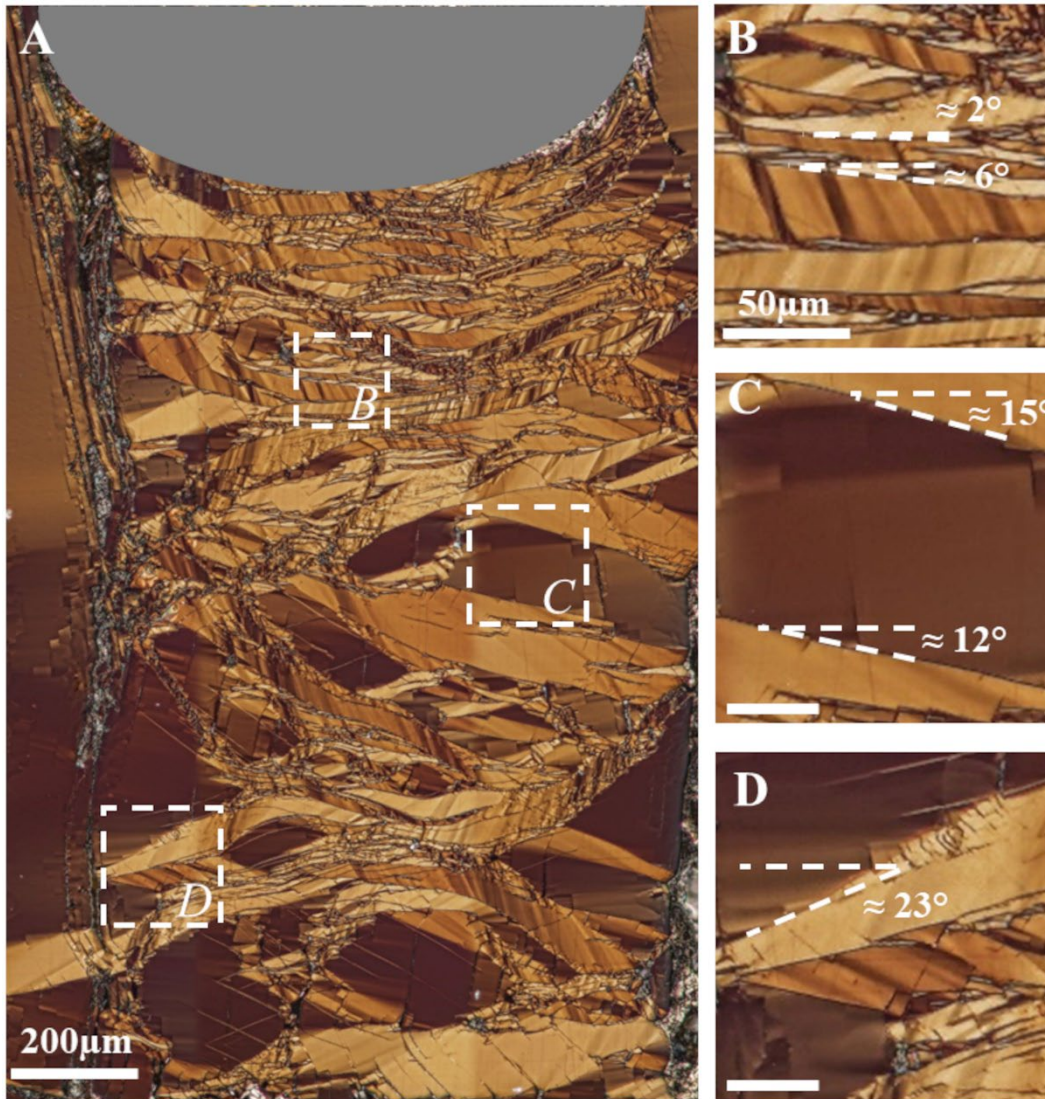


Fig. S3. Irreversible poly-crystallization in a constrained single crystal specimen of Cr_2AlC post *in-situ* indentation. (A) Post-deformation polarized light optical microscopy image showing the remnant impression of the indenter and the irreversible poly-crystallization throughout the initial single crystal specimen. (B) High magnification image of the region marked with a dashed box labelled B in (A) showing kinking-induced grains underneath the indenter that are relatively thin with grain boundaries almost normal to the indentation axis. (C-D) High magnification images of the regions marked with dashed boxes labeled C and D, respectively, in (A) showing kinking-induced grains in the regions away from the indenter that are rather thick with grain boundaries inclined at relatively larger angles. The inclination of select kinking-induced grain boundaries are marked in (B-D). The scale bars in (B-D) are the same.

