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RPPR Final Report

as of 03-May-2018

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INVESTIGATOR(S):

Name: Carl C. Koch
Email: cckoch@ncsu.edu
Phone Number: 91951573400000
Principal: N

Name: Yuntian Zhu
Email: ytzhu@ncsu.edu
Phone Number: 9195130559
Principal: Y

Organization: **North Carolina State University**

Address: 2701 Sullivan Drive, Raleigh, NC 276957514

Country: USA

DUNS Number: 042092122

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Final Report for Period Beginning 05-Dec-2011 and Ending 04-Sep-2015

Title: Probing Deformation Mechanisms of Nanostructured Mg Alloys for Unprecedented Strength and Good Ductility

Begin Performance Period: 05-Dec-2011

End Performance Period: 04-Sep-2015

Report Term: 0-Other

Submitted By: Yuntian Zhu

Email: ytzhu@ncsu.edu

Phone: (919) 513-0559

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STEM Degrees: 4

STEM Participants: 4

Major Goals: The major goal of the proposed project is to probe fundamental deformation mechanisms with an aim to produce ultrastrong Mg alloys with good ductility. Both alloying and nanocrystallization will be used as effective tools to activate deformation mechanisms that might yield high strength and good ductility. This proposed project is a continuation of our ARO Short Term Innovative Research (STIR) project, which has successfully demonstrated the possibility of producing deformation twins and stacking faults in Mg alloys. Specifically, this project will probe the following three fundamental issues:

- 1) Deformation twinning in nanostructured Mg alloys and the effect of grain size.
- 2) Grain boundary mediated dislocation activities, including partials that create stacking faults on the basal plane.
- 3) Formation of clusters of alloy elements and second phase particles assisted by dislocations and grain boundaries, and the interactions between them.

The mechanical behaviors of the nanostructured Mg and its alloys will also be studied to reveal how the deformation mechanisms affect the mechanical properties, which is the secondary focus of the proposed project. The knowledge obtained in this study will be used to guide the design of nanostructured Mg alloys for superior mechanical properties.

Accomplishments: 1. Discovered a previously-unobserved metastable phase (bT). The bT phase is found to have an orthorhombic structure with a stoichiometry of Mg₅RE. The details was reported Phil. Mag.
2. We studied the effect of Ag on segregation of alloy elements at twin boundaries, stacking faults and grain boundaries in the Mg-Gd system. Specifically, for the first time a spinal-shaped periodic segregation is observed at the { } twin boundary and high-angle lamellar grain boundary in a Mg-Gd-Y-Zr alloy due to the presence of the Ag addition. The segregation consists of Gd- and Ag-rich columns. It appears that high Ag content in the spinal-shaped segregation induces fcc-like cells structures. This as reported in Acta Materialia.
3. We also made for the first time in-situ atomic-scale observation of the nucleation and growth of voids in hexagonal close-packed magnesium under electron irradiation. The voids are found to first grow into a platelet shape, followed by a gradual transition to a nearly equiaxial geometry. The initial growth in length is controlled by slow nucleation kinetics of vacancy layers on basal facets and anisotropic vacancy diffusivity. The subsequent

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thickness growth is driven by thermodynamics to reduce surface energy. The detail was reported in a Nature Communication paper. At higher irradiation doses, we also found that some voids continued to grow while others shrank to disappear, depending on the nature of their interactions with nearby self-interstitial loops. This finding was reported in Materials Research Letters paper. Finally, we experimentally observed the formation mechanisms of c-component interstitial dislocation loops and their interactions before the formation void in Mg. This was published in Acta Materialia.

4. We analyzed dislocation interactions with SFs, and then propose a physics-based model to explain the observed relationship between yield strength and SFs spacing. Similar to the empirical Hall-Petch relationship for grain size, it is expected that this strengthening mechanism will hold true for a variety of materials engineered with parallel spaced stacking faults over a wide range of fault spacing. This was published in Applied Physics Letters.

5. We report a new strengthening mechanism, high density of SFs, in a conventional hot rolled Mg-8.5Gd-2.3Y-1.8Ag-0.4Zr (wt.%) alloy. Introducing high density of basal plane SFs was demonstrated to be effective in obstructing dislocation motion and retaining moderate strain hardening rate. As the mean spacing between adjacent SFs decreased, strength of the processed Mg alloy substantially increased without loss of ductility. An unprecedented strength and reasonably good ductility (~600 MPa of UTS, ~ 575 MPa of YS and ~ 5.2 % of uniform ductility) were obtained in the rolled Mg alloy with the mean spacing between SFs of ~16.3 nm. This was published in Materials Research Letters.

The major papers published in this project are attached.

Training Opportunities: Four Ph.D. students were trained in this project: Weiwei Jian, Weizong Xu, Xiaolong Ma and Jordan Moore.

Results Dissemination: The research results from this project have been reported in papers and over 30 conferences, workshops and academic institutions.

In addition, a high-school student, J. Malkin, from the North Carolina School of Science and Mathematics (NCSSM) has been trained, which resulted in a paper publication.

Honors and Awards: Albert Sauveur Achievement Award, ASM International, 2014.
Alcoa Foundation Distinguished Engineering Research Award, NC State University, 2014
Highly Cited Researchers 2014, among 147 in Materials Science, Thomson Reuters (ISI)
Leadership Award, TMS, 2015
IUMRS Sômiya Award, International Union of Materials Research Societies, 2015
Highly Cited Researchers 2016, Thomson Reuters (ISI)
Fellow, The Minerals, Metals and Materials Society (TMS) (2017)

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Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: Faculty

Participant: Carl C. Koch

Person Months Worked: 2.00

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: Y

Other Collaborators:

Funding Support:

Participant Type: Graduate Student (research assistant)

Participant: Weiwei Jian

Person Months Worked: 15.00

Project Contribution:

Funding Support:

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International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Weizong Xu

Person Months Worked: 8.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Xiaolong Ma

Person Months Worked: 5.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Jordan Moor

Person Months Worked: 4.00

Funding Support:

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International Collaboration:
International Travel:
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Other Collaborators:

Participant Type: Faculty

Participant: Yuntian Theodore Zhu

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Journal: Materials Research Letters
Publication Identifier Type: **Publication Identifier:**
Volume: 1 **Issue:** 2 **First Page #:** 61
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Publication Location:

Article Title: Ultrastrong, Stiff and Multifunctional Carbon Nanotube Composites

Authors:

Keywords: Stacking Faults, Mg, Strength, Ductility, Dislocations

Abstract: Mg alloys are among the lightest alloys but they are usually weak. Here we report a new mechanism to make them ultrastrong while maintaining good ductility. Stacking faults with nanoscale spacing were introduced into a Mg–8.5Gd–2.3Y–1.8Ag–0.4Zr (wt%) alloy by conventional hot rolling, which produced a yield strength of 575 MPa, an ultimate strength of 760 MPa, and a uniform elongation of 5.2 %. Low stacking fault (SF) energy enabled the introduction of a high density of SFs, which impeded dislocation slip and promoted dislocation accumulation. These findings provide guidance for developing Mg alloys with superior mechanical properties.

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Volume: 4 **Issue:** 0 **First Page #:** 2288
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Publication Location:

Article Title: In-Situ Atomic-Scale Observation of Void Formation Induced by Electron Radiation

Authors:

Keywords: Mg, irradiation, void, In-situ observation, TEM

Abstract: The formation of voids in an irradiated material significantly degrades its physical and mechanical properties. Void nucleation and growth involve discrete atomic-scale processes that, unfortunately, are not yet well understood due to the lack of direct experimental examination. Here we report for the first time in-situ atomic-scale observation of the nucleation and growth of voids in hexagonal close-packed magnesium under electron irradiation. The voids are found to first grow into a platelet shape, followed by a gradual transition to a nearly equiaxial geometry. Using atomistic simulations, we show that the initial growth in length is controlled by slow nucleation kinetics of vacancy layers on basal facets and anisotropic vacancy diffusivity. The subsequent thickness growth is driven by thermodynamics to reduce surface energy. These experiments represent unprecedented resolution and characterization of void nucleation and growth under irradiation, and might help with understanding th

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Publication Identifier Type: DOI **Publication Identifier:** 10.1080/14786435.2014.913115
Volume: 94 **Issue:** 21 **First Page #:** 0
Date Submitted: **Date Published:**
Publication Location:

Article Title: A new metastable precipitate phase in Mg–Gd–Y–Zr alloy

Authors:

Keywords: magnesium alloys; metastable phases; base-centred orthorhombic structure; phase transformations

Abstract: Mg–RE alloys are among the strongest Mg-based alloys due to their unique precipitation structures. A previously unobserved metastable phase (γ) is found to coexist with reported β and δ metastable phases under peak ageing conditions in a Mg–Gd–Y–Zr alloy. The position of the RE elements within the γ phase is identified using atomic-resolution high-angle annular dark field scanning transmission electron microscopy imaging, and the γ phase is shown to have an orthorhombic structure with a stoichiometry of Mg₅RE. Based on these observations, a new precipitation sequence is proposed.

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Journal: Materials Research letters
Publication Identifier Type: DOI **Publication Identifier:** 10.1080/21663831.2013.765927
Volume: 1 **Issue:** 2 **First Page #:** 0
Date Submitted: **Date Published:**
Publication Location:

Article Title: Ultrastrong Mg Alloy via Nano-spaced Stacking Faults

Authors:

Keywords: Stacking Faults, Mg, Strength, Ductility, Dislocations

Abstract: Mg alloys are among the lightest alloys but they are usually weak. Here we report a new mechanism to make them ultrastrong while maintaining good ductility. Stacking faults with nanoscale spacing were introduced into a Mg–8.5Gd–2.3Y–1.8Ag–0.4Zr (wt%) alloy by conventional hot rolling, which produced a yield strength of 575 MPa, an ultimate strength of 760 MPa, and a uniform elongation of 25.2 %. Low stacking fault (SF) energy enabled the introduction of a high density of SFs, which impeded dislocation slip and promoted dislocation accumulation. These findings provide guidance for developing Mg alloys with superior mechanical properties.

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Journal: Applied Physics Letters
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Article Title: Physics and model of strengthening by parallel stacking faults

Authors:

Keywords: Mg, strengthening, stacking faults, Physics

Abstract: We have recently reported that parallel stacking faults (SFs) can tremendously increase the strength of a magnesium alloy. The strengthening is found to increase linearly with the reciprocal of the mean SF spacing, d . In this study we analyze dislocation interactions with SFs, and then propose a physics-based model to explain the observed relationship between yield strength and SFs spacing. Similar to the empirical Hall-Petch relationship for grain size, it is expected that this strengthening mechanism will hold true for a variety of materials engineered with parallel spaced stacking faults over a wide range of fault spacing.

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Article Title: In-situ atomic-scale observation of irradiation-induced void formation

Authors:

Keywords: In-situ, irradiation, void formation

Abstract: The formation of voids in an irradiated material significantly degrades its physical and mechanical properties. Void nucleation and growth involve discrete atomic-scale processes that, unfortunately, are not yet well understood due to the lack of direct experimental examination. Here we report an in-situ atomic-scale observation of the nucleation and growth of voids in hexagonal close-packed magnesium under electron irradiation. The voids are found to first grow into a plate-like shape, followed by a gradual transition to a nearly equiaxial geometry. Using atomistic simulations, we show that the initial growth in length is controlled by slow nucleation kinetics of vacancy layers on basal facets and anisotropic vacancy diffusivity. The subsequent thickness growth is driven by thermodynamics to reduce surface energy. These experiments represent unprecedented resolution and characterization of void nucleation and growth under irradiation, and might help with understanding the irradiation

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Article Title: Dynamic Void Growth and Shrinkage in Mg under Electron Irradiation

Authors:

Keywords: Void, Coalescence, Growth, Electron Irradiation, Magnesium

Abstract: We report in situ atomic-scale investigation of late-stage void evolution, including growth, coalescence and shrinkage, under electron irradiation. With increasing irradiation dose, the total volume of voids increased linearly, while the nucleation rate of new voids decreased slightly and the total number of voids decreased. Some voids continued to grow while others shrank to disappear, depending on the nature of their interactions with nearby self-interstitial loops. For the first time, surface diffusion of adatoms was observed to be largely responsible for the void coalescence and thickening. These findings provide fundamental understanding to help with the design and modeling of irradiation-resistant materials.

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Volume: 111

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Date Submitted:

Date Published:

Publication Location:

Article Title: Extraordinary strain hardening by gradient structure

Authors:

Keywords: Gradient structure, Nano metls, Strain hardening, Ductility

Abstract: Gradient structures have evolved over millions of years through natural selection and optimization in many biological systems such as bones and plant stems, where the structures change gradually from the surface to interior. The advantage of gradient structures is their maximization of physical and mechanical performance while minimizing material cost. Here we report that the gradient structure in engineering materials such as metals renders a unique extra strain hardening, which leads to high ductility. The grain-size gradient under uniaxial tension induces a macroscopic strain gradient and converts the applied uniaxial stress to multiaxial stresses due to the evolution of incompatible deformation along the gradient depth. Thereby the accumulation and interaction of dislocations are promoted, resulting in an extra strain hardening and an obvious strain hardening rate up-turn. Such extraordinary strain hardening, which is inherent to gradient structures and does not exist in homogeneous

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Publication Identifier: 10.1080/21663831.2014.935821

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Article Title: Synergetic Strengthening by Gradient Structure

Authors:

Keywords: Gradient Structure, Synergetic Strengthening, Stress Gradient, Mechanical Incompatibility

Abstract: Gradient structures are characterized with a systematic change in microstructures on a macroscopic scale. Here, we report that gradient structures in engineering materials such as metals produce an intrinsic synergetic strengthening, which is much higher than the sum of separate gradient layers. This is caused by macroscopic stress gradient and the bi-axial stress generated by mechanical incompatibility between different layers. This represents a new mechanism for strengthening that exploits the principles of both mechanics and materials science. It may provide for a novel strategy for designing material structures with superior properties.

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Dislocation–twin interactions in nanocrystalline fcc metals

Y.T. Zhu^{a,*}, X.L. Wu^b, X.Z. Liao^c, J. Narayan^a, L.J. Kecskés^d, S.N. Mathaudhu^d

^a Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695, USA

^b State Key Laboratory of Nonlinear Mechanics, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

^c School of Aerospace, Mechanical and Mechatronic Engineering, University of Sydney, Sydney, NSW 2006, Australia

^d US Army Research Laboratory, Aberdeen Proving Ground, MD 21005, USA

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Abstract

Dislocation interaction with and accumulation at twin boundaries have been reported to significantly improve the strength and ductility of nanostructured face-centered cubic (fcc) metals and alloys. Here we systematically describe plausible dislocation interactions at twin boundaries. Depending on the characteristics of the dislocations and the driving stress, possible dislocation reactions at twin boundaries include cross-slip into the twinning plane to cause twin growth or de-twinning, formation of a sessile stair-rod dislocation at the twin boundary, and transmission across the twin boundary. The energy barriers for these dislocation reactions are described and compared.

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Keywords: Nanocrystalline materials; Dislocations; Twin boundaries; Interactions; fcc

1. Introduction

Twins have been reported to significantly affect the mechanical properties of nanostructured face-centered cubic (fcc) metals and alloys [1–10]. Importantly, twins have been shown to be able to simultaneously increase the strength and ductility of nanostructured metals, which is attributed to the dislocation interaction with and accumulation at twin boundaries. Since deformation twinning usually occurs simultaneously with the slip of perfect and partial dislocations, interactions between twins and gliding dislocations inevitably occur at twin boundaries. Nanocrystalline fcc metals have been found to deform via twinning more readily than their coarse grained counterparts [11–22]. This increases the probability of interactions between dislocations and twins in nanocrystalline fcc metals. Furthermore, nanocrystalline fcc metals usually have high strength, and the resulting high flow stress may provide enough driving force to activate some energetically

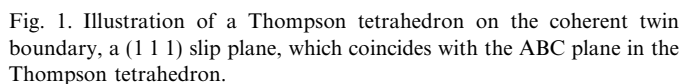
unfavorable dislocation reactions at the twin boundaries. Therefore, it is of scientific interest and practical importance to understand how the dislocations react at twin boundaries.

Dislocation reactions at twin boundaries have been observed both experimentally [2,3,23–32] and by molecular dynamics (MD) simulations [33–41]. However, no systematic investigation has been reported. It is the objective of this paper to systematically describe plausible dislocation reactions at twin boundaries.

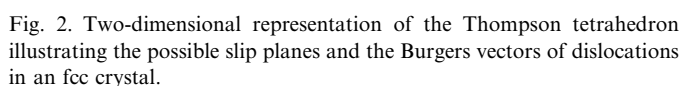
2. Possible dislocations to react with twin boundaries

There are only four types of dislocations in the fcc structure that may react at a twin boundary. They can be described with the assistance of Fig. 1, which shows a Thompson tetrahedron on the twin boundary. Note that the twin boundary is also the (1 1 1) slip plane, i.e. the ABC plane in the Thompson tetrahedron. The other three slip planes on the tetrahedron are the ACD, ABD and BCD planes. Before a dislocation reacts at a twin boundary it first needs to slip on one of these three planes. When the

* Corresponding author. Tel.: +1 919 513 0559; fax: +1 919 515 3419.
E-mail address: ytzhu@ncsu.edu (Y.T. Zhu).



To make the discussion easier, we unfold the Thompson tetrahedron onto a two-dimensional representation, as shown in Fig. 2. Assuming that a dislocation glides on the BCD, i.e. $(\bar{1}1\bar{1})$, plane toward the twin boundary, the orientation of the dislocation line will become parallel to BC when it reaches the twin boundary. From Figs. 1 and 2 it can be deduced that this dislocation can be one of four possible types: (a) a 30° Shockley partial dislocation, i.e. the partial's Burgers vector is at a 30° angle to the dislocation line; (b) a 90° Shockley partial dislocation; (c) a screw perfect dislocation with the Burgers vector parallel to the



As shown in Fig. 3c, after the $\delta\mathbf{B}$ glides to the right the twin thickness is reduced by one atomic plane, i.e. de-twinning occurred during the process. The partial $\mathbf{B}\alpha$ advances to the new twin boundary under the original applied stress, and can repeat the above process to annihilate the whole twin.

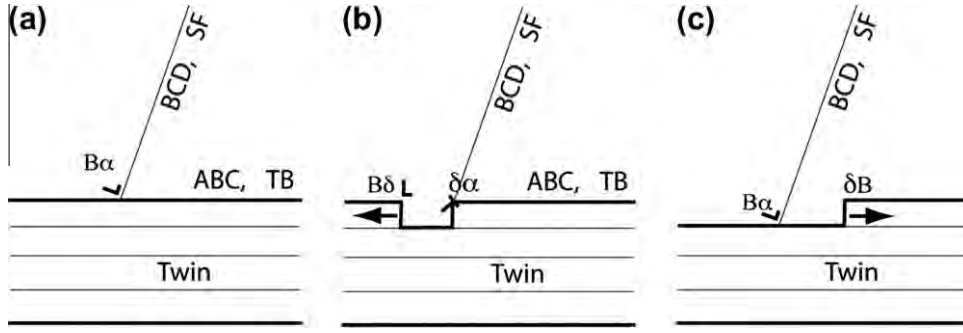


Fig. 3. De-twinning process caused by the interaction of a 30° partial, $B\alpha$, with the twin boundary. SF marks the stacking fault, TB marks the twin boundary (thick black lines). BCD and ABC represent the BCD and ABC slip planes in the Thompson tetrahedron, respectively.

There is an energy barrier to the dislocation reactions described in Eqs. (1) and (2), because the reactions increase the total energy of the dislocations. To estimate the energy barrier we invoke the isotropic elastic dislocation energy per unit dislocation line length [43]:

$$E_\beta = \frac{Gb^2(1 - \nu \cos^2 \beta)}{4\pi(1 - \nu)} \ln \frac{R}{r_0} \quad (3)$$

where E_β is the energy per unit length of a dislocation with a Burgers vector is at an angle β to the dislocation line, G is the shear modulus, ν is the Poisson's ratio, R can be estimated as the grain size d , and r_0 can be estimated as the Burgers vector b [44]. Eq. (3) can be rewritten as:

$$E_\beta = \frac{Gb^2(1 - \nu \cos^2 \beta)}{4\pi(1 - \nu)} \ln \frac{d}{b} \quad (4)$$

The dislocation core energy is not included in Eq. (4). For covalent and ionic crystals, the core energy is relatively high and also a strong function of orientation [45,46]. For metals with a close-packed structure, such as fcc metals, the core energy is about $0.1\text{--}0.05Gb^2$. The calculation of core energies of a dislocation is still a topic of computational and analytical study. One way to incorporate the core energy into Eq. (4) is to choose a smaller r_0 , i.e. $r_0 = b/\alpha$, where α can be calculated as [45]:

$$\alpha = \frac{\sqrt{3}e^{1+\gamma}(1 - \nu)}{\sqrt{2}[\sin^2 \beta + e^\gamma(1 - \nu)\cos^2 \beta]} \quad (5)$$

where $\gamma = (1 - 2\nu)/4(1 - \nu)$. Therefore, the total dislocation energy can be described as:

$$E_\beta = \frac{Gb^2(1 - \nu \cos^2 \beta)}{4\pi(1 - \nu)} \ln \frac{\alpha d}{b} \quad (6)$$

Note that for fcc metals the magnitudes of the Burgers vector are $a/\sqrt{2}$ for a perfect dislocation, $a/\sqrt{6}$ for a partial dislocation, and $a/3\sqrt{2}$ for the stair-rod dislocation $\delta\alpha$. These quantities will be used to estimate the dislocation energy changes for dislocation reactions.

The energy increase (energy barrier) for a dislocation reaction can be calculated by subtracting the total energy of the initial dislocations from that of the dislocation(s) produced by the reaction. For example, for the reaction described in Eq. (1) the energy barrier can be calculated as:

$$\Delta E_{eq,1} = E_{B\delta} + E_{\delta\alpha} - E_{B\alpha} \quad (7)$$

According to the Thompson tetrahedron both $B\alpha$ and $B\delta$ are 30° partials, i.e. $\beta = 30^\circ$, while the stair-rod dislocation $\delta\alpha$ is an edge dislocation ($\beta = 90^\circ$). Substituting Eq. (6) into Eq. (7) and using the appropriate magnitudes of Burgers vectors, the energy barrier for the dislocation reaction in Eq. (1) can be calculated as:

$$\Delta E_{eq,1}^{B\alpha \rightarrow B\delta + \delta\alpha} = \frac{Ga^2}{72\pi(1 - \nu)} \ln \frac{\sqrt{2}d}{a} + \frac{Ga^2}{72\pi(1 - \nu)} \ln 3\alpha \quad (8)$$

The first term on the right side of Eq. (8) represents the isotropic elastic energy, while the second term represents the core energy. In fact, since both $B\alpha$ and $B\delta$ are 30° partials, $E_{B\alpha} = E_{B\delta}$. This leads to $\Delta E_{eq,1}^{B\alpha \rightarrow B\delta + \delta\alpha} = E_{\delta\alpha}$. For easy comparison we will hereafter define

$$\hat{E} = \frac{Ga^2}{72\pi(1 - \nu)} \ln \frac{\sqrt{2}d}{a} = \tilde{E} \ln \frac{\sqrt{2}d}{a} \quad (9)$$

Assuming hereafter that the Poisson's ratio is approximately 1/3, which is a reasonable approximation for most fcc metals, one can easily calculate $\Delta E_{eq,1}^{B\alpha \rightarrow B\delta + \delta\alpha} = \hat{E} + 2.0\tilde{E}$. Note that $\hat{E}$ is much larger than $\tilde{E}$. For example, assuming the grain size is 50 nm and a is 0.4 nm, we have $\hat{E} \approx 5\tilde{E}$.

Following a similar procedure, the energy barrier for the dislocation reaction in Eq. (2) can be calculated as:

$$\begin{aligned} \Delta E_{eq,2}^{\delta\alpha \rightarrow \delta B + B\alpha} &\approx \frac{Ga^2(10 - 9\nu)}{144\pi(1 - \nu)} \ln \frac{\sqrt{2}d}{a} + 5.5\tilde{E} \\ &\approx 3.5\hat{E} + 5.5\tilde{E} \end{aligned} \quad (10)$$

This indicates that the second reaction requires a much higher applied stress to overcome the energy barrier. If the applied stress is high enough to activate the reaction described in Eq. (1) but not the reaction in Eq. (2), then a step will be produced at the twin boundary. Twin boundaries with steps have been extensively studied experimentally and by MD simulations [33,36,37]. For example, Yamakov et al. [36] show that a partial dislocation can interact with a twin boundary, which forms a stair-rod dislocation and a step at the twin boundary and, consequently, thickens or reduces the twin by one atomic layer.

3.2. Transmission of the 30° partial across the twin boundary

To understand how the 30° partial $B\alpha$ on the BCD slip plane can be transmitted across the twin boundary we need to invoke the double Thompson tetrahedron [28], illustrated in Fig. 4. As shown, the Thompson tetrahedron above the (1 1 1) twin boundary represents matrix slip systems, while the bottom tetrahedron represents twin slip systems. The twin boundary plane is shared by the matrix above it and the twin below it. Therefore, the matrix tetrahedron and the twin tetrahedron share the same base, which is ABC. In other words, dislocations with Burgers vectors AB , BC , CA , $A\delta$, $B\delta$, and $C\delta$ can slip both in the matrix and in the twin.

From Fig. 4 the 30° partial $B\alpha$ on the BCD slip plane in the matrix, can have the following dislocation reaction to release another partial in the twin:



where $B\alpha'$ is a partial that can slip away in the twin from the twin boundary on the BCD' plane, and $\alpha'\alpha$ is a new type of stationary stair-rod dislocation across the twin boundary. Since the dislocation line is parallel to BC, it can be seen from Fig. 4 that $\alpha'\alpha$ is an edge dislocation with its Burgers vector perpendicular to both the dislocation line and the twin boundary (1 1 1). The magnitude of $\alpha'\alpha$ can be calculated from the geometry of the double tetrahedron as $2a/3\sqrt{3}$. The dislocation configuration after the reaction is illustrated in Fig. 5, which shows two stacking faults from the two sides of the twin boundary meeting at the twin boundary and connected by the stair-rod dislocation $\alpha'\alpha$.

The energy barrier of the dislocation reaction described in Eq. (11) can be calculated as:

$$\begin{aligned} \Delta E_{Eq11}^{B\alpha \rightarrow B\alpha' + \alpha'\alpha} &\approx \frac{Ga^2}{27\pi(1-\nu)} \ln \frac{\sqrt{2}d}{a} + 4.1\tilde{E} \\ &\approx 2.7\tilde{E} + 4.1\tilde{E} \end{aligned} \quad (12)$$

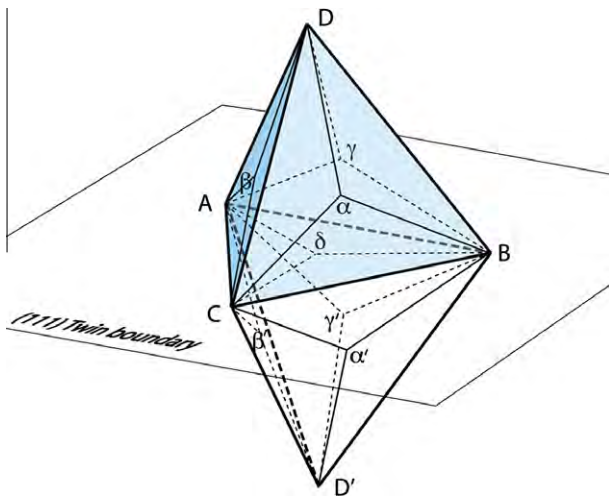


Fig. 4. Illustration of a double Thompson tetrahedron. The top tetrahedron above the (1 1 1) twin boundary represents matrix slip systems, while the bottom tetrahedron represents twin slip systems.

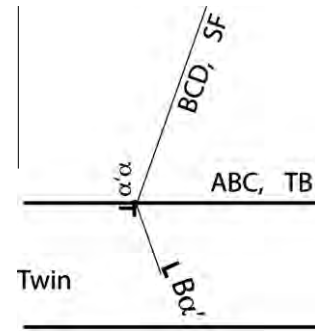


Fig. 5. The dislocation configuration after the partial $B\alpha$ penetrates the twin boundary to release another partial $B\alpha'$ on the BCD' plane inside the twin, leaving a stair-rod dislocation $\alpha'\alpha$ on the twin boundary. This configuration is viewed from the BC orientation.

This indicates that the energy barrier for the 30° partial $B\alpha$ to be transmitted across the twin boundary is smaller than that in reaction 2, suggesting that this scenario is energetically plausible under an appropriate applied stress.

4. A 90° partial at the twin boundary

Assuming that a 90° Shockley partial dislocation $D\alpha$ glides on the BCD plane towards the coherent twin boundary, we describe plausible dislocation reactions at the twin boundary below.

4.1. Cross-slip of the 90° partial at the twin boundary

The cross-slip of 90° partials at the coherent twin boundary has been reported to be responsible for the formation of fivefold twins [47,48], which have been experimentally observed and also verified by MD simulation [49]. Since this has been reported before, we will give only a brief description here.

A deformation twin can be defined by the twin plane K_1 , shear direction η_1 , undistorted plane K_2 , and direction η_2 (see Fig. 6) [45]. Deformation twins in an fcc metal are of compound type, in which a twin formed by Shockley partials with Burgers vectors parallel to η_1 gliding on K_1 is the same as a twin formed by partials with Burgers vectors parallel to η_2 gliding on K_2 . In the current situation K_1 and K_2 correspond to the ABC and BCD planes in the Thompsons tetrahedron, respectively. η_1 is parallel to the 90° partial $A\delta$ and η_2 is parallel to another 90° partial $D\alpha$. In other words, when the 90° partial $D\alpha$ on the BCD plane reaches the twin boundary it becomes equivalent to another 90° partial $A\delta$ on the ABC plane. Under an appropriate external shear stress the $A\delta$ partial could glide to the left or right, which consequently grows or shrinks the twin by one atomic layer. Note that since both $D\alpha$ and $A\delta$ are the same type of partial, there is no energy change (barrier) in this dislocation reaction. Therefore, orientation of the applied stress becomes a critical factor influencing this cross-slip.

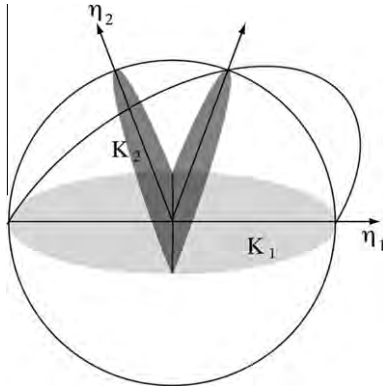


Fig. 6. Illustration of twinning elements η_1 , η_2 , K_1 and K_2 .

4.2. Transmission of the 90° partial across the twin boundary

To understand how a 90° partial $D\alpha$ can be transmitted across the twin boundary to activate a partial dislocation in the twin we need to take a careful look at the double Thompson tetrahedron to determine the dislocation reactions that can translate the Burgers vector of the 90° partial into a partial in the twin. As shown in Fig. 4, the 90° partial $D\alpha$ can dissociate as:

$$D\alpha \rightarrow D\delta + \delta\alpha \quad (13)$$

The double Thompson tetrahedron indicates that the Burgers vector $D\delta$ is identical to $\delta D'$ in the twin, i.e. $D\delta = \delta D'$, which can dissociate into a 90° partial $\alpha' D'$ and a stair-rod dislocation $\delta\alpha'$, i.e.

$$D\delta = \delta D' \rightarrow \delta\alpha' + \alpha' D' \quad (14)$$

The 90° partial $\alpha' D'$ can glide in the twin to move away from the twin boundary. Other similar reactions that can also produce a 90° partial include:

$$\delta D' \rightarrow \delta\beta' + \beta' D' \quad (15)$$

and

$$\delta D' \rightarrow \delta\gamma' + \gamma' D' \quad (16)$$

The 90° partials $\beta' D'$ and $\gamma' D'$ can glide on the ACD' and ABD' slip planes, respectively, in the twin.

The magnitude of $D\delta$ and $\delta D'$ is $a/\sqrt{3}$ according to the double Thompson tetrahedron. The energy barrier of the dislocation reaction described in Eq. (13) can be calculated as:

$$\Delta E_{Eq13}^{D\alpha \rightarrow D\delta + \delta\alpha} \approx \frac{Ga^2}{18\pi(1-\nu)} \ln \frac{\sqrt{2}d}{a} + 4.4\tilde{E} = 4\hat{E} + 4.4\tilde{E} \quad (17)$$

The energy barrier of the dislocation reaction described in Eq. (14) can be calculated as:

$$\Delta E_{Eq14}^{\delta D' \rightarrow \delta\alpha' + \alpha' D'} \approx -\frac{Ga^2}{36\pi(1-\nu)} \ln \frac{\sqrt{2}d}{a} - 0.3\tilde{E} \approx -2\hat{E} - 0.3\tilde{E} \quad (18)$$

The energy barriers for the reactions in Eqs. (15) and (16) are the same as that in Eq. (14). Therefore, the dislocation reaction described in Eq. (13) has a very high energy barrier while the reactions in Eqs. (14)–(16) are energetically favorable.

The high energy barrier in Eq. (13) is caused by creation of the dislocation $D\delta$ (or $\delta D'$), which has a large Burgers vector with a magnitude of $a/\sqrt{3}$. If the dislocation reaction path changes to avoid the formation of $D\delta$ ($\delta D'$), the energy barrier will be lower. Assuming that the dislocation reactions in Eqs. (13)–(15) take place in one step without forming $D\delta$ ($\delta D'$), we can substitute Eq. (14) into Eq. (13), which yields:

$$D\alpha \rightarrow \delta\alpha + \delta\alpha' + \alpha' D' \quad (19)$$

Similarly, $\beta' D'$ and $\gamma' D'$ can also be formed by the following reactions:

$$D\alpha \rightarrow \delta\alpha + \delta\beta' + \beta' D' \quad (20)$$

and

$$D\alpha \rightarrow \delta\alpha + \delta\gamma' + \gamma' D' \quad (21)$$

The energy barrier for the reaction in Eq. (19) can be calculated as:

$$\Delta E_{Eq19}^{D\alpha \rightarrow \delta\alpha + \delta\alpha' + \alpha' D'} \approx \frac{Ga^2}{36\pi(1-\nu)} \ln \frac{\sqrt{2}d}{a} + 4.0\tilde{E} \approx 2.0\hat{E} + 4.0\tilde{E} \quad (22)$$

Therefore, the energy barrier for the reaction in Eq. (19) is half of the energy barrier in Eq. (13). The energy barriers for the reactions in Eqs. (20) and (21) are identical to that in Eq. (19).

There are two stair-rod dislocations in Eqs. (19)–(21). Both stair-rod dislocations remain at the twin boundary and could react to form a dislocation structure with lower energy. With the help of the double Thompson tetrahedron the stair-rod reactions can be described by:

$$\delta\alpha + \delta\alpha' \rightarrow 4/9A\delta \quad (23)$$

$$\delta\alpha + \delta\beta' \rightarrow 2/9\delta C \quad (24)$$

$$\delta\alpha + \delta\gamma' \rightarrow 2/9\delta B \quad (25)$$

Substituting Eqs. (23)–(25) into Eqs. (19)–(21) yields:

$$D\alpha \rightarrow 4/9A\delta + \alpha' D' \quad (26)$$

$$D\alpha \rightarrow 2/9\delta C + \beta' D' \quad (27)$$

and

$$D\alpha \rightarrow 2/9\delta B + \gamma' D' \quad (28)$$

The energy barrier for reaction in Eq. (26) is:

$$\Delta E_{Eq26}^{D\alpha \rightarrow 4/9A\delta + \alpha' D'} \approx \frac{2Ga^2}{243\pi(1-\nu)} \ln \frac{\sqrt{2}d}{a} + 1.4\tilde{E} \approx 0.6\hat{E} + 1.4\tilde{E} \quad (29)$$

The energy barriers for the reactions in Eqs. (27) and (28) are:

$$\Delta E_{Eq27,28} \approx \frac{2Ga^2(1-3\nu/4)}{486\pi(1-\nu)} \ln \frac{\sqrt{2}d}{a} + 0.2\tilde{E} \approx 0.1\hat{E} + 0.2\tilde{E} \quad (30)$$

Therefore, the energy barriers for dislocation reactions in Eqs. (26)–(28) are very low, which makes it easier for the 90° partial $\mathbf{D}\alpha$ to be transmitted across the twin boundary to emit another 90° partial in the twin. However, it is also noted that the reaction products in these equations include dislocations with Burgers vectors that are a fraction of that of a partial, which may make the energy higher than described in Eqs. (29) and (30), since they do not correspond to stable or metastable atomic positions.

5. Reaction of a perfect screw dislocation at the twin boundary

If we assume that a perfect screw dislocation $\mathbf{BC}$ glides on the BCD plane toward the twin boundary (see Fig. 4) it could be dissociated into two 30° partials with a stacking fault in between, i.e.



when this dissociated $\mathbf{BC}$ reaches the twin boundary it could constrict to again form a perfect dislocation. Since $\mathbf{BC}$ is parallel to the dislocation line, it can either cross-slip into the ABC plane on the twin boundary or onto the BCD' plane in the twin, depending on the orientation of the applied stress. Therefore, a screw dislocation can easily cross-slip on the twin boundary or be transmitted across the twin boundary. The interaction of a screw dislocation with a coherent twin boundary has been observed by MD simulation [34].

6. Reaction of a perfect 60° dislocation at the twin boundary

If we assume that a perfect 60° dislocation $\mathbf{BD}$ glides on the BCD plane towards the twin boundary (see Fig. 4) it could be dissociated into a 30° partial $\mathbf{B}\alpha$ and a 90° partial $\alpha\mathbf{D}$ with a stacking fault between them, i.e. $\mathbf{BD} \rightarrow \mathbf{B}\alpha + \alpha\mathbf{D}$. These partials ($\mathbf{B}\alpha$ and $\alpha\mathbf{D}$) with a stacking fault ribbon can glide together under an applied stress towards the twin boundary. Since the perfect 60° dislocation cannot easily cross-slip or be transmitted across the twin boundary, there are several plausible scenarios that could occur, which are described below.

6.1. Perfect dislocation $\mathbf{BD}$ constricts before reaction

We begin by describing the scenario where the partials are constricted to form the perfect dislocation $\mathbf{BD}$ before the dislocation reacts at the twin boundary. Such a scenario can happen more easily when the stacking fault energy is relatively high and the distance between the leading and trailing partials is small. This has been observed experimentally [32] and by MD simulations [33,35,50]. It can be seen from the double Thompson tetrahedron (Fig. 4) that $\mathbf{BD}$ is

at a 60° angle to the dislocation line $\mathbf{BC}$. The dislocation reaction for $\mathbf{BD}$ to cross-slip onto the ABC plane is:



The energy barrier for such a reaction is:

$$\Delta E_{Eq32}^{BD \rightarrow BC+CD} \approx \frac{Ga^2}{8\pi} \ln \frac{\sqrt{2}d}{a} + 7.2\tilde{E} \approx 6\hat{E} + 7.2\tilde{E} \quad (33)$$

This energy barrier is so high that such a cross-slip is almost impossible.

Another possible dislocation reaction is for $\mathbf{BD}$ to be transmitted across the twin boundary to emit a perfect dislocation in the twin. The following analysis yields possible dislocation reactions. First, $\mathbf{BD}$ can dissociate according to:



where $\delta\mathbf{D}$ is equivalent to $\mathbf{D}'\delta$, which can further react to emit perfect dislocations in the twin according to:



Substituting Eqs. (35)–(37) into Eq. (34), and also considering $\mathbf{B}\delta + \mathbf{A}\delta = \delta\mathbf{C}$ and $\mathbf{B}\delta + \mathbf{C}\delta = \delta\mathbf{A}$, we have:



The energy barriers for the dislocation reactions in Eqs. (38)–(40) can be described by:

$$\begin{aligned} \Delta E_{Eq38}^{BD \rightarrow 2B\delta+D'B} &\approx \frac{Ga^2(1-3\nu/4)}{12\pi(1-\nu)} \ln \frac{\sqrt{2}d}{a} + 7.5\tilde{E} \\ &\approx 4.5\hat{E} + 7.5\tilde{E} \end{aligned} \quad (41)$$

$$\begin{aligned} \Delta E_{Eq39}^{BD \rightarrow \delta C+D'A} &\approx \frac{Ga^2}{24\pi(1-\nu)} \ln \frac{\sqrt{2}d}{a} + 3.9\tilde{E} \\ &\approx 3.0\hat{E} + 3.9\tilde{E} \end{aligned} \quad (42)$$

$$\begin{aligned} \Delta E_{Eq40}^{BD \rightarrow \delta A+D'C} &\approx \frac{Ga^2}{24\pi(1-\nu)} \ln \frac{\sqrt{2}d}{a} + 3.9\tilde{E} \\ &\approx 3.9\hat{E} + 3.9\tilde{E} \end{aligned} \quad (43)$$

Therefore, the dislocation reactions in Eqs. (39) and (40) have smaller energy barriers. In these two reactions one partial will glide on the twin plane, which will grow or shrink the twin by one atomic plane and leave behind a step on the twin boundary depending on the gliding direction. At the same time a perfect 60° dislocation is emitted in the twin, which will also produce a step on the twin boundary. In comparison, the dislocation reaction in Eq. (38) will release two partials on the ABC plane, which may grow or shrink the twin by two atomic planes if they glide on two slip planes.

6.2. 30° leading partial $\mathbf{B}\alpha$ reacts first at the twin boundary

If we assume that the 60° dislocation $\mathbf{BD}$ glides on the BCD plane toward the twin boundary it can be dissociated

as $\mathbf{BD} \rightarrow \mathbf{B}\alpha + \alpha\mathbf{D}$, with the 30° partial $\mathbf{B}\alpha$ as the leading partial. The leading partial $\mathbf{B}\alpha$ could either cross-slip onto the twin boundary plane or be transmitted across the twin boundary. We will discuss these two cases below.

6.2.1. Leading 30° partial $\mathbf{B}\alpha$ cross-slip onto the twin boundary plane

When the stacking fault energy is relatively low and under an appropriate applied stress $\mathbf{B}\alpha$ can cross-slip onto the ABC twin boundary plane to emit a partial $\mathbf{B}\delta$ following the dislocation reaction described in Eq. (1), leaving behind a stair-rod dislocation $\delta\alpha$ and the 90° partial $\alpha\mathbf{D}$, still on the BCD plane, as shown in Fig. 7a. Such a dislocation structure has been observed both experimentally [3,51] and by MD simulation [9,33,37], and it has been assumed to be very effective in blocking other dislocations and, consequently, causing strain hardening [9].

As shown in Fig. 7a, under a high applied stress the trailing partial $\alpha\mathbf{D}$ may be driven to the twin boundary to react with the stair-rod dislocation $\delta\alpha$:



The energy barrier for this reaction is:

$$\begin{aligned} \Delta E_{Eq44}^{\delta\alpha + \alpha\mathbf{D} \rightarrow \delta\mathbf{D}} &\approx -\frac{Ga^2}{36\pi(1-\nu)} \ln \frac{\sqrt{2}d}{a} + 0.3\tilde{E} \\ &\approx -2\hat{E} + 0.3\tilde{E} \end{aligned} \quad (45)$$

Therefore, the dislocation reaction in Eq. (44) is energetically favorable.

From the double Thompson tetrahedron $\delta\mathbf{D}$ is equivalent to $\mathbf{D}'\delta$. The latter can dissociate as:



where $\mathbf{D}'\alpha'$ can slip away on the BCD' plane in the twin. This scenario is schematically illustrated in Fig. 7b. The energy barrier for this reaction is:

$$\begin{aligned} \Delta E_{Eq46}^{\mathbf{D}'\delta \rightarrow \mathbf{D}'\alpha' + \alpha'\delta} &\approx \frac{Ga^2}{36\pi(1-\nu)} \ln \frac{\sqrt{2}d}{a} - 0.3\tilde{E} \\ &\approx 2\hat{E} - 0.3\tilde{E} \end{aligned} \quad (47)$$

This energy barrier is reasonably low for it to occur during real deformation.

Another scenario is for the stair-rod dislocation $\delta\alpha$ in Fig. 7a to further dissociate into two partial dislocations

according to Eq. (2), $\delta\alpha \rightarrow \delta\mathbf{B} + \mathbf{B}\alpha$, where the partial $\delta\mathbf{B}$ glides on the twin boundary in the opposite direction to $\mathbf{B}\delta$ to reduce the twin thickness by one atomic plane, as illustrated in Fig. 7c. Such a process can be repeated to reduce the twin, as described in Section 3.1. The energy barrier for such a reaction is about $3.5\hat{E} + 5.5\tilde{E}$, making it more difficult than the reaction in Eq. (46). The cutting of a stacking fault by a dislocation has been observed by MD simulation [36]. The de-twinning process is similar to cutting of the stacking fault, suggesting that such a scenario could happen under an appropriate applied stress.

6.2.2. Leading 30° partial $\mathbf{B}\alpha$ transmits across the twin boundary

As discussed in Section 3.2 (see Eq. (11) and Fig. 5), the 30° partial $\mathbf{B}\alpha$ may be transmitted across the twin boundary, leaving behind a large stair-rod dislocation $\alpha\alpha'$. If the trailing partial $\alpha\mathbf{D}$ remains on the BCD plane it will have a unique dislocation configuration where one stacking fault links $\alpha\alpha'$ with partial $\mathbf{B}\alpha'$, while another stacking fault links $\alpha\alpha'$ with trailing partial $\alpha\mathbf{D}$, as shown in Fig. 8a. The trailing partial $\alpha\mathbf{D}$ can also cross-slip onto the twin boundary plane, becoming a partial $\delta\mathbf{A}$ that slips to the left to increase the twin by one atomic plane (as described in Section 4.1), forming a dislocation configuration, as shown in Fig. 8b.

The trailing partial $\alpha\mathbf{D}$ can also react with the stair-rod $\alpha\alpha'$ and be transmitted across the twin boundary considering $\alpha\mathbf{D} \rightarrow \delta\mathbf{D} + \alpha\delta$ and $\alpha\alpha' \rightarrow \delta\alpha + \alpha'\delta$:



From the double Thompson tetrahedron (Fig. 4) it can be seen that $\delta\mathbf{D} = \mathbf{D}'\delta = \alpha'\delta + \mathbf{D}'\alpha'$. Therefore, Eq. (48) can be rewritten as:



The energy barrier for the reaction in Eq. (49) can be described by:

$$\Delta E_{Eq49}^{\mathbf{D}\alpha + \alpha\alpha' \rightarrow 2\alpha'\delta + \mathbf{D}'\alpha'} \approx \frac{Ga^2}{18\pi(1-\nu)} \ln \frac{\sqrt{2}d}{a} = 4\hat{E} \quad (50)$$

The dislocation reaction in Eq. (49) can release one partial ($\mathbf{D}'\alpha'$) in the twin, leaving behind a double stair-rod dislocation ($2\delta\alpha'$). However, this reaction apparently has a high energy barrier.

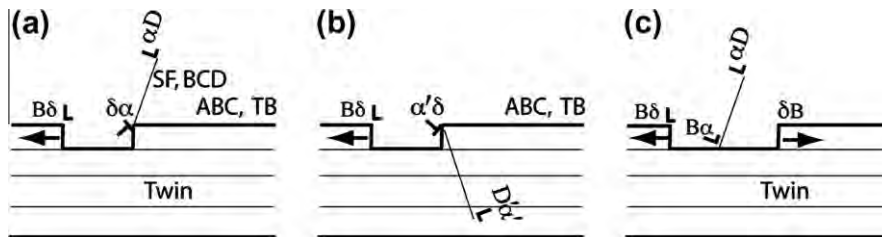


Fig. 7. Reaction of dissociated 60° dislocation $\mathbf{BD}$ with a 30° leading partial at the twin boundary. (a) The leading partial cross-slips onto the ABC twin boundary, leaving behind a stair-rod dislocation and the 90° trailing partial still on the original BCD slip plane. (b) After the trailing partial $\alpha\mathbf{D}$ reacts with the stair-rod dislocation $\delta\alpha$ and transmits across the twin boundary (Eqs. (44) and (46)). (c) The stair-rod dislocation dissociates according to $\delta\alpha \rightarrow \delta\mathbf{B} + \mathbf{B}\alpha$ to reduce the twin by one atomic layer.

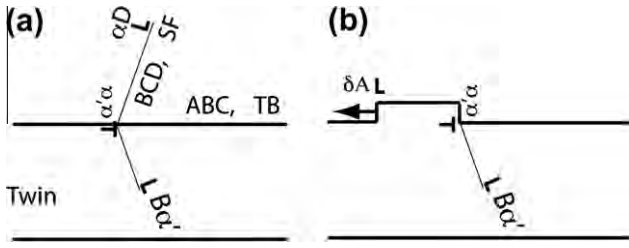


Fig. 8. (a) Dislocation configuration after the leading 30° partial $B\alpha$ transmits across the twin boundary and the trailing 90° partial αD remains on the BCD plane. (b) After the trailing partial αD cross-slips into the ABC plane to grow the twin by one atomic plane.

Similarly to Eqs. (36) and (37), δD could also dissociate according to the two equations: $\delta D = D'\delta = D'\beta' + \beta'\delta$ and $\delta D = D'\delta = D'\gamma' + \gamma'\delta$. However, the final energy barrier for such reactions will be even higher than that of the reaction in Eq. (49). Therefore, these reactions will not be described in detail here.

6.3. 90° leading partial αD reacts first at the twin boundary

If the 90° leading partial αD is the leading partial it could either cross-slip onto the twin boundary plane or transmit across the twin boundary. We will discuss these two cases below.

6.3.1. Leading 90° partial αD cross-slips onto the twin boundary plane

The leading partial αD can cross-slip to form δA , which slips on the twin boundary plane ABC as described in Section 4.1. The trailing partial $B\alpha$ can also cross-slip onto the twin boundary to form $B\delta$ on the ABC plane, following the procedure described in Section 3.1, leaving behind a stair-rod dislocation $\delta\alpha$. $B\delta$ and δA can glide together on the twin boundary with a stacking fault between them.

On the other hand, the trailing 30° partial $B\alpha$ can also be transmitted across the twin boundary to emit a partial $B\alpha'$ in the twin, as described in Section 3.2 and Fig. 5. This leaves behind a stair-rod $\alpha'\alpha$ at the twin boundary.

6.3.2. Leading 90° partial αD transmits across the twin boundary

The leading partial αD can be transmitted across the twin boundary, which is energetically not too difficult, as described in Section 4.2. With the help of Eqs. (19)–(21) in Section 4.2, which describe the dislocation reactions of $D\alpha$, the αD reactions for transmission across the twin boundary can be described by:

$$\alpha D \rightarrow \alpha\delta + \alpha'\delta + D'\alpha' \quad (51)$$

$$\alpha D \rightarrow \alpha\delta + \beta'\delta + D'\beta' \quad (52)$$

and

$$\alpha D \rightarrow \alpha\delta + \gamma'\delta + D'\gamma' \quad (53)$$

where the partial dislocations $D\alpha'$, $D'\beta'$ or $D'\gamma'$ will glide away in the twin, leaving behind two stair-rod dislocations

at the twin boundary. When the trailing partial $B\alpha$ reaches the twin boundary it can react with the stair-rod dislocation in all three cases, i.e.

$$B\alpha + \alpha\delta \rightarrow B\delta \quad (54)$$

This reaction is energetically favorable with an energy reduction of $-\hat{E} - 2.0\tilde{E}$. The $B\delta$ can glide on the ABC plane, which either increases or reduces the twin thickness by one atomic plane, depending on the slip direction. The slip direction is determined by the orientation of the applied shear stress.

The trailing partial $B\alpha$ can also react with stair-rod dislocations (as shown in Eqs. (51)–(53)) at the twin boundary to release a Shockley partial dislocation in the twin:

$$B\alpha + \alpha\delta + \alpha'\delta \rightarrow B\alpha' + 2\alpha'\delta \quad (55)$$

$$B\alpha + \alpha\delta + \beta'\delta \rightarrow B\alpha' + \alpha'\delta + \beta'\delta \quad (56)$$

and

$$B\alpha + \alpha\delta + \gamma'\delta \rightarrow B\alpha' + \alpha'\delta + \gamma'\delta \quad (57)$$

At first sight the energy barrier should be 0 for the reactions in Eqs. (55)–(57) because the number of partial dislocations and stair-rod dislocations do not change. However, as described in Eqs. (23)–(25), the reacting stair-rod dislocation pairs on the left can combine to form a dislocation with lower energy, while the stair-rod dislocation pairs on the right form a dislocation with higher energy when they combine together. These energy differences can be regarded as the energy barrier, which are described by:

$$\Delta E_{Eq55} \approx \frac{23Ga^2}{486(1-\nu)} \ln \frac{\sqrt{2}d}{a} + 2.7\tilde{E} \approx 3.4\hat{E} + 2.7\tilde{E} \quad (58)$$

$$\Delta E_{Eq56,Eq57} \approx 2.8\hat{E} + 3.7\tilde{E} \quad (59)$$

Therefore, the energy barrier for the trailing 30° partial to be transmitted across the twin boundary is very high.

7. Discussion

Plausible dislocation reactions at the twin boundaries and the energy barriers associated with the reactions are listed in Table 1. It should be noted that the energy barrier is not the only factor that determines a dislocation reaction. Other factors that may play a role in the dislocation reaction include the orientation and magnitude of the applied stress, as well as the stacking fault energy of the material. If the grains are nearly randomly oriented without much texture it can be assumed that the orientation of the applied stress does not affect the global probability of which types of dislocation reaction occur.

Stacking fault energy should play a significant role in determining which types of dislocation reaction predominantly occur. Specifically, if the stacking fault energy is relatively high it will be difficult for partial dislocations to nucleate and slip, which leads to fewer interactions

Table 1

Summary of dislocation reactions at twin boundaries and their isotropic energy barriers. TB = twin boundary, which is the ABC plane.

Reaction description	Equation	Eq.#	Isotropic energy barrier
30° Partial, Bα			
Cross-slip onto the TB	$B\alpha \rightarrow B\delta + \delta\alpha$	1	$\hat{E} + 2.0\tilde{E}$
Stair-rod dislocation dissociation	$\delta\alpha \rightarrow \delta B + B\alpha$	2	$3.5\hat{E} + 5.5\tilde{E}$
Transmit across the TB	$B\alpha \rightarrow B\alpha' + \alpha'\alpha$	11	$2.7\hat{E} + 4.1\tilde{E}$
90° Partial, Dα			
Cross-slip onto the TB	$D\alpha \rightarrow A\delta$		0
Transmit across the TB	$D\alpha \rightarrow \delta\alpha + \delta\alpha' + \alpha'D'$	19	$2.0\hat{E} + 4.0\tilde{E}$
	$D\alpha \rightarrow \delta\alpha + \delta\beta' + \beta'D'$	20	$2.0\hat{E} + 4.0\tilde{E}$
	$D\alpha \rightarrow \delta\alpha + \delta\gamma' + \gamma'D'$	21	$2.0\hat{E} + 4.0\tilde{E}$
	$D\alpha \rightarrow 4/9A\delta + \alpha'D'$	26	$0.6\hat{E} + 1.4\tilde{E}$
	$D\alpha \rightarrow 2/9\delta BC + \beta'D'$	27	$0.1\hat{E} + 0.2\tilde{E}$
	$D\alpha \rightarrow 2/9\delta + \gamma'D'$	28	$0.1\hat{E} + 0.2\tilde{E}$
Cross-slip of perfect screw dislocation, BC			
No dislocation reaction needed			0
Perfect 60° dislocation			
Cross-slip onto TB	$BD \rightarrow BC + CD$	32	$6.0\hat{E} + 7.2\tilde{E}$
Transmit across the TB	$BD \rightarrow 2B\delta + D'B$	38	$4.5\hat{E} + 7.5\tilde{E}$
	$BD \rightarrow \delta C + D'A$	39	$3.0\hat{E} + 3.9\tilde{E}$
	$BD \rightarrow \delta A + D'C$	40	$3.0\hat{E} + 3.9\tilde{E}$
	$D'\delta \rightarrow D'\alpha' + \alpha'\delta$	46	$2.0\hat{E} - 0.3\tilde{E}$
30° Leading partial cross-slip onto TB and trailing 90° partial transmit across TB			
30° Leading partial transmit across TB first and the 90° trailing partial transmit cross TB second	$D\alpha + \alpha\alpha' \rightarrow 2\alpha'\delta + D'\alpha'$	49	$4.0\hat{E}$
90° Leading partial and 30° trailing partial transmit across TB sequentially	$B\alpha + \alpha\delta + \alpha'\delta \rightarrow B\alpha' + 2\alpha'\delta$	55	$3.4\hat{E} + 2.7\tilde{E}$
	$B\alpha + \alpha\delta + \beta'\delta \rightarrow B\alpha' + \alpha'\delta + \beta'\delta$	56	$2.8\hat{E} + 3.7\tilde{E}$
	$B\alpha + \alpha\delta + \gamma'\delta \rightarrow B\alpha' + \alpha'\delta + \gamma'\delta$	57	$2.8\hat{E} + 3.7\tilde{E}$

$$*\hat{E} = \frac{Ga^2}{72\pi(1-\nu)} \ln \frac{\sqrt{2}d}{a}, \tilde{E} = \frac{Ga^2}{72\pi(1-\nu)}.$$

between individual partials and twin boundaries. In addition, a higher stacking fault energy makes it easier for a dissociated perfect dislocation to constrict at the twin boundary before the leading partial reacts at the twin boundary. This is especially significant for perfect screw dislocations, which, once constricted, can cross-slip into the twin boundary plane or be transmitted across the twin boundary to glide on a slip plane in the twin, without any dislocation reaction.

If the stacking fault energy is very low partial dislocations can be emitted in large numbers from grain boundaries and other sources [52,53]. These partials can cross-slip into the twin boundaries with small energy barriers (see Table 1), which generate steps on the twin boundaries. It can also be seen from Table 1 that the energy barriers for 90° partials to be transmitted across twin boundaries are much lower than the energy barrier for 30° partials to be transmitted across a twin boundary. In addition, a low stacking fault energy makes it difficult for a dissociated perfect dislocation to constrict. This could produce a scenario in which the leading partial cross-slipped into the twin boundary plane or was transmitted across the twin boundary, while the trailing partial remains on the original slip plane in the matrix. Such a dislocation structure is believed to be effective in improving the work hardening rate [9].

8. Summary

In this paper we have systematically described the plausible dislocation reactions at twin boundaries. Such reactions and subsequent dislocation slips determine how the twins affect the deformation behavior of nanocrystalline fcc metals. Plausible dislocation reactions and the energy barriers associated with the reactions are listed in Table 1. It should be noted that the equations used to calculate the dislocation elastic energies are based on isotropic elasticity. Therefore, the energy barriers listed in Table 1 are isotropic energy barriers. The energy barrier determines the feasibility of a dislocation reaction. A lower energy barrier indicates that the reaction is statistically more likely to occur. However, other factors, including the orientation and magnitude of the applied stress and the stacking fault energy also play important roles. It should be noted that most of the dislocation–twin reactions described in this paper may not occur in coarse grained fcc metals and alloys because of their requirement of high applied stresses to overcome the energy barriers.

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Deformation twinning in a nanocrystalline hcp Mg alloy

X.L. Wu,^a K.M. Youssef,^b C.C. Koch,^b S.N. Mathaudhu,^c L.J. Kecskés^c and Y.T. Zhu^{b,*}

^aState Key Laboratory of Nonlinear Mechanics, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, China

^bDepartment of Materials Science & Engineering, North Carolina State University, Raleigh, NC 27695-7919, USA

^cU.S. Army Research Laboratory, Aberdeen Proving Ground, MD 21005, USA

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Nanocrystalline (nc) hexagonal close-packed (hcp) metals are rarely observed to deform by twinning, which is contrary to face-centered cubic metals. Here we report that, after alloying Mg with 10 at.% Ti, deformation twins are observed in an nc Mg–Ti alloy processed by mechanical attrition. The formation of deformation twins is attributed to the alloying effect, which may change the energy path for twinning. These results point to a promising approach to design nc hcp alloys for superior mechanical properties. © 2010 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Twinning; Nanocrystalline; hcp; Mg; Alloying

Nanocrystalline (nc) materials usually have high strength, but disappointingly low ductility [1]. Early attempts to increase the ductility often resulted in decrease in strength [2,3], although in some cases both high strength and good ductility are observed [4]. Twins in nc face-centered cubic (fcc) materials have been reported to increase both the strength and the ductility by accumulating dislocations at the twin boundaries [5]. Fortunately, fcc materials have been found to deform by twinning easily in their nc state [6,7]. This makes deformation twinning one of the most promising strategies for simultaneously increasing the strength and ductility of nc fcc metals and alloys [8–11]. However, this important strategy for improving the strength and ductility has so far not been available to nc hexagonal close-packed (hcp) metals and alloys because they rarely deform by twinning [12].

The twinning behavior of hcp materials is very different from that of fcc metals. For fcc metals, with decreasing grain size it becomes more difficult to deform by twinning in the coarse-grain size range [13], but twinning becomes easier once the grain size is smaller than 100 nm [6], although twinning may become difficult again when the grain size is too small (inverse grain size effect) [14]. In contrast, coarse-grained hcp metals usually need twinning to accommodate plastic deformation in addition to dislocation slip due to their lack of sufficient slip systems. However, twinning is rarely observed

in nc hcp metals and alloys, with the exception of nc Zr processed by surface mechanical attrition [15]. The reason for the observed grain size effect on twinning in hcp materials is not clear. It would be scientifically and technically important to activate deformation twinning in nc hcp metals.

It is the objective of this investigation to activate deformation twinning in hcp Mg by adding Ti as the alloying element. Alloying will change the energy path for twinning, i.e. the general planar fault energy (GPFE) curves, and this will affect propensity for twinning [16]. We choose Mg as a model material in this study because it has the lowest density among structural metals except for Be. Ti is chosen as the alloying element because it has a high solubility in Mg when processed by ball milling [17,18].

Nanocrystalline Mg–10 at.% Ti samples were prepared by ball milling in a SPEX 8000 mill, using a steel vial and balls. Starting materials were elemental powders of Mg (99.9%) and Ti (99.5%). X-ray analysis reveals the Bragg peaks corresponding to the hcp Mg phase after milling for 24 h, indicating that no new phases formed and the Ti formed a solid solution with Mg (see Fig. 1a). Note the shift in the Mg alloy peaks to higher 2θ angles, indicative of a contraction of the lattice parameter. This is important because only when Ti forms a solid solution can it lower the stacking fault energy. For simplicity, the Mg–10 at.% Ti alloy is hereafter referred to as the Mg–Ti alloy. Shown in Figure 1b is the statistical distribution of grain sizes with an average grain size of 33 nm.

* Corresponding author. Tel.: +1 919 5130559; e-mail: ytzhu@ncsu.edu

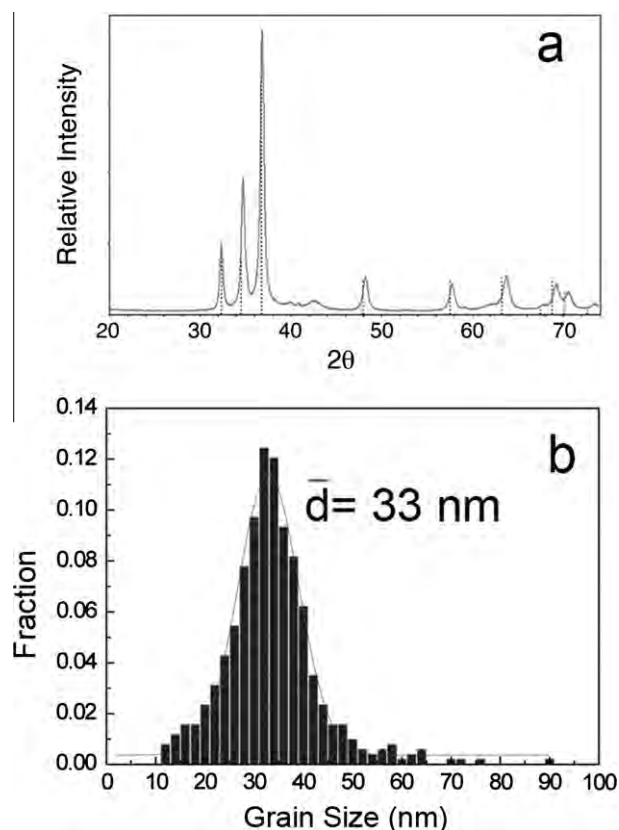


Figure 1. (a) X-ray diffraction pattern indicating a single hcp Mg phase. (b) Statistical distribution of grain sizes in the as-processed nc Mg–Ti alloy, measured from over 500 grains in transmission electron microscopy micrographs. The average grain size is 33 nm.

Figure 2 shows high-resolution electron microscopy (HREM) images of two deformation twins in the as-processed nc Mg–Ti alloy. The images are viewed from a $[1\bar{1}23]$ zone axis. Coherent twin boundaries and mirror images of atomic arrangements are clearly shown, verifying that they are indeed twins. Importantly, a two-atomic-layer step on the coherent twin boundary is shown in both Figure 2a and b (marked by 2). In addition, there also exist two one-layer steps on the coherent twin boundary in Figure 2a and one one-layer step in Figure 2b (marked by 1). The most common twinning system observed in hcp Mg is $\{10\bar{1}2\}\langle 10\bar{1}1 \rangle$ [19,20]. The $\{10\bar{1}1\}\langle 10\bar{1}2 \rangle$ deformation twins observed in this study are consistent with the twinning mode observed in MD simulation of Mg under compression [19]. Interestingly, this twinning system was also observed in hcp Ti and Zr processed by severe plastic deformation under pressure, although the twinning only happened in large grains [21,22]. MD simulation predicted that $\{10\bar{1}1\}\langle 10\bar{1}2 \rangle$ deformation twins grow by the slip of a zonal twinning dislocation, $\frac{1}{2}\langle 10\bar{1}2 \rangle$, on the coherent $(10\bar{1}1)$ twin boundary, followed by atomic shuffling. This zonal dislocation involves two $(10\bar{1}1)$ planes, forming a two-layer step on the twin boundary. Such two-layer steps are indeed observed in Figure 2, which clearly verifies this twinning mechanism predicted by the MD simulation. The MD simulation also predicted that the one-layer steps are immobile and that the four-layer steps are unstable and can spontaneously

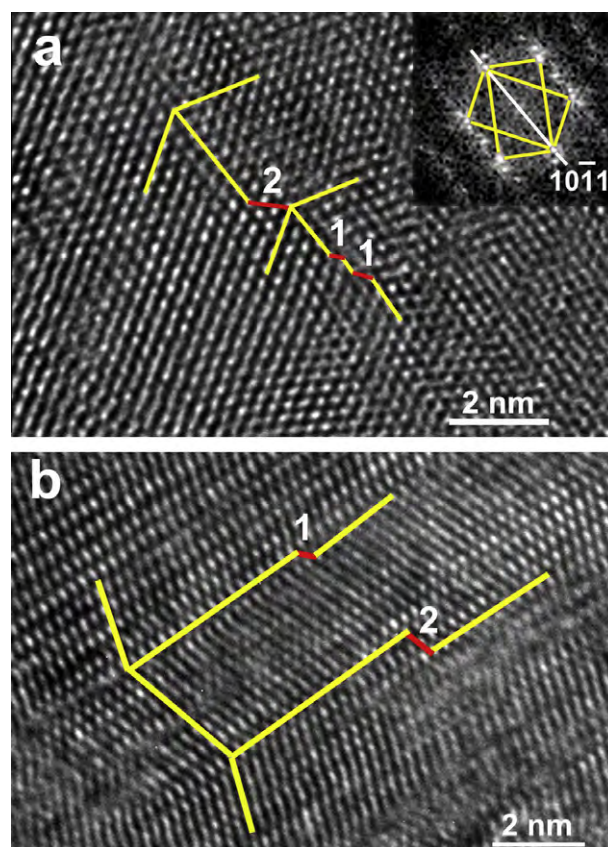


Figure 2. (a) HREM micrograph showing a deformation twin in the nc Mg–Ti alloy, viewed along a $[1\bar{1}23]$ zone axis. The twin system is $\{10\bar{1}1\}\langle 10\bar{1}2 \rangle$. A two-atomic-layer step and two one-layer steps are on the twin boundary. (b) HREM micrograph showing another deformation twin with a two-layer step on the lower twin boundary and a one-layer step on the upper twin boundary.

dissociate into two two-layer steps [19]. The one-layer steps are experimentally observed in Figure 2, while no four-layer steps have been observed in our samples. Interestingly, Figure 2a shows two one-layer steps next to each other, which could merge to form a two-layer step, i.e. a zonal twinning dislocation. Over 50 grains in nc Mg–Ti alloy were observed from $[1\bar{1}23]$ zone axis, all of which contain deformation twins. It has been reported that ball-milled nanocrystalline Mg with grain sizes similar to the our nc Mg–Ti alloy do not deform by twinning [23,24].

Figure 3 shows several $\langle 1\bar{1}23 \rangle$ dislocations in the nc Mg–Ti alloy (marked by T), lying on the $\{10\bar{1}1\}$ planes. The $\{10\bar{1}1\}\langle 1\bar{1}23 \rangle$ slip system can produce strain in both the a -axis and the c -axis directions. This is very important because the slip system of coarse-grained Mg is usually $\{0001\}\langle 1120 \rangle$, which cannot produce strain in the c -axis direction. The activation of the $\{10\bar{1}1\}\langle 1\bar{1}23 \rangle$ slip system should help with the plastic deformation of the nc Mg–Ti alloy. This also indicates that the nc hcp Mg–Ti alloy deforms via slip systems that are normally not active in coarse-grained Mg, a phenomenon similar to that observed in nc fcc materials.

Although X-ray analysis verified that Ti solute completely dissolved into the Mg matrix to form a hcp solid solution (Fig. 1a), there remains the questions of

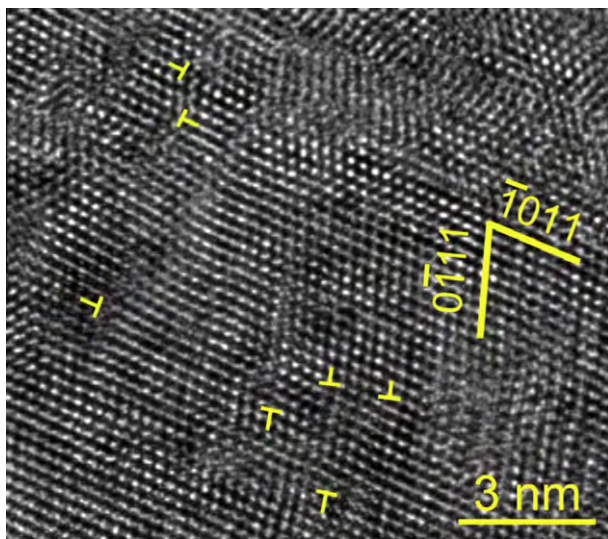


Figure 3. HREM image showing $\langle \bar{1}\bar{1}23 \rangle$ dislocations on $\{10\bar{1}1\}$ planes. The zone axis is $[\bar{1}2\bar{1}3]$.

whether the Ti solute is uniformly distributed in the Mg matrix and if there is a grain size effect. To answer these questions, we performed energy-dispersive X-ray (EDX) analysis on grains of the nc Mg–Ti alloy. Shown in Figure 4a are two grains with sizes of 35 and 50 nm, respectively. Figure 4b shows that the Ti atoms are distributed uniformly in the small grain. However, in the large grain, Ti has a higher concentration in the area near the grain boundary than in the area near the grain cen-

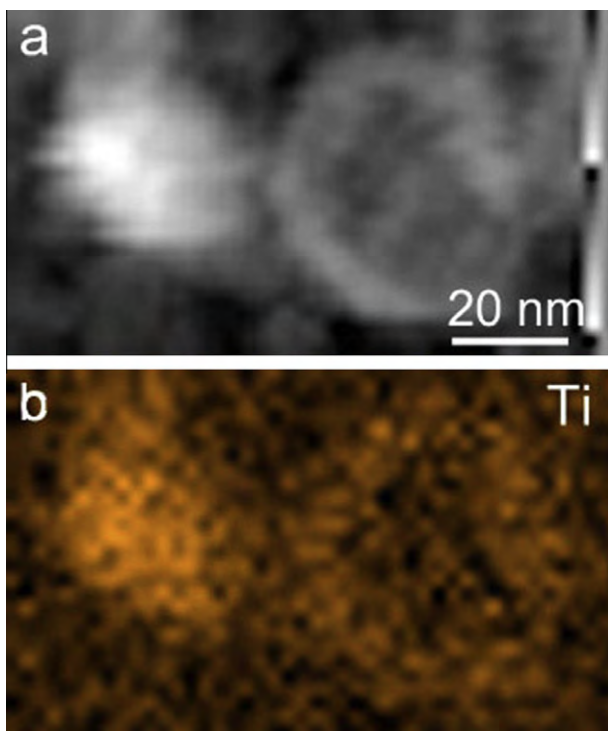


Figure 4. (a) EDX images of a small grain (left) and a large grain (right). (b) EDX analysis reveals uniform Ti distribution in the small grain, but in the large grain Ti has higher concentration in the region near the grain boundary than in the region near the center.

ter. This indicates that the elastic strain near the grain boundary facilitates the mixing of the Ti solute atoms into the Mg lattice. Figure 4b also shows that the small grain has a higher concentration of Ti, suggesting that the solubility of Ti increases with decreasing grain size. No intermetallic compound is observed in the EDX analysis, which is consistent with the X-ray analysis.

The segregation of Ti atoms to the region near the grain boundaries could have helped with the nucleation and growth of deformation twins observed in the nc hcp Mg–Ti alloy. It is reported that dislocation nucleation and emission from the grain boundaries became a major deformation mode in nc fcc metals because of the lack of dislocation source in the grain interior [6,25–27]. The dislocation nucleation and emission likely also play a major role in nc hcp metals. Since the GPFE energies primarily affect the dislocation nucleation [28], the segregation of Ti atoms to the grain boundary region should strengthen the alloying effect on the dislocation nucleation, and might consequently help with the formation of deformation twins observed in the nc hcp Mg–Ti alloy.

The twinning system in the nc Mg–Ti alloy is $\{10\bar{1}1\}\langle 10\bar{1}2 \rangle$, which can provide strain in the c -axis direction. In addition, a new slip system, $\{10\bar{1}1\}\langle \bar{1}\bar{1}23 \rangle$, is also activated, which can also provide strain in the c -axis direction. In other words, both the deformation twinning and the newly activated slip system can facilitate plastic strain in the c -axis direction. This is significant for the nc hcp Mg–Ti alloy because it makes the total number of independent deformation systems larger than five, as required by the von Mises criterion for compatibility [29].

The activation of deformation twinning in the nc hcp Mg–Ti alloy is most likely caused by the change in the GPFE curves caused by Ti alloying. This statement is supported by the following observations. First, nc hcp metals and alloys have rarely been observed to deform by twinning [12], although twinning is a major deformation mechanism in their coarse-grained counterparts. Ball-milled nanocrystalline Mg with grain sizes similar to our nc Mg–Ti alloy has been reported not to deform by twinning [23,24]. Second, twins were observed in all nc Mg–Ti grains with an $\langle 11\bar{2}3 \rangle$ zone axis, which indicates the prevalence of deformation twins in the nc Mg–Ti alloy. It should also be noted that the high strain rate used in the ball milling should also have promoted twinning in the nc Mg–Ti alloy [14]. This is because a higher strain rate usually leads to a higher flow stress.

Three important energies act on the GPFE curves: the stacking fault energy, the unstable stacking fault energy and the unstable twin fault energy [16]. These are energy barriers associated with the nucleation and gliding of partial and twinning dislocations. They have been reported to significantly affect the twinning tendency in fcc metals and alloys [16,30,31], and a similar effect should also apply to hcp metals such as Mg. For example, it is known that lowering the stacking fault energy promotes the deformation twinning in nc fcc metals and alloys [9–11,32–34]. Also, a lower unstable twin fault energy should make twinning easier. It would be of interest to calculate the GPFE curves of the hcp Mg–Ti alloy as a function of Ti concentration in the future.

In conclusion, deformation twinning has been activated in an nc hcp Mg–Ti alloy, which is most likely caused by the modification of GPFEs through Ti alloying. The segregation of the Ti atoms near the grain boundaries makes the alloying effect stronger. These results suggest that it might be possible to design nc hcp Mg alloys to activate deformation twinning for improving the mechanical properties. In addition, new slip systems that are not available to their coarse-grained counterparts could be activated in nc hcp Mg alloys. Further studies are needed to investigate which elements are most effective in promoting deformation twinning in nc Mg alloys. In addition, the physics of the grain size effect on deformation mechanisms of nc hcp metals also needs further investigation.

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REPORT

Ultrastrong Mg Alloy via Nano-spaced Stacking Faults

W. W. Jian^a, G. M. Cheng^a, W. Z. Xu^a, H. Yuan^a, M. H. Tsai^a, Q. D. Wang^b, C. C. Koch^a,
 Y. T. Zhu^{a*} and S. N. Mathaudhu^{a,c*}

^aDepartment of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695, USA;

^bSchool of Materials Science and Engineering, Shanghai Jiaotong University, Shanghai, People's Republic of China;

^cMaterials Science Division, U.S. Army Research Office, Research Triangle Park, NC 27709, USA

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Mg alloys are among the lightest alloys but they are usually weak. Here we report a new mechanism to make them ultrastrong while maintaining good ductility. Stacking faults with nanoscale spacing were introduced into a Mg–8.5Gd–2.3Y–1.8Ag–0.4Zr (wt%) alloy by conventional hot rolling, which produced a yield strength of ~575 MPa, an ultimate strength of ~600 MPa, and a uniform elongation of ~5.2%. Low stacking fault (SF) energy enabled the introduction of a high density of SFs, which impeded dislocation slip and promoted dislocation accumulation. These findings provide guidance for developing Mg alloys with superior mechanical properties.

Keywords: Stacking Faults, Mg, Strength, Ductility, Dislocations

Magnesium and its alloys have attracted extensive attention in the recent years due to their abundance, low-density, good castability and recyclability [1–4]. However, the application of Mg alloys has been substantially hindered by their relatively low strengths (tensile yield strength: ~100–250 MPa for commercial casting Mg alloys [5,6]) and limited ductility (elongation: 2–8% [5–7]) at room temperature. Outside of traditional precipitation control, Mg-alloy strengthening typically relies on two general approaches: non-traditional, esoteric processing and grain refinement. An example of non-traditional processing for high strength is rapid solidification/powder metallurgy, which was used to obtain a yield strength of ~600 MPa in a Mg–Zn–Y alloy with uniform distribution of long-period ordered structures [8]. While the resultant properties are remarkable, such unconventional processing technologies limit potential industrial application. In addition, the ultra-high strength is usually accompanied by marked losses in ductility [8].

The second general approach of grain refinement for strengthening has been used to obtain ultrafine (<1 μm) grains in Mg alloys [9–12]. The high concentration of grain boundaries (GBs) in the ultrafine-grained

microstructure provides barriers to motion of dislocations and consequently promotes the strength improvement. Nevertheless GB strengthening mechanism alone provided limited contribution to macroscopic yield strengths, which, in these reports [9–12], are typically less than 400 MPa. More importantly, refining the grain size is reported to suppress the propensity of deformation twinning which, in addition to dislocation slip is an important mechanism for enhancing strength and ductility [13–18]. Ultrafine-grained microstructures also suffer from strength reduction via grain growth at a relatively low temperature (0.32 T_m) [19], thus limiting the potential for further shaping or processing.

In this letter, we report a new mechanism for inducing ultrahigh strengths (yield strength: ~575 MPa, ultimate strength: ~600 MPa) and maintaining moderate ductility (uniform elongation: ~5.2%) via conventional processing (hot rolling) of a Mg-alloy (Mg–8.5Gd–2.3Y–1.8Ag–0.4Zr (wt%)) with relatively large grain sizes (13 μm). We posit that the introduction of a high density of stacking faults (SFs) with nanoscale spacing provides for a high density of barriers to block and pin dislocations and retention of work hardening for enhanced ductility.

*Corresponding authors. ytzhu@ncsu.edu, suveen.n.mathaudhu.civ@mail.mil

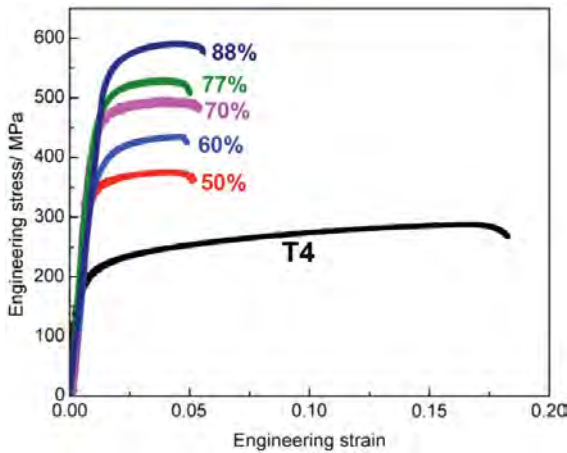


Figure 1. Engineering stress–strain curves of Mg alloy samples under T4 treatment and hot rolling with different thickness reductions (marked by the curves).

