

Undulating Slip in Laves Phase and Implications for Deformation in Brittle Materials

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By combining density-functional theory calculations and aberration-corrected transmission electron microscopy, dislocations in Laves phase (a typical complex intermetallic compound) are shown to slip in an undulating path. During the slip, the dislocation cores jump up and down between a weakly bound plane and an adjacent strongly bound plane for gliding and atomic shuffling, respectively. This is different from the conventional slip process in simple metals, which is continuous within a single plane, as described in the paradigm of the generalized stacking fault energy.

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Attributed to their unique chemical, physical, and mechanical properties, intermetallic compounds have attracted increasing research attention [1–3]. In order to obtain wide applications, the brittleness of intermetallics has to be overcome. To improve the ductility of materials, effective plastic deformation is necessary, which is usually carried out by nucleation and slip of dislocations. Intermetallic compounds generally possess complex structures in which dislocations slip in groups, even involving short-range diffusion along different directions [4]. For instance, special zonal dislocations were proposed for the different displacements on differing slip planes [5]. However, the physical processes of dislocation glide with such local mutual motion of atoms are still largely speculative. In this work, we have chosen a Laves phase as a model system for complex intermetallics. The Laves phases represent a large family of intermetallic compounds. They exhibit exceptional properties for high-temperature applications, owing to their high melting temperature, high strength at high temperatures, and remarkable resistance to creep deformation [6]. While the deformation in Laves phases is believed to correspond to thermal activation [6], conventional shear processes seem to contradict such a feature. However, there is little information about the deformation mechanisms in Laves phases at the atomic scale.

In this Letter, we report on the slip process of dislocations in the Cr₂Nb Laves phase and its implications on the mechanical properties of the material. The structure of the dislocation core was clearly imaged by using aberration-corrected high-resolution transmission electron microscopy (HRTEM) [7,8] and the focal series exit-wave reconstruction technique [9], which can resolve all atoms in the crystal. First-principles calculations have revealed that such core structure is generated in an undulating slip mechanism, requiring the moving dislocations to jump between different slip planes. The nature of this novel mechanism leads to a general concept for dislocation slip

in complex-structured materials that atoms prefer to break weak bonding in order to initiate dislocation slip and accomplish the slip with a minimum energy path even by switching between different slip planes. These results may help understand the brittle-to-ductile transition (BDT) of intermetallic compounds. Finally, we show that the dislocation cores have an abnormal strain field, which is presumably related to the complex dissociation of dislocations in the material, as revealed by the lattice distortion analysis (LADIA) method [10,11].

HRTEM experiments.—In order to produce a lot of dislocations in the brittle Laves phase for the present study, the Cr₂Nb grains were embedded in a relatively “soft” NiAl matrix. Dislocations were then introduced into the Cr₂Nb Laves phase by compression at 1073 K, which is well below its BDT temperature. By comparing microstructures before and after the deformation, abundant partial dislocations were confirmed to be generated by the mechanical deformation. Substantial partial dislocations were arrested in the Cr₂Nb grains. This makes the investigation of dislocation cores feasible by HRTEM.

The Laves phases with S₂L stoichiometry are composed of smaller atoms S and larger atoms L [12]. Their crystal structure can be subdivided to two units: a single layer of a kagome network of S atoms, which is denoted by capital Latin letters (A, B, C) and a triple layer of $\alpha c\beta$ ($\beta a\gamma$ or $\gamma b\alpha$), which has a stacking sequence like the face-centered cubic structure, where the Greek letters (α , β , γ) denote L atoms and the lower case Latin letters (a , b , c) denote S atoms. The interplanar spacing between the triple and single layers [corresponding to plane 1 in Fig. 1(a)] is 3 times that of the interplanar spacing within the triple layer (corresponding to plane 2), and the interatomic force between the triple and single layers is considerably weaker than that within the triple layer. The single layer and the triple layer stack alternately to form the Laves phase, where all the L atoms are situated at the centers of