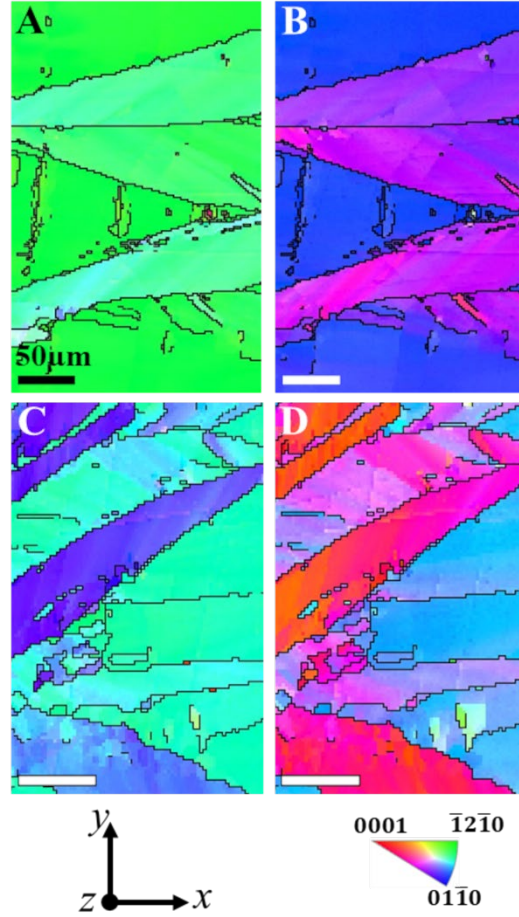


Fig. S4. Kinking-induced crystal reorientation in a constrained single crystal specimen of Cr_2AlC post *in-situ* indentation. (A-B) EBSD y - and z -IPF maps, respectively, of the region shown in Fig. 4A. (C-D) EBSD y - and z -IPF maps, respectively, of the region shown in Fig. 4D. Note that $\langle 11\bar{2}0 \rangle$ and $\langle 0001 \rangle$ crystallographic orientations of the initial single crystal specimen were along y - and x -axes, respectively. The scale bars in (A-D) are the same.