The casting procedure used to produce the Mg–8.5Gd–2.3Y–1.8Ag–0.4Zr (wt%) (hereafter referred to as “Mg alloy ingot”) can be found in reference [20]. The Mg alloy was then T4 treated (solution treatment at 500°C for 12 h in a vacuum furnace and quenched in room temperature silicon oil); the T4 conditions serve as a baseline for property assessment. Prior to each rolling pass, specimens were heated in a furnace at 450°C for 15 min and rolled on a conventional hot roller with a thickness reduction of <5% per pass to a total rolling reduction of 50%–88%. Rolled specimens were air-cooled to room temperature. Tensile test samples were cut on the rolling plane and pulled to failure in the direction parallel to rolling direction using a strain rate of $2.35 \times 10^{-3} \text{ s}^{-1}$. The gauge length and width of the testing samples are 7 and 1 mm, respectively. The surfaces of gauge region were polished to mirror-like surfaces before tensile testing and at least three samples for each rolling parameter were tested. For transmission electron microscopy (TEM) studies, specimens were gently polished and then ion milled to perforation on a cold stage with low angle and low-energy ion beam, and microscopy was conducted on a JEM-2000FX and a JEM-2010F operating at 200 kV.

Figure 1 shows the tensile engineering stress–strain curves of the Mg alloy samples after T4 treatment, and after hot rolling to different thickness reductions. Both the tensile yield strength and ultimate strength of the rolled samples increase as the rolling strain increases. At 88% rolling reduction, the grain size was refined to $\sim 13 \mu\text{m}$, and the maximum tensile yield strength and ultimate strength reached 575 and ~ 600 MPa, respectively, which are more than two times the values of the T4 treated baseline. Compared with the yield strength and uniform elongation values of various Mg alloys [9,11,21–54] as shown in Figure 2, the current result is an extraordinary combination of ultrahigh strength and reasonably good ductility. Importantly, the elongation to failure of

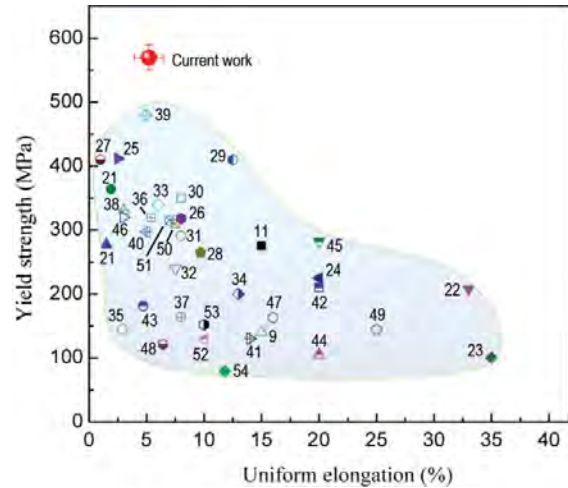


Figure 2. Summary of room temperature tensile yield strength and uniform elongation of previous reports and our current work. The criteria used to summarize and reproduce this figure are (1) only room temperature uniaxial tensile test results were included, (2) the gauge length of tensile test sample was larger than 5 mm and (3) the stress–strain curve must be indicated in the individual report in order to reproduce the uniform elongation. The reference number is adjacent to the data point. Note: Ref. [8] reported a Mg alloy with a yield strength of 600 MPa, but its uniform elongation is not available.

the processed Mg alloy retains a moderate level (5–6%) without diminishing during the hotrolling process.

The TEM analysis was performed to probe the main microstructural features that are responsible for the observed strengthening in the hot rolled Mg–8.5Gd–2.3Y–1.8Ag–0.4Zr (wt%) alloy. It was observed that beyond 50% thickness reductions, basal plane SFs become the primary crystalline defects (see Figure 3). The (0001) basal plane SFs are further verified by the presence of streaking along the [0001] direction in the selected area diffraction pattern [55] (Figure 3(d)). The average spacing between adjacent SFs, d , decreases with rolling thickness reduction. At 88% thickness reduction, nano-spaced SFs with an average spacing $d \sim 16$ nm were formed in most of the coarse ($\sim 13 \mu\text{m}$) grains. The formation of high density of SFs is due to the low SF energy (SFE) of this Mg alloy. It has been reported that both Gd and Y lower the SFE of Mg [56,57]. The SFs can be formed by the dissociation of a full dislocation into two partial dislocations on the basal plane during plastic deformation. The partial dislocations can be driven apart by applied stress to form a wide planar SF ribbon [58]. Our primary TEM observations also indicate that there was a transition stage in the rolling thickness reduction range of $\sim 30\%$ to $\sim 50\%$, in which deformation mechanism transitioned from dislocation slip to SFs-mediated process. Further study on this transition is underway and will be reported in the future.

Plotting the yield strength against the reciprocal of average spacing of SFs, $1/d$, reveals a linear relationship

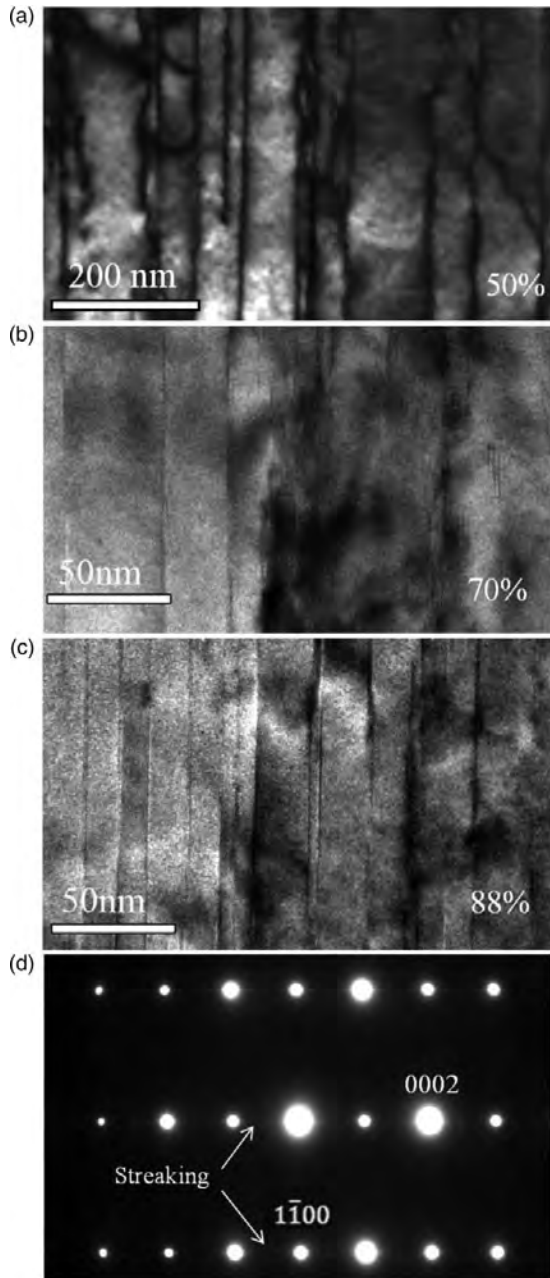


Figure 3. TEM images of Mg alloy samples with various rolling thickness reductions: (a) 50%, $d = 55$ nm, (b) 70%, $d = 25$ nm and (c) 88%, $d = 16$ nm. Image (d) is the SAD pattern of the 70% rolled sample in which the streaking verifies the basal plane SFs.

(Figure 4), i.e.

$$\sigma_{0.2} = \sigma_0 + \frac{k}{d}, \quad (1)$$

where d is the mean spacing between adjacent SFs, σ_0 is the total strength contributed by strengthening mechanisms other than SFs. This relationship is similar to the empirical Hall–Petch equation and its physical model is being developed and will be published in the future. In the current Mg alloy, a number of typical strengthening

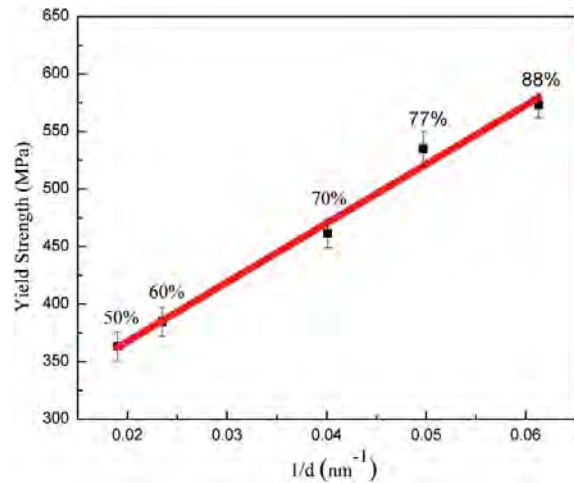


Figure 4. Yield strength vs the reciprocal of mean spacing between SFs of rolled samples with different thickness reduction. The number by each data point indicates the thickness reduction by hot rolling.

mechanisms such as solid solution strengthening, grain refinement, dynamic precipitation and textural strengthening are expected to be active [8,20]; however, strengthening contributions from these are not expected to be the primary cause of the ultrahigh strength observed.

The large slope of the linear correlation between the strength and $1/d$, the reciprocal of the SF spacing indicates that the SFs are very effective in improving the strength. Fitting the data in Figure 4 with Equation (1) yields $\sigma = 340$ MPa, and $k = 3780$ MPa nm. Therefore, introducing SFs with an average spacing of 16 nm increased the yield strength of the Mg alloy by 70% from 340 to 575 MPa. This indicates that SFs are very effective in improving the strength of Mg alloys. The fact that SFs increased the strength, but did not decrease the ductility (see Figure 1) makes SFs very attractive for improving mechanical properties of Mg alloys. This discovery is especially important for hexagonal close-packed (hcp) metals and alloys, because twinning, an effective approach for improving strength and ductility for face centered cubic (fcc) metals and alloys, becomes very difficult to activate in hcp metals when the grain sizes are below a few hundred nanometers [13,14], making it very difficult to combine the strengthening effects of refining grains and introducing twins.

SFs on basal planes are expected to provide similar effect on impeding dislocation movement as reported for nano-twinned electrodeposited Cu [17]. As dislocations slip and encounter SF boundaries, they can either (1) cut or interact with SFs in order to move and facilitate plastic deformation or (2) accumulate around SF boundaries and accommodate a moderate strain hardening [59].

In order to probe the dislocation interactions with SFs, postmortem TEM observation (Figure 5) was conducted on tension-tested samples that were hot rolled

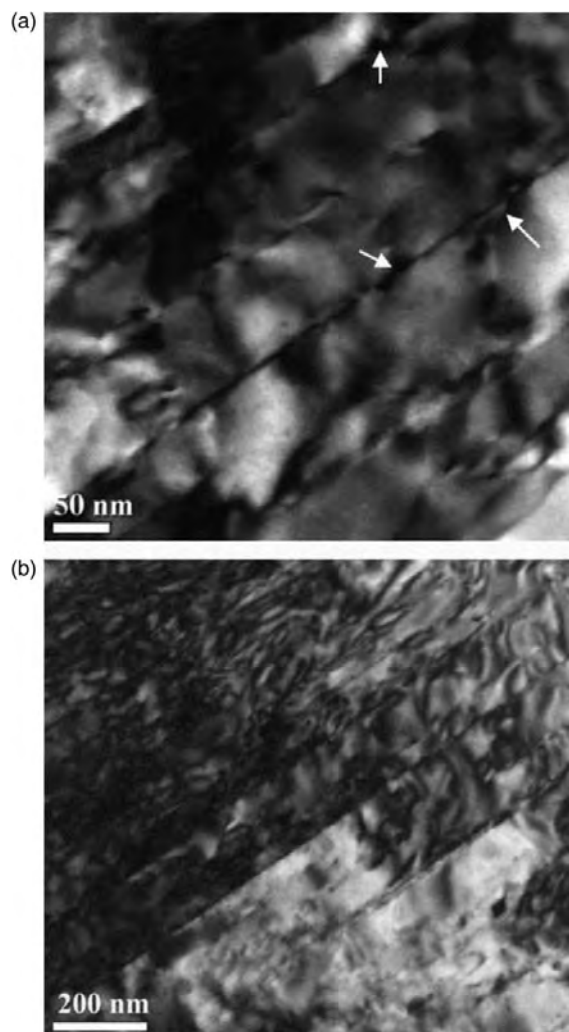


Figure 5. TEM images of 88% hot rolled sample after tensile test. (a) Fragments of SFs cut by the dislocations marked by white arrows (b) High density of dislocations was trapped between SFs.

to 88% to produce nano-spaced SFs Figure 5(a) shows the distinctly different features of fragmented SFs as compared to Figure 3(c). Some SFs have been broken into short segments (Figure 5(a)), and a high density of dislocations are trapped between SFs (Figure 5(b)). As shown in Figure 5(a), some SF segments are well aligned along a line, suggesting that they were most likely formed from a single SF that was cut by dislocations (marked by white arrows) slipping on pyramidal or prismatic planes.

Since the slip systems in hcp Mg are limited at room temperature, it is necessary to activate $\langle c \rangle$ and/or $\langle c + a \rangle$ dislocations to slip on the pyramidal or prismatic slip planes. Such dislocation slip will encounter SFs and cut SFs into segments, which are additional pinning sites to block dislocation motion. These dislocation-SF interactions are similar in some way to the dislocation-twin interactions in an fcc system [59] More investigation is needed to study these interaction details.

The blocking of dislocations by SFs and the cutting of SFs by dislocations will hinder the slip of dislocations, which consequently increases the yield strength. The high density of dislocations between SFs after tensile testing indicates that SFs are effective in blocking and accumulating dislocations, which will enhance strain-hardening rate and consequently help with ductility retention. This explains why no ductility reduction is observed with increasing strength when a high density of SFs is introduced into the Mg alloy.

In summary, conventional hot rolling was conducted on a T4treated Mg–8.5Gd–2.3Y–1.8Ag–0.4Zr (wt%)Mg alloy with thickness reduction up to 88%. Unprecedented strength and moderate ductility (YS $\sim$ 575 MPa, UTS $\sim$ 600 MPa and uniform elongation $\sim$ 5.2%) were observed in the resultant coarse-grained alloy. TEM studies show that a high density of nano-spaced SFs are the main defects inside of the grains and their density increased as rolling thickness reduction increased. The strength of the processed Mg alloy was found to increase as the mean spacing between adjacent (SFs) decreased. Nano-spaced SFs are found to be tremendously effective in impeding the movement of dislocations and retaining strain hardening. Activation of nonbasal dislocations during tensile testing accounts for the detected moderate ductility, in addition to the capability of retaining strain hardening. It is expected that optimization of approaches that introduce a high density of nano-spaced SFs will enable other Mg alloys with concurrent high strength and good ductility.

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ARTICLE

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In-situ atomic-scale observation of irradiation-induced void formation

Weizong Xu¹, Yongfeng Zhang², Guangming Cheng¹, Weiwei Jian¹, Paul C. Millett³, Carl C. Koch¹, Suveen N. Mathaudhu⁴ & Yuntian Zhu¹

The formation of voids in an irradiated material significantly degrades its physical and mechanical properties. Void nucleation and growth involve discrete atomic-scale processes that, unfortunately, are not yet well understood due to the lack of direct experimental examination. Here we report an *in-situ* atomic-scale observation of the nucleation and growth of voids in hexagonal close-packed magnesium under electron irradiation. The voids are found to first grow into a plate-like shape, followed by a gradual transition to a nearly equiaxial geometry. Using atomistic simulations, we show that the initial growth in length is controlled by slow nucleation kinetics of vacancy layers on basal facets and anisotropic vacancy diffusivity. The subsequent thickness growth is driven by thermodynamics to reduce surface energy. These experiments represent unprecedented resolution and characterization of void nucleation and growth under irradiation, and might help with understanding the irradiation damage of other hexagonal close-packed materials.

¹Department of Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina 27695, USA. ²Fuels Modeling and Simulations, Idaho National Laboratory, Idaho Falls, Idaho 83415, USA. ³Department of Mechanical Engineering, University of Arkansas, Fayetteville, Arkansas 72701, USA. ⁴Materials Science Division, US Army Research Office, Research Triangle Park, North Carolina 27709, USA. Correspondence and requests for materials should be addressed to Y.Z. (email: ytzhu@ncsu.edu).

Irradiation resistance is one of the critical material properties that is important for many applications including nuclear energy^{1–4}, outer space systems⁵ and other industrial applications^{6,7}. Materials under irradiation of high-energy particles, such as neutrons, ions and electrons, will develop point defects or defect clusters, which may subsequently evolve into microstructural flaws, such as voids, dislocation loops, solute segregation or precipitation^{3,8–12}. Such defects and flaws not only deteriorate the physical properties of irradiated materials, but also cause direct structural failure. In particular, the void formation will lead to volumetric swelling and eventual failure.

Voids could form in almost all materials under irradiation^{8,9,13–20}. They nucleate from the agglomeration of mobile vacancies, and evolve with the absorption and emission of vacancies or self-interstitials at the void surfaces²¹. In many cases, they appear as a polyhedron bounded by several low-energy flat surfaces. Experimental investigations reported so far have concentrated on void growth behaviours, such as void growth rate, size and spatial distribution^{9,13,15,21–24}. Although attempts have been made to observe void formation^{23,25,26}, no atomic-scale observation of void nucleation and early growth has been reported because of experimental difficulties. The lack of understanding of void formation behaviour at the atomic scale has adversely affected the development of advanced theoretical models to predict void evolution under irradiation. This is evidenced by the fact that existing models^{27–37} cannot accurately predict the void evolution at the atomic level that is experimentally observed in the current study. Specifically, it is observed here that the void formation is largely controlled by the atomic process on the void surfaces, a phenomenon that has not been reported before and can only be observed *in situ* at atomic scale. A fundamental understanding of the void formation mechanism is of both scientific and technical importance to advance the design of new irradiation-resistant materials.

Here we report an *in-situ* observation of the nucleation and early growth mechanisms of voids in Mg at the atomic scale. Mg is chosen as a model hexagonal close-packed (hcp) material. This is motivated primarily by its low-melting point and very-low-electron damage threshold of 100 kV (refs 38–40), making it feasible to use high-resolution transmission electron microscopy (HRTEM) to simultaneously induce electron irradiation damage and to observe the resulting damage evolution *in situ* at atomic scale in a commercial electron microscope operating at 200 kV at room temperature.

Results

Void nucleation and early length growth. We observed that under electron irradiation, self-interstitial atom (SIA) loops first form on basal planes in the grain interior. Subsequently, voids nucleate in the vicinity of these SIA loops, which act as biased sinks for SIAs, thus creating an adjacent vacancy supersaturation zone²¹, as shown in Fig. 1a. In addition, SIAs may also diffuse to free surface of the transmission electron microscopy (TEM) foil (70 nm in thickness), which helps enhance the excess vacancy concentration. The void nuclei observed here usually have a thickness of 1.0–1.6 nm (four to six atomic layers and 0.26 nm per layer) and a length of 3.0–4.0 nm. Some small voids are observed to appear for a short period of time and then disappear (see Supplementary Movie 1), which suggests the existence of a critical nucleus size, below which the void is not stable. This also indicates that the void nucleation is a thermally activated process that is similar to the nucleation process in a phase transformation. After their nucleation, voids first grew in two dimensions on the basal plane ($\langle a \rangle$ direction, hereafter referred to as Stage 1) and then thicken in the direction perpendicular to the basal plane

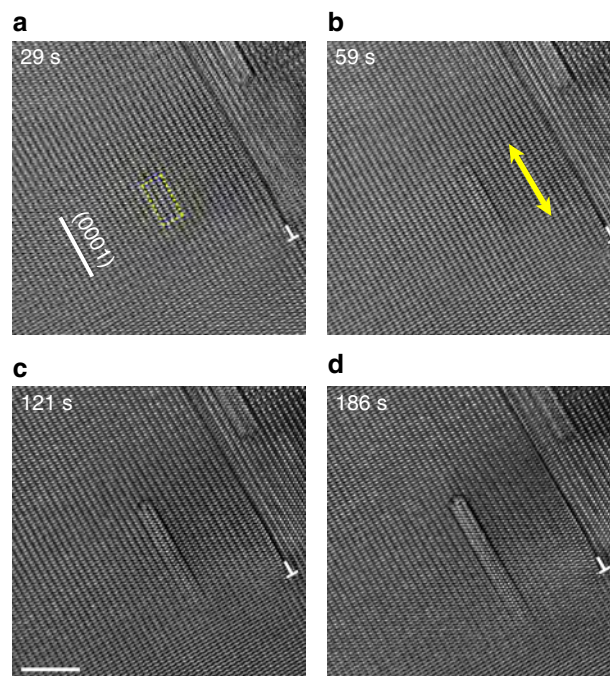


Figure 1 | A series of HRTEM images of void length growth under electron irradiation. (a) A void (outlined by dashed lines) nucleated near the interstitial dislocation loop. (b–d) Stage 1 growth of the void, where it grew in length but not in thickness. The length growth direction is indicated by the yellow arrow. Detailed growth process is shown in Supplementary Movie 2. The specimen is irradiated over a dose range of 0.95–1.17 displacement-per-atom (d.p.a.). Scale bar, 5 nm.

($\langle c \rangle$ direction, hereafter referred to as Stage 2). The Stage 1 is demonstrated by a series of still images, Fig. 1b–d, picked sequentially from an *in-situ* HRTEM video (see Supplementary Movie 2). As shown, the void grew to the SIA loop edge but did not grow beyond it. The thickness of the void did not change in this stage (about 1.56 nm or six atomic layers), whereas the length grew to 15–20 nm. The elongated void morphology in Fig. 1d is similar to that observed in electron-irradiated zirconium^{23,41}, which was pre-irradiated by fast neutrons. It should be noted that the voids have a plate-like polyhedron shape in three dimensions with their broad face on the (0001) basal plane. Our HRTEM images and videos were taken along an $[2\bar{1}10]$ orientation, which resulted in two-dimensional images with void thickness along the c -axis and length on the basal plane (see Fig. 4 and Supplementary Fig. S1). For simplicity, the void dimension on the basal plane is hereafter referred to as void length.

Void thickness growth. In the Stage 2, voids started to grow in thickness. This growth process is found to be discrete, rather than smooth and continuous, whereby the void thickness grew one vacancy layer at a time. This is demonstrated in a typical void growth evolution shown in Fig. 2. First, a vacancy layer nucleated on a basal plane that is adjacent to the void surface and near the centre of the void's (0001) facet, as marked by the yellow arrow in Fig. 2a. After its nucleation, it takes this vacancy layer about 20 s to spread over the whole (0001) facet, making the void one atomic plane (~ 0.26 nm) thicker (Fig. 2b,c). However, it takes another 50 s to nucleate the next vacancy layer near the centre of the (0001) facet (Fig. 2d). This process as described above can be viewed in Supplementary Movie 3.

As the void thickens, its side facets grow larger, as shown in Fig. 3. The sidewalls of the void are composed of $\{01\bar{1}1\}$ facets

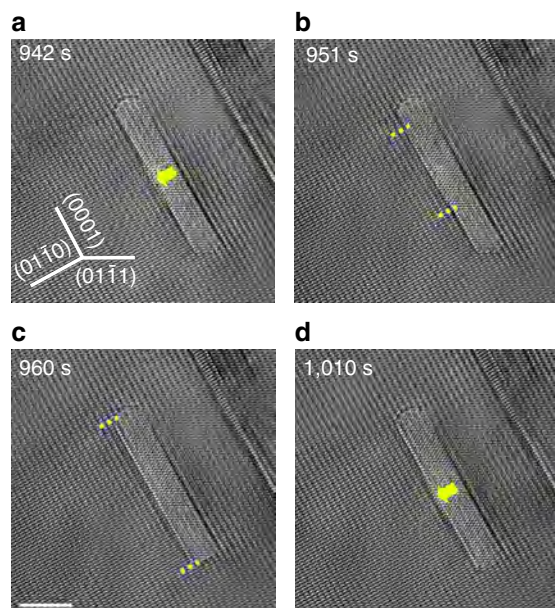


Figure 2 | Void thickness growth in Stage 2 over a dose range of 2.27 to 2.36 d.p.a. (a) First vacancy layer nucleates on the top of the (0001) facet as indicated by the yellow arrow. (b) The spreading of the vacancy layer on the (0001) facet, the size of the vacancy layer is designated by the dashed lines. (c) Vacancy layer extends over the whole (0001) facet surface. (d) Subsequent nucleation of a new vacancy layer (see Supplementary Movie 3 for more details). Scale bar, 5 nm.

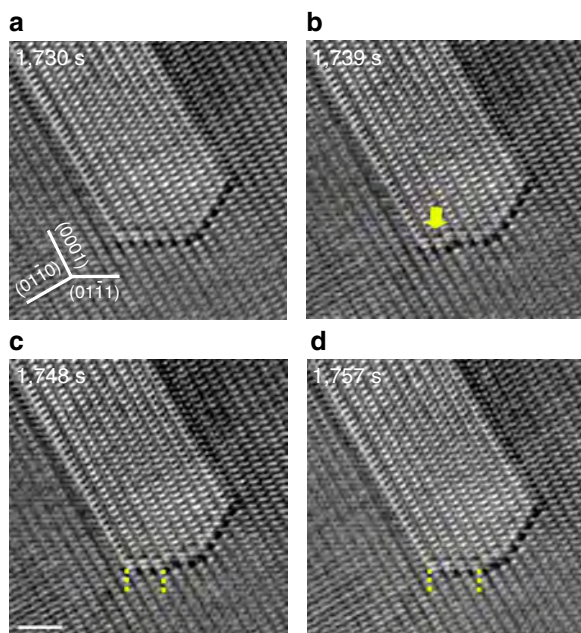


Figure 3 | Formation of void side facets over a dose range of 3.37 to 3.41 d.p.a. (a) Facet plane indexes. (b) A vacancy layer nucleated on the (0111) facet near its intersection with the (0001) facet as indicated by the yellow arrow. (c) The vacancy layer extended on the (0111) facet, which leads to d, the growth of the (0110) facet in the thickness direction. See Supplementary Movie 3 for more details. Scale bar, 2 nm.

when the thickness is small (Fig. 4a); and {0110} facets appear when the thickness is larger (Fig. 4b). The void length growth occurs slowly via vacancy layer nucleation and growth on the sidewalls in this stage. The growth of the sidewalls starts with the

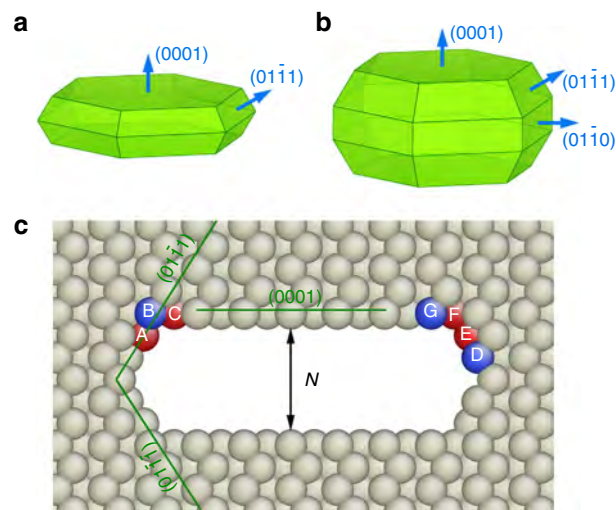


Figure 4 | Void shape and vacancy inter-facet diffusion paths. (a) Illustration of three-dimensional geometry and facet indexes of a void with small thickness bounded by {0001} and {0111} facets. (b) Geometry and facet indexes of a void with larger thickness bounded by {0001}, {0110} and {0111} facets. (c) Atomic configuration for vacancy diffusion paths between a (0001) facet and the {0111} facets (A-B-C or D-E-F-G) for a five-atomic-layer-thick void ($N=5$). The image is projected along a $[2\bar{1}0]$ direction. Two possible different diffusion paths are considered due to the double lattice structure in hcp⁴⁹.

nucleation of a vacancy layer on a (0111) facet at its intersection with the (0001) basal facet as marked in Fig. 3b. The vacancy layer extends its size on the (0111) facet (Fig. 3c) until it reaches the other corner bounded by the (0110) facet (Fig. 3d), which enlarges the (0110) facet area by one atomic layer. This process grows the (0110) facet without growing the void in the length direction. Further void growth in this direction needs the formation of a vacancy layer on the (0110) facet directly (see Supplementary Movie 3).

The voids have a polyhedral geometry bounded by {0001}, {0111} and {0110} facets after the Stage 2 growth, as determined by viewing the voids along $\langle 2\bar{1}10 \rangle$, $\langle 0001 \rangle$ and $\langle 1\bar{1}00 \rangle$ zone axes (see Supplementary Fig. S1). This is consistent with the void morphology in magnesium observed under neutron irradiation¹⁴. Given the fact that the surface energies of the {0001} and {0111} surfaces are similar, and slightly lower than that of {0110}^{42,43}, the equilibrium void shape should be approximately equiaxed^{14,43}. However, the early-stage voids observed here are mostly plate-shaped with their thickness much smaller than their length. The formation energy calculation shows that the plate-shaped voids are less stable than that in near equiaxed voids in a similar volume size (see Supplementary Fig. S2). Therefore, the geometry of the voids observed here is not in thermodynamic equilibrium.

The observed non-equilibrium void geometry is caused by their anisotropic growth kinetics. The void length is measured to grow at a speed of $\sim 2.8 \text{ nm min}^{-1}$ at the Stage 1, which is more than an order of magnitude faster than the growth in the thickness direction, $\sim 0.2 \text{ nm min}^{-1}$, as observed in the Stage 2 (see Supplementary Fig. S3 for more details). The thickening of the void in the Stage 2 is driven by thermodynamics, that is, the reduction of the total surface energy, which favours a near-equiaxed void geometry.

The slow growth kinetics in the thickness direction is caused by both the void growth mechanism and the anisotropic diffusion kinetics of vacancies. Figure 2 shows that it takes 50 s to nucleate

a new vacancy layer on the {0001} void facet, which is about 2.5 times longer than the time it takes for the vacancy layer to extend across the whole facet. This suggests that the slow growth kinetics in the thickness direction is primarily caused by the difficulty in vacancy layer nucleation, which is similar to what was predicted in silicon⁴⁴. Furthermore, vacancies diffuse along $\langle a \rangle$ directions about two times faster than along $\langle c \rangle$ directions at room temperature^{45,46}. Therefore, a higher flux of vacancies will flow to {0111} and {0110} sidewalls than to the {0001} facets. This diffusion anisotropy is therefore partially responsible for the slow growth in the $\langle c \rangle$ direction.

Energy barriers for vacancy inter-facet diffusion. To help understand the void growth behaviour further, the energy barriers for the vacancy diffusion between a basal {0001} facet and {0111} side facets are calculated by means of molecular dynamics (MD) simulation using the nudged-elastic-band method⁴⁷ and an empirical potential developed by Liu *et al.*⁴⁸ Because of the double lattice structure of hcp crystals⁴⁹, there are two possible diffusion paths for vacancy to diffuse between the {0001} and {0111} facets, that is, A-B-C and D-E-F-G paths as shown in Fig 4c.

Figure 5 shows the calculated free energy change along the diffusion paths A-B-C and D-E-F-G for different void thickness. As shown, there are several energy barriers along each diffusion path, with the highest one limiting the overall diffusion rate along the path. For instance, as indicated by the arrow in Fig. 5, the

barrier for the A $\rightarrow$ B $\rightarrow$ C path is determined as 0.20 eV, whereas a larger barrier for the reverse path C $\rightarrow$ B $\rightarrow$ A is 0.41 eV, suggesting that the net vacancy diffusion direction should be A $\rightarrow$ B $\rightarrow$ C. As shown in Fig. 4c, symbols A $\rightarrow$ B $\rightarrow$ C and D $\rightarrow$ E $\rightarrow$ F $\rightarrow$ G represent vacancy diffusion paths from {0111} facets to {0001} facets, hereafter referred to as the forward diffusion, whereas C $\rightarrow$ B $\rightarrow$ A and G $\rightarrow$ F $\rightarrow$ E $\rightarrow$ D represent reverse diffusion paths. The corresponding energy barriers for the forward and reverse diffusions are illustrated in Fig. 6.

Discussion

Figure 6 shows that when the void is over five atomic layers thick, the energy barriers for the reverse vacancy diffusion (C $\rightarrow$ B $\rightarrow$ A and G $\rightarrow$ F $\rightarrow$ E $\rightarrow$ D) are smaller than those for the forward diffusion (see Fig. 6). As a result, vacancies will diffuse from {0001} facets to {0111} facets to help voids to grow in length, which is consistent with the experimental observation in the Stage 1. It should be noted that, during the Stage 2 growth, the diffusion energy barrier effect is overwhelmed by the thermodynamic effect, where the voids grow in thickness to reduce the total surface area and to lower the overall Gibbs free energy.

The diffusion of vacancies along the path of C $\rightarrow$ B $\rightarrow$ A and G $\rightarrow$ F $\rightarrow$ E $\rightarrow$ D also helps to explain the nucleation location of the vacancy layer on the {0001} and {0111} facets. As vacancies diffuse from the edge of a {0001} facet to the edges of intersecting {0111} facets, vacancies will be depleted in the region near

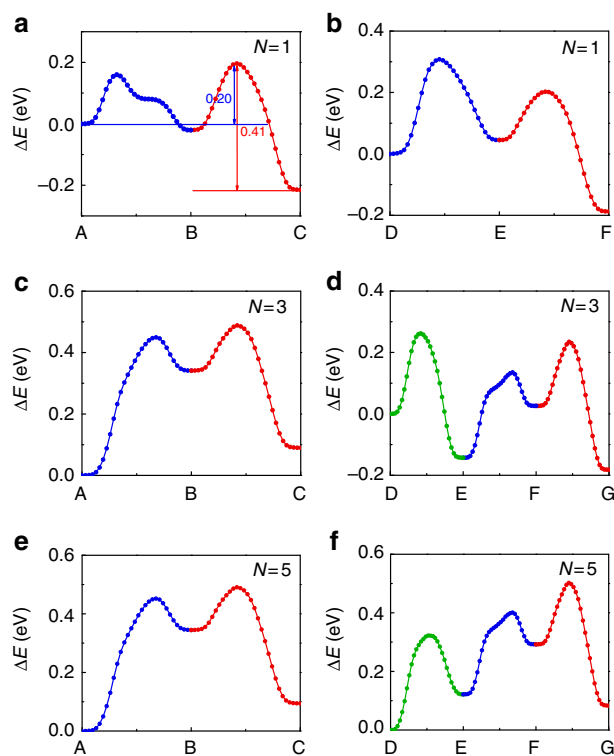


Figure 5 | Free energy change of a vacancy along inter-facet diffusion paths. (a,b) Diffusion paths A-B-C and D-E-F with void thickness $N=1$, respectively. (c,d) Diffusion path A-B-C and D-E-F-G with $N=3$, respectively. (e,f) $N=5$. The vacancy inter-facet diffusion barrier along the whole diffusion path is estimated as the difference between maximum potential energy and that of the initial configuration. For example, the overall barrier for A $\rightarrow$ B $\rightarrow$ C path is determined as 0.20 eV (blue arrow), and the barrier for the reverse path C $\rightarrow$ B $\rightarrow$ A is 0.41 eV (red arrow). Note that when a void is one-atomic-layer thick ($N=1$), position G does not exist in the atomic configuration.

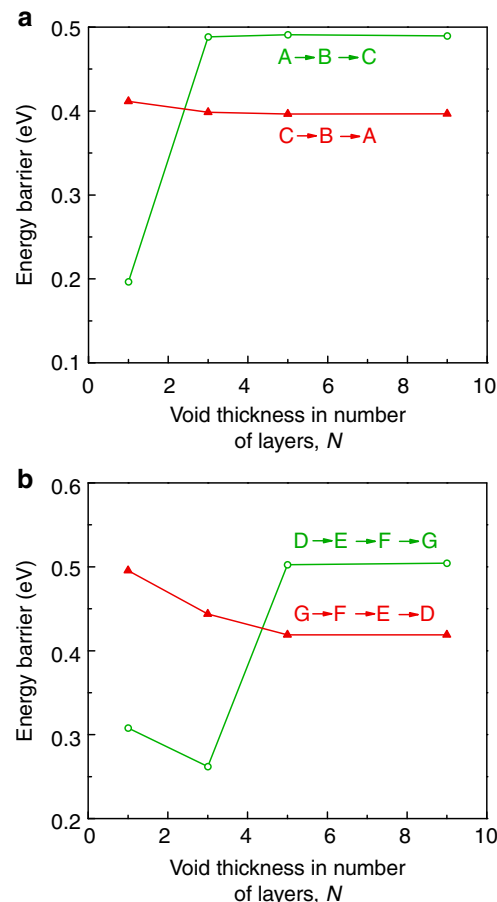


Figure 6 | Energy barriers for vacancy diffusion between {0001} and {0111} facets. (a) Energy barriers for forward diffusion along the path A $\rightarrow$ B $\rightarrow$ C and its reverse diffusion (C $\rightarrow$ B $\rightarrow$ A) as a function of void thickness N . (b) Energy barriers for forward diffusion along the path D $\rightarrow$ E $\rightarrow$ F $\rightarrow$ G and its reverse diffusion (G $\rightarrow$ F $\rightarrow$ E $\rightarrow$ D).

the edge of the {0001} facet, making it nearly impossible for vacancy layer to nucleate in these regions, because a supersaturation of vacancies is the prerequisite for the nucleation of a new vacancy layer. This is why the vacancy layer always nucleates near the centre of the {0001} facets, as observed in Fig. 2. On the other hand, the vacancy diffusion leads to the supersaturation of vacancies near the edges of the {0111} facets, which promotes the vacancy layer formation, as observed experimentally in Fig. 3.

The vacancy diffusion from {0001} facets to {0111} facets also contributed to the observed maintenance of void thickness during the Stage 1 growth. In this stage, as the area of a {0001} facet is relatively small, the vacancy diffusion from the {0001} facets to the {0111} facets depletes vacancies on the {0001} facets, making it difficult to nucleate a new vacancy layer on the {0001} facets. This will suppress the thickening of the void until it grows laterally to a size larger than a critical value. At this critical size, vacancies near the centre area of the {0001} facets are able to accumulate to a supersaturated state to nucleate a vacancy layer, which transits the Stage 1 length growth to the Stage 2 thickness growth.

Figure 6 also shows that before the void nucleus reaches a critical thickness, the diffusion barriers for the forward diffusion $A \rightarrow B \rightarrow C$ and $D \rightarrow E \rightarrow F \rightarrow G$ are lower than their reverse diffusions. In other words, more vacancies will diffuse from the sidewalls to the {0001} facets. This could help the void to thicken to a critical value at the Stage 1. The transition of the diffusion barriers could be closely related to the geometrical change for the atomic configurations of the void in terms of the number of atomic layers or void thickness. The thickness-dependent inter-facet diffusion barriers for vacancies here are quite similar to the three-dimensional Ehrlich–Schwoebel barriers for the surface adatoms diffusion⁵⁰. As seen in Supplementary Fig. S2, a void nucleus with a thickness of a few atomic layers is energetically more stable than a basal plane vacancy dislocation loop when the total number of vacancies is small. Similar calculation results are also reported for α -Zirconium^{51,52}. This suggests that a void with a thickness of a few atomic layers should not collapse when the total number of vacancies is small.

Our *in-situ* HRTEM observation revealed for the first time the irradiation-induced void nucleation and growth at the atomic scale. Under irradiation, interstitial loops form first, producing supersaturated vacancy zones in their vicinity, where voids are nucleated. A void nucleus larger than a critical size will grow in the length direction first (Stage 1) and then in thickness (Stage 2). These observations may help us with the understanding of void formation of other hcp systems or under other irradiation conditions. For example, the void thickness growth in the Stage 2 observed here is similar to what was observed in Zr via low-resolution TEM under high-voltage electron irradiation (1 MeV) at elevated temperature (573 K)^{23,41}. Although the void nucleation and early growth process in Zr has not been reported, it might be similar to what we have observed in Mg. This needs further studies to clarify.

The shape of the void in Mg is observed as a polyhedron bounded with {0001}, {0111} and {0110} facets under electron irradiation. The same void geometry was observed for facet voids in Mg under neutron irradiation¹⁴. Interestingly, similar morphology of faceted voids were also found in other hcp materials, such as Ti²⁰ and Zr⁴¹, although fast neutrons produce defects in a manner that is very different from those by electrons. Therefore, the void formation mechanisms observed here could potentially help with the understanding of void formation in other hcp materials and/or under other irradiation conditions, and may inspire new ideas with the development of better predictive modelling.

Methods

TEM sample preparation. Magnesium with 99.9% purity was used in this investigation. The major impurity elements are Fe = 0.0510 wt%, Mn = 0.0320 wt%, C = 0.0089 wt%, Al = 0.0054 wt%, Na = 0.0027 wt%, Zn = 0.0026 wt%, H = 0.0010 wt% and O = 0.0007 wt%. TEM foil was electro-polished in a solution of 5.3 g lithium chloride, 11.16 g magnesium perchlorate, 100 ml 2-butoxy-ethanol and 500 ml methanol at -30°C and 200 mA, then low energy ion-milled on a cold stage and plasma cleaned for HRTEM observation.

Thickness measurement. The sample thickness in the irradiated region is close to 70 nm as determined by electron energy-loss spectra (EELS) using the log-ratio method⁵³, given as $t/\lambda = \ln(I_t/I_0)$, where λ is the inelastic scattering mean free path ($\lambda = 150$ nm for Mg⁵⁴), I_0 and I_t are the total area under the zero-loss peak and the whole spectra, respectively (see Supplementary Fig. S4).

Electron irradiation conditions. The electron irradiation and *in-situ* observation were performed in a JEM-2010F transmission electron microscope operating at 200 kV at room temperature. The electron beam current is about $8.2 \times 10^{23} \text{ e m}^{-2} \text{ s}^{-1}$, which corresponds to a damage rate of $\sim 1.4 \times 10^{-3}$ displacement-per-atom (d.p.a.) s^{-1} . The void in Fig. 1 nucleated at a dose of around 0.95 d.p.a. The listed times in Figs 1–3 are times from the starts of video recording and are listed in Supplementary Movies 2 and 3. Similar void growth behaviour is observed in samples with various thickness (105, 155, 195, 300 and 460 nm), as shown in Supplementary Figs S5–S7.

Energy barrier calculation. To calculate the energy barriers for vacancy inter-facet diffusion, a periodic simulation cell with the size of $6.0 \times 6.0 \times 1.6 \text{ nm}^3$ along the x ([0110]), y ([0001]) and z ([2110]) directions is used. The system size has been tested with negligible size effect on the results. A centre void is created along the z direction with the side surfaces being {0001}, {0111} and {0111}. The length of the void along x is about 3.0 nm and the thickness N along z increases from one to nine atomic layers to study the effect of thickness. The interatomic interaction is described by the embedded atom method potential developed by Liu *et al.*⁴⁸, which well reproduces the surface formation energy and vacancy formation energy with reference to experiments. After relaxing the simulation cell, the barrier is calculated at 0 K using the nudged-elastic-band method⁴⁷.

Formation energy calculation. The formation energies are calculated using MD simulations with the same embedded atom method potential developed by Liu *et al.*⁴⁸ For all configurations, the simulation cells are first equilibrated at 300 K until the potential energy converges. The temperature is then quenched down to 0 K for the energy calculation. The specific formation energy E_v^f is defined as $E_v^f = (E_{\text{total}} - N_A E_{\text{coh}})/N_v$. In the equation, E_{total} is the total potential energy of the system with N_A atoms and N_v vacancies. E_{coh} is the cohesive energy of hcp Mg.

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Author contributions

W.X. conceived and designed the experiments. Y.Z. performed the MD calculations. G.C. and W.J. contribute to the general discussions with extensive assistance. Y.Z., C.C.K., S.N.M. and P.C.M. supervised the project and provided guidance for the analysis. W.X. and Y.Z. co-wrote the paper.

Additional information

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Physics and model of strengthening by parallel stacking faults

W. W. Jian,¹ G. M. Cheng,¹ W. Z. Xu,¹ C. C. Koch,^{1,a)} Q. D. Wang,^{2,a)} Y. T. Zhu,^{1,a)}
 and S. N. Mathaudhu^{1,3,a)}

¹Department of Materials Science & Engineering, North Carolina State University, Raleigh,
 North Carolina 27695, USA

²School of Materials Science and Engineering, Shanghai Jiaotong University, Shanghai, China

³Materials Science Division, U.S. Army Research Office, Research Triangle Park, North Carolina 27709, USA

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We have recently reported that parallel stacking faults (SFs) can tremendously increase the strength of a magnesium alloy. The strengthening is found to increase linearly with the reciprocal of the mean SF spacing, d . In this study we analyze dislocation interactions with SFs, and then propose a physics-based model to explain the observed relationship between yield strength and SFs spacing. Similar to the empirical Hall-Petch relationship for grain size, it is expected that this strengthening mechanism will hold true for a variety of materials engineered with parallel spaced stacking faults over a wide range of fault spacing. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4822323>]

Traditionally, one or more of the following mechanisms have been used to strengthen metals and alloys: solid solution, precipitates, grain boundary, and cold-working. The precipitates, boundaries, or defects introduced by these strategies serve as barriers to dislocation motion, and consequently, increase the macroscopic strength of the material. Grain boundary strengthening has historically followed the empirical Hall-Petch relationship, where within a certain range of grain sizes (e.g., 20 nm to hundreds of micrometers^{1–9}), the yield strength of metals and alloys increases linearly with the reciprocal of square root of grain size,^{9–13} as represented by the equation $\sigma_{0.2} = \sigma_0 + \frac{k}{\sqrt{d}}$.^{14,15}

More recent studies have shown that a twin boundary, which is a type of coherent internal boundary, can also be effective in blocking dislocation motion and when present in sufficient volume densities, enable increased strain hardening.¹⁴ Lu *et al.* showed that the twin thickness (the spacing between two adjoining twin boundaries) can also be taken as a characteristic structural dimension that affects the yield strength in the same manner as grain boundaries for nanocrystalline Cu, i.e., follows the Hall-Petch relationship.^{16–18}

In heavily deformed metals with sufficiently low stacking fault energies (SFE), another type of coherent planar defect, stacking faults (SFs), is commonly observed.^{19–23} This is especially true for face-centered cubic metals when the grain sizes are smaller than a critical nanosize.^{24,25} The formation of SFs involves dissociation of a full dislocation into partial dislocations that bound a planar stacking fault ribbon,²⁶ or emission of partial dislocations from grain boundaries.²⁵ Analogous to coherent twin boundaries, stacking faults should impede dislocation movement and thus strengthen the material. However until recently, there were no systematic studies or reports indicating this as a tractable mechanism.

Recently, a high density of SFs with nano-scale spacing was introduced in a Mg-8.5Gd-2.3Y-1.8Ag-0.4Zr (wt. %) alloy

through conventional hot rolling.^{27–30} Addition of certain alloying elements, such as Gd and Y, can significantly decrease the SFE of Mg alloys and, thus, promote the formation of SFs during deformation.^{31,32} TEM investigation showed that the mean spacing of the SFs, d , decreased as the rolling strain increased. The nano-spaced stacking faults were demonstrated to make the main strengthening contribution to the observed ultrahigh strength (600 MPa ultimate tensile strength and 575 MPa tensile yield strength). More interestingly, as shown in Fig. 1, the room temperature yield strength of the Mg alloy, $\sigma_{0.2}$, increased linearly with the reciprocal of d (d^{-1} dependence),²⁷ expressed as $\sigma_{0.2} = \sigma_a + k \cdot d^{-1}$, instead of the commonly observed Hall-Petch relationship ($d^{-1/2}$ dependence) and where σ_a is the flow stress stemming from all other strengthening mechanisms other than parallel stacking faults, as marked by the blue arrow in Fig. 1.

In this paper, we elucidate the fundamental deformation physics that underlies this difference by first identifying the dislocations activated during the room temperature tensile testing of the Mg-alloy with nano-spaced SFs on the basal plane, and, based on the experimental observation, we propose a physical model to explain the d^{-1} dependent relationship between yield strength and SF spacing.

Hot rolling typically results in a strong texture in Mg alloys with the close packed basal plane parallel to the rolling direction.^{33,34} Since the tensile testing direction is parallel to the basal plane in this study, deformation by contributions from basal and prismatic slip as well as extension twinning are minimized,³⁵ and $\langle c+a \rangle$ dislocations (Fig. 2) are necessary for slip on the pyramidal slip planes to accommodate overall plastic deformation.³⁶ Figs. 2(a)–2(c) show detailed TEM characterization using the two-beam technique on the 88% rolled sample after tensile testing. According to the visibility criterion, $\vec{g} \cdot \vec{b} \neq 0$, the $\langle a \rangle$ dislocation should be visible in a TEM image when the incident beam tilts to the two-beam condition with $\vec{g} = [11\bar{2}0]$ and $\langle c \rangle$ dislocation should be visible in the TEM image with $\vec{g} = [0002]$. Furthermore, the $\langle c+a \rangle$ dislocations should be visible in both the $\vec{g} = [11\bar{2}0]$ and $\vec{g} = [0002]$ conditions.^{37,38} With this analysis, the TEM images show that $\langle c+a \rangle$

^{a)}Authors to whom correspondence should be addressed Electronic addresses: carl_koch@ncsu.edu, wangqudong@sjtu.edu.cn, ytzhu@ncsu.edu, and suveen.n.mathaudhu.civ@mail.mil.

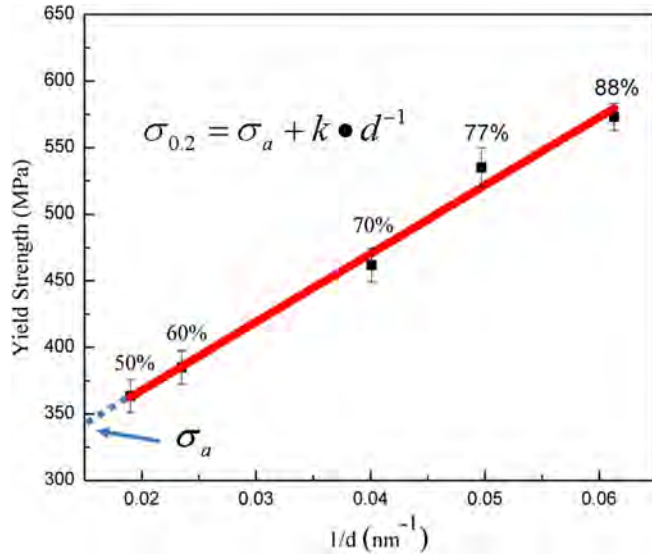


FIG. 1. Yield strength, $\sigma_{0.2}$, vs. the reciprocal of mean spacing between SFs, d , of rolled samples with different thickness reduction. The number by each data point indicates the thickness reduction by hot rolling. The yield strength of rolled Mg alloy can be expressed as $\sigma_{0.2} = \sigma_a + k \cdot d^{-1}$, where σ_a is the flow stress stemming from all other strengthening mechanism other than parallel stacking faults.

dislocations (Fig. 2) were activated and cut the SFs on the basal plane during the tensile testing.²⁷ Recently, the observation of $\{c+a\}$ dislocations being the main dislocations activated during deformation of a similar alloy has been reported, which validates our observations of the activation of $\langle c+a \rangle$ dislocations.³⁹

In Mg alloys, $\langle c+a \rangle$ dislocations, such as $\frac{1}{2}\langle 1\bar{2}13 \rangle$ type, usually slip on the pyramidal plane, $\{\bar{1}2\bar{1}2\}$,³⁶ as shown in Fig. 3(a). Here we assume that $\langle c+a \rangle$ dislocation is an edge dislocation and its dislocation line is straight. When a $\langle c+a \rangle$ dislocation encounters a SF and cuts through it (Fig. 3(c)), extra energy per unit length of dislocation line, E_S , is consumed.

For simplicity, assuming a dislocation with a unit length and a Burgers vector b glides a distance of x on a pyramidal slip plane (e.g., $\{\bar{1}2\bar{1}2\}$) as shown in Fig. 3. During this process, the dislocation cuts n SFs with an average spacing of d . According to Fig. 3, n can be calculated as

$$n = \frac{x}{d/\sin\theta}. \quad (1)$$

The extra energy consumed by cutting the n SFs can be calculated as

$$\Delta E = nE_S = \frac{x E_S}{d/\sin\theta}. \quad (2)$$

This extra energy is supplied by the extra work done by the extra applied resolved shear stress, $\Delta\tau$, to move the unit dislocation for the distance x , which can be described by

$$\Delta W = \Delta\tau x b \quad (3)$$

The extra work should be equal to the extra energy consumed by cutting the n SFs, i.e., $\Delta W = \Delta E$, which leads to

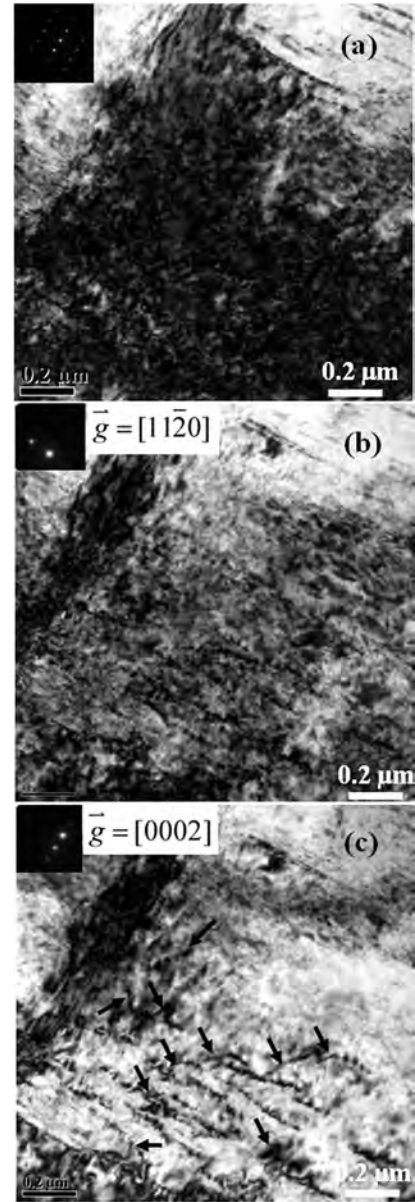


FIG. 2. TEM image of 88% hot rolling Mg-8.5Gd-2.3Y-1.8Ag-0.4Zr (wt. %) alloy samples: (a) after tensile test (b) and (c) two-beam bright field images with different g vectors indicated by the diffraction patterns. The non basal $\langle c+a \rangle$ are marked by short black arrows. Note that some dislocations were also activated and this may due to slight orientation alteration of Mg grain during tensile testing.

$$\Delta\tau x b = \frac{x E_S}{d/\sin\theta}. \quad (4)$$

Simplifying Eq. (4), the extra applied shear stress that is needed to cut the stacking faults can be described as

$$\Delta\tau = k/d, \quad (5)$$

where $k = E_S \sin\theta/b$ is a constant.

Thus, the extra applied shear stress that is needed for a dislocation to move on a non-basal slip plane and cut through SFs is linearly proportional to the reciprocal of the mean spacing between adjacent SFs, d . Assuming that the shear stress needed for the dislocation to overcome all other sources of resistance, including lattice friction (Peierls stress),

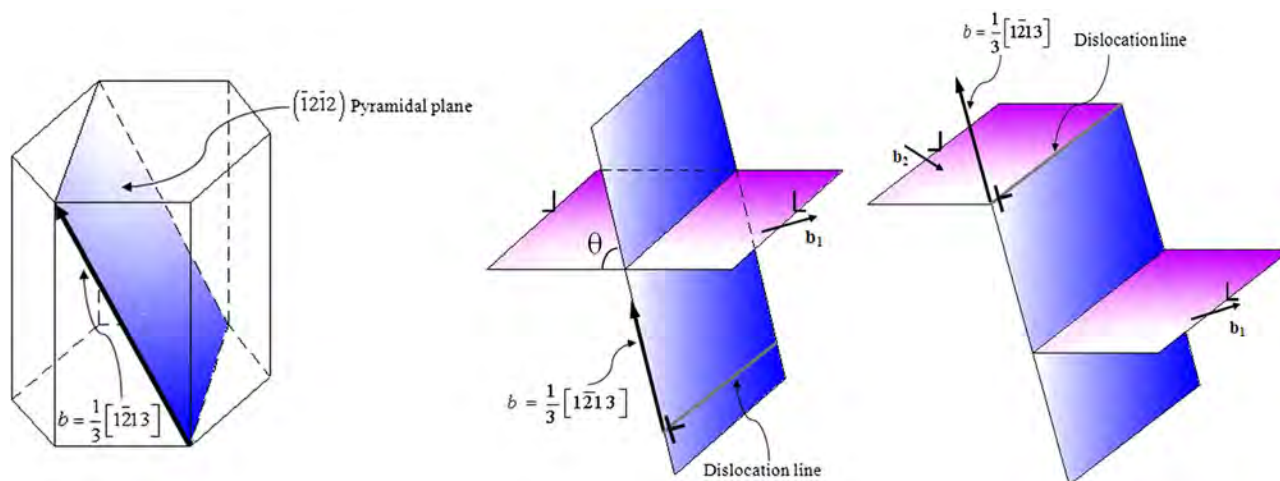


FIG. 3. Schematic illustration of (a) a $\langle c+a \rangle$ dislocation, (b) $\langle c+a \rangle$ dislocation motion and interaction with a basal stacking fault, and (c) $\langle c+a \rangle$ dislocation cutting through the stacking fault.

grain boundary, etc., is τ_α , the strength of an alloy with high density of SFs can be described as

$$\tau = \tau_\alpha + k/d. \quad (6)$$

Equation (6) can be also expressed in the form of normal yield strength

$$\sigma = \sigma_\alpha + k/d. \quad (7)$$

Equation (7) is similar to the Hall-Petch relationship except that the yield strength is dependent on d^{-1} instead of $d^{-1/2}$ as in the latter.

Note that the condition for Eq. (7) to be valid is that dislocations interact and cut through SFs. This equation is applicable to hcp metals, where the $\langle c+a \rangle$ dislocation slip can accommodate plastic deformation, and more so in our experiments where plasticity by basal slip and extension twinning is suppressed by the strong basal texture and the geometry of the loading conditions.^{40,41} For this physical model, we assume that bulk plasticity occurs via the emission of $\langle c+a \rangle$ dislocations that subsequently cut the SFs on the basal plane. The conditions of validity for Eq. (7) may also only be when the grain size is relatively large ($> 1 \mu\text{m}$). It is generally reported that as the grain size of an alloy is refined to the nanometer range ($< 100 \text{ nm}$), conventional lattice dislocation slip is suppressed and that plasticity is significantly mediated by deformation mechanisms that occur through the motion of grain boundary (GB) defects such as grain boundary sliding.^{42–44} Theoretically, Eq. (7) should also be applicable to other crystal systems such as face-centered cubic (fcc) and body-centered cubic alloys as long as the stacking fault energy is sufficiently low, and the cutting of the generated SFs by dislocations is a significant deformation mechanism. Further investigations are ongoing to clarify these issues.

It should also be noted that some dislocations accumulated between segmented SFs during the room temperature tensile testing, as opposed to all cutting through and also, some dislocations were observed when the two-beam condition was set to $\bar{g} = [11\bar{2}0]$ (Fig. 2).²⁷ These observations suggest that dislocation pileup may also play some roles in the

deformation and strengthening of the alloy. If the dislocation piling up near the SFs becomes dominant, the SFs become similar to twin boundaries in terms of impeding dislocation motion and enhancing dislocation accumulation, in which case the Hall-Petch relationship should apply.^{16–18} It appears that this is not the case in the Mg alloy studied here.

In summary, we have posited a physical model for strengthening in materials with parallel stacking faults. This model is based on the physics of dislocations cutting stacking faults. It describes a linear relationship between the applied stress and the reciprocal of the mean spacing between stacking faults, and thus explains the d^{-1} dependence (d is the average spacing between stacking faults) observed in an Mg alloy with high density of stacking faults. It is expected that this model will be valid for any metallic alloy where cutting of stacking faults by dislocations is a significant deformation mechanism. This also points out a new strengthening and toughening mechanism for hcp metals and alloys: lowering stacking fault energy and choose appropriate processing parameters to form a high-density of parallel spaced stacking faults.

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Extraordinary strain hardening by gradient structure

XiaoLei Wu^{a,1}, Ping Jiang^a, Liu Chen^a, Fuping Yuan^a, and Yuntian T. Zhu^{b,c,1}

^aState Key Laboratory of Nonlinear Mechanics, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, China; ^bDepartment of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695; and ^cSchool of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, China

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Gradient structures have evolved over millions of years through natural selection and optimization in many biological systems such as bones and plant stems, where the structures change gradually from the surface to interior. The advantage of gradient structures is their maximization of physical and mechanical performance while minimizing material cost. Here we report that the gradient structure in engineering materials such as metals renders a unique extra strain hardening, which leads to high ductility. The grain-size gradient under uniaxial tension induces a macroscopic strain gradient and converts the applied uniaxial stress to multiaxial stresses due to the evolution of incompatible deformation along the gradient depth. Thereby the accumulation and interaction of dislocations are promoted, resulting in an extra strain hardening and an obvious strain hardening rate up-turn. Such extraordinary strain hardening, which is inherent to gradient structures and does not exist in homogeneous materials, provides a hitherto unknown strategy to develop strong and ductile materials by architecting heterogeneous nanostructures.

gradient structured metal | nanocrystalline metal

Man kind has much to learn from nature on how to make engineering materials with novel and superior physical and mechanical properties (1, 2). For examples, the clay-polymer multilayers mimicking naturally grown seashells are found to have exceptional mechanical properties (3). Another example is the gradient structure, which exists in many biological systems such as teeth and bamboos. A typical gradient structure exhibits a systematic change in microstructure along the depth on a macroscopic scale. Gradient structures have been evolved and optimized over millions of years to make the biological systems strong and tough to survive nature. They are greatly superior to manmade engineering materials with homogeneous microstructures.

Here we report the discovery of a hitherto unknown, to our knowledge, strain hardening mechanism, which is intrinsic to the gradient structure in an engineering material. The gradient structure shows a surprising extra strain hardening along with an up-turn and subsequent good retention of strain hardening rate. Strain hardening is critical for increasing the material ductility (4–6). We also show a superior ductility–strength combination in the gradient structure that is not accessible to conventional homogeneous microstructures.

Microstructural Characterization of Gradient Structure

We demonstrate these behaviors in a grain-size gradient-structured (GS) sample, i.e., two GS surface layers sandwiching a coarse-grained (CG) core, produced by the surface mechanical attrition treatment (SMAT) (7) in a 1-mm-thick CG interstitial free (IF)-steel sheet (*SI Materials and Methods*). The GS layers on both sides have a gradual grain-size increase along the depth (Fig. 1*A*). In the outermost layer of ~25- μ m thickness are nearly equiaxial nanograins with a mean size of 96 nm (Fig. 1*B*). The grain size increases gradually to 0.5 and 1 μ m at the depths of ~60 and 90 μ m, respectively, with subgrains or dislocation cells smaller than 100 nm. For convenience, we define the top 90- μ m-depth as a nanostructured layer (8–10) with a grain-size gradient. The whole gradient layer is 120 μ m thick, including the deformed CG layer with either dislocation tangles or dislocation cells of

sizes ranging from submicrometers to micrometers. The central strain-free CG core has an average grain size of 35 μ m (Fig. 1*C*).

Unique Mechanical Responses Under Uniaxial Tension

Fig. 2*A* shows the engineering stress–strain (σ_e – ϵ_e) curves. The gradient-structured (GS–CG) sample exhibits not only a large tensile uniform elongation (E_U), comparable to that of the homogeneous CG sample, but also yield strength that is ~2.6 times as high. In contrast, the freestanding nanostructured (NS) film becomes unstable soon after yielding. Interestingly, the GS–CG sample shows a transient hardening in the regime of small tensile strains on its σ_e – ϵ_e curve between two inflection points (Fig. 2*B*, *Inset*). This caused an up-turn in the strain hardening rate Θ (Fig. 2*B*, *Inset*). Meanwhile, the unloading–reloading σ_e – ϵ_e curves also reveal a similar Θ -up-turn upon each reloading (GS–CG⁺, red curves in Fig. 2*B*). More importantly, the GS–CG sample shows an even slower Θ -reduction than that of the CG sample (Fig. 2*B*), indicating a better Θ -retention in the GS–CG sample. In contrast, the freestanding GS layer and CG core do not show any Θ -up-turn (see the GS layer and CG curves in Fig. 2*B*), suggesting that the unique behavior is produced only when these two types of layers form an integral bulk.

The dramatic hardening behavior raises a critical issue: where in the GS–CG sample is strain hardening generated? To answer this question, we measured the microhardness (H) along the depth of GS–CG samples after testing them to varying strains. As shown in Fig. 2*C*, the H values increase with increasing tensile strain. The border, where H values in the untested sample no longer drop, demarcates the GS layer and CG core. Fig. 2*D* shows H increments, ΔH , along the depth caused by testing at various tensile strains. ΔH is an indicator on the magnitude of

Significance

Nature creates the gradient structure (GS) for a purpose: to make biological systems strong and tough to survive severe natural forces. For the grain-size GS, the deformation physics is still unclear. One wonders if the grain-size GS in the nanomicroscale would also benefit materials engineered by mankind. In this paper, a universal strain hardening mechanism is revealed in the GS. We discovered a unique extra strain hardening that is intrinsic to the GS. Its mechanism is the presence of strain gradient together with the stress state change. A superior combination of strength and ductility that is not accessible to conventional homogeneous materials is obtained. As a novel mechanism, extra strain hardening renders high ductility in the GS materials.

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¹To whom correspondence may be addressed. E-mail: xlwu@imech.ac.cn or ytzh@ncsu.edu.

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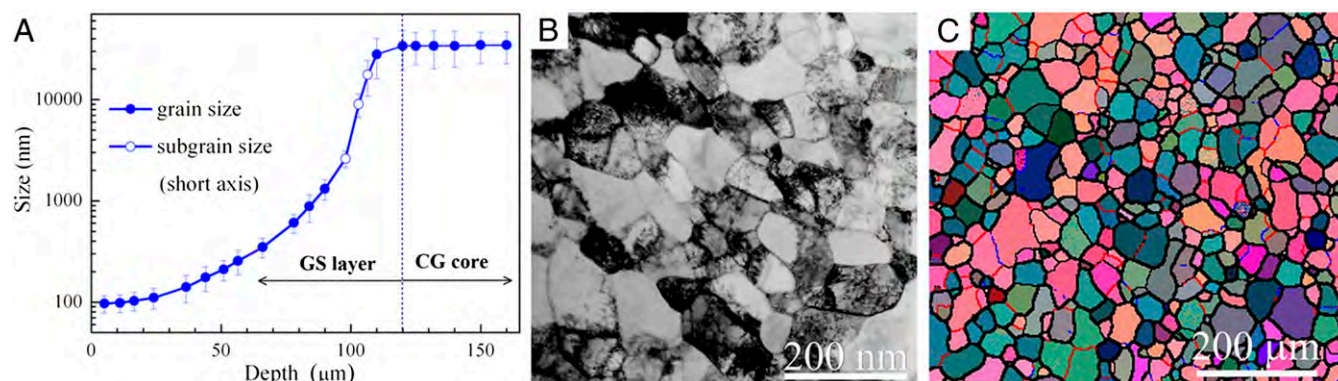


Fig. 1. Gradient structure by SMAT. (A) Variation of average grain sizes along the depth. The error bars represent the SD of the grain sizes. The GS sample was produced by means of SMAT for 5 min on both sides of a CG IF-steel sheet. (B) Cross-sectional TEM bright-field image of the nanograins with a mean grain size of 96 nm at the depth of ~10 μm. (C) Electron back-scatter diffraction image of coarse grains with a mean grain size of 35 μm.

hardening retained after unloading. For comparison, the ΔH values are also measured in both the freestanding GS layer (failure strain of 0.05 in Fig. 2A) and homogeneous CG after tensile testing them to the strain of 0.05. Remarkably, the layer in GS-CG exhibits a unique extra strain hardening, i.e., a much higher ΔH than that of the freestanding GS layer (dotted area in Fig. 2D). This extra hardening originates in the gradient layer, and its peak moves inward and finally penetrates into the CG core at higher strains. This indicates again that the gradient layer needs to form an integral bulk with the CG core to be effective in producing strain hardening.

The above unique hardening behavior is inherent to the GS-CG and is caused by the gradient-generated multiaxial stresses

and strain gradient. Under uniaxial tension (Fig. 3A), necking instability readily occurs in the NS surface layers at very low tensile strains (see the NS-film curve in Fig. 2A), which is characterized by their fast lateral shrinking. However, lateral instability is constrained and quickly stopped by the neighboring stable layer. Consequently, the strain gradient is produced near the border between the unstable surface layers and the stable central core (11, 12), where strain continuity is required to keep material continuity.

The mutual constraint between the unstable surface layers and stable central core leads to stress state changes, as schematically shown in Fig. 3A. When the shrinking surface layers are constrained by the central core, the constraint is realized in the form of lateral tensile stress in the surface layers, i.e., (σ_x^+) as shown

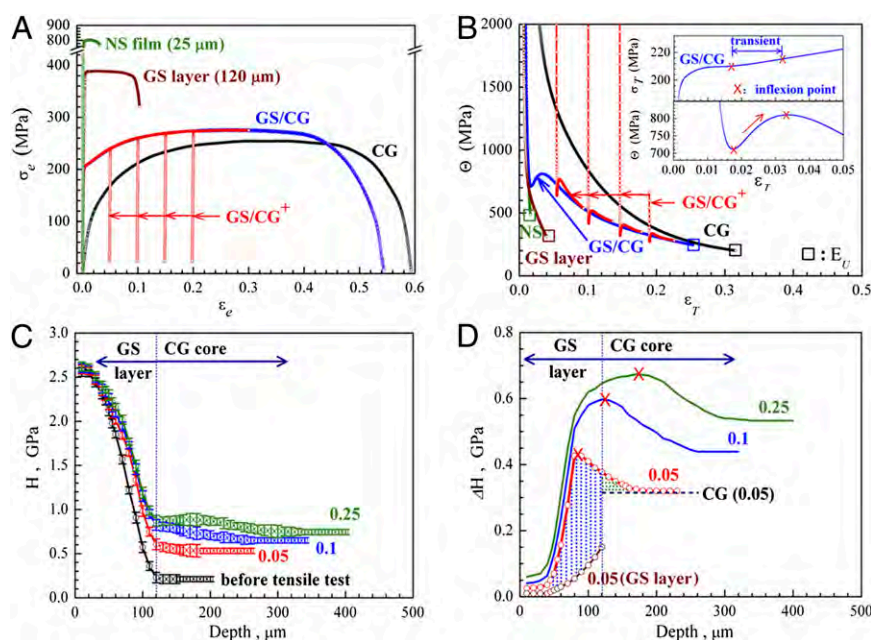


Fig. 2. Hardening rate up-turn and unique extra strain hardening. (A) Tensile engineering stress-strain (σ_e - ϵ_e) curves at a quasistatic strain rate of $5 \times 10^{-4} \text{ s}^{-1}$. CG: standalone homogeneous CG sample; GS layer: grain-size GS layer of 120-μm thickness; GS-CG: sandwich sample of 1-mm thickness. NS: freestanding, quasihomogeneous nanostructured film of 20-μm thickness peeled from the top surface of GS; GS-CG⁺: the same sandwich sample subjected to unloading-reloading tensile testing at four separate strains of 0.05, 0.1, 0.15, and 0.2. All tensile samples were dog-bone-shaped, with a gauge dimension of 8 mm $\times$ 2.5 mm. (B) Strain hardening rate ($\Theta = d\sigma/d\epsilon$) vs. true strain (ϵ_T) curves. (Inset) Transient response on the σ_T - ϵ_T curve of the GS-CG sample between two inflection points marked by "x," corresponding to the Θ -up-turn on its Θ - ϵ_T curve. GS-CG⁺ (red curve) shows Θ -up-turn upon each reloading. (C) Vickers microhardness (H) vs. depth. The H values were measured on the cross-sectional GS-CG sample after tensile testing them to varying strains (labeled on the curves). The border between GS layer and CG core is located at 120-μm depth. (D) ΔH (H increment) vs. depth after varying tensile strains. The dotted area indicates the extra hardening in the GS-CG sample.

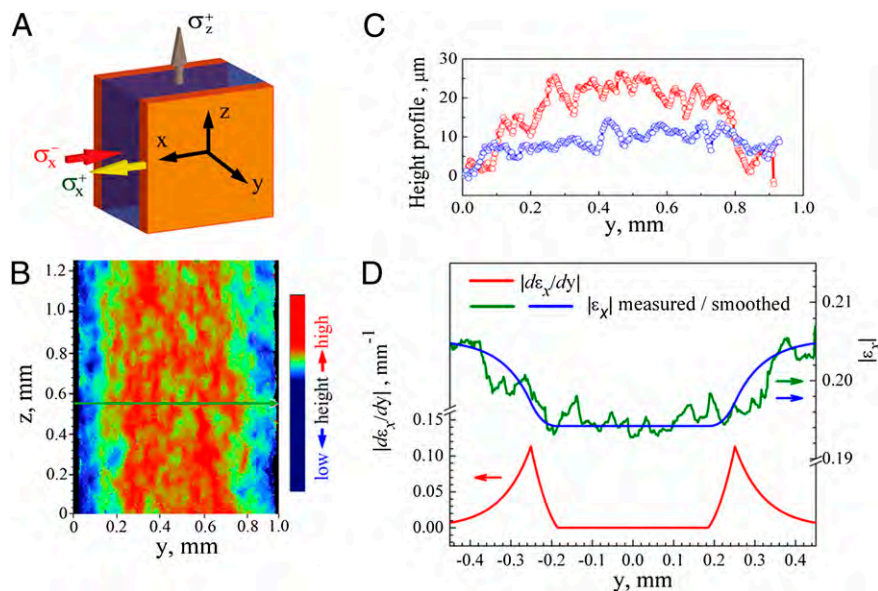


Fig. 3. Stress state change and strain gradient. (A) Schematic stress state change during uniaxial tension in a GS-CG sample. Outer layers: the plastically unstable layers. Core: the stable layer. σ_z^+ is the lateral tensile stress in the outer layers, and σ_x^- is the lateral compressive stress in the inner layer in the x direction. σ_z^+ is the applied uniaxial stress. (B) Measured height contour on the side surface, vertical to the x axis, within the gauge section of GS-CG sample at the tensile strain of 0.25. (C) Measured height profiles covering the thickness of both GS-CG sample (along the green line in B) and a standalone homogeneous CG sample after tensile testing to a strain of 0.3. (D) Distribution of lateral strain (ϵ_x) and strain gradient ($d\epsilon_x/dy$) across the thickness along the green line in B.

Fig. 3A. Because no external lateral stress is applied to the sample, the tensile stresses in the outer surface layers have to be balanced by a lateral compressive stress (σ_x^-) in the inner stable core. Therefore, the applied uniaxial tensile stress is converted to complex 2D stress states with the outer surface layers under a tension-tension stress state and the central stable layer under a tension-compression stress state.

To evaluate the strain gradient, the height profiles on the lateral surface, i.e., vertical to the x axis in Fig. 3A, were measured after suspension of a tensile testing at the strain of 0.25, as shown in Fig. 3B (also Fig. S14). The GS-CG sample exhibits marked height difference, i.e., lower on both sides and higher in the middle (see the red curve in Fig. 3C) (also Fig. S1B). This is the direct evidence that nonuniform lateral deformation in GS-CG occurred, with the outer GS layers shrunk more than the central zone. In contrast, a homogeneous standalone CG sample only shows surface roughness without a systematic height difference (see the blue curve in Fig. 3C). The lateral strain ϵ_x was calculated as $\epsilon_x = \delta x/x_0$, where $\delta x = x - x_0$ was measured from the contour (Fig. 3C) and x_0 is the initial width. This strain is negative due to shrinking, and the distribution of its absolute values along the green line in Fig. 3B is plotted in Fig. 3D. It is also fitted with a smooth curve $\epsilon_x(y)$ (blue curve). As shown, the absolute value of ϵ_x is essentially unchanged in the stable central layer except for the effect of surface roughness. However, the $|\epsilon_x|$ increases gradually toward the surface, which produces strain gradient $d\epsilon_x/dy$ across the sample thickness as plotted in Fig. 3D (red curve). As shown, there exists a maximum strain gradient near the interface. As discussed later, this maximum strain gradient will promote the accumulation of geometrically necessary dislocations (GNDs) (11,12) to produce a peak of extra strain hardening.

To probe the physical origin behind the Θ -up-turn, dislocation evolution with strains in GS sample is studied by stress relaxation tests, which is complemented by transmission electron microscopy (TEM) observations. Fig. 4A shows a $\sigma_e - \epsilon_e$ curve as a function of relaxation time at varying strains (Fig. 4A, *Inset*), which were selected carefully to cover the strain range where the Θ -up-turn occurs (Fig. 2B, *Inset*). The ratio $Re = \rho_m/\rho_{m0}$

represents the relative mobile dislocation density evolution (13). Fig. 4B shows the evolution of the ρ_m/ρ_{m0} with relaxation time and its inset reveals how the ρ_m/ρ_{m0} varies with tensile strain. As shown, with increasing tensile strain, the Re first drops (Fig. 4B, *Inset*) and then reaches the minimum value at the strain of 0.015, after which Re increases rapidly to reach a near-saturated value at the strain of 0.05. Interestingly, the strain value of 0.015 almost coincides with the strain at which minimum Θ is observed in the GS-CG sample (Fig. 2B, *Inset*). This observation indicates rapid exhaustion of mobile dislocations at low strains, which is consistent with what was reported in nanocrystalline Ni (14). In addition, the strain of 0.015 is also near the onset of necking instability for the NS film (see the green curve in Fig. 24), suggesting that the exhaustion of mobile dislocations promoted instability of the GS layers (15). On the other hand, this also creates more space for dislocation accumulation later, setting the stage for Θ -up-turn (Fig. 4E).

TEM observations provide us with information on the evolution of dislocation structures in the nanograins. At very small strain of 0.008 (soon after yielding), tangled high-density dislocations are visible either in their interior or at boundaries and subboundaries (Fig. 4C). At higher strain of 0.015 (before the Θ -up-turn), debris of dislocations is visible (Fig. 4D), indicating the occurrence of disentanglement and annihilation of the initial dislocation structure (16). Further increasing strain to 0.035 (soon after Θ -up-turn) regenerates dislocation structures (Fig. 4E). These observations are consistent with and provide insight into the evolution of mobile dislocations and Θ -up-turn in the GS-CG sample.

Discussion and Summary

The extra strain hardening (Fig. 2D) is caused by the strain gradient (Fig. 3D), which needs to be accommodated by the generation of the GNDs (17–20). The GNDs interact and tangle with mobile dislocations to further promote the dislocation storage (18). These dislocation activities effectively promote the dislocation accumulation near the border demarcating the unstable and stable layers, which produces the observed extra hardening (ΔH) peak as shown in Fig. 2D. With increasing applied

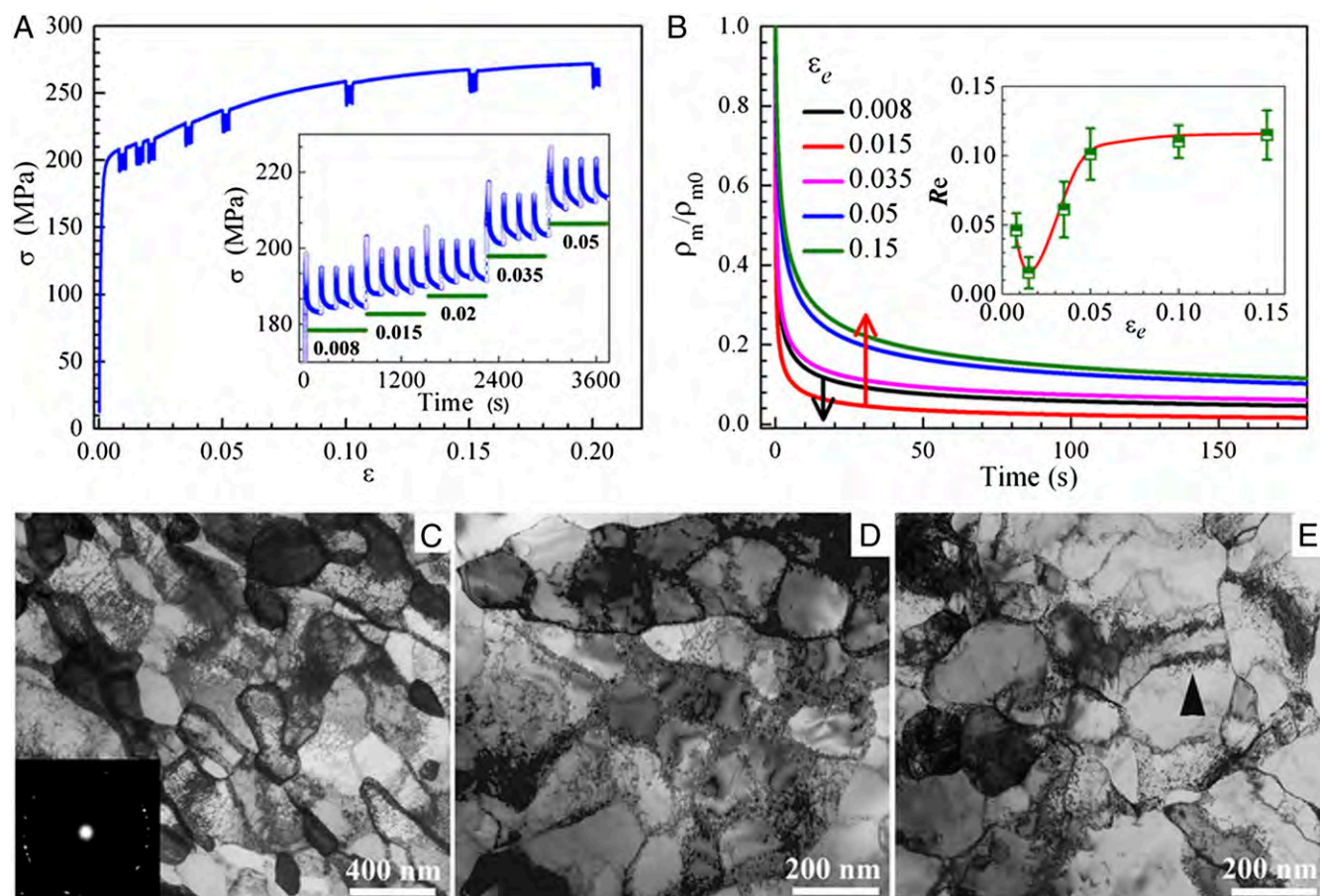


Fig. 4. Evolution in mobile dislocation density. (A) σ_e – ϵ_e curve from a stress relaxation test at eight starting strains. (Inset) Stress–relaxation time curve. Four relaxation tests are performed at each starting strain. (B) Evolution of the mobile dislocation density ρ_m/ρ_{m0} with the first stress relaxation (180 s) at varying starting strains. ρ_m is the mobile dislocation density, whereas ρ_{m0} is the dislocation density at the onset of each relaxation cycle. Two arrows indicate the first drop and later rise in ρ_m/ρ_{m0} with strain. (Inset) $R_e = \rho_m/\rho_{m0}$ after relaxation as a function of starting strain. (C–E) Cross-sectional TEM bright-field images of GS–CG samples after suspension of tensile testing at varying strains. (C) Dislocation-tangled grain boundaries and subboundaries at the strain of 0.008 (~20 μm deep). (D) Dislocation debris left inside grain interior and on their boundaries at the strain of 0.015 (~20 μm deep). (E) Newly formed dislocation subboundaries (indicated by a triangle) at the strain of 0.035 (~25 μm deep).

strain, stable layers will become unstable, which leads to migration of the border and consequently the ΔH peak toward the CG core. This leaves in its wake high densities of dislocations. This explains why the ΔH peak becomes flatter and moves inward as the tensile strain increases. In other words, the extra strain hardening is accumulative with the dynamically moving border. This is the reason why the GS–CG sample has a slower decrease in Θ than the homogeneous CG core with strain (Fig. 2B). Furthermore, the multiaxial stress state will activate more slip systems (16, 21), which makes it more likely for dislocations to interact and entangle with each other (Fig. 4E), following the initial depletion of dislocations (Fig. 4B). The GNDs caused by the strain gradient and the dislocation accumulation caused by the multiaxial stress state are the primary causes for the observed dramatic hardening rate up-turn and its good retention.