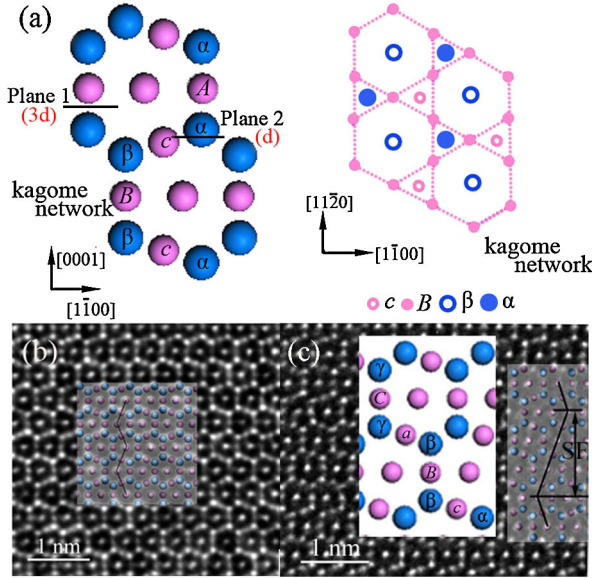


FIG. 1 (color online). Structures of the C14 Laves phase and a stacking fault of it. (a) Model of the C14 structure viewed along the $[11\bar{2}0]$ and $[0001]$ directions, respectively. The $\alpha c\beta$ -type triple layers are separated by single layers of kagome network. (b) High-resolution transmission electron micrograph (HRTEM) of an undeformed C14 Laves phase viewed along the $[11\bar{2}0]$ direction, recorded with the aberration-corrected high-resolution transmission electron microscope. (c) An HRTEM image of a stacking fault in the deformed C14 Laves phase.

hexagons in the kagome networks. The hexagonal C14 structure of a Laves phase [Fig. 1(b)] can be defined as

$$\beta B \beta c \alpha A \alpha c \beta B \beta c \alpha A \alpha c \beta B \beta c \alpha A \alpha c.$$

Figure 1(c) shows a partial dislocation which has glided through the (0001) basal plane of the C14 Cr_2Nb and where the stacking sequence of the triple layer is changed from $\beta c \alpha$ to $\beta a \gamma$. Consequently, the structure becomes

$$\beta B \beta c \alpha A \alpha c \beta B \beta | a \gamma C \gamma b \alpha A a b \gamma C \gamma b.$$

Here the vertical line marks the stacking fault left by the glide of the partial dislocation.

The HRTEM image (Fig. 2) shows the characteristics of shearing in the dislocation core. After magnifying the image, it can be seen that not only two α -A- α bond chains within the dislocation core region are distorted, but also the atomic positions in the triple layer are slightly changed. In particular, the position of the Nb atom denoted by α at the center in Fig. 2(b) is higher than its counterparts in undistorted regions in the same triple layer. These features indicate that four layers, $\alpha A \alpha c$, are involved in the slip process.

Atomistic simulations.—To reveal the physical process of the dislocation slip, we have performed theoretical calculations with the nudged elastic band (NEB) method [13,14], which can reveal the potential surface for the slip process without any artificial interferences. The activated

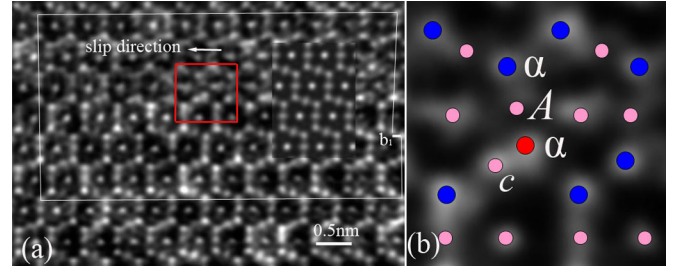


FIG. 2 (color online). (a) An aberration-corrected HRTEM image of the partial dislocation. The closure failure of the Burgers circuit implies that the dislocation has a Burgers vector, $\mathbf{b}_1$, of $\langle -1100 \rangle / 3$ and moves from right to left. The simulated image of the stacking fault is shown as an inset with a thickness of 2.4 nm and a focus value of 9 nm. (b) A magnified image of the dislocation core shown in the red box in (a).

atoms are assumed to move along the minimum energy path in response to the applied stress, since the minimum energy path typically has the greatest statistical possibility among all possible paths. No assumption is made about the intermediate states of the dislocation slip in the NEB calculation; only the initial and final states are fixed. This method has been successfully used to calculate the cross-slip process of screw dislocations in copper [15].