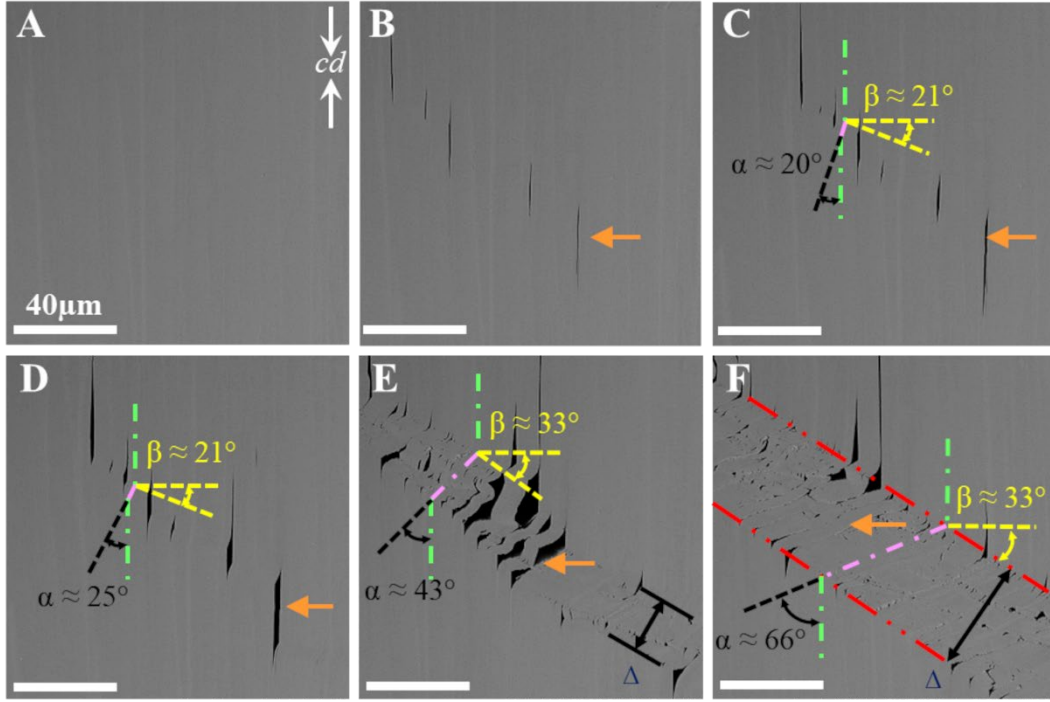


Fig. S5. Evolution of cracking, kinking and crack-healing in a constrained single crystal specimen of Cr_2AlC during *in-situ* indentation. A series of SEM images showing the sequence of events leading to crack-healing at a fixed location (roughly 300 μm) away from the indenter tip during progressive indentation. **(A)** Initial state of the region away from the indenter with basal plane and indentation direction marked as ‘*cd*’. **(B)** Initiation of multiple cleavage cracks along the basal planes. **(C)** Growth and opening of the cleavage cracks and buckling and kinking of the ligaments between these cracks. **(D-E)** Initiation and growth of a kink-band resulting in crack growth arrest and initiation of secondary cracks within the kink-band. **(F)** Crack-healing by growth and widening of the kink-band. An arrow follows the growth, opening, rotation and finally healing of one of the basal plane cracks through (C-F). The average in-plane rotation (α) of the material in the kink-band together with the inclination (β) of the kink-band boundary are traced in (C-F). The boundary of the fully developed kink-band in (F) is traced by broken (red) lines. The scale bars in (A-F) are the same.