The nanograined layers play critical roles in producing high extra strain hardening although no significant extra hardening occurs in the nanograined layers themselves (Fig. 2D). First, the nanograined layers have a much higher flow stress than the larger-grained inner layer. This ensures high lateral stresses (Fig. 3A) during necking instability of the nanograined layer, which is constrained by the stable central layer. The high lateral stress will promote the operation of additional slip systems to help with dislocation storage. Second, the early necking by the nanograined layers activates the multiaxial stresses and strain gradient

at an early stage of the mechanical testing, which consequently starts the extra strain hardening process in an early stage.

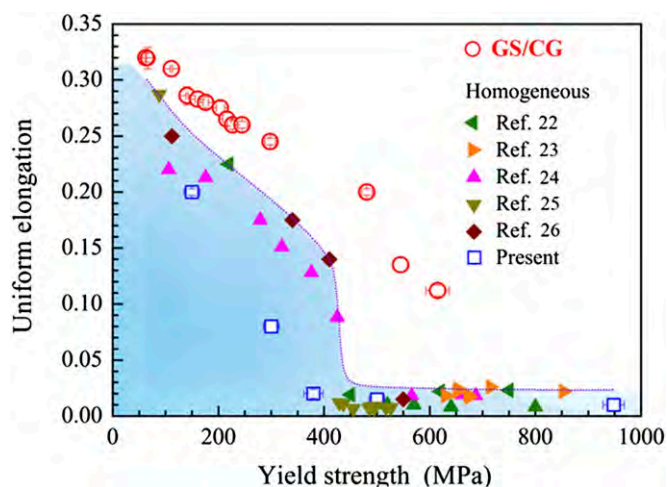


Fig. 5. Superior mechanical property. Strength and ductility in the GS–CG samples of IF-steel compared with their homogeneous counterparts.

Our preliminary results also suggest that there is a minimum SMAT processing time above which the strain hardening rate up-turn occurs. This minimum time is associated with a minimum GS layer thickness. It is our hypothesis that there should be an optimum GS layer thickness that produces the most significant Θ -up-turn and the most extra strain hardening. Further systematic investigation is needed to verify this hypothesis. Also note that the mechanism for good ductility observed here is totally different from that in gradient nanograined Cu (8), where high ductility was attributed to grain growth due to the low structural stability of the nanograined Cu. No grain growth is observed in the GS IF-steel in the current study (Fig. S2).

Due to the extra strain hardening, the gradient structure provides for an effective route to a superior combination of good ductility and

high strength (Fig. 5). When the homogeneous IF-steel is deformed to increase strength, its ductility usually drops dramatically, especially when the strength is above 400 MPa (22–26). In contrast, the ductility of GS sample is 5–10 times higher than that of the homogeneous nanograined structures within the strength range of 450–600 MPa. More importantly, the GS sample can be easily produced in metallic materials in a cost-effective and large-scale way and therefore is expected to be conducive to industrial production.

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A new metastable precipitate phase in Mg–Gd–Y–Zr alloy

H. Zhou^{a,b}, W.Z. Xu^b, W.W. Jian^b, G.M. Cheng^b, X.L. Ma^b, W. Guo^{a,c},
S.N. Mathaudhu^{b,d}, Q.D. Wang^{a,c,*} and Y.T. Zhu^{b,*}

^aNational Engineering Research Center of Light Alloy Net Forming, Shanghai Jiao Tong University, Shanghai 200240, China; ^bDepartment of Materials Science & Engineering, North Carolina State University, Raleigh, NC 27695, USA; ^cKey State Laboratory of Metal Matrix Composite, Shanghai Jiao Tong University, Shanghai 200240, China; ^dMaterials Science Division, US Army Research Office, Research Triangle Park, Durham, NC 27709, USA

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Mg–RE alloys are among the strongest Mg-based alloys due to their unique precipitation structures. A previously unobserved metastable phase (β_T) is found to coexist with reported β'' and β' metastable phases under peak ageing conditions in a Mg–Gd–Y–Zr alloy. The position of the RE elements within the β_T phase is identified using atomic-resolution high-angle annular dark field scanning transmission electron microscopy imaging, and the β_T phase is shown to have an orthorhombic structure with a stoichiometry of Mg_5RE . Based on these observations, a new precipitation sequence is proposed.

Keywords: magnesium alloys; metastable phases; base-centred orthorhombic structure; phase transformations

Introduction

Magnesium alloys are becoming increasingly attractive for potential use in a wide range of structural applications because of their low density, good machinability and good recyclability [1–4]. However, some applications are limited due to their relatively low strength and poor room temperature ductility. Recently, progress has been made in developing high-strength Mg alloys by means of grain refinement, age hardening and introduction of stacking faults [5–10]. Of these, precipitation hardening provides a promising strategy to enhance the mechanical properties in Mg alloys containing rare earth (RE). Wang et al. [11] found that the yield strength of Mg–Gd–Y–Ag and Mg–Gd–Y alloys can be improved by 75 and 81%, respectively, after appropriate peak ageing wherein a super-high-tensile strength of up to 403 MPa was reported.

To understand the strengthening that occurs in Mg–RE alloys, it is critical to investigate the structure and formation process of precipitates. He et al. [12] proposed a precipitation sequence for Mg–Gd–Y alloys, which consisted of four stages of S.S.S.S (Supersaturated Solid solution) $\rightarrow \beta'' \rightarrow \beta' \rightarrow \beta_1 \rightarrow \beta$. Under peak ageing condition, β' phase was shown to coexist with β'' as the main strengthening phase [13]. Similarly, Honma found that β'' and β' are metastable and isomorphic with the HCP Mg [14]. The structure of the β' phase has been suggested to be base-centred orthorhombic (b.c.o)

*Corresponding authors. Email: wangqudong@sjtu.edu.cn (Q.D. Wang); ytzhu@ncsu.edu (Y.T. Zhu)

with lattice parameters of $a = 0.64$ nm, $b = 2.22$ nm, and $c = 0.52$ nm, and its composition is reported as Mg_7RE [15–18]. While the structure of the β' phase is well observed and reported, the phase structure of β'' is still somewhat controversial. Many researchers believe that β'' has D0_{19} crystal structure (hexagon, $a = 0.640$ nm and $c = 0.520$ nm) [12,19,20], and TEM and three-dimensional atom probe studies suggest that the β'' phase likely has a stoichiometric composition Mg_3RE [21]. In either case, the majority of reports [12,16–18] on the precipitation sequence of Mg–Gd–Y alloy suggest that the β'' phase precipitates at the early stages of ageing, and prior to β' , however, the mechanisms by which β'' may transform to β' are still unknown. Given that the β' phase is the main strengthening phase in the Mg–RE alloys, it is therefore crucial to fully understand its formation and growth mechanisms.

In the present work, we report a previously unobserved metastable phase (hereafter named β_{T}) that coexists with the β'' and β' phases. The crystal structure and elemental composition of the new β_{T} phase are identified by both experiments and simulations. We also report conclusive evidence of the morphology and atomic arrangements of both metastable phases, β' and β'' , and propose a formation sequence among the β'' , β_{T} and β' phases.

Experimental methods

The casting procedure to produce the Mg–9.8Gd–2.7Y–0.4Zr (wt%) alloy can be found in [22]. Ingots with a diameter of 180 mm were homogenized at 500 °C for 12 h followed by quenching in hot water (i.e. T4 treatment). Subsequently, repeated upsetting was carried out at 350 °C for eight passes via route B (rotating the billet 90° for each pass) [23]. Isothermal ageing was carried out at 200 °C in silicon oil for 0–64 h. TEM specimens were cut from the aged samples and thinned by mechanical polishing to a thickness of ~90 μm . Twin-jet electropolishing was carried out in a solution of 5.3 g lithium chloride, 11.16 g magnesium perchlorate, 500 mL methanol and 100 mL 2-butoxy-ethanol, at –55 °C and 100 mA [24]. Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) on a Cs-corrected FEI Titan³ 80–300 STEM operated at 200 kV was used to probe the atomic structure. Diffraction pattern simulation was carried using CaRIne software.

Results

Figure 1 shows the low-magnification HAADF images of the sample aged at 200 °C for 64 h. Figure 1(a) was obtained with a beam parallel to the $[0\ 0\ 0\ 1]$ zone axis of the α -Mg matrix, whereas Figure 1(b) was taken from $[1\ 1\ \bar{2}\ 0]$ of the α -Mg matrix. For simplicity, all zone axes mentioned in the text hereafter are those of the α -Mg matrix. The morphology of the precipitates from $[0\ 0\ 0\ 1]$ direction is an elliptical main body and protrusions. This morphology agrees with reports by Nie, He and Nishijima [12,17,25]. These earlier reports also concluded that both the main body and its surrounding protrusions are composed of metastable β' phase. However, as shown in Figure 1(a), the space between the white stripes in the main body is 1.1 nm, which is smaller than that in the protrusions (1.5 nm). This observation suggests that the main body and the protrusions might have different crystal structures. To clarify this, we used higher resolution STEM images to probe the composition and crystal structure of the main body and the protrusions.

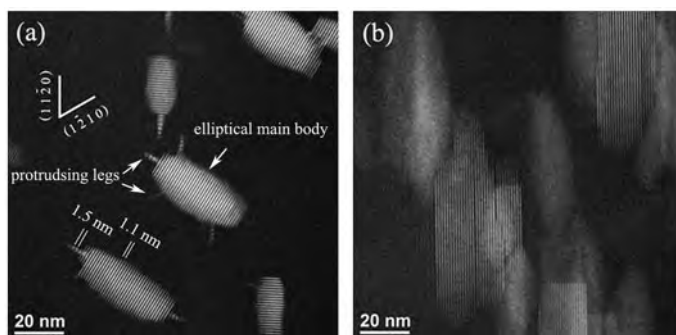


Figure 1. Dark-field STEM micrographs of the sample aged at 200 °C for 64 h: (a) micrograph taken with the incident beam parallel to the $[0\ 0\ 0\ 1]$ axis and (b) with beam parallel to the $[1\ 1\ 2\ 0]$ axis.

Figure 2 shows the schematics and high-resolution HAADF-STEM images that clearly reveal very different crystal structure between the main body and the protrusions. Moreover, there is a third type of crystal structure that exists at some tips of the protrusions (Figure 2(a)). Colour atomic models based on the HAADF-STEM images are used to illustrate the atomic structures clearly. The light blue spheres represent magnesium atoms, whereas the purple ones represent the rare earth elements. Figure 2(b) and (c) show the HAADF images and corresponding models of the protrusions from the $[0\ 0\ 0\ 1]$ and $[1\ 1\ 2\ 0]$ zone axis, respectively. The unit cell viewed from the $[0\ 0\ 0\ 1]$ zone axis is marked by a black rectangle in Figure 2(b). Figure 2(d) and (e) show the structure of the main body, which is the same as what has been reported for the β' phase. The crystal structures of both the main body and the protrusions are body-centred orthorhombic (b.c.o.). However, their lattice parameters are quite different, as indicated by the rectangle in Figure 2(c) and (d). Therefore, the protrusions are from a new phase that is different from the phase of the main body. This new phase has never been reported before, and is defined herein as the metastable β_T phase. The lattice parameters of the β_T phase and the β' phase are found to have the following inter-relationship:

$$a_{\beta_T} = a_{\beta'}, b_{\beta_T} = 1.5b_{\beta'}, c_{\beta_T} = c_{\beta'}$$

As mentioned earlier, a third type of precipitate structure was found at the tip of some protrusions (Figure 2(f) and (g)). Its structure is the same as that reported for the β'' phase ($D0_{19}$). The lattice parameters in this case are $a_{\beta''} = 2a_{\text{Mg}}$ and $c = c_{\text{Mg}}$. Therefore, the new metastable phase β_T coexists with both the β'' and β' under peak ageing conditions in this Mg–Gd–Y alloy.

The simulated three-dimensional structure model of the β'' , β_T and β' are presented in Figure 3(a). The new established β_T phase is b.c.o structure with a lattice of $a = 0.64$ nm, $b = 3.33$ nm, and $c = 0.52$ nm. If the atomic type is not considered, this structure is the same as the hcp Mg. In other words, the β_T phase can be formed simply by substituting Mg atoms with RE atoms in an ordered way in the hcp lattice. The Mg to RE ratio is 5:1, so the stoichiometry of this new phase can be described as Mg_5RE which

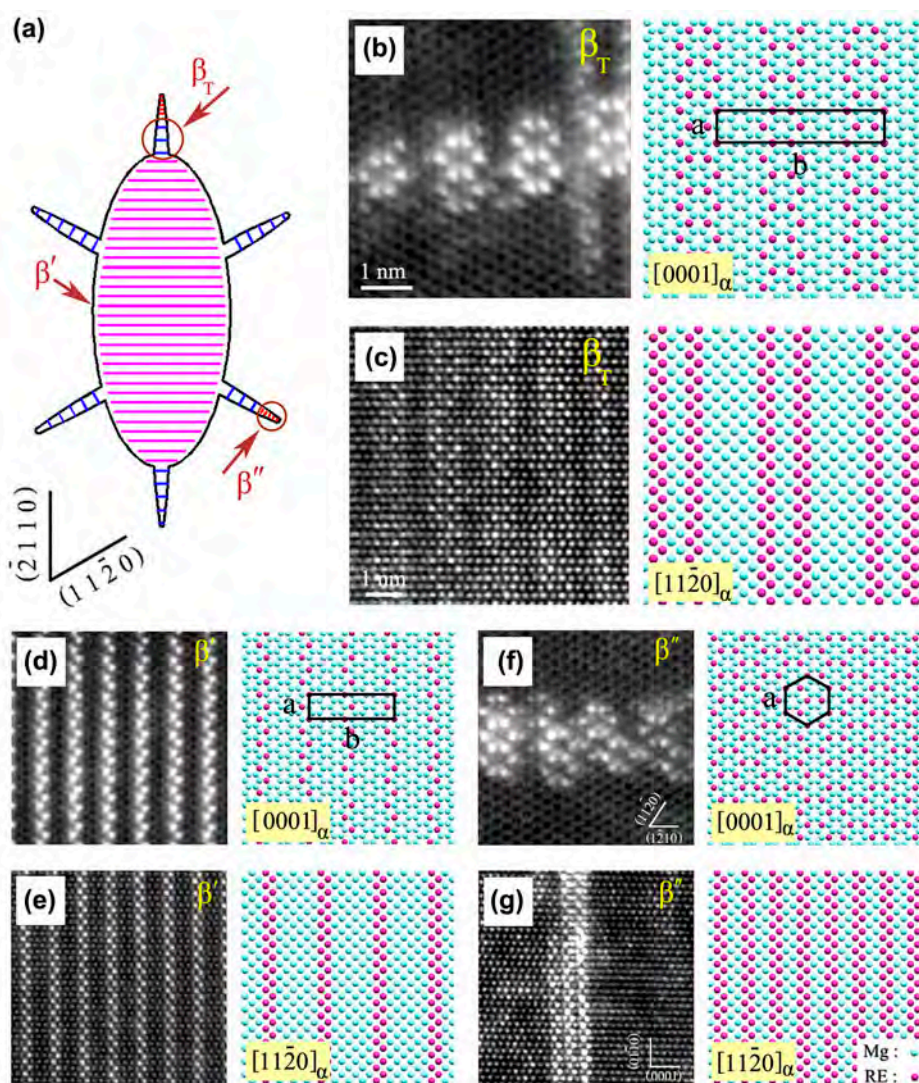


Figure 2. (colour online) (a) Schematics of the precipitate in $[0001]_{\alpha}$ direction, and HAADF-STEM images and atomic models for: (b) β_T , (d) β' and (f) β'' taken with the incident beam parallel to the $[0001]_{\alpha}$ axis, and (c) β_T , (e) β' and (g) β'' from $[11\bar{2}0]_{\alpha}$ direction.

is different from the compositions of either β'' (Mg_3RE) or β' (Mg_7RE). Due to the narrow width of β_T and β'' phases ($<5\text{ nm}$), it is hard to obtain a clear diffraction pattern, even with use of selected area electron diffraction. Thus, fast Fourier transforms (FFTs) of the high resolution STEM images and the simulation patterns of β'' , β_T and β' models are shown in Figure 3(b)–(d) with $[0001]$ and $[11\bar{2}0]$ zone axes. The simulation results are consistent with the FFT results, and provide a clearer depiction of the orientation relationship of these phases to α -Mg matrix. From the simulations, it can be seen that the orientation relationship between a β_T precipitate and the matrix is:

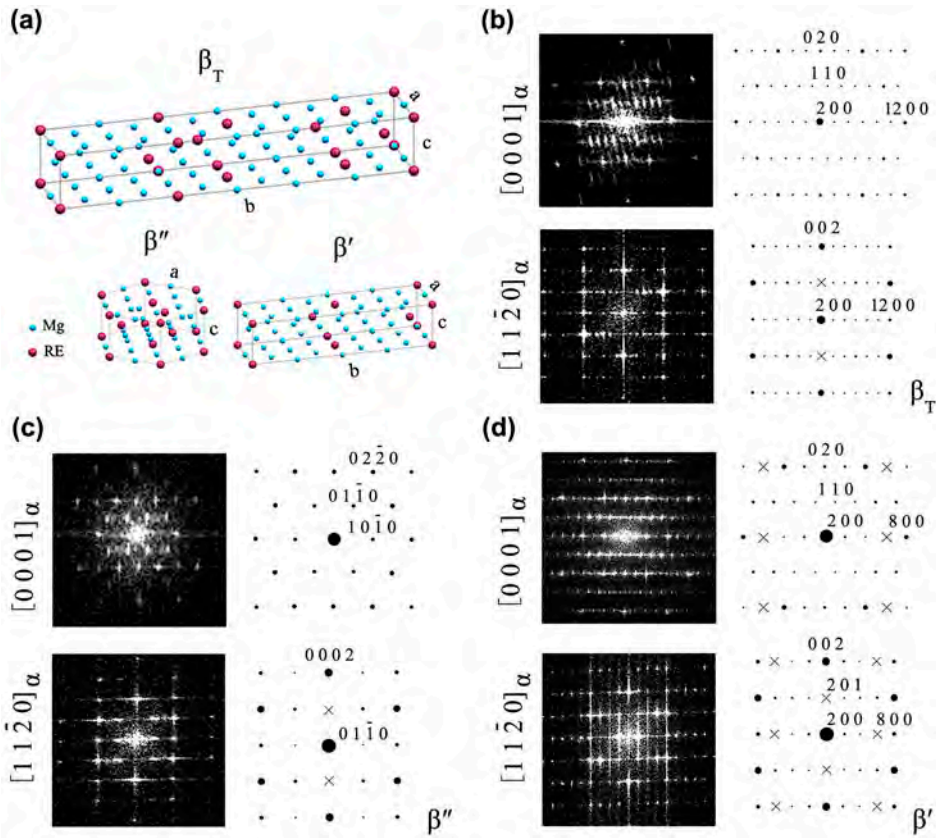


Figure 3. (colour online) (a) Atomic models of β_T , β'' and β' deduced from STEM images, and (b)–(d) FFT and simulation patterns of β_T , β'' and β' , from $[0001]_\alpha$ and $[11\bar{2}0]_\alpha$ zone axis.

$$(100)\beta_T // (11\bar{2}0)_\alpha \text{ and } [001]\beta_T // [0001]_\alpha,$$

This is the same as that between β' and α -Mg. However, the spacing of the (100) crystal plane of β_T is 1.5 times that of β' .

In Figure 2, the newly identified metastable β_T phase is shown to be between the β'' and β' phases. This contradicts earlier observations under lower resolution TEM, which showed the whole protrusion being composed of the β' phase [17,18,26]. It is likely that conventional TEM did not meet the resolution requirement needed to identify the difference among the β'' , β_T and β' phases [13]. For example, dark-field TEM images of β'' and β' phases would show superimposed diffraction patterns in peak-aged materials. In our work, HAADF-STEM can form images via high-angle scattered electrons. The brighter contrast in the image will indicate larger atomic numbers (Z-contrast) [27]. Consequently, HAADF-STEM studies is an effective tool to determine the ordered arrangement of RE atoms in the β'' and β' phases, which offers an opportunity to identify of precipitate structure and also investigate the transformations among different metastable phases.

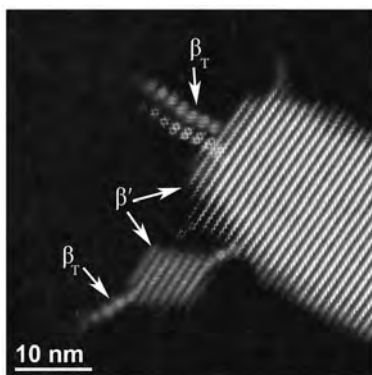


Figure 4. Dark-field STEM micrographs of a sample aged at 200 °C for 64 h: taken with the incident beam parallel to the $[0\ 0\ 0\ 1]_{\alpha}$ zone axis.

As is shown in Figure 4, a β' nucleus was formed in the middle of the β_T phase, which suggested that the β_T could provide nucleation site for the β' phase. In addition, the β_T phase protrusions are connected with the main body β' phase (Figure 4). This suggests that the β_T phase might be the precursor of the β' phase. In some cases, the tip of the needle-shaped β_T phase is connected to β'' phase, however, there is not enough evidence to know if the formation of β_T phase is formed from the β'' phase. But in view of RE composition change among these phases, it is feasible that the transformation occurred from β'' (Mg_3RE) to β_T (Mg_5RE), then to β' (Mg_7RE). Therefore, a five-stage precipitation sequence for Mg–Gd–Y–Zr alloys is proposed as follow: $\text{S.S.S.S} \rightarrow \beta'' \rightarrow \beta_T \rightarrow \beta' \rightarrow \beta_1 \rightarrow \beta$, where some phases may coexist under an ageing conditions.

Conclusion

In summary, a new metastable phase (β_T) is observed in an aged Mg–Gd–Y–Zr alloy by aberration-corrected HAADF-STEM. The β_T phase has an orthorhombic crystal structure with lattice parameters of $a = 0.64$ nm, $b = 3.33$ nm and $c = 0.52$ nm, with a composition of Mg_5RE . The β_T phase is postulated to play a key role in the sequential formation of the strengthening β' phase. According to our observations, a precipitation sequence of $\text{S.S.S.S} \rightarrow \beta'' \rightarrow \beta_T \rightarrow \beta' \rightarrow \beta_1 \rightarrow \beta$ is proposed, where some phases may coexist under some ageing conditions.

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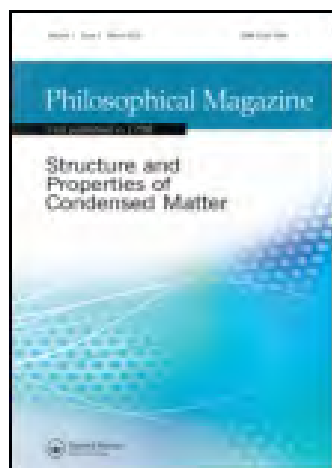
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Strengthening at nanoscaled coherent twin boundary in f.c.c. metals

Pei Gu^a, Ming Dao^b & Yuntian Zhu^c

^a Department of Engineering Mechanics, Hohai University, Nanjing, Jiangsu 210098, China

^b Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

^c Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695, USA

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Strengthening at nanoscaled coherent twin boundary in f.c.c. metals

Pei Gu^{a*}, Ming Dao^b and Yuntian Zhu^c

^a*Department of Engineering Mechanics, Hohai University, Nanjing, Jiangsu 210098, China;*

^b*Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA;* ^c*Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695, USA*

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This paper analyses slip transfer at the boundary of nanoscaled growth twins in face-centred cubic (f.c.c.) metals for strengthening mechanism. The required stress for slip transfer, i.e. inter-twin flow stress, is obtained in a simple expression in terms of stacking fault energy and/or twin boundary (TB) energy, constriction energy and activation volume. For nanotwinned Al, Cu and Ni, inter-twin flow stress versus twin thickness remarkably shows Hall–Petch relationship. The Hall–Petch slope is rationalized for various reactions of screw and non-screw dislocations at the TB. Additionally, strengthening at the boundary of nanoscaled deformation twins in f.c.c. metals is analysed by evaluating required twinning stress. At small nanograin size, the prediction of deformation twin growth stress shows inverse grain-size effect on twinning, in agreement with recent experimental finding.

Keywords: nanostructures; dislocations; strengthening mechanisms

1. Introduction

Growth twins with tens of nanometres as twin thickness embedded in ultrafine grains of several hundred nanometre size, such as nanotwinned Cu (nt-Cu), are introduced by pulsed electrodeposition [1–3]. Such nanotwins have been shown to be effective for enhancing strength and preserving ductility compared to nanograins without twinning, because coherent twin boundary (TB) acts as both barrier to dislocation motion and source for dislocation generation. In molecular dynamics (MD) simulations, various reactions of screw and non-screw dislocations in the forms of absorption to TB and/or transmission to adjacent twin lamella were discovered [4–6]. The role of these dislocation reactions at TB in strengthening was investigated in mechanistic model [7–10]. In recent slip transfer model [11], inter-twin flow stress, the required shear stress for absorption to TB and/or transmission to adjacent twin lamella, is quantified to be strongly dependent on twin thickness (twin density). Such inter-twin flow stress is the counterpart of intra-twin flow stress [9], which governs slip when the loop extends within a twin lamella. For nt-Cu, it was shown in Ref. [11] that the obtained inter-twin flow stress for various reactions of screw and non-screw dislocations that were observed

*Corresponding author. Email: pei_gu@yahoo.com

in MD simulations [4,5] is consistent with experimental measurement of flow stress [2]. But, no study of inter-twin flow stress has been done for other nanotwinned metals.

Twinning does occur in other face centered cubic (f.c.c.) metals such as Al and Ni [12,13], which have much higher stacking fault energies than Cu. Crystallographic analysis and MD simulation showed various reactions at TB for impinging screw and non-screw dislocations [4,5,14]. Therefore, the study of slip transfer in nanotwinned Al (nt-Al) and nanotwinned Ni (nt-Ni) is important to understand their deformation behaviour for enhancing strength and preserving ductility. But, since there are no activation volume data for nt-Al and nt-Ni, it is impossible to directly apply the size dependent slip transfer model [11] to these nanotwins. In this study, the activation volumes of nt-Al and nt-Ni are obtained from the concept of structural length equivalence in the unified mechanistic model [9] and then used to evaluate required stresses of slip transfers observed in MD simulations for nt-Al and nt-Ni. Similar to nt-Cu, the results show that these inter-twin flow stresses of nt-Al and nt-Ni are strongly size dependent and are in a comparable range to flow stresses of their counterparts, nanograined Al (nc-Al) and Ni (nc-Ni). When plotting the inter-twin flow stress versus the inverse of the square root of twin thickness, we find remarkably that the inter-twin flow stress of nt-Al and nt-Ni, as well as nt-Cu, follows Hall–Petch relationship. Grain boundary strengthening leading to Hall–Petch relationship was discussed in [15], which established the Hall–Petch slope as the stress intensity for slip transfer to activate the slip system of adjacent grain, and was later extended to rationalize nanocrystalline materials in [16]. Comparing to grain boundary, the unique structure of nanotwin, its coherent TB and symmetry with respect to the other side of the TB, allows us to develop analytical expressions of flow stress for these dislocation reactions observed in MD simulations in terms of nanotwin's unique properties (TB energy, stacking fault energy and twin thickness) and investigate the cross-slip of each dislocation reaction for strengthening in detail.

Nanoscaled deformation twins are another type of twinning for strength enhancement where the twins are formed during deformation in the nanograins (less than 100 nm), see [17]. For this type of TB strengthening, we discuss the formation and growth of nanoscaled deformation twins by slip and slip transfer from a proposed mechanistic model. The required stresses are obtained in a simple form in terms of stacking fault energy, TB energy, as well as the structural length scale in this case, grain size. It is shown that for small grain size, stress required for deformation twin growth is larger than stress required for the slip of partial dislocations without twinning so that twinning tendency becomes small. This prediction is in agreement with recent experimental finding of inverse grain-size effect on twinning [13].

The plan of the paper is as follows. In Section 2, we present the slip transfer model for various reactions of screw and non-screw dislocations at nanoscaled TB of aluminium, copper and nickel; associated inter-twin flow stress is quantified in terms of structural deformation properties and written into a simple generic form. In Section 3, we investigate TB strengthening in two aspects: from the slip transfer model in Section 2, we analyse inter-twin flow stresses and Hall–Petch slopes for slip transfer at the TB in nt-Al, nt-Cu and nt-Ni; from a nanoscaled mechanistic twinning model, we evaluate deformation twin growth stress and discuss the inverse grain-size effect on twinning.

2. TB slip transfer model

2.1. Screw dislocation

The coherent TB and slip system in a nanotwinned f.c.c. metal are schematically illustrated in Figure 1. In the pile-up cross-slip model, Figure 2, an array of screw dislocations is lined up against the TB; under external loading, a partial dislocation disassociated from the first screw dislocation is either absorbed onto the TB with orientation angle ϕ_1 or transmitted onto the slip plane of the next twin lamella with orientation angle ϕ_2 . At the intersection with TB, the two partials which form the screw dislocation **BA** are constricted in order to cross-slip [18,19]. At the initiation of cross-slip, consider a small half-circular loop of partial dislocation with radius r moving onto the TB or the slip plane of adjacent twin lamella from the portion of constriction. From the previous work [7,9], the energy of the cross-slipped half-circular loop is given as $F_1 = 0.3125 Gb_1^2 r \ln(r/r_0)$, where b_1 is the magnitude of the partial dislocation's Burgers vector and $r_0 \approx b_1$ is the core cut-off radius. The energy of the initial partial dislocation segment before slip transfer, which corresponds to the half-circular loop of the cross-slipped partial dislocation, is taken to be the energy per unit length of a straight partial dislocation scaled by the initial segment length $2r$, that is $F_2 = 2r[Gb_1^2 \ln(r/r_0)/(4\pi)]$. Combining these two expressions, the energy change due to the lengthening of the loop in the cross-slip process is $F = F_1 - F_2 = 0.1533 Gb_1^2 r \ln(r/r_0)$. It is noted that rigorous mathematical treatment of the loop energy change, which is in complicated form, is not sought here; this fair approximation leads to a simple and clear expression for inter-twin flow stress, which is shown later to be consistent with experimental data. The free energy change for the cross-slip of the pile-up screw dislocations is [7,20],

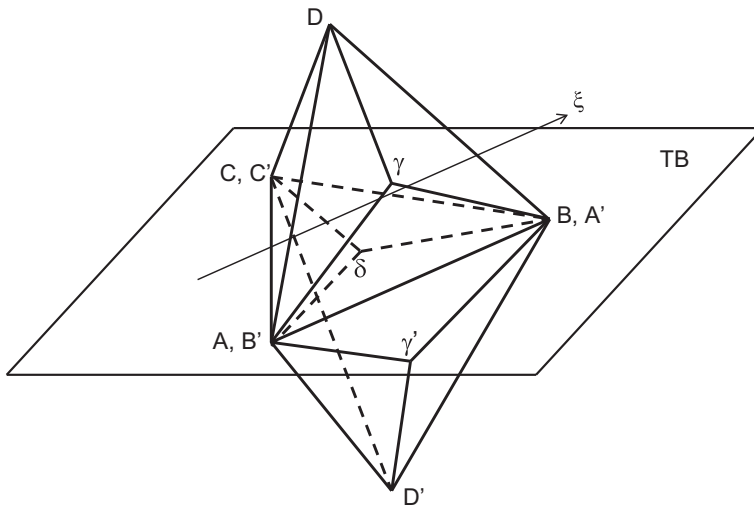


Figure 1. Dislocations in twinned f.c.c. material. In the lamella above the TB, slip system is given by Thompson tetrahedron **ABCD**; below the TB, slip system is given by Thompson tetrahedron **A'B'C'D'**. Dislocation is defined by clockwise Burgers circuit when sighting down the positive direction of ξ , see Ref. [21].

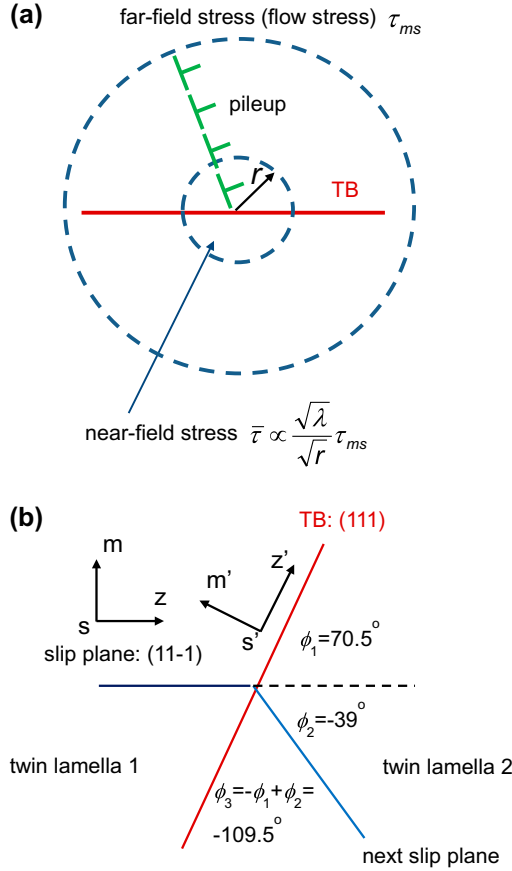


Figure 2. (colour online) (a) Pile-up dislocation slip transfer model showing the relation between the near-field stress and far-field stress. (b) Slip plane orientation: original slip plane, next slip plane and TB.

$$\Delta F = \Phi r \ln \frac{r}{r_0} - H \left(r^{\frac{3}{2}} - r_0^{\frac{3}{2}} \right) + P(r^2 - r_0^2) + 2Ur. \quad (1)$$

Here, $\Phi = 0.1533 Gb_1^2$; $P = \pi\Gamma/2$; $\Gamma = \Gamma_S$ (stacking fault energy) for transmission; $\Gamma = \Gamma_T$ (TB energy) for absorption; U is the constriction energy (energy/unit length). There should be a constant term in Equation (1) for point constriction energy [19]. It is excluded here because it does not contribute to inter-twin flow stress, which is obtained from the derivative of the free energy change as seen later. The far-field shear stress τ_{ms} to drive the screw dislocation to TB acts on the original slip plane $\mathbf{m}$ (for $\mathbf{m}$ - $\mathbf{s}$ - $\mathbf{z}$ coordinate system, see Figure 2(b)) and along the direction of the Burgers vector $\mathbf{BA}$, which is defined by clockwise Burgers circuit when sighting down the positive dislocation line ζ [21]. The shear stress near the intersection of the slip plane and the TB is the near-field stress, given by the mode III crack tip stress field [20],

$$\tau_{m's'} = \frac{K_{III}}{\sqrt{2\pi R}} f_{III}(\phi) = \frac{K_{III}}{\sqrt{2\pi R}} \cos\left(\frac{\phi}{2}\right), \quad (2)$$

where $K_{III} = \sqrt{2\pi\lambda}\tau_{ms}$; λ is twin thickness; ϕ is the orientation angle measured from the original slip plane, see Figure 2(b); R is the distance from the intersection of slip planes along $\mathbf{z}'$ axis (for this axis, as well as $\mathbf{m}'$ and $\mathbf{s}'$ axes used later, see Figure 2(b)). Note that such pile-up model resulting in stress concentration due to dislocation accumulation, which has the similarity to a crack in fracture mechanics, was also used in previous studies of cross-slip [20,22]. Consider the first cross-slipped partial dislocation's Burgers vector on the slip plane $\mathbf{m}'$ is $\mathbf{b}_1$ with its component along $\mathbf{s}'$ axis being $b_{1s'}$. The work done by shear stress for the extension of $\mathbf{b}_1$ is the integration of $\tau_{m's'}b_{1s'}$ over the half-circular area of cross-slip, and using Equation (2), is given as:

$$\int \frac{K_{III}}{\sqrt{2\pi r \sin \theta}} f_{III}(\phi) b_{1s'} dA = 1.4K_{III}f_{III}(\phi)b_{1s'}(r^{\frac{3}{2}} - r_0^{\frac{3}{2}}) = H(r^{\frac{3}{2}} - r_0^{\frac{3}{2}}). \quad (3)$$

Here, the area element for the half-circular area is $dA = r dr d\theta$ and $0 \leq \theta \leq \pi$. The factor in Equation (3), $r \sin \theta$, is the distance along the $\mathbf{z}'$ axis between the area element and the intersection of slip planes. From Equation (3), we obtain H in Equation (1),

$$H = 1.4K_{III}f_{III}(\phi)b_{1s'}. \quad (4)$$

Using K_{III} defined above and $b_{1s'} = b_1 \cos 30^\circ$, we get $H = 1.98\sqrt{\pi\lambda}\tau_{ms} b_1 \cos(\phi/2) \cos 30^\circ$.

Considering slip transfer as the non-homogeneous creation of a half-circular loop on the cross-slipped plane [9–11], the cross-slipped loop activates when the free energy change reaches maximum at activation size: $\partial\Delta F/\partial r = 0$ at $r = r_a$. Here, r_a is the activation size given by $r_a = \sqrt{2V/(\pi b)}$, which depends on both twin thickness and grain size. The activation volume V for nt-Cu was characterized in Figure 7 of Ref. [9] for nt-Cu. The above maximum condition leads to,

$$\tau = \frac{0.06725 Gb_1}{\sqrt{\lambda} r_a \cos(\phi/2)} \left(1 + \frac{1}{2} \ln \frac{r_a}{r_0 e} + \frac{r_a P}{\Phi} + \frac{U}{\Phi} \right). \quad (5)$$

Here, $\tau \equiv \tau_{ms}$, the required shear stress for cross-slip which is referred to as inter-twin flow stress. The absorption flow stress is obtained by taking $\phi = \phi_1$, and transmission flow stress is obtained by taking $\phi = \phi_2$, in Equation (5). In transmission, a trailing partial follows the leading partial. In absorption, when first twinning partial is activated, the second twinning partial is repealed to move in the opposite direction $\phi = -\pi + \phi_1$ [4,6,8]. The first twinning partial is chosen along the direction ϕ_1 because the driving force $\tau_{m's'}b_{1s'}$ is larger in this direction than another twinning direction $\phi_3 = -\pi + \phi_1$. If the two twinning partials are activated at the same time, the energy change associated with both partials needs to be accounted for. The first and third terms in the right side of Equation (1) are scaled by a multiplier 2, whereas the second term needs to include the work done by shear stresses along both twinning directions. Following the above maximizing procedure, the inter-twin flow stress in the case of both twinning partials' activation at the same time is

$$\tau = \frac{0.1345 Gb_1}{\sqrt{\lambda} r_a [\cos(\phi_1/2) + \sin(\phi_1/2)]} \left(1 + \frac{1}{2} \ln \frac{r_a}{r_0 e} + \frac{r_a P}{\Phi} + \frac{U}{2\Phi} \right). \quad (6)$$

Our calculation shows shear stress from Equation (5) is close to that from Equation (6), so we take Equation (5) as the absorption flow stress. Also note that when the obtained inter-twin flow stress and activation size are substituted into Equation (1), we obtain activation energy, which was discussed in Ref. [11].

2.2. Non-screw dislocation

Obeying the conservation of Burgers vectors, non-screw dislocations' cross-slip to TB and/or next twin lamella is possible. The reactions for 60° degree dislocation at the TB were discussed in MD simulation [5]. We calculate the inter-twin flow stress resulting from 60° degree dislocation's slip transfer by extending the approach for screw dislocation discussed above. According to the dislocation definition [21], for **DA**, the shear stress acting along its Burgers vector direction on the original slip plane **m** drives the dislocation to the TB; when reversing the dislocation's Burgers vector to **AD**, the shear stress is reversed also. To calculate the work done by shear stress in slip transfer, we project the shear stress on a cross-slipped plane **m'** into the axes **s'** and **z'** shown in Figure 2(b). The shear stress along the axis **s'** on the cross-slipped plane is the resolved shear stress from $\tau_{ms} = \tau/2$ on the original slip plane before cross-slip, and the shear stress along the axis **z'** on the cross-slipped plane is the resolved shear stress from $\tau_{mz} = \tau\sqrt{3}/2$ on the original slip plane before cross-slip. For **DA**, in the coordinate system in Figure 2(b), the sign of τ is positive; for **AD**, the sign of τ is negative. The shear stress along the axis **s'** near the intersection of the slip plane and the TB (near-field stress) is given by Equation (2). The shear stress along the axis **z'** near the intersection of the slip plane and the TB (near-field stress) is obtained from mode II crack tip field [20,23] as

$$\tau_{m'z'} = \frac{K_{II}}{\sqrt{2\pi R}} f_{II}(\phi) = \frac{K_{II}}{\sqrt{2\pi R}} \left[\frac{1}{4} \cos\left(\frac{\phi}{2}\right) + \frac{3}{4} \cos\left(\frac{3\phi}{2}\right) \right], \quad (7)$$

where $K_{II} = \sqrt{2\pi\lambda}\tau_{mz}$. Consider the first cross-slipped partial dislocation's Burgers vector on the slip plane **m'** is **b₁** with its components being $b_{1s'}$ and $b_{1z'}$ along the axes **s'** and **z'**, respectively. The work done by shear stress for the extension of **b₁** is the integration of $\tau_{m's'}b_{1s'} + \tau_{m'z'}b_{1z'}$ over the half-circular area of cross-slip, and using Equations (2) and (7), is given as:

$$\int \left(\frac{K_{III}}{\sqrt{2\pi r \sin \theta}} f_{III}(\phi) b_{1s'} + \frac{K_{II}}{\sqrt{2\pi r \sin \theta}} f_{II}(\phi) b_{1z'} \right) dA = H \left(r^{3/2} - r_0^{3/2} \right), \quad (8)$$

where $H = 1.4[K_{III}f_{III}(\phi)b_{1s'} + K_{II}f_{II}(\phi)b_{1z'}]$. The area element dA in Equation (8) was given in Section 2.1. For cross-slip to more than one cross-slip direction in the dislocation reaction, the H is the sum of the contribution of each cross-slip direction,

$$H = \sum_j 1.4 [K_{III}f_{III}(\phi_j)b_{1s'j} + K_{II}f_{II}(\phi_j)b_{1z'j}], \quad (9)$$

where the cross-slip direction $\phi_j = \phi_1, \phi_2, \phi_3$, as shown in Figure 2(b). When the dislocation reaction leads to partials' cross-slip to all three directions, the free energy change is written in the form similar to Equation (1),

$$\Delta F = 3\Phi r \ln \frac{r}{r_0} - H \left(r^{\frac{3}{2}} - r_0^{\frac{3}{2}} \right) + P^* (r^2 - r_0^2) + 2Ur, \quad (10)$$

where $P^* = \pi(2\Gamma_T + \Gamma_S)/2$. If the cross-slip directions are 2, say ϕ_2 and ϕ_3 , the sum in Equation (9) is for the contributions of these two directions; the multiplier in the first term on the right side of Equation (10) is 2; and $P^* = \pi(\Gamma_T + \Gamma_S)/2$. If the cross-slip direction is 1, the sum in Equation (9) is for the contribution of this direction; the multiplier in the first term on the right side of Equation (10) is 1; $P^* = \pi\Gamma_S/2$ (ϕ_2) or $P^* = \pi\Gamma_T/2$ (ϕ_1 or ϕ_3). Similar to the screw dislocation case, the inter-twin flow stress is obtained by maximizing Equation (10) at the activation size.

Reactions observed in MD simulations [5] for non-screw dislocations in Al, Cu and Ni are used to evaluate associated inter-twin flow stresses. For non-screw dislocation **DA** in nt-Al and nt-Cu, the reaction at TB results in a twinning partial **Cδ** and two partials on the slip plane of adjacent twin lamella $\gamma'\mathbf{D}'$ (leading) + $\mathbf{A}'\gamma'$ (trailing). We consider that the required shear stress for cross-slip activates the twinning partial **Cδ** and the leading partial $\gamma'\mathbf{D}'$. Since the two are 90° twinning partials, using K_{II} and f_{II} in Equation (7) and the cross-slipped Burgers vectors' components along $\mathbf{z}'$ axes of the two cross-slipped planes, we obtain from Equation (9),

$$H = 1.4K_{II}f_{II}(\phi_2)b_1 - 1.4K_{II}f_{II}(\phi_3)b_1 = 3.665\sqrt{\lambda}\tau b_1. \quad (11)$$

For **DA** in nt-Ni, the reaction at TB results in a twinning partial **δA** and a partial $\gamma'\mathbf{D}'$ on the slip plane of adjacent twin lamella, plus sessile dislocations at the intersection of the slip planes and TB $1/6[001] + 1/18[111]$. The sessile dislocations do not contribute to the free energy change in Equation (10). Using K_{II} , K_{III} , f_{II} and f_{III} in Equations (2) and (7) with the cross-slipped Burgers vectors' components along $\mathbf{s}'$ and $\mathbf{z}'$ axes, we obtain from Equation (9),

$$H = 1.4K_{II}f_{II}(\phi_2)b_1 - 1.4K_{II}f_{II}(\phi_3)\frac{1}{2}b_1 + 1.4K_{III}f_{III}(\phi_3)\frac{\sqrt{3}}{2}b_1 = 3.665\sqrt{\lambda}\tau b_1. \quad (12)$$

Since both reactions have the same initial cross-slip loop number for activation, 2, and the same H , we obtain the inter-twin flow stress for them from maximizing the free energy in Equation (10),

$$\tau = \frac{0.1115 Gb_1}{\sqrt{\lambda}r_a} \left(1 + \frac{1}{2} \ln \frac{r_a}{r_0 e} + \frac{r_a P^*}{2\Phi} + \frac{U}{2\Phi} \right), \quad (13)$$

where $P^* = \pi(\Gamma_T + \Gamma_S)/2$.

For non-screw dislocation **AD** in nt-Al, the reaction at TB results in two twinning partials, **δC** which glides along ϕ_3 and **Ad** which glides along ϕ_1 , plus a sessile dislocation $1/2[\bar{1}\bar{1}0]$. For **AD** in nt-Cu and nt-Ni, the reaction at TB results in a partial $\gamma'\mathbf{A}'$ on the slip plane of adjacent twin lamella, plus sessile dislocations $1/3[001] + 1/9[111]$. The inter-twin flow stress for **AD** can be obtained from Equation (10) in a similar way as that for **DA**. For **AD** in nt-Al,

$$\tau = \frac{0.1164 Gb_1}{\sqrt{\lambda}r_a} \left(1 + \frac{1}{2} \ln \frac{r_a}{r_0 e} + \frac{r_a P^*}{\Phi} + \frac{U}{\Phi} \right), \quad (14)$$

where $P^* = \pi\Gamma_T/2$. Following the argument in Section 2.1 for the case that both cross-slip directions ϕ_1 and ϕ_3 are involved, we consider three cases: (i) **δC** is activated first

along ϕ_3 ; (ii) $\mathbf{A}\delta$ is activated first along ϕ_1 ; (iii) both partials glide at the same time. Equation (14) is for the case of smallest inter-twin flow stress among the three, the case (i). For $\mathbf{AD}$ in nt-Cu and nt-Ni,

$$\tau = \frac{0.0855 Gb_1}{\sqrt{\lambda}r_a} \left(1 + \frac{1}{2} \ln \frac{r_a}{r_0 e} + \frac{r_a P^*}{\Phi} + \frac{U}{\Phi} \right), \quad (15)$$

where $P^* = \pi\Gamma_S/2$.

Combining above solutions as well as those in Sections 2.1, the generic expression for inter-twin flow stress is written as:

$$\tau = \frac{AGb_1}{\sqrt{r_a}} \left(1 + \frac{1}{2} \ln \frac{r_a}{r_0 e} + \frac{r_a P}{k\Phi} + \frac{U}{k\Phi} \right) \frac{1}{\sqrt{\lambda}}. \quad (16)$$

Here, k is the number of initial cross-slip directions in Figure 2(b). Inside the parentheses, the first two terms represent the contribution of loop growth during cross-slip, whereas the last two terms represent the contributions of TB energy, stacking fault energy and constriction energy. When using the approximation $r_a \approx b_1 e$ [7.8.20], the second term is removed. It is noted that for the cases involving sessile dislocations, for subsequent incoming dislocations to cross-slip at the TB, further reactions are needed to dissolve dislocation locks; otherwise, strain hardening is expected.

3. Evaluating strengthening at TB

Since there are no experimental data available for the activation volume of nt-Al and nt-Ni currently, and it is also impossible to determine the parameter in the non-homogeneous nucleation model [9] for activation volume without the experimental data, it is required to estimate the activation volume for nt-Al and nt-Ni in order to use Equation (16). We recall the competition of grain size and twin thickness in [9]. For nanotwinned materials with large grain size, it was found that the effect of twin thickness on properties is equivalent to the effect of the grain size in nanograined materials (without twins) on properties, also see [2,24,25]. Specifically, the flow stress, activation volume and strain-rate sensitivity of nanotwins versus twin thickness provide good correlation for size dependence just like the grain size is used for these three physical parameters of nanograins without twinning. In such case, the activation volume of nanotwins is considered to be equivalent to that of nanograins, when the value of nanotwin thickness is the same as the value of nanograin size. For nc-Al and nc-Ni, there are limited data for their grain-size-dependent activation volume. The parameter in the non-homogeneous nucleation model, from which the activation volume is obtained in the entire nanometre range, was determined in Ref. [10] for nc-Al and nc-Ni. These grain-size-dependent activation volumes of nc-Al and nc-Ni obtained from the non-homogeneous nucleation model are used as twin-thickness-dependent activation volumes of nt-Al and nt-Ni here according to above size equivalence argument. It is noted that this treatment from the size equivalence conception is an approximation. As seen by comparing Figure 5 with Figure 7 in Ref. [9], the value of activation volume of nt-Cu is not the same as that of nc-Cu for the same structural length, but they are close. However, the results below show that the Hall–Petch slope is insensitive to the activation volume.

The construction energy U for Cu obtained in MD simulation was shown to be in the same range as that obtained from dislocation theory for recombining two partials from their equilibrium distance [26]. Here, we use the recombination energies from dislocation theory as the values of U for Al, Cu and Ni in numerics. Additional material properties in our calculations are as follows. Stacking fault energies for Al, Cu and Ni are 0.146 J/m^2 , 0.054 J/m^2 and 0.194 J/m^2 [27,28], respectively. The TB energy is $\Gamma_T = \Gamma_S/2$ [29,30]. Shear moduli for Al, Cu and Ni are 35, 50 and 76 GPa, respectively; Burgers vectors for Al, Cu and Ni are 0.25, 0.255 and 0.248 nm, respectively.

Figures 3 and 4 show the prediction of inter-twin flow stress for nt-Al and nt-Ni against the inverse of square root of twin thickness. Also plotted in the two figures are the flow stress data for nc-Al and nc-Ni [10,31]. The inter-twin flow stress of nt-Cu discussed in [11] is plotted in Figure 5 together with experimental data for nt-Cu [2] against the inverse of square root of twin thickness. The horizontal axis for the structural length in these figures is in the nanorange below 100 nm. The flow stress of a nanotwinned material includes two portions, i.e. inter-twin flow stress and intra-twin flow stress. Intra-twin dislocation and inter-twin dislocation are two types of dislocation activities in nanotwins, and experiments suggest both exist [25]. Intra-twin flow stress drives dislocation extension inside twin lamella, whereas inter-twin flow stress drives dislocation to cross-slip the TB. For nt-Cu, comparison of the inter-twin flow stress obtained here and the intra-twin flow stress discussed in Ref. [9] with experimentally measured flow stress suggests the three are in the same range; for nt-Al and nt-Ni, this is also expected to be true. In Figures 3 and 4, the fact that the flow stress data for nanograins are in the same range as the inter-twin flow stresses of nanotwins again

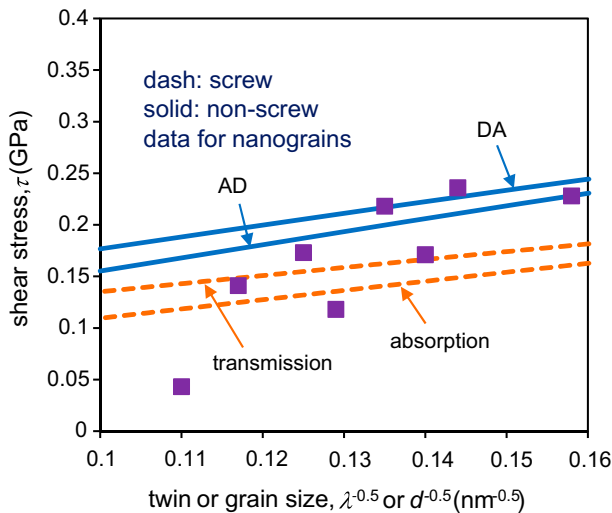


Figure 3. (colour online) Inter-twin flow stresses of screw dislocation **BA** and non-screw dislocations **DA** and **AD** versus twin thickness for nt-Al. The experimental data are flow stress versus grain size for nc-Al from Ref. [10]. As structural length scale, the twin thickness of nt-Al is equivalent to the grain size of nc-Al. The predicted inter-twin flow stress of nt-Al is in the same range as the flow stress data of nc-Al. The nearly straight curves suggest Hall–Petch slopes for strengthening of slip transfer, which is also true for nt-Ni and nt-Cu as shown in Figures 4 and 5.

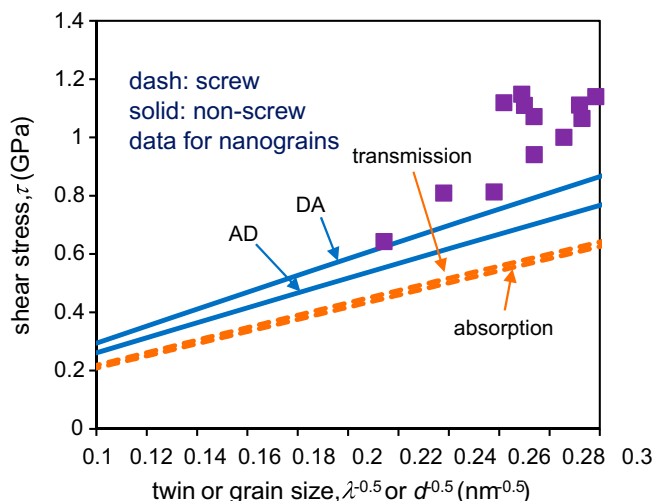


Figure 4. (colour online) Inter-twin flow stresses of screw dislocation **BA** and non-screw dislocations **DA** and **AD** versus twin thickness for nt-Ni. The experimental data are flow stress versus grain size for nc-Ni from Ref. [31]. The twin thickness of nt-Ni is equivalent to the grain size of nc-Ni; the predicted inter-twin flow stress of nt-Ni is in the same range as the flow stress data of nc-Ni.

points to the equivalence of grain size for a nanograined material to the twin thickness for its nanotwinned counterpart whose grain size is in the ultrafine range. On the other hand, the flow stress of a nanograined material is not exactly the same as the flow stress of its nanotwinned counterpart, because crystallographic details of the two structures are different and experimental flow stress data can be scattered. In Figure 5, the agreement of predicted curves with experimental data is better than Figures 3 and 4, since both are for nt-Cu, whereas the predicted curves are for nanotwins and the experimental data are for nanograins in Figures 3 and 4.

From the nearly straight lines for the inter-twin flow stress in Figures 3, 4 and 5, we see remarkable evidence of Hall–Petch slope for each of the dislocation reaction at the TB. In other words, the pre-expression of $(1/\sqrt{\lambda})$ in Equation (16) is nearly a constant, weakly varying with the twin-thickness-dependent activation size $r_a(\lambda)$. For example, in screw dislocation transmission of nt-Al, the Hall–Petch slope is 1.13 and 1.25 for the twin thickness 39 and 70 nm, respectively. This weak dependence proves the early treatment of using $r_a = b_1 e$ when maximizing the free energy of cross-slip [7,8,20]. The calculated Hall–Petch slopes for dislocation reactions are listed in Table 1. Also given in the table are the averages for the reactions of nt-Al, nt-Cu and nt-Ni. For the same material, the slope for non-screw dislocation is larger than that for screw dislocation, because the edge component is more difficult to cross-slip from its crystallographic orientation. The ranking of the slope from small to large is as follows: nt-Al, nt-Cu and nt-Ni. This is because that Equation (16) is proportional to shear modulus and the ranking of shear modulus of the three materials is the same as above ranking for the slope. Such dependence of the slope on shear modulus is consistent with previous theoretical work of micrograins and nanograins [16,32,33]. Although more dislocation reactions at the TB for each material in the table may be discovered later, the

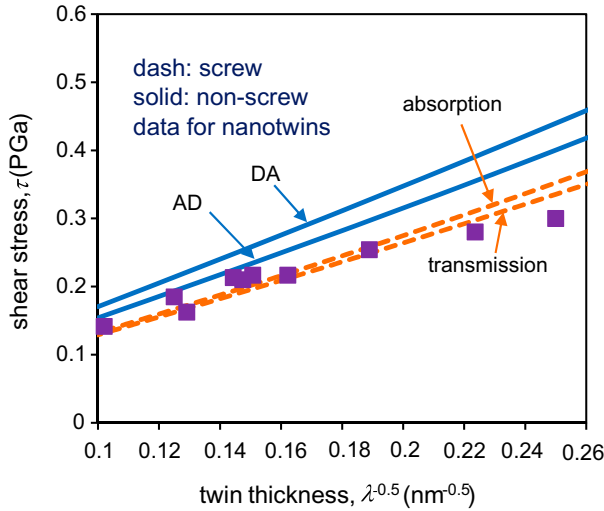


Figure 5. (colour online) Inter-twin flow stresses of screw dislocation **BA** and non-screw dislocations **DA** and **AD** versus twin thickness for nt-Cu. The experimental data for nt-Cu are from Ref. [2].

Table 1. Hall–Petch slope for slip transfer at nanoscaled TB ($\text{GPa}\sqrt{\text{nm}}$).

	Dislocations				Average
	Screw transmission	Screw absorption	Non-screw AD	Non-screw DA	
Al	1.24	1.05	1.50	1.64	1.35
Cu	1.36	1.44	1.60	1.76	1.54
Ni	2.18	2.08	2.59	2.90	2.43

averaged value given here is expected as a reasonable evaluation for the slope of Hall–Petch relationship of the nanotwinned material.

When absorption occurs and when absorbed partials extend to larger loop on the TB, the inter-twin flow stress for the activation of the cross-slip no longer drives the loop extension. Instead, the extension on the TB is the competition of the TB energy, loop’s self-energy and the interaction of different portions of the larger loop, comparable to the grain size. Similar to the approach for the intra-granular flow stress [34], the required shear stress for the large extension on the TB can be evaluated. When a partial extends on the TB across the entire grain from one side to the opposite side, or two cross-slipped partials in the middle of the TB extend in opposite directions across it, the required shear stress is (taking $\beta = 1$ in Ref. [34])

$$\tau_m = \frac{\Gamma_T}{b} + 0.306 \frac{Gb}{d}. \quad (17)$$

Here, d is grain size. The process causes TB migration: one side of the twin lamella decreases by one atomic layer and another side increases by one atomic layer. In the case of deformation twins [17,35,36], above τ_m is deformation twin growth stress or

deformation twin reduction stress in nanograins. Asaro and Suresh in [7] proposed a deformation twin initiation criteria based on the generalized stacking fault energy curve and showed that deformation twins of Al, Cu and Ni are achievable in comparison with partials' glide without twinning. Among various pathways, the formation of a nano-scaled deformation twin can be done by successful grain boundary emission of partials extending in parallel adjacent slip planes to the opposite grain boundary consecutively; or a two-step cross-slip of a partial at the TB: $\mathbf{B}\gamma = \mathbf{B}\delta + \delta\gamma$; $\delta\gamma = \delta\mathbf{B} + \mathbf{B}\gamma$, where $\mathbf{B}\delta$ and $\delta\mathbf{B}$ extend in the opposite directions across the grain under shear stress to grow the twin by one atomic layer and $\mathbf{B}\gamma$ in the second reaction extends one atomic layer further in the original slip plane of the matrix (untwined region) to continue this twinning process [37]. Here, we use above model for nanoscaled deformation twins to examine their required stresses. Obviously, in this twinning mechanism, the structural length for nano-scaled deformation twin formation and growth is grain size, as seen in Equation (17). However, Equation (17) is not the required stress for deformation twin formation, which is the stress to create the first layer, the stacking fault, across the entire grain and which is given from the approach in Ref. [34] as

$$\tau_t = \frac{\Gamma_s}{b} + 0.306 \frac{Gb}{d}. \quad (18)$$

Previous work [12,38] gave similar functional form as Equation (18), but did not determine the slope for grain size dependence in twin formation. Using material properties given above, for Al, $\tau_t = 1036$ MPa when $d = 6$ nm; for Cu, $\tau_t = 298$ MPa when $d = 46$ nm; for Ni, $\tau_t = 1039$ MPa when $d = 23$ nm. These calculated values for τ_t from Equation (18) are consistent with those reported in Ref. [17]. The nanograins' flow stress for partials' glide without twinning is [31].

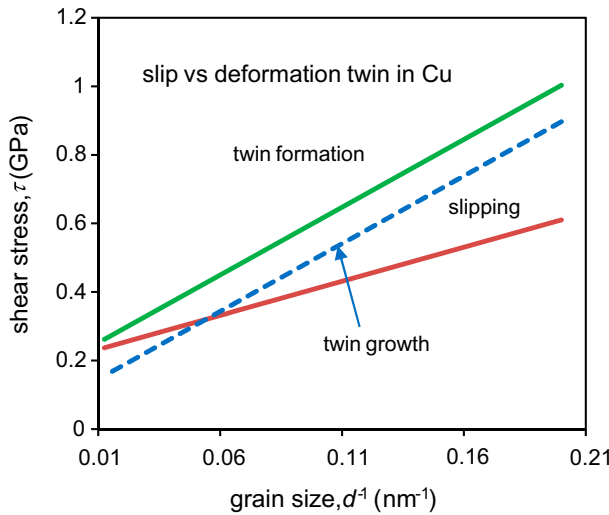


Figure 6. (colour online) Required stresses for deformation twin formation and growth versus required stress for the slip of partial dislocation without twinning in nanograined Cu. For small grain size, stress required for deformation twin growth is larger than stress required for the slip of partial dislocation such that twinning tendency becomes small.

$$\tau_f = \frac{\Gamma_s}{b} + 0.156 \frac{Gb}{d}. \quad (19)$$

The three flow stresses above, τ_m , τ_t and τ_f , follow the generalized Hall–Petch relationship [39], $\tau = k_1 + k_2/d^\alpha$. In agreement with previous observation, the slope of the deformation twin formation stress is larger than that of the flow stress for partials' glide without twinning in nanograins [17], but is smaller than the slope of Hall–Petch relationship for deformation twins in micrograins [35]. The three required stresses for Cu are plotted versus grain size in Figure 6, which shows that for small grain size, stress required for deformation twin growth is larger than stress for the slip of partials without twinning. Hence, twinning tendency becomes small for small grain size, in agreement with experimental finding of inverse grain-size effect on twinning [13]. Such inverse grain-size effect can be explained by examining Equations (17) and (19), in which, for small grain size, the grain-size-dependent terms are dominant and the slope for twin growth is larger than the slope for the slip of partials without twinning. The transition grain size is estimated from the two equations as $d \propto Gb^2/(\Gamma_s - \Gamma_T)$.

4. Concluding remark

In summary, the present mechanistic model elaborates the role of slip and slip transfer at nanoscaled growth and deformation twin boundaries in strengthening. It provides a means to evaluate inter-twin flow stress and activation energy for dislocation reactions at the TB. Quantified inter-twin flow stress of nanoscaled growth twins, as well as previously studied intra-twin flow stress [9], is related to activation volume, strain-rate sensitivity, nanostructural size, as well as other dislocation properties such that the strengthening mechanisms of nanotwins can be investigated through coupled modelling and experiment for optimizing performance. The influence of slip as well as slip transfer to the formation and growth of nanoscaled deformation twins is analysed, and the required stresses for their formation and growth are examined within the mechanistic model to show the inverse grain-size effect on twinning.

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A model for $\langle c+a \rangle$ dislocation transmission across nano-spaced parallel basal stacking faults in a HCP alloy

Pei Gu^{a*}, Yuntian Zhu^{b,c} and Suveen N. Mathaudhu^{b,d}

^aDepartment of Engineering Mechanics, Hohai University, Nanjing, Jiangsu 210098, China;

^bDepartment of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695, USA; ^cSchool of Materials Science and Engineering, Nanjing University of Science and

Technology, Nanjing, Jiangsu 210094, China; ^dDepartment of Mechanical Engineering, University of California at Riverside, Riverside, CA 92521, USA

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We develop a model for recently observed $\langle c + a \rangle$ dislocation transmission across nano-spaced parallel basal stacking faults in hexagonal close-packed (HCP) Mg microcrystalline grains. The model theoretically predicts nano-space-dependent yield strength that is in good agreement with experimental data. Additionally, it theoretically predicts activation volume and strain rate sensitivity.

Keywords: nano-structure; flow stress; stacking fault; plastic deformation

1. Introduction

The refinement of grain size to the nanoscale for metals significantly increases their strength, but at the same time often reduces their ductility as compared to their micro-grained counterparts [1–3]. However, the introduction of subgrain features such as nanoscale growth or deformation twins [4–6] not only enhances strength but also preserves considerable ductility, since coherent twin boundary in face-centred cubic (FCC) metals acts as both dislocation slip barriers to induce strain hardening and dislocation generation sources. Experimental and modelling studies have been done within the past decade to characterize nanotwins through the three important size-dependent plastic deformation parameters: flow stress, activation volume, and strain rate sensitivity, which allow the nano-twinned materials to be designed for optimized mechanical properties [5,7–14].

Alternative paths exist to make nanoscale subgrain features within micrograins for achieving superior plastic deformation behaviours. Recently, a micrograined hexagonal close-packed (HCP) Mg alloy, Mg-8.5Gd-2.3Y-1.8Ag-0.4Zr (wt.%), with high-density of nano-spaced parallel basal stacking faults (BSFs) was obtained by hot rolling following T4 heat treatment [15,16]. The Mg was alloyed with rare earth elements Gd and Y to achieve low stacking fault energy, which promoted the formation of BSFs during the rolling process in the thickness reduction range of 50–88%. This produced nano-spaced BSFs whose interspacing decreased with rolling strain. The resulting specimens showed high tensile strength and also considerably preserved ductility compared to

*Corresponding author. Email: pei_gu@yahoo.com

micrograined Mg without subgrained parallel BSFs. TEM images showed $\langle c + a \rangle$ dislocation transmissions across the parallel BSFs in the HCP crystal structure in Refs. [15,16], where it was proposed that the interaction of these $\langle c + a \rangle$ dislocations with nano-spaced parallel BSFs is the predominant plastic strengthening mechanism for the HCP material, and it was observed that the flow stress varies linearly with $1/d$, with d being the average nanoscale interspacing between adjacent parallel BSFs. In another study [17] from both TEM and DFT (density function theory) calculation, it was reported that adding rare earth element Y to Mg can reduce basal stacking energy and thus generate BSFs that interact with $\langle c + a \rangle$ dislocations. Although their alloying elements differ from those reported in Refs. [15,16], I_1 BSFs in the non-deformed state and a high activity of pyramidal dislocations after some plastic deformation were observed.

Motivated by the experimental observation of Refs. [15–17], we probe $\langle c + a \rangle$ dislocation extension and transmission in materials with nano-spaced planar boundaries using an advanced model. The size (BSF interspacing) dependency of flow stress is obtained, which analytically determines the coefficients of the linear relationship between the flow stress and $1/d$. We show that the $\langle c + a \rangle$ dislocation transmission across BSFs is likely the major mechanism in strengthening when the BSF interspacing is in the nanometre scale. In the second portion of the article, we theoretically evaluate the activation volume and strain rate sensitivity for the $\langle c + a \rangle$ dislocation transmission from the non-homogeneous nucleation model [12,13].

2. Model

The model of $\langle c + a \rangle$ dislocation extension between parallel BSFs and transmission across the BSFs is shown in Figure 1. Consider a $\langle c + a \rangle$ dislocation on the pyramidal slip plane that moves from lower side to upper side under the required shear stress.

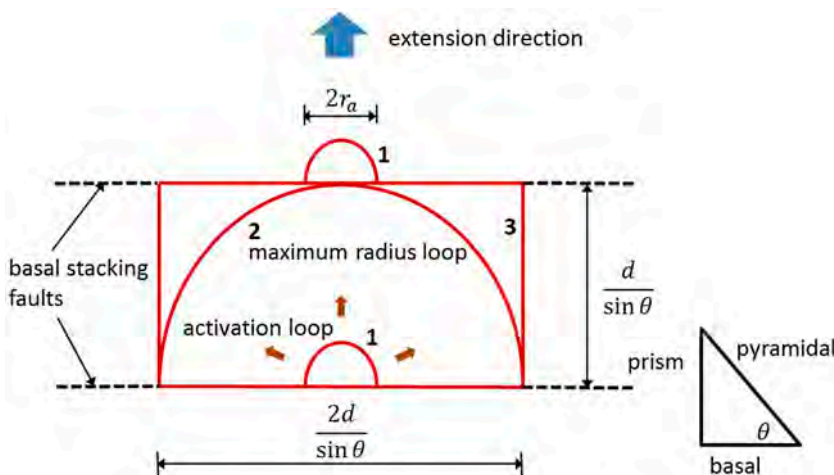


Figure 1. A $\langle c + a \rangle$ dislocation model for HCP micro-grains with nano-spaced BSFs. First step: loop activation in the nanospace by transmission across the BSF; second step: loop extension in the nanospace to maximum radius and then lying on the next BSF.

As illustrated in the figure, the process consists of two steps: (1) transmission of the loop across the lower BSF from previous nanospace by generating a small dislocation loop to reach its activation size; (2) extending the activated dislocation loop in the nanospace to the maximum radius $d/\sin\theta$ (as shown in the triangle in Figure 1, the interspacing is $d/\sin\theta$ because the dislocation extends on the pyramidal plane), where θ is the angle between the basal and pyramidal slip planes, and continuing the growth of the loop to be absorbed onto the upper BSF in Figure 1. These two steps are repeated for the next nanospace. The left end and right end of the loop are pinned to the grain boundary where the $\langle c+a \rangle$ dislocation is emitted into the first nanospace. From above, the maximum size of the loop within a nanospace is $d/\sin\theta$. An activation methodology similar to that in the step (1) appears in the recent study of dislocation transmission across twin boundary in nano-twinned FCC metals [18,19]; a loop growth scheme similar to that used in the step (2) was employed in the study of intra-granular dislocation emitted from grain boundaries of nano-grained FCC metals [20–23].

The free energy change during the transmission in Step (1) is given by Refs. [18,19]

$$\Delta F = \Phi r \ln \frac{r}{r_0} - \frac{\pi}{2} \tau b C_S (r^2 - r_0^2), \quad (1)$$

where r is the radius of the newly initialized loop in the nanospace; b is the magnitude of Burgers vector for $\langle c+a \rangle$ dislocation, $b = \sqrt{11/3}a$ with a being the lattice parameter in the hexagonal plane (twice the atomic radius); the dislocation core cut-off radius r_0 is on the order of the lattice parameter a ; the coefficient $\Phi = 0.1533Gb^2$ [18], with G being the shear modulus; C_S is the local stress concentration factor at a non-homogeneous nucleation site [13]. The embryo of the dislocation loop grows to reach its activation size (or activation volume) in order to extend further into the nanospace. At the activation size r_a , the free energy change ΔF attains its maximum. This condition $\partial\Delta F/\partial r = 0$ at $r = r_a$ gives the required shear stress,

$$\tau = \frac{0.09759Gb}{C_S r_a} \left(1 + \frac{1}{2} \ln \frac{r_a}{r_0 e} \right). \quad (2)$$

Here, e is the natural logarithm base. Activation size relates to activation volume by $r_a = \sqrt{2V/\pi/b}$, which depends on the characteristic structural length (grain size for nanograins; twin thickness for nanotwins) and was characterized for nano-grained Cu and nano-twinned Cu [12]. For the HCP Mg alloy with nano-spaced parallel BSFs, the structural length is the interspacing d . However, experimental data to characterize the interspacing-dependent activation volume are not available currently, and are expected in the order of b . Here, we take $r_a = b$ and $r_a/r_0/e \approx 1$. Using this activation size, Equation (2) becomes

$$\tau = 0.09759 \frac{G}{C_S}. \quad (3)$$

In reality, the activation loop is likely to be a half-elliptic loop, which can be pinned at the left and right end points of the loop marked by the number 2 in Figure 1. However, for simplicity, in deriving Equations (2) and (3), we use a half-circular loop with the activation area considered the same as that of the half-elliptic loop.

Next, we consider Step (2). The required shear stress is calculated from the half-circular loop of maximum radius, which is the result of extending the activated loop in Step (1). In this intra-nanospace extension stage, the work done by the shear stress increases the loop energy. Upon reaching the maximum radius, the work done by the shear stress is the half circle area multiplied by the driving force τb , which gives $\pi\tau b(d/\sin\theta)^2/2$; the loop energy increase is the energy in the half-circular loop $\pi Gb^2d/\sin\theta/2$ minus the energy in the straight loop on the BSF before bow-out $Gb^2d/\sin\theta$, which gives $Gb^2(\pi - 2)d/\sin\theta/2$. Here, the loop energy per unit length is taken as $Gb^2/2$. Balancing of the two energies leads to

$$\tau = 0.3633 \frac{Gb \sin \theta}{d}. \quad (4)$$

Following the maximum radius, the loop lies on the BSF. In this stage, since the characteristic loop size $d/\sin\theta$ does not change, the required shear stress for the loop to lie on the BSF would be the same as in Equation (4).

As shown in Figure 1, for a $\langle c + a \rangle$ dislocation to transmit across a BSF, the dislocation loop needs to be at its maximum radius to contact the BSF, while at the same time exert enough force on the BSF to be able to generate a small dislocation loop with an activation size in the next nanospace. On the other hand, in order for the loop to grow to the maximum radius, it must be activated in the nanospace by reaching the activation size. Therefore, one step of the two is the consequence of the other, and the yield strength for the HCP nanostructure should consist of a portion to overcome the resistance of crossing the BSFs and another portion to overcome the dislocation line tension to extend inside the nanospace to maximum radius. Hence, it is the sum of Equations (3) and (4), which gives,

$$\sigma = MG \left(0.09759 \frac{1}{C_s} + 0.3633 \frac{b \sin \theta}{d} \right). \quad (5)$$

Here, M is the Taylor factor to correlate the tensile flow stress with shear flow stress for nano-polycrystals. Equation (5) is in agreement with the $1/d$ linear relationship observed in [15,16]. If a pile-up of dislocations against the BSF occurs, the second term on the right side of Equation (1) is replaced by $-3.5094 \sqrt{d/\sin\theta} \tau b (r^{3/2} - r_0^{3/2})$ [18,19]. A similar derivation leads to following tensile flow stress,

$$\sigma = MG \left(0.05824 \frac{\sqrt{b \sin \theta}}{\sqrt{d}} + 0.3633 \frac{b \sin \theta}{d} \right), \quad (6)$$

for dislocation pile-up.

Because the alloy is a polycrystalline material in which the orientations of the grains are randomly distributed, we are looking for the critical resolved shear stress of each of the possible slip activities. In addition to transmission across the BSFs, dislocation extension parallel to them is possible. Consider a side extension of the rectangle loop with both upper and lower sides lying on BSFs, marked as the number 3 in Figure 1, by the distance Δx . The energy balance for this extension is simply $\tau b \Delta x d / \sin\theta = 2(Gb^2/2)\Delta x$, which leads to the tensile flow stress for side extension $\sigma = MGb \sin\theta/d$. This flow stress is a counterpart of that given in Equation (5) or (6).

When the logarithm factor is included in the dislocation line energy per unit length, the tensile flow stress for side extension is

$$\sigma = \frac{3MGb \sin \theta}{4\pi d} \ln\left(\frac{d}{b \sin \theta}\right), \quad (7)$$

assuming the Poisson ratio is 1/3. Note, in material defect study using an elasticity solution, there are two ways of treating the dislocation energy per unit length of a loop. One is taking it as the exact elasticity solution to include the logarithm function $\ln(R/r_0)$, where R is the characteristic loop size and r_0 is the core cut-off radius. Because of the uncertainty of the core cut-off and the ill-behaved logarithm function for small r_0 , the second way as we did is to simply take the energy per unit length of the loop as $Gb^2/2$.

The flow stress given by Equation (5), along with that for side extension given above (with and without the logarithm factor), is plotted in Figure 2 against $1/d$, together with experimental data for the Mg alloy with nano-spaced parallel BSFs [15,16]. In plotting, we take $G = 17$ GPa, $b = 0.61$ nm, $M = \sqrt{3}$, $C_S = 12$ and $\sin \theta = \sqrt{8/11}$. The $\langle c + a \rangle$ dislocation transmission model, Equation (5), agrees with experimental data better than the $\langle c + a \rangle$ dislocation pile-up model, Equation (6). For the pile-up model, when the first dislocation transmits across the BSF and extends to the end of the new nanospace, it cannot transmit again due to insufficient driving stress and needs to wait for the building-up of dislocation pile-up to accumulate sufficient stress concentration to reactivate the transmission. As shown in the figure, such a pile-up scenario can occur when the interspacing of the BSFs is larger than a critical value.

Figure 2 shows for d larger than about 50 nm, side extension dominates plastic flow since it requires less stress than that for transmission across the BSFs, provided that there are no other dislocation loops in the nanospace to block the side extension.

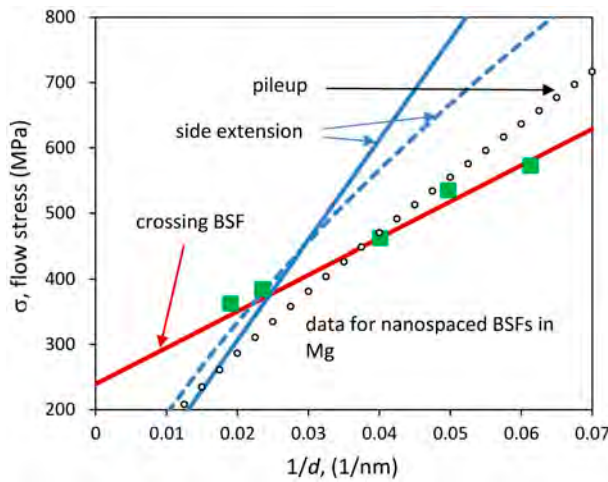


Figure 2. Predicted nanospace-dependent flow stress for microcrystalline Mg with parallel BSFs. Data are from Refs. [15,16]. For side extension, the dashed line is plotted using Equation (7) and the solid line is plotted using $\sigma = MGb \sin \theta/d$.

The critical d for the transition is different for different materials (with the same HCP structure), since it relates to the magnitude of Burgers vector and local stress field near the BSF (C_S) from Equations (5) and (6). An additional contribution to the flow stress from surrounding dislocations was estimated as $\propto Gb/\lambda$, where λ is the distance to the nearest dislocation, in modelling confined dislocations within BCC/FCC nano-multilayers [24]. From Figure 2, this contribution does not appear to be significant for the transmission across BSFs since the prediction by Equation (5), without the term, is in agreement with experimental data, that is, λ is considered to be large enough. However, the contribution of surrounding dislocations to the side extension flow stress shifts the transition point to the left. Overall, the model strongly suggests $\langle c + a \rangle$ dislocation transmission across BSFs is the dominate mechanism in the observed linear relationship between the yield stress and interspacing of BSFs.