We used the perfect crystal and the stacking fault structures of C14 Cr_2Nb as the initial and final states for the glide of the partial dislocation, respectively. The density-functional theory calculations were performed with the projector-augmented wave method [16] in the VASP software [17], where the generalized gradient approximation [18] was used for the exchange and correlation functional. The atomic configurations during the slip process are schematically shown in Fig. 3(a), where the upper half-crystal moves from right to left relative to the lower half. While shuffling of the layers α and c is involved during the process (described in detail below), the top view is also given in Fig. 3(b) to clearly illustrate the motion of the two layers, below which the layer β of Nb and the kagome layer B of Cr are shown as a reference for the motion of α and c . The process is composed of three steps (I–III; see also movie 1 in the supplemental material [19]).

(I) In the first stage, the upper half-crystal above plane 1, as labeled in Fig. 3(a), moves in the slip direction. This is the characteristic feature of the so-called crystallographic slip [20]. During this stage, the atoms highlighted by the red triangle in plane A are getting closer and closer to α along the direction of the black arrow in Fig. 3(c). The layers α and c also move in the slip direction, but to a much less extent. This is because the A- α spacing is 3 times the α - c and c - β spacings, leading to weaker bonding between A and α . Another reason for the blockade of the motion of α and c is that their destinations within the slip plane are already occupied by c and α , respectively.

(II) A simultaneous shuffling of α and c occurs on plane 2, as outlined in the red box in Fig. 3(a). The motion

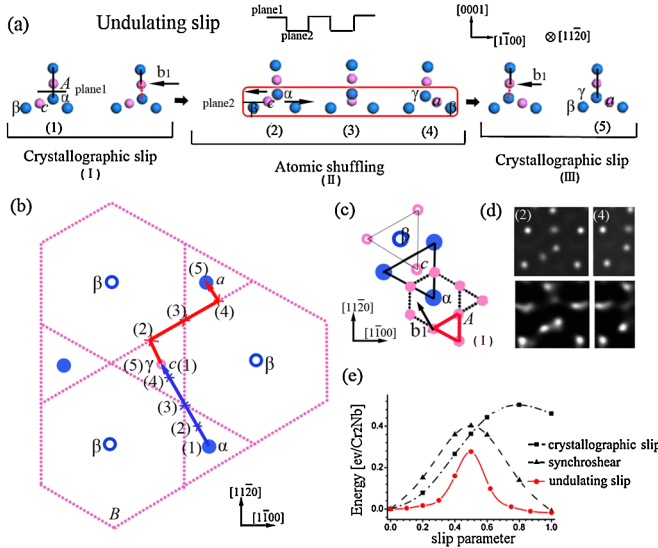


FIG. 3 (color online). Results of the NEB calculation for the slip process. (a) Side view of the atomic configurations (1)–(5) during the slip, which contains a crystallographic slip in plane 1 and an atomic shuffling in the triple layer. (b) Top view of the atomic configurations during the slip. The blue path denotes the movement of Nb from the site α to γ , and the red path denotes the motion of Cr from c to a . The shuffling occurs from the configuration (2) to (4). (c) Top view of the crystallographic slip, showing the moving direction of the kagome layer A relative to the layer α below it. (d) A comparison between the calculated and experimental results. The upper two images are the simulated ones for the configurations (2) and (4). The lower two are the corresponding experimental images, which are from the center and from the right side of the dislocation core, respectively. (e) Energy profiles for different slip mechanisms. The undulating slip has a path with the lowest energy.

of α towards γ is in the slip direction, the same as in the first stage. The motion of the layer c [denoted as the section from point (2) to (4) in Fig. 3(b)], however, is *perpendicular* to the slip direction. The jumping away of α leaves vacancies for c to jump into, avoiding the overlapping of α and c within the slip plane. At the same time, it is also avoided for the layer α to get too close to the red triangle in the layer A above it. As shown in the energy profile of the crystallographic slip in Fig. 3(e), a too close distance between α and A would give a large increase in energy. The point (3) is the saddle point in the shuffle process (also the saddle point in the whole slip process), at which the layer c is located directly above one third of the atoms in the next-nearest kagome layer B . The layer α is directly above another one third of the atoms in the kagome layer B , which is the third-nearest layer to α . At the end of this stage, the stacking sequence of the triple layer changes from $\beta c \alpha$ of configuration (2) to $\beta a \gamma$ of configuration (4).

(III) The slip switches back to plane 1 for crystallographic slip. In this final stage, all the atoms in the upper half-crystal move again in the slip direction. Since the

moving frontier of the dislocation core switches between plane 1 and plane 2, the whole slip process is called the undulating slip.