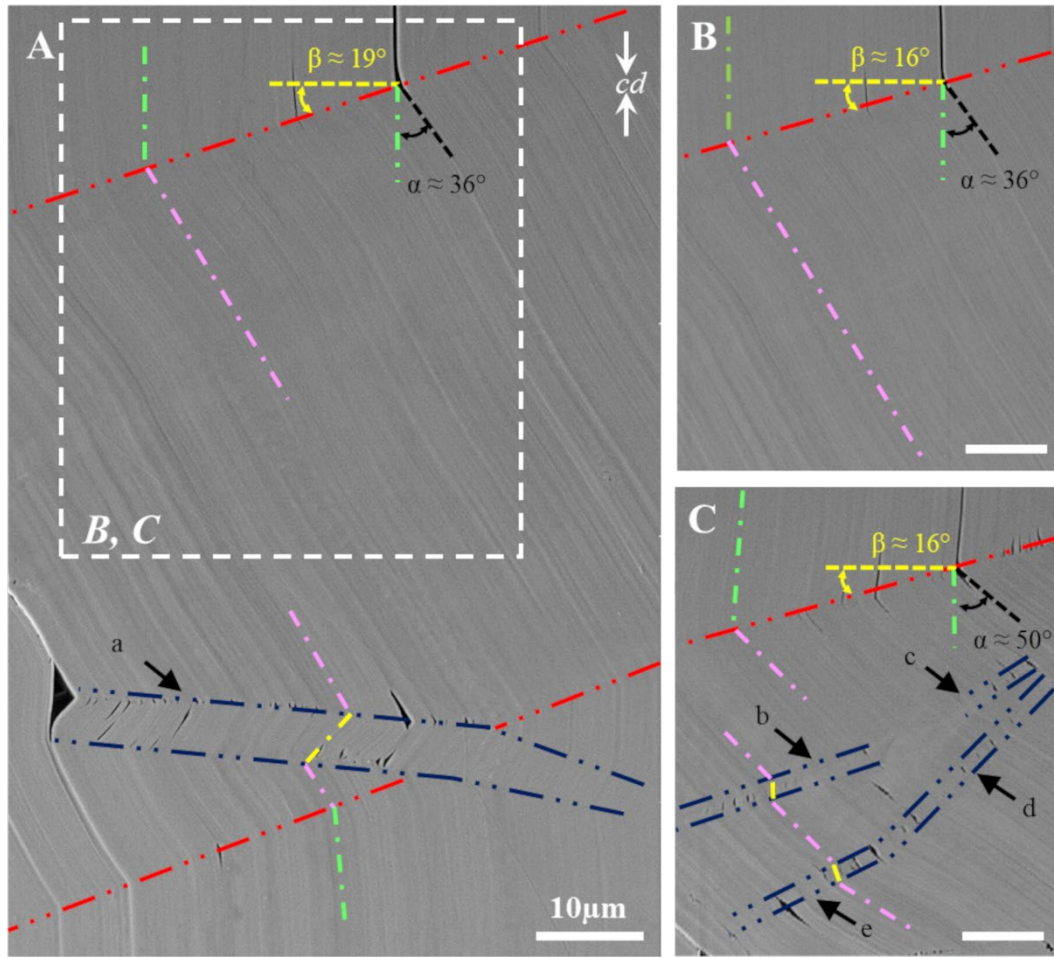


Fig. S6. Initiation of secondary kink-bands within a primary kink-band at higher indentation depths in a constrained single crystal specimen of Cr_2AlC during *in-situ* indentation. (A) An SEM image showing a kink-band traced by broken (red) lines and a secondary kink-band within the primary kink-band traced by broken (blue) lines at a location (roughly 120 μm) away from the indenter tip. (B-C) SEM images of the regions marked with a (white) dashed box in (A) showing initiation of multiple secondary kink-bands traced by broken (blue) lines within the primary kink-band with increasing indentation loading. The indentation direction is marked as 'cd' in (A). The scale bars in (A-C) are the same.

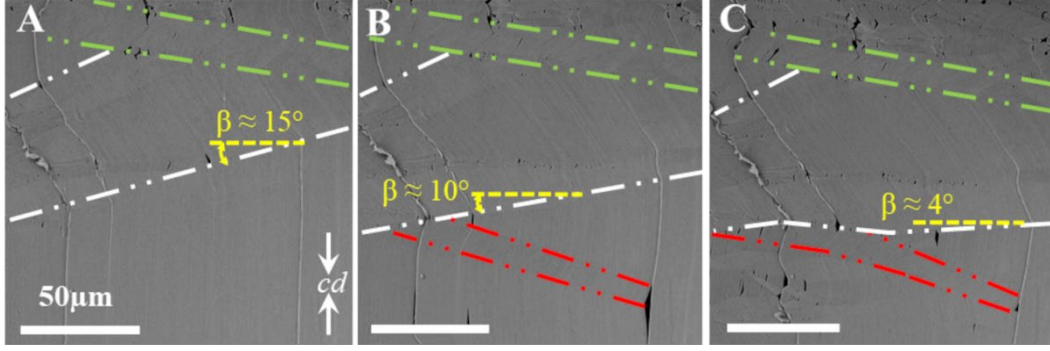


Fig. S7. Rotation of the kink-band boundaries away from the indentation axis and secondary kinking at higher indentation depths in a constrained single crystal specimen of Cr_2AlC during *in-situ* indentation. (A) An SEM image showing two kink-bands marked with broken (white and green) lines together with the inclination (β) of one of the kink-band boundaries at a location (roughly 100 μm) away from the indenter tip. (B-C) Rotation of the kink-band boundary away from the indentation axis as marked by the decreasing value of β and initiation of a secondary kink-band traced by broken (red) lines, with increasing indentation loading. The indentation direction is marked as ' cd ' in (A). The scale bars in (A-C) are the same.