From the non-homogeneous nucleation model [12,13], the interspacing-dependent activation size for the $\langle c + a \rangle$ dislocation's transmission across BSF is predicted from Equation (2) as $r_a = 0.09759 GbM/C_S/\sigma$, where σ is the flow stress in Equation (5). The activation size for its side extension can be estimated using the side extension flow stress in the same way. In general, $r_a \propto GbM/C_S/\sigma$. The activation volume is obtained from $V = \pi r_a^2 b/2$, and the activation energy is obtained by substituting the activation size and flow stress into Equation (1). The prediction of activation volume and activation energy is plotted in Figure 3a against the inverse of the interspacing for the Mg alloy with nano-spaced parallel BSFs. Also plotted are the experimental data for the activation volume of nano-grained Mg-5Al (wt.%) [25], referred as nc-Mg in the figure, against the inverse of grain size. For the nano-grained Mg-5Al, other slip systems, which have different Burgers vectors than that of $\langle c + a \rangle$ dislocation, may be active. In order to compare, both activation volumes in the plot are scaled by the lattice parameter in the hexagonal plane. Despite different slip planes, the activation volume for the Mg alloy with nano-spaced BSFs is in a comparable numerical range to that for the nano-grained Mg-5Al. The predicted activation volume for side extension matches the data better since the nc-Mg data are in the characteristic structural length range >50 nm, in which the side extension dominates according to Figure 2.

The strain rate sensitivity is obtained using the obtained flow stress and the predicted activation volume from $\sqrt{3}kT/\sigma/V$, where k is Boltzmann constant and T is absolute temperature [12]. The prediction of strain rate sensitivity is plotted in Figure 3b together with the experimental data of nano-grained Mg-5Al [25]. The strain rate sensitivity for the Mg alloy with nano-spaced parallel BSFs is also in a comparable numerical range to that for the nano-grained Mg-5Al. Note that in general $V \propto r_a^2 b$ from dimensional consideration, so that accurate prediction of activation volume, as well as strain rate sensitivity, depends on accurate evaluation of activation size. Currently, no experimental data for activation volume and strain rate sensitivity of the Mg alloy with nano-spaced parallel BSFs are available. Therefore, the predicted values in Figure 3a and b serve as a theoretical estimation of their size dependence to be verified by future experimental measurements. For the Mg alloy with nano-spaced parallel BSFs, the ability of $\langle c + a \rangle$ dislocations to transmit across BSFs, possibly from one side of the grain boundary to the other side, enhances strength and maintains certain ductility.

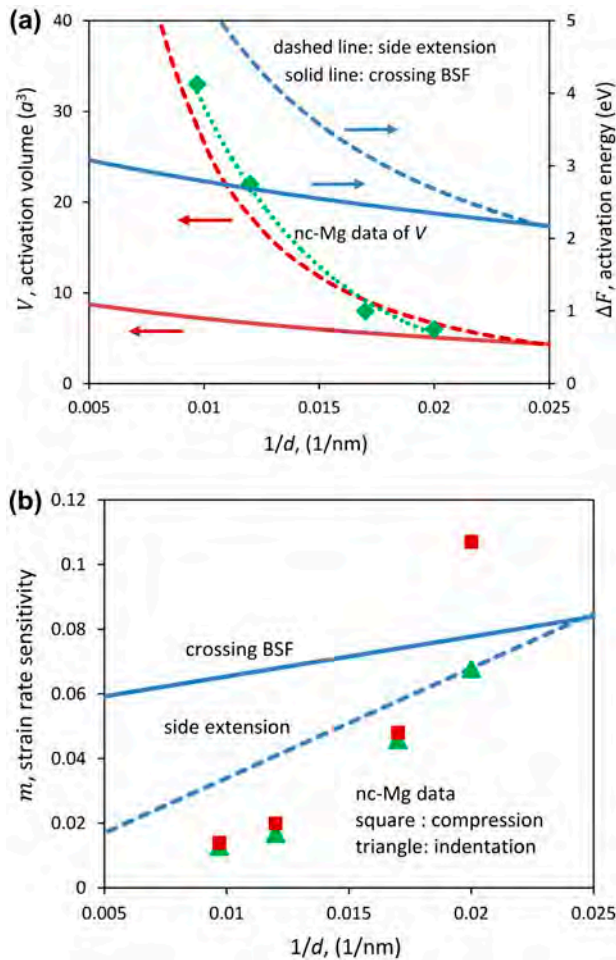


Figure 3. Predicted (a) activation volume and (b) strain rate sensitivity for microcrystalline Mg with parallel BSFs. Data are for nano-grained Mg-5Al (wt.%) from Ref. [25].

3. Discussion

A dislocation model is developed for a microcrystalline HCP structure with nano-spaced parallel BSFs. The simple expression shows the coupled effect of observed $\langle c + a \rangle$ dislocations' transmission across the BSFs and extension within the nanospace for strengthening. Prediction of flow stress, activation volume and strain rate sensitivity compares favourably with experimental data for microcrystalline Mg with nano-spaced parallel BSFs and nano-grained Mg. Analysis also suggests that for larger BSF interspacing, other mechanisms such as dislocation pile-up and/or dislocation extension sideways between the BSFs may become active.

In our Mg-Gd-Y-Ag-Zr alloy, nano-spaced parallel BSFs formed during hot rolling serve as obstacles for the glide of $\langle c + a \rangle$ dislocations generated during subsequent mechanical testing, enhancing strength and also maintaining certain ductility. In fact,

recent experiment and MD simulation have shown the importance of $\langle c + a \rangle$ dislocation in reducing anisotropic plastic deformation and thus achieve super strength and ductility [26]. However, the complexity of HCP deformation behaviour [27] has not been well understood. Further study such as *in situ* TEM for this alloy will be able to elaborate detailed mechanisms. Also, this dislocation model is developed based on available low strain rate observations and rationalizations. For dislocation activation and interaction with defects at high strain rate [28–30], investigation will be performed when test data for this alloy become available.

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YTZ and SNM acknowledge the support from U.S. Army Research Office under grant W911NF-12-1-0009. YTZ also acknowledges additional support from U.S. National Science Foundation under grant DMR-1104667.

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Dynamic Void Growth and Shrinkage in Mg under Electron Irradiation

W. Z. Xu^a, Y. F. Zhang^b, G. M. Cheng^a, W. W. Jian^a, P. C. Millett^c, C. C. Koch^a,
S. N. Mathaudhu^d and Y. T. Zhu^{a,*}

^aDepartment of Materials Science and Engineering, North Carolina State University, Raleigh, NC, 27695, USA;

^bFuels Modeling and Simulations, Idaho National Laboratory, Idaho Falls, ID 83415, USA; ^cDepartment of Mechanical Engineering, University of Arkansas, Fayetteville, AR 72701, USA; ^dMaterials Science Division, U.S. Army Research Office, Research Triangle Park, NC 27709, USA

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We report *in situ* atomic-scale investigation of late-stage void evolution, including growth, coalescence and shrinkage, under electron irradiation. With increasing irradiation dose, the total volume of voids increased linearly, while the nucleation rate of new voids decreased slightly and the total number of voids decreased. Some voids continued to grow while others shrank to disappear, depending on the nature of their interactions with nearby self-interstitial loops. For the first time, surface diffusion of adatoms was observed to be largely responsible for the void coalescence and thickening. These findings provide fundamental understanding to help with the design and modeling of irradiation-resistant materials.

Keywords: Void, Coalescence, Growth, Electron Irradiation, Magnesium

The irradiation resistance of a material determines its performance and service life in many applications such as nuclear energy, [1–5] outer space systems [6] or other industrial applications.[7,8] Radiation produces crystalline and microstructural defects in materials, which causes degradation of their properties. Extensive effort has been taken to investigate the evolution of irradiation-induced defects, including dislocations, stacking fault tetrahedrons, voids, element segregation and precipitation in metals and ceramics.[9–27] Particularly, void formation has attracted extensive attention since it may cause volumetric swelling and eventual material failure.

Voids have been reported to form in almost all crystalline materials under irradiation.[9–12,28–32] They are formed from the aggregation of vacancies or vacancy clusters in irradiated materials.[9] Voids usually take the morphology of faceted polyhedrons, bounded with low-energy surfaces. The growth process of voids is found complex and dynamic,[33,34] influenced by defect production, temperature, crystal anisotropy and the density of crystalline defects such as dislocations and grain boundaries.[9,16,17,35–41] Dislocations, in particular, are believed to facilitate the void nucleation and growth,

since they act as stronger sinks for self-interstitial atoms (SIA) than for vacancies, known as dislocation bias.[42] Consequently, voids may evolve simultaneously with dislocations. The interaction of voids and dislocations is thus believed to significantly affect the evolution and stability of voids in materials.[9,42,43]

SIA dislocation loops on a basal plane are usually produced under electron irradiation in hexagonal close-packed (hcp) Mg as an additional (0001) interstitial layer.[22,31,44] The SIA dislocation loops are also called c-component dislocation loops since their Burgers vector contains the $\frac{1}{2}$ [0001] component. The formation of the c-component loop is believed to promote void formation and growth in hcp Ti and Zr metals.[32,45] However, little is known about the relationship between voids and the c-component SIAs loops in Mg so far.

We have recently reported the nucleation and early-stage growth of voids in Mg, which were observed *in situ* at atomic scale using high-resolution transmission electron microscopy (HRTEM).[46] Voids were readily formed under electron radiation in a commercial 200 kV electron microscope at room temperature due to the relatively low melting point and low electron damage

*Corresponding author. Email: ytzhu@ncsu.edu

threshold of Mg.[47] The early-stage growth of voids involves lengthening to a plate-like shape, and then thickening to a more equiaxed shape, which is determined by the growth kinetics and thermodynamics. Interestingly, the evolution of surface ledges on various void facets was observed to affect void evolution. Such a process on void facets is rarely reported before and can only be observed *in situ* at the atomic scale.

In this paper, we further report on void evolution behaviors during their late-stage growth. This stage is characterized with the interaction between voids and SIA dislocation loops. Void coalescence is also observed, which involves surface diffusion of adatoms. These findings represent new fundamental understandings of void growth mechanisms.

1. Experimental Procedures Commercial purity magnesium (99.9%) was used in this study. Major impurities include (wt%) 0.0510% Fe, 0.0320% Mn, 0.0089% C, 0.0054% Al, 0.0027% Na, 0.0026% Zn. The transmission electron microscopy (TEM) foil was prepared using a Struers TenuPol-2 electro-polishing machine in an electrolyte of 5.3 g lithium chloride, 11.16 g magnesium perchlorate, 100 ml 2-butoxy-ethanol and 500 ml methanol at -30°C and 200 mA, then low energy ion-milled on a cold stage and plasma cleaned for high-resolution TEM observations.

The electron irradiation and *in situ* observation were carried out in a JEM-2010F TEM operating at 200 kV at room temperature. The electron beam flux is about $8.2 \times 10^{23} \text{ e} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$, which corresponds to a damage rate of $\sim 1.4 \times 10^{-3} \text{ dpa} \cdot \text{s}^{-1}$. The listed times in Figures 3–6 are times from the starts of video recording, which corresponds to the time listed in the Supplementary Movies 1–4, respectively. The recording time in the movie is expressed as minutes:seconds.

A series of HRTEM images taken along a $[2\bar{1}\bar{1}0]$ orientation are used for void volume calculations. According to previous studies,[29,46] the voids are found to have a polyhedron shape, bounded by $\{0001\}$, $\{01\bar{1}1\}$ and $\{01\bar{1}0\}$ facets. The schematic illustration of the void shape is shown in Supplementary Figure S1. Volume V of a void is calculated using the following equation, which is derived from the void geometry:

$$V = 2\sqrt{3}L^2W - 2\sqrt{3}L(W - S)^2 \tan \theta + \sqrt{3}(W - S)^3 \tan^2 \theta, \quad (1)$$

where L is the void length, which is the void dimension on the (0001) basal plane, W is the void thickness, which is the void dimension along $[0001]$ direction, S is the projected length of the $\{01\bar{1}0\}$ facets, θ is the acute angle between $\{01\bar{1}1\}$ and $\{01\bar{1}0\}$ plane, which is 33.8° .

2. Statistics of Void Evolution The data reported here are from an irradiated region observed under *in situ* HRTEM. It has an approximate area of about $180 \text{ nm} \times 100 \text{ nm}$ and a thickness of $\sim 70\text{--}100 \text{ nm}$. Figure 1(a) shows that the total volume of the voids steadily increased with irradiation dose. Figure 1(b) shows that the average void length increased from 12 to 15.8 nm, and the average thickness increased from 2.2 to 5.7 nm. In other words, the average thickness increased sharply by about 160%, while the average length increased by only 32%. This is similar to the previous finding that the void nuclei tend to grow in the thickness direction after first lengthening to a plate-like shape.[46]

While the total volume of voids increased, the total number of voids decreased during the irradiation as shown in Figure 2. This indicates that some voids grew larger while others became smaller and eventually disappeared. Interestingly, new voids continued to nucleate,

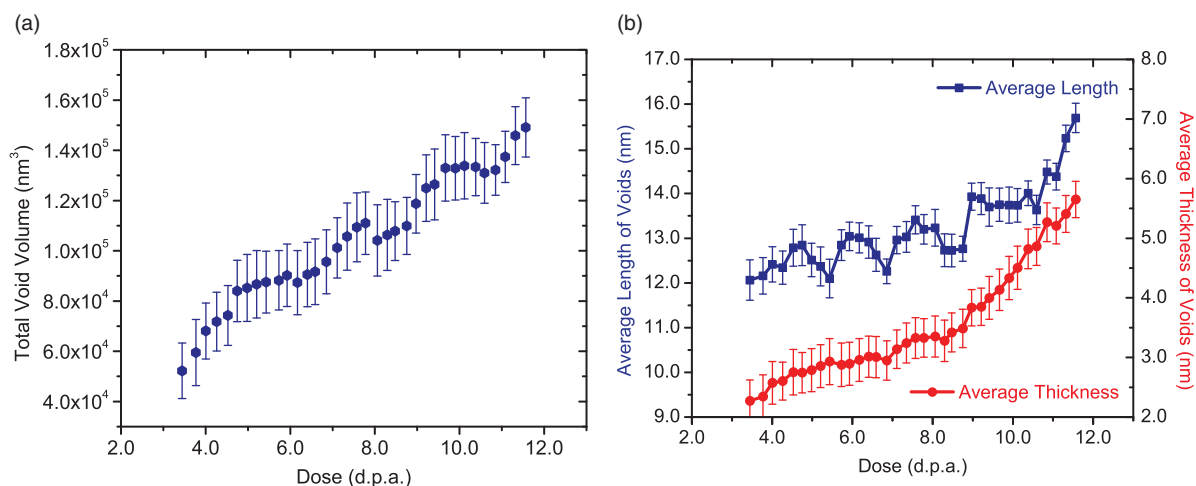


Figure 1. Statistics of void evolution behavior in the observed region with increasing irradiation dosage (a) total void volume, (b) average void length and thickness.

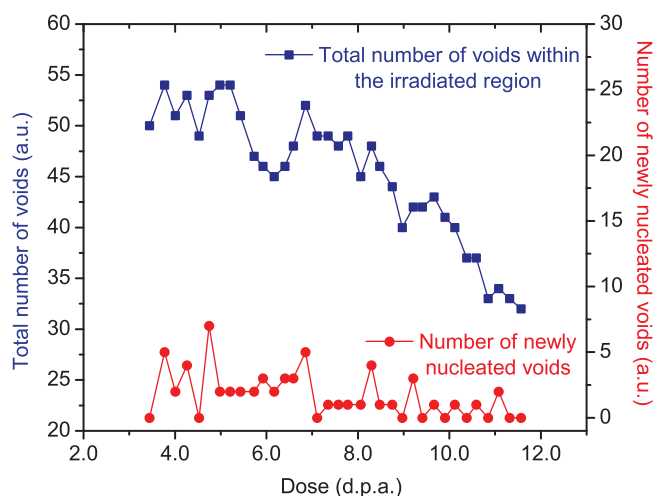


Figure 2. Evolution of (a) total number of voids and (b) number of newly nucleated voids within the irradiated region with increasing irradiation dosage.

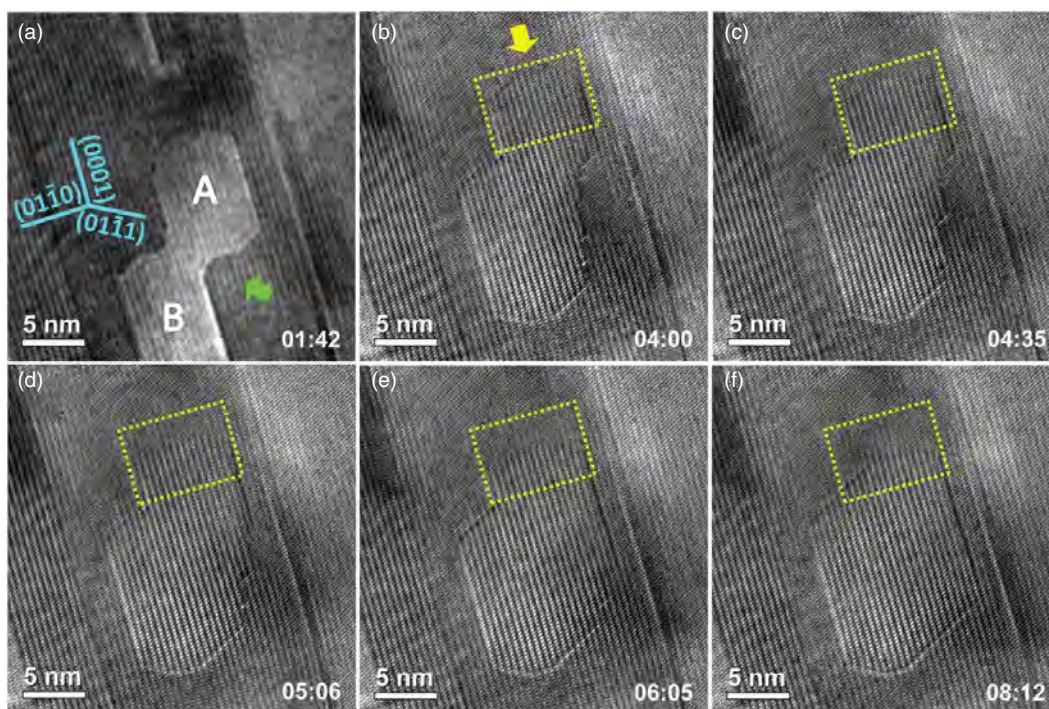


Figure 3. The coalescence of two voids (a) Ledges were formed when two voids met each other, as indicated by the green arrow. (b)–(f) Atoms on the ledges gradually diffused out and filled the cavity in the dashed frame. The total length of the two voids decreased after coalescence (see Supplementary Movie 1).

which caused the fluctuation of the total number of voids. Such simultaneous nucleation of new voids suggests a very different evolution kinetics from the conventional growth and ripening process.[48]

3. Void Coalescence As shown in Figure 3, when voids A and B initially contacted each other, a big step was formed on the (0001) facet that bridged the two voids, as shown in Figure 3(a). This big step evolved into many small steps along the (0001) facet (Figure 3(b)).

The small steps moved along (0001) plane and merged to the side of the neighboring step or the facet. As shown in Figure 3(b)–(f), six steps merged to four steps, two steps, one step and finally formed one void without any step, respectively. As seen, the stepped (0001) facet evolved to form a flat facet in the end.

It is interesting that the length of void A shortened as the steps on the (0001) facet vanished, as shown in Figure 3(b) and 3(d). Moreover, the removal of steps during the void coalescence occurred much faster than a

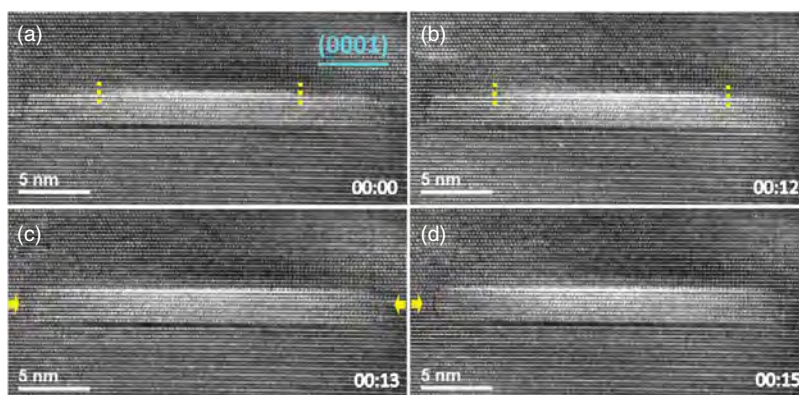


Figure 4. The shortening of void length during Stage 2 growth. (a) and (b) A vacancy layer on a (0001) facet was extending to the sidewalls, as marked by the dashed yellow lines. (c) and (d) The shortening of void length happened when this vacancy layer extended over the (0001) facet (see Supplementary Movie 2).

typical void thickness growth process via the nucleation and extension of vacancy layers on the (0001) facet.[46] These observations indicate that the atoms on surface steps most likely diffused along the void's inner surfaces [46] (from {0001} facets to $\{01\bar{1}1\}$ and $\{01\bar{1}0\}$ sidewalls) to reshape the void. The fast diffusion of adatoms leads to fast coalescence of the voids, because the energy barrier is much smaller for adatom diffusion than for vacancy diffusion.[49]

The adatom diffusion on the inner surfaces of voids also occurred during the void thickening process. Figure 4(c) and 4(d) show that one or a few atomic layers of void length suddenly vanished during its thickness growth as marked by the yellow arrow (see Supplementary Movie 2). This occurred when the vacancy cluster was extending on a (0001) facet. In other words, the remaining atoms on the edge of the (0001) facet diffused away quickly to the sidewalls of the void, which is quite similar to what occurred during void coalescence. The diffusion of these excess atoms on the (0001) facet to the void sidewalls not only directly contributed to the length shortening but also might have reduced the vacancy concentration on the sidewalls. This will make it more difficult for the nucleation of new vacancy layers on the sidewall facets, which hinders the void growth in the length direction. In Figure 4(a) and 4(b), the extension of a vacancy layer on the (0001) facet involves vacancy diffusion from the matrix to the void surface, which is expected to be a slow process. The phenomenon of length shortening during the void thickness growth was also observed in Zirconium under 1 MeV electron irradiation.[20,50] The detailed evolution process in Zr could be very similar to the finding here in Mg, which needs to be clarified in future studies.

4. Interaction Between SIA Loop and Void

Figure 5 shows an SIA loop eating away a void while extending along a basal plane from the up-left corner to

bottom-right side. The void happened to lie in front of the loop. The void gradually shrank in length as it interacted with the SIA loop edge (Figure 5(b)–(d)), and eventually disappeared after the SIA loop passes through it (see Supplementary Movie 3). It should be noted that there is a transient thickening process of the void observed in Figure 5(a) and 5(b). The void thickness largely remained un-shrunk during the process until the length and thickness are comparable in size, and then the thickness is reduced. The void volume is measured as a function of time to confirm that it is a void shrinkage process rather than a geometry change as shown in Supplementary Figure 2.

Figure 6(a) and 6(b) shows another observation that the void shrank in its size when it was located in front of the SIA loop edge similar to the previous observation in Figure 5. Interestingly, the void did not vanish after the loop passed it, but rather increased again in length (Figure 6(c) and 6(d)). The void growth began when it was located at the broad side of the loops indicated in Figure 6(e), suggesting such a void position could promote void growth. The broad sides of the loop are also found to be typical locations of void nucleation.[46]

The above observation indicates that the evolution of a void is significantly affected by its interaction with nearby SIA loops. A void tends to grow if it is located near the broad side of an SIA loop, and shrink if located in front of an SIA loop edge. This can be understood by considering the stress-induced diffusion of point defects around the loops. The SIA loop can be regarded as a Frank dislocation with compressive stress field near the broad side and the tensile stress field near the outer side. The compressive stress field would attract vacancies,[51] thus helping void grow larger in this region. However, the tensile stress field would attract SIAs, causing the void to shrink. Therefore, a transition from shrinkage to growth is expected when the void is positioned from the tension region to compression region, as shown

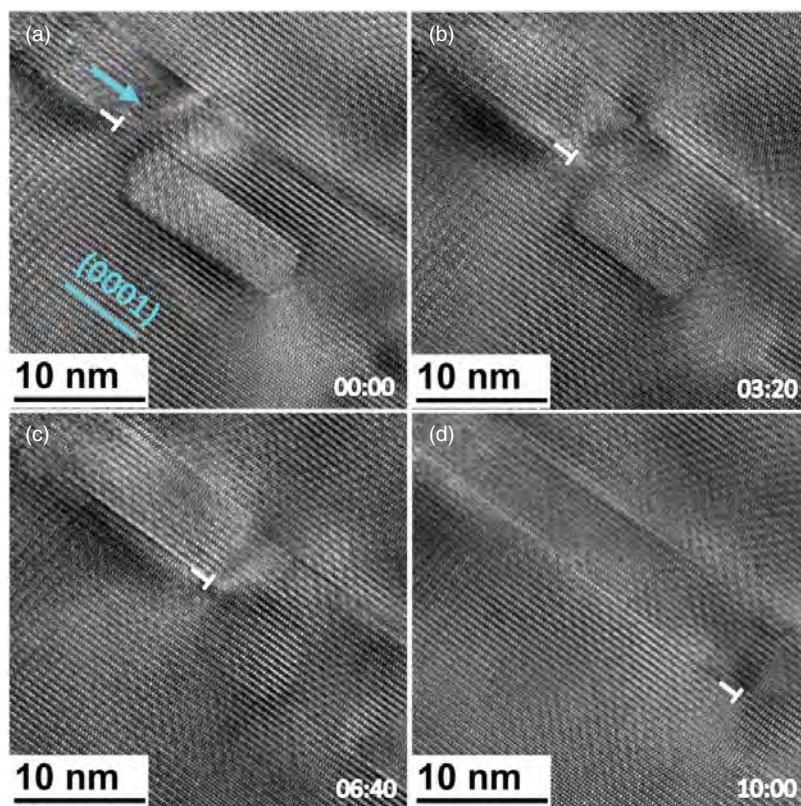


Figure 5. The void shrank in length when it contacted the edge of an extending SIA loop. (a) The loop is extending along (0001) basal plane toward the void. The direction of loop extension is indicated by the blue arrow. (b) and (c) The void shrank along length direction. (d) The void vanished after the SIA loop extends over. (see Supplementary Video 3).

in Figure 6(a)–(c). In addition, pipe diffusion through an SIA dislocation loop may occur when it comes in direct contact with the void, which was suggested to be responsible for the void shrinkage observed in an earlier study.[52]

Void growth or shrinkage is closely related to the dynamic evolution of SIA loops. The diameters of SIA loops were observed to grow. SIA loops were also observed to migrate along the $\langle c \rangle$ direction in some occasions. The SIA loops are not stationary in the matrix. They continue to grow or climb until they meet other dislocation loops [53] or a void. The dynamic evolution of SIA loops is also commonly seen in other materials under electron irradiation.[9,43,54]

The dynamic evolution of SIA loops could also result in the nucleation of new voids if the required condition of local vacancy super-saturation is attained. As shown in Figure 2, the nucleation of new voids could simultaneously occur during the entire irradiation period. These newly nucleated voids follow the same growth pattern as reported in our previous paper on early-stage void growth,[46] and then evolved as observed in this study.

The voids were observed to shrink mostly in length, and rarely in thickness (Figure 5(a) and 5(b)). The void

shrinkage in thickness only occurred when the void became small and equiaxed in shape. These phenomena were caused due to the following reasons. First, the length shortening process is energetically favorable, since it causes a void to evolve into a more equiaxed shape, which lowers the overall surface energy.[29,46] The thickness reduction, on the contrary, is thermodynamically unfavorable. Second, in order to reduce void thickness, an atom layer should form on the void (0001) facet. However, this process turned out to be very difficult. On the one hand, the formation energy of an adatom on the {0001} surface is 0.61 eV in Mg, which is much larger than those on the void sidewalls, which are 0.46 eV on the {01 $\bar{1}$ 1} facets and 0.34 eV on the facets.[49] In other words, it is more difficult to form an adatom on the {0001} surface than on the {01 $\bar{1}$ 1} or {01 $\bar{1}$ 0} surface. On the other hand, for a typical elongated void, a (0001) facet is larger than a {01 $\bar{1}$ 1} facet or a {01 $\bar{1}$ 0} facet. Therefore, it takes more adatoms to fill the entire (0001) facet, and a step needs to form first. As seen in the void coalescence, the step on the (0001) facet is energetically unfavorable and will be quickly removed via adatom diffusion through the inner facets to the sidewalls. This makes the formation of an atom layer on the (0001) surface more difficult.

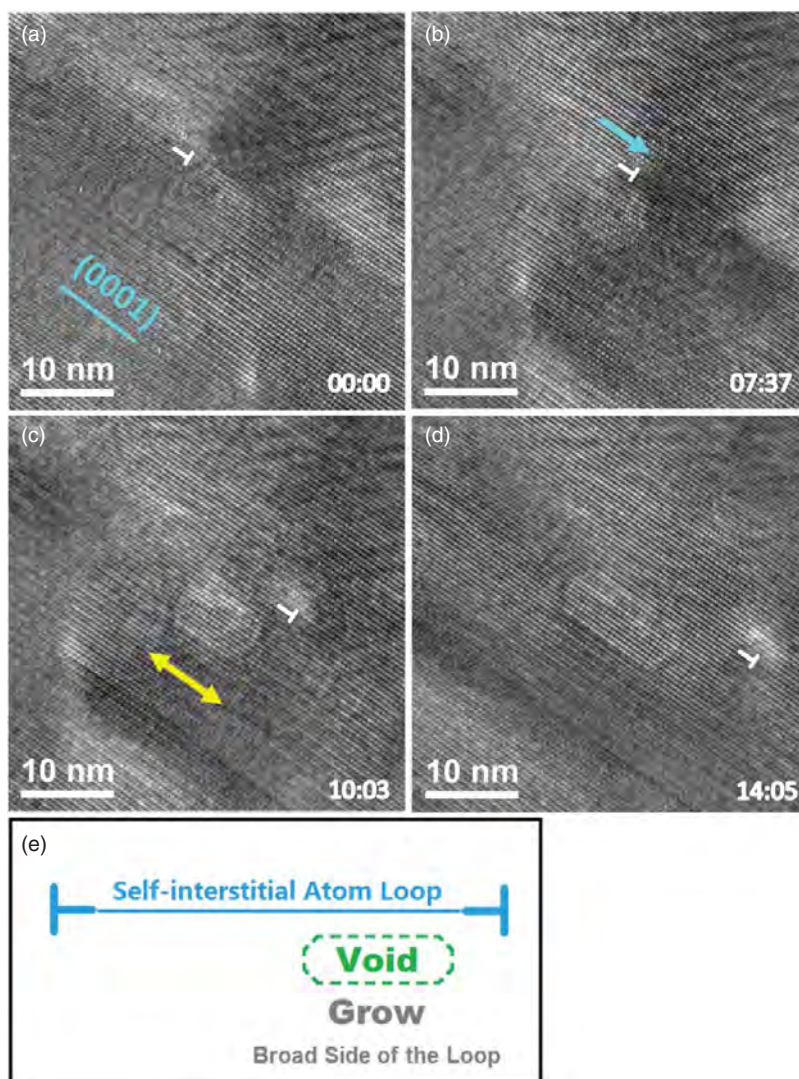


Figure 6. The void length grew as an SIA loop was passing through it. (a) and (b) The void shrank in size when it was located in front of an extending SIA loop edge. The extending direction of the SIA loop is indicated by the blue arrow. (c) and (d) The void began to grow in length when the SIA loop moved to its side (see Supplementary Movie 4). (e) Schematic illustration of a void located at the broad side of an SIA loop. A void tends to grow on this side.

5. Conclusion With increasing irradiation dosage, the total volume of voids increases and the number of voids decreases, while new voids still nucleate but with decreasing nucleation rate. The evolution of voids in Mg under active irradiation is significantly affected by their interactions with SIA loops. A void will grow if it is on the broad side of an SIA loop, and shrink if it is located in front of the loop edge. Two voids close to each other may coalesce with each other via the formation and elimination of steps on the $\{0001\}$ facets. The fast diffusion of adatoms on the $\{0001\}$ facets is believed to be largely responsible for the fast coalescence of voids. Void growth in thickness is usually accompanied by shrinking in length. Elongated voids usually do not shrink in thickness (c -axis) until their length is reduced to an extent that

the void becomes equiaxed. This is attributed to the difficulty in nucleating an atomic layer on the $\{0001\}$ facets as well as to thermodynamics, which favor equiaxed voids.

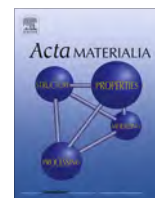
Supplementary Online Material. A more detailed information on experiments is available at <http://dx.doi.org/10.1080/21663831.2014.904826>.

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Effect of Ag on interfacial segregation in Mg–Gd–Y–(Ag)–Zr alloy



H. Zhou^{a,b}, G.M. Cheng^b, X.L. Ma^b, W.Z. Xu^b, S.N. Mathaudhu^c, Q.D. Wang^{a,*}, Y.T. Zhu^{b,d,*}

^a National Engineering Research Center of Light Alloys, Net Forming and State Key Laboratory of Metal Matrix Composite, Shanghai Jiao Tong University, 200240 Shanghai, PR China

^b Department of Materials Science & Engineering, North Carolina State University, Raleigh, NC 27695, USA

^c Department of Mechanical Engineering, University of California, Riverside, CA 92521, USA

^d School of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, PR China

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ABSTRACT

Interfaces such as twin boundaries, stacking faults and grain boundaries often play an important role in controlling mechanical properties of metals through interaction with dislocations. Segregation of alloy elements and impurities to these interfaces can stabilize them and produce a large strengthening effect. Here we report the effect of Ag on segregation of alloy elements at twin boundaries, stacking faults and grain boundaries in the Mg–Gd system. Specifically, for the first time a spinal-shaped periodic segregation is observed at the {1 0 1 2} twin boundary and high-angle lamellar grain boundary in the Mg–Gd–Y–Zr alloy due to the presence of the Ag addition. The segregation consists of Gd- and Ag-rich columns. It appears that high Ag content in the spinal-shaped segregation induces fcc-like cell structures.

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1. Introduction

Due to their lightweight, magnesium alloys are becoming increasingly attractive for structural applications in aerospace, automotive, and electronic industries [1,2]. Extensive effort has been made to improve their mechanical strength [3], formability [4], creep resistance [5] and corrosion resistance [6]. Reported strategies to enhance strength of Mg alloys include grain refinement [7], age hardening [8,9] and introduction of stacking faults [10–12]. Moreover, by combining these strengthening mechanisms, several high-strength magnesium alloys containing rare earth elements (Mg–RE) have been developed. For example, Homma et al. [13] developed a high-strength Mg–Gd–Y–Zn–Zr alloy that has yield strength of 473 MPa by combining significant grain refinement with age hardening.

Since the solubility of the rare earth alloying elements decreases with decreasing temperature, Mg–RE alloys can be significantly hardened by precipitation of second phase particles. It has been reported that the precipitation process in Mg–Gd–Y alloy follows the sequence of S.S.S.S (Supersaturated Solid

solution) → β'' → β_T → β' → β_1 → β [14]. The precipitates, especially the peak aged β' phase, enhance the mechanical strength by blocking dislocation slip [15]. Moreover, rare earth atoms tend to segregate at interfaces such as grain boundaries [16,17], twins boundaries [18], and stacking faults [19]. Such segregation is believed effective in pinning dislocations, which leads to further strengthening [20,21].

Previous studies revealed that additional Zn element in Mg–RE alloys induced a novel type of long period stacking ordered (LPSO) structures during annealing and consequently enhanced strength. This has led to a recent increase in research of magnesium alloy strengthening via this mechanism [22–27]. Interestingly, other alloying elements, such as Ag, also show similar strengthening effect in Mg–RE alloys [28]. Wang et al. [29] found that the tensile strength of as-cast Mg–Gd–Y alloys was further improved by adding ~2 wt.% of Ag. The tensile strength of peak aged Mg–Gd–Y–Ag alloy reached a high ultimate tensile strength (UTS) of 403 MPa without compromising elongation. Jian et al. [10,11] also found that the rolled Mg–Gd–Y–Ag alloy shows much higher yield strength than a Mg–Gd–Y alloy that has similar elemental composition of Gd and Y. Their hypothesis was that the induced stacking faults played a critical role in the improvement of mechanical properties. However, it is still not well understood how Ag element affects microstructure evolution of Mg–RE alloys during deformation and heat treatment.

In this work, two Mg–RE alloys with similar compositions except for Ag content were studied in order to investigate how

* Corresponding authors at: Department of Materials Science & Engineering, North Carolina State University, Raleigh, NC 27695, USA. Tel.: +1 919 513 0559 (Y.T. Zhu). Tel.: +86 21 54742715 (Q.D. Wang).

E-mail addresses: wangqudong@sjtu.edu.cn (Q.D. Wang), ytzhu@ncsu.edu (Y.T. Zhu).

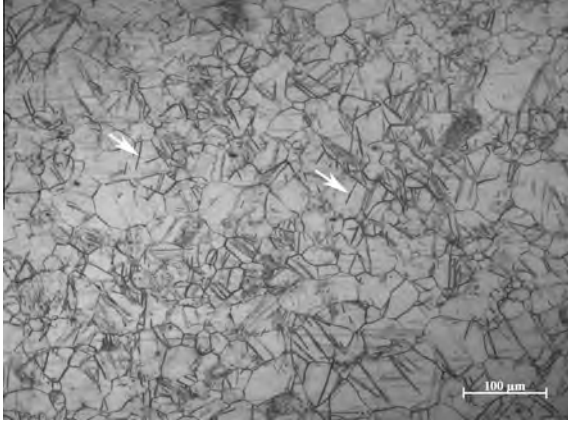


Fig. 1. Optical micrograph of the microstructure of the Mg-Gd-Y-(Ag)-Zr alloy subjected to 75% hot-rolling.

the Ag addition affects segregation at various interfaces such as twin boundaries, stacking faults, and grain boundaries. Atomic-scale characterization was carried out using high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) with an ultra-high spatial resolution of ~ 0.10 nm, which provided a more precise and reliable structural interpretation of chemical ordering, and a better understanding of the atomic configuration [30,31]. Since the differences in atomic numbers between the constituent elements are fairly large (Mg: 12, Gd: 64, Y: 39, Ag: 47), we were able to obtain Z (atomic number) – contrast images to differentiate segregated heavy solute atoms. Basing on comprehensive analysis of electron diffraction patterns, atomic resolution images and also sub-nanometer chemical analysis with energy-dispersive X-ray spectroscopy (EDS), we were able to establish models of atomic segregation at coherent twin boundaries, stacking faults and grain boundaries.

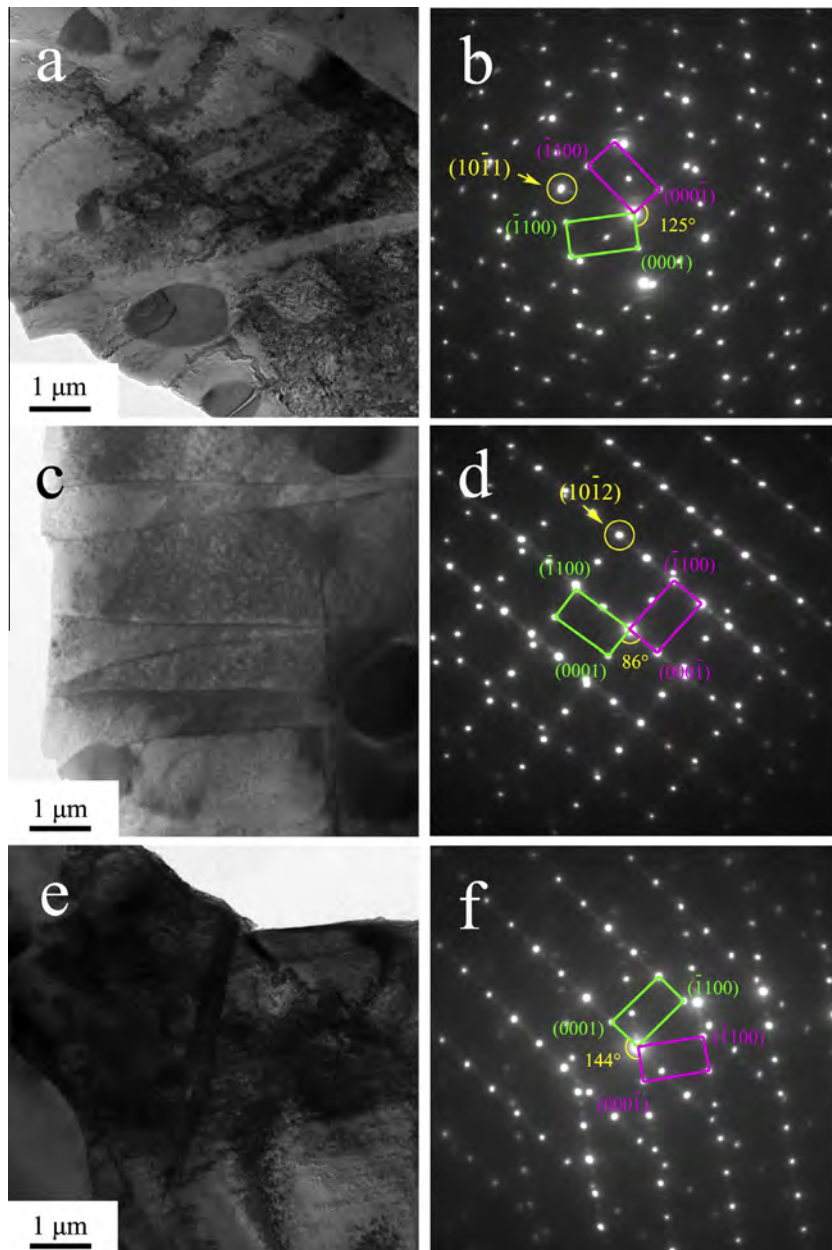


Fig. 2. TEM images and selected area diffraction of lamellae structures in the hot rolled Mg-Gd-Y-(Ag) alloy: (a) and (b) $\{10\bar{1}1\}$ twin (TBI); (c) and (d) $\{10\bar{1}2\}$ twin (TBII); and (e) and (f) lamellar grain boundary (LGB).

Table 1
Lamellar structures in the Mg–Gd–Y–(Ag)–Zr alloy subjected to 75% hot rolling.

Lamellar Structures	Abbreviation	Definition	Misorientation between two {0001} planes
{10 $\bar{1}$ 1} twins	TBI	Compression twin	$\sim 125^\circ$
{10 $\bar{1}$ 2} twins	TBII	Tensile twin	$\sim 86^\circ$
Lamellar grain boundary	LGB	Special grain boundary	$146^\circ, 144^\circ, 140^\circ, 102^\circ$, etc.

2. Experimental procedures

The casting procedure used to produce the Mg–10.1Gd–3.5Y–0.45Zr and Mg–10.4Gd–1.6Y–(2.0Ag)–0.13Zr (wt.%) ingots can be found in reference [32]. For simplicity, these two alloys are hereafter referred to as the Mg–Gd–Y alloy and Mg–Gd–Y–Ag alloy, respectively. The as-cast ingots were solution treated at 500 °C for 12 h in a vacuum furnace and quenched to room temperature in silicon oil (T4 treatment). The T4-treated samples with dimensions of $20 \times 25 \times 2$ mm³ were used as the starting material for hot rolling. Specimens for hot rolling were heated at 450 °C for 15 min before each rolling pass, and then rolled on a conventional hot roller with a thickness reduction of ~ 0.1 mm per pass and total rolling reduction of 75%. Annealing after rolling was performed at 250 °C for 0.5 h. The specimens for optical microscopy

characterization were ground with sandpaper of 320, 600, and 800 grits, and then polished by a woolen cloth with 1 μ m diamond suspension. Final polishing was done using magnesia suspension on polishing cloth to a mirror finish. The etching solution was comprised of 100 ml ethyl alcohol with 5 g picric acid and 5 g acetic acid. Cross-sectional TEM specimens were cut from the rolling sheet and gently polished to a thickness of ~ 25 μ m. Perforation by ion milling was carried out on a cold stage (~ -50 °C) with low angle ($< 3.5^\circ$) and low energy ion beam (< 3 KeV). Atomic-resolution high-angle annular dark-field (HAADF) observation was conducted on an aberration-corrected scanning transmission electron microscope (STEM) (FEI Titan 80-300) operated at 200 kV. EDS mapping was conducted at an accelerating voltage of 80 kV to avoid excessive irradiation damage to the Mg alloy samples [33].

3. Results

3.1. Microstructure

The microstructure of 75% hot-rolled Mg–Gd–Y–Ag alloy is shown in Fig. 1. Straight lamellar structures were frequently observed in coarse grains (~ 15 μ m). Previous investigations regarded them as deformation twins, which had specific orientation from parent grains [34,35]. Deformation twinning is a

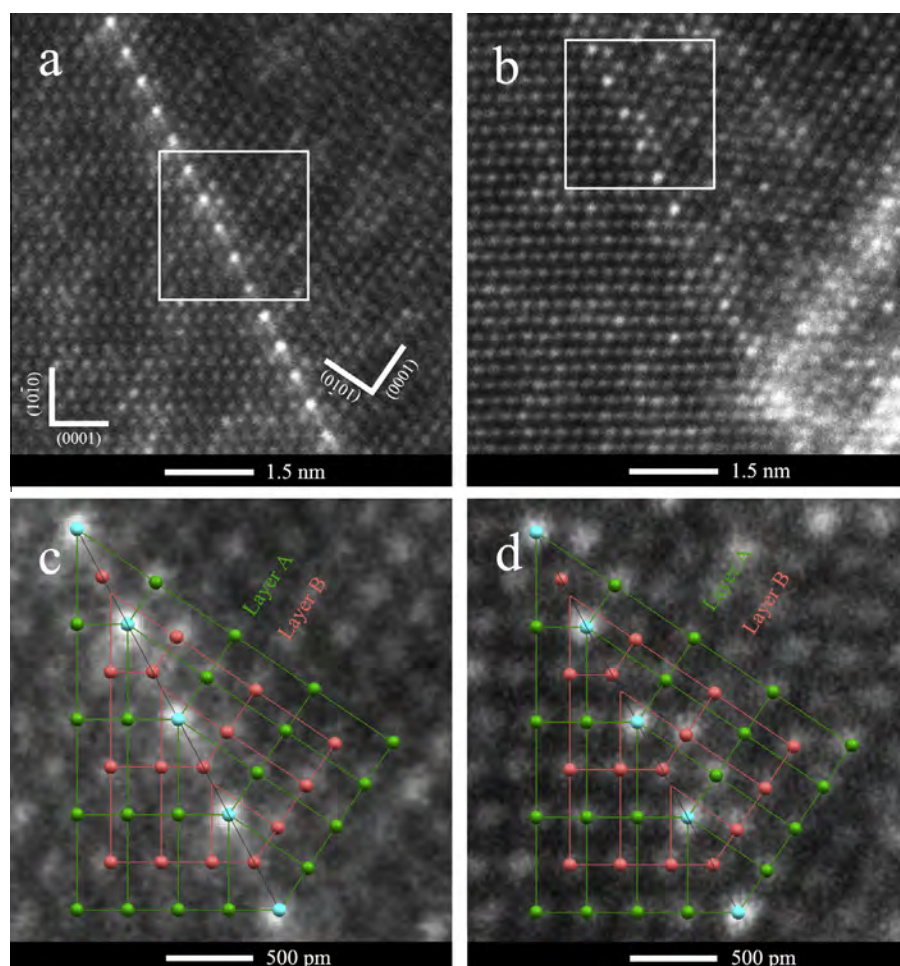


Fig. 3. HAADF-STEM images of TBI with the incident beam parallel to the [1120] axis: (a) and (c) Mg–Gd–Y alloys and enlarged image marked by the atomic model; (b) and (d) Mg–Gd–Y–Ag alloy and enlarged image marked by the atomic model. Green and pink spheres representing atoms in layer A and B of Mg crystal, respectively, and turquoise spheres representing the segregated solute atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

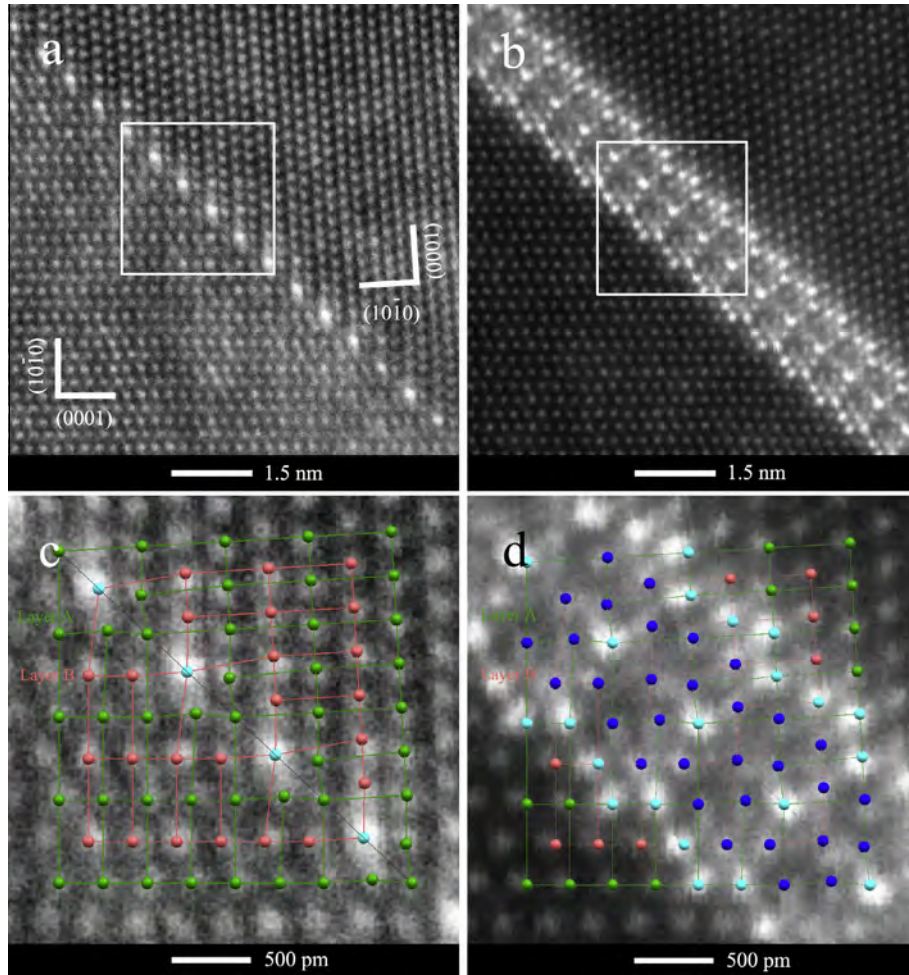


Fig. 4. HAADF-STEM images of TBII with the incident beam parallel to the $[1\bar{1}20]$ axis: (a) and (c) Mg-Gd-Y alloys annealed for 30 min, at 250 °C and the enlarged image by the atomic model; (b) and (d) Mg-Gd-Y-Ag alloy and the enlarged image marked by the atomic model. Green and pink spheres represent atoms in layers A and B of the Mg lattice, respectively, turquoise spheres represent the brightest spots, and blue spheres represent the spots with weaker brightness. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

common and important mechanism for plastic deformation in hexagonal close-packed (hcp) metals [36]. There are theoretically at least seven twinning modes in hcp metals, involving different twinning planes, including $\{10\bar{1}1\}$, $\{10\bar{1}2\}$, $\{10\bar{1}3\}$, $\{11\bar{2}1\}$, $\{11\bar{2}2\}$, $\{11\bar{2}3\}$ and $\{11\bar{2}4\}$ [37]. Among them, $\{10\bar{1}1\}$, $\{10\bar{1}2\}$ and $\{10\bar{1}3\}$ twins (hereafter referred to TBI, TBII and TBIII, respectively) are the most common types observed in Mg alloys, which can be clearly observed in the $[1\bar{1}20]$ zone axis [18]. For simplicity, all zone axes and crystal planes are hereafter those of the α -Mg matrix. Three types of lamellar structures were identified by using selected area diffraction as shown in Fig. 2. Classification of the lamellar structures in hot-rolled Mg-Gd-Y-(Ag)-Zr alloy is summarized in Table 1. The first lamellar structure is TBI with twin plane (K_1) of $\{10\bar{1}1\}$ as shown in Fig. 2a and b. The angle between the twin $\{0001\}$ planes and the matrix $\{0001\}$ planes is $\sim 125^\circ$ as viewed from the $[1\bar{1}20]$ zone axis. TBI is a compression twin since it typically forms under compressive stress [38]. Wu et al. observed TBI twins in an hcp Mg-Ti alloy [39], which was favored under compression. Fig. 2c and d shows the typical morphology of TBII, which is the predominant lamellar structure in hot-rolled samples. The angle between the two $\{0001\}$ planes is 86° as marked in Fig. 2d. TBII is the most common twinning system observed in hcp Mg [40].

We also observed another kind of lamellar structure that had a unique orientation relative to the traditional twins, as shown in

Fig. 2e and f. We define it as a special lamellar grain boundary (LGB), where neighboring grains shared the same $[1\bar{1}20]$ zone axis. Such LGBs are easy to study under high-resolution TEM because atomic structures on both sides can be clearly imaged, which provides an opportunity to observe relevant structures on both sides of grain boundary. The misorientation angles across LGBs were found to vary. Table 1 lists at least four different angles observed in our alloy systems. In the following, the LGB with a typical angle of $\sim 144^\circ$ is used for segregation investigations. The formation mechanism of these LGBs will be discussed in Section 4.1.

3.2. Segregation at coherent twin boundaries

Shown in Fig. 3 are the atomic-resolution HAADF-STEM images of TBI in Mg-Gd-Y and Mg-Gd-Y-Ag alloys observed from the $[1\bar{1}20]$ zone axis. After annealing at 250 °C for 30 min, single-line segregation along TBI occurred in both the 75% rolled Mg-Gd-Y and Mg-Gd-Y-Ag alloys, as shown in Fig. 3a and b, respectively. Models on their atomic structures are shown in the magnified images in Fig. 3c and d to demonstrate the different Z-contrasts caused by different elements. The green and pink spheres represent atoms in layers A and B in magnesium matrix, respectively. Turquoise spheres represent solute atoms that have bright contrast in HAADF-STEM image. It shows that the atoms at the twin interface are not perfectly close-packed. The atoms in

layer A are close to the exact lattice sites, while atoms in layer B are located in compression sites [18]. Compression sites are caused by lattice distortion that makes their distance to surrounding atoms smaller. In contrast, extension sites are those that have larger space than sites in perfect lattice. Both alloys exhibit similar segregation behaviors at the interface of TBI: Mg atoms on layer A are replaced by solute atoms while no replacement occurred on layer B.

In contrast, TBII shows different segregation phenomena in the alloys with and without Ag. Fig. 4a and b shows the HAADF-STEM images of TBI in Mg–Gd–Y and Mg–Gd–Y–Ag alloys after annealing, respectively. Corresponding atomic models are provided in Fig. 4c and d, which use the same color schemes as those in Fig. 3. The blue atoms represent spots with weaker brightness. The morphology of interfacial segregation at TBII of Mg–Gd–Y alloy is still single-line shaped, as shown in Fig. 4a, while the alloy containing Ag shows a unique segregation with periodic structures as shown in Fig. 4b. From the $[1\bar{1}20]$ direction, the structure looks like a “spine” along the twin boundary. It is clear from the figure that the central column and two side columns of atoms are

brightest, while the atoms between them are dimmer but still brighter than Mg atoms in the matrix. It has been reported that segregated atoms increase the pinning effect on the twin boundary [18]. The number of segregated atom sites in Mg–Gd–Y–Ag alloy (Fig. 4b) is much larger than those in the alloy without Ag (Fig. 4a), suggesting that Ag helps to stabilize the twin boundary. The atomic model in Fig. 4c and d indicates that the atomic stacking of TBII is not perfect. The compression sites are located in layer A, which is different from TBI. By measuring the distance of neighboring atoms, the compression sites are found to occupy more space in TBII than those in TBI. Another crucial difference is that layer B in TBII is located in extension sites, which is not observed in TBI. The atomic models of Mg–Gd–Y and Mg–Gd–Y–Ag alloys indicate that the addition of Ag also changes the positions where atomic replacement occurs in TBII.

In order to confirm the effects of Ag on the interfacial segregation directly, EDS mapping was carried out at twin boundaries as shown in Fig. 5. For simple comparison, a region containing both TBI and TBII was selected for the mapping as shown in Fig. 5a. Fig. 5c and d shows significant segregation of Gd and Ag in both

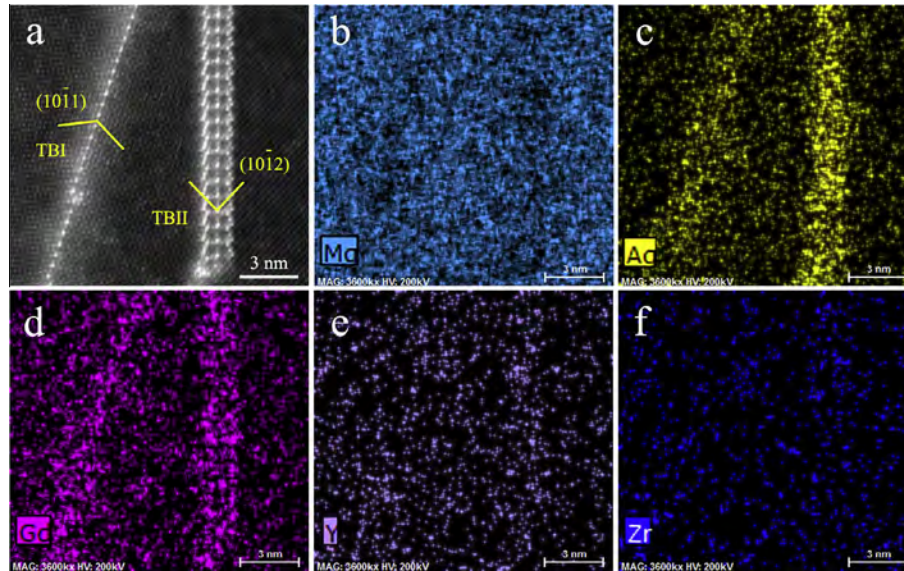


Fig. 5. EDS chemical mapping of the twin boundary segregations in Mg–Gd–Y–Ag–Zr alloy: (a) the corresponding HAADF-STEM image, (b) Mg–K α ; (c) Ag–K α ; (d) Gd–K α ; (e) Y–K α ; and (f) Zr–K α .

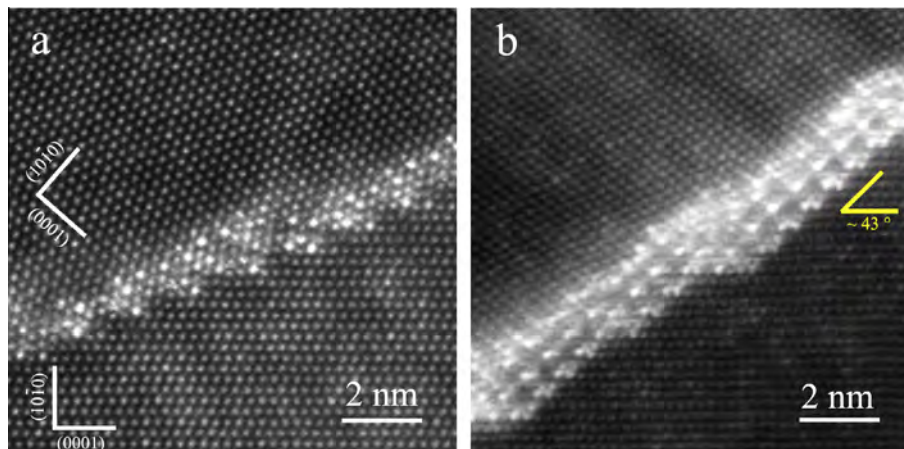


Fig. 6. HAADF-STEM images of grain boundaries with the incident beam parallel to the $[1\bar{1}20]$ axis: (a) Mg–Gd–Y alloy; (b) Mg–Gd–Y–Ag alloy.

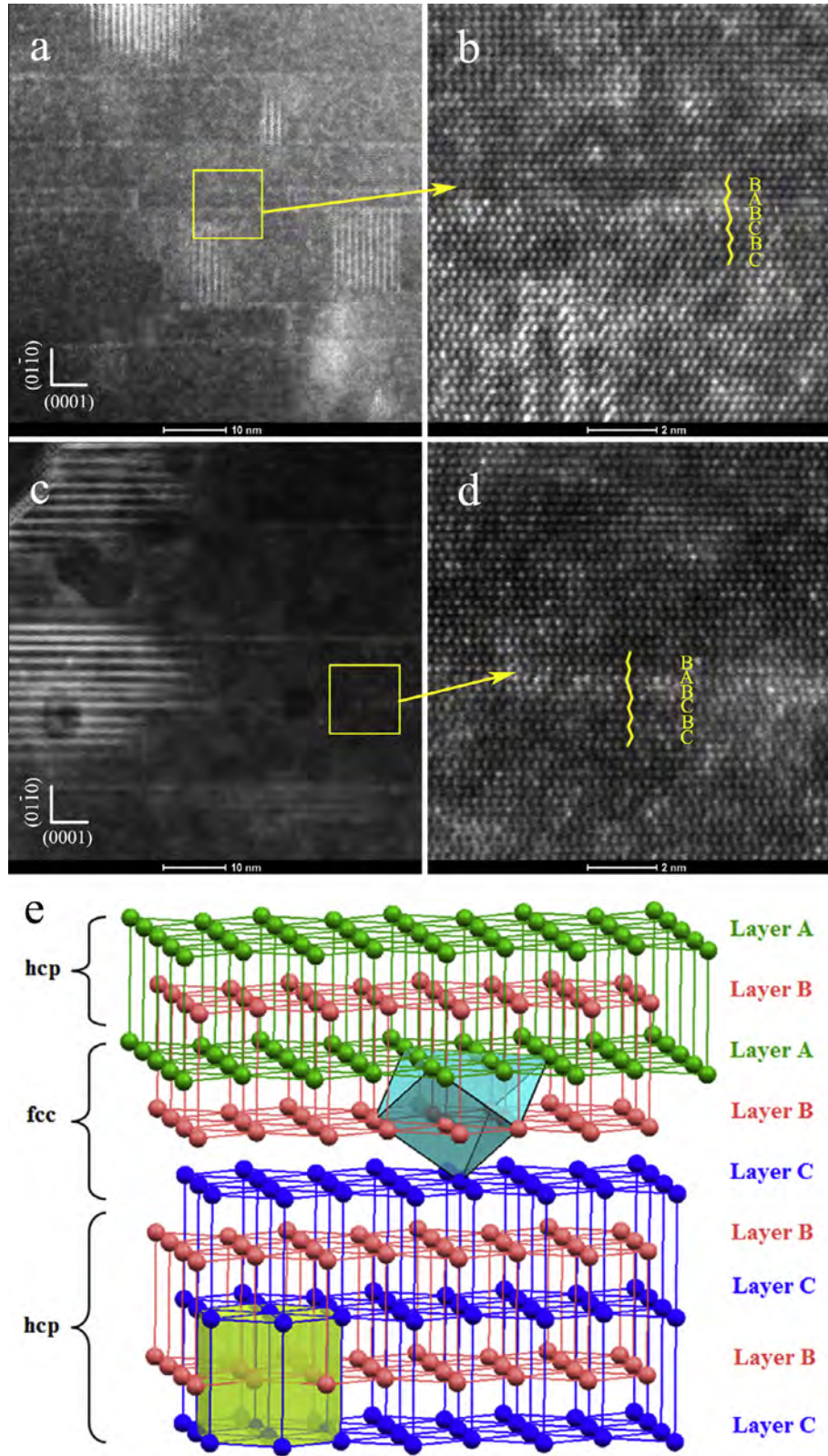


Fig. 7. HAADF-STEM images of segregation at stacking faults: (a) and (b) Mg-Gd-Y-Zr alloy, (c) and (d) Mg-Gd-Y-Ag-Zr alloy, and (e) atomic model of I1 stacking faults.

TBI and TBII in Mg-Gd-Y-Ag alloy. In contrast, Y is not obviously segregated to either twin boundaries (Fig. 5e). Fig. 5f indicates that Zr was not segregated either, which is consistent with a literature report [41].

3.3. Segregation at grain boundaries

Fig. 6 shows the segregation at lamellar grain boundaries (LGBs) of Mg-Gd-Y and Mg-Gd-Y-Ag alloys. In order to make valid

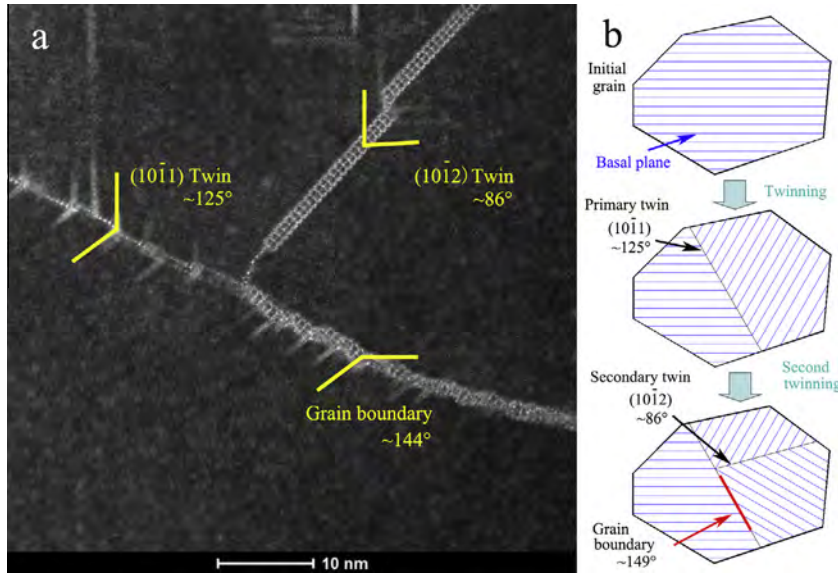


Fig. 8. (a) HAADF-STEM images of grain boundaries with the incident beam parallel to the $[11\bar{2}0]$ axis, and (b) schematic of formation process of special grain boundary.

comparisons, the same grain boundary angle of $\sim 144^\circ$ is chosen for comparison in both alloys. Different segregation phenomena are observed at the grain boundaries in the alloys with and without Ag, which is similar to the observations for TBII. The alloy with Ag shows spinal-shaped segregation structures, however, this “spine” at the LGB is not continuous, and appears to be pieced together of several parallel segments. It appears to try to follow both the $(10\bar{1}2)$ plane as on the TBII and the LGB, but the $(10\bar{1}2)$ plane does not coincide with the LGB, which leads to the segmented feature shown in Fig. 6b. This observation also indicates the importance of the $(10\bar{1}2)$ twin boundary (TBII) in the formation of the spinal-shaped segregation.

3.4. Segregation at stacking faults

Fig. 7a and c shows the low magnification HAADF-STEM images of 75% rolled Mg–Gd–Y and Mg–Gd–Y–Ag samples. A high density of stacking faults appeared in both alloys, which tend to be generated in twins or lamellar grains mentioned above. Jian et al. reported the role of the nano-spaced stacking faults to improve the mechanical properties of magnesium alloys [10,11]. The yield strength follows a linear relationship with the reciprocal of average spacing of stacking faults [10]. In this work, the spacing of stacking faults in the two alloys is in the range of 10–20 nm. High resolution images in Fig. 7b and d show that the stacking faults in the alloys are mainly I1 type, which has a stacking sequence of ABABABCBCB. I1 stacking faults introduce a thin three-layer of face-center cubic (fcc) stacking structure into the hcp matrix as shown in Fig. 7e. After annealing at 250 °C for 0.5 h, Suzuki

segregation of solute atoms to the three fcc layers of stacking faults occurred, which is also reported in Mg–Y–Zn alloys [19]. The Suzuki segregation on stacking faults is different from the reported LPSO structure in Mg alloys [8]. First, the structure of Suzuki segregation only appeared in the local fcc layers at the stacking faults. Furthermore, the Suzuki segregation does not show any periodicity along the c -axis as in the LPSO periodic structures.

4. Discussion

4.1. Proposed formation mechanism for special lamellar grain boundary

Grain boundaries with neighboring grains sharing the same $[11\bar{2}0]$ zone axis are widely observed in our deformed samples. We hypothesize that they were formed by multiple twinning. Note that the size of a virgin grain may be too large (see Fig. 1) to be fully captured by TEM, but local feature analysis could shed some light on this issue. Fig. 8a shows a local triple-junction area including TBI, TBII and the resulting LGB. The formation of such morphology from the virgin grain is schematically illustrated in Fig. 8b. First, assuming that there is an initial grain that has a $[11\bar{2}0]$ zone axis perpendicular to the page, then the horizontal

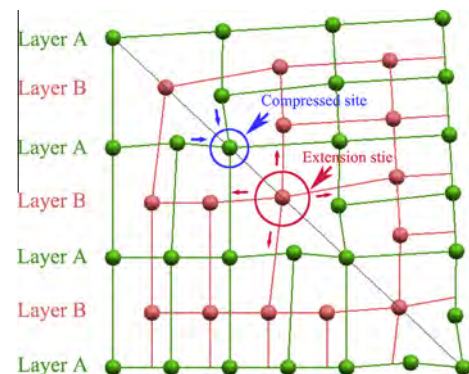


Fig. 9. Crystal structure of TBII in the direction of $(11\bar{2}0)$ α plane.

Table 2
Possible angle of LGBs induced by two and three twinning events.

The number of twins	Twinning type	Possible angle of LGB
2 – twinning	TBI + TBI	110°
	TBII + TBII	172°
	TBI + TBII	141° and 149°
3 – twinning	TBI + TBI + TBI	165°
	TBII + TBII + TBII	102°
	TBI + TBII + TBII	117° and 147°
	TBI + TBI + TBII	164° and 156°

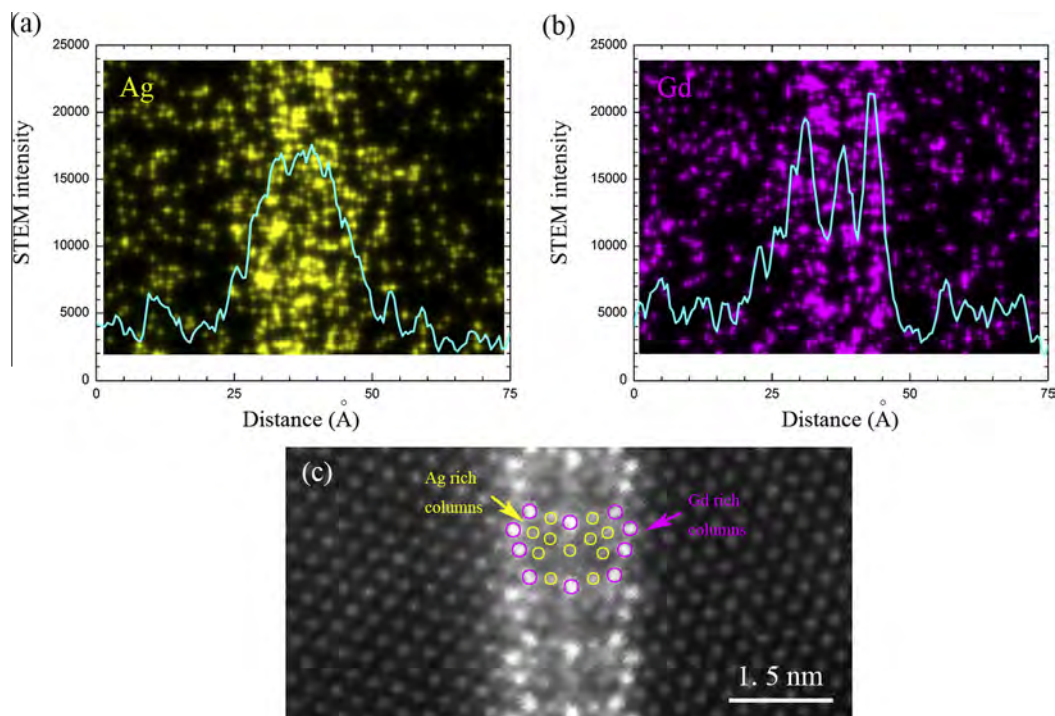


Fig. 10. Integration of the STEM intensity of (a) Ag and (b) Gd across a TBII, and (c) HAADF-STEM image of TBII of Mg-Gd-Y-Ag alloy with the incident beam parallel to the $[1\bar{1}20]$ zone axis. The yellow circles represent Al-enriched sites and the purple circles represent the Gd-enriched sites. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

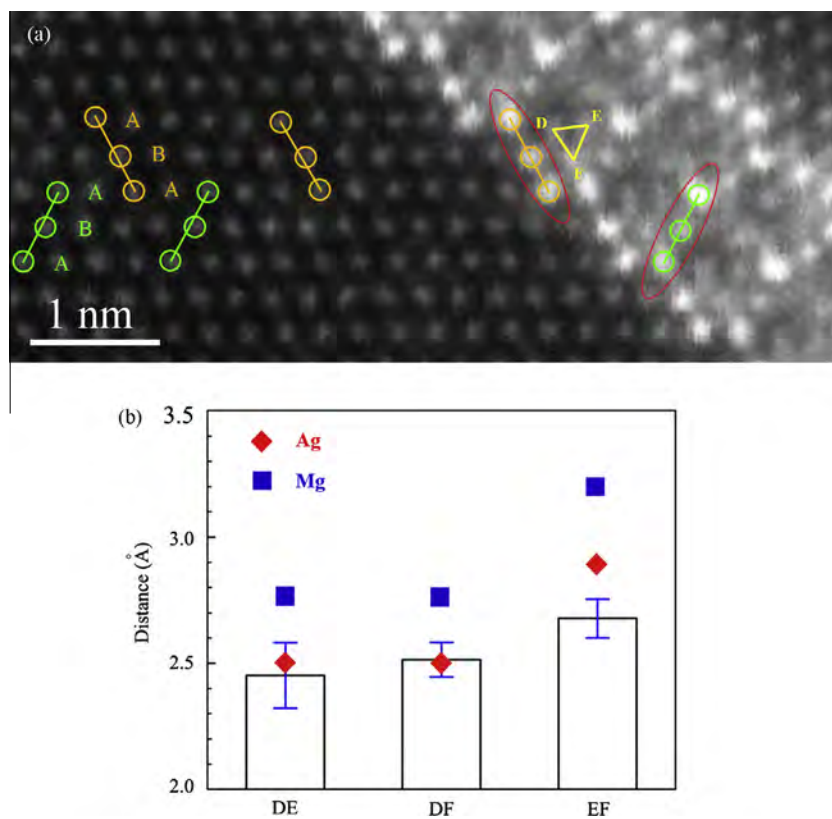


Fig. 11. (a) HAADF-STEM image of TBII of Mg-Gd-Y-Ag alloy with the incident beam parallel to the $[1\bar{1}20]$ zone axis, and (b) statistical distance of DE, DF and EF.

Table 3
Twin boundaries energy in Mg [41].

Twin boundary	$\Gamma(10\bar{1}1)$	$\Gamma(10\bar{1}2)$	$\Gamma(10\bar{1}3)$	$\Gamma(11\bar{2}1)$	$\Gamma(11\bar{2}2)$	$\Gamma(11\bar{2}3)$	$\Gamma(11\bar{2}3)$
Energy (mJ/m ²)	143	189	~189	148	145	~145	~145

blue lines in Fig. 8b represent the basal planes of the grain. When the alloy is subjected to rolling, a primary twin forms, which changes the orientation of the right part of TBI as shown in Fig. 8b. Further deformation leads to the formation of the secondary twin in the primary twin. Thus, the right part of the grain will be re-oriented again due to the secondary twinning. Now the red marked boundary becomes one of the special LGBs observed in this study, which has $[1\bar{1}20]$ zone axis for both sides with a misorientation angle of 149° . If the basal planes interact with other defects such as dislocations, the resulting misorientation angles could be slightly different from the predicted value, as observed in this study. As mentioned earlier, the misorientation angles may vary, depending on the type and number of multiple twinning modes. Table 2 lists all possible angles produced by two and three twinning events. Note that there may be other cases where grain boundary angle is formed by more than three consecutive twinning events.

4.2. Proposed mechanism of segregation at interfaces

As shown in Fig. 9, there are two types of lattice sites alternating along the TBII: the compression site and extension site. The space of compression site is smaller than a normal Mg atom would occupy, whereas the extension site is larger. Therefore, TBII is an interface with alternative tensile and compressive elastic strains. It has been reported that the size of solute atoms affects the segregations at twin boundaries [18]: solute atoms larger than Mg tend to segregate to the tension sites, while those smaller than Mg tend to segregate to the compression sites. In our case, if the same segregation trend is followed, the large Gd and Y (0.188 nm) atoms should segregate to tension sites, while the smaller Ag atoms should segregate to the compression sites.

A careful EDS analysis is carried out to investigate the segregation of the alloy elements. Fig. 10a and b shows the integration of the brightness contrast along a TBII. As shown in Fig. 10a, Ag atom distribution has only one peak within the width of ~ 1.5 nm, which is very close to the width of spinal-shaped segregation in TBII. In other words, Ag is almost uniformly distributed across TBII. However, the distribution of Gd has three apparent peaks across TBII (Fig. 10b), indicating three separate Gd atom concentration columns across the TBII. It should be noted that the intensity of the middle peak is slightly weaker than the two side peaks. Based on this information, the atomic structure of alloy segregation can be schematically illustrated in Fig. 10c. Combining with the fact that Gd has the highest atomic number of the three elements in the alloy (64 for Gd, 47 for Ag, and 12 for Mg), it is reasonable to assume that the brightest spots correspond to atomic sites of higher Gd concentrations, as indicated by purple circles in Fig. 10c. The atomic sites between them have median brightness and are probably Ag-enriched, as marked by yellow circles in Fig. 10c.

The Ag enrichment appears to affect the lattice structure of local area near TBII. As is shown in Fig. 11a, the area far away from twin boundary follows an ABAB ... hcp stacking sequence. However, three adjacent layers of atoms in the area near twin boundary appear to arrange in a straight line as marked by the red ellipse. This kind of atomic stacking is similar to that in fcc lattice with a packing sequence of ABCABC ... ABC. Statistics on the interatomic distances between three typical Ag-rich columns of D, E and F is shown in Fig. 11b, which was analyzed from 36 different atom

pairs along TBII. Their values are compared with that of pure Ag and Mg, as shown in Fig. 10b and c. It is obvious that they match better with pure Ag than pure Mg. This further indicates that the atomic packing in the spinal-shaped segregation is close to that of fcc Ag, possibly due to the high Ag content in this area.

The above observations indicate that segregation varies with interface types. Capolungo [42] reported first-principle calculations of the twin boundary energies for seven different types of twins in Mg (shown in Table 3). The stacking fault energy on the basal plane in Mg is $\Gamma^{\text{SF}} = 14$ mJ/m² (which is the upper value of theoretical prediction) [43,44]. It is generally accepted that grain boundary energy is usually higher than coherent twin boundary energy [45]. Therefore, the sequence of interfacial energies concerned in this paper is: $\Gamma^{\text{LGB}} > \Gamma^{\text{TBII}} > \Gamma^{\text{TBI}} > \Gamma^{\text{SF}}$. The periodic spinal-shaped segregation only occurs in TBII and LGBs with higher energies, which suggests that with Ag addition, spinal-shaped segregation only occurs in interfaces with high energies.

5. Conclusion

This study revealed interfacial segregation of solute atoms to interfaces including grain boundaries, twin boundaries, and stacking faults in Mg–Gd–Y–(Ag)–Zr alloys using atomic-resolution HAADF-STEM imaging and EDS mapping. Ag addition was found to significantly affect segregations at high-energy interfaces. The following are new understandings gained from this study:

1. Ag-assisted segregation at $\{10\bar{1}2\}$ twin boundaries (TBII) and lamellar grain boundaries (LGB) exhibits a new periodic spinal-shaped structure that is different from the single-lined segregation in the alloy without Ag. The segregation at $\{10\bar{1}1\}$ twin boundaries (TBI) shows the same periodic single-line segregation with or without Ag addition. The segregation at I1 stacking faults is random without any periodicity in both Mg–Gd–Y and Mg–Gd–Y–Ag alloys.
2. EDS mapping revealed significant segregation of Gd and Ag at both TBI and TBII in Mg–Gd–Y–Ag alloy. Ag atoms are uniformly distributed across TBII, while the Gd atoms have three distribution peaks. In the spinal-shaped segregation at TBII, the brightest spots are proposed as Gd-rich columns, and the median-brightness spots between them are Ag-rich columns. The addition of Ag induced many local quasi-fcc structures.
3. Interfacial energy affects the interfacial segregation. The sequence of interfacial energy in this paper is: $\Gamma^{\text{LGB}} > \Gamma^{\text{TBII}} > \Gamma^{\text{TBI}} > \Gamma^{\text{SF}}$. The periodic spinal-shaped segregation only occurs in TBII and LGBs with higher energies, and is absent at lower energy TBI and I1 stacking faults.
4. The lamellar grain boundaries with unique orientation were found in rolled Mg alloys, which was proposed formed by multiple twinning. Possible mis-orientation angles of LGB are 110° , 141° , 149° and 172° after secondary twinning, and are 102° , 117° , 147° , 156° , 164° and 165° after tertiary twinning.