Configurations (2) and (4) in Fig. 3 can be considered as the transition points between the crystallographic slip and the atomic shuffling. High-resolution electron microscopy images were simulated based on their atomic configurations, as shown as the upper two images in Fig. 3(d). They match well with the experimental images [the corresponding lower two in Fig. 3(d)] at the dislocation core, consistent with the undulating slip mechanism described above. The intermediate states within the shuffling process, which are of high energies, are not observable in the current static study. In this regard, the ultrafast electron microscopy (or 4D electron microscopy) [21] could give interesting results when atomic resolution is realized there in the future.

The onset of plastic deformation is controlled by the atomic shuffling which is closely related with the thermal activation of atoms in the triple layers. This is probably the reason that dislocations were only observed in the present alloys deformed at high temperatures. Atoms with different activation energies in the triple layers could facilitate or impede the atomic shuffling, and hence influence the nucleation and motion of dislocations at a given temperature. These observations should help understand alloying effects on plastic deformation of such brittle materials [22]. It may shed new light on the means for lowering the BDT temperature and thus improving the formability of these materials at lower temperatures. The feature of thermal activation will also help understand the high hardness of Laves phases [6], as hardness is high when plastic deformation is prevented [23,24].

The occurrence of this novel slip mechanism is likely due to the fact that the low initial energy plays an important role in the dislocation slip. According to the generalized stacking fault model by shearing two blocks of material against each other [25], the energy profiles of synchroshear [26,27] and crystallographic slip [20] have also been calculated by the first-principles method [Fig. 3(e)]. Conventionally, the unstable stacking energy γ_{us} is frequently used to judge the slip mechanisms. Therefore, the synchroshear slip, which operates only within the triple layers but has lower γ_{us} than the crystallographic slip, could be regarded as energetically most favorable [20]. In the present study, however, the lower initial energy of crystallographic slip suggests that the weakly bonded plane in a structure is the location to start a slip process. In the undulating slip mechanism, after lowering the initial energy by starting with the crystallographic slip, the overall γ_{us} is actually also reduced.

Strain analysis.—Figure 4(a) shows a strain map of the ϵ_{xx} component, i.e., the strain along the slip direction, at the atomic scale determined from an experimental high-resolution image of the dislocation by the LADIA method

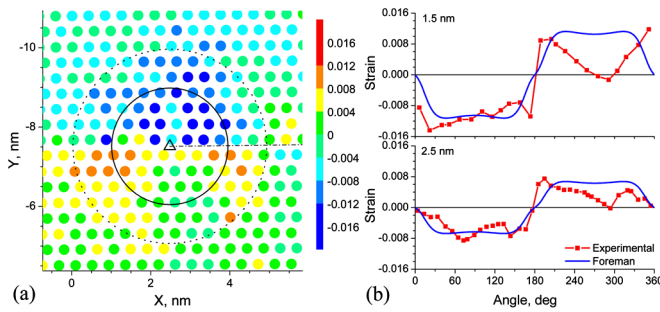


FIG. 4 (color online). Results of the strain field analysis. (a) ϵ_{xx} strain map obtained from an experimental HRTEM image of the dislocation by the LADIA method. The triangle denotes the center of the dislocation core and circles mark the location of measurements shown in Fig. 4(b) with distances of 1.5 nm (solid line) and 2.5 nm (dotted line), respectively, from the core. (b) Angular variation of strain fields measured experimentally and calculated with the Foreman model.

[10,11]. It clearly shows that the strain is compressive in the region of the extra half-plane above the dislocation, and tensile below the dislocation as expected. Nevertheless, while the compressive strain concentrates around the area right above the dislocation, the tensile strain locates in two petal-shaped areas. In order to analyze the strain field around the dislocation, two circles with distances of 1.5 and 2.5 nm, respectively, from the dislocation core were selected to measure the variation of the strain with the azimuth angle [Fig. 4(b)]. The experimental strain profiles satisfactorily agree with calculated results with the Foreman model [28] except for the area right below the core. This suggests that the strain or stress field of dislocations should be calculated with the consideration of the lattice structure of dislocation cores in such complex-structured crystals, as where complex dissociations of dislocations are likely to take place.

As there are similar stacking sequences in C15 and C14 structures, our results may be directly applied to understand the mechanical behavior of materials of these structures, and to design new alloys with improved ductility and toughness. In a broader view, the aberration-corrected electron microscopy, the first-principles NEB calculations, and the lattice distortion analysis show their potential for revealing the dynamic processes of dislocations in complex materials, or relatively simple materials but with complex dislocation behaviors involved (like silicon [29,30]).

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