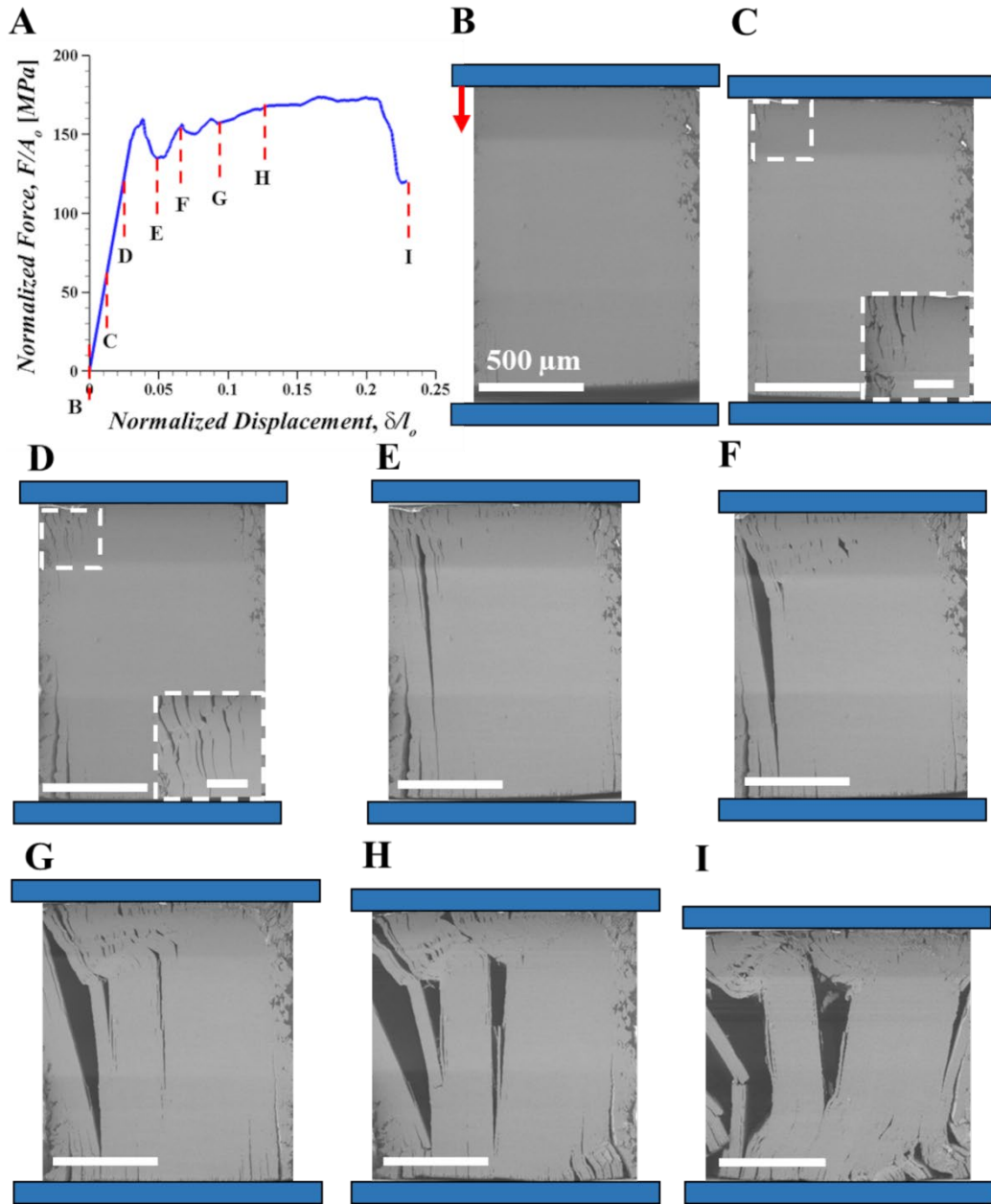


Fig. S8. In-situ uniaxial compression of an as-grown single crystal of Cr_2AlC . (A) Normalized force (F/A_0) – displacement (δ/l_0) response, where A_0 and l_0 are the initial cross-sectional area and length of the specimen, respectively. (B-I) SEM images showing the progressive initiation and growth of cleavage cracks along the basal planes i.e., $\{0001\}$ planes and limited buckling of the ligaments between the cracks and kinking underneath the punch. High resolution SEM images of early-stage crack initiation underneath the punch is shown as inserts in (C-D). The scale bars in (B-I) for the main figures are the same while the scale bars for the inserts in (C-D) are 100 μm . The imposed uniaxial displacement corresponding to SEM images in (B-I) is marked in (A).