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Heterogeneous lamella structure unites ultrafine-grain strength with coarse-grain ductility

Xiaolei Wu^{a,1}, Muxin Yang^a, Fuping Yuan^a, Guilin Wu^b, Yujie Wei^a, Xiaoxu Huang^b, and Yuntian Zhu^{c,d,1}

^aState Key Laboratory of Nonlinear Mechanics, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, China; ^bCollege of Materials Science and Engineering, Chongqing University, Chongqing 400044, China; ^cSchool of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, China; and ^dDepartment of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695

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Grain refinement can make conventional metals several times stronger, but this comes at dramatic loss of ductility. Here we report a heterogeneous lamella structure in Ti produced by asymmetric rolling and partial recrystallization that can produce an unprecedented property combination: as strong as ultrafine-grained metal and at the same time as ductile as conventional coarse-grained metal. It also has higher strain hardening than coarse-grained Ti, which was hitherto believed impossible. The heterogeneous lamella structure is characterized with soft micrograined lamellae embedded in hard ultrafine-grained lamella matrix. The unusual high strength is obtained with the assistance of high back stress developed from heterogeneous yielding, whereas the high ductility is attributed to back-stress hardening and dislocation hardening. The process discovered here is amenable to large-scale industrial production at low cost, and might be applicable to other metal systems.

back-stress hardening | heterogeneous lamella structure | ductility | strength | strain partitioning

Strong or ductile? For centuries engineers have been forced to choose one of them, not both as they would like to. This is because a material is either strong or ductile but rarely both at the same time. High strength is always desirable, especially under the current challenge of energy crisis and global warming, where stronger materials can help by making transportation vehicles lighter to improve their energy efficiency. However, good ductility is also required to prevent catastrophic failure during service.

Grain refinement has been extensively explored to strengthen metals. Ultrafine-grained (UFG) and nanostructured metals can be many times stronger than their conventional coarse-grained (CG) counterparts (1–5), but low ductility is a roadblock to their practical applications. The low ductility is primarily due to their low strain hardening (6–12), which is caused by their small grain sizes. To further exacerbate the problem, their high strengths require UFG metals to have even higher strain hardening than weaker CG metals to maintain the same ductility according to the Considère criterion. This makes it appear hopeless for UFG materials to have high ductility and it has been taken for granted that they are super strong but inevitably much less ductile than their CG counterparts.

Microstructure of Heterogeneous Lamella Structure

Here we report that a previously unidentified heterogeneous lamella (HL) structure possesses both the UFG strength and the CG ductility, which to our knowledge has never been realized before. The HL structure was produced by asymmetric rolling (13, 14) and subsequent partial recrystallization (see *Materials and Methods* for details). The asymmetric rolling elongated the initial equiaxed grains (Fig. 1A) into a lamella structure (Fig. 1B), which is heterogeneous with some areas having finer lamella spacing than others. This was due to the variation of slip systems and plastic strain in grains with different initial orientation (15). The asymmetric rolling also imparts a higher strain near the sample surface (14), which produces a nanostructured surface layer (Fig. 1C) as well as a slight structure gradient before and after

recrystallization. During the subsequent partial recrystallization, the lamellae with finer structure recrystallized to form soft microcrystalline lamellae while others underwent recovery to maintain the hard UFG structure (15) (Fig. 1D). Fig. 1E shows the distribution of recrystallized grains (RGs) with sizes larger than 1 μm after blacking out UFG areas. Interestingly, most RGs cluster into long lamellae along the rolling direction, which are distributed within black UFG lamellae. Fig. 1F is a transmission electron microscopy (TEM) image showing a lamella of RGs between two UFG lamellae. The RGs are equiaxed and almost dislocation-free. In contrast, the smaller UFG grains still contain a high density of dislocations. Fig. 1G shows that the volume fraction of RGs decreases through the depth but their sizes increase slightly. The weak gradients in microstructure before and after recrystallization are reflected in the microhardness (Hv) variation in Fig. 1H. Tensile samples with different thickness were prepared by polishing away equal-thickness layers from both sides of the recrystallized sample (Fig. 1H).

Mechanical Properties and Strain Hardening of HL Structure

Fig. 2A and B shows that HL Ti, e.g., both HL60 and HL80 from the central 60- μm and 80- μm -thick layer, respectively, is as strong as UFG Ti and as ductile as CG Ti. The squares in Fig. 2A mark the start of necking according to the Considère criterion. Both HL60 and HL80 are three times as strong as CG Ti while maintaining the same ductility (the uniform tensile elongation) (Fig. 2A). Furthermore, all other HL Ti samples are also much stronger and more ductile than CG Ti (Fig. 2B). In contrast, the UFG Ti becomes mechanically unstable soon after yielding.

The HL Ti samples derive their high ductility from their high strain-hardening rate ($\Theta = d\sigma/d\epsilon$), which becomes unprecedentedly higher than that of CG Ti after some plastic straining (Fig. 2C).

Significance

For centuries it has been a challenge to avoid strength–ductility trade-off, which is especially problematic for ultrastrong ultrafine-grained metals. Here we evade this trade-off dilemma by architecting a heterogeneous lamella structure, i.e., soft micrograined lamellae embedded in hard ultrafine-grained lamella matrix. The heterogeneous deformation of this previously unidentified structure produces significant back-stress hardening in addition to conventional dislocation hardening, rendering it higher strain hardening than coarse-grained metals. The high back-stress hardening makes the material as strong as ultrafine-grained metals and as ductile as coarse-grained metals.

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¹To whom correspondence may be addressed. Email: xlwu@imech.ac.cn or ytzh@ncsu.edu.

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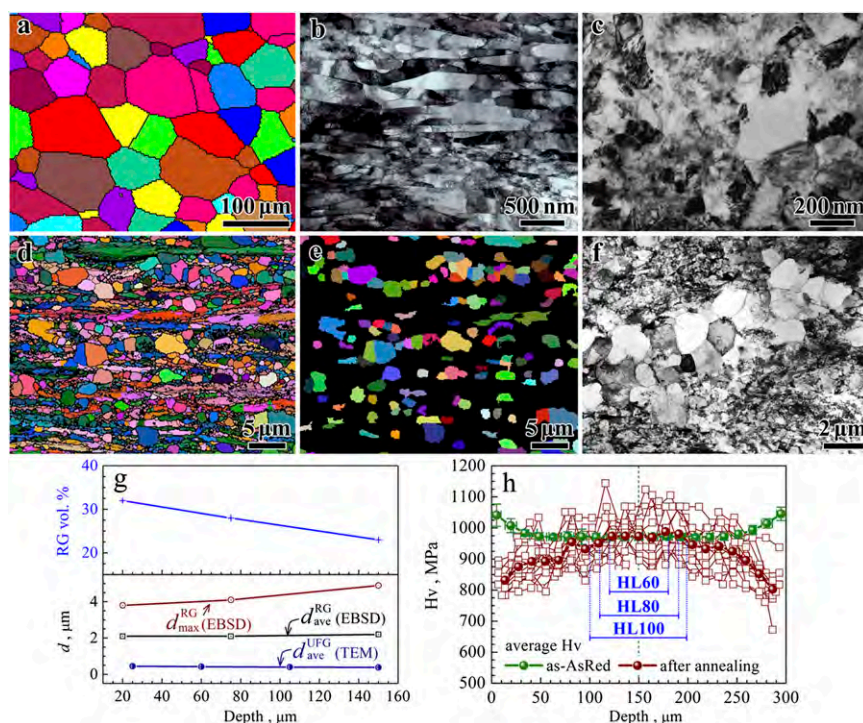


Fig. 1. Microstructure of HL Ti. (A) EBSD image of initial CG Ti. (B and C) TEM images showing nonuniform elongated lamellae in the central layer and nanograins in the top $\sim 25\text{-}\mu\text{m}$ surface layer after AsR. (D) EBSD image of HL Ti after partial recrystallization. (E) EBSD image of recrystallized grains (RGs) larger than $1\text{ }\mu\text{m}$. (F) Cross-sectional TEM image of RG lamellae with two UFG lamellae on two sides. (G) Weak gradient distribution of RG volume fraction, RG average grain size ($d_{\text{ave}}^{\text{RG}}$), maximum size ($d_{\text{max}}^{\text{RG}}$), and mean grain size of UFG lamellae ($d_{\text{ave}}^{\text{UFG}}$) through the depth measured by EBSD and TEM. (H) Hv gradient in the as-rolled state and after partial recrystallization, together with the location of the tensile samples (e.g., HL60 means $60\text{ }\mu\text{m}$ in thickness). The large scattering in Hv data after partial recrystallization reflects the heterogeneous nature of HL Ti.

More remarkably, the HL60 sample has much higher strain hardening than the CG sample for the entire plastic deformation. Thicker HL Ti samples have a distinctive two-stage strain-hardening behavior, with initial low Θ , but higher Θ at larger plastic strains. Specifically, in stage I, Θ shows a steep drop at first followed by a steep upturn, typical of discontinuous yielding. This is due to the shortage of mobile dislocations at the onset of plastic deformation (8, 16), which makes it necessary for dislocations to glide faster to accommodate the applied constant strain rate. Higher stress is needed to move dislocations faster. Upon yielding, dislocations quickly multiply, leading to quick Θ increase due to dislocation interaction and entanglement. In stage II, Θ continues to rise, albeit at a relatively slow rate. This is surprising and, to our knowledge, has never been observed in either UFG or conventional CG metals, both of which have a typical monotonic drop in Θ .

Surprisingly, the weak Hv gradient disappeared after tensile testing (Fig. 2D), in contrast with what was observed in gradient structured steel (11). This indicates that the RGs were dramatically hardened by plastic deformation and the weak gradient in microstructure did not play a major role in mechanical properties. Note that Hv values are still scattered after tension, indicating that the heterogeneous mechanical properties remained after the tensile testing.

Bauschinger Effect and Back Stresses

The observed extraordinarily high strength of HL Ti can be attributed to its composite lamella nature. Under tensile loading, the soft lamellae of recrystallized micrograins will start plastic deformation first. However, they are constrained by surrounding hard lamellae so that dislocations in such grains are piled up and blocked at lamella interfaces, which are actually also grain boundaries.

This produces a long-range back stress (17–19) to make it difficult for dislocations to slip in the micrograined lamellae until the surrounding UFG lamellae start to yield at a larger global strain. In other words, the internal back stress has significantly increased the flow stress of the soft lamellae by the time the whole sample is yielding. This is the primary reason for the observed high yield strength of HL Ti samples, as verified later by the back-stress calculation. This observation is consistent with the high strength caused by back stresses in passivated thin films (20–22) and nanopillars (23, 24).

To probe the origin of the high strain hardening of HL Ti and the contribution of back stress to the observed high yield strength, we conducted loading–unloading–reloading (LUR) testing (Fig. 3A) to investigate the Bauschinger effect, from which we can estimate the contributions of the back stress and dislocation hardening to the flow stress. Interestingly, HL Ti shows a very strong Bauschinger effect: during unloading, the reverse plastic flow (σ_{rev}) starts even when the applied stress is still in tension (Fig. 3B). A larger hysteresis loop during the unloading–reloading represents a stronger Bauschinger effect. As shown in Fig. 3B, the hysteresis loop becomes larger with increasing tensile strain for the HL Ti. Importantly, the hysteresis appeared even during the first unloading–reloading cycle near the yield point. In contrast, the CG Ti has negligible hysteresis (Fig. 3B). As schematically shown in Fig. 3C, the Bauschinger effect can be described by the reverse plastic strain (ϵ_{rp}) normalized by the yield strain (ϵ_y) (21, 24), which increases with increasing plastic strain (Fig. 3D). The back stress can be calculated as $\sigma_b = \sigma_f - \sigma_{\text{eff}}$ and $\sigma_{\text{eff}} = ((\sigma_f - \sigma_{\text{rev}})/2) + (\sigma^*/2)$ (25), where σ_f denotes the flow stress, and σ_{eff} , σ_{rev} , and σ^* are defined in Fig. 3C.

As shown in Fig. 3D, the back stress is about 400 MPa near the yield point. The soft lamellae in HL Ti need to overcome this

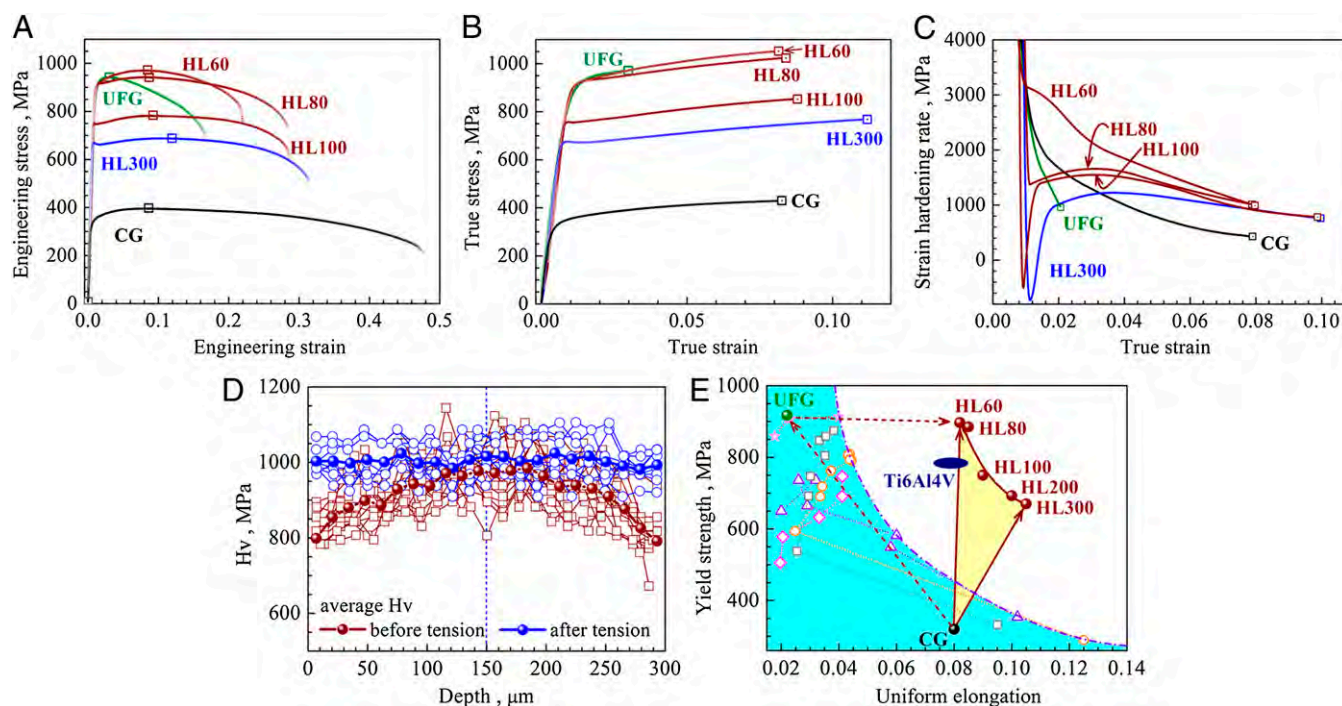


Fig. 2. Mechanical properties and strain hardening of HL Ti. (A) Tensile engineering stress–strain curves in HL Ti at a quasi-static strain rate of $5 \times 10^{-4} \text{ s}^{-1}$ in comparison with UFG Ti and CG Ti. UFG sample: 300 μm thick as processed by AsR. HL Ti: annealed UFG at 475 $^{\circ}\text{C}$ for 5 min. The number after HL indicates the sample thickness (μm). The tensile samples were flat and dog-bone-shaped, with gauge dimension of 10 mm $\times$ 2.5 mm. (B) Tensile true stress–strain curves in HL Ti. (C) Strain hardening rate ($\Theta = d\sigma/d\varepsilon$) versus true strain of HL Ti. (D) Hv change before and after tensile testing at tensile strain of 10% in HL300. Solid points indicate the mean Hv values, whereas open indicate the experimentally measured values obtained by 10 time tests. Note the disappearance of a weak Hv gradient across the thickness after tensile testing. (E) Yield strength and uniform tensile elongation of HL Ti. Other data of Ti as well as Ti6Al4V are also shown for comparison.

additional high back stress to deform plastically, which contributes significantly to the observed high yield strength of the HL samples, especially the HL60 and HL80 samples. In other words, the observed high yield strength of HL samples resulted from the high back stress.

The back stress increased with plastic strain, especially at the early strain stage, which contributed to the high strain hardening. This is the primary reason why the strain hardening in HL Ti increased with applied global strain and surpassed that of CG-Ti, as shown in Fig. 2C. The homogeneous CG Ti does not show measurable Bauschinger effect or back stress, and its strain hardening decreased monotonically with the global strain. The effective stress, which includes the dislocation hardening and Peierls stress, is much lower than the back stress, which is consistent with an earlier report in constrained nanopillars (23). The increase in the effective stress with tensile strain should be primarily caused by dislocation density, i.e., dislocation hardening. Therefore, the high strain hardening originates from both back stress hardening and dislocation hardening. To the authors' best knowledge, the significant back-stress hardening has never been reported before.

The back-stress hardening is caused by the pile-up and accumulation of geometrically necessary dislocations. With increasing tensile strain, dislocation sources in the softer microcrystalline lamellae are activated first. However, the soft lamellae are surrounded and constrained by hard UFG lamellae, which are still deforming elastically. Therefore, dislocations in the soft lamellae cannot transmit into hard UFG lamellae. As shown in Fig. 4A, which is a TEM micrograph from an HL Ti sample tested at a tensile strain of 2%, dislocations piled up at several locations. All dislocations in an individual pile-up are from the same dislocation source and have the same Burgers vector. They consequently

produce a long-range back stress to stop the dislocation source from emitting more dislocations. That is, soft lamellae constrained by hard lamella matrix appear much stronger than when they are not constrained. This explains why the HL60 and HL80 samples can be as strong as the UFG Ti, although they contain

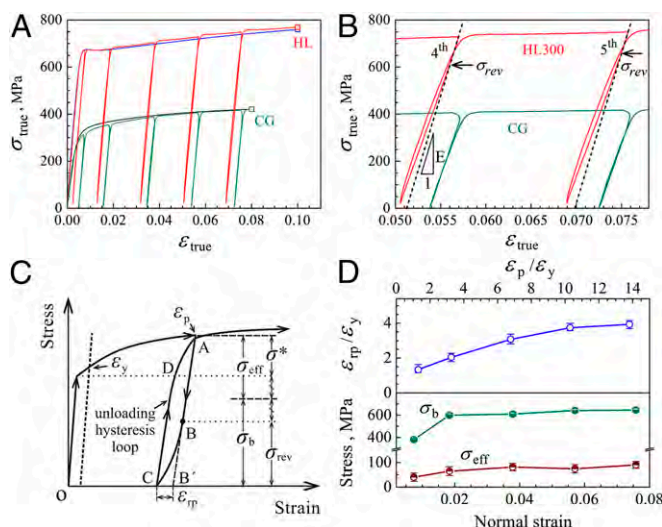


Fig. 3. Bauschinger effect and back stress of HL Ti. (A) LUR stress–strain curves of HL Ti and CG Ti. (B) Hysteresis loops. The two arrows indicate the reverse flow stress, i.e., σ_{rev} , deviating from the initial elastic behavior during unloading. (C) Schematic of calculating back stress (25). (D) Normalized reverse plastic strain, back stress, and effective stress versus applied strain.

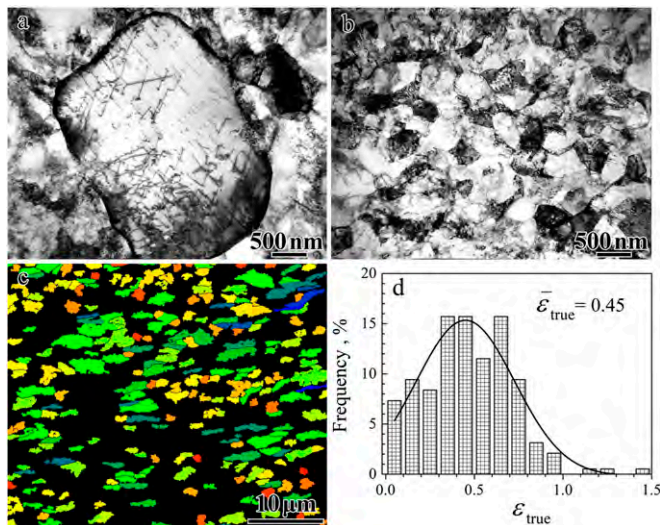


Fig. 4. Strain partitioning in HL Ti. (A) TEM image showing pile-up of dislocations in a recrystallized micrometer-sized grain at tensile strain of 2%. (B) TEM image showing equiaxed UFG in a sample tested to a tensile true strain of 9.4%. (C) EBSD image showing elongated RG along tensile direction at true strain of 9.5%. (D) Distribution of strains in RG with an average true strain of 0.45.

over 20% softer microcrystalline lamellae. It appears that the full constraint of the soft lamellae by the hard matrix is a prerequisite for this phenomenon.

Strain Partitioning

Beyond the yield point, the whole HL Ti sample is deformed plastically. However, the softer lamellae are easier to deform than hard lamellae. This causes plastic strain partitioning where the soft lamellae carry much higher plastic strain than hard lamellae. Indeed, after tensile testing for 9% true strain, the UFG in hard lamellae remain largely equiaxed (Fig. 4B), whereas most of the recrystallized micrometer-sized grains were deformed from equiaxed shape to elongated shape along the tensile direction (Fig. 4C). The true strain in each grain can be calculated from its aspect ratio α as $\epsilon = (2/3)\ln \alpha$ (see the [Supporting Information](#)). After the HL Ti was deformed for a global true strain of 9.4%, the average true strain in recrystallized micrometer-sized grains was 45% (Fig. 4D). It should be noted that the real strain in the UFG lamella cannot be estimated using the grain geometry change because other deformation mechanisms such as coordinated deformation, grain boundary sliding, and grain rotation may also contribute to plastic strain when the grain sizes are very small (26). Nevertheless, the plastic strain in the hard UFG lamellae should be less than 9.4% because the soft lamellae carry much higher plastic strain of 45%. The strain has to be continuous at the interlamella interfaces, which further leads to strain gradient near these interfaces. Geometrically necessary dislocations (GNDs) will be generated to accommodate the strain gradient (27–29), which will generate long-range back stress near the interfaces. In other words, back-stress hardening in the HL Ti during plastic deformation is associated with strain partitioning, i.e., inhomogeneous plastic strain.

In addition to back stress, dislocation hardening, which is related to the increase in total dislocation density (29), should also contribute to the observed high strain hardening. The HL structure promotes the generation and accumulation of two types of the dislocations during the testing. One is the aforementioned GNDs, and the other is incidental type of dislocations that do not produce long-range back stress. It should be noted that local complex 3D stress states may develop from the applied uniaxial stresses due to

the plastic incompatibility between the soft and hard lamellae. The stress state change will promote dislocation accumulation and interaction by activating more slip systems (11, 30, 31), similar to what occurs in gradient structures (11, 31). This will effectively increase the incidental dislocation density.

The HL structure can be considered as a special case of bimodal structure, but is much more effective in producing strain hardening than the reported conventional bimodal structure (6). Compared with the conventional bimodal structure, the HL structure possesses the following unique features that are essential for producing the observed extraordinary mechanical behavior: (i) the lamellar nature of the structure, (ii) the full constraint of the soft lamellae by harder matrix, and (iii) the high density of interlamella interfaces. First, it has been reported that the elongated inclusions produce higher strain hardening than spherical ones, especially when its long axis is aligned in the loading direction (32), which is the case in this study. The lamella geometry makes mutual constraint between the soft and hard lamellae more effective, which produces higher back stresses. Second, the full constraint of the soft lamellae by the hard lamella matrix makes it more effective to constrain the plastic deformation of the soft lamellae to develop higher back stresses than the conventional bimodal structure. Third, the HL structure has the high density of interlamella interfaces, where dislocation can pile up and accumulate to enhance back-stress hardening and dislocation hardening.

This work opens a new frontier toward high tensile ductility without sacrificing the high strength of UFG metals. Back stresses are primarily responsible for the observed high strength. Both back-stress hardening and dislocation hardening are responsible for the observed extraordinary strain-hardening rate and consequent high ductility. The lamella geometry, high constraint of the soft lamellae by hard matrix, and the high density of interfaces make it effective for developing back stress and dislocation hardening. The observations here provide a new principle for designing metals with mechanical properties that have not been reachable before. Importantly, the lamella structure is fabricated by asymmetric rolling followed by annealing, which is an industrial process that can be easily scaled up for large-scale production at low cost. The process discovered here might be applicable to other engineering metals and alloys, and needs further study.

Materials and Methods

Materials. Commercial pure titanium sheets 2.4 mm thick were used in the present study. The composition was (wt %) 0.10 C, 0.05 N, 0.015 H, 0.25 O, 0.30 Fe, bal. Ti. The sheets were vacuum-annealed at 700 °C for 2 h to achieve a fully homogeneous CG microstructure with a mean grain size of 43 μm .

HL-Structured Ti by Asymmetrical Rolling. Ti sheets 2.4 mm thick were processed by asymmetrical rolling (AsR) at room temperature. Rolling was conducted on a rolling mill with 45-mm-diameter rolls. The top and bottom rolls were driven at velocities of 1 m/s and 1.3 m/s, respectively, and a rolling reduction was 0.1 mm per pass. The Ti sheet was flipped over, and feeding direction was alternated from one end to the other between AsR passes. The sheets were finally rolled to 300 μm thick after 20 rolling passes with a total rolling reduction of 87.5%. No cracks were observed on the surface of the AsR-processed Ti sheets. The subsequent partial recrystallization was conducted in AsR-processed HL Ti sheets 300 μm thick at 475 °C for 5 min.

Tensile Test and LUR Test. All tensile specimens were dog-bone-shaped, with a gauge length of 10 mm and a width of 2.5 mm. To obtain reproducible tensile property, all tensile tests were repeated at least 3–5 times. The direction of tensile specimens was parallel to the rolling direction. Tensile samples, containing the central layer of various thicknesses, e.g., HL100, HL80, and HL60, etc. (number indicates the sample thickness, μm), was further obtained by taking off the equal thickness from two sides simultaneously in 300- μm -thick annealed HL samples.

Quasi-static uniaxial tensile tests were carried out using an Instron 5582 testing machine at strain rate of $5 \times 10^{-4} \text{ s}^{-1}$ at room temperature. An extensometer was used to measure the strain during the tensile deformation. LUR tensile tests were conducted using an Instron 5966 testing machine at

room temperature. Five loading–unloading cycles were conducted during each tensile test. Upon straining to a designated strain (e.g., 2%) at strain rate of $5 \times 10^{-4} \text{ s}^{-1}$, the specimen was unloaded by the stress-control mode to 20 N at the unloading rate of $200 \text{ N} \cdot \text{min}^{-1}$, followed by reloading at a strain rate of $5 \times 10^{-4} \text{ s}^{-1}$ to the same applied stress before the next unloading.

Electron Back-Scattered Diffraction and TEM Observations. The cross-sectional and longitudinal electron back-scattered diffraction (EBSD) and TEM observations were conducted to investigate the microstructural evolution in HL Ti before

and after tensile tests. TEM samples were cut from the gauge sections of tensile samples.

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Fundamentals of Superior Properties in Bulk NanoSPD Materials

R.Z. Valiev^{a,b*}, Y. Estrin^{c,d}, Z. Horita^{e,f}, T.G. Langdon^{g,h}, M.J. Zehetbauerⁱ and Y.T. Zhu^{j,k}

^a*Institute of Physics of Advanced Materials, Ufa State Aviation Technical University, Ufa 450000, Russia;*
^b*Laboratory for Mechanics of Bulk Nanomaterials, Saint Petersburg State University, Saint Petersburg 198504, Russia;* ^c*Centre for Advanced Hybrid Materials, Department of Materials Engineering, Monash University, Clayton, VIC 3800, Australia;* ^d*Laboratory of Hybrid Nanostructured Materials, Moscow Institute of Steel and Alloys, Moscow 119049, Russia;* ^e*Department of Materials Science and Engineering, Faculty of Engineering, Kyushu University, Fukuoka 819-0395, Japan;* ^f*WPI, International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, Fukuoka 819-0395, Japan;* ^g*Departments of Aerospace & Mechanical Engineering and Materials Science, University of Southern California, Los Angeles, CA 90089-1453, USA;*
^h*Materials Research Group, Faculty of Engineering and the Environment, University of Southampton, Southampton SO17 1BJ, UK;* ⁱ*Research Group Physics of Nanostructured Materials; Faculty of Physics, University of Vienna, Wien A-1090, Austria;* ^j*School of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, People's Republic of China;* ^k*Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695, USA*

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Bulk nanoSPD materials are materials with nanostructural features, such as nanograins, nanoclusters, or nanotwins, produced by severe plastic deformation (SPD) techniques. Such nanostructured materials are fully dense and contamination free and in many cases they have superior mechanical and functional properties. Here, we provide a critical overview of such materials, with a focus on the fundamentals for the observed extraordinary properties. We discuss the unique nanostructures that lead to the superior properties, the underlying deformation mechanisms, the critical issues that remain to be investigated, future research directions, and the application potential of such materials.

Keywords: Severe Plastic Deformation, Ultrafine-grained Materials, Nanostructures, Properties

1. Introduction In recent years there has been growing interest in bulk nanostructured materials produced by severe plastic deformation (SPD) processing, as demonstrated by the increasing number of publications with high citations [1] as well as numerous specialized conferences, workshops and symposia on the subject (www.nanosspd.org).

The critical feature of SPD, in which heavy straining is applied under high pressure with accumulated strains ε in excess of ~ 4 – 6 , makes it possible to produce ultrafine grains (UFG) with sizes smaller than 1,000 nm.[2–5] Processing by SPD may also lead to a dissolution of second phases, precipitation, amorphization, and other processes producing various nanostructural features such as deformation twins, non-equilibrium grain boundaries, dislocation substructures, solute segregation,[6]

and clusters. These changes in the inner make-up of the material may affect the deformation mechanisms and, consequently, change the material properties in a fundamental way. As a result, new structural and functional metals and alloys having superior and unique properties have been developed by SPD processing.[4,7–10]

Over the last decade there has been extensive research into the mechanical and functional properties of bulk nanostructured materials as well as their origin and relationship to fundamental physics. This report gives a critical overview of this research with special attention directed to the extraordinary properties that are enabled by SPD. Our views on the prospects for future developments in the area of nanoSPD materials are also outlined.

*Corresponding author. Email: rzvaliev@mail.rb.ru

2. Grain Boundaries and Other Crystal Lattice Defects Generated by SPD Grain boundaries in nanostructured materials affect their properties in very significant ways and quite often the UFG metals are referred to as ‘interface-controlled materials’. Different types of grain boundaries are formed by SPD processing and they may be classified as [2,7]

- Low- vs. high-angle boundaries;
- Special vs. random boundaries;
- Equilibrium vs. non-equilibrium boundaries with strain-distorted structures.

In addition, SPD may also produce other structural features in alloys, such as second-phase particles, nanotwins, and solid segregations at the grain boundaries. Such modifications of the make-up of the material at the nano scale can have a strong effect on the material properties. The use of advanced imaging and structural characterization techniques over the past decade has brought about the discovery of three significant nanostructural features of SPD-processed alloys,[8,10–16] which give rise to their remarkable mechanical and functional properties. These are outlined below.

2.1. Nanotwins. A high density of nanotwins produced by SPD was found to increase both the strength and ductility of nanostructured metals and alloys. Figure 1 shows a transmission electron microscopy (TEM) image of UFG Cu after equal-channel angular pressing (ECAP) and cryorolling at the liquid nitrogen temperature; twins 10–20 nm in width are clearly visible.[12] To promote the formation of nanotwins, the following intrinsic material properties and external deformation conditions are required [11]: (1) a relatively

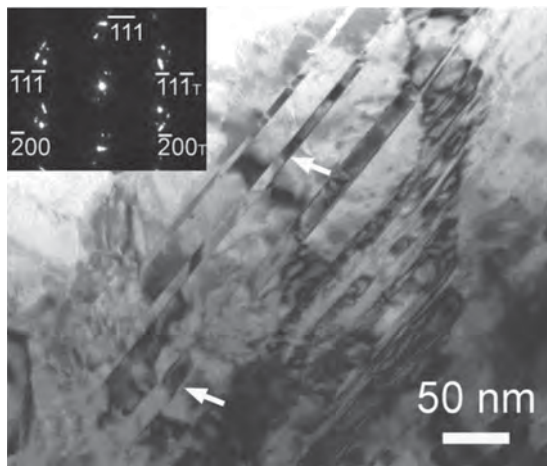


Figure 1. Typical bright-field TEM images of a grain with high density of deformation nanotwins in UFG Cu that was subjected to ECAP and subsequent cryogenic rolling.[12]

low stacking fault energy, (2) a low deformation temperature, and (3) a high strain rate. It should be noted that there is an optimum grain size range conducive for deformation twinning.[11,17–19] This optimum grain size for the formation of deformation twins is affected by both intrinsic properties of the material mentioned above, and it can be estimated using the following equation [11]:

$$\frac{d_m}{\ln(\sqrt{2}d_m/a)} = \frac{9.69 - \nu}{253.66(1 - \nu)} \frac{Ga^2}{\gamma}, \quad (1)$$

where γ is the stacking fault energy, a is the lattice parameter, ν is Poisson’s ratio, G is the shear modulus, and d_m is the optimum grain size.

2.2. Clusters and Segregations. It was found by 3D atom probe tomography that SPD may hinder the formation of precipitates in age-hardenable alloys and instead promote clustering and segregation of alloying elements.[7,15,20–22] For example, the data in Figure 2 [23] show that segregations at grain boundaries make-up clusters ~ 3 –5 nm wide in the age-hardenable Al alloy 7075. Moreover, the concentration of alloying elements may be an order of magnitude higher at grain boundaries than in the grain interior.[8,20,22,23]

2.3. Nanosized Particles and Secondary Phase Precipitations. In many alloys subjected to SPD after solid-solution hardening, high densities of nanosized particles appear.[8,10,24] Figure 3 shows an example of nanoparticles that are ~ 10 –20 nm in size in the UFG Al alloy 6061 after ECAP.[24] The presence of

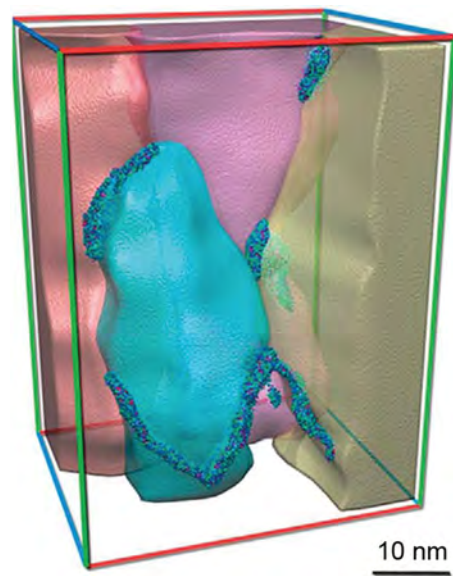


Figure 2. Tomographic image of nanostructure of UFG Al alloy 7075. Segregations of alloying elements on grain boundaries and at triple junctions are shown.[22]

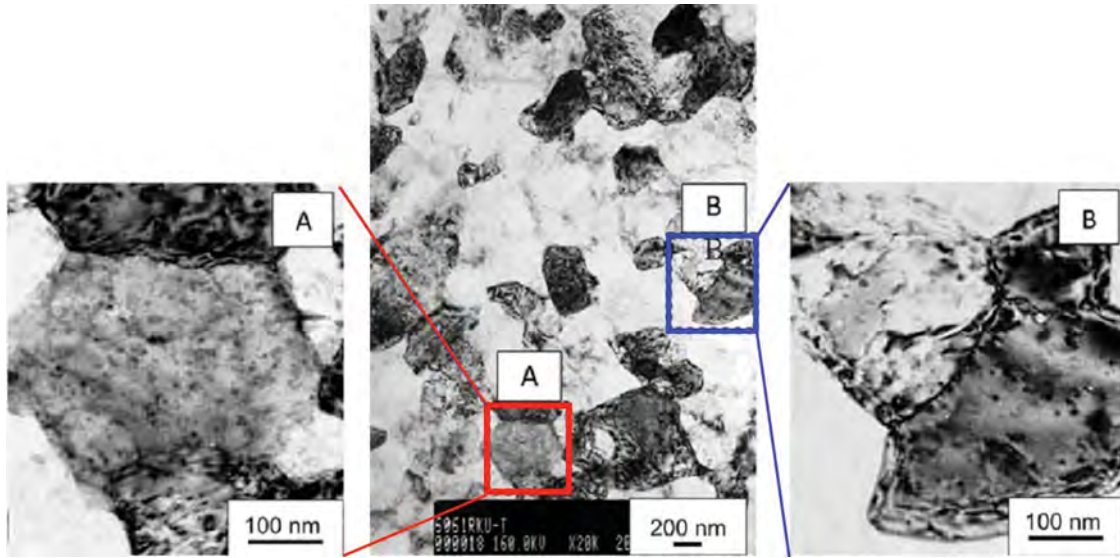


Figure 3. UFG structure of Al alloy 6061 after ECAP in parallel channels (four passes): nanosized precipitations in grains are clearly visible in areas A and B at higher magnification.[24]

these nanoparticles is due to dynamic aging and the high density of nucleation sites generated by entangled dislocations. The small size and high density of such particles effectively block and accumulate dislocations not only causing higher strength but also promoting ductility.[13,23–25]

Thus, UFG metals and alloys produced by SPD methods are characterized by a number of nanostructural features which can strongly influence their behavior. In many demonstrated cases, the properties induced by SPD processing are unique to these materials, as will be shown in the following sections.

3. Mechanical Properties of Bulk Nanostructured Materials Three major properties, namely strength, fatigue behavior and superplasticity, are considered in this section.

3.1. Superior Strength and Ductility. A primary advantage of SPD processing is strength enhancement. Even though the well-known Hall–Petch relation between the yield stress σ_y and the grain size d ,

$$\sigma_y = \sigma_0 + K_{HP}d^{-1/2}, \quad (2)$$

may break down for nanomaterials, it commonly holds for UFG materials produced by SPD. Here, σ_0 and K_{HP} are constants for a given material. Typically, extreme grain refinement by SPD can improve the strength of pure metals or dilute alloys by a factor of 3–8.[26–30] For SPD-processed alloys, grain refinement is often accompanied by phase transformations leading to the formation of nanoclusters, segregations, nanotwins, and

dislocation substructures, which provide additional hardening mechanisms. In particular, the formation of grain boundary segregations in the UFG alloys by SPD may suppress the generation of dislocations at grain boundaries and lead to considerable additional hardening.[23] For example, Figure 4 shows the tensile stress–strain curves of the Al alloys 1570 and 7475. It is seen that the alloys which acquired their UFG structure by high-pressure torsion (HPT) are more than twice as strong as those subjected to conventional hardening.

It was shown [23] that for bulk nanostructured alloys with a grain size of 100–130 nm, the magnitude of σ_y is considerably higher than the value calculated from the Hall–Petch relationship. This phenomenon of super-strength of nanostructured alloys was recently demonstrated in various SPD-processed materials, including Al alloys,[24,31] Ti alloys,[8] carbon steels and stainless steels,[32–34] and in an Al–Mg nanocomposite.[35] However, increasing strength of metals and alloys through grain refinement by SPD usually leads to an undesirable drop in their ductility.[8,10,36,37]

The low ductility is caused by the reduction of the strain-hardening capability of a severely deformed material. This can be rationalized in terms of the Considère criterion which states that failure by necking under tensile loading will not occur if the following inequality is fulfilled:

$$\left(\frac{d\sigma^T}{d\varepsilon^T} \right)_{\dot{\varepsilon}} \geq \sigma^T, \quad (3)$$

where σ^T and ε^T denote the true stress and true strain, respectively. On the other hand, grain refinement enhances the strain rate sensitivity (SRS) of the flow stress and this helps preventing necking.[38] Therefore,

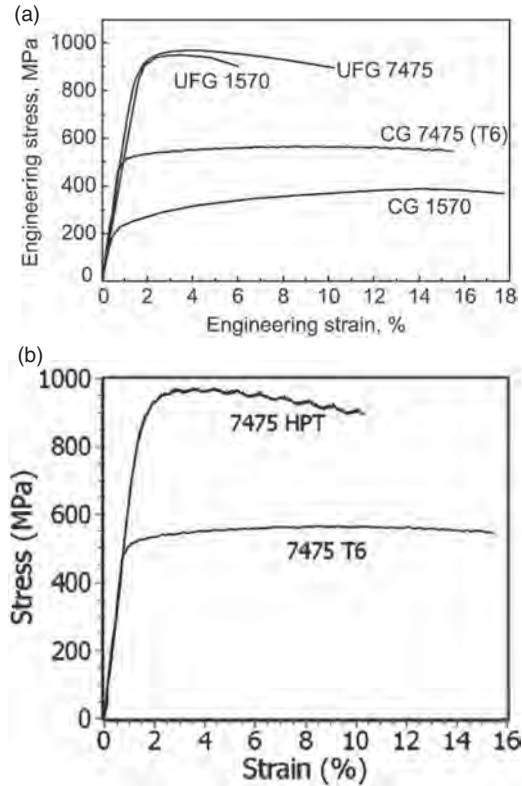


Figure 4. Engineering stress–strain curves of the UFG alloys Al 1570 (a) and Al 7475 (b) processed by HPT in comparison with standard treatment.[23]

these two factors compete with each other in affecting the tensile ductility.[39] The effect of the SRS increase is usually weaker than the effect of the strain-hardening reduction, which explains the low ductility of UFG materials except at relatively high homologous temperatures. Indeed, high ductility was reported in nanostructured zinc [40,41] which has a low melting point of 692.68 K.

There have been some exceptions where UFG and nanostructured metals exhibited both high strength and high ductility.[42–47] The primary reason for the low ductility of nanostructured and UFG metals and alloys is their low strain-hardening rate. In recent years, great efforts were made to design microstructures and deformation mechanisms that will increase the strain-hardening rate, some of which lead to an increase in both strength and ductility.[5,25] Reported successful strategies include inducing effects that promote the occurrence of a high density of twin boundaries,[12,48,49] lowering the stacking fault energy to activate deformation twinning,[12,14,50] introducing a high density of second-phase nanoparticles,[13,51] or through grain boundary engineering.[52,53] More recently, an alternative strategy that relies on gradient structures was shown to be very effective in improving ductility.[54–57]

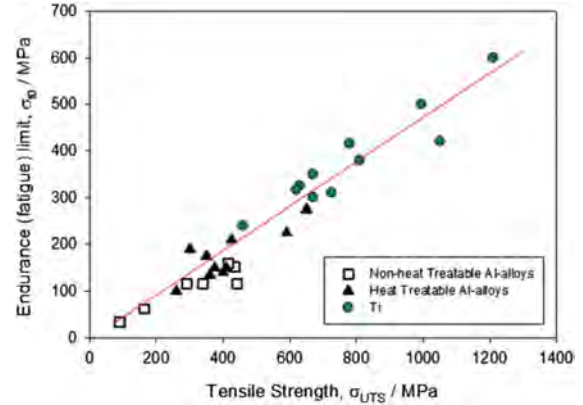


Figure 5. Empirical correlation between the fatigue limit and the UTS for UFG Ti and Al alloys.[59]

3.2. Fatigue Behavior. Fatigue resistance is important for many applications of UFG materials and there has been extensive research in this area. Recent literature surveys on fatigue properties of SPD-processed materials can be found elsewhere.[9,58,59] Empirically, the fatigue limit of coarse-grained materials is proportional to the ultimate tensile strength (UTS) (Figure 5) [59] which may be used to estimate the fatigue limit. However, the fatigue behavior of SPD-processed metals in general is determined by both strength and ductility. Specifically, high-cycle fatigue (HCF) is controlled by the resistance of the material to crack initiation, while low cycle fatigue (LCF) is governed by crack propagation. The life under LCF is largely controlled by ductility while that under HCF is dictated by the fracture strength. Consequently, when SPD processing raises the tensile strength at the cost of ductility, the HCF life is improved while the LCF life is decreased. Again, there are fortunate exceptions to this disadvantageous juncture. It was found [60,61] that ECAP of dilute Cu–Cr–Zr alloys followed by an aging treatment leads to a remarkable improvement of tensile strength and fatigue strength in the HCF regime without sacrificing ductility and LCF properties. Similarly, extrusion + ECAP processing of the ZK60 Mg alloy was shown to lead to an excellent combination of strength and ductility [62] and also brought an impressive improvement of fatigue properties over the entire range of stress amplitudes tested (see Figure 6).[63]

SPD processing also produces good fatigue performance in other metals and alloys. For example, it was reported [64] that an ECAP-processed stainless steel had a record-high fatigue limit due to profuse deformation twinning induced by severe straining. Another example is SPD-processed commercial purity titanium that showed record values of fatigue strength (which were close to or in excess of those for the conventional alloy Ti-6Al-4V).[65–67] These results make it promising to replace this potentially toxic alloy with pure Ti in biomedical applications (see Section 4.8).

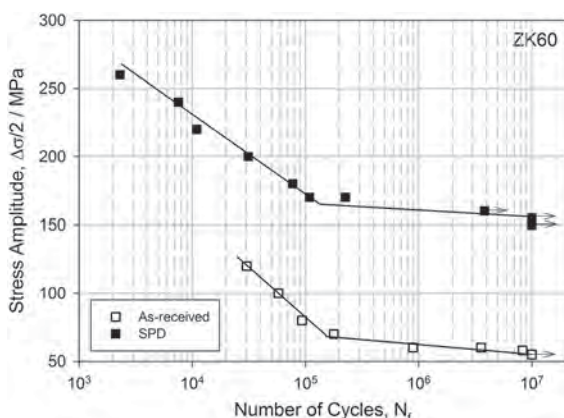


Figure 6. Wöhler plot for Mg alloy ZK60 in the as-received condition (open symbols) and after processing by integrated direct extrusion and ECAP.[63]

3.3. Superplasticity. Superplasticity refers to the ability of a polycrystalline specimen to pull out to a very high strain, defined typically as an elongation of at least 400%, [68] when tested in tension. The development of a superplastic capability in polycrystalline materials is significant because of the increasing importance of the superplastic-forming industry in the manufacture of complex parts having curved surfaces. [69] Superplasticity requires a small grain size, typically below $\sim 10 \mu\text{m}$, and it is now recognized that the dominant flow process is grain boundary sliding in which the strain rate varies inversely with the grain size raised to a power of 2. [70] This means in practice that the extremely small grain sizes produced by SPD processing provide a possibility for achieving superplastic flow at exceptionally rapid strain rates. This was first demonstrated in early experiments on two commercial aluminum-based alloys where elongations of up to 1,000% were attained at strain rates of 10^{-2} s^{-1} . [71] This result suggests that an SPD material should exhibit a rapid superplastic-forming capability directly after processing and this was demonstrated by using a biaxial gas-pressure-forming facility and blowing a dome in an SPD-processed Al–Mg–Sc alloy in the short period of only 60 s. [72] Experiments also confirmed that the superplastic properties were retained when the material was processed by ECAP and then rolled into a sheet. [73]

Although it is relatively easy to achieve exceptional grain refinement in face-centered cubic metals, the situation becomes more difficult in hexagonal close-packed metals such as magnesium because of the limited number of available slip systems. To overcome these difficulties, a two-step processing route was developed in which some initial grain refinement is introduced through extrusion prior to processing by ECAP. [74] The effect of this procedure is illustrated in Figure 7 where results are shown for a Mg–8% Li alloy tested in tension over a range of strain rates at 473 K in a cast condition,

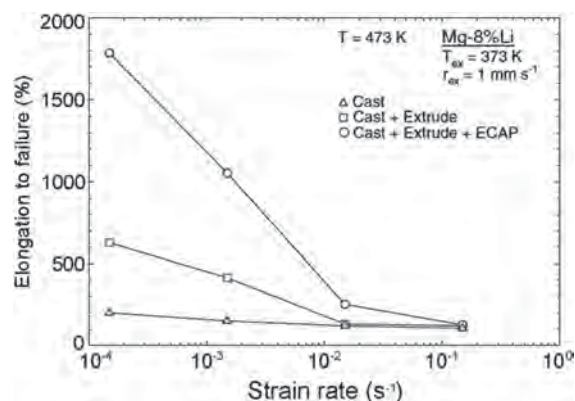


Figure 7. Elongation vs. strain rate at 473 K for a Mg–8% Li alloy in the cast condition, after casting and extrusion, and after casting and extrusion followed by ECAP. [75]

after casting and extrusion and after casting and extrusion followed by processing by ECAP. [75] The changes introduced by these different processing routes are dramatic because the alloy is not superplastic in the cast condition, it is only marginally superplastic after casting and extrusion, but in the cast + extrusion + ECAP condition it is possible to achieve high elongations of up to 1,800%. Using this two-step processing route, it is feasible to achieve excellent superplastic elongations in magnesium alloys and an example is shown in Figure 8 where a ZK60 Mg–Zn–Zr alloy was pulled to failure at an elongation of 3,050%. [76] In practice, even larger superplastic elongations may be attained in aluminum-based alloys processed by ECAP and there is a recent report of an elongation of 4,100% in an Al–Mg–Sc–Zr alloy when tested at 723 K at a strain rate of $5.2 \times 10^{-2} \text{ s}^{-1}$. [77] Finally, it is important to note that, despite the very small cross-sectional areas of the tensile specimens processed by HPT, it is again possible to achieve excellent superplastic properties with an elongation of 1,800% recorded in an HPT-processed Zn–22% Al eutectoid alloy when pulled to failure at 473 K at a strain rate of $1.0 \times 10^{-1} \text{ s}^{-1}$. [78]

4. Functional Properties of BNM Nanostructuring of metals may also enhance various functional properties or produce new physical and chemical properties, thereby making them attractive for innovative engineering and medical applications. This section reviews the features and nature of the unusual functional properties observed in bulk nanostructured materials.

4.1. Electrical Conductivity in Ultrafine-grained Materials. It is well known that Ag, Cu, Au, and Al are metals with high electrical conductivity (111%, 100%, 78%, and 64% International Annealed Copper Standard [IACS], respectively). In addition to high

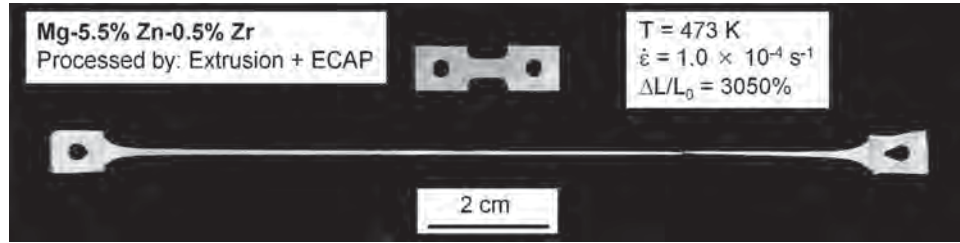


Figure 8. Appearance of a tensile specimen of a ZK60 magnesium alloy pulled to failure at 3,050% after extrusion and ECAP; the upper specimen is untested.[76]

conductivity, high mechanical strength of these metals is required for certain applications. Strengthening is generally achieved through strain hardening, solid-solution hardening, precipitation hardening and grain refinement. However, these strengthening mechanisms also lead to lower conductivity because of electron scattering by crystal lattice defects. Recent studies reveal new ways of solving this problem by grain refinement.

The evolution of mechanical properties and electrical conductivity with strain was investigated for pure Cu processed by ECAP,[79–82] accumulated roll bonding (ARB),[83–85] and HPT.[82] As summarized in Figure 9, in pure Cu (99.99%) the hardness increases and electrical conductivity decreases with increasing equivalent strain in the early stages of straining and both level off to constant levels (130 Vickers hardness, 88% IACS) at equivalent strains exceeding ~ 20 . [82] However, the electrical conductivity decreased by only $\sim 12\%$ whereas the hardness increased by $\sim 270\%$ at this saturation level. Subsequent annealing improved the electrical conductivity to 97% IACS while the hardness increment was maintained at a higher level of $\sim 160\%$ (80 Vickers hardness) when compared to the annealed state (50 Vickers hardness). A Corson alloy was processed by HPT and achieved a high strength (~ 1 GPa). [86] Furthermore, subsequent aging increased the strength to ~ 1.1 GPa and improved the electrical conductivity to an acceptable level of $\sim 30\%$ IACS.

The advantageous effects of HPT processing on the strength and electrical conductivity of Cu–0.7%Cr, Cu–0.9%Hf, and Cu–0.7%Cr–0.9%Hf alloys were demonstrated.[87] It was reported that pure copper exhibits a high strength over 1 GPa and an electrical conductivity as high as 97% IACS.[48] The sample was synthesized using a pulsed electrodeposition technique which produced grain sizes of 100–1,000 nm containing a high density of nanotwins. The significance of nanotwinning is that twin boundaries block dislocation motion but have little effect on the electrical resistivity. Such combinations of properties are yet to be matched by SPD processing but the above examples suggest that this is potentially achievable.

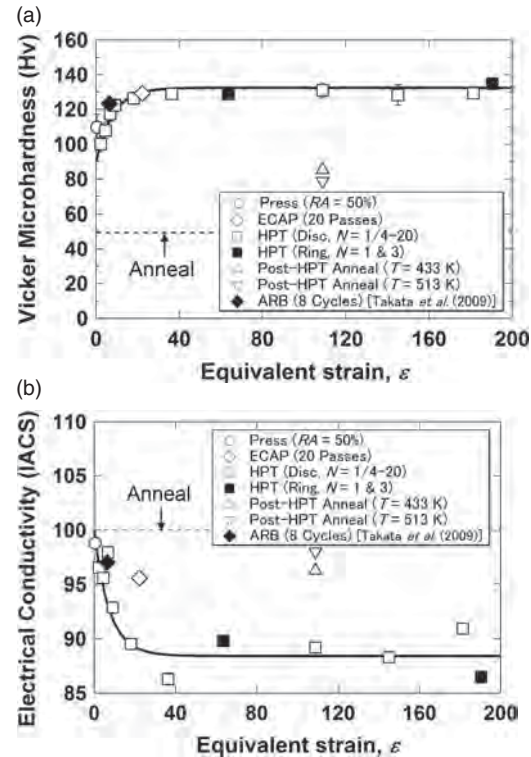


Figure 9. (a) Vickers microhardness and (b) electrical resistivity/conductivity plotted against equivalent strain for samples processed by SPD methods.[82]

Another requirement for electrical conductors is light weight and this is especially important for applications in motors, robots, and power transmission lines. Aluminum is the lightest among the high conductivity metals. It was reported [88,89] that UFG Al–Mg–Si alloys processed by ECAP and HPT exhibit a good combination of increased mechanical properties and enhanced electrical conductivity. The increased conductivity was due to second-phase precipitation which reduced the solute concentration in the Al matrix. It was proposed that processing at elevated temperatures to induce dynamic aging may be promising for continuous wire production.[90] Taking advantage of the low solubility of Fe in Al (~ 0.05 wt%) and a fine eutectic structure at ~ 1.8 wt%Fe, an Al–Fe alloy was processed

by HPT and subsequent aging which resulted in a high strength of 600 MPa and a high conductivity of $> 50\%$ IACS.[91,92]

4.2. Giant Magnetoresistance (GMR) Produced by HPT. When ferromagnetic particles are finely dispersed in a non-magnetic matrix, magnetoresistance (MR) appears with an isotropic feature. This isotropic MR is called GMR if the MR ratio reaches a magnitude of more than a few tens of percent.[93–100] The Cu–Co system is known as a good candidate for GMR as ferromagnetic Co particles with little solubility of Cu coexists in the Cu matrix.[101] A Cu–10wt%Co alloy was processed using HPT to achieve a fine dispersion of ferromagnetic particles and MR was reported at a level $\sim 2.5\%$ at 77 K with an isotropic feature (Figure 10).[102] The appearance of MR was also confirmed in a Cu–22wt%Fe alloy.[103] While the achieved magnitudes of the MR do not qualify as GMR, the results show that HPT is at least potentially promising for creating GMR in alloys.

4.3. Enhanced Hydrogen Storage Performance of SPD-processed Materials.

4.3.1. Mg and Mg Alloys. Since 2004, ECAP has been used to process nanometals for hydrogen storage, particularly Mg and its alloys (ZK60) (Figure 11).[104–106] The advantages of ECAP over ball milling include prevention of oxidation, which can seriously inhibit absorption/desorption of H_2 , and the low production cost as large volumes of material can be efficiently processed using ECAP. Furthermore, ECAP avoids health hazards common to toxicity-prone nanopowder-based processes.

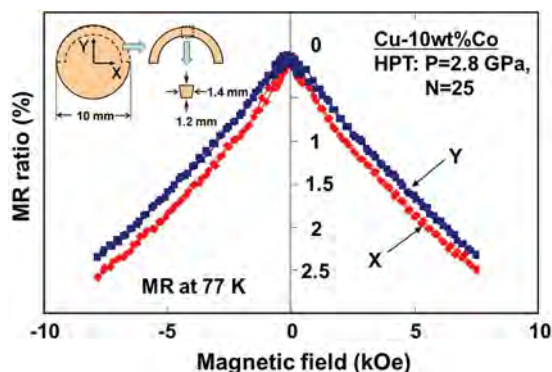


Figure 10. Variation of MR ratio with magnetic field in two different directions (X and Y) for HPT sample after $N = 25$ revolutions, where the definition of X and Y is as illustrated.[102]

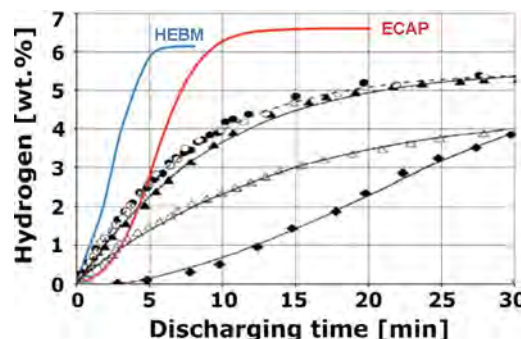


Figure 11. Hydrogen storage kinetics showing high performance of ECAP-processed ZK60 alloy compared to its ball-milled counterpart (desorption,[104,105]).

A critical requirement for energy storage is stability of the storage capacity and the absorption/desorption kinetics over large numbers of cycles. Ball-milled Mg and Mg alloys rarely meet this requirement unless catalysts are added.[107] As seen in Figure 12, ECAP-processed ZK60 shows high stability of both its capacity for hydrogen uptake and the hydrogenation/dehydrogenation kinetics for at least 1,000 cycles.[105] This was also confirmed for HPT-processed ZK60 for at least 100 cycles (Figure 13,[108]). However, not all SPD-processed materials show high stability. There are several reports [109–111] that ARB- or HPT-processed MgH_2 powder has good kinetics but low stability and this was confirmed by a recent high-cycle study [108] as shown in Figure 14. After 40 cycles, the capacity of hydrogen loading clearly decreased. Comparing the long-time stability of SPD-processed materials ZK60 and MgH_2 , it was concluded that the SPD processes in both materials provide nucleation sites for hydride formation which are, however, not stable in the case of SPD-processed pure MgH_2 . In that material, it is the comparably large volume of the hydride particles which decreases the hydrogen loading capacity as the hydrogen diffusion becomes sluggish compared with the non-hydrogenated substance.[108]

4.3.2. TiFe Alloys. The TiFe intermetallic with B2-type crystal structure is a well-known candidate for stationary hydrogen storage because of its low hydrogenation temperatures, reversible hydrogenation features, high hydrogen storage capacity, and low price. However, its practical application is limited as it requires an activation process before hydrogenation, which includes exposure to hydrogen atmosphere under high pressures at high temperatures. There have been many attempts to overcome this limitation.[112–120] Recent studies have shown that SPD processing is the way to achieve that, as such an activation process is no longer required when the TiFe is pre-processed by

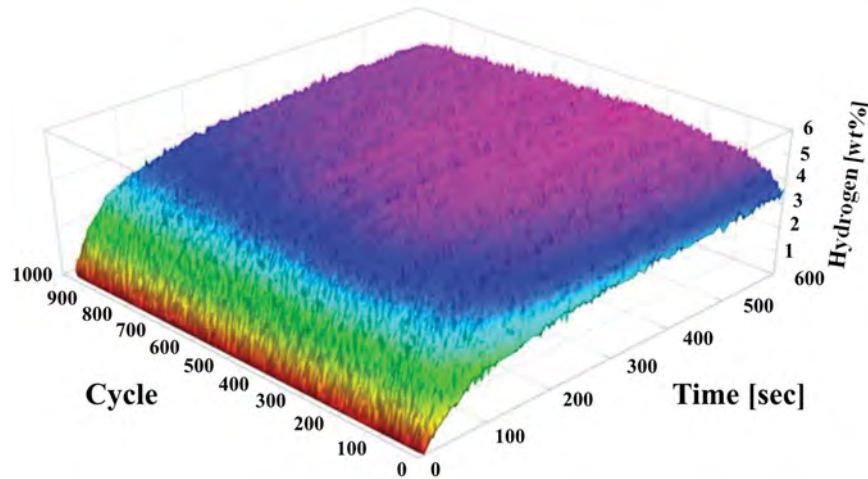


Figure 12. Long time characteristics of hydrogen storage (absorption) measured in the ECAP-processed ZK 60 alloy (from [105]).

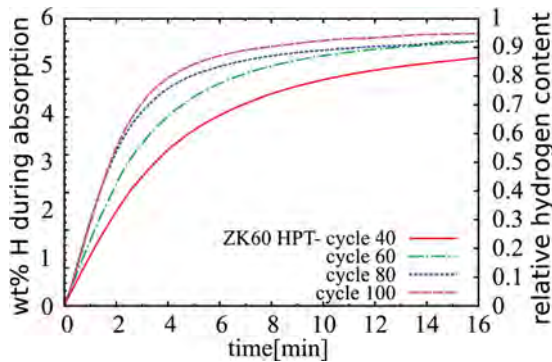


Figure 13. Hydrogen absorption of ZK60 after HPT processing at room temperature after different numbers of cycles of hydrogen loading and unloading, according to [108].

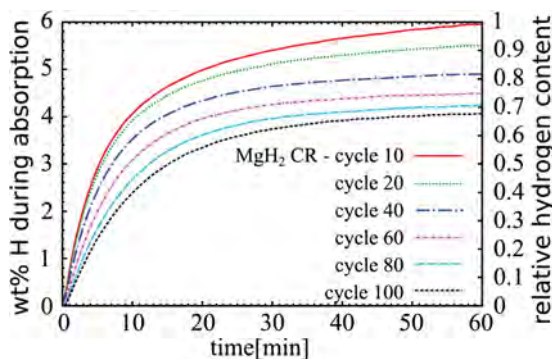


Figure 14. Hydrogen absorption of MgH_2 after cold rolling at room temperature after different numbers of cycles of hydrogen loading and unloading, according to [108].

HPT (Figure 15).[121] Furthermore, the HPT-processed sample is not deactivated even after storage in air for a prolonged period of time.[122] The mechanism enabling hydride formation without activation is associated with

enhanced diffusion of hydrogen that occurs via HPT-induced microcracks and nanograin boundaries. A further study on TiFe also showed that plastic straining is important in these hard intermetallics. Another SPD process, specifically groove rolling of encapsulated billets, was shown to be effective in activating TiFe samples as well.[123]

4.4. Production of Nanograins in Semiconductors and Occurrence of Photoluminescence.

When crystalline Si is subjected to high pressure, allotropic transformations occur from the diamond cubic structure (Si-I) to high-pressure phases with different crystal structures. These include Si-II with the β -Sn structure, Si-III with body-centered cubic structure, and other phases.[124] Because such high-pressure phases are semi-metallic in nature, they are more likely to deform plastically at room temperature under high pressure. An early study [125] and more recent studies [126,127] reported the formation of nanograins in crystalline Si processed by HPT. The mechanism for the nanograin formation is not understood but it is probably associated with enhanced dislocation activity or transformation-induced grain refinement.[2,128,129] It is interesting to note that nanocrystalline Si (*nc*-Si) exhibits unique optical properties such as visible photoluminescence (PL) because of quantum confinement.[130] It was shown that annealing after HPT gave rise to a reverse transformation of Si-III and Si-XII to Si-I while retaining the nanograin structure (Figure 16).[127] This is reflected in a broad PL peak centered around 600 nm due to the quantum confinement effect in the Si-I nanograins (Figure 17).[127] The application of HPT to Ge and GaAs also produced nanograins [131,132] and a similar PL peak was also observed for GaAs owing to the nanograin formation by HPT processing and subsequent

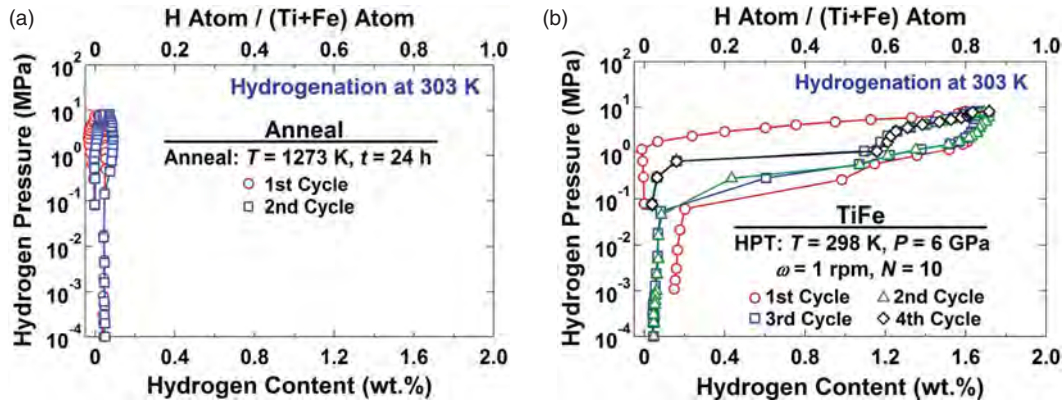


Figure 15. Pressure–concentration (P–C) isotherms at 303 K for samples processed by (a) annealing at 1,273 K for 24 h and (b) HPT processing for 10 turns. Fourth cycle in (b) was terminated after absorption for conducting XRD analysis.[121]

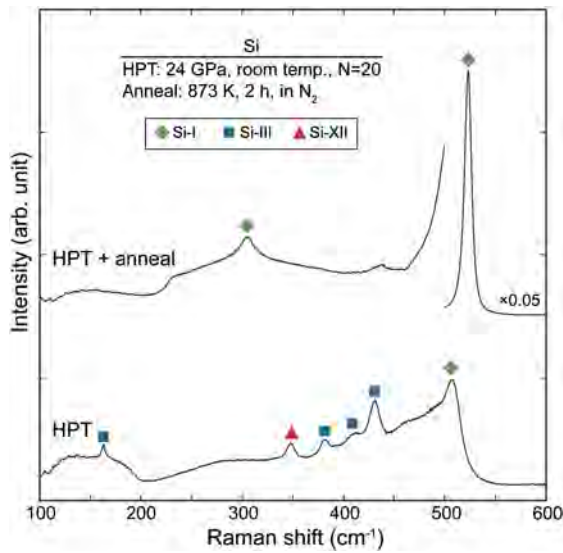


Figure 16. Raman spectra after HPT processing for 20 revolutions and annealing. Each Raman spectrum was taken at about 2 mm from the disk center.[127]

annealing.[132] It should be noted that *nc*-Si is commonly produced by ion implantation,[133] electrochemical etching,[134] and chemical vapor deposition,[135] all of which are suitable for low-dimensional nanostructures such as porous Si and Si dots. It is important to emphasize that the nano-grained semiconductors were obtained in *bulk* form by virtue of HPT. Thus, the HPT processing of semiconductors can be of great interest for potential applications to optoelectronic devices.

4.5. Superconductors in Nanograin Structures.

Superconducting properties such as the critical temperature T_c , critical current density J_c , and upper critical field H_{c2} may be affected when the sample size is reduced to the superconducting coherence length (ξ) due to the quantum-confinement effect.[136–138] Although the size effect on the superconducting transition was studied

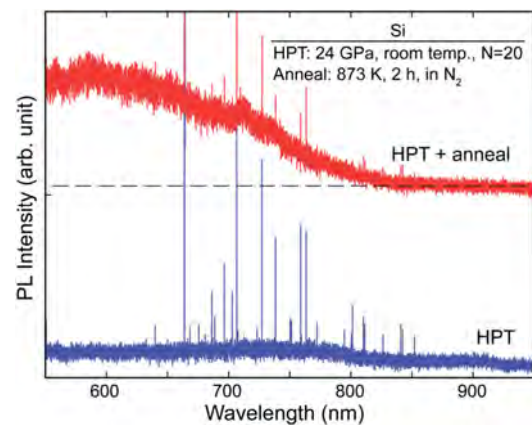


Figure 17. PL spectra after HPT processing for 20 revolutions and annealing. Some of the sharp luminescence peaks are due to laser plasma lines.[127]

by fabricating an ultrathin lead film [139] and an aluminum nanowire,[140] a recent report [141] examined the effect of grain size on the superconducting properties of bulk polycrystalline Nb whose grain size was reduced to ~ 250 nm using HPT processing.[142] This grain size is equivalent to $\sim 5\xi$ and the effect was appreciable. It was shown that the values of T_c , J_c , and H_{c2} were increased due to grain refinement by HPT processing (Figure 18). The increase in J_c can be attributed to the enhanced vortex pinning due to crystal lattice defects such as dislocations and grain boundaries. It was also shown that the residual resistivity ρ_0 is governed by the amount of strain imposed by the HPT processing.

Superconductivity was also studied for a well-known system used for superconducting magnets, a Nb-47wt%Ti alloy, to examine the effect of HPT processing on T_c . [143] It was found that T_c occurred below 9 K, it decreased with increasing shear strain but rose again with annealing. Although the grain size of the material was comparable with the coherence length (about 8ξ),[144] the trend of T_c with the imposed strain was

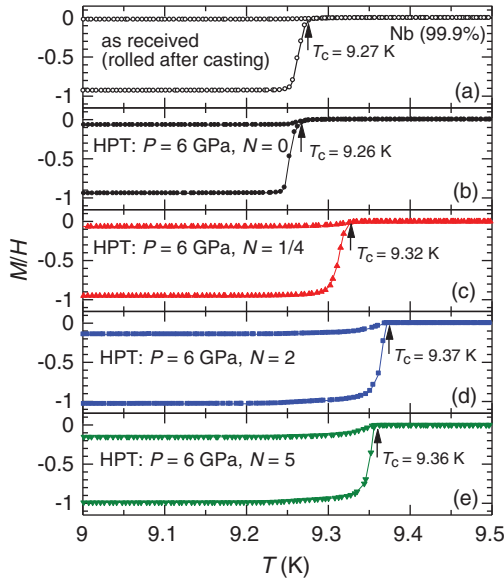


Figure 18. Temperature dependence of the magnetization $M(T)$ of Nb in the magnetic field $H = 2$ Oe. (a) As-received sample; (b)–(e) HPT-processed samples with different revolution numbers N . [141]

opposite to pure Nb [141] and this was attributed to dissolution of Ti in Nb with straining by HPT. The increase in T_c upon annealing was due to Ti decomposition from a supersaturated state after HPT processing. An important conclusion is that the application of the HPT processing to the Nb-47wt%Ti alloy in conjunction with subsequent annealing leads to an increase in tensile strength as well as bending strength while also maintaining T_c above the value obtained after solution treatment (Figure 19).

4.6. Thermoelectrics. In the field of thermoelectrics, so far mainly two groups of materials were considered in the context of SPD processing (for a detailed review, see [145]): (i) Bi–Te alloys for low-temperature applications and (ii) skutterudites for high-temperature applications. The successes of SPD processing can be judged upon the efficiency of processed thermoelectrics in terms of the so-called figure-of-merit:

$$ZT = \frac{S^2 T}{\rho \lambda}. \quad (4)$$

A large ZT -value is reached either via a high thermovoltage represented by the Seebeck coefficient S or by a decrease in electrical resistivity ρ as well as a decrease in the thermal conductivity λ . The S -value can be enhanced by increasing the gradient of the density of states, for example, by limiting the sample dimensions to a few nanometers or even to the atomic scale as in topological semiconductors, like graphene or silicon [146]). As such dimensions are usually not reached in SPD processing, efforts so far have concentrated on

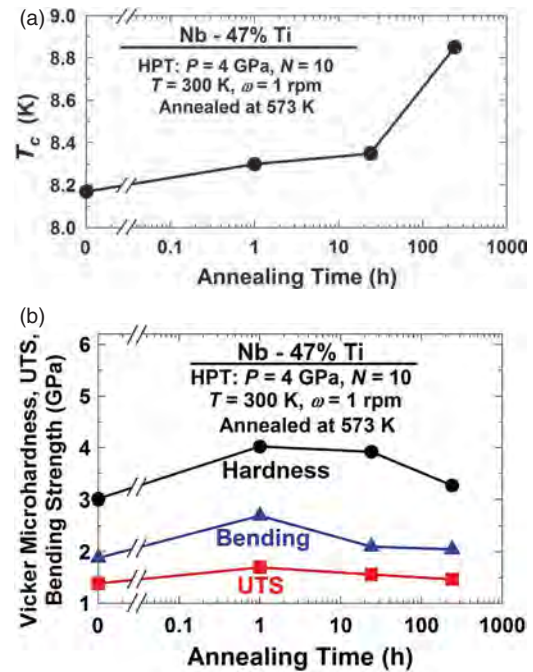


Figure 19. Variation of (a) transition temperature for superconductivity, T_c , and (b) Vickers microhardness, UTS, and bending strength against annealing time for samples processed by HPT for $N = 50$ turns and annealed at 573 K. [143]

the decrease of ρ and λ . Now the problem arises of controlling these two quantities independently. This problem needs to be tackled individually for the two groups of materials considered.

The *low-temperature thermoelectric Bi–Te alloys* exhibit a large crystal anisotropy which means that the texture of the SPD-processed materials is even more important for the resultant ZT value than the decrease in grain size leading to a smaller thermal conductivity through additional phonon scattering. There have been several attempts to increase ZT by application of SPD, mainly HPT [147] and ECAP. [148] HPT processing gave rise to an increased power factor S^2/ρ due to a (110) texture contributing to both a low resistivity and a high Seebeck coefficient (Figure 20, [147]). A real increase in ZT by an SPD method was achieved by the ECAP procedure [148] by carefully choosing the ECAP temperature (773 K) and path (Route A where there is a rotation of the billet by 180° after each pass) in order to obtain high carrier mobility (Figure 21), thus minimizing the electrical resistivity and thereby achieving a figure of merit as high as $ZT = 2.3$.

From among *high-temperature thermoelectrics*, so far *skutterudites* have been the subject of SPD processing. Ball-milled skutterudite nanopowder was successfully consolidated by means of HPT at a distinctly lower temperature than the conventional hot pressing, thus yielding much smaller grain sizes. [149] It was found that the thermal conductivity was strongly decreased by

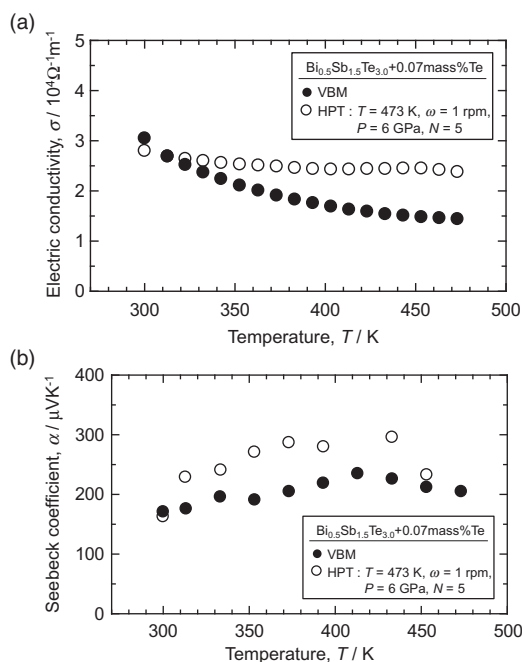


Figure 20. Electrical conductivity (a) and Seebeck coefficient (b) vs. temperature, for p -type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_{3.0}$ after processing by the Vertical Bridgman Method and HPT.[147]

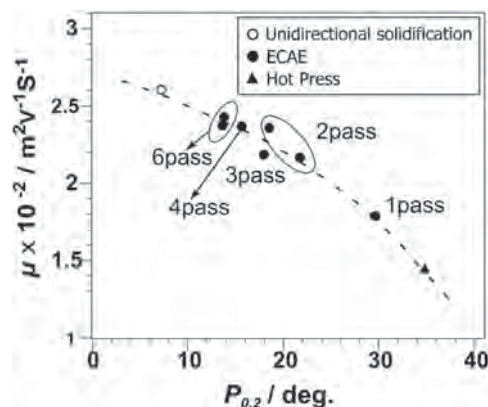


Figure 21. Dependence of carrier mobility μ on preferred orientation angle $P_{0,2}$, after applying different numbers of passes of Route 4 ECAP (labeled 'ECAE' in the original figure (from [148])).

HPT-induced lattice defects although cracks and voids were also generated and increased the electrical resistivity far more so that the overall ZT dropped. This problem was addressed by suitably increasing the HPT processing temperature in order to avoid the formation of cracks and voids, thus keeping the increase in resistivity sufficiently low to achieve an overall increase in ZT (Figure 22).[145,150] By optimizing the HPT-processing temperature, pressure, and strain, ZT was further increased by a factor of 2–3 ([145,150]; Figure 22) compared with the value before HPT. Finally, with $\text{ZT} = 1.9$, a world record for n -type skutterudites was set using this strategy

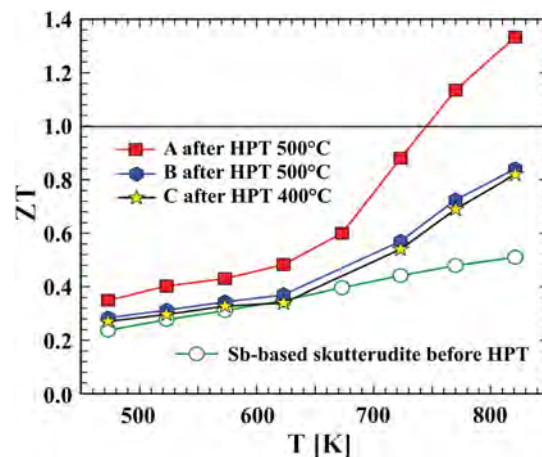


Figure 22. Increase in ZT in an n -type skutterudite after HPT processing at temperatures 400°C and 500°C. Letters A, B, and C refer to different strains achieved by HPT (from [145]).

([151]; Figure 23). Most recently, another world record $\text{ZT} = 1.45$ was also established for p -type skutterudites [152] by means of a similar preparation procedure. It should be mentioned that this procedure does not introduce new phases,[153] unlike in many alloys processed by SPD,[154] and instead there are changes only in the density and arrangement of SPD-induced crystal lattice defects.[153] Among the latter, there clearly were some which increased the electrical resistivity but without decreasing the lattice thermal conductivity. It must be left to further research whether, in the interest of maximizing ZT, it is possible to remove such defects without losing those that significantly reduce λ .

4.7. SPD-processed Materials in Biomedical Applications. One application where SPD technologies have achieved one of their most significant successes is the area of medical implant materials. The contemporary development of metallic implant materials is driven by the need for improved mechanical performance and biocompatibility. Different paradigms govern this development for permanent and temporary (bioresorbable) implants. While materials for permanent implants, such as bone or tooth replacement, obviously need to be as inert as possible, those for temporary implants are required to degrade at a rate commensurate with the rate of tissue healing. Various materials are being explored as candidates for such applications with an aim to improve their properties by SPD processing.[155] The archetypal alloy systems that offer the best performance for these two kinds of applications are arguably those based on titanium and magnesium. Indeed, Ti forms a protective surface layer of titania and is considered to be bio-inert (thus being suitable for permanent implants) whilst Mg is very reactive and biodegradable.

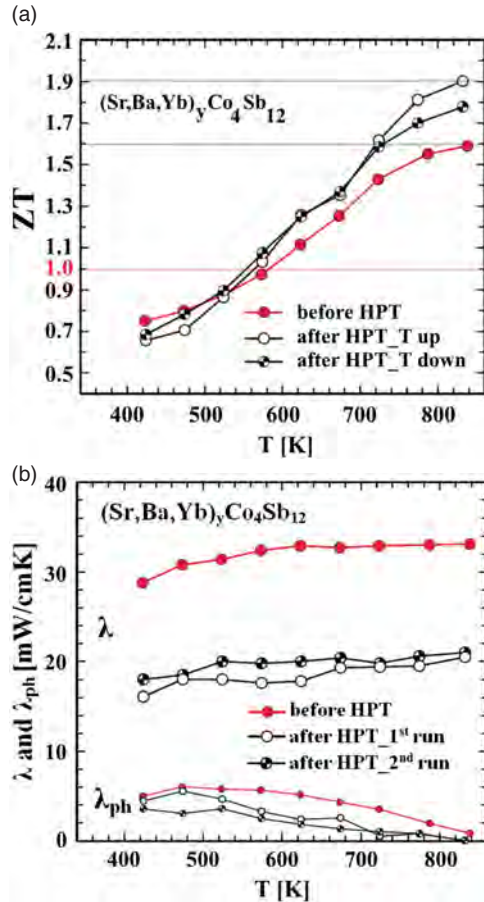


Figure 23. (a) Increase in ZT to a world record $ZT = 1.9$ by HPT processing; the increase is mainly due to the decrease in thermal lattice conductivity λ_{ph} shown in (b) [151]

For titanium-based alloys, among which Ti-6Al-4V is currently most used, a great challenge is the real or perceived toxicity of the alloying elements. Commercial purity titanium grades are thus becoming the materials of choice. To compensate for the loss of strength associated with alloying, SPD techniques are employed, such as ECAP and, recently, its continuous modification ECAP-Conform.[66,155–158] In this way, extreme grain refinement, almost down to the nano scale, is attained, and this leads to an enhancement of tensile strength of pure titanium to the levels of the conventional alloy Ti-6Al-4V and higher with UTS > 1,300 MPa.[66,156,158] Similar encouraging results were obtained for the fatigue strength and this makes it possible to improve the design of medical implants with better functionality (Figure 24).[156,158] Recent reviews compile the results obtained by ECAP, as well as by more involved SPD processing routes.[66,155] It is especially encouraging that biocompatibility of Ti does not suffer from the ultrafine crystallinity.[159] On the contrary, enhanced rates of attachment and proliferation of osteoblast and fibroblast cells, as well as stem

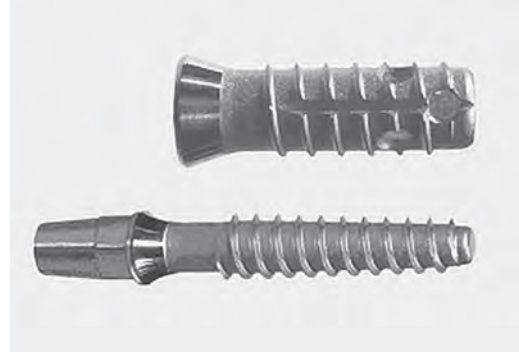


Figure 24. 3.5 mm diameter Timplant® (above) and the new 2.4 mm diameter Nanoimplant® produced from superstrong n -Ti (below).[156,158]

cells,[156,157,160] were obtained in a number of *in vitro* assays. *In vivo* studies, while not confirming such enhancement, demonstrated that a spectacular improvement of the mechanical performance of ECAP-modified commercial purity Ti was not accompanied by a loss of biocompatibility.[161]

To further improve biocompatibility, it has been attempted (i) to replace Al and especially V with more biocompatible elements and (ii) to make Young's modulus close to that of bone in order to avoid the so-called 'stress shielding'. [162] In particular, Ti-Nb alloys have attracted a great deal of interest. Not only do they meet both these requirements, but they also show good biocorrosion properties.[162] However, since a low Young's modulus is inherently connected with a relatively low strength, some additional strengthening is required if this material is to be used for medical applications as in implants or prostheses. Processing by SPD can improve the strength via grain refinement.[163–168] However, due to the potential of SPD processing to change phase stability as a result of shear combined with hydrostatic pressure, additional phases may form and this may produce undesired changes—mostly increases—of the overall Young's modulus (see, e.g.[166]) except when a new phase has a low Young's modulus too.[167] Also, SPD processing of ternary and quaternary alloys obtained by replacing some of the Nb content by other constituents such as Ta, Zr, and Sn may affect the Young's modulus in a similar way. Nevertheless, if care is taken in choosing the SPD parameters, such as limited pressure and strain, as well as the number and type of alloy constituents, the strength may be increased by 30–120% (Figures 25 and 26,[157,168]). The selection of an SPD method is also important if a good ductility is required for the intended application. Hydro-Extrusion (HE) may be the SPD method of choice, thereby sacrificing some strength for higher ductility. It is important to emphasize that with all different SPD methods applied to date (Rolling and Folding (R & F), HE, and HPT [168]),

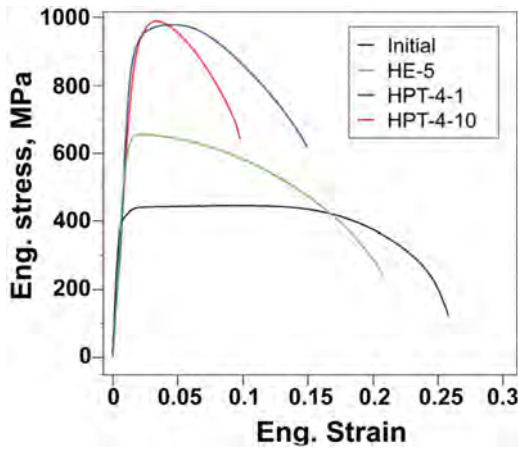


Figure 25. Stress–strain curves for initial and SPD-processed Ti-45Nb samples. HE-5 stands for 97% area reduction by HE, HPT-4- X for High-Pressure Torsion at a pressure of 4 GPa and X revolutions.[168]

a low Young's modulus was maintained (Figure 26). Smaller changes may happen according to the texture evolution which, again, is specific to the particular SPD method chosen ([168]; Figure 26). While with HPT processing the evolving texture is weak, this is not so for the R & F technique, the Young's modulus becoming even lower than initially, so that the elastic behavior of the material is closer to that of bone.

Magnesium is very promising for medical applications because of its light weight and bioresorbability. [169,170] As the lightest of all structural metals (except beryllium), the use of magnesium can reduce the weight of many medical structures from wheelchairs and stretchers to surgical tools, to vascular stents and orthopedic implants.[171,172] Magnesium is also among the most biocompatible of metals.

The prospect of nanostructuring magnesium and its alloys to achieve novel properties was recognized more than 20 years ago.[2,173,174] Grain refinement has been regarded as one of the most attractive methods to enhance the performance of magnesium alloys.[175] In addition to grain refinement, substantial texture effects are induced in hcp magnesium alloys by SPD processing. The latter are sometimes sufficiently large to introduce significant mechanical anisotropy, and they are large enough in magnitude to cause net softening upon ECAP [176,177] which is to be avoided through appropriate process design.

Nanostructuring of magnesium alloys offers several advantages and alternatives for biomedical applications, for example in vascular stents. First, reducing the grain size alters the corrosion rate. An AZ31 alloy was processed by ECAP and it was found that the corrosion rate in Hank's solution was reduced, although not sufficiently to make it suitable for stent applications.[178] An AZ80 alloy was deformed by ECAP and extrusion to

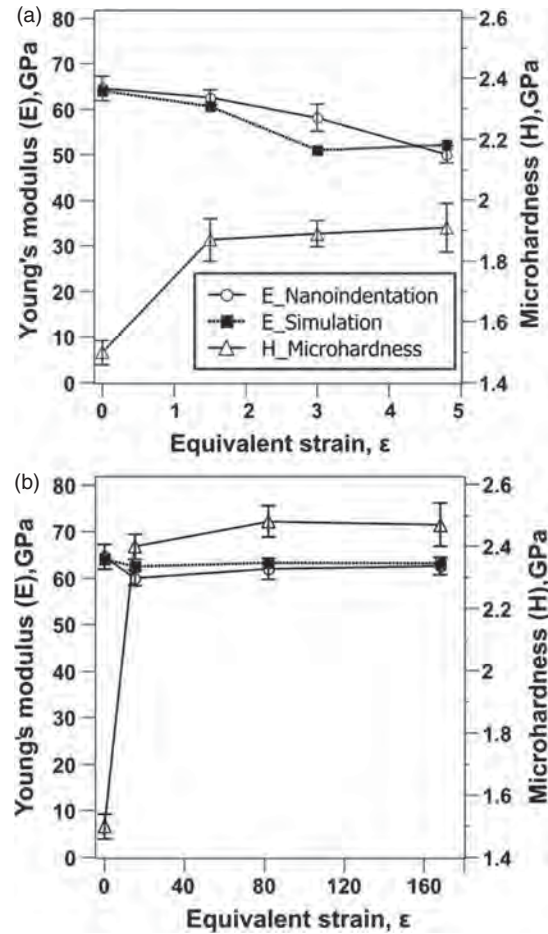


Figure 26. Young's modulus E as measured by nanoindentation (open circles), and microhardness H (open triangles), as a function of von Mises equivalent strain ϵ , for R & F (a) and HPT samples (b). The values of E were also calculated from texture data (full squares).[168]

obtain an UFG structure that enhanced the electrochemical properties.[179] The polarization layers produced remained stable and completely resisted degradation for up to 96 h. More recently, the electrochemical characteristics of AE21 and AE42 alloys were evaluated after processing by ECAP for eight passes.[180] It was found that the smaller grain size resulting from ECAP enhanced the corrosion rate in AE21 due to increased chemical activity at the grain boundaries whereas, by contrast, the corrosion rate in AE42 was reduced after the same ECAP treatment. In the latter case, the larger effect of increased uniformity of the spatial distribution of alloying elements offsets the effect of a smaller grain size. Clearly, the effects of nanostructuring are complex and alloy dependent and accordingly they must be carefully evaluated for any prospective magnesium alloy.

In particular, osteoconductive characteristics of nanostructured surfaces need further exploration. The *in vivo* characteristics of both conventional and nanostructured magnesium alloys need to be researched to

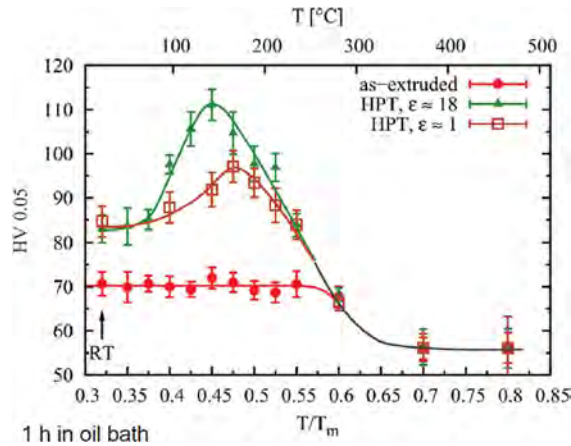


Figure 27. Microhardness of samples of Mg_{0.2}Zn_{0.5}Ca as a function of homologous annealing temperature T/T_m (T and T_m denoting the annealing temperature and the melting temperature in Kelvin, respectively): (i) after 1 h annealing (full circles) and (ii) after HPT processing and annealing (squares and triangles). HPT processing was done at a pressure of 4 GPa up to von Mises equivalent strains ϵ indicated.[183]

establish the basis for realizing the high potential of magnesium-based stents and orthopedic devices.

As noted earlier, the ability of Mg to be resorbed in bodily fluids makes it a good candidate for biodegradable implants. Various Mg alloys have been tested with respect to their biodegradability. Mg–Zn–Ca alloys have proven to exhibit two advantages at the same time, a good biodegradability and high strength.[181] However, recent experiments with these alloys show that, with respect to the time necessary for tissue healing, these alloys may either degrade too quickly and/or the concomitant hydrogen evolution is faster than the organism can absorb. It was found that the lower the alloying element and/or impurity content of the Mg-alloy, the longer it takes for the alloy to degrade.[182] On the other hand, this means that the potential of the alloy for high strength becomes smaller because second-phase particles cannot form and also solid-solution hardening becomes insignificant. It also becomes harder to reduce the grain size of the Mg alloy below 1 μm with the presence of fewer second-phase particles and/or atoms in solid solution. Very recently, it was reported that strengthening of Mg and its dilute alloys can be affected by the agglomeration of surplus vacancies in vacancy clusters or loops.[183] Figure 27 presents this strengthening effect for the case of biodegradable alloy Mg_{0.2}Zn_{0.5}Ca, which was HPT processed to generate vacancies [184,185] and annealed at homologous temperatures up to about 0.5 T_m (where T_m is the melting temperature in Kelvin) in order to induce agglomeration of these vacancies. Depending on the HPT strain applied, the strength increment amounted to almost 60% of the strength of the as-extruded material (Figure 27). By comparison, grain size strengthening yielded a strength

increment of only 19% and this is irrespective of the HPT strain applied (Figure 27;[183]). The hypothesis that vacancies are responsible for the observed strengthening effect is supported by two facts, namely that (i) very similar hardening effects with respect to extent and annealing treatment have been reported for quenched-in vacancies [186] and (ii) careful checks by Atom Probe Tomography [183] ruled out the formation of a second phase as an alternative cause for strengthening.

5. Summary The results of numerous studies reported in this article demonstrate clearly that various superior properties, both mechanical and functional, can be obtained in bulk nanostructured materials produced by SPD. The results of numerous studies reported in this article demonstrate clearly that various superior properties, both mechanical and functional, can be obtained in bulk nanostructured materials by SPD. The basic mechanical properties considered include superior strength, enhanced fatigue endurance, and superplasticity. These studies generate a great deal of interest with regard to scientific foundations of the phenomena involved and their practical applications in new structural materials. Recent discoveries have also demonstrated new opportunities for SPD processing with respect to improving functional properties of materials. These include increased electrical conductivity in metals and alloys, giant magnetoresistance, enhanced hydrogen storage performance, occurrence of photoluminescence in nanogained semiconductors, superior thermoelectric properties, and many other unique phenomena that are of immediate interest for various functional applications.

Observations performed during the last decade with a suite of modern techniques including TEM/HREM, X-ray diffraction, 3D-atom probe, and others reveal that not only can SPD processing form UFGs but it can also be used to engineer grain boundary structure and generate nanoparticles, segregations or nanoclusters and other structural elements at nano scale. The type and morphology of such nanostructured elements, as well as their number density, determine new deformation and transport mechanisms responsible for improvement of mechanical, chemical and physical properties of bulk nanostructured materials through SPD techniques.

Over the last few years, studies of bulk nanostructured materials tend to be oriented more toward the development of their advanced and superior properties and in this context the concept of nanostructural design plays an important role. In addition to grain refinement down to the nanometer range, grain boundary structure engineering is also important because boundaries having different structures can exhibit specific transport mechanisms, in terms of deformation and diffusion, and this can be used to control the properties.[7,187] This opens up the potential for developing new ways for improving the properties of ultrafine-grained materials.

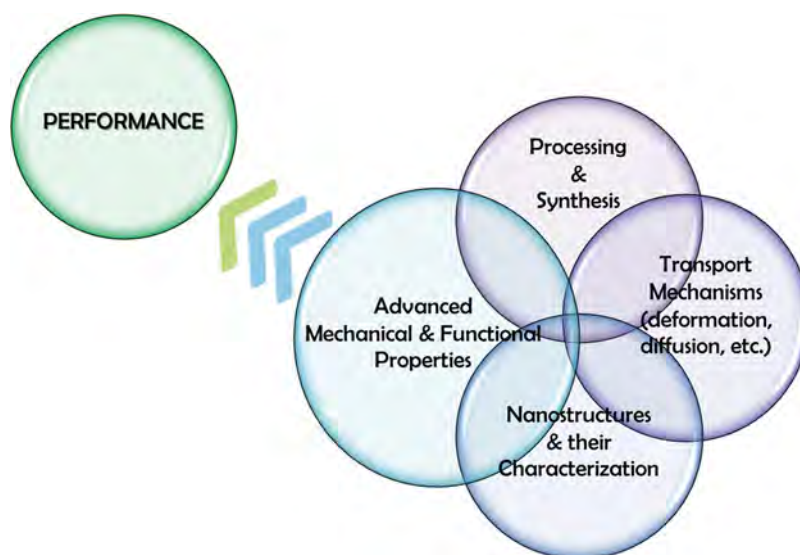


Figure 28. Principles of nanostructural design of bulk nanostructured materials.[5]

The concept of the nanostructural design of materials is schematically illustrated in Figure 28 [5] using a pictorial representation which modifies and further develops the well-known concept of the contemporary creation of novel materials through the integration of theory and modeling, structure characterization, processing and synthesis, as well as studies of the properties. In comparison with traditional materials design, nanostructuring of bulk materials deals with a far larger number of structural parameters related to the grain size and shape, lattice defects in the grain interior, as well as with rich grain boundary structure, and also with the presence of segregations and second-phase nanoparticles. This provides the possibility to vary the transport mechanisms and change the properties of materials in a desired way. Not only does nanostructuring of bulk materials by SPD processing permits a considerable enhancement of mechanical and physical properties, but it may also be used to create multifunctional materials.[4,8,9,31,188,189] In this respect, it can be anticipated that in the very near future the nanostructuring of materials by SPD processing techniques under different controlled regimes will provide new breakthroughs in the development of materials with superior properties for advanced structural and functional applications.

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Producing Bulk Ultrafine-Grained Materials by Severe Plastic Deformation: Ten Years Later

RUSLAN Z. VALIEV,^{1,2} YURI ESTRIN,^{3,4} ZENJI HORITA,^{5,6}
TERENCE G. LANGDON,^{7,8,12} MICHAEL J. ZEHETBAUER,⁹
and YUNTIAN ZHU^{10,11}

1.—Institute of Physics of Advanced Materials, Ufa State Aviation Technical University, 12 K. Marx str., Ufa 450000, Russia. 2.—Laboratory for Mechanics of Bulk Nanomaterials, Saint Petersburg State University, 28 Universitetsky prospekt, Peterhof, Saint Petersburg 198504, Russia. 3.—Department of Materials Science and Engineering, Monash University, Clayton, VIC 3800, Australia. 4.—Laboratory of Hybrid Nanostructured Materials, NUST MISIS, Moscow 119490, Russia. 5.—Department of Materials Science and Engineering, Faculty of Engineering, Kyushu University, Fukuoka 819-0395, Japan. 6.—WPI, International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, Fukuoka 819-0395, Japan. 7.—Departments of Aerospace & Mechanical Engineering and Materials Science, University of Southern California, Los Angeles, CA 90089-1453, USA. 8.—Materials Research Group, Faculty of Engineering and the Environment, University of Southampton, Southampton SO17 1BH, UK. 9.—Research Group Physics of Nanostructured Materials, Faculty of Physics, University of Vienna, Vienna, Austria. 10.—Departments of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695, USA. 11.—School of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, China. 12.—e-mail: langdon@usc.edu

It is now well established that the processing of bulk solids through the application of severe plastic deformation (SPD) leads to exceptional grain refinement to the submicrometer or nanometer level. Extensive research over the last decade has demonstrated that SPD processing also produces unusual phase transformations and leads to the introduction of a range of nanostructural features, including nonequilibrium grain boundaries, deformation twins, dislocation substructures, vacancy agglomerates, and solute segregation and clustering. These many structural changes provide new opportunities for fine tuning the characteristics of SPD metals to attain major improvements in their physical, mechanical, chemical, and functional properties. This review provides a summary of some of these recent developments. Special emphasis is placed on the use of SPD processing in achieving increased electrical conductivity, superconductivity, and thermoelectricity, an improved hydrogen storage capability, materials for use in biomedical applications, and the fabrication of high-strength metal-matrix nanocomposites.

AUTHORS' NOTE

An article titled "Producing Bulk Ultrafine-Grained Materials by Severe Plastic Deformation" was published in JOM in the issue dated April 2006 (<http://link.springer.com/article/10.1007/s11837-006-0213-7>). This article was designed to summarize the fabrication of bulk ultrafine-grained (UFG) materials through the application of severe plastic deformation (SPD) with special emphasis on defining the fundamental terms and the major techniques used in SPD processing. The article was a remarkable success. It is currently shown on the Thomson Reuters Web of Science website with a total of more than 600 citations. It is listed as a Highly Cited Paper which places it in the top 1% of all papers in the field of Materials Science published in 2006. It is also easily, by a factor of more than three, the all-time most cited paper to appear in JOM. The current article is designed to provide, exactly ten years later, an update to this fast-moving and challenging field and to give a description of new developments in the production and properties of UFG materials.

INTRODUCTION

Processing through the application of severe plastic deformation (SPD) has now become widely accepted as a promising tool for the fabrication of bulk ultrafine-grained (UFG) materials. An earlier report defined the terms associated with this type of processing¹ and the various experimental procedures that may be used to achieve grain refinement to the submicrometer or even the nanometer level. The present article, published 10 years later, describes the more recent developments in this rapidly expanding research field with special emphasis on the potential for achieving exceptional physical, mechanical, and functional properties that cannot be attained through the use of conventional techniques. New activities, including a classic development within the general framework of SPD processing, have been described in several recent reviews,^{2–14} but the present article offers the first opportunity to provide a more detailed overview of some of the important developments since the earlier article in 2006.

NEW PROPERTIES ACHIEVED THROUGH SPD PROCESSING

The effect of processing by SPD is not limited to extreme grain refinement. Indeed, processing by SPD may also result in unusual phase transformations associated with the dissolution of second phases, precipitation, amorphization, and other processes that produce various nanostructural features. These include deformation twins, nonequilibrium grain boundaries, dislocation substructures,

vacancy agglomerates, solute segregation, and clusters.^{7,9,12} These changes in the inner makeup of the material may affect the deformation mechanisms and, consequently, change a material property in a radical way. As a result, new structural and functional metals and alloys with uniquely superior properties can be developed by SPD processing.^{8,9,13} The following sections present several recent examples of extraordinary properties achieved by SPD processing that convincingly demonstrate the large innovation potential of bulk nanomaterials.

Currently, many different SPD processing techniques are available,^{3,9,10,12} but most attention to date has concentrated on two processes: equal-channel angular pressing (ECAP) and high-pressure torsion (HPT). Both are especially attractive for research because they produce materials having smaller grain sizes and higher fractions of high-angle grain boundaries than most other SPD techniques.^{3,5} These two main techniques are applied in the examples now described.

Strength and Ductility of UFG Materials Processed by SPD

It has been a perpetual endeavor for materials scientists to make materials with both high strength and high ductility.^{15,16} This issue has become more urgent under the current challenge of global warming and the energy crisis. Stronger materials can make transportation vehicles lighter and consequently more energy efficient. UFG materials processed by SPD techniques usually have much higher strength than their coarse-grained (CG) counterparts.¹³ However, improving their poor ductility without sacrificing their strength has been challenging. This problem is further compounded by the confusion of ductility with plasticity in the academic community and the difficulty of using standard samples to measure the ductility of UFG materials.

Ductility is measured under tensile loading, and can be considered a special case of plasticity, i.e., tensile plasticity. At room temperature, ductility is controlled largely by the strain-hardening capability and, to a lesser extent, the strain rate sensitivity of the flow stress. At higher temperatures, the strain rate sensitivity is high, which may considerably improve the ductility. Ductility is significantly affected by the microstructure, such as grain size, and the distribution of second-phase particles. On the other hand, plasticity is largely determined by the intrinsic properties of a metal such as the crystal structure and, in particular, the availability of the slip systems and dislocation mobility. For example, hexagonal-close-packed (hcp) metals commonly have lower plasticity than face-centered-cubic (fcc) and body-centered-cubic (bcc) metals.

UFG metals usually have low ductility but high strength. The low ductility is primarily a result of the low strain-hardening capability of UFG metals. According to the Considère criterion, uniaxial tensile deformation is stable when the inequality

$$d\sigma/d\varepsilon \geq \sigma \quad (1)$$

is fulfilled. Here σ is the true flow stress, ε is the true strain, and $d\sigma/d\varepsilon$ is the strain-hardening rate under a constant strain rate. Therefore, the high flow stress of UFG metals requires them to have an even higher strain-hardening rate than their CG counterparts to maintain the same ductility.¹⁶

To improve the ductility of UFG metals, the most effective way is to increase their strain-hardening rate. In other words, it is necessary to design UFG structures that can effectively block and accumulate dislocations. Grain boundaries are no longer effective for dislocation accumulation because, when the grain sizes are very small, grain boundaries become dislocation sources and sinks without much dislocation accumulation.¹⁷ It follows that dislocation barriers are required within the grain interior where dislocations can be blocked and accumulate. Some successful strategies to this end include the use of growth twins,¹⁸ deformation twinning,^{19–21} stacking faults,^{22,23} and second-phase particles/precipitates²⁴ as barriers. Since these approaches can also increase the strength, they often lead to a simultaneous increase in both strength and ductility. It should also be noted that UFG metals processed by SPD techniques often contain a high density of dislocations. This leaves little room for dislocation accumulation during tensile testing before saturation is reached. Therefore, annealing to lower the dislocation density without increasing the grain size is expected to improve the strain hardening and ductility. Indeed, it has been found

that processing the UFG metals to a very large strain or annealing SPD-processed UFG metals for a very short time can enhance the ductility,^{20,25,26} which could be due to both a lower dislocation density and a higher fraction of high-angle grain boundaries.

It should be noted that for UFG metals and alloys with low melting temperatures, room temperature may represent a relatively high homologous temperature that, coupled with the small grain size, may lead to grain boundary sliding during deformation and consequently to high strain rate sensitivity to enhance ductility.^{27–29}

Lastly, it has been found recently that a heterogeneous lamellar (HL) Ti with ~25 vol.% of recrystallized grains (~4 μm) embedded in a UFG hard matrix has a strain-hardening rate and ductility higher than that of CG Ti with a grain size of 43 μm while maintaining the strength of UFG Ti (Fig. 1).¹⁶ Such a combination of strength and ductility was previously believed impossible according to conventional knowledge. These superior mechanical properties are attributed to a significant development of back-stress strengthening and back-stress strain hardening caused by plastic incompatibilities between the various microstructural regions during the deformation. The plastic incompatibility generates a dramatic strain gradient that must be accommodated by geometrically necessary dislocations. This represents a new paradigm in designing metals and alloys to fully use their potential in mechanical properties to unprecedented new levels, and it should be further explored. In the same vein, it was recently proposed to embed thin layers of soft CG material in the UFG matrix to achieve the desired combination of high strength and ductility in the resulting hybrid material.³⁰

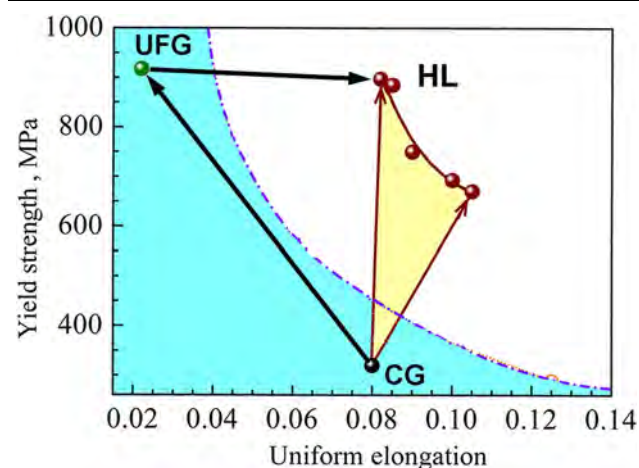


Fig. 1. Heterogeneous lamellar (HL) Ti with ~25 vol.% of recrystallized grains (~4 μm) embedded in the UFG hard matrix has a strain-hardening rate and ductility higher than CG Ti with a grain size of 43 μm while maintaining the strength of UFG Ti.¹⁶

Fabricating High-Strength Metal-Matrix Nanocomposites by High-Pressure Torsion

Processing by HPT is usually undertaken on disk-shaped specimens,³¹ although the processing has been extended also to cylindrical^{32–34} and sheet³⁵ samples. The conventional HPT disks are generally cut from a single metal or alloy, but recently it was shown that semicircular disks of Al and Cu may be successfully bonded through a solid-state reaction at ambient temperature by using HPT processing through up to 100 turns.³⁶ A similar procedure was used later in which separate disks of commercial-purity aluminum and a commercial ZK60 magnesium alloy, cut and polished to thicknesses of ~0.8 mm, were stacked in the HPT facility as three disks in the sequence Al/Mg/Al and processed by HPT at room temperature under an applied pressure of 6.0 GPa.³⁷ This processing was conducted under quasi-constrained conditions in which there is a small outflow of material around the periphery of the stack during the processing operation.³⁸

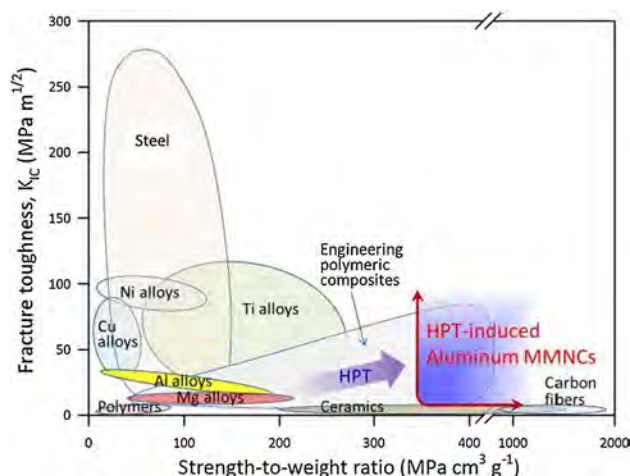


Fig. 2. A pictorial representation of fracture toughness versus strength-to-weight ratio for many metals and other materials⁴³ including a depiction of the HPT-induced aluminum MMNC where, in the absence of experimental data, no upper limit is specified.⁴⁰

Inspection of the stacked disks after processing revealed Al-rich and Mg-rich phases, but near the edges of the disks after five and ten turns there was a homogeneous distribution of very fine Mg phases confined within the Al matrix. Furthermore, careful microstructural analysis revealed a true nanostructure in the Al-Mg disks after processing with average grain sizes near the edges of the disks of ~ 190 nm and ~ 90 nm when processing through five and ten turns, respectively.³⁷ It was shown by using energy-dispersive x-ray spectroscopy (EDS) that an intermetallic compound, β - Al_3Mg , was formed in the Al matrix as thin layers with thicknesses of ~ 20 nm and ~ 30 nm after five and ten turns, respectively, thereby producing an intermetallic-based, Al metal-matrix nanocomposite in the highly deformed regions near the edges of the disks. In addition, an intermetallic compound of γ - $\text{Al}_{12}\text{Mg}_{17}$ was identified in the Al matrix using x-ray diffraction, and this was attributed to rapid diffusion of Mg from the Mg-rich phases.³⁷ Measurements of the Vickers microhardness, H_v , revealed a very significant increase in hardness to $H_v = 135$ near the edge of the disk after five turns and an even higher hardness of $H_v = 270$ near the edge after ten turns. This hardness was attributed to a combination of Hall-Petch strengthening, solid solution strengthening, and precipitation hardening where these strengthening processes can occur simultaneously because of the use of very rapid processing at a relatively low temperature that prevents the occurrence of significant recovery. It is important to note that the hardness values in the pressed material are exceptionally high by comparison with the highest attainable hardness in the ZK60 alloy of $H_v = 105$ – 110 after processing through five turns of HPT.³⁹ Color-coded contour maps are available to provide visual displays of the variations in hardness within the cross sections of the HPT disks.^{40,41}

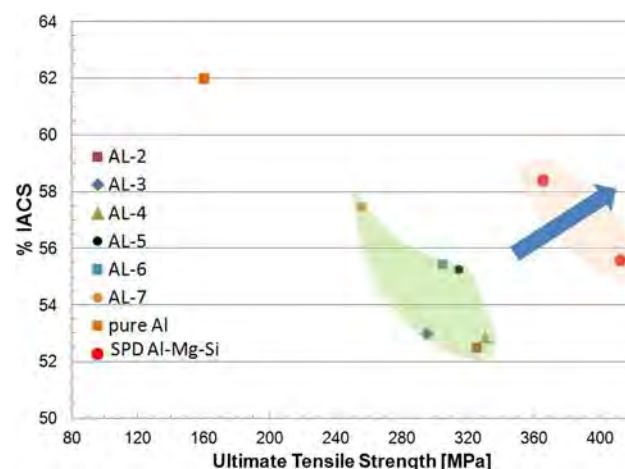


Fig. 3. Electrical conductivity (in % IACS) of the various Al-Mg-Si alloys (AL-2-AL-7) used in electrical engineering for overhead power lines plotted against their ultimate tensile strength⁵⁰ and compared with the properties of a nanostructured AA6201 produced by two-step SPD processing.⁵¹

The microstructures associated with these processed disks are complex after five or more turns, ranging from a multilayered structure at the center of the disk to a metal-matrix nanocomposite (MMNC) in the peripheral region. It is now recognized that these gradient-type structures provide an excellent potential for the future development of superior mechanical properties.^{18,42} It is instructive to consider this new MMNC with reference to the toughness-strength diagram, which was developed recently to depict, in a simple form, the optimum conditions for many different metals and other materials.⁴³ This diagram is shown in Fig. 2 where the HPT-induced aluminum MMNC lies at the right with a strength-to-density ratio in excess of $350 \text{ MPa cm}^3 \text{ g}^{-1}$, which is derived from the measured hardness of $H_v = 270$, equivalent to a strength of ~ 865 MPa, and a density of 2.48 g cm^{-3} . In the absence of any specific data, no upper limit is delineated for the MMNC region in Fig. 2.⁴⁰ Nevertheless, it is important to note that this region is far removed from the regions on the diagram at much lower strength-to-weight ratios for conventional Al and Mg alloys. Based on these results, there appears to be a significant opportunity for making use of this approach in the development of a wide range of high-strength materials.

Nanostructured Al and Cu Alloys with Enhanced Strength and Conductivity

Mechanical strength and electrical conductivity are the most important properties of conducting metallic materials used in electrical engineering. Today, there is a growing need in this field for innovative conductor materials with improved properties. However, high electrical conductivity and high strength are usually mutually exclusive as a result of the physical nature of these properties.

Alloying of pure metals results in a significant increase of their mechanical strength, whereas the electrical conductivity drops because of the scattering of electrons at solutes and precipitates, provided the latter are densely spaced.⁴⁴

Recent studies have shown that microstructural design in Al, Cu, and their alloys can result in a favorable combination of high mechanical strength with enhanced electrical conductivity.^{45,46} It was demonstrated that both properties are primarily controlled by the microstructure of these materials of which the grain size, morphology of second phases and their distribution, as well as the dislocation structure are the most important parameters. In this case, nanostructuring the alloys by SPD is of special interest, and this raises fundamental questions concerning new mechanisms of strength and electrical conductivity as well as the innovation potential for practical applications of nanostructured materials.^{47–49}

It was shown that nanostructuring of Al and Cu alloys by SPD processing can significantly increase their mechanical strength with simultaneous improvement in their electrical conductivity (Fig. 3).^{49–52} The development of metallic conductors with such attractive properties is one of the most topical subjects in modern electrical engineering.⁵⁰ Given that the global consumer market of Al-Mg-Si alloys for overhead power transmission lines⁵³ accounts for about 450,000 tons/year and continues to grow, the R&D activities focused on the improvement of their properties are of keen interest. One of the largest aluminum producers in the world, RUSAL, is currently developing a new manufacturing line for mass production of nanostructured Al-Mg-Si alloys with improved mechanical strength and electrical conductivity for overhead power lines.⁵⁴ An experimental extruder will be built that will use SPD to produce nanostructured alloys. Current research activities also focus on the development of novel Al alloys for applications in electrical engineering. For example, the HPT technique has been used⁵⁵ for fabrication of Al-Fe thin wires having a diameter of 80 μm . Fe is an ideal alloying element for electrical conductivity of Al because of its low solubility in the matrix, and simultaneously, Fe can provide some strength and creep resistance if intermetallic particles are finely dispersed. Processing by HPT enabled the formation of mostly equiaxed ultrafine grains with high dislocation densities and fine dispersions of eutectic phases whose microstructures were ideal to increase not only the strength but also the formability to allow further wire drawing with 25:1 area reduction.⁵⁵ The HPT-processed Al-Fe alloy after wire drawing showed very good surface quality. The electrical conductivity of the drawn wires ranged from 49% to 51% of IACS and increased to 52–54% of IACS after aging at 200°C for 1 h. There is a great potential to further improve the electrical conductivity of the Al-Fe alloys with an optimized aging

treatment.⁵⁵ Such thin wires can be useful for applications in microelectromechanical systems (MEMS).

Nanostructured pure copper would be an innovative solution for electric circuitry and connectors (e.g. in electrical engines and voltage current converters). In the field of microelectronics materials, and more precisely in copper interconnects, the electrical performance must not compromise the resistance to creep and electro-voiding when the channel and size of the system is reduced. In particular, mechanical properties become dependent on the sample size when the characteristic dimensions of the sample are below a few tens of micrometers. There are two reasons for this: (I) the microstructural scale (grain size) is sample size dependent and (II) the confinement of plasticity to small dimensions leads to new phenomena that make mechanical properties sample size dependent.⁴⁶ The potential application of nanostructured Cu with improved wear resistance has been highlighted as a material for reversible electrical contacts⁴⁶ where an optimal design for such contacts was also proposed.

Nanostructured Biomaterials

An area where SPD technologies have come close to industry-scale applications is in the manufacturing of medical implants. In the quest for materials with high mechanical performance and good biocompatibility, titanium alloys have come to the fore as the materials of choice for permanent implants, including bone replacement and dental applications. In the case of titanium, significant efforts go into enhancing the strength characteristics of commercial-purity (CP) grades to avoid potential biotoxicity of alloying elements, especially in dental implants. In the case of magnesium alloys, a great challenge is the excessively high rate of their degradation, which is problematic in terms of both the durability of the implant and the high rate of hydrogen evolution during corrosion as in vascular stent applications.

Although grain refinement by SPD cannot resolve all of these issues, it has been extremely effective in enhancing the property profile of the candidate implant materials.^{56–60} Not surprisingly, the mechanical performance of CP Ti of biomedical grades was improved significantly upon processing by ECAP. A recent study of the properties of Ti processed by a combination of ECAP-Conform and drawing⁶¹ returned record values of the ultimate tensile strength (1330 MPa) and fatigue strength (620 MPa). What is less evident is that extreme grain refinement of the bulk of the metal down to the nanoscale appears to transpire to surface morphology, which turns out to be conducive for enhanced adhesion and growth of living cells. Indeed, proliferation of the preosteoblast cells,⁶² fibroblast cells,⁵⁶ and stem cells⁶³ on the polished surface of nanostructured Ti processed by ECAP

was shown to be promoted by grain refinement. However, in the implant manufacturing industry, implants undergo special surface treatments, such as grit-blasting, plasma-spraying, acid-etching, and anodization.⁶⁴ The effect of grain refinement of the bulk of the material on the surface characteristics, which in turn control fatigue properties and cellular response, may be weakened by such surface treatments. A recent study⁶⁰ shed some light on the effect of sand-blasting combined with acid-etching (the SLA process⁶⁵) on the fatigue performance of CP Ti. The study demonstrated that the SLA surface treatment of Ti with different bulk microstructures gave rise to different levels of surface roughness. A greater increment of fatigue strength was achieved for the CG variant of Ti. Nevertheless, the fatigue properties of CP titanium processed by ECAP followed by SLA treatment were superior to those of CG CP titanium.

It should also be understood that the exceptional improvement of mechanical properties of Ti by such SPD processes as ECAP or its modifications, while not causing a deterioration of cell response, are not necessarily accompanied with its appreciable enhancement. This has been demonstrated by *in vivo* assays based on histology and micro-CT analyses.⁶⁶ Still, the overall performance of SPD-processed titanium makes it very suitable for bone and tooth replacement. The ultimate proof for that has been provided in a most recent clinical study.⁶¹

Among the Ti alloys, SPD-processed β -alloys of the Ti-Nb system have attracted special interest. Not only do they show good biocorrosion and biocompatibility properties, but they also have a favorable Young's modulus close to that of bone. This helps to avoid the detrimental effects of stress shielding on the bone tissue healing.⁶⁷ SPD processing ensures that the relatively low strength of as-cast Ti-Nb is significantly improved through grain refinement,^{68,69} suggesting that this material still qualifies for bone replacement applications. However, the SPD parameters need to be chosen carefully to avoid the occurrence of deformation-induced new phases that may raise the Young's modulus of the alloy to undesirably high levels (see, for example, Panigrahi et al.⁶⁸).

For temporary (bioresorbable) implants, magnesium alloys have advanced as favorite materials because of their high biodegradation rate. Current research focuses on improving the biocompatibility and the mechanical performance of these systems through variations in alloy composition, microstructure, and surface treatment. Mg-Zn-Ca alloys have proven to exhibit both these advantages at the same time.⁶⁹ With respect to the time necessary for tissue healing, however, these alloys may degrade too quickly and the concomitant hydrogen evolution is faster than the human body can absorb. The degradation was found to take longer with less alloyed Mg systems,⁷⁰ albeit at the cost of their

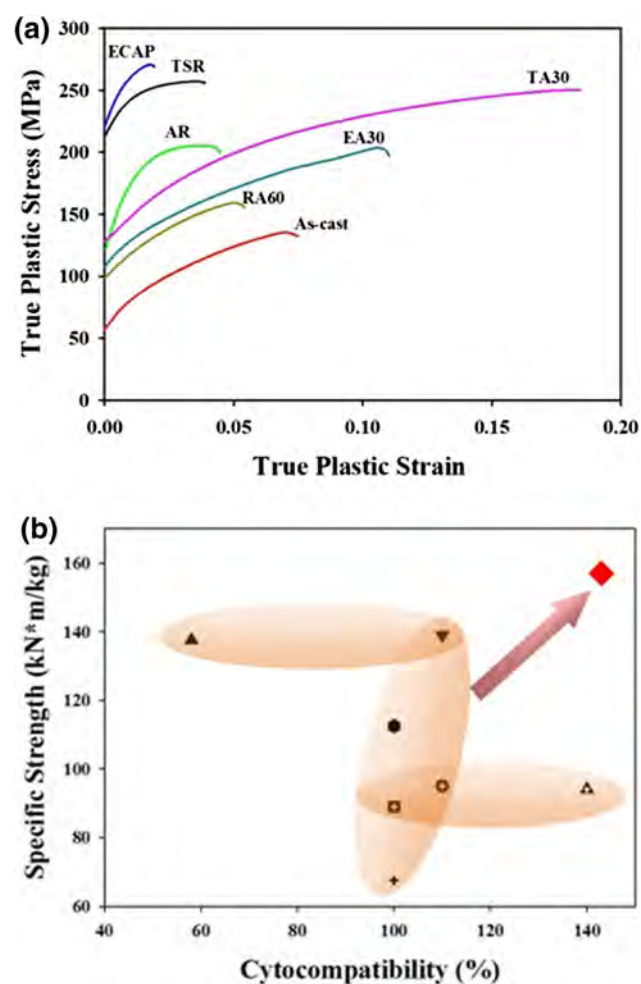


Fig. 4. Properties of the ultralight UFG alloy Mg-4Li-1Ca: (a) tensile properties (TSR = two-step rolling, TA30 = TSR + 30 min annealing, EA30 = ECAP + 30 min annealing; RA60 = rolling + 60 min annealing); (b) comparison of the specific strength of the alloy (ultimate tensile strength/density) in TA condition (diamond) with those of its commercial "competitors" (data adopted from the literature): AZ91 (filled up-pointing triangle), ZK60 (filled inverted triangle), pure Mg (cross), Mg-6Zn-1Ca (square), Mg-1Ca (up-pointing triangle), Mg-8.5Li-1Al (white circle), WE43 (hexagon).⁷⁴

strength. The application of SPD has shown to bring back or even surpass the original level of strength by means of grain refinement,^{70,71} phase formation, and the generation of vacancy agglomerates.⁷²

Significant improvements of the biocorrosion resistance by means of SPD processing were observed in earlier studies of Mg-based alloys showing that the corrosion current for Mg immersed in simulated body fluids is smaller for small grain sizes. This was recently confirmed for ultra-light UFG alloy Mg-4Li-1Ca (LX41).^{13,73} Both two-step rolling and ECAP were shown to lead to a record-breaking specific strength of the alloys and a good tensile ductility.⁷⁴ A very good cytocompatibility of the alloy (Fig. 4) makes it a perfect candidate for bone replacement as well as for maxillofacial and other medical implant applications.

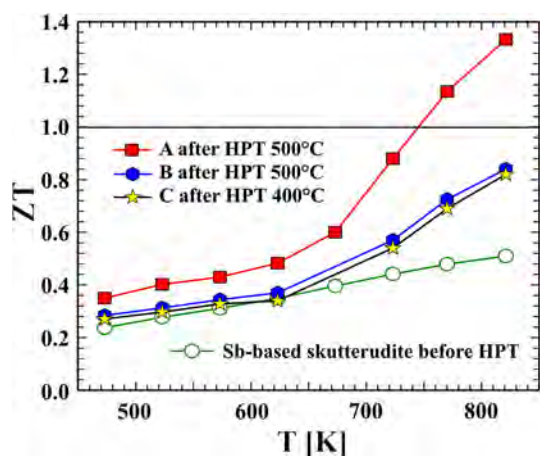


Fig. 5. Increase of ZT in an *n*-type skutterudite after HPT processing at temperatures 400°C and 500°C. Letters A, B, and C refer to different strains achieved by HPT.⁷⁵

In summary, the emergence of UFG materials for permanent and biodegradable medical implants demonstrates in an exemplary way the great potential that SPD techniques have in developing novel materials in general.

Thermoelectricity and Superconductivity

In recent years, SPD processing has achieved outstanding benefits in thermoelectric properties that are described in terms of the so-called figure-of-merit:

$$ZT = (S^2T)/(\rho\lambda). \quad (2)$$

SPD processing activities concentrated on decreasing the denominator of Eq. 2 by a decrease of electrical resistivity ρ via reduced electron scattering or by a decrease of the thermal conductivity λ via enhancement of phonon scattering at a fixed absolute temperature T , leaving the other quantity unchanged or accepting only a slight increase in it; S denotes the so-called Seebeck coefficient. SPD processing has been undertaken with two groups of materials (for a detailed review, see Rogl et al.⁷⁵): (I) Bi-Te alloys for low-temperature applications and (II) skutterudites for high-temperature applications.

The low-temperature thermoelectrics such as Bi-Te alloys exhibit a large crystal anisotropy that is more important for the resultant ZT value than the decrease of grain size leading to a smaller thermal conductivity through additional phonon scattering. HPT processing gave rise to an increased power factor S^2/ρ caused by a (110) texture contributing to both a low resistivity and a high Seebeck coefficient,⁷⁶ whereas a real increase of ZT was achieved by the ECAP procedure⁷⁷ by carefully choosing the ECAP temperature and path to obtain a high carrier mobility, thus minimizing the electrical resistivity and thereby achieving a figure of merit as high as $ZT = 2.3$.

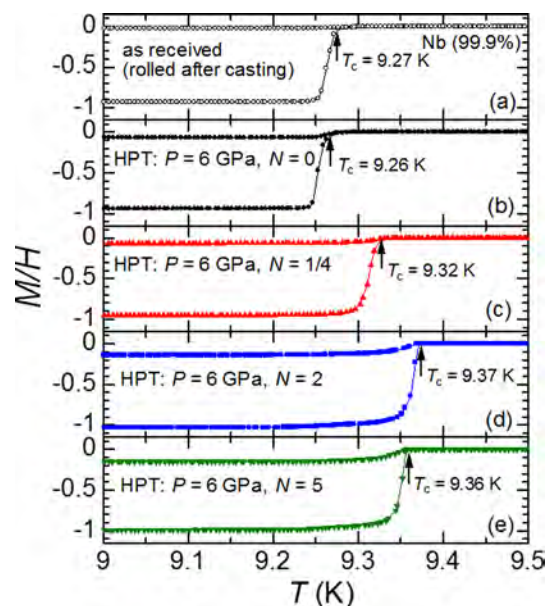


Fig. 6. Temperature dependence of the magnetization $M(T)$ of Nb in the magnetic field $H = 2$ Oe: (a) as-received sample and (b–e) HPT-processed samples with different revolution numbers N .⁸⁹

From high-temperature thermoelectrics, so far skutterudites have been subject to SPD processing, in replacing the conventional hot pressing consolidation of ball-milled skutterudite nanopowder. In applying HPT at a distinctly lower temperature than the conventional hot pressing,⁷⁸ a much smaller grain size and thus significantly lower thermal conductivity could be achieved. However, cracks and voids were also generated and increased the electrical resistivity far more so that the overall ZT dropped. Nevertheless, the latter effect may be avoided by suitably increasing the HPT processing temperature so that ZT was increased by a factor of 2–3^{75,79} (Fig. 5) compared to the value before HPT. Finally, with $ZT = 1.9$, a world record for *n*-type skutterudites was set using this strategy.⁸⁰ Most recently, another world record, $ZT = 1.45$, was also established for *p*-type skutterudites⁸¹ by means of a similar preparation procedure. It should be mentioned that in this case SPD does not introduce new phases and instead there are changes only in the density and arrangement of SPD-induced crystal lattice defects.⁸² These defects, however, show differences in their specific electrical resistivity and lattice thermal conductivity so that aimed modifications of SPD processing with respect to further enhancements of ZT seem possible.

In recent years, it has been shown that superconductivity properties such as the critical temperature T_c , critical current density J_c , and upper critical magnetic field H_{c2} may be affected when the sample size is reduced to the superconducting coherence length (ξ) as a result of the quantum-confinement effect.^{83–85} This encouraged the use of HPT for

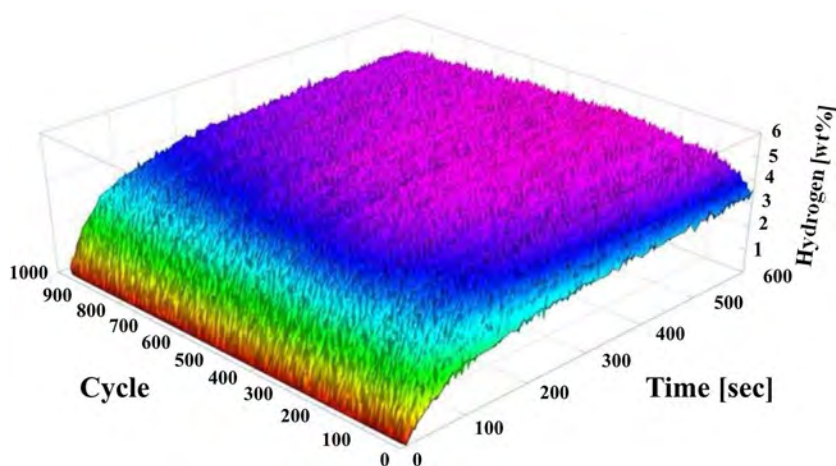


Fig. 7. Long-time characteristics of hydrogen storage (absorption) measured in ECAP-processed ZK 60 alloy.⁹²

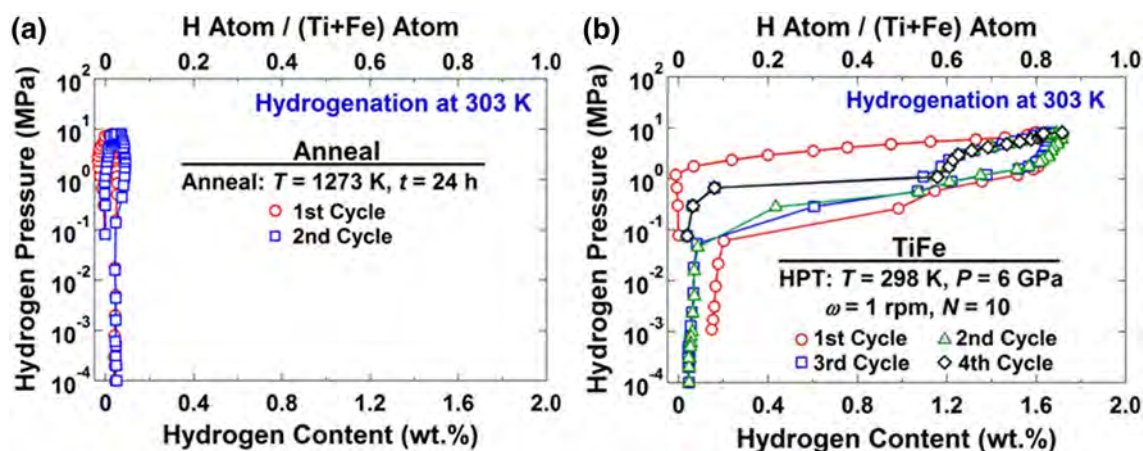


Fig. 8. Pressure–concentration (P–C) isotherms at 303 K for samples processed by (a) annealing at 273 K for 24 h and (b) HPT processing for 10 turns. Fourth cycle in (b) was terminated after absorption for conducting XRD analysis.⁹⁷

examining the effect of grain size on the superconductivity properties, thus reaching grain sizes of ~ 250 nm⁸⁶ in polycrystalline Nb, which is equal to about 5ξ . HPT-induced grain refinement markedly increased the values of T_c , J_c , and H_{c2} , as shown in Fig. 6. The increase in J_c can be attributed to the enhanced vortex pinning on crystal lattice defects such as dislocations and grain boundaries.

The SPD impact on superconductivity was also studied for the Nb-47 wt.% Ti alloy, a well-known system used for superconducting magnets.⁸⁷ T_c decreased with increasing shear strain but rose again with annealing. Although the grain size of the material was comparable with the coherence length (about 8ξ),⁸⁸ the trend of T_c with the imposed strain was opposite to pure Nb⁸⁹ as a result of the dissolution of Ti in Nb with increased HPT straining. The application of HPT in conjunction with subsequent annealing led to an increase in strength while T_c was maintained above the value obtained after solution treatment.

SPD-Processed Hydrogen Storage Materials

SPD processing has been reported to lead to significant improvements in the kinetics of hydrogen storage in metallic materials, mainly those in Mg-based and Ti-based alloys.

The use of Mg-based alloys for hydrogen storage is attractive for on-board mobile applications in the automotive industries because of their light weight.⁹⁰ Not only the fast absorption/desorption kinetics but also the lower operating temperature are important requirements. It has been shown that ECAP processing at least achieves the kinetics of ball-milled, nanostructured, Mg-based alloys with a promise of a simpler, purity-conserving, and low-cost production, free of potential hazards of handling of fine Mg powders (see recent reports^{91,92} and reviews^{93,94}). Furthermore, the stability of the storage capacity and the absorption/desorption kinetics were maintained over a large number of cycles (Fig. 7) even without use of catalysts when the alloys had been processed by ECAP and HPT.^{92,95} It

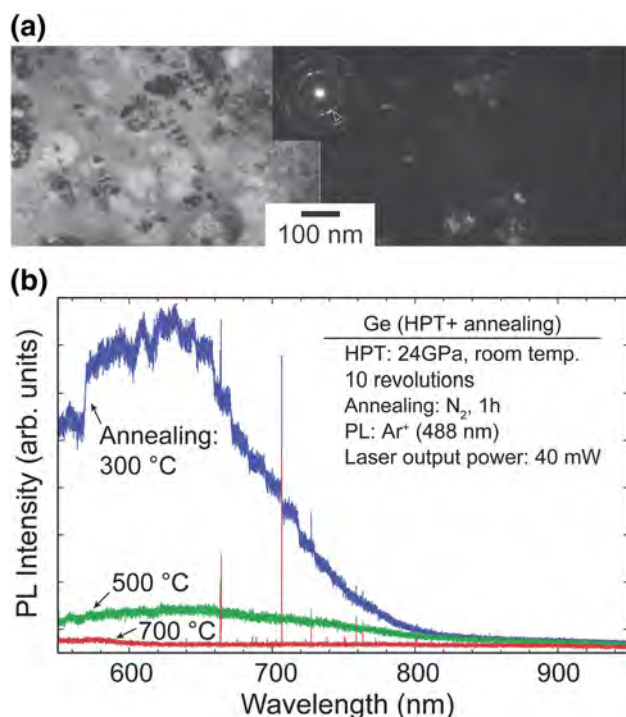


Fig. 9. (a) TEM bright-field (left) and dark-field (right) images and SAED patterns (center) of nanograins after HPT processing for 10 revolutions and successive annealing at 300°C and (b) PL spectra after HPT processing for 10 revolutions and successive annealing at 300°C, 500°C, and 700°C.¹⁰²

turned out that SPD-induced lattice defects other than grain boundaries act as nucleation sites for hydrogenation and that their stability is critical for the overall reproducibility of the absorption/desorption kinetics. Another work studying the hydrogen kinetics in an HPT-processed Mg₂Ni alloy⁹⁶ gave evidence that a high density of HPT-induced planar lattice defects, such as crystallite boundaries and stacking faults, is responsible for the enhancement of hydrogen sorption kinetics.

Among the Ti-based systems, the TiFe intermetallic alloy is a well-known candidate for stationary hydrogen storage. However, its practical application is limited as it requires exposure to hydrogen atmosphere under high pressures at high temperatures. This problem can be eliminated when TiFe is preprocessed by HPT (Fig. 8)⁹⁷ or by other SPD techniques because hydrogen diffusion is facilitated through the introduction of a high density of microcracks and grain boundaries. Furthermore, the HPT-processed sample is not deactivated even after storage in air.⁹⁸

SPD-Processed Nanocrystalline Semiconductors

Over the last several years, considerable progress has also been made in application of SPD to semiconductor materials. In particular, the feature of high pressure as part of the HPT technique has

yielded several attractive results. When crystalline Si is subjected to high pressure, allotropic transformations occur from the original diamond cubic structure (Si-I) to high-pressure phases with different crystal structures. Because such high-pressure phases are semi-metallic in nature, they are more likely to deform plastically at room temperature under high pressure. Thus, the application of HPT gives rise to the formation of nanograins in crystalline Si as a consequence of enhanced dislocation activity or transformation-induced grain refinement. Annealing after HPT leads to a reverse transformation to Si-I while retaining the nanograined structure.⁹⁹ Because nanocrystalline Si exhibits visible photoluminescence (PL) as a result of a quantum confinement effect, a broad PL peak appears centered around 600 nm. The application of HPT to Ge and GaAs also produces nanograins (Fig. 9a),^{100–102} and a similar PL peak is observed owing to the nanograin formation by HPT processing and subsequent annealing (Fig. 9b).^{101,102} It should be emphasized that the nanograined semiconductors were obtained in *bulk* form by virtue of HPT. Thus, HPT processing of semiconductors is of great interest for potential applications to optoelectronic devices.

CONCLUSIONS

The results of recent studies reported in this article demonstrate that various superior properties, both mechanical and functional, can be achieved in bulk nanostructured materials produced by SPD. These results shed light on the mechanisms underlying the special properties of these materials and open up avenues for their practical applications as new structural and functional materials. Recent discoveries have also demonstrated new opportunities for SPD processing with respect to improving the physical and chemical properties of materials. These include increased electrical conductivity, superconductivity, and thermoelectricity in metals and alloys; improved hydrogen storage capability; enhanced biocompatibility; and many other unique phenomena that are of interest for various functional applications.

As shown in this overview, over the last decade a solid scientific foundation has been laid for enhancing the properties of materials by SPD-induced nanostructuring through extensive research. A greater understanding has been gained of the defining role of the grain boundary structure and further nanostructural features, such as nanoclusters, nanoparticles, and nanotwins, on the deformation properties and diffusion transport mechanisms. These nanostructural features are closely related to the regimes of SPD in which they were produced as a result of extreme straining, high pressures, and/or unusual phase transformations. With this new knowledge, it is reasonable to anticipate that, in the not-so-distant future, nanostructural design by

SPD processing will provide new breakthroughs in the development of various materials with superior properties for advanced structural and functional applications.

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Synergetic strengthening far beyond rule of mixtures in gradient structured aluminum rod

Jordan Moering^a, Xiaolong Ma^a, Jacob Malkin^b, Muxin Yang^c, Yuntian Zhu^{a,d}, Suveen Mathaudhu^e

^a Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695, USA

^b North Carolina School of Science and Mathematics, Durham, NC, USA

^c State Key Laboratory of Nonlinear Mechanics, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, PR China

^d School of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, People's Republic of China

^e Department of Mechanical Engineering, University of California, Riverside, CA, 92505, USA

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ABSTRACT

Gradient structured metals have been reported to exhibit high strength and high ductility. Here we report that the strength of gradient structured aluminum rod is much higher than the value calculated using the rule of mixtures. The mechanical incompatibility in the gradient structured round sample produced 3D stress states, extraordinary strengthening and good ductility. An out of plane {111} wire texture was developed during the testing, which contributes to the evolution of the stress state and mechanical behavior.

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Metals exhibiting gradient microstructures have recently become the focus of research for their remarkable ability to produce a superior combination of strength and ductility in metallic systems [1–3]. Gradient structures can be defined as microstructures with macroscopic gradients in one or a combination of the several types of microstructural features including, but not limited to, grain size [1–5,7–9], texture [4], dislocation density, twin density [6], precipitates, etc. The most common and well studied gradient structure is grain size gradient structure [1–5], which often consist of nanocrystalline or ultrafine grains at the surface of a tensile sample, which gradually transition to coarse grains in the interior over distances of ~50 μm or longer. Although the means by which gradient microstructures can be created include Surface Mechanical Grinding Treatment, Surface Mechanical Attrition Treatment (SMAT), Ultrasonic Shot Peening [11], Wire Brushing [12], and Air Blast Shot Peening [13], most of the seminal work was undertaken with SMAT [1,10,12,14–16]. Much like conventional shot peening, SMAT uses round balls to repeatedly impact the surface of a material. However, the number of impacts and the energy of impacts is often much greater, leading to surface grain refinement to the nanocrystalline regime.

Gradient structures synthesized by SMAT or other approaches are relatively well characterized, but their general effect on global mechanical response is poorly understood. For example, SMAT of IF Steel improved the yield strength by a factor of ~2.5 while the ductility was

only reduced by ~15% [2]. However, SMAT of pure iron led to similar strength improvements, though ductility was reduced by >50% [15]. In general, yield strength is universally improved in gradient structures, though it seems ductility can either decrease [15], remain more or less unchanged [3], or increase [1]. The discrepancy, in part, must be explained by the mechanism or mechanisms by which gradient structures deform and has been attributed to grain growth, dynamic hardening, strain partitioning, and dislocation accumulation at grain boundaries, to name a few [1,2,16–18]. One mechanism that has been experimentally verified is the evolution of a multi-axial stress state during tensile testing of the gradient structure [3]. The stress state evolution necessarily rises due to mechanical incompatibility of the hard surface layer and ductile core, and has been observed in flat gradient structures [2,3]. The net result of this interaction is that the applied 1D tensile stress is converted into a 2D stress state in flat gradient structures during uniaxial tensile deformation. However, in round samples, the ductile core is fully confined by the hard shell and unable to contract in the early tension stage like flat samples due to the lack of freestanding directions. This should lead to a more complex stress state upon loading and could have a greater strengthening effect compared to flat samples [19].

Here we report that gradient structured aluminum rods processed with SMAT have strength that is twice as high as what is predicted by the rule of mixtures, which is dramatically higher than the synergetic strengthening observed in gradient-structured flat samples [3]. To

probe the mechanisms behind this surprising observation, the gradient structures of round samples are characterized and the texture evolution was studied with EBSD to explore the stress state evolution during tensile testing.

1350 Al wire was used for this study and was machined into tensile specimens with a gauge diameter of 5 mm and a gauge length of 20 mm. The samples were annealed (O tempered) at 370 °C for 21 h under vacuum to produce homogenized, coarse grains. This annealing also produced a recrystallized cube texture, which was confirmed with Electron Back Scattered Diffraction (EBSD). The SMAT treatment was conducted using a modified SPEX Mill for 5 min using 7 stainless steel balls 6 mm in diameter. By nature of the randomized impacts, the tensile sample was free to rotate in the vial and exhibited uniform deformation across the gauged section. The resulting “as-SMAT” sample was cross sectioned and prepared for imaging by conventional polishing techniques and ion milling for 45 min. EBSD data was acquired with an Oxford EBSD detector installed in the dual Beam FEI Quanta 3D FEG. Microhardness testing was conducted on the ion polished surface using a Mitutoyo Model HM-11 with a Vickers diamond indenter at a load of 0.001 N. An average of 10 indentations was used for the microhardness profile and Kikuchi patterns from EBSD revealed the prepared sample was free from polishing damage. Fig. 1 shows the gradient structure produced by the SMAT surface, the tensile test results, and the resulting hardness profile from surface to interior

As can be seen in Fig. 1, the O tempered aluminum exhibited a yield strength of 27 MPa which is dramatically increased to 59 MPa after SMAT treatment. Examining the cross section of the as-SMAT sample, it is clear that a deformation gradient, characterized by dislocation accumulation and subgrain boundaries, extends to a depth of ~250 μm from the surface. However, the microhardness results show that the hardened layer extends to a depth of 600 μm from the surface, and the hardness of the surface layer is only improved by ~50%. In order to surmise the effect of the hardened surface layer, rule of mixtures estimations were calculated using hardness data and the volume fraction of each hardened layer, shown to scale in Fig. 1E. This rule of mixtures analysis has been successfully used in other gradient samples to further reveal the hardening effect of the surface layer [1,16].

There is some debate in the community regarding the relationship between microhardness, yield strength, and ultimate tensile strength.

The initial construction by Tabor predicted yield strength in the absence of strain hardening, and found the commonly used empirical relationship, $3\sigma_y = Hv$ [20]. When including the effects of strain hardening for soft aluminum alloys, various models have been proposed, but the raw data deviates very little from a linear relationship when plotted manually [21,22]. In addition, there is also strong experimental evidence corroborating the linear relationship between microhardness and yield strength in 1000 series aluminum [22–27]. Some data show a deviation in the linear relationship between σ_y and Hv in the softened state, but assume a y-intercept of zero, which is not necessarily consistent with experimental results, where y-intercepts of >100 have been reported [28,29]. Therefore, it can generally be assumed that yield strength and microhardness measurements are proportional such that

$$\sigma_y = KHv,$$

where K is a constant, which may deviate from 3. Therefore, rule of mixtures predictions can be written as follows:

$$\frac{\sigma_{gs}}{\sigma_{cg}} = \frac{K \sum V_f H_{gs}}{K H_{cg}} = \frac{\sum V_f H_{gs}}{H_{cg}}$$

where σ_{gs} is the yield strength of the gradient structured rod, σ_{cg} is the yield strength of the coarse grained O tempered rod, H_{gs} is the hardness of each layer in the gradient and its respective volume fraction, V_f , and H_{cg} is the hardness of the coarse grained O tempered rod. Examining the data, we see that

$$\frac{\sigma_{gs}}{\sigma_{cg}} = 2.2; \quad \frac{\sum V_f H_{gs}}{H_{cg}} = 1.1$$

Therefore, there is significant strengthening that is not accounted for by rule of mixtures predictions.

To examine possible strengthening mechanisms at hand, the SMAT-produced microstructure gradient was characterized in cross section using EBSD. Fig. 2 shows various maps of the aluminum sample and the inverse pole figures of local areas. Typical deformation structures in aluminum can be seen at various depths, including subgrain boundaries, slip bands, and dislocation cells. Although the grain size has not

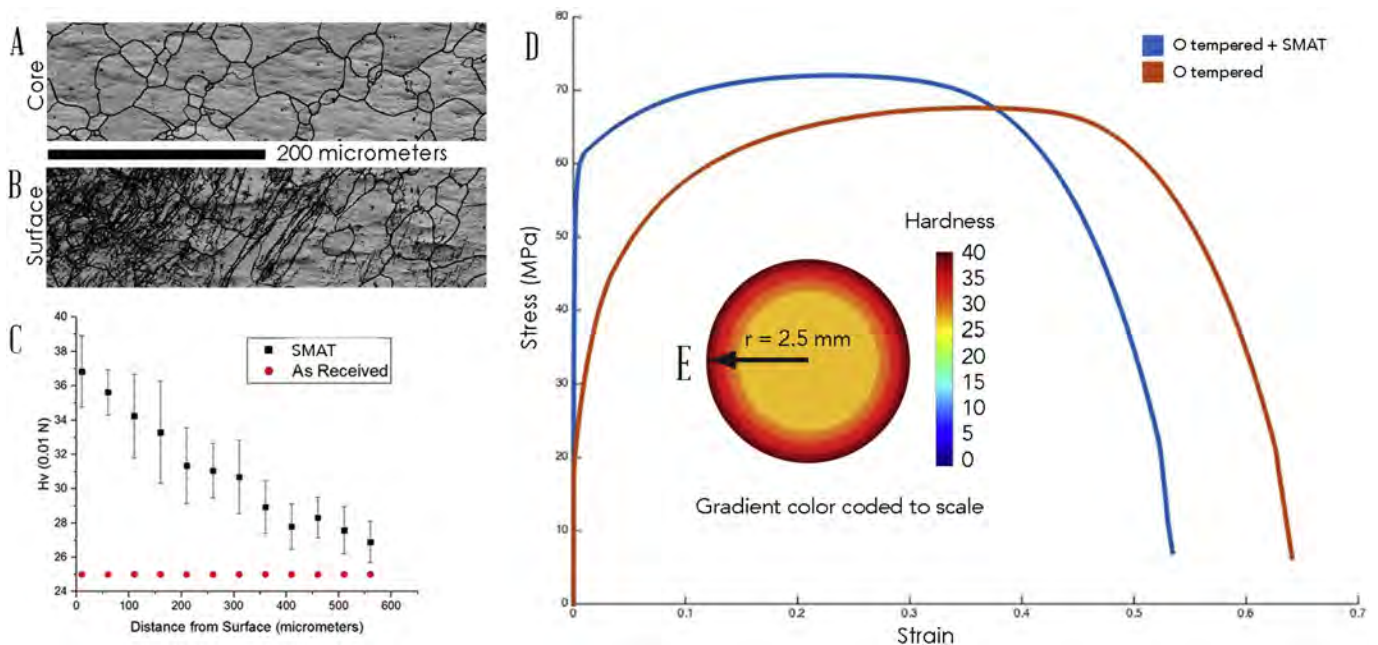


Fig. 1. (a) EBSD map of the O tempered aluminum and (b) after SMAT processing. (c) Microhardness profile at various depths and (d) Tensile test results of the SMAT and as-annealed samples with arrow indicating the rule of mixtures prediction of yield strength. (e) Color coded hardness map showing depth of the gradient to scale.

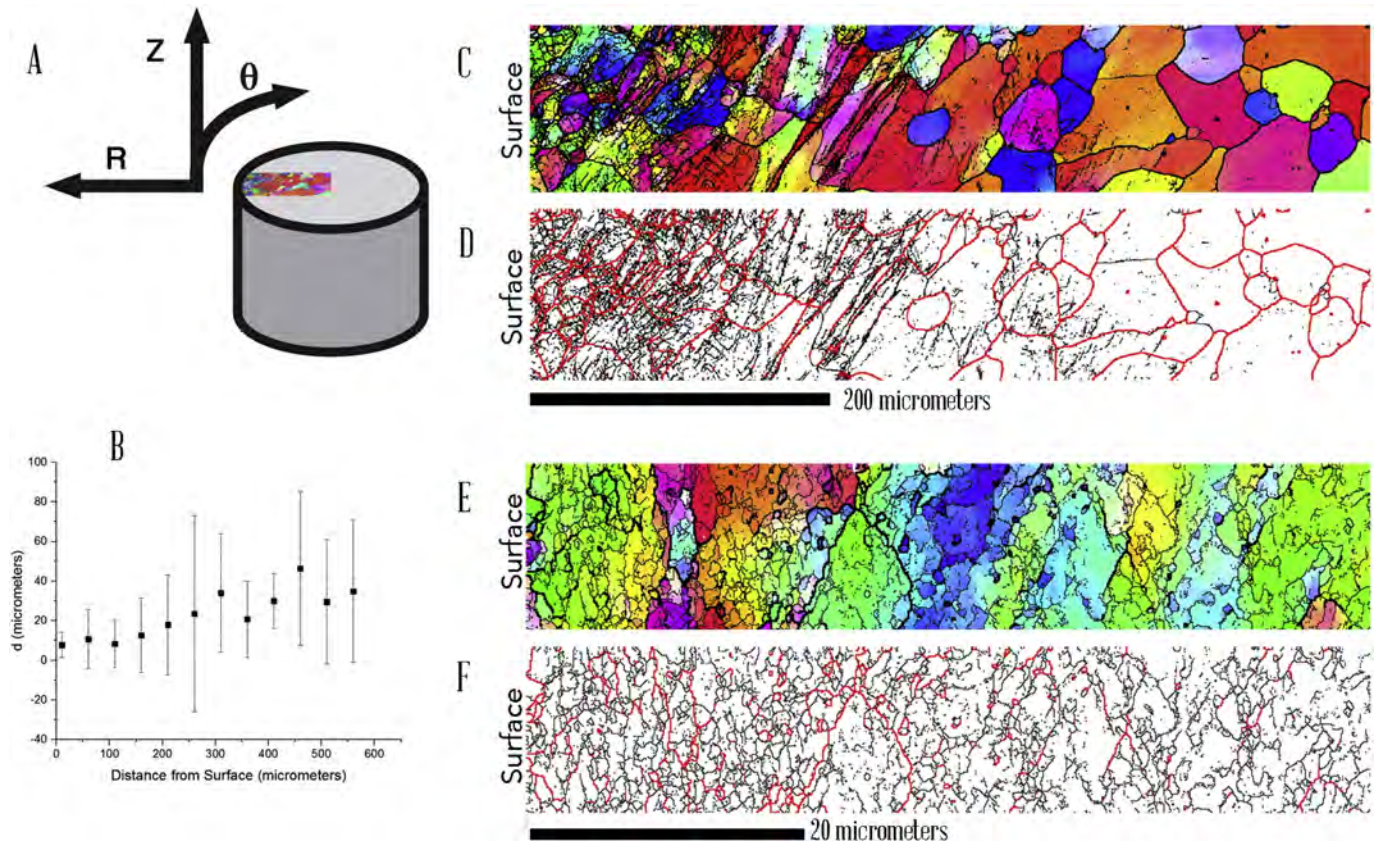


Fig. 2. (a) Convention used for axis of the round SMAT sample along the surface normal (R), tensile direction (Z), and radial direction (θ). (b) Grain size gradient. (c and d) EBSD map of the SMAT sample projected along Z and grain boundary map, respectively. For the grain boundary maps, red lines indicate misorientation of $>10^\circ$ and the black lines indicate misorientations $>2^\circ$. (e and f) High resolution EBSD map of the very top surface layer showing numerous subgrain boundaries when projected along Z and its grain boundary map, respectively.

been reduced to the nanocrystalline regime, magnification of the surface in Fig. 1 (e–f) shows the subgrain boundary size approaches $\sim 3 \mu\text{m}$. These subgrain boundaries are typical of the early stages of SMAT processing, and have been observed in samples subjected to small revolutions of High Pressure Torsion (HPT) [10,30]. However, the degree of grain refinement is quite mild at the surface of the SMAT sample which correlates well to the mild improvement in hardness at the surface, as seen in Fig. 1.

Beyond the microstructure, there could be other mechanisms that improve the strength of the SMAT sample. It is well known that SMAT samples exhibit high compressive residual stresses, and can develop multiaxial stress states in tension [31,32]. In fact, strengthening from both the initial stress state and the stress state evolution would not be accounted for in the rule of mixture predictions since this model neglects transverse stresses and interaction between layers within the gradient. It is well known that the compressive residual stresses in SMAT structures can exceed the yield strength of the coarse grained core by a factor of 3 and extend to depths of nearly 1 mm [31,33]. In shot peening, similar compressive stresses were shown to increase the yield strength of samples by $\sim 2\times$ and therefore some of the hardening beyond rule of mixtures can be accounted for by this phenomenon [5]. In some cases, 40% of the strengthening of gradient structures has been attributed to this residual stress [34]. In addition to this effect, the multiaxial stress evolution, which arises from the mechanical incompatibility between early-plastic and stable elastic regions, should also contribute to strengthening [2]. At low strains, the stress applied will exceed the yield strength of the coarse grained region, inducing plastic deformation while the surface is still deforming elastically. As the inner region attempts to contract, the surface must develop a compressive stress to remain coherent with the shrinking interior, and this phenomenon has been observed experimentally in flat samples [2,3].

In round samples, however, the gradient confines the interior layer, creating 3D internal stresses. Direct observation of the strain accumulation within the gradient is not possible with round samples as with flat samples. Using EBSD, it is possible to get clues about the deformation mechanism of the gradient structure by examining the post-mortem microstructure of the SMAT sample.

In order to investigate the stress state evolution of the gradient layer, samples were taken from the post-mortem “as-annealed” and SMAT samples from the uniformly elongated region to compare the microstructure using EBSD. Because the texture symmetry depends on the deformation symmetry, the texture evolution gives insight to the stresses evolved during yielding. If out of plane stresses are operating on the gradient, then the symmetry of these stresses should be evident in the pole figures. After tensile testing, as seen in Fig. 3, the post-mortem EBSD maps clearly differed, and the Z and θ {111} and {110} axis projection pole figures of the top layer of both samples showed a similar symmetry but the SMAT sample showed out of plane texture symmetry.

In the as-annealed sample, the Z projection pole figure shows some {111} character, and some symmetric “smearing” of the {110} about the tensile (Z) axis, all of which is the common texture seen in uniaxial drawing of aluminum [35–37]. Interestingly, the pole figures from the SMAT sample show a similar symmetry, but not around the tensile axis as seen in Fig. 3F. It is clear from the pole figures that the θ direction develops a similar wire texture to Z direction of the as-annealed sample. This out of plane texture is evidence that a multiaxial stress state evolves during tensile testing that is not present in samples lacking gradient structures. The mechanical mismatch between the hard surface and ductile core causes these multiaxial stresses to develop as the gradient is deforming, causing non-uniform deformation and enhanced strengthening while maintaining good ductility.

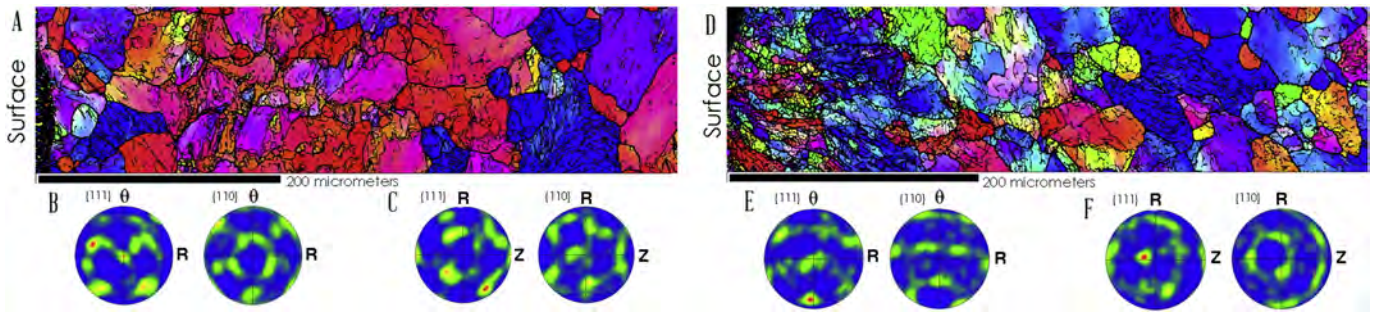


Fig. 3. a) Z projection EBSD map of the uniformly elongated “as-annealed” sample after tensile testing and corresponding pole figures showing b) Symmetric smearing of {110} about the tensile (Z) axis and c) θ axis projection. d) Z projection EBSD map of the uniformly elongated SMAT sample after tensile testing and corresponding pole figures projected along e) the Z axis and f) the θ axis. There is a clear symmetry that develops along the θ axis in the post-mortem SMAT sample not present conventional samples.

Despite the evidence of out of multiaxial stress state evolution, it is very difficult to discern the primary strengthening mechanism of this gradient structured aluminum alloy. It was not possible to quantify the residual compression, which has been shown in some cases to greatly affect mechanical performance [5,34]. In addition, the effect of residual stresses on the microhardness testing could skew the hardness due to the compression at the surface and tension in the core. Another factor that could increase the yield strength is the high back stress developed at the plastic-elastic interface of the gradient structure [18]. Also, although the linear relationship between hardness and yield strength was used to predict rule of mixtures calculations in this study, the high rate of strain hardening in aluminum could introduce error into this prediction especially in the measurements of the ductile core and this analysis was used only as an approximation for the gradient structure yield strength. Further studies should explore these confounding effects in more detail to elucidate the strengthening mechanisms in gradient structured aluminum rod. Further, deviations in strength predictions from the rule of mixtures model should be investigated, since this model neglects multiaxial stresses which have been reported here and elsewhere to be non-trivial role in strengthening [3].

Our data demonstrate that aluminum treated by SMAT exhibits a yield strength far beyond what is predicted by rule of mixtures. The gradient structure produced by SMAT-produced some improvement in hardness and EBSD maps showed the hardening is accompanied by dislocation accumulation, subgrain boundaries, and very little grain refinement. EBSD of the post-mortem samples showed that the gradient structured aluminum developed an out of plane texture that indicates a complex, multiaxial stress evolution during tensile testing that is not present in its coarse grained counterpart.

Unlike previous reports of gradient structures where increased strength and ductility were attributed to grain growth, dislocation accumulation at grain boundaries, and other mechanisms, this report provides evidence that strengthening in round SMAT samples is due to both the complex initial stress state of the material as well as the dynamic strain hardening that occurs within the mismatched layers, which produced 3D complex stress states. These effects lead to synergistic strengthening far beyond of what is predicted by the rule of mixtures in gradient structured rod. Further investigation of the residual stress effect and stress state evolution in gradient structures should shed light on the magnitude of contributions by these strengthening mechanisms.

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Full length article

Mechanical properties of copper/bronze laminates: Role of interfaces



Xiaolong Ma^a, Chongxiang Huang^{b, **}, Jordan Moering^a, Mathis Ruppert^c,
Heinz Werner Höppel^c, Mathias Göken^c, Jagdish Narayan^a, Yuntian Zhu^{a, d, *}

^a Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC, 27695, USA

^b School of Aeronautics and Astronautics, Sichuan University, Chengdu, 610065, China

^c Department of Materials Science and Engineering, Institute I: General Materials Properties, Friedrich-Alexander Universität Erlangen-Nürnberg, Martensstr. 5, 91058, Erlangen, Germany

^d School of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing, 210094, China

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ABSTRACT

Interfaces play a crucial role in mechanical behaviors of both laminated and gradient structured materials. In this work, copper/bronze laminates with varying interface spacing were fabricated by accumulative roll bonding and subsequent annealing to systematically study the interface effect on mechanical properties. Heterogeneities exist in chemical composition, grain size, hardness and texture across the interfaces. Simultaneous improvement of strength and ductility with decreasing interface spacing is found in tensile tests. Extra geometrically necessary dislocations (GNDs) are found to accumulate in the vicinity of interfaces, which is due to mechanical incompatibility across the interfaces. Importantly, an interface-affected zone spanning a few micrometers was found, which is not affected by interface spacing. These observations suggest the existence of an optimum spacing, which may produce the highest hardening capacity and ductility without sacrificing strength.