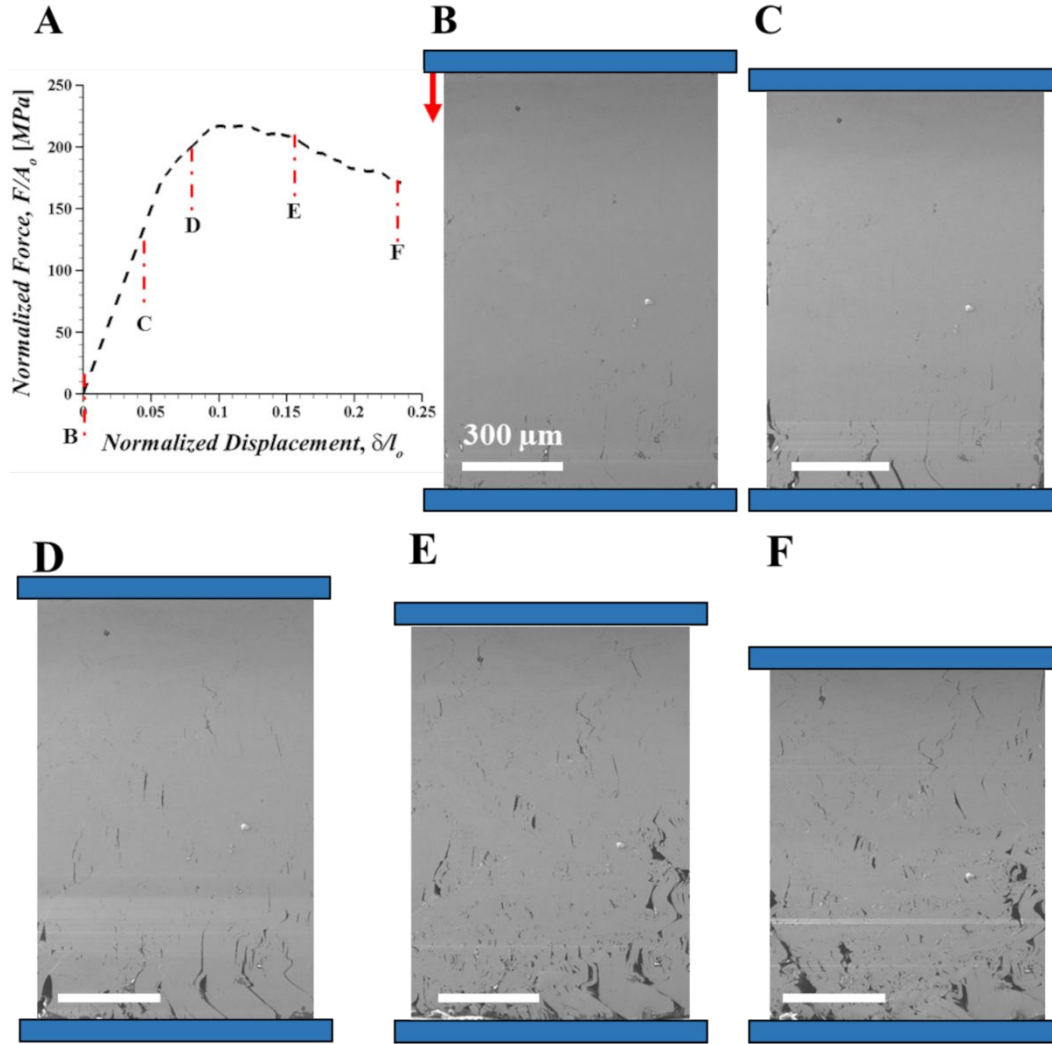


Fig. S9. *In-situ* uniaxial compression of a kinking-healed specimen of Cr_2AlC . The kinking-healed specimen considered here is taken from the single crystal specimen that was subjected to *in-situ* indentation under deformation constraint normal to the basal planes, Fig. S3. **(A)** Normalized force (F/A_0) – displacement (δ/l_0) response, where A_0 and l_0 are the initial cross-sectional area and length of the specimen, respectively. **(B-F)** SEM images of the specimen surface at various levels of imposed uniaxial displacement showing extremely limited initiation and growth of cleavage cracks in the kinking-healed specimen. Note that in this specimen cracks first initiate in the bottom part of the specimen that comprises relatively large pockets of unkinked regions, while cracks in the top part of the specimen that predominantly comprises kinked regions occurs at much higher load levels. The scale bars in (B-F) are the same. The imposed uniaxial displacement corresponding to SEM images in (B-F) is marked in (A).

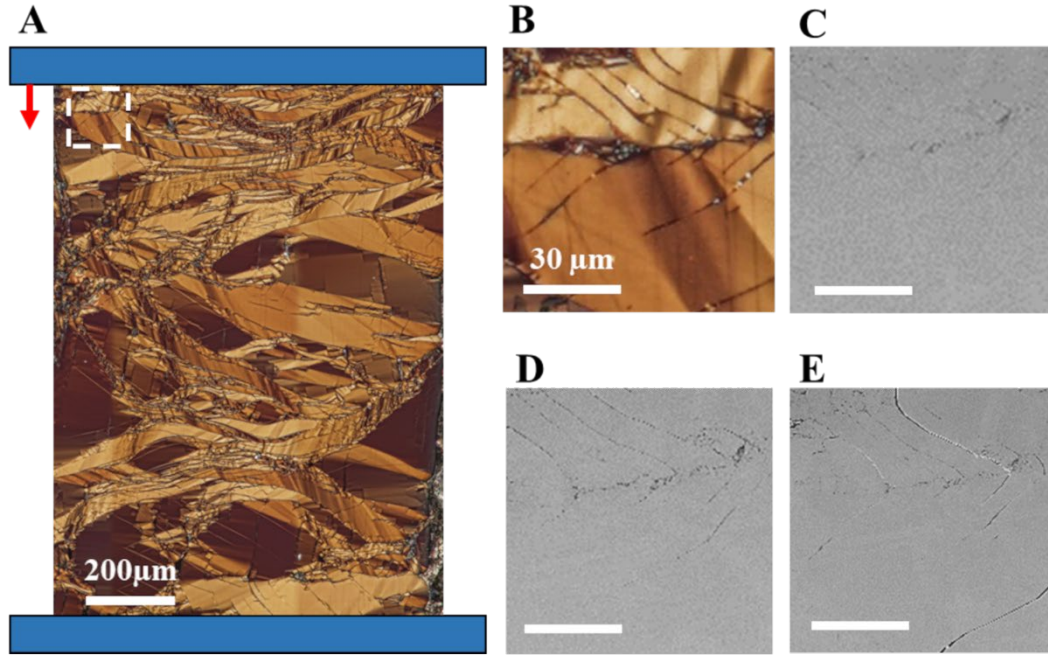


Fig. S10. Reopening resistance of the healed cracks during *in-situ* uniaxial compression of a kinking-healed specimen of Cr_2AlC . The kinking-healed specimen considered here is taken from the single crystal specimen that was subjected to *in-situ* indentation under deformation constraint normal to the basal planes, Fig. S3. **(A)** Schematic of the experimental set-up in which a kinking-healed specimen is subjected to uniaxial compression together with the polarized light optical microscopy image showing the kinking-induced poly-crystallized microstructure in the entire specimen. **(B)** High magnification image of the region marked with a dashed box in (A) showing inclined hairline-like features inside the kink-bands that are surface marks from physically healed cracks. **(C-E)** SEM images of the same region in (B) showing negligible opening of the healed cracks during uniaxial compression. The imposed uniaxial displacement corresponding to SEM images in (C-E) are marked in Fig. S9A as C-E. The scale bars in (B-E) are the same.