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1. Introduction

Laminate and gradient structured metals have recently attracted extensive interests in the materials community for their potential in achieving outstanding mechanical properties [1–6]. Fang et al. and Wu et al. reported that gradient structures with nanocrystalline surface layers and coarse-grained interior produced a superior combination of strength and ductility [1,5,7]. Wu et al. reported that heterogeneous lamella-structured pure Ti possessed both the high strength of ultrafine grains and the decent ductility of the coarse grains [8]. Both laminate and gradient structures contain interfaces, across which there are differences in chemical compositions and/or microstructures, such as grain sizes and crystallographic orientations (texture) [9–11]. Interfaces were believed to significantly contribute to the observed high strain hardening and ductility in both laminate and gradient materials [3,12–15]. Kümmel et al. [16] attributed this to an additional grain refinement

caused by an increasing number of interface, which, however, is not an intrinsic effect from interfaces. Some researchers proposed that gradient distribution of stress near the interface enhances working hardening in multi-layered and gradient structured metals [3,17–19]. Wu and Zhu found that strain gradient and the associated back-stress strengthening near the interfaces played a critical role in the high strength and high strain hardening rate [5,8,20,21].

Early literatures have linked microstructural heterogeneity with strain gradient evolution and subsequent generation of geometrically necessary dislocations (GNDs) during plastic deformation [22–25]. Applying this general theory to laminates, Ashby et al. developed a reciprocal relationship between the average GND density and interface spacing in an idealized laminate structure with a single crystal matrix and equally spaced rigid plate-like particles [22]. However, this theory was based on simple assumptions, which does not represent real complex materials very well. In fact, laminate components are mostly engineered from polycrystalline matrix and none of them are absolutely rigid [26,27]. Additionally, the details of GND density configuration and their dependence on interface spacing are not well described in the conventional theory and have been rarely investigated experimentally. These issues are critical to understanding the fundamental mechanisms and imperative to practical material design.

* Corresponding author. Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695, USA.

** Corresponding author. School of Aeronautics and Astronautics, Sichuan University, Chengdu, 610065, China.

E-mail addresses: chxhuang@scu.edu.cn (C. Huang), ytzhu@ncsu.edu (Y. Zhu).

For example, to what extent and distance does an interface exert influence during deformation? Does the width of the interface-affected zone depend on the interface spacing/layer thickness? Very few systematic studies have been reported to explore these issues.

It has been a grand challenge to investigate the aforementioned issues through direct experimental observations. First, in gradient structures, the microstructural interfaces also act as elastic/plastic and necking/stable interfaces during tensile testing. Thus, rather than being stationary, those interfaces migrate dynamically across the samples during deformation due to the strength/ductility gradient, which makes it difficult to identify or track them experimentally [1,5,7]. Second, even for laminate structures with stationary interfaces, it is not trivial to fabricate samples with varying interface spacing and also with similar microstructure across the interface in terms of the grain size and texture. For example, the majority of laminate metallic structures fabricated by accumulative roll bonding (ARB) always have finer microstructures with increasing rolling cycles [28,29]. Furthermore, even atomic structure of interface might change with decreasing interface spacing [4,30]. To effectively probe the effect of interfaces on mechanical performance, identical or very similar interfaces and interfacial structures with varying interface spacing are needed. Third, it is technically difficult to determine the deformation characteristics, such as dislocation density and their evolutions, near the interface using conventional approaches such as transmission electron microscopy (TEM) because of the inhomogeneous nature of dislocation slips [31].

In the present study, copper and bronze (Cu-10 wt%Zn) laminates with varying interfacial spacing were fabricated using ARB processing and post-annealing. These samples have maintained almost the same level of microstructural difference across their interfaces. Using ex-situ electron back-scattering diffraction (EBSD) technique, the deformation history of interface regions under tension were successfully recorded, which revealed how and to what extent do these interfaces affect GND activities [32–34]. Unloading-reloading tension tests were performed to further confirm the role of the interfaces in back stress evolution.

2. Experimental methods

Commercial pure copper (ASM-C11000) and bronze (ASM-C22000) were selected for this work. The chemical compositions and general mechanical properties of these raw materials are listed in Table 1 [35,36]. The advantage of these two materials is their similar elastic constants so that we don't have to consider the effect of elastic mismatch. 1 mm-thick raw copper and bronze sheets were ARB-processed with 2, 3 and 5 cycles to achieve 4, 8 and 32 layers, respectively. Prior to each ARB cycle, the sample surfaces were cleaned by acetone and then wire brushed in order to remove oxide layer and to ensure a well-defined surface roughness and

sufficient bonding strength. Subsequently, the two treated surfaces were stacked with an alternate sequence of copper and bronze, and roll-bonded at room temperature using a four high rolling mill (BW 200, CarlWezel, Mühlacker, Germany) at a nominal thickness reduction of 50% per cycle. The bonded sheets were air cooled and halved before performing the next cycle. The edge regions where sheets tend to tear from each other were cut away and the central part with good initial bonding strength was used for following processing. Details of ARB processing can be found in early works [26,37]. The as-ARB processed samples were annealed together at 250 °C for 2 h in a vacuum tube furnace under argon atmosphere and thereafter labeled as N2, N3 and N5, respectively.

Samples for Ion Channeling Contrast Microscopy (ICCM), micro-hardness testing and EBSD observation were first cut from the annealed samples and then mechanically polished to achieve a mirror-like surface. Electrochemical polishing was then performed for <30 s to remove the strained top-surface layer that may affect following tests. The electrolyte consisted of a phosphoric acid (concentration of 85%), ethanol and deionized water with a volume ratio of 1:1:2. ICCM and EBSD were conducted under an FEI Quanta 3D FEG dual-beam instrument. Texture analysis was based on EBSD maps with a view area of $30 \times 100 \mu\text{m}^2$ to capture the global characteristic. For local misorientation mapping, each EBSD scan was performed under 30 kV and 16 nA electron beam and with a bin size of 2×2 to achieve a decent angular resolution [38,39]. Scan step size was set at 100 nm to ensure appropriate spatial resolution.

TEM foils were prepared by mechanically polishing specimen to a thickness of $\sim 30 \mu\text{m}$, followed by ion milling to perforation. The milling process was performed at $-50 \text{ }^\circ\text{C}$ to avoid potential grain growth. TEM observation was performed in a JEM-2010F microscope operating at 200 kV at room temperature. Dog-bone shaped tensile samples with a gauge dimension of $10 \times 2 \times 1 \text{ mm}^3$ were machined from the annealed sheets and tested under uniaxial tension on a Shimadzu AGS machine. Both normal and unloading-reloading tension tests were carried out at room temperature at a strain rate of $9 \times 10^{-4} \text{ s}^{-1}$ and each test was repeated for at least 3 samples to ensure data reproducibility. Ex-situ EBSD mapping in the interfacial region was carried out on the same specimen at three strain levels: 0%, 3% and uniform elongation strain. The interfacial region of interest was carefully marked by a milling feature.

3. Results

3.1. Microstructures

Fig. 1a–c are the optical microscopy images of all sample, which show clearly well-defined laminate structure with uniform layer thickness and varying interface spacing. The red color indicates the copper layers. The layer thickness for N2, N3 and N5 samples are 250, 125 and 31 μm , respectively. ICCM micrographs (Fig. 1d–f) reveal similar microstructures in all samples subjected to different ARB cycles. Coarse copper grains with considerable annealing twins are observed in all N2, N3 and N5 samples. The annealing twins were formed by recrystallization during annealing, which is further confirmed by texture analysis later. In contrast, the bronze layer maintained largely the rolling structure in all samples due to its higher thermal stability. Fig. 1 shows slightly larger grain size in the bronze layer of the N2 sample than in the N3 and N5 samples. This is probably resulted from the relatively low rolling strain in the N2 sample. However, as shown later, the differences in their hardness and texture are not significant. Small quantities of nanocrystalline bronze grains were locally dispersed in the vicinity of the interfaces, which is observed in all samples under ICCM.

Table 1
Chemical compositions and general material properties of raw materials [35,36].

	Chemical compositions (wt.%)					
	Cu	Pb	Fe	O	Zn	Others
Copper	≥ 99.90	–	–	0.04	–	≤ 0.06
Bronze	89.0–91.0	≤ 0.05	≤ 0.05	–	10.0	–
	Material parameters					
	a (Å)	γ_{SF} (mJ/m ²)	E (GPa)	ν	G (GPa)	
Copper	3.61	45	115	0.324	44	
Bronze	3.64	35	115	0.307	44	

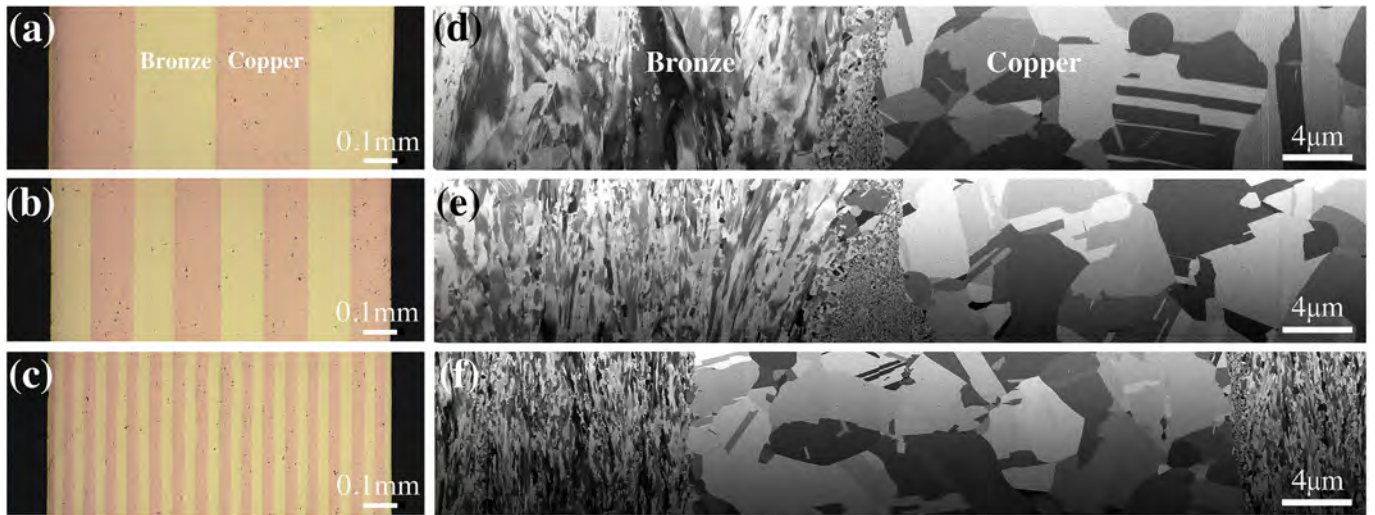


Fig. 1. Optical microscopy of (a) N2, (b) N3, (c) N5 samples, respectively. It clearly shows the inter-layer contrast and the interface spacing. Ion channeling contrast microscopy images of microstructures at copper/bronze interfaces in (d) N2, (e) N3 and (f) N5 samples.

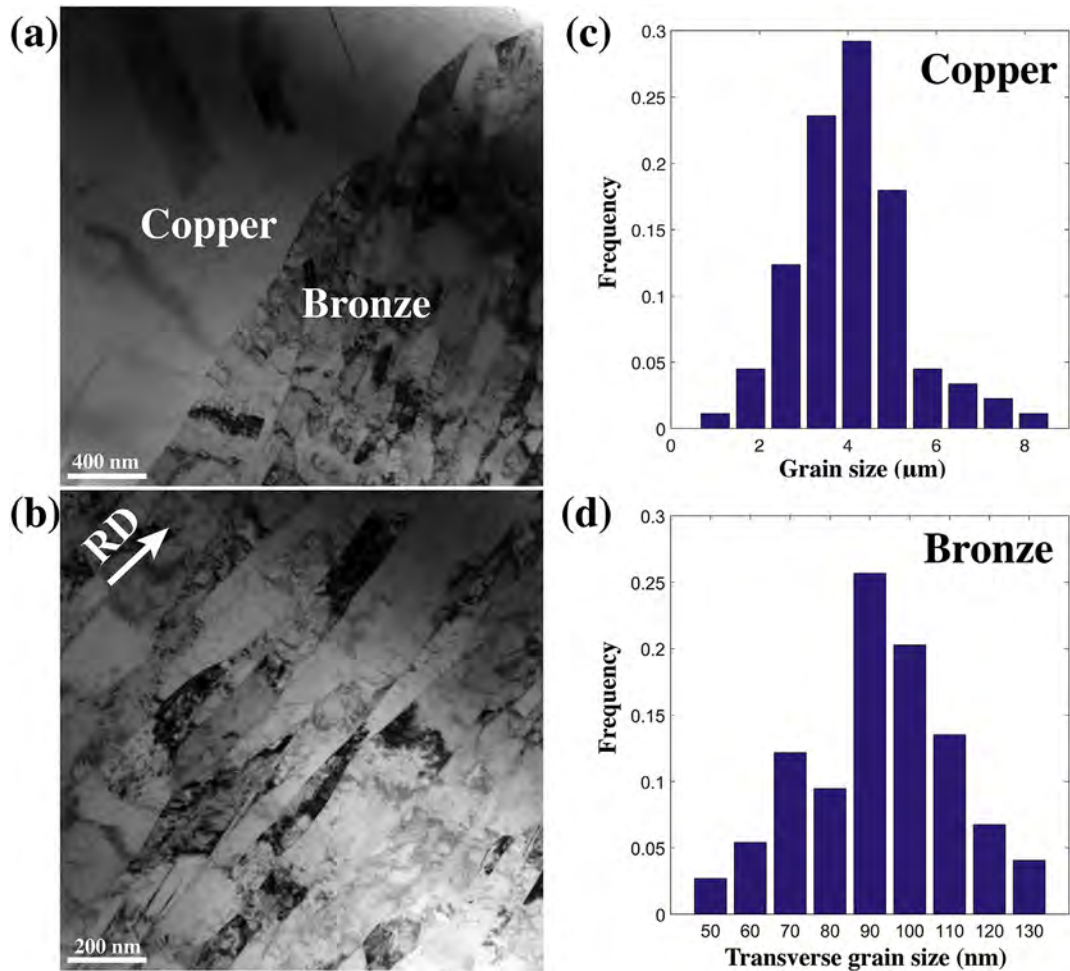


Fig. 2. (a) TEM micrograph of a copper/bronze interface in the ARB N5 sample shows well-bonded interface and big grain size difference across it. (b) Retained rolling microstructure in the bronze layer. The arrow indicates the rolling direction. (c) Grain size distribution in the copper layers based on ICCM images. (d) Transverse grain size distribution in bronze layers based on TEM micrographs.

3.2. Heterogeneity across interfaces

A representative copper/bronze interface in the N5 sample is shown in Fig. 2a, which reveals a transition from coarse-grained copper to nanostructured bronze across the interface. Clearly, the recrystallized coarse-grained Cu grains are much larger and exhibit less dislocation contrast than the bronze layer. The latter still exhibit a deformed microstructure. Fig. 2b shows more microstructural details in the bronze layer, which reveals elongated grains along the rolling direction as well as dislocation cells and areas with high dislocation density. The statistical distributions of (transverse) grain sizes in the copper and bronze layers are shown in Fig. 2c and d, respectively. As shown, the bronze layer has an average feature size of ~100 nm, while the copper layer has an average grain size of ~5 μm . Such grain size and composition difference are expected to produce a significant mechanical incompatibility across the interface.

The microstructural and compositional difference across the interface led to sharp difference in hardness. As shown in Fig. 3a, the nanostructured bronze layer has a hardness of ~1500 MPa, which is more than twice that in microcrystalline copper layer (~700 MPa). It is noted that the micro-hardness of both copper and bronze layers are very close in all samples, given the measurement errors, despite varying interface spacing. Crystallographic orientation (texture) was also found to differ remarkably across the interfaces. As shown in Fig. 3b, copper exhibits a strong cube texture component $\{001\}\langle 100\rangle$, which is resulted from both recrystallization and grain growth [40]. In contrast, bronze shows $\{110\}\langle 112\rangle$

texture with slight variation [40,41], which is consistent with previous reports of brass-type rolling texture in FCC alloys with low stacking-fault energy [42]. Post-annealing after ARB did not change the rolling texture of the bronze layer much, which is consistent with the TEM observation of rolling microstructure in Fig. 2. Note that the present pole figures are scanned from the N3 sample, but N2 and N5 exhibit similar textures in the copper and bronze layers.

The above observations indicate that the ARB processing and appropriate annealing produced interfaces with varying spacing but similar microstructure, micro-hardness and texture. This allows us to study the interface effect on the mechanical properties without complications from other structural factors.

3.3. Uniaxial tensile tests

Fig. 4a shows the tensile stress-strain curves for N2, N3 and N5 samples. Inset is a photograph of a sample. As shown, both the strength and uniform tensile elongation (ductility) increased with decreasing interface spacing. Interestingly, the yield strength did not increase as much as the ultimate strength, indicating that decreasing the interface spacing is more effective in enhancing the strain-hardening rate than yield strength. Fig. 4b summarizes the variation of ultimate strength and ductility, which confirms their reproducibility. It's worth noting that some earlier ARB studies also reported similar simultaneous improvements in strength and ductility with increasing rolling cycles, but most of these studies attributed this phenomenon to microstructure change instead of the interface spacing [29,43,44].

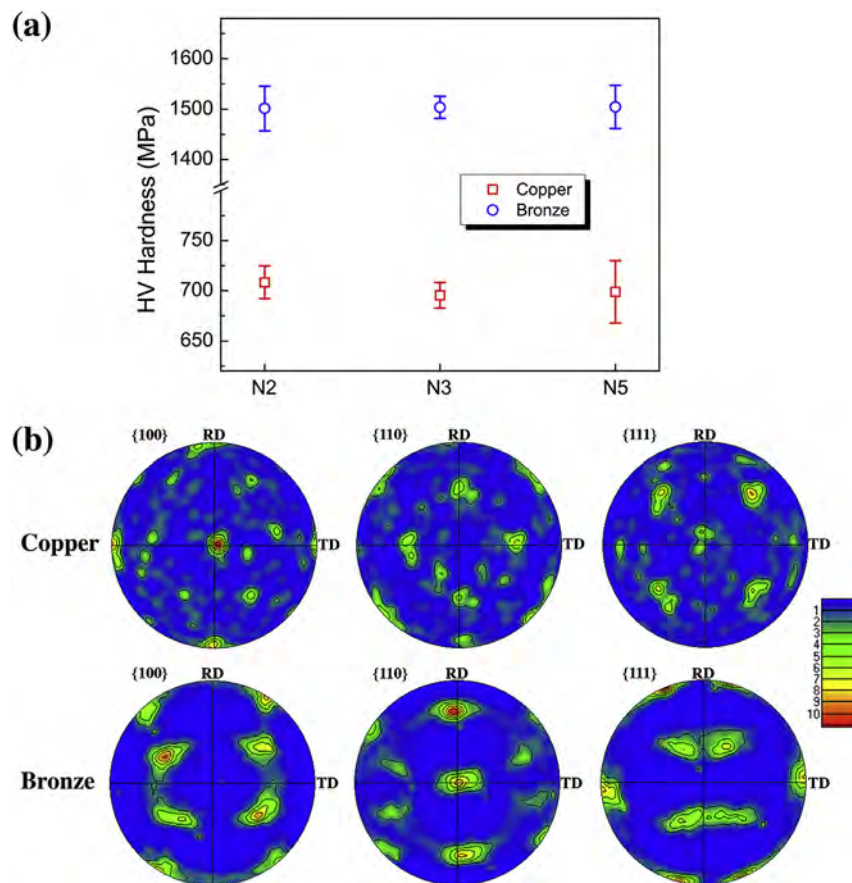


Fig. 3. (a) Micro-hardness (with a 15 g load) in both the copper and bronze layers in N2, N3, N5 samples after annealing. (b) $\{100\}$, $\{110\}$, $\{111\}$ Pole figures in both copper and bronze layers in N3 sample after annealing, showing a strong cube texture and a brass-type texture with slight deviation, respectively. N2 and N5 have similar texture characteristics.

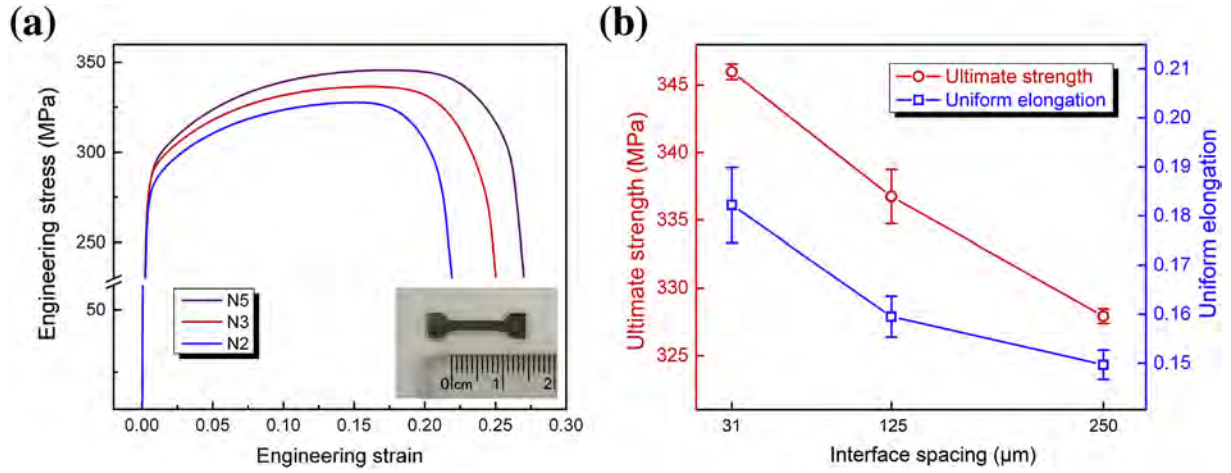


Fig. 4. (a) Tensile curves of N2, N3 and N5 samples show simultaneous increase of strength and elongation with increasing number of layers. (b) Summary of tensile results. Error bars represent standard deviation from at least 3 data sets.

3.4. Ex-situ EBSD mapping and GND characterization

Fig. 5 shows EBSD inverse pole figure mappings of the copper layers along the transverse direction, at zero strain, 3% tensile strain and uniform elongation strain for each sample. Arrows indicate interfaces. Generally, the indexing rate is more than 97% even for copper grains near interfaces, making following interfacial analysis reliable. For the N5 sample, the whole copper layer is captured because it is thin. For each sample, the local crystal orientation in a region near an interface was measured at the above selected tensile strains to study the GND evolution. In this study, we used the kernel average misorientation (KAM) method to determine the local

misorientation from the EBSD orientation data [34]. First, we defined the limit of the general grain boundary misorientation as 3° . Any misorientation greater than this value was excluded in local misorientation calculation since it is caused by a grain boundary, not by GND accumulation. The local misorientation of every single point ($100 \times 100 \text{ nm}^2$) was then determined by the 24 surrounding points:

$$\theta_0 = \frac{\sum_{i=1}^{24} \theta_i \cdot I_{(\theta_i < \alpha)}}{\sum_{i=1}^{24} I_{(\theta_i < \alpha)}} \quad (1)$$

where θ_0 represents the resulted local misorientation for the

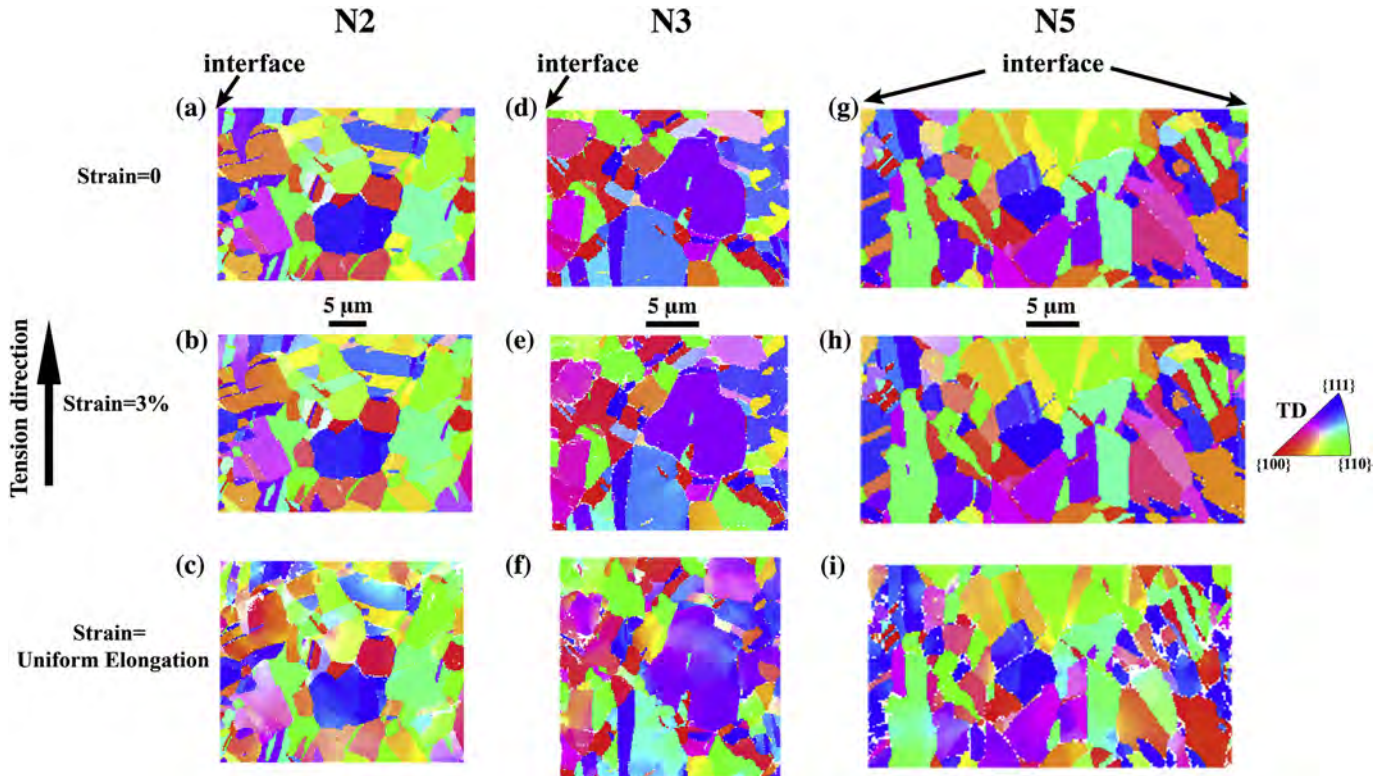


Fig. 5. Transverse-direction (TD) inverse pole figure mapping of the regions around interfaces in (a–c) N2, (d–f) N3 and (g–i) N5 samples under different tensile strain levels: 0%, 3% and maximum uniform elongation.

corresponding point and θ_i is the misorientation between this point and its neighbor point i . $I(\theta_i < \alpha)$ is an indicator function and α is the predefined grain boundary misorientation threshold (3° here). To extrapolate the GND density information, we use a simple method from the strain gradient theory by Gao and Kubin [25,45]:

$$\rho^{\text{GND}} = \frac{2\theta}{ub} \quad (2)$$

where ρ^{GND} is the GND density at points of interest, θ represents the local misorientation, b is the Burger's vector (0.255 nm for copper) and u is the unit length (100 nm) of the point. The resulted GND density maps are shown in Fig. 6 for all samples under corresponding tensile strains. Clearly, the overall level of GND density is elevated with increasing tensile strain. This is expected from the deformation of polycrystalline materials, which is inhomogeneous [22,31,32]. It is also noted that the GND density is not uniform across the whole mapping region, which is not considered in the conventional theory [22,24]. Fig. 7 shows the histogram distribution of GND density for each map. The GND distributions in the three samples are very similar at each tensile strain. Here, we need to mention the measurement error in the study. Previous researches on EBSD technique indicated that the measurement error might dominate when the misorientation to measure is very small and the relative error decreases when increasing real misorientation [39,46]. Taking the extreme case by assuming that the misorientation under zero strain is caused by measurement error, the resulted upper limit of measurement error of GND density is less than $1.73 \times 10^{14} \text{ m}^{-2}$, which is reasonable compared to an early report [47].

Fig. 7 also shows that the variation of GND density increases with tensile strain. This is definitely a true deformation phenomenon, rather than measurement error, because the latter has an inverse trend [46]. Since the GND density is related to the strain

gradient [22,25], these results indicate that the strain gradient is not uniform and this becomes more severe with increasing plastic strain. One source for the non-uniform strain gradient and GND density is the randomly distributed polycrystalline grain boundaries. They serve as barriers to dislocation motion and therefore locally generate GNDs [32,34]. The GND density is also affected by the crystallographic orientation, which varies from grain to grain. Another important source would be the macroscopic interfaces, which is the central interest in this study. To extract the effect of interfaces, the mapped regions in Fig. 5 were sliced parallel to the interface and the average GND density in each slice was randomly sampled [48] to minimize the interference from grain boundaries, crystallographic orientation and other irrelevant factors. The resulted GND densities versus their equivalent distance from interfaces are shown in Fig. 8, which reveals the development of a gradient in GND density near the interface. In other words, there is an *interface-affected zone* where the GNDs were accumulated during the tensile deformation. This zone spans only a few micrometers, and is observed in all three samples and becomes more pronounced with increasing applied tensile strain. It is also noted that the GND density in the layer interior becomes rather lower and uniform across all samples, i.e. the interface effect declined quickly with increasing distance from the interface.

4. Discussions

4.1. Dislocation pile-up model for the GND density close to interfaces

The heterogeneity in grain size, strength, stacking fault energy and texture between the copper and bronze layers makes them mechanically incompatible during deformation. However, the two different layers are forced to deform together, which generates

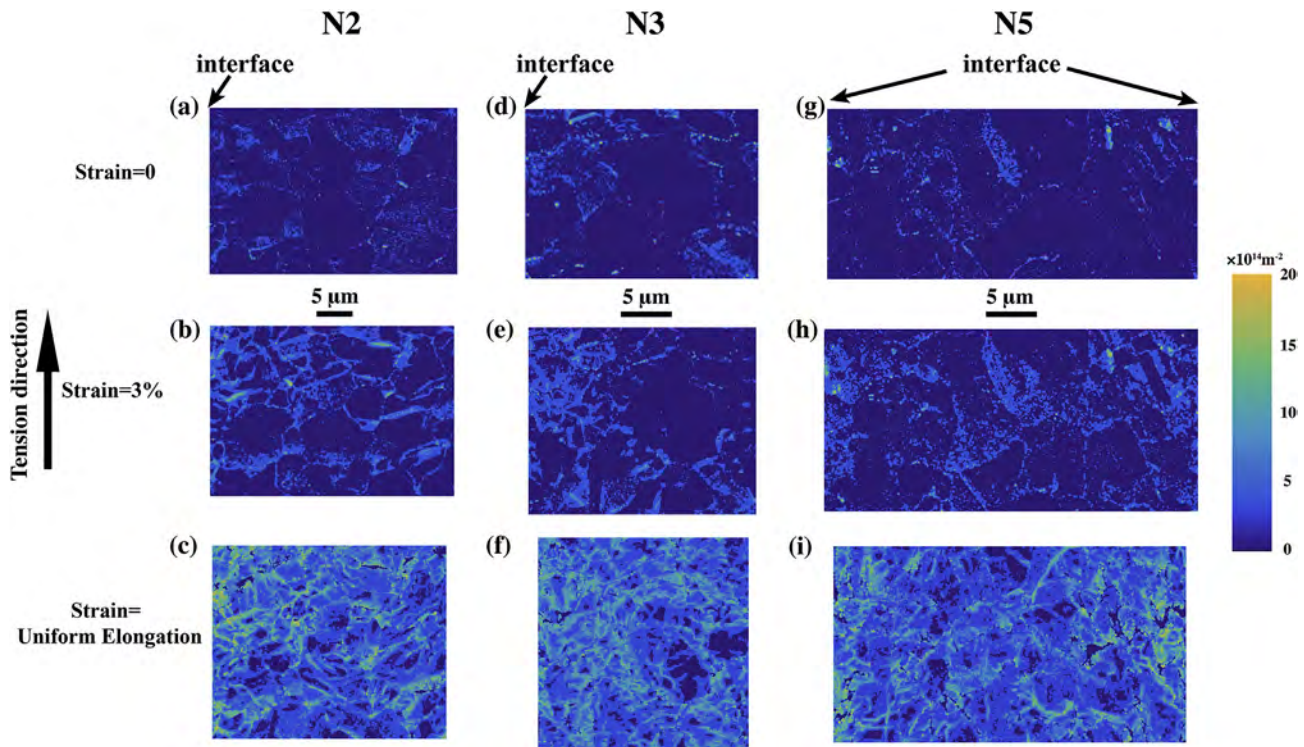


Fig. 6. GND density mapping based on local misorientation results in (a–c) N2, (d–f) N3 and (g–i) N5 samples under different tensile strains: 0%, 3% and maximum uniform elongation.

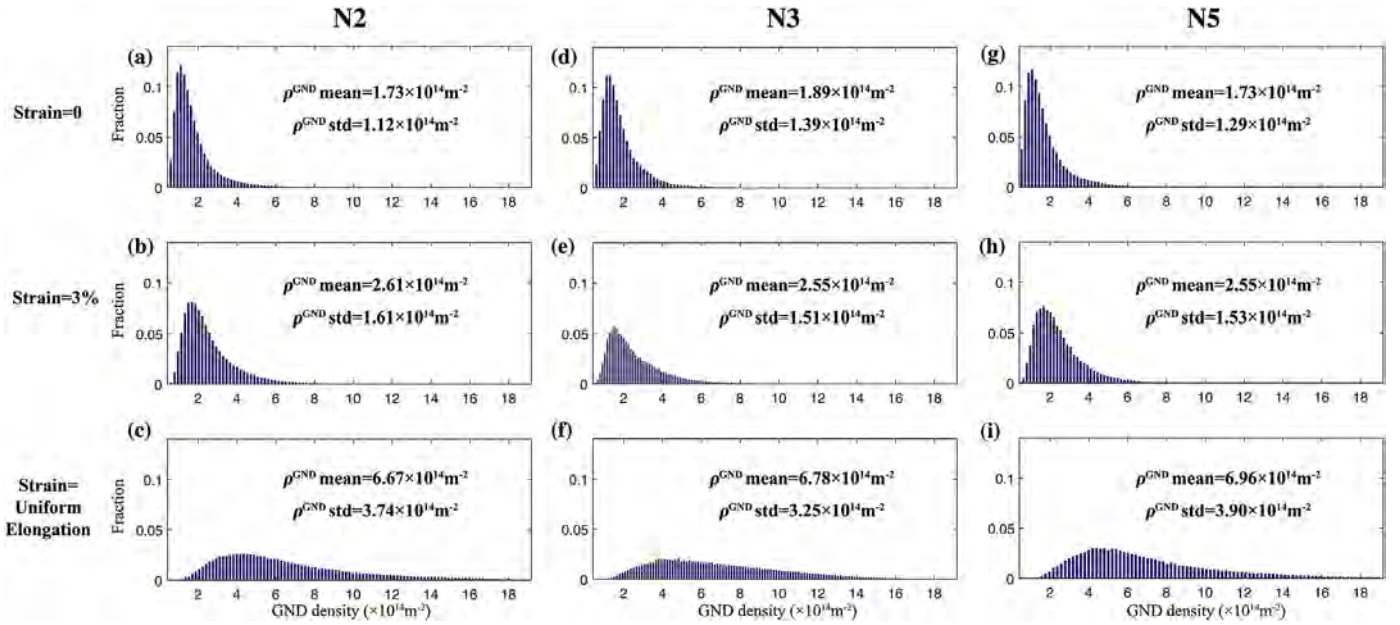


Fig. 7. Global GND density distribution on corresponding mapping results in Fig. 6. The mean value of GND density and the standard deviation are labeled in each histogram.

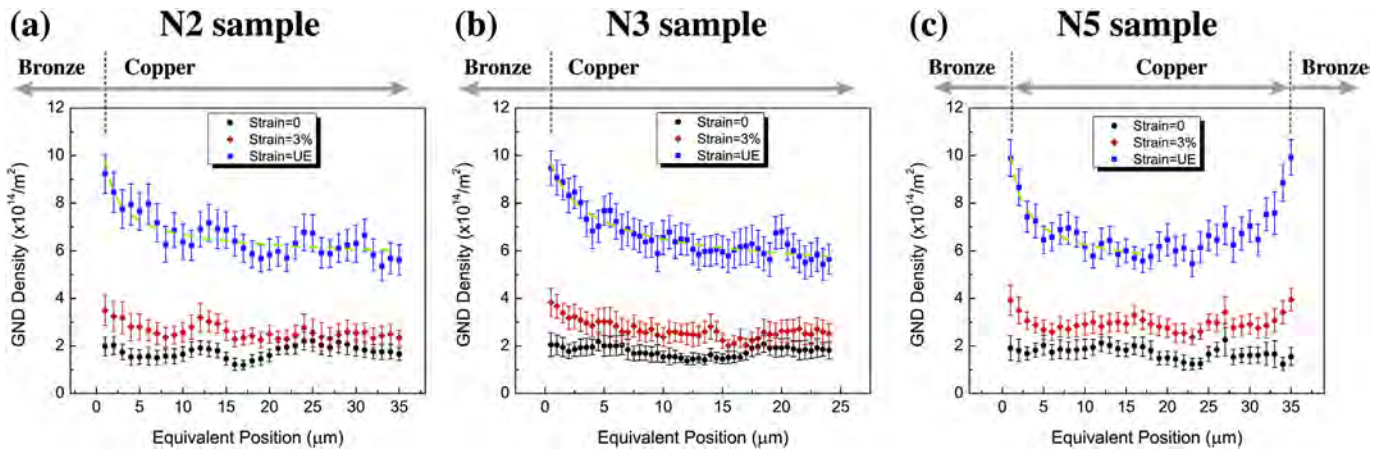


Fig. 8. Averaged GND density in copper layer versus the equivalent distance from the interfaces at different strain levels of (a) N2 sample, (b) N3 sample, (c) N5 sample. Dashed green lines represent pile-up model fitting results. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

strain gradient near the interface to fit the different strains across the interface. The strain gradient needs to be accommodated by GND, in the form of dislocation pile-up near the interface [49–51]. GND distributions were derived based on the conventional pile-up model [50], where the GND density $\rho^{\text{GND}}(x)$ is inversely proportional to $k/\sqrt{x(a-x)}$. Here, x is the distance from the interface, k and a are constants [50]. Defining the averaged GNDs arose from the grain boundary and orientation effects as ρ_0^{GND} , the fitting function can be modified as

$$\rho^{\text{GND}}(x) = \frac{k}{\sqrt{x(a-x)}} + \rho_0^{\text{GND}} \quad (3)$$

Data sets from the uniform elongation strain level are used to fit the model because they are least affected by measurement noise. The fitting results (dashed green lines) of GND density are superimposed on the measured data in Fig. 8, which demonstrate that the dislocation pile-up model can well describe the GND accumulation at interfaces in laminate structures. The fitting results also reveal that the ρ_0^{GND} values are very close for three samples with

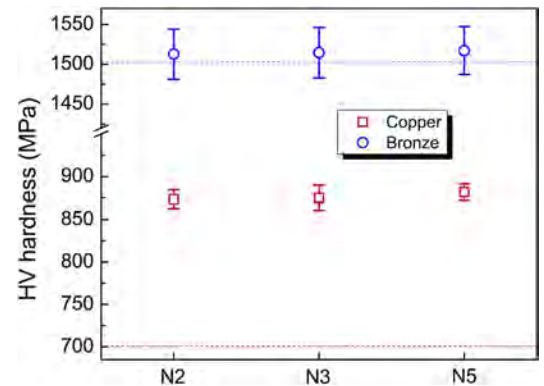


Fig. 9. Micro-hardness in layer interior at uniformly elongated sample region after tension. Dashed lines represent the base level before tensile tests.

different interface spacing: $\rho_0^{\text{GND}} = 5.1, 4.8$ and $4.9 \times 10^{14} \text{ m}^{-2}$ in N2, N3 and N5 samples, respectively. Fig. 8 also shows that GND density close to interface is $\sim 10 \times 10^{14} \text{ m}^{-2}$, indicating that interfaces doubled GND density locally.

Consistent with fitted ρ_0^{GND} in Fig. 8, Fig. 9 shows that the microhardness values in the copper and bronze layers after tensile testing to uniform elongation are almost the same in three samples. This indicates that the hardening capacities of the layer interior are approximately the same regardless of different interface density in samples. Therefore, the improved mechanical properties in Fig. 4 are largely caused by the interface effect.

4.2. Role of interface in deformation of nanostructured bronze

The average transverse grain size in the bronze layers is about 100 nm, which makes it difficult to characterize the deformation history by the current EBSD technique due to its resolution limit. But the extra accumulation of GNDs is still expected to occur in the bronze side as well. Although the hardening in the bronze layer interior during tension is not as high as in the Cu layer (see Fig. 9), extra hardening by GND accumulation could be generated in the nanostructured layer close to interfaces, which has been observed in gradient structures [5,14].

In addition, interfaces are also expected to facilitate other deformation mechanisms in the nanostructured bronze, such as deformation twinning [52], to promote strain hardening and ductility. Such mechanisms could be activated in grains near the interface for the following reasons. First, the aforementioned dislocation pile-up will produce a shear stress field near the interface and this stress field is expected higher than that from ordinary pile-ups at conventional grain boundaries because the plastic incompatibility across such interface is higher [49,50]. Second, bi-metal interfaces could act as dislocation sources and sinks to facilitate plastic deformation [30]. Fig. 10a shows a TEM micrograph of the copper/bronze interface after tensile deformation. Fig. 10b is the corresponding high-resolution micrograph. On the right side of the interface is a large copper grain with an annealing twin and the left is a bronze grain with only 30 nm grain size. A deformation twin in the bronze grain is probably nucleated at the interface by the transmission of the Shockley partial from the annealing Cu twin [30,53].

4.3. Effect of interface spacing on back stress hardening

Dislocation pile-up will produce back stress, which is a long-

range stress field that prohibits further dislocation emission from the dislocation source [50,54]. In other words, higher plastic flow stress is needed to overcome this field to sustain further deformation. This mechanism is highlighted in a recent work on Ti lamella microstructures [8]. The macroscopic interfaces here are expected to have similar effect. We calculated the back stress from unloading-reloading test curves at different tensile strains (see Fig. 11a) using an equation recently proposed by Yang et al. [21]. As shown in Fig. 11b, the resulted back stress is higher in samples with smaller interface spacing (higher interface density). This can be rationalized with the help of Fig. 8, which reveals that each interface produces an interface-affected zone by considerable GND pile-ups. Consequently, higher interface density amounts to more GND pile-ups in a certain sample volume, leading to a higher observed back stress at the present spacing scale.

However, further enhancement of back stress hardening and ductility may be limited when the interface spacing is smaller than a critical value since the transition of deformation mechanisms may occur [55]. This hypothesis is supported by reports that nanolaminates usually exhibit very high strength but disappointing tensile ductility [56–58]. In other words, there should be an optimum interface spacing that generates the extra GND pile-ups across the whole layer and yields the highest back stress hardening and ductility while maintaining high strength. We propose that this optimum spacing is comparable to the observed width of interface-affected zone, i.e. a few micrometers, which is consistent with recent report of aluminum alloy laminate composites [16] but still needs further investigations.

It should be also noted that further reducing interface spacing via ARB method will probably give rise to the preferred crystallographic orientations (textures) at bi-metal interfaces [2,4,59]. Such local and stable texture affects deformation and mechanical properties in its own way. When each layer is much thicker than the grain size dimension, its influence is trivial and the general interface effect governs the case [60], like in this work. The effect of interfacial texture is expected to interact with the general interface effect, which needs to be further studied.

5. Conclusion

In summary, we have systematically studied the effect of the copper/bronze interface on the deformation behavior and mechanical properties of laminate structures. The main conclusions are:

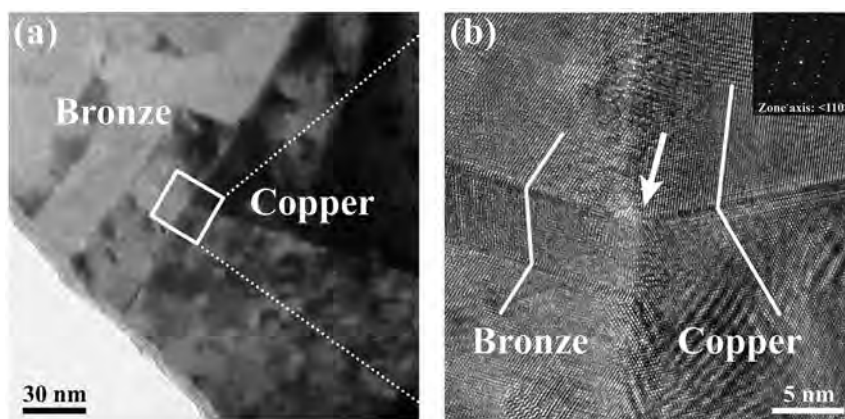


Fig. 10. (a) A TEM micrograph of copper/bronze interface in the N5 sample after tensile test. (b) The high-resolution image of the marked square in (a). Inset is a diffraction pattern, which shows the zone axis of copper side is $\langle 110 \rangle$. The symmetric diffraction spots reveal the annealing twin in the copper grain, which is also marked in the image. A deformation twin in bronze side is highlighted as well. Nucleation site for the deformation twin is marked by an arrow.

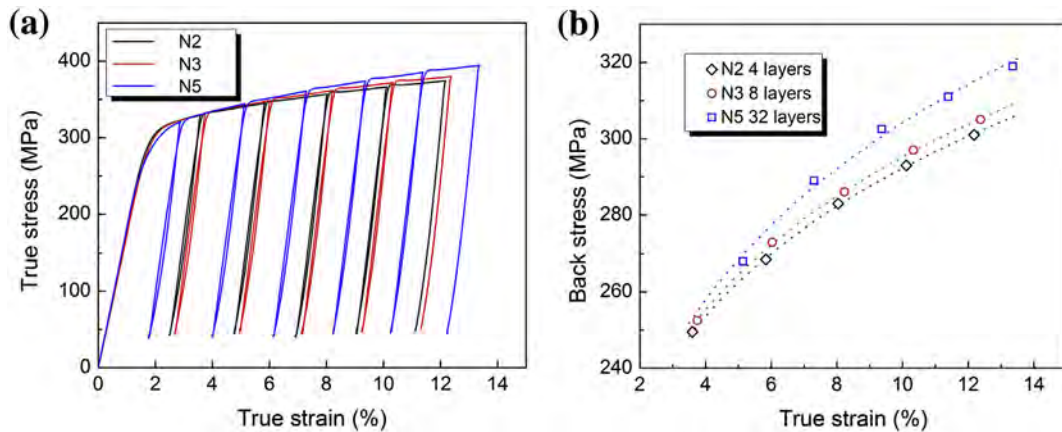


Fig. 11. (a) Unloading-reloading tensile curves of N2, N3, N5 samples. (b) The calculated back stress at corresponding strain levels.

- (1) The copper/bronze laminates were produced by means of ARB and post-annealing with varying interface spacing but similar heterogeneity across the interfaces including chemical composition, grain size, micro-hardness and texture.
- (2) Both ultimate strength and ductility in uniaxial tension are improved with decreasing interface spacing, which can be primarily attributed to the effect of interfaces since other variables are kept almost the same.
- (3) An interface-affected zone during deformation was experimentally observed. It spans a few micrometers regardless of varying interface spacing. Within this zone, non-uniform strain gradient and GND accumulation were generated via dislocation pile-up. In contrast, hardening capacity in the layer interior is about the same across samples.
- (4) Interfaces affect adjacent layers during deformation and promotes back stress hardening by producing more GND pile-ups. It's our hypothesis that there exists an optimum interface spacing, comparable to the width of interface-affected zone, for the highest ductility without sacrifice of strength.

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Deformation twinning in nanocrystalline materials

Y.T. Zhu^{a,*}, X.Z. Liao^b, X.L. Wu^c

^a Department of Materials Science & Engineering, North Carolina State University, Raleigh, NC 27695, USA

^b School of Aerospace, Mechanical and Mechatronic Engineering, The University of Sydney, NSW 2006, Australia

^c State Key Laboratory of Nonlinear Mechanics, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100080, China

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ABSTRACT

Nanocrystalline (nc) materials can be defined as solids with grain sizes in the range of 1–100 nm. Contrary to coarse-grained metals, which become more difficult to twin with decreasing grain size, nanocrystalline face-centered-cubic (fcc) metals become easier to twin with decreasing grain size, reaching a maximum twinning probability, and then become more difficult to twin when the grain size decreases further, i.e. exhibiting an inverse grain-size effect on twinning. Molecular dynamics simulations and experimental observations have revealed that the mechanisms of deformation twinning in nanocrystalline metals are different from those in their coarse-grained counterparts. Consequently, there are several types of deformation twins that are observed in nanocrystalline materials, but not in coarse-grained metals. It has also been reported that deformation twinning can be utilized to enhance the strength and ductility of nanocrystalline materials. This paper reviews all aspects of deformation twinning in nanocrystalline metals, including deformation twins observed by molecular dynamics simulations and experiments, twinning mechanisms, factors affecting the twinning, analytical models on the nucleation and growth of deformation twins, interactions between twins and dislocations, and the effects of twins on mechanical and other properties. It is the authors' intention for this review paper to serve not only as a valuable reference for researchers in the field of nanocrystalline metals and alloys, but also as a textbook for the education of graduate students.

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* Corresponding author. Tel.: +1 919 513 0559; fax: +1 919 515 3419.

E-mail address: ytzhu@ncsu.edu (Y.T. Zhu).

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1. Introduction

When a metal or alloy is plastically deformed, its shear strain is usually produced by dislocation slip and/or deformation twinning, especially at low temperatures and low strain rates [1,2]. Other deformation mechanisms include grain rotation, grain boundary sliding, and diffusion, but these mechanisms only become significant at relatively high temperatures, especially when the grain sizes are large [3]. Deformation twinning is a common and important phenomenon in metals and alloys. The twinning tendency of a face-centered-cubic (fcc) metal is largely determined by its stacking fault energy. For example, coarse-grained fcc metals with high stacking fault energies such as Al and Ni normally deform by dislocation slip, while fcc metals with low stacking fault energy such as Ag primarily deform by twinning [4,5]. The following deformation conditions also promote deformation twinning [1,2,6–11]: (1) high strain rate and (2) low deformation temperature. Deformation twinning in coarse-grained materials has been reviewed by Christian and Mahajan [1], and therefore will not be reviewed in detail in the present paper. The focus of this paper is on nanocrystalline fcc metals. Nanocrystalline bcc and hcp metals have not been extensively studied, and will only be briefly discussed.

Nanocrystalline (nc) materials can be defined as solids with grain sizes in the range of 1–100 nm [12]. They have been reported to be considerably stronger than their coarse-grained counterparts, but their ductility is usually disappointingly low [13]. Bulk nc materials are usually synthesized by either two-step approaches such as nano-powder synthesis and consolidation [14,15], or one-step approaches such as severe plastic deformation (SPD) [16–18]. The low ductility of nc materials synthesized by the two-step approach is usually attributed to flaws such as cracks, air bubbles, etc. [19]. SPD is capable of synthesizing flaw-free nc materials with higher ductility than those synthesized by nano-powder consolidation. However, even these flaw-free nc materials usually exhibit very low uniform tensile elongation (the strain before necking), which is the measure for useful ductility. It should be also noted that very small samples are often used to measure the mechanical properties of nc materials, due to the difficulty in synthesizing large nc samples. This presents a serious problem because small sample size (e.g. gauge length smaller than 5 mm) may lead to an artificially high ductility, although the yield strength is not affected [20,21].

The mechanical properties, including ductility, of nc materials are controlled by their unique deformation mechanisms [6,9,10,18,22,23]. Deformation mechanisms identified in nc materials include partial dislocation emission from grain boundaries [8,24–31], deformation twinning [8,24–30,32], perfect dislocation slip [24,26,28], grain boundary sliding [24,33–37], and grain rotation [25,28,38,39]. In addition, since deformation twinning usually occurs simultaneously with the slip of perfect and partial dislocations, interactions between twins and gliding dislocations at twin boundaries inevitably occur and have been observed both experimentally [40–44] and by molecular dynamics (MD) simulations [45–50]. These interactions make twins effective in simultaneously increasing the strength and ductility of nc materials [40,51]. In addition, it is also reported that nc Cu with high density of twins have good electrical conductivity and excellent resistance to current-induced diffusion [40,52]. Therefore, deformation twinning in nc materials is of both fundamental and practical importance, and can be utilized to design nc materials for superior mechanical and physical properties.

Significant progress has been made in understanding the deformation twins in the last decade. In this paper we review all aspects of deformation twinning in nc metals and alloys, including deformation twins observed by MD simulations and experiments, twinning mechanisms, factors affecting the twinning, analytical models on the nucleation and growth of deformation twins, and the effects of deformation twinning on mechanical and other properties.

This paper is organized in the following way. We will first briefly introduce some basics on the deformation twinning to help with the reading of the paper, especially for those young scientists such as graduate students. The deformation twinning in coarse-grained fcc materials will be briefly reviewed to provide a comparison for the twinning in nc materials. Then the deformation mechanisms in nc materials will be discussed to put the deformation twinning in an appropriate perspective relative to all other active mechanisms in nc materials. This is followed by all aspects of deformation twin-

ning in nc materials. The interaction between dislocations and twin boundaries will be reviewed because it significantly affects the mechanical properties of nc materials. Finally, the effect of twinning on the mechanical behaviors and electrical conductivity of nc materials will be discussed.

2. Basics of deformation twinning in fcc metals

Deformation twinning as a common deformation mechanism has been described in textbooks [53] as well as specialized books dealing with dislocations and deformation of metals [54]. Here we will only briefly describe some selected aspect of it to help with the discussions in the following sections of the paper. Conventionally, deformation twins in fcc metals are believed to be formed by the glide of partial dislocations with the same Burgers vector on successive [55] planes. This collectively produces a macroscopic strain to accommodate the imposed strain. The twinning partial in fcc metals has a Burgers vector of $\mathbf{b}_1 = a/6\langle 1\ 1\ 2 \rangle$ with a magnitude of $a/\sqrt{6}$. As shown in Fig. 1 [56], if deformation twinning occurs above the twin boundary a spherical grain via partials with a Burgers vector $\mathbf{b}_1$, a grain will be sheared into a new shape. Note that a grain boundary kink will be produced at the twin boundary with a kink angle of 141° , which is twice of the angle between two close-packed $\{1\ 1\ 1\}$ planes.

The twinning partial dislocations are all Shockley partials that can glide on the slip plane. There are three equivalent Shockley partials on each slip plane. For example, as shown in Fig. 2, on the $(1\ 1\ 1)$ slip plane the three partials are $\mathbf{b}_1 = \mathbf{B}\delta = a/6[2\ \bar{1}\ \bar{1}]$, $\mathbf{b}_2 = \mathbf{A}\delta = a/6[\bar{1}\ 2\ \bar{1}]$, and $\mathbf{b}_3 = \mathbf{C}\delta = a/6[\bar{1}\ \bar{1}\ 2]$. Note that there are also three partials with opposite Burgers vectors, $-\mathbf{b}_1$, $-\mathbf{b}_2$, and $-\mathbf{b}_3$. The implications of these partials with opposite Burgers vectors will be discussed later.

Fig. 2b shows the magnitude and orientation of the three Burgers vectors of partial dislocations, $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$, as overlaid on the close-packed atoms in the $(1\ 1\ 1)$ slip plane. It also shows the atomic stacking positions A, B, and C. For fcc metals, the stacking sequence of atoms in successive close-packed planes is ABCABCABC. When a partial dislocation glides across a slip plane, a stacking fault is produced and all atoms above the stacking fault change their positions. From magnitude and orientation of the Burgers vectors shown in Fig. 2b, the atom stacking position shift caused by the gliding of a partial dislocation can be described below:

Partial $\mathbf{b}_1$: A $\rightarrow$ B, B $\rightarrow$ C, C $\rightarrow$ A

Partial $\mathbf{b}_2$: A $\rightarrow$ B, B $\rightarrow$ C, C $\rightarrow$ A

Partial $\mathbf{b}_3$: A $\rightarrow$ B, B $\rightarrow$ C, C $\rightarrow$ A

In other words, although the three Burgers vectors have different orientations, they cause the same stacking position shift. As will be shown later, this has important implications for deformation twinning in nc fcc metals. Note that partials with opposite orientations, i.e. $-\mathbf{b}_1$, $-\mathbf{b}_2$, and $-\mathbf{b}_3$, will shift the stacking sequence to the opposite direction, i.e. B $\rightarrow$ A, C $\rightarrow$ B, A $\rightarrow$ C.

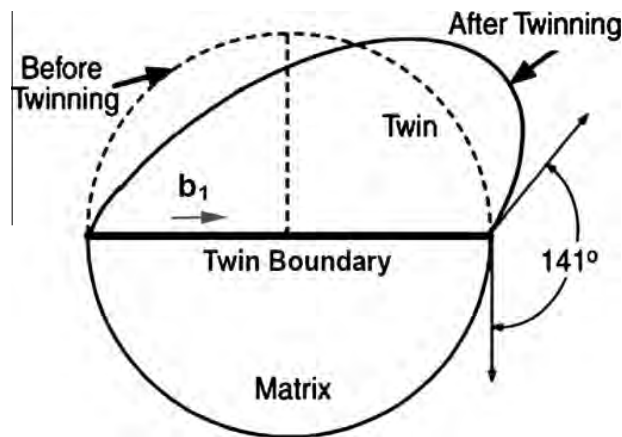


Fig. 1. Conventional deformation twinning by the gliding of partials on successive slip planes above the twin boundary changes the shape of the spherical grain above the twin boundary [56].

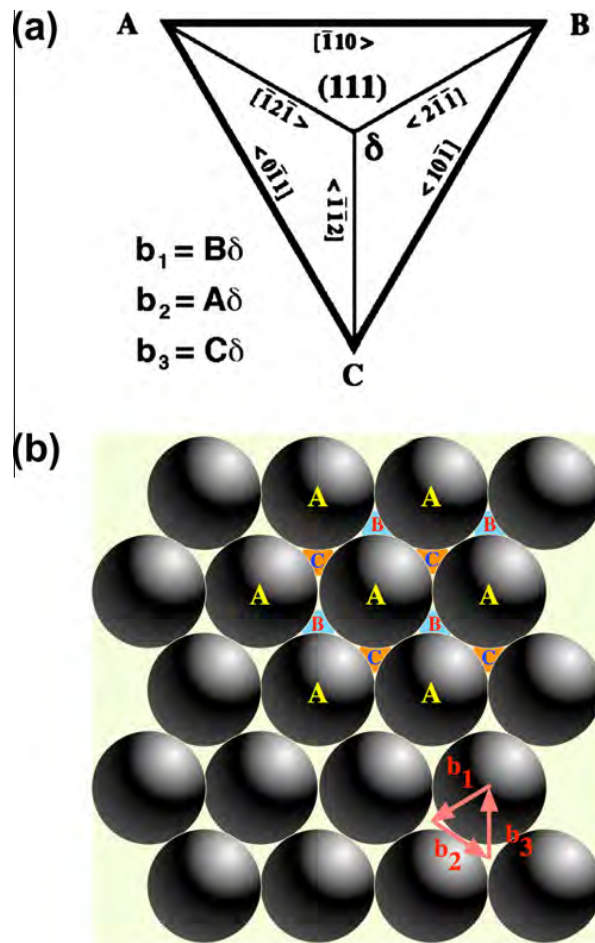


Fig. 2. (a) Three equivalent Burgers vectors $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$ on the (1 1 1) slip plane for Shockley partials. (b) The magnitude and orientation of the three partial Burgers vectors, $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$, on the (1 1 1) plane of closely-packed atoms, and the atomic stacking positions A, B, C (note that they are not related to the letter A, B and C in (a)).

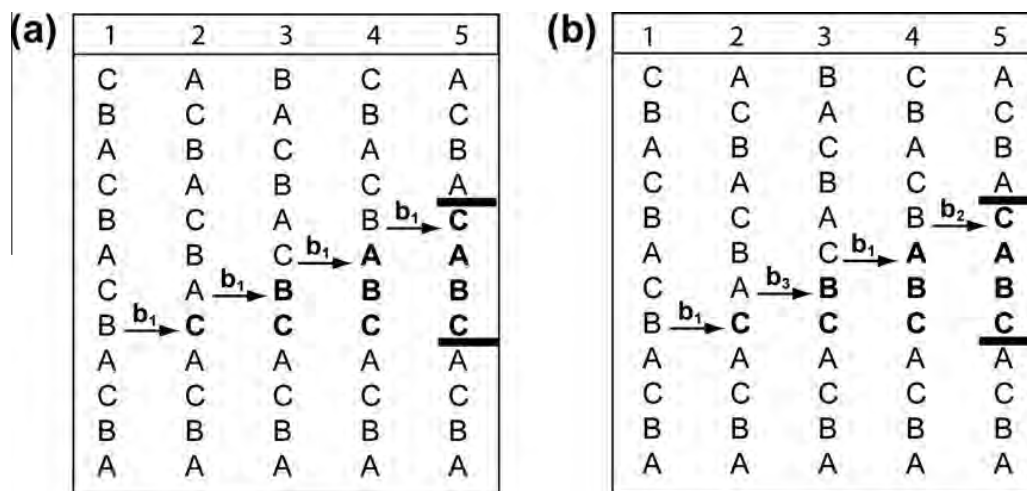


Fig. 3. (a) The process of forming a four-layer deformation twin by the slip of four partials with the same Burgers vector ($\mathbf{b}_1$) on successive slip planes. (b) The process of forming a four-layer deformation twin by the slip of four partials with a mixture of Burgers vectors $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$ on successive slip planes.

As stated earlier, a deformation twin can be formed by the slip of Shockley partials on successive slip planes. Fig. 3a shows the formation of a four-layer twin via the slip of partials with the same Burgers vector, marked by the bold letter **CBAC**. As shown, the column 1 has a normal fcc stacking

sequence ABCABCABC. The slip of first partial $\mathbf{b}_1$ produces an intrinsic stacking fault (see the bold letter **C** in column 2), which is identical to removing a layer of B atoms. The slip of the second $\mathbf{b}_1$ partial on an adjacent slip plane converts the stacking fault into a two-layer twin nucleus (**CB**, see column 3) [34,42,56–59]. Note that the two-layer twin nucleus is also identical to an extrinsic stacking fault, e.g. a stacking fault formed by inserting an extra C layer between the A and B layers. [54]. Further slip of $\mathbf{b}_1$ partials grows the twin nucleus into a four-layer twin **CBAC**, with the twin boundaries represented by two horizontal lines (see column 5). Since the twinning process described in Fig. 3a involves only partials with the same Burgers vector, we name such a process as monotonic twinning process.

Fig. 3b shows that a four-layer twin with identical stacking sequence as in Fig. 3a can also be produced by the slip of four partials with mixture of three Burgers vector ($\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$) on successive slip planes. In other words, a twin can be formed by the slip of identical partials or different partials. This is because the three partials, $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$, produce the same stacking sequence shifts despite of their orientation difference.

It should be noted that the macroscopic strain produced by the two twinning processes described in Fig. 3 are very different. In Fig. 3a, all partials have the same Burgers vector, and therefore produce a shear strain in the same direction. This can collectively produce a relatively large macroscopic strain and change the grain shape as shown in Fig. 1. In contrast, the twinning process described in Fig. 3b will produce a much smaller macroscopic strain because partials with different Burgers vectors shear the lattice to different directions.

The two twinning processes described in Fig. 3 will have implications in the twin morphologies. As discussed later, most twinning mechanisms proposed for the fcc metals with coarse grains are consistent with the twinning process described in Fig. 3a, while the twinning process described in Fig. 3b could be very common in nanocrystalline fcc metals. Materials with grain sizes in the range of 1 μm to 1000 μm are hereafter defined as coarse-grained materials [3,16,18,28,60–64].

A crystallographic feature of the twin is the mirror symmetry of atomic arrangement across the coherent twin boundary plane. For an fcc metal, this symmetry can be best viewed along the $[1\ 1\ 0]$ orientation that is on the coherent twin boundary plane (see Fig. 4a). As shown, the coherent twin boundary plane is the $(1\ \bar{1}\ 1)$ close-packed plane, and it has a 70.53° angle with other close packed planes. Each lattice point in the two-dimensional illustration (Fig. 4a) represents an atom column, with the dark circles below the light circle by a distance of atomic radius, i.e. $1/4[1\ 1\ 0]$. However, under the high-resolution electron microscope, these two types of columns give identical images, as shown in Fig. 4b. The mirror symmetry in the high-resolution electron microscopy (HREM) image shown in Fig. 4b is often used to identify twins in fcc metals.

Regular low-resolution transmission electron microscopy (TEM) is also often used to identify deformation twins in metals, although it cannot obtain atomic-resolution images. TEM can detect the microstructural feature of twins, which is often in a plate shape with straight twin boundaries. Examples of low-resolution twin images are shown in Fig. 5a. However, in nc fcc metals, multiple twins often form, which show no obvious plate-like morphology (see Fig. 5b) [34,42,56,65–70]. Under such circumstances, HREM is needed to identify and study the deformation twins.

3. Deformation twinning in coarse-grained fcc metals

3.1. Twinning mechanisms in coarse-grained fcc metals

Deformation twinning in coarse-grained fcc metals and alloys has been comprehensively reviewed by Christian and Mahajan [1]. Therefore, we will only give a brief summary here. Coarse-grained fcc metals are believed to twin via several conventional mechanisms including the pole mechanism [71], prismatic glide mechanism [72], faulted dipole mechanism [73], or other mechanisms [74–76]. These mechanisms often require a dislocation source in the grain interior to operate. As will be discussed later, this poses a problem for nc metals and alloys since their grain interior are often free of dislocations [25,61], although dislocations can exist in nc grains under certain deformation conditions [77,78]. In addition, the deformation mechanisms in nc materials are dramatically different from those in their coarse-grained counterparts due to a strong grain size effect below 100 nm.

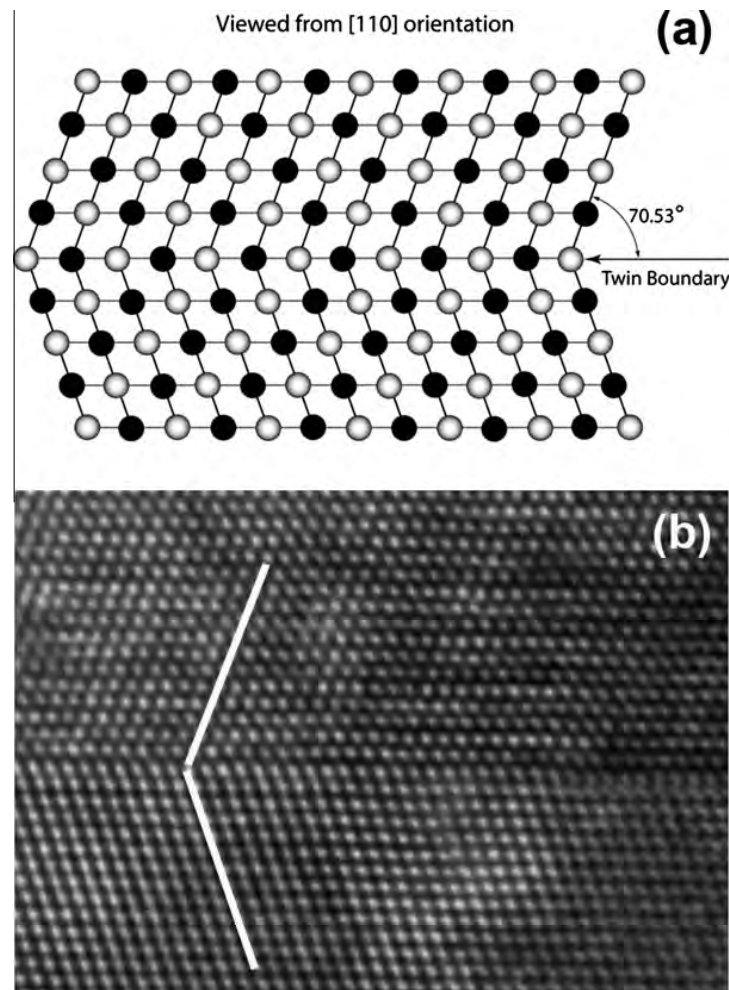


Fig. 4. (a) The mirror symmetry of atoms in a twin in fcc metals, when viewed from a $[1\ 1\ 0]$ direction that is on the coherent twin boundary plane. A dark filled circle represents an atom column that is shifted for half an atomic distance below an atom column represented by a light circle. (b) A typical HREM image of a twin in an fcc metal. Columns represented by lighter and dark circles in (a) are not differentiated by HREM in (b).

One exception is a 3-layer twin nucleation model proposed by Mahajan and Chin for fcc metals [74]. In theory, this model can be easily applied to nc metals. Furthermore, Kibey et al. recently calculated the critical stress for the nucleation of such a three-layer twin, incorporating the general planar fault energies (GPFE) obtained from the *ab initio* density functional theory (DFT) [79]. The predicted stress is very close to experimentally measured values for many fcc metals. However, the “three-layer” twin nucleation is yet to be observed in nc fcc metals.

3.2. Grain size effect

According to the experimental results reported in the literature, smaller grain size impedes deformation twinning [11,80–83] in coarse-grained metals and alloys, irrespective of their crystal structure. Meyers et al. [11] summarized the Hall–Petch slopes for both perfect dislocation slip and twinning in a number of *coarse-grained* metals with fcc, body-centered cubic (bcc) and hexagonal-close-pack (hcp) crystal structures. In each case, the experimentally observed Hall–Petch slope for twinning is much higher than that for the slip of perfect dislocations. In other words, for coarse-grained metals, the stress required for activating twinning increases much faster with decreasing grain size than the stress for perfect dislocation slip, as illustrated in Fig. 6. Therefore, smaller grain size make the deformation twinning more difficult. The grain size effect was demonstrated in many examples. El-Danaf et al. [81] reported that 70/30 brass showed much greater twin density in samples with the grain size of 250 μm than in samples with grain sizes of 9 and 30 μm . Meyers et al. [84] observed that shock compression at

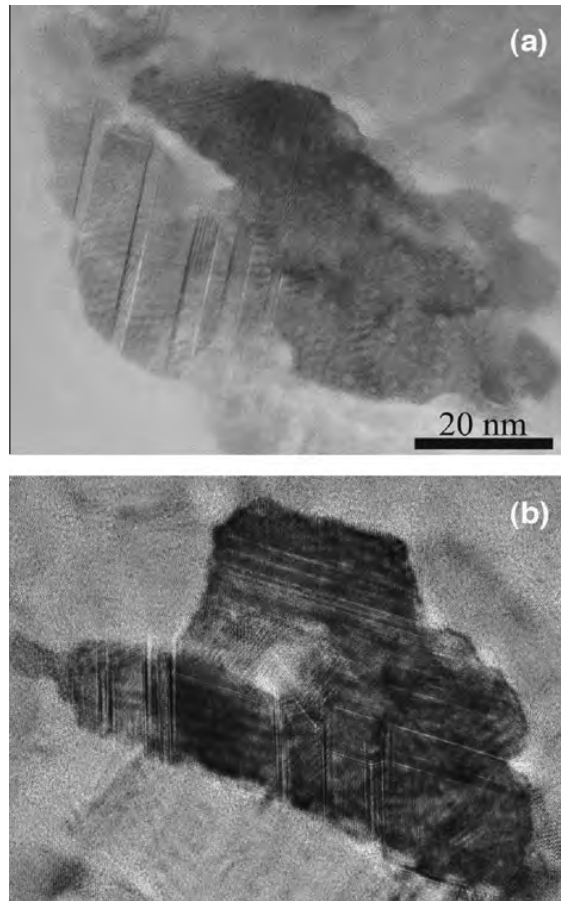


Fig. 5. Morphology of deformation twins in nc fcc Cu under low resolution. (a) Twins with plate-like morphology. (b) Multiple twins without obvious plate-like morphology. Both (a) and (b) are from the original HREM images with reduced resolutions.

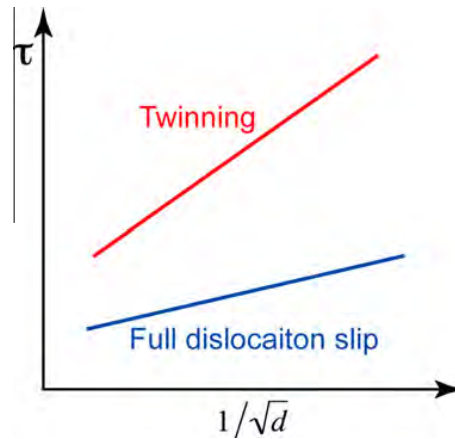


Fig. 6. The schematic of Hall–Petch relationship for twinning and full dislocation slip in coarse-grained metals and alloys. τ is the shear stress and d is the grain size. The higher slope for twinning indicates that twinning is more difficult than the slip of full dislocations in smaller grains.

35 GPa produced profuse deformation twins in Cu samples with average grain sizes of 117 and 315 μm , but virtually no twin in Cu samples with an average grain size of 9 μm .

3.3. Temperature and strain rate effect

The strain rate and temperature effect on deformation twinning in coarse-grained fcc metals and alloys have been summarized by Meyers et al. [11] and by Christian and Mahajan [1]. There is a

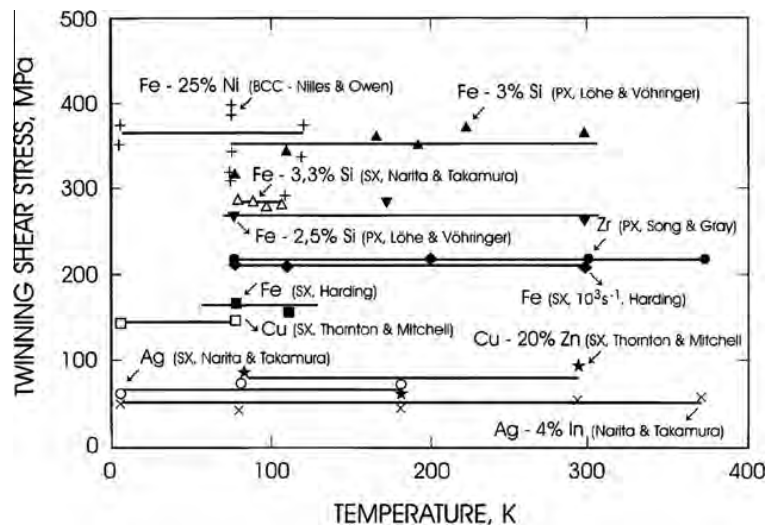


Fig. 7. Effect of temperature on twinning stress for several single crystalline and polycrystalline metals and alloys [11].

general equivalency of low temperature and high strain rate [1]. Specifically, lower temperature and higher strain rate usually promote deformation twinning. For example, fcc Cu was found to deform by twinning at 4 K at a low strain rate [85], although it only deforms by dislocation slip at room temperature and low strain rate. Therefore, there is a transition to twinning with decreasing temperature. This transition temperature increases with decreasing stacking fault energy [1]. Generally, the tendency for twinning increases rather slowly with decreasing temperature but much faster with increasing strain rate. For example, shock deformation has been found to produce twins in metals and alloys with medium-to-high stacking fault energy [84,86–88], which usually does not deform by twinning at quasi-static strain rate and room temperature.

The observed temperature and strain rate effect can be understood from two aspects. The first is how the critical twinning stress varies with the temperature and strain rate, and the second is how the material flow stress changes with the temperature and strain rate. Meyers et al. [11] summarized the twinning stress as a function of temperature for a number of single-crystal and polycrystalline metals and alloys (see Fig. 7), and found that the twinning stress is insensitive to temperature. However, there are debates on this issue [89–92]. Mahajan suggested that the bcc metals have a negative twinning stress dependence on temperature, while fcc metals have a slight positive twinning stress dependence on temperature [1]. The strain rate effect on twinning stress is not well studied. Harding [93,94] found that the twinning shear stress increased from 170 MPa to 220 MPa when the strain rate was increased from 10^{-3} s^{-1} to 10^3 s^{-1} .

The flow stress of metals and alloys usually increases with decreasing temperature and/or increasing strain rate. The increase in flow stress at low temperature is believed caused, at least in part, by the strong dependence of the work-hardening on temperature, which may increase the flow stress to the critical twinning stress. During the deformation process, dynamic hardening and recovery occurs simultaneously. The dynamic recovery process needs the climbing of dislocations, which is a thermally activated process [95]. It becomes slower at lower temperatures [28,95–104], and this causes higher work-hardening rate, and consequently higher flow stress. At higher strain rate the overall work hardening rate increases because the dislocation generation rate is faster than the dislocation annihilation, which leads to the increase in flow stress. Therefore, the increase in twinning tendency at low temperatures and higher strain rates can be largely attributed to the increase in flow stress.

4. Deformation mechanisms in nanocrystalline materials

Due to their small grain size, nc materials deform via mechanisms that are different from those in their coarse-grained counterparts [6,8,9,22–24,27,42,66]. As discussed in the introduction, several deformation mechanisms have been identified in nc materials. The significance of each deformation

mechanism changes with decreasing grain size. For example, for fcc metals and alloys with medium-to-high stacking fault energy, perfect dislocation slip dominates in large grains (e.g. larger than 50 nm) [3]. However, more than one deformation mechanisms may be active at any grain size, although the significance of each mechanism changes with grain size. In other words, for each deformation mechanism, there is a grain size range in which it plays a significant role. In the following subsections, we will briefly summarize several deformation mechanisms to set the stage for the detailed review of deformation twinning in Section 5.

It should be noted that the HREM observations have been extensively used to support proposed twinning mechanisms. These observations were mostly postmortem because of the difficulty of in situ HREM. Early HREM observations were mostly used to validate twinning mechanisms observed by molecular dynamics (MD) simulations. New twinning mechanisms were later proposed based on analysis of postmortem HREM observations. Some of these HREM findings were verified by MD simulations. HREM and MD simulations are complementary means for studying deformation twinning, and then are especially powerful when combined to study deformation mechanisms in nc materials.

4.1. Grain boundary sliding

Grain boundary sliding in nc materials was first observed by MD simulations [24,36,37,105], later reported experimentally [27,106–108], and modeled analytically [109–112]. Importantly, such grain boundary sliding may occur in a coordinated way [27,105–107,113–115]. For example, shown in Fig. 8 is the alignment of grain boundaries of many grains to facilitate the grain boundary sliding [107]. The small grain sizes of nc materials [37] make it easier for the grain alignment [80,116]. Such a coordinated grain boundary sliding may play a significant role in the deformation of nc materials, as shown in Fig. 9, which reveals prevalent grain boundary aligning in nc Ti. More study is needed on this issue.

4.2. Grain rotation

Grain rotation in nc metals was first observed under in situ HREM by Ke et al. [38], and later confirmed by Shan et al. [25,117], Jin et al. [118] and Wang et al. [119]. Grain rotation as a deformation mechanism was also revealed by MD simulations [105,120,121] and has been analytically modeled [111,122,123]. The unambiguous means to observe grain rotation is in situ TEM. However, experimental evidence of grain rotation from such observation is also controversial because the TEM samples are very thin and may not represent bulk nc materials. More recently, texture measurement confirmed that grain rotation indeed plays a significant role in the deformation of bulk nc materials [28,124–127]. However, the grain rotation was also found to accompany grain growth during the deformation

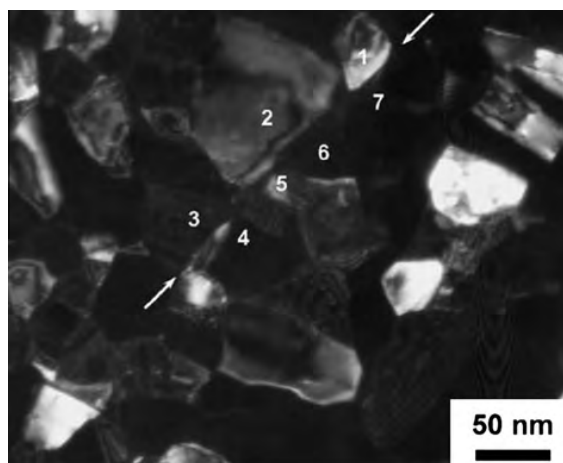


Fig. 8. The alignment of grains in nc Pd after deformation by high-pressure torsion, suggesting coordinated grain boundary sliding [107].

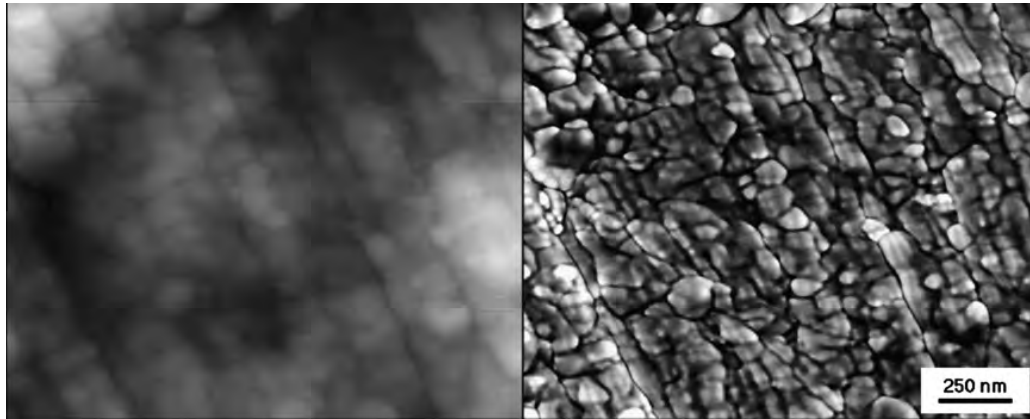


Fig. 9. Atomic Force Microscope (AFM) topography (left) and phase contrast (right) images taken from the surface of a nc Ti sample processed by HPT after being tested in tension at 250 °C for a strain of ~30%.

[28,39,124,125,128]. Such stress (strain) assisted grain growth has been reported by several groups [28,39,118–121,124–126,128–139] and can occur at even liquid nitrogen temperature [129,130]. These observations suggest that grain rotation play a significant role in the deformation of nc metals and alloys and it often leads to grain growth. Wang et al. concluded that grain rotation first converts high-angle grain boundaries to low-angle grain boundaries. The low-angle grain boundaries will then disappear, leaving behind higher density of dislocations, which is consistent with MD simulations by Haslam et al. [128].

4.3. Dislocation emission from grain boundaries

Grain boundaries become the primary dislocation source and sink when the grain is smaller than a critical size [140–143]. This is because dislocation sources often no longer exist in the grain interior of nc materials. For example, in ultrafine-grained hexagonal close-packed (hcp) Ti processed by severe plastic deformation [142], grains and subgrains smaller than 100 nm are often dislocation free (see Fig. 10). This critical grain size is determined by material properties such as stacking fault energy and deformation parameters such as temperature and strain rate. High stacking fault energy and low melting temperature make dislocation recovery easier, which consequently leads to larger critical grain size. For example, for pure Al, which has high stacking fault energy (122 mJ/m² [54,144]) and

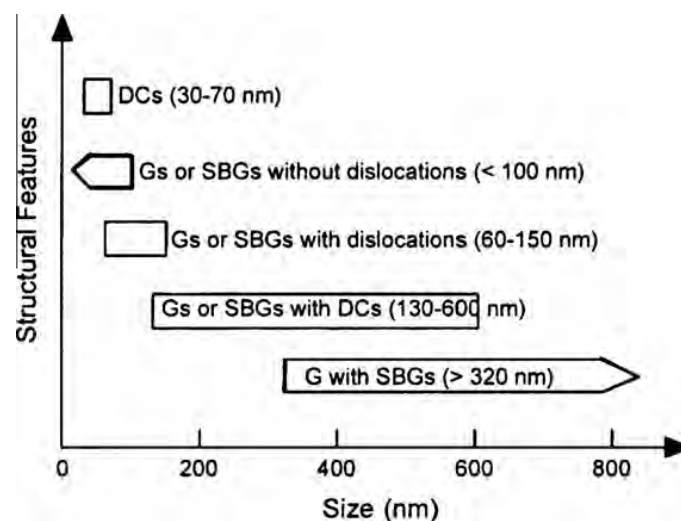


Fig. 10. Hierarchy of microstructure in Ti processed by severe plastic deformation [142]. The acronyms are G – grains, SBG – subgrains, DC – dislocation cells.

low melting temperature (660.32 °C), the critical grain size is relatively large. Grains of a few hundred nanometers may be dislocation free [145–147]. The lack of dislocation in the grain interior has been attributed to the lacking of strain hardening in nc materials [51,140,148–154].

When dislocation source is unavailable inside the grain interior, grain boundary becomes the primary source for dislocation generation. Indeed, in situ TEM revealed extensive emission of dislocations from grain boundaries of nc materials [25,143,155,118,156]. However, in situ TEM is often done under low-resolution mode and cannot differentiate partial dislocations from perfect dislocations. Partial dislocation emissions from grain boundaries were extensively observed by MD simulations [9,10,26,22,144,157,158], and was verified experimentally by ex situ HREM observations [8]. As will be discussed in later sections, the emission of dislocations from the grain boundaries play a critical role in the nucleation and growth of deformation twins in nc fcc metals, and is responsible for several unique twinning mechanisms.

It should be noted that under certain deformation conditions, high-dislocation density is still possible in nc metals and alloys. For example, high-density of dislocation defect structure was found in the grain interior of nc Ni deformed under constrained rolling at liquid nitrogen temperature [77].

4.4. Stacking fault and deformation twinning

In coarse-grained fcc and bcc materials, stacking faults and deformation twins usually occur in metals and alloys with low stacking fault energy, although high strain rate and low deformation temperature can significantly promote twinning. In coarse-grained hcp metals and alloys, twinning is a common deformation mechanism because their small number of slip systems [56,159–170]. In comparison, nc materials have a very different behavior in the formation of stacking faults and deformation twins. First, nc hcp metals are rarely observed to deform by twinning. Second, nc fcc metals are found to generally deform by twinning more easily, especially in those fcc metals with medium to high stacking fault energy, although twinning may become difficult again at very small grain sizes [171]. Deformation twinning in nc fcc metals and alloys is the focus of this review, and is discussed in detail in the next section.

5. Deformation twinning in nanocrystalline fcc materials

5.1. Molecular dynamics simulations

The MD simulation of deformation twinning in nc fcc materials has been comprehensively reviewed by Wolf et al. [22]. Here we will only give a brief summary on the features of MD simulations as well as the major results on deformation twinning obtained by MD simulations. Early insights on the deformation mechanisms of nc materials are almost exclusively obtained by MD simulations [9,24,26,36,105,144,157,172–176], largely because of the difficulty in synthesizing nc materials for experimental studies. For example, extensive early studies were performed on nc samples synthesized by inert gas condensation [15,177–184], which did not have clean grain boundaries and had flaws such as cracks and pores after consolidation due to the adsorption of O, H, and N atoms during the synthesis of nano-powders. It is still a challenge even today to synthesize nc materials with certain structural characteristics to systematically investigate a specific deformation mechanism.

MD simulation has several advantages over experimental investigation, which makes it a powerful tool for studying nc materials [22]. First, MD simulation can elucidate the atomic level deformation mechanisms in nc materials in a degree of detail that cannot be obtained experimentally. Second, it is capable of investigating the real-time deformation behavior, including twinning and detailed defect evolution and interaction, which are not possible by any experimental technique. Third, it can simulate a well-characterized and idealized model nc system to study specific deformation mechanisms. Fourth, it is capable of deforming samples to very large plastic strains, which make it possible to investigate the deformation behavior under high dislocation densities.

MD simulation also has its own limitations [22]. First it is typically limited to relatively small model systems. As a result, many researchers often use model systems with very small grain sizes. This could

sometimes lead to serious problems because it is known that grain sizes affect the deformation mechanisms [24,37,57,59,171,185]. For example, it was observed by MD simulations that nc Al, Cu and Ni rarely deform by twinning [10], which contradicts the experimental observations [2,6,23,33–35,66,68,77,186–189]. This controversy was later found caused by the grain size effect, i.e. the small grain size used in the MD simulation is so small that the deformation twins are hard to form, due to an inverse grain size effect on twinning [171]. This limitation will be gradually relaxed as faster computers become more available to researchers. The second limitations of MD simulations is its short time duration [22], which results in extremely high strain rate (typically larger than 10^7 s^{-1}). Although such high strain rate is physically plausible [190–192], they are much higher than what we can normally obtain experimentally. This makes it more complex to compare with experimental results, because it is well known that the strain rate has significant effect on deformation mechanisms. For example, it is generally agreed that higher strain rate promotes deformation twinning [2,11,80,84,171,188,193–195].

MD simulation has revealed many important deformation mechanisms of nc materials despite of its limitations. Below we will list only a few that are relevant to deformation twinning: First, emission of Shockley partials from grain boundaries are extensively observed by several groups [9,10,24,26,37,45,46,144,157,158,185,196–210]. Second, three mechanisms for twin nucleation and growth were clearly revealed by Yamakov et al. (see Fig. 11) [9]. As shown in Fig. 11, a twin nucleus (marked by A) is formed by the overlapping of two extended dislocations on adjacent slip planes. There are also three other similar twin nuclei in the same grain. A twin marked by B is formed by successive emission of five Shockley partials from the grain boundary. C represents a twin formed by grain boundary splitting and migration, which leaves behind a coherent twin boundary (marked by α) and produces another coherent twin boundary (marked by β), while the migrating twin boundary (marked by δ) consists of a Shockley partial dislocations.

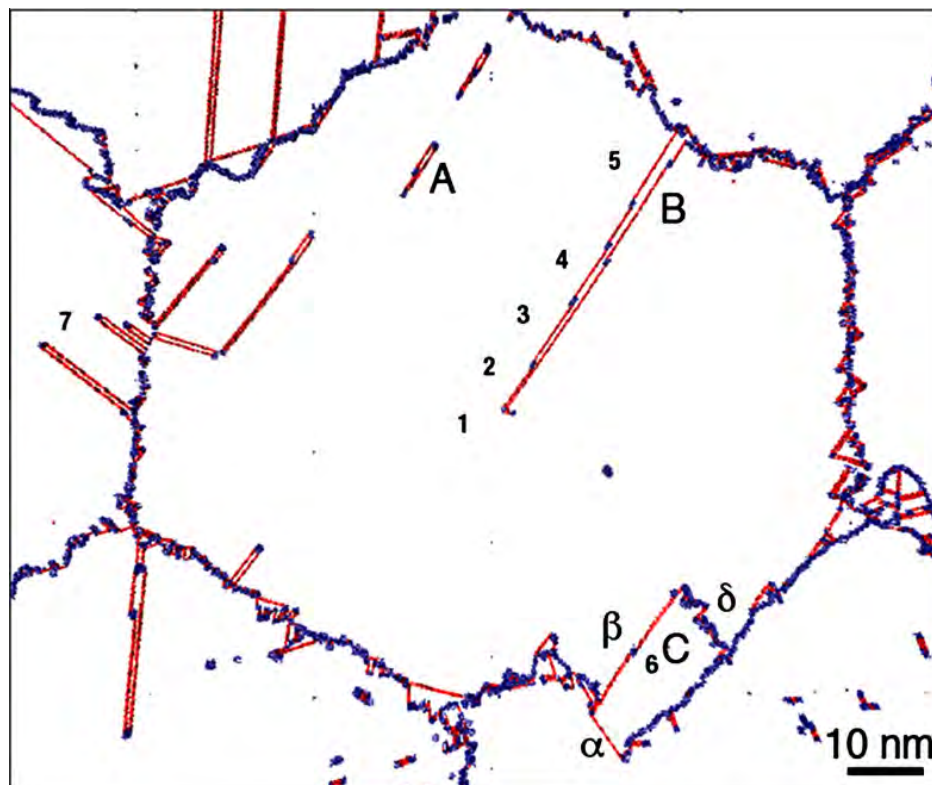


Fig. 11. Three twinning mechanisms are revealed in this MD simulation snapshot of nc Al with columnar grains [9]. As marked in the figure, A represents a twin nucleus formed by the overlapping of two extended dislocations on adjacent slip planes, B represents a twin formed by successive emission of Shockley partials from the grain boundary, and C represents a twin formed by grain boundary splitting and migration. Seven marks a few partial dislocations emitted from the grain boundary.

5.2. Experimental observations

The experimental observations of deformation twins were summarized in a previous paper [56]. Experimental results can validate and provide input to the MD simulations. Nanocrystalline samples for experimental studies are usually much larger and more complex than the model systems used by MD simulations, and therefore may reveal some deformation phenomena that are missed by the MD simulations. Early experimental observations of deformation twins were limited to the validation of MD simulation results. Examples include the experimental observation of partial dislocations emitted from grain boundaries (see Fig. 12) [6–8,23,186,211,212], and deformation twinning [3,6–8,18,23,31,65,66,186,213,214]. In recent years, several new phenomena have been first revealed by experimental investigations, including fivefold twins [8,65,70], twins with reduced macroscopic strain [2], inverse grain size effect on twinning [171], V-shaped twins by a self-thickening mechanism [67,69], and reversible twinning process [215]. Interestingly, a proposed formation mechanism [70] based on the experimentally observations for fivefold twins was later verified by MD simulation [216].

Experimental techniques for investigating deformation twinning include HREM, in situ HREM, and diffraction analysis (X-ray, synchrotron or neutron analysis). HREM is used most because it is easily accessible and provides direct atomic-resolution observation of twins. However, it is a postmortem technique, which makes the analysis of the twinning process non-trivial. In recent years, in situ HREM has been used to observe the twinning process, twin-dislocation interactions and other deformation mechanisms in nc materials [119,156,215,217,218]. Such experiments are still relatively difficult, and the quality of the atomic images is expected to improve in the near future. X-ray analysis has been used to analyze the twin boundary density in nc materials [51,149,153,219–222]. However, such analysis is usually qualitative and the absolute value of density of twin boundaries may depend on the method/model used in the analysis. Nevertheless, relative comparison of twin densities can be made if the X-ray diffraction data are taken and analyzed in a consistent manner.

The samples used for experimental studies have been prepared by mechanical attrition [65], physical vapor deposition [6], high-pressure torsion [8], surface mechanical attrition [223], electro-deposition [35,40,41,68], inert gas condensation [15], etc. Each of these methods may have its own intrinsic issue such as impurities, unclear grain boundaries, and non-equilibrium grain boundaries. One common feature of experimental samples is the relatively wide grain size distribution, especially in samples produced by deformation methods. In comparison, MD simulations often use relatively

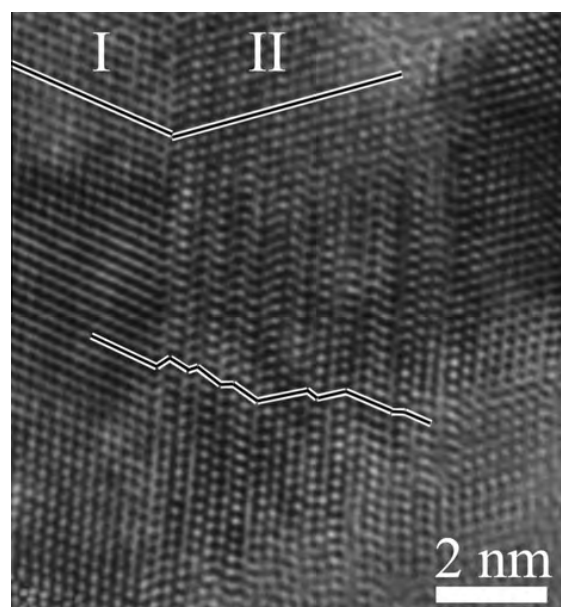


Fig. 12. An HREM image of nc Cu processed by high-pressure torsion (HPT), showing Shockley partial dislocations that were emitted from the lower grain boundary and stopped in the grain interior before reaching the upper grain boundary, leaving behind stacking faults [8].

uniform grain sizes. The wide grain size distribution may be an advantage in some cases. For example, the inverse grain size effect on deformation twinning was found by statistical HREM investigation of electro-deposited Ni with grain sizes ranging from 10 nm to 76 nm [171].

Experimental techniques available so far have much lower spatial and temporal resolutions than the MD simulations. It is also a challenge to observe the deformation process and defect evolutions in real time. Therefore, it would be desirable to combine experiments and MD simulations to probe the deformation process of nc materials.

5.3. Twinning mechanisms

In this section, we will describe the twinning mechanisms that are proposed basing on the experimental observations and MD simulation results.

5.3.1. Overlapping of stacking fault ribbons

The nucleation of deformation twins via overlapping of two stacking fault ribbons are first observed by MD simulations (see Fig. 11) [9]. Fig. 13 shows an HREM image of such a twin nucleus with a thickness of two atomic planes in the interior of a nc Al grain. It was formed by the dynamic overlapping of two extended partial dislocations with stacking faults on adjacent slip planes. As shown, the two stacking faults are only partially overlapped. The twin can grow thicker by adding more SFs on either side of the twin. However, no deformation twins of this type that are thicker than two layers have been reported. Therefore, this twinning mechanism does not play a significant role in the deformation of nc materials. This is because of the lacking of a continuous mechanism for it to grow. It depends on the incidental overlapping of other slipping dissociated dislocations with stacking fault ribbons to grow.

A variant of this twinning mechanism is the overlapping of a dissociated dislocation with a stacking fault connected with the grain boundary [187]. As shown in Fig. 14, close to the grain boundary, the two-layer twin nucleus turned into a stacking fault. This suggests that a stacking fault was first formed from the grain boundary and extended toward grain interior. A dissociated dislocation with a wide stacking fault slipped toward the grain boundary on an adjacent slip plane and then incidentally overlapped with the stacking fault, forming a two-layer twin nucleus. Such a twin nucleus was also predicted by MD simulation (see Fig. 11).

If the leading partial of the dissociated dislocation shown in Fig. 14 reaches the grain boundary, the twin nucleus will become identical to a normal twin nucleus formed by emission of two Shockley partials from the grain boundary. This twin nucleation mechanism could be significant in nc materials with non-equilibrium grain boundaries. High density of dissociated partials with one end pinned on the grain boundary has been observed in nc Ni with non-equilibrium grain boundaries (see Fig. 15) [187], which provides a high probability for such a mechanism to operate.

The two scenarios of twin nucleation via overlapping of stacking faults are schematically illustrated in Fig. 16, in which the thin hairlines across the grain represent the slip planes and the thick shorter lines represent the stacking faults. A twin is nucleated when two stacking faults on two adjacent slip

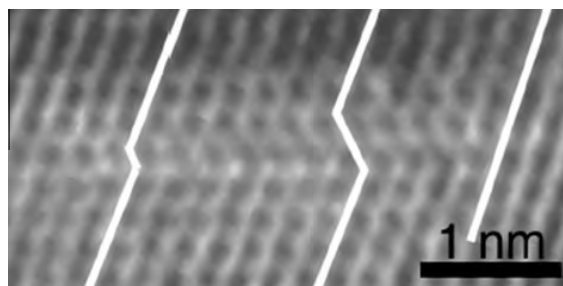


Fig. 13. A deformation twin formed by the overlapping of two extended dislocations on adjacent slip planes in the interior of a grain of nc Al deformed by ball-milling [23].

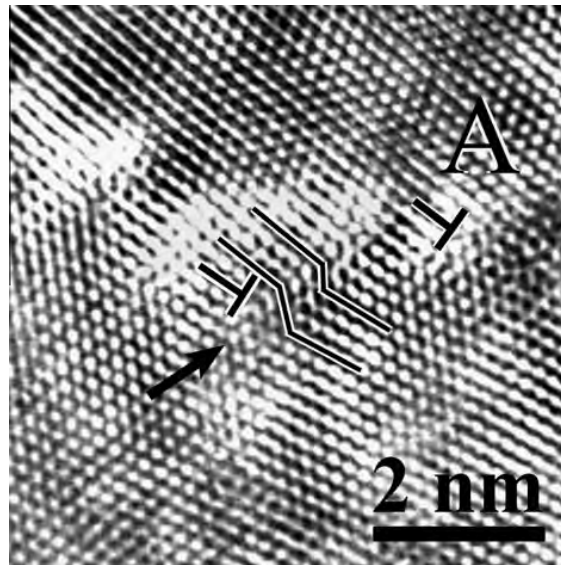


Fig. 14. A twin nucleus formed by overlapping of a dissociated dislocation with a stacking fault from grain boundary in nc Ni [187].

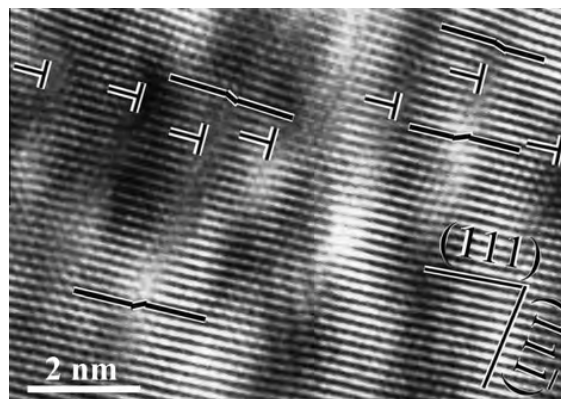


Fig. 15. HREM images showing 60° dislocations that are dissociated into Shockley partials bounding stacking faults.

planes overlap with each other. The twin nucleus marked as A corresponds to that in Fig. 13, while the twin nucleus marked as B corresponds to that in Fig. 14.

5.3.2. Partial emission from grain boundaries

Formation of deformation twins via emission of Shockley partials from grain boundaries was first predicted by MD simulations (see Fig. 11) [9]. Such deformation twins were later verified by HREM. For example, Fig. 17a shows a deformation twin, T_1 , which has a curved twin boundary with the matrix, T_2 , in nc Ni deformed by surface mechanical attrition treatment (SMAT) [56,224]. This twin was formed by successive emission of Shockley partials from the grain boundary on the left. However, the partials did not reach the other side of the grain, and the stopped front of these partials formed a curved twin boundary (see the broken white line). Another example is seen in Fig. 17b, which shows a single twin growing from a grain boundary but terminated inside a grain [214]. The twin was formed by plastically deforming an electrodeposited nc Ni. Such a twin can only be formed by the partial emissions from the grain boundary on the left.

To form the twins shown in Fig. 17, Shockley partials need to be emitted from the grain boundaries on successive slip planes. This type of twinning is the most commonly observed in nc fcc metals and alloys [6,8,9,23,37,66,157,187,203,214]. Therefore, it is scientifically important to understand how the partials are emitted from the grain boundary. It has been reported that partial dislocations can readily

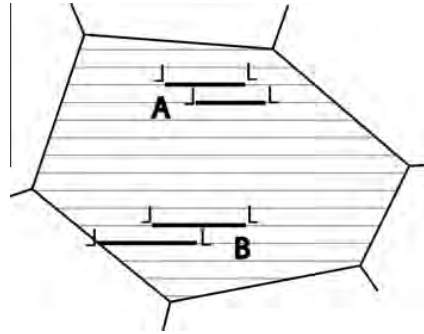


Fig. 16. Two scenarios of twin nucleation via overlapping of stacking faults. The thin hairlines across the grain represent the slip planes and the thick shorter lines represent the stacking faults. Each “L” at the end of a stacking fault indicates a partial dislocation. The twin nucleus marked as A corresponds to that in Fig. 13, while the twin nucleus marked as B corresponds to that in Fig. 14.

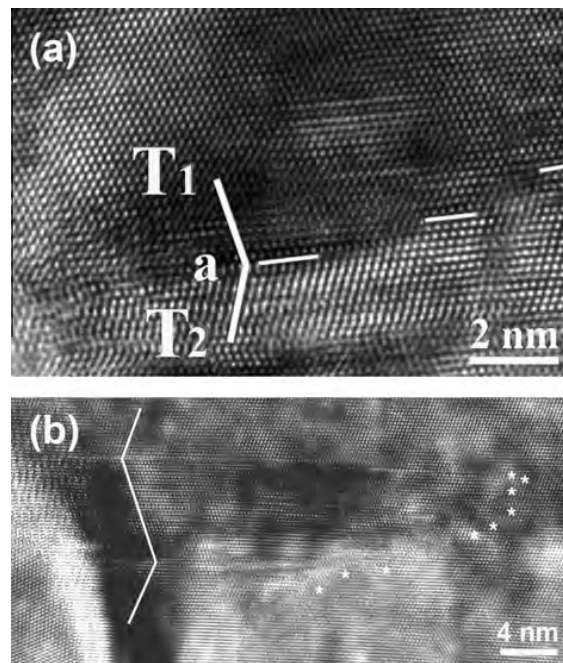


Fig. 17. (a) A deformation twin (T_1) formed by successive emission of partials on adjacent slip planes from the grain boundary on the left in nc Ni deformed by surface mechanical attrition treatment [56]. (b) An HREM image of a twin formed by plastically deforming electrodeposited nc Ni. The twin was formed by the emission of partials from the grain boundary on the left, and it ended in the grain interior as marked by the white asterisks [214].

emit from non-equilibrium grain boundary to nucleate a deformation twin [7,187,225]. However, it is statistically and practically impossible for a partial dislocation to exist on every slip plane to grow a single twin. Nucleation of a new partial on every slip plane is difficult because of the required high energy. Therefore, there must be a partial multiplication mechanism at the grain boundary that will supply a twinning partial on every successive slip plane for twin nucleation and growth. This has been proposed recently by Zhu et al. [214], and is delineated below.

Two dislocation reaction and cross-slip mechanisms have been proposed to supply twinning partials on successive slip planes from the grain boundary to grow a twin continuously. The first mechanism involves the emission of partials with the same Burgers vector, while the second mechanism involves the emission of partials with two different Burgers vectors, which produce a single twin with reduced shear strain. The details of these two mechanisms are described below.

For simplicity, a square grain is used in the description of the two mechanisms. As shown in Fig. 18, the line parallel to the left grain boundary represents a full dislocation with a Burgers vector of

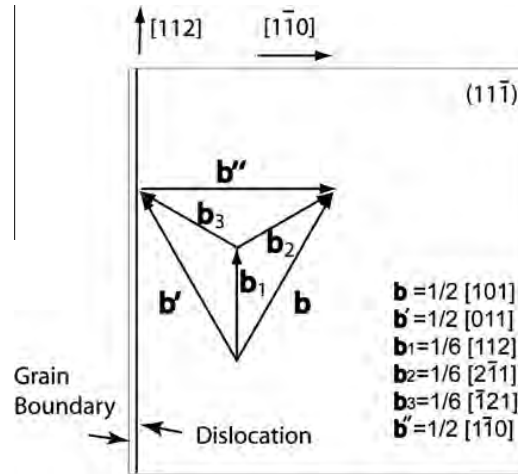


Fig. 18. Schematics of a square grain with a dislocation line parallel to the grain boundary [207]. The slip plane is $(11\bar{1})$, which is parallel to the page. The dislocation line near at the left grain boundary has a Burgers vector of $\mathbf{b} = 1/2[101]$. Other Burgers vectors in the figure are $\mathbf{b}' = 1/2[011]$, $\mathbf{b}_1 = 1/6[112]$, $\mathbf{b}_2 = 1/6[2\bar{1}1]$, $\mathbf{b}_3 = 1/6[\bar{1}21]$, $\mathbf{b}'' = 1/2[1\bar{1}0]$.

$\mathbf{b} = 1/2[101]$. The orientation of the dislocation line is $[112]$. The plane represented by the square is the $(11\bar{1})$ close-packed slip plane. Below we will delineate the first mechanism for Shockley partial multiplication.

5.3.2.1. Mechanism A: multiplication of partials with the same Burgers vector. Let's start with Fig. 18, the perfect dislocation, $\mathbf{b}$, dissociates into two partials under an appropriate applied stress,

$$\mathbf{b} \rightarrow \mathbf{b}_1 + \mathbf{b}_2 \quad (1)$$

where $\mathbf{b}_1 = 1/6[112]$ is parallel to the dislocation line, while $\mathbf{b}_2 = 1/6[2\bar{1}1]$ has a 60° angle with the dislocation line. This dissociation is energetically favorable and therefore can proceed easily. Under an applied shear stress with appropriate orientation, the partial with the Burgers vector $\mathbf{b}_2$ glides on the $(11\bar{1})$ slip plane across the grain to form a stacking fault. Partial $\mathbf{b}_1$ is a pure screw partial and cross-slips to the next $(11\bar{1})$ plane, where it undergoes the following dislocation reaction

$$\mathbf{b}_1 \rightarrow \mathbf{b} + (-\mathbf{b}_2) \quad (2)$$

where $-\mathbf{b}_2$ stays at the grain boundary and the perfect dislocation $\mathbf{b}$ is driven toward the grain interior by the applied stress. The reaction in Eq. (2) has a very high energy barrier and therefore needs a large applied stress to activate. The $\mathbf{b}$ can subsequently dissociate into $\mathbf{b}_1$ and $\mathbf{b}_2$ according to Eq. (1), forming a wide stacking fault ribbon [212]. $\mathbf{b}_2$ would be the leading partial because the applied stress favors its slip. The slip of $\mathbf{b}_2$ nucleates a single twin, and $\mathbf{b}_1$ returns to the grain boundary due to insufficient resolved shear stress to drive it across the grain. Note that in the above process $\mathbf{b}_1$ separates $-\mathbf{b}_2$ and $\mathbf{b}_2$ and keeps them at a large distance to reduce their mutual attraction so that $\mathbf{b}_2$ can easily glide away.

Repetition of the above dislocation reactions (Eqs. (1) and (2)) and cross-slip of $\mathbf{b}_1$ enables the single twin to grow continuously. Such a twin growth process leaves a partial $-\mathbf{b}_2$ on the left grain boundary and another partial $\mathbf{b}_2$ on the right grain boundary on every slip plane in the twin. This changes the grain shape from the original square to what is shown in Fig. 19, as viewed in the $\mathbf{b}' = [011]$ direction, which is perpendicular to $\mathbf{b}_2$.

In an HREM micrograph taken from any $\langle 110 \rangle$ direction that is on the twin boundary plane, the atomic-scale image has mirror symmetry across the coherent twin boundary. This is the way to identify a twin using HREM. As shown in Fig. 18, there are three orientations from which a twin with $(11\bar{1})$ twinning plane can be viewed by HREM: $\mathbf{b} = 1/2[101]$, $\mathbf{b}' = 1/2[011]$, and also $\mathbf{b}'' = 1/2[1\bar{1}0]$. The view from $\mathbf{b}'$ is illustrated in Fig. 19, which shows a 141° grain boundary kink. However, if the twin is viewed from the $\mathbf{b}$ and $\mathbf{b}''$ direction, the projection of the twinning partial $\mathbf{b}_2$ on the direction perpendicular to the $\mathbf{b}$ and $\mathbf{b}''$ in the $(11\bar{1})$ plane will be reduced by half because the $\mathbf{b}$ and $\mathbf{b}''$ has a 30°

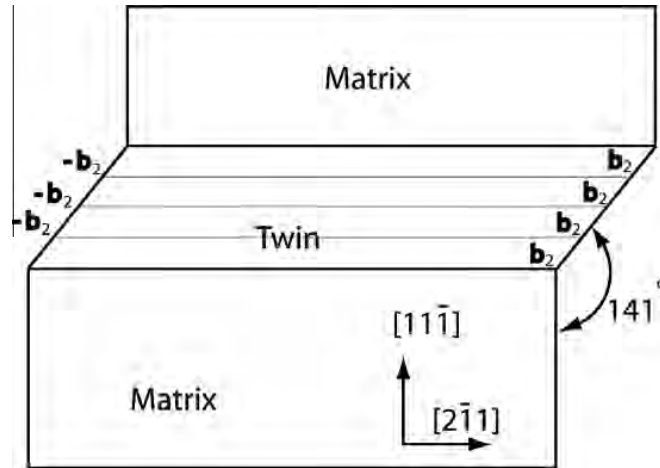


Fig. 19. The grain shape change caused by the first twinning mechanism in which all twinning partials have the same Burgers vector [207]. The 141° grain boundary kink can be seen from an orientation perpendicular to the Burgers vector of the twinning partial and parallel to the slip plane.

angle with the $\mathbf{b}_2$. In other words, the grain boundary kink angle will now be increased to 158° , as shown in Fig. 20. This makes twinning strain appear less than what is viewed from $\mathbf{b}'$ orientation (Fig. 19).

5.3.2.2. Mechanism B: multiplication of partials with the two different Burgers vectors. Next we will describe the second twinning mechanism, which involves the emission of partials with two different Burgers vectors, $\mathbf{b}_2$ and $\mathbf{b}_3$. It produces less macroscopic strain than the twinning mechanism A. One can see from Fig. 19 that, after cross-slip, the partial $\mathbf{b}_1$ under appropriate applied stress can have another dislocation reaction:

$$\mathbf{b}_1 \rightarrow \mathbf{b}' + (-\mathbf{b}_3) \quad (3)$$

where $\mathbf{b}_3 = 1/6[\bar{1}21]$ and $\mathbf{b}' = 1/2[011]$. The partial $-\mathbf{b}_3$ stays at the grain boundary and the perfect dislocation $\mathbf{b}'$ dissociates into $\mathbf{b}_1$ and a new partial $\mathbf{b}_3$. The applied shear stress drives the new partial $\mathbf{b}_3$ away from the grain boundary to glide on the $(11\bar{1})$ plane across the grain, which grows the twin.

If the dislocation reactions described in Eqs. (2) and (3) occur on alternative slip planes or occur for approximately the same number of times, the grain will change its shape along the $\mathbf{b}_1$ direction (see

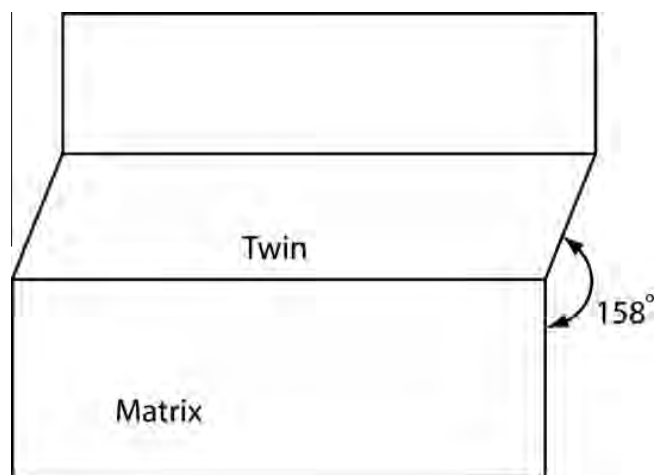


Fig. 20. The grain shape change caused by the first twinning mechanism in which all twinning partials have the same Burgers vector, but viewed from the orientation of $\mathbf{b}$ and $\mathbf{b}'$ [207]. The grain boundary kink is 158° . As will be described later, this can also be caused by the second twinning mechanism in which approximately equal numbers of $\mathbf{b}_2$ partials and $\mathbf{b}_3$ partials are involved. In the second twinning mechanism, the 158° grain boundary kink can be seen from an orientation perpendicular to $\mathbf{b}_1$.

Fig. 18), but the macroscopic strain will be only half of that shown in Fig. 19. This is because the slip of the partial $\mathbf{b}_2$ produces a strain of $a/\sqrt{6}$ along the $\mathbf{b}_2$ direction, while the slip of the partial $\mathbf{b}_3$ produces a strain of $a/\sqrt{6}$ along the $\mathbf{b}_3$ direction. From Fig. 18 we have the following relationship $\mathbf{b}_2 + \mathbf{b}_3 = \mathbf{b}_1$. Therefore, the total strain in every two slip planes is $a/\sqrt{6}$ along the $\mathbf{b}_1$ direction, producing a change in grain shape as shown in Fig. 20 when viewed from the $[1\bar{1}0]$ orientation (along $\mathbf{b}''$). However, if the twin is viewed from the $\mathbf{b}$ or $\mathbf{b}'$ orientation, the grain boundary kink angle will be $\sim 169^\circ$ (see Fig. 21). Note that it is also possible to form a twin by the mixture of the first and the second mechanisms. This could happen when the twinned grain rotates during the twinning process, which changes the stress orientation.

As described in Figs. 19–21, three possible grain boundary kinks could be observed under HREM if a twin is formed by the mechanism A or B. If the HREM image shows a twinned grain with a 141° grain boundary kink as shown in Fig. 19, then the twin was formed by the mechanism A described by Eq. (2), in which only one type of twinning partial is involved to produce the twin. On the other hand, if the HREM image shows a twinned grain with a 158° grain-boundary kink as shown in Fig. 20, it is not possible to determine if the twin is produced by the first mechanism or the second mechanism. However, if the HREM image shows a twinned grain with a 169° grain-boundary kink as shown in Fig. 21, the twin is formed by the Mechanism B, in which about equal number of $\mathbf{b}_2$ partials and $\mathbf{b}_3$ partials are involved.

In practice, the grain boundary kink in an HREM micrograph is sharp enough for angle measurement only when the grain boundary is close to the edge-on orientation, which does not happen very often statistically. This makes the kink-angle measurement a tedious task. For example, the grain boundary kinks in Fig. 17 are not obvious because grain boundary is far from the edge-on condition.

In the above discussion, we specified the dislocation type and Burgers vector so that $\mathbf{b}_1$ is a pure screw partial dislocation, making it easy for $\mathbf{b}_1$ to cross-slip into the next $(1\bar{1}\bar{1})$ plane. This is the easiest path for twin growth. However, we shall point out that even if $\mathbf{b}_1$ is a pure edge or a mixed type, it can still move to the next $(1\bar{1}\bar{1})$ slip plane by climbing alone or by climbing plus cross-slip, although higher applied stress is needed for such a process. Note also that the dislocation climbing on the grain boundary should be much easier than in the grain interior because of higher diffusion rate at the grain boundary and the probability of higher local residual stress.

5.3.3. Twinning with low macroscopic strain

In the last section, we demonstrated that deformation twins in nc fcc metals may have a grain boundary kink of 141° if formed by partials with the same burger vector and viewed from an appropriate $\langle 1\bar{1}0 \rangle$ orientation under HREM (see Fig. 22) [2]. This represents the highest macroscopic strain that can be formed by a deformation twin in fcc materials. It is also demonstrated that if the partials

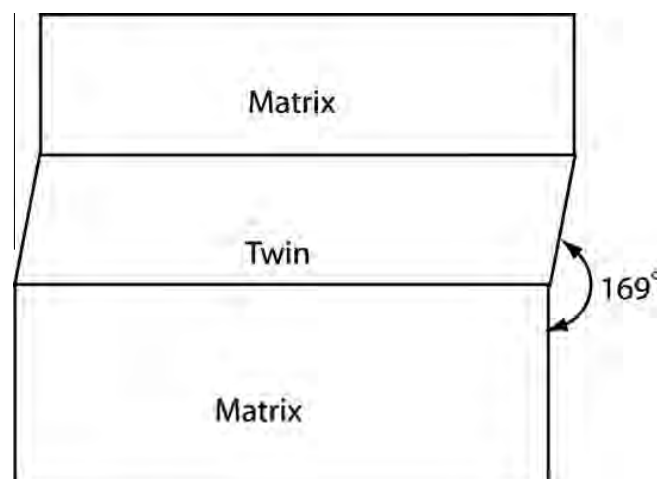


Fig. 21. The grain shape change caused by the second twinning mechanism (Mechanism B) in which approximately equal numbers of $\mathbf{b}_2$ partials and $\mathbf{b}_3$ partials are involved. The 158° grain boundary kink can be seen from the orientation of $\mathbf{b}''$.

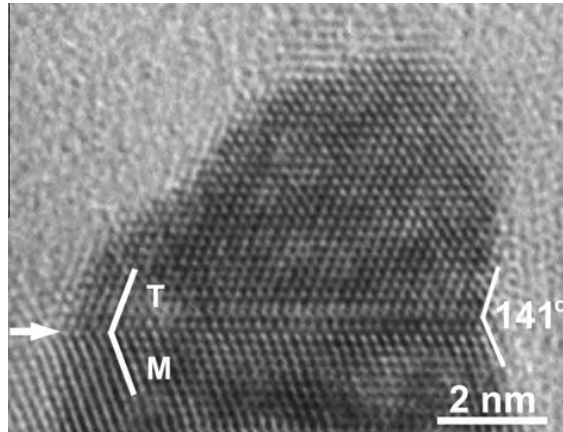


Fig. 22. HREM micrograph of a twin in nc Cu synthesized by high-pressure torsion. The arrow indicates the twin boundary. The grain boundary has a 141° kink at its intersection with the twin boundary. This twin was formed by partials with the same Burgers vector [2]. Note that this twin morphology is the same as that of a deformation twins in coarse-grained fcc metals.

have different Burgers vectors, the macroscopic strain will be lower. In this section, we further deliberate on the observation and mechanisms of deformation twins with low or even zero macroscopic strain.

Fig. 23 shows typical HREM images of deformation twins in nc Al, Ni and Cu that were produced by cryogenic milling, cryo-tension, and high-pressure torsion, respectively [2]. As shown, the grain boundary segments are smooth even at locations where they intersect the twin boundaries, suggesting that the deformation twins shown in Fig. 23 did not change the morphology of the grains.

It is proposed that the twins shown in Fig. 23 were formed via a twinning mechanism named *random activation of partials* (RAP) [2]. Fig. 2 illustrates a set of Shockley partials involved in the RAP process. As shown, on the (1 1 1) slip plane, there are three Shockley partials, $\mathbf{b}_1 = \mathbf{B}\delta$, $\mathbf{b}_2 = \mathbf{A}\delta$ and $\mathbf{b}_3 = \mathbf{C}\delta$. Note that $\mathbf{A}\delta$ means a Burgers vector that starts at $\mathbf{A}$ and ends at δ . It is obvious that

$$\mathbf{b}_1 + \mathbf{b}_2 + \mathbf{b}_3 = 0 \quad (4)$$

As discussed in Section 2 and Fig. 3, a twin can be formed by the slip of identical partials or different partials, because the three partials, $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$, produce the same stacking sequence shifts despite of their orientation difference. Therefore, if all of the three partials propagate in equal number of times, one after another, there will be no net accumulation of macroscopic strain.

The RAP mechanism involves three Shockley partials with different Burgers vectors. Below we discuss how the emission of three Shockley partials can be realized in a nano grain with the help of

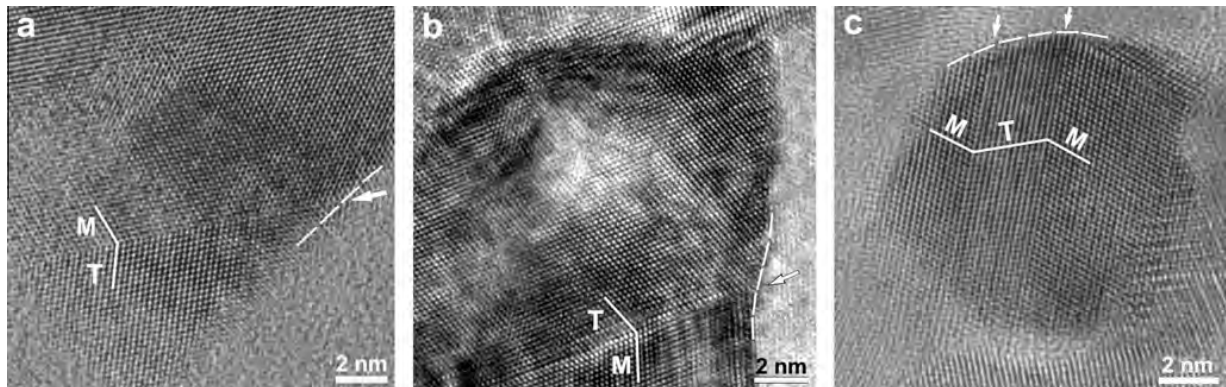


Fig. 23. HREM images of typical deformation twins in three nc fcc metals. (a) Al processed by cryo-milling, (b) electro-deposited Ni deformed by cryo-tension, and (c) Cu processed by high-pressure torsion. It is evident that the deformation twins did not change the shape of the grains. The arrows indicate the twin boundaries. The broken curves indicate grain boundaries. Twins and matrix are labeled T and M, respectively [2].

Fig. 24. Consider a Shockley partial dislocation loop on a (1 1 1) plane with the Burgers vector $\mathbf{b}_1 = 1/6[2\bar{1}\bar{1}]$. **Fig. 24** illustrates such a dislocation loop emitted from a grain boundary triple junction and deposited on other segments of the grain boundary of a hexagonal grain. Part of the dislocation line segments parallel to grain edges AB and DE has pure screw character and can easily cross-slip in the GB to the next slip plane. On the next slip plane, $\mathbf{b}_1$ can slip by itself under appropriate stress or produce other dislocations via the following two reactions:

$$\frac{a}{6}[2\bar{1}\bar{1}] = \frac{a}{6}[\bar{1}2\bar{1}] + \frac{a}{2}[1\bar{1}0] \quad (5)$$

$$\frac{a}{6}[2\bar{1}\bar{1}] = \frac{a}{6}[\bar{1}\bar{1}2] + \frac{a}{2}[10\bar{1}] \quad (6)$$

From **Fig. 2a**, we can also rewrite Eq. (5) as $\mathbf{b}_1 = \mathbf{BA} + \mathbf{b}_2$, and Eq. (6) as $\mathbf{b}_1 = \mathbf{BC} + \mathbf{b}_3$. Thus it is possible to randomly emit the three Shockley partials, $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$, on the next (1 1 1) slip plane.

A global shear stress cannot drive the three partials simultaneously. So what drives the $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$ partial slip? It is argued that it is possible for these partials to randomly nucleate and slip one at a time, driven by changing local shear stresses [2]. These stresses could significantly differ from the global shear stress. That such a scenario is possible is revealed by atomistic simulations of stress concentration of 3–3.5 GPa, which is many times higher than the applied shear stress, near the edge of a stacking fault [203]. Furthermore, grain boundary sliding and grain rotation, significant in nc materials [25,38,39,108], alter local stress state [80] and/or change the orientation of the twinning grain. These local stress variations can promote the random emission of partials. Other locations for high local stress concentration include triple junctions, and grain boundary steps. Also, once a twin is nucleated, it is relatively easy to grow the twin [57,59,226], thus explaining why the RAP twins could form instead of producing many stacking faults. It has been recently reported that the three partials $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$ can indeed move in the same direction by a stop-and-start mechanism. This mechanism has been predicted by MD simulation and verified by in situ TEM observation at the incoherent twin boundaries in Cu film produced by magnetron sputtering [227]. This mechanism can also produce deformation twins without macroscopic strain.

A global strain is necessary to relieve the global stress. Although the grains with RAP twins do not change their shape, they indeed contribute to the global strain by grain boundary sliding and grain rotation. Also, during the RAP twinning, the applied stress, and the attendant accumulated energy, is effectively dissipated locally by the random nucleation and slip of three Shockley partials from grain boundaries. However, their Burgers vectors add up to zero macroscopic strain, without violating laws of thermodynamics. It should be noted that although the RAP twins have negligible direct contribution to the macroscopic deformation at the grain level, they indirectly contribute to the bulk deformation by favorably reorienting the crystal lattice to change the applied resolved shear stresses on slip systems.

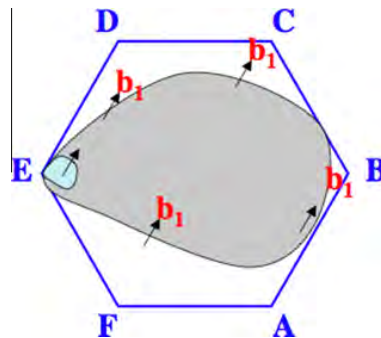


Fig. 24. A Shockley partial dislocation loop with Burgers vector $\mathbf{b}_1$ emitted from a grain boundary triple junction at E, grows, and deposits on other grain boundaries of a hexagonal grain [2]. Part of the dislocation line segments parallel to grain edges AB and DE has pure screw character and can move along the grain boundary to the next slip plane.

Note that the RAP twins form only if the numbers of $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$ partials are about the same. If this condition is not met, there will be macroscopic strain in the twinned grain. The magnitude of the strain is determined by the relative numbers of the three partials.

5.3.4. Grain boundary splitting and migration

This type of twins was first proposed by Ashby and Harper in 1967 [228]. The twinning mechanism was first verified by the MD simulation [157], and then experimentally observed recently [66]. This twinning mechanism was already shown in Fig. 11 and described in Section 5.1. Fig. 25 is an HREM image of a twin formed by grain boundary splitting and migration in nc Al processed by cryogenic ball milling. As shown, some segments of the boundary are straight, coherent (111) twin boundaries as indicated by white arrows. Mirror images typical of twins are shown on the two sides of these coherent twin boundaries. These segments, which are connected by non-crystallographic segments, form a zigzag boundary between the twinned area and the matrix. A twin lamella was formed via the migration of the new twin boundary. The boundaries of twin lamellae formed at different time frames joined together to form the zigzag boundary.

The non-crystallographic segments observed here were actually the new twin boundaries in this mechanism. As discussed earlier in Section 5.1, the non-crystallographic segments are formed by Shockley partial dislocations, which exist on every slip plane. It is likely that these partials are $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$ mixed in about the equal numbers, because if all partials have the same Burgers vector, there should be a large strain field in front of the non-crystallographic twin boundary. Such a strain field should be reflected by lattice distortion and/or high density of dislocations in the matrix in front of the non-crystallographic twin boundary, which is not observed in Fig. 25.

5.3.5. Sequential twinning mechanism

The mechanism of sequential twinning via emissions of Shockley partials from grain boundaries and twin boundaries was proposed based on the experimental observation of multifold twins, including fivefold twins (see Fig. 26) [70]. Fivefold twins were often observed to form by the nucleation and growth mechanism in nanosized particles, annealed nc fcc metals, or nano-wires [229–233]. However, these fivefold *growth* twins are very different from the fivefold *deformation* twins discussed here, which are formed by the partial-dislocation mediated sequential twinning mechanism. Fivefold deformation twins have been observed in an nc Al alloy [65], pure Cu [8,70,234], and an ultrafine-grained Cu alloy [235]. In this twinning mechanism, a regular twofold twin will be formed first, and then a threefold twin is formed by the successive interaction of Shockley partials with the twin boundary. Repetition of this process leads to the formation of fourfold and fivefold twins. This twinning mechanism was later verified by MD simulation [216]. More details are described below.

The first step of this mechanism is the formation of a simple twin with domains I and II (Fig. 27a) via partial dislocation emissions from grain boundaries. Such a type of twins occur frequently in nc fcc metals [7,70,214], and can be formed via several twinning mechanisms [42,214]. The second step (Fig. 27b) starts with the emission of a 90° Shockley partial, $\mathbf{b}_1 = 1/6[\bar{1}12]$, from the upper grain boundary in domain II. The partial glides on a (11 $\bar{1}$) slip plane toward the twin boundary TB1. A 90° Shockley partial has a Burgers vector perpendicular to the dislocation line.

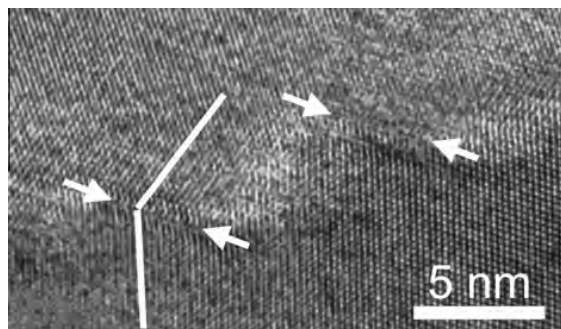


Fig. 25. A deformation twin formed by GB splitting and migration in nc Al deformed by ball milling [66].

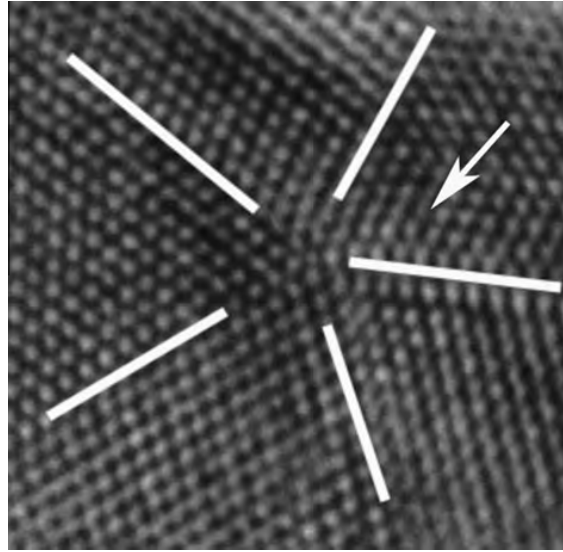


Fig. 26. A fivefold twin formed by the sequential twinning in nc Cu deformed by high-pressure torsion [70].

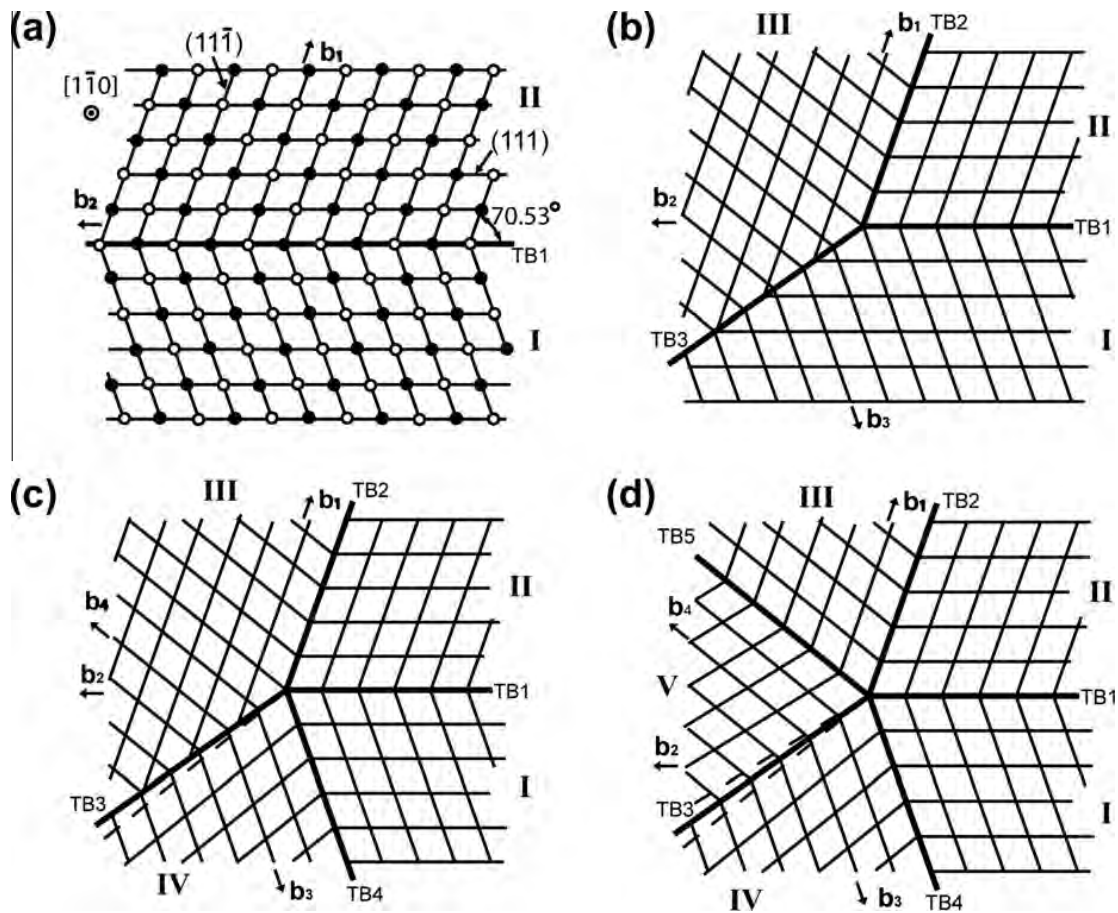


Fig. 27. (a) Illustration of a regular twin (step 1). (b) A threefold deformation twin (step 2) formed by the emission of a series of 90° partials, $\mathbf{b}_1$. These partials form new 90° partials with a Burgers vector $\mathbf{b}_2$ on the twin boundary TB1, which glides away from TB1, forming a new twin boundary TB3. (c) A fourfold deformation twin (step 3) formed from a threefold deformation twin by emitting a series of 90° partials, $\mathbf{b}_3$. (d) A fivefold deformation twin (step 4) formed from a fourfold deformation twin by emitting a series of 90° partials, $\mathbf{b}_4$. The dotted lines form an angle of 7.33° , which has to be accommodated by elastic strain [70].

A deformation twin can be defined by the twin plane K_1 , shear direction η_1 , undistorted plane K_2 , and direction η_2 . η_2 lies on K_2 (see Fig. 28) [54]. Deformation twins in an fcc metal are of compound type, in which a twin formed by Shockley partials with the Burgers vector parallel to η_1 gliding on K_1 is the same as a twin formed by partials with the Burgers vector parallel to η_2 gliding on K_2 . In Fig. 27a, we can regard K_1 and K_2 as $(1\ 1\ \bar{1})$ and $(1\ 1\ 1)$ slip planes, respectively. η_1 is parallel to $\mathbf{b}_1$, and η_2 is parallel to another 90° Shockley partial $\mathbf{b}_2 = 1/6[1\ 1\ \bar{2}]$. In other words, when a 90° Shockley partial $\mathbf{b}_1$ reaches the twin boundary TB1, it becomes equivalent to another 90° partial $\mathbf{b}_2$ on the $(1\ 1\ 1)$ plane. Under an appropriate external shear stress, the $\mathbf{b}_2$ partial could glide to the left, which consequently moves the twin boundary downward by one atomic plane. When a series of Shockley partials with a Burgers vector $\mathbf{b}_1$ emit from the grain boundary successively on adjacent $(1\ 1\ \bar{1})$ planes, with each $\mathbf{b}_1$ partial converting to a $\mathbf{b}_2$ partial that glides to the left, a twin domain III will form, which effectively converts the regular twin in Fig. 27a into a threefold twin as shown in Fig. 27b. An incoherent twin boundary, TB3, is also formed.

A threefold deformation twin can be transformed into a fourfold deformation twin via the emissions of a series of 90° Shockley partials from a grain boundary in domain I or III (step 3). Assuming that a 90° Shockley partial $\mathbf{b}_3$ first emits from a point on a grain boundary in domain I (see Fig. 2) and moves toward the twin boundary TB3, a stacking fault will form, and a twin will nucleate and grow on both side of the stacking fault via the stress-controlled twin growth mechanism, resulting in a new twin domain IV (Fig. 27c). The fourfold deformation twin can be transformed into a fivefold deformation twin (step 4) by emitting another series of Shockley partials ($\mathbf{b}_4$) from grain boundaries in

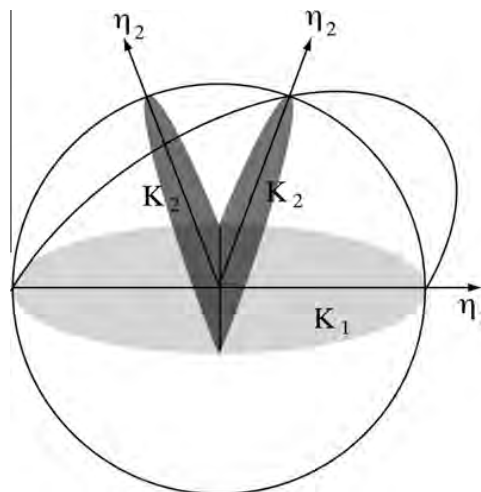


Fig. 28. Illustration of twinning elements η_1 , η_2 , K_1 and K_2 .

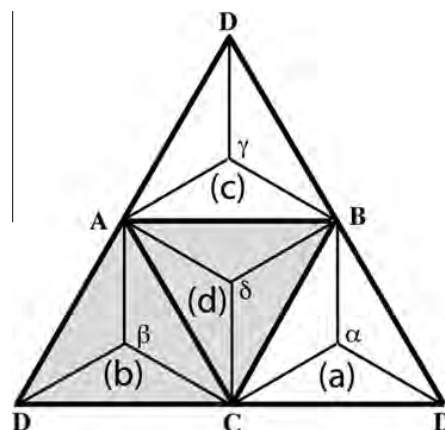


Fig. 29. The Thompson tetrahedron illustrating the possible slip systems and dislocations thereof in an fcc crystal.

twin domain III (Fig. 27c), following the same process as the formation of twin domain IV. When a Shockley partial with a Burgers vector $\mathbf{b}_4$ reaches the twin boundary TB3, it forms an edge dislocation in the displacement shift complete (DSC) lattice, with a Burgers vector opposite to the Burgers vector of the edge dislocation previously formed by a $\mathbf{b}_3$ partial in the DSC lattice. Therefore, these two types of edge dislocations will cancel each other, which converts TB3 into a coherent twin boundary. In addition, another coherent twin boundary, TB5, is also formed, which transforms the fourfold twin into a fivefold twin. It is also possible that the $\mathbf{b}_3$ and $\mathbf{b}_4$ partials are activated simultaneously, directly transforming a threefold deformation twin into a fivefold deformation twin.

Note that the above ideal twinning process would leave a 7.33° gap (see the angle between the two dashed lines in Fig. 27d). This is because the angle between two $\langle 111 \rangle$ planes in an fcc metal is $\sim 70.53^\circ$, which is 1.47° smaller than the 72° that is required to cover 360° by five twins. This angle difference is accommodated by elastic strain [229,236]. The lattice distortion from elastic strain can be seen near twin boundaries of the fivefold twin in Fig. 26 (see the white arrow).

5.3.6. Partial multiplication at twin boundaries

One of the major issues in the formation of deformation twins in nc fcc metals is the source of partial dislocations that are needed on consecutive $\{111\}$ slip planes. As discussed earlier, in coarse-grained fcc metals, several continuous partial-supply mechanisms have been proposed, including the pole mechanism [71], prismatic glide mechanism [72], faulted dipole mechanism [73], and others [1,74–76]. However, these mechanisms cannot operate in nc metals due to the lack of dislocation sources in the grain interior. The partial multiplication mechanisms discussed in Section 5.3.2 and the RAP mechanism discussed in Section 5.3.3 are two examples of partial dislocation self-generation mechanisms via dislocation reaction at grain boundaries. Below we will describe several mechanisms for partial multiplication at twin boundaries, which can form single and multiple twins in a self sustained way [42].

To assist with the description of the twinning mechanisms, we show the unfolded Thompson tetrahedron in Fig. 29. As shown, the four $\{111\}$ slip planes (represented by four triangles) can be denoted as (a)–(d). The (b) and (d) planes are shaded here because they will be used to help describe the formation of deformation twins in the following sections. Note also that points α , β , γ and δ are at the center of the triangles BCD, ACD, ABD, and ABC, respectively. The lines that link the center of a triangle with its corners, e.g. $\mathbf{A}\beta$, and $\delta\mathbf{C}$, represent the Burgers vectors of partial dislocations on that slip plane. $\mathbf{A}\beta$ represents a Burgers vector from A to β . Other Burgers vectors herein are defined in the same way. A dislocation whose Burgers vector links the centers of two slip planes is defined here as a stair-rod dislocation (e.g. $\beta\delta$), which follows the definition by Thompson [54,76].

5.3.6.1. Single twin via partial reactions at twin boundary. As shown in Fig. 30a, a partial dislocation, $\mathbf{C}\beta$, glides on the (b) plane toward a stacking fault, SF, on the (d) plane, and is stopped on the slip plane next to the SF. Driven by applied stress, the partial $\mathbf{C}\beta$ dissociates into a partial dislocation $\mathbf{C}\delta$ on the (d) plane and a stair rod dislocation $\delta\beta$ according to Fig. 29:



According to Fig. 30b, $\mathbf{C}\delta$ glides to the right to nucleate the twin, leaving behind the stair-rod dislocation $\delta\beta$. The stair-rod dislocation $\delta\beta$ can further dissociate into a partial $\delta\mathbf{C}$ on the (d) plane and a partial $\mathbf{C}\beta$ on the (b) plane according to Fig. 29:

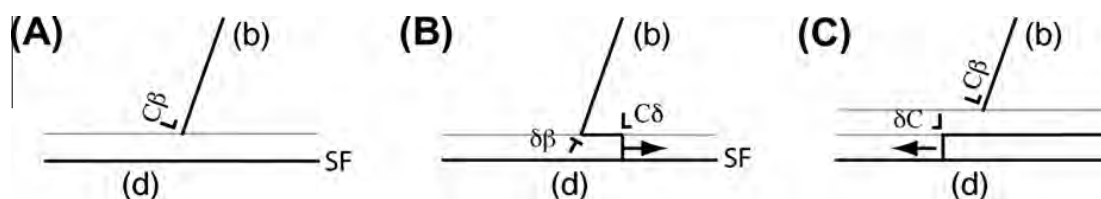


Fig. 30. Schematics of dislocation reactions between partial $\mathbf{C}\beta$ on the (b) plane and a stacking fault, SF, on the (d) plane to nucleate a single twin. Repetition of these reactions leads to the growth (thickening) of this twin [42].



This reaction, and others to follow, needs applied stress to overcome the energy barrier. As shown in Fig. 30c, δC glides to the left to extend the twin nucleus and the partial $C\beta$ glides up by one atomic plane.

The above dislocation reactions at the stacking fault SF nucleate a two-layer twin, and leave behind the original partial dislocation $C\beta$ at the twin boundary. The partial $C\beta$ can continue the above dislocation reaction and slip with each reaction cycle growing the twin by one slip plane.

In this twinning mechanism, the self partial-multiplication mechanism involves a Shockley partial at the twin boundary (see Fig. 30c). This Shockley partial should be associated with, and located at the end of, a stacking fault. Therefore, we should see a twin in the (d) plane and a stacking fault in the (b) plane. Such a configuration is indeed observed in nc Cu processed by high-pressure torsion, as shown in Fig. 31.

5.3.6.2. V-shaped twin via dislocation reaction and cross-slip [42,67,69]. This mechanism is different from the cross-slip mechanism proposed by Fujita and Mori [237]. The latter does not provide for a mechanism for the twin to grow (thicken) by itself. To describe this mechanism, we start with the situation described in Fig. 30a, in which the partial $C\beta$ is stopped at the stacking fault SF. The partial $C\beta$ now dissociates into the following dislocations (see Fig. 29) under an applied stress with appropriate stress magnitude and orientation:



$A\delta$ glides to the right to nucleate a twin on the (d) plane, while CA cross-slips to the next intersection of the (d) and (b) planes (see Fig. 32a). The stair-rod dislocation $\delta\beta$ is sessile. CA now dissociates into two partials on the (b) plane:



βA glides upward to nucleate a twin on the (b) plane, forming the nucleus of a V-shaped twofold twin (see Fig. 32b).

The partial $C\beta$ can repeat the above dislocation reactions and processes, causing growth (thickening) of the twofold twin, as illustrated in Fig. 32c. As shown, there is a stair-rod dislocation $\delta\beta$ at every intersection of the (d) and (b) planes. This results in a high stress at the ends of the stair-rod pileup at the intersecting boundary of the two twins. When the stress is very high, partial or perfect dislocations could be emitted or absorbed to relieve these stress concentrations.

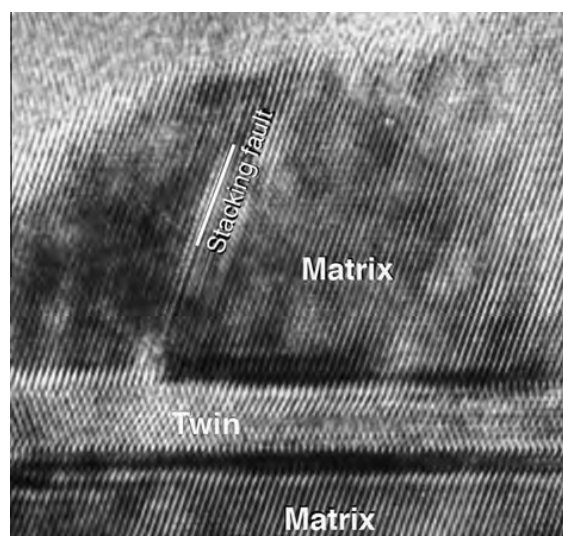


Fig. 31. A single twin that is consistent with the self-multiplication mechanism [42].

Such a V-shaped twin has been observed in electrodeposited nc Ni after cryo-rolling at liquid nitrogen temperature [69]. Shown in Fig. 33a is the HREM image of a nc Ni grain marked as A. The image inside the white frame is shown in Fig. 33b. As shown, two intersecting twins are visible, labeled as T_1 and T_2 , respectively. The T_1 is observed to extend all the way from the grain boundary on the right side. One end of the T_2 intersects with T_1 in the area marked by B, while the other end terminates inside the grain (marked as D). This V-shaped twin was formed by the *dislocation reaction and cross-slip* mechanism illustrated in Fig. 32.

5.3.6.3. T-shaped twin via dislocation reaction and cross-slip. A T-shaped twin can be formed in a process similar to the V-shaped twin. Assuming that a V-shaped twin is already formed (see Fig. 34A). A partial dislocation $C\delta$, emitted from the grain boundary or another source, glides to the right on a (d) plane adjacent to the original stacking fault (see Fig. 34A). The partial $C\delta$ is stopped by the twin boundary and dissociates into the following dislocations (see Fig. 29) under the applied stress:

$$C\delta \rightarrow CA + A\beta + \beta\delta \quad (11)$$

$A\beta$ glides upward to nucleate a twin on the (b) plane, while CA cross-slips to the intersection of the next (d) plane and (b) plane (similar to that shown in Fig. 32a). The stair-rod dislocation $\beta\delta$ is sessile and cannot move. CA now dissociates into two partials on the (d) plane:

$$CA \rightarrow C\delta + \delta A \quad (12)$$

δA lides to the left to grow the twin on the (d) plane (see Fig. 34B). The partial $C\delta$ can repeat the above dislocation reactions and processes, causing growth (thickening) of the T-shaped twin, as illustrated in Fig. 34c.

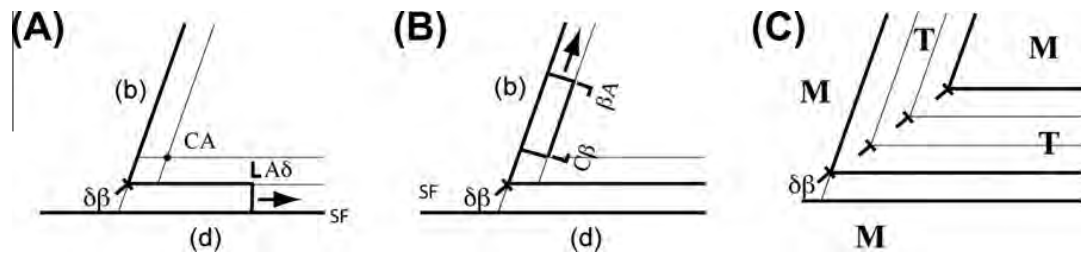


Fig. 32. Schematics of the nucleation and growth of a V-shaped twofold deformation twin by dislocation reaction and cross-slip at the twin boundary. (A) Nucleation of a twin on the (D) plane. (B) Nucleation of the second twin on the (B) plane. (C). A V-shaped twofold twin after some growth. A stair-rod dislocation $\delta\beta$ is at every intersection of the (D) and (B) planes [42].

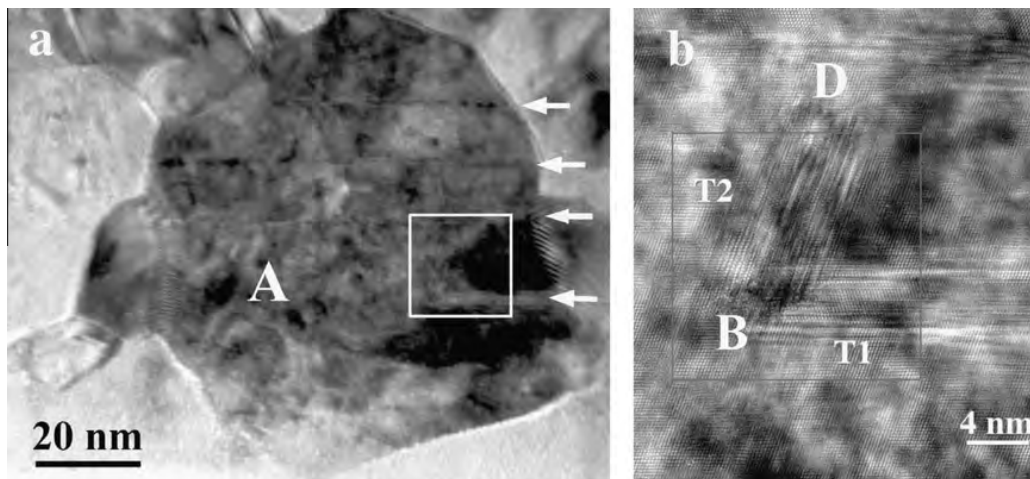


Fig. 33. HREM images showing (a) a grain that contains a cross-slip twin in the white frame and (b) an enlarged image of the area in the white frame in (a) [66].

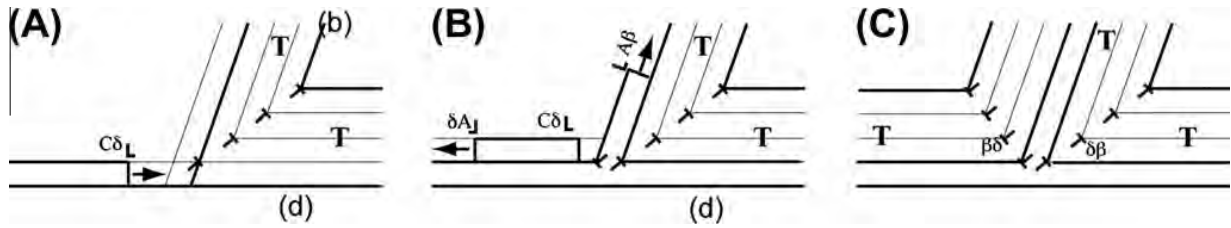


Fig. 34. Formation of a T-shaped twin. (A) A partial, $C\delta$, slip toward the twin boundary. (B) After the dislocation reactions (Eqs. (5) and (6)), a T-shaped twin is nucleated, leaving behind the partial $C\delta$ to repeat another dislocation reaction cycle. (C) The final T-shaped twin with two arrays of stair-rod dislocations [42].

As shown in Fig. 34C, the above process produces a stair-rod dislocation $\beta\delta$ at every intersection of (d) and (b) planes, which is of the opposite sign to the $\delta\beta$ stair-rod dislocations formed earlier in the twofold twin. The arrays of $\beta\delta$ and $\delta\beta$ stair-rod dislocations partially cancel each other's long-range stress fields [238]. However, the pileup tips would still have local stress concentration. Note that following the processes similar to what are described in the Figs. 32 and 34, an X-shaped twin can also form [42].

5.3.7. Dislocation rebound mechanism

The single and multiple twins could also be formed by the dislocation rebound mechanism [239]. The elastic field of a partial dislocation is reflected (or partially reflected) at grain boundaries or twin boundaries (analogous to shock wave reflection) [239]. The reverse shear field can aid in nucleation of an opposite-sign dislocation where the first one impinged, especially if the velocity of the dislocation approaches the Rayleigh velocity (sound velocity) [42,48,239]. This dislocation rebound mechanism can produce the single twin, V-shaped twin, T-shaped twin, and X-shaped twins described above [42]. The rebound mechanism is deliberated in the following sections.

As shown in Fig. 35a, a partial, $C\delta$ nucleates from the grain boundary on the left, glides to the right to form a stacking fault. Such events have been observed both in MD simulations [9,10] and by HREM [8]. The elastic field of the partial dislocation is reflected by the grain boundary on the right, which helps with the nucleation of a partial dislocation with an opposite sign, δC on the next slip plane. This partial glides to the left, nucleating a single twin, as shown in Fig. 35b. Note that the nucleation and glide of δC leaves behind a partial of opposite sign, $C\delta$, on the right grain boundary (see Fig. 35b).

5.4. Grain size effect

Grain size is an essential factor that affects the formation of deformation twins in metals and alloys. It has been extensively reported in the literature that larger grain sizes are more favorable to twin nucleation for conventional coarse-grained (CG) materials [11,240]. This is rationalized as follows. Both the critical stresses σ for dislocation slip and twinning follow a Hall–Petch type (H–P) behavior, $\sigma = \sigma_0 + kd^{-\alpha}$, where d is grain size, σ_0 and k are constants and α is an exponent typically equal to 0.5. For many CG metals and alloys, the H–P slope for deformation-twinning-mediated plasticity (k_{DT}) is

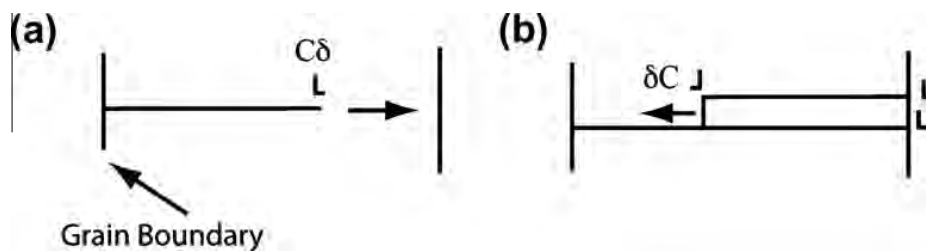


Fig. 35. The formation of a single twin by the rebound mechanism. (a) A partial $C\delta$ glides to the right to form a stacking fault. (b) $C\delta$ rebounds as δC from a grain boundary or twin boundary to nucleate a single twin. Two partials $C\delta$ are left superposed on the grain boundary at the right [40].

much larger (up to 10 times) than that for dislocation slip (k_{DS}) [11,81]. Therefore, for coarse-grained metals and alloys, decreasing grain size favors dislocation slip and makes twinning more difficult. The physical reason for such a grain size effect in coarse-grained metals is not understood. Yu et al. [241] recently attempted to explain such a phenomenon by a “stimulated slip” mechanism. More studies are needed to probe its fundamental physics.

However, when the grain size is further refined down to nanometer regions (below 100 nm), deformation twinning has been frequently observed even in materials with medium to high stacking fault energies such as copper and nickel. Therefore, twinning was considered as one of the major plastic deformation mechanisms of nanostructured materials [8,24–30]. The grain size effect on deformation twinning in the nc fcc Ni was systematically investigated in a recent study [171]. An electrodeposited nc-Ni foil with grains in the range of 10–75 nm and an average grain size of ~ 25 nm were deformed at liquid nitrogen temperature at a strain rate of $3 \times 10^{-3} \text{ s}^{-1}$ to a strain of 5.5% and at a flow stress of 1.5 GPa. About 130 grains were examined under HREM to check if they contain deformation twins and stacking faults. Fig. 36 shows the histograms of (a) grain size distribution, (b) the number of grains containing stacking faults and twins, and (c) fractions of grains containing stacking faults and twins in samples deformed under tension. Fig. 36b shows that with decreasing grain size the number of grains containing twins (hereafter referred to as twinned grains) first increases and then decreases, while the number of grains containing stacking faults increases monotonically. The fraction of twinned grains is a good statistical indicator of twinning propensity. Therefore, Fig. 36 indicates that the twinning

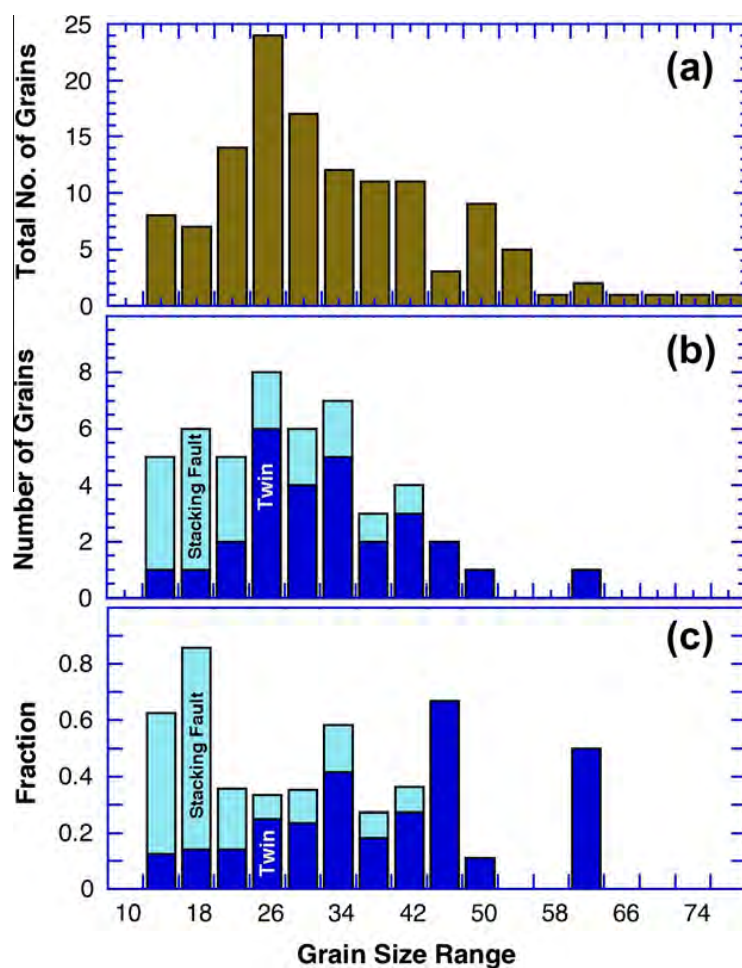


Fig. 36. Statistical grain size effect on the formations of stacking faults and deformation twins in nc Ni deformed under tension at liquid nitrogen temperature. The twin is defined as consisting of two or more layers of stacking faults on consecutive slip planes. (a) The size distribution of all grains examined under TEM. (b) The number distributions of grains containing stacking faults and twins. (c) The fraction distribution of grains containing stacking faults and twins. Each fraction was calculated as the ratio of the number of grains containing stacking faults and twins to the total number of grains in the corresponding size range [164].

propensity first increases and then drops with decreasing grain size. The decrease of twinning propensity with decreasing grain size is called the *inverse grain-size effect* [171]. This inverse grain size effect was also verified by synchrotron and neutron diffraction [242], and later observed in nc Cu [243], which has a lower stacking fault energy and very different general planar fault energies from the Ni. This suggests that it is a common phenomenon in nc fcc metals.

The experimental observation of grain size effect shown in Fig. 36 is consistent with what is predicted by an analytical model of Zhu et al. [57,59]. Fig. 36 shows an optimum grain size at which the twinning is easiest, which is also predicted by the model. The details of this model will be discussed later in Section 5.8.3.

One of the salient features of the data in Fig. 36 is that no inverse grain-size effect exists for stacking faults. This is due to the effect of generalized planar fault energies on the nucleation of twins, which make it more difficult to activate twinning partial than to activate the first partial to form stacking fault. In other words, the grain size effect on the deformation twins and stacking faults can be explained by the combined effect of grain size effect described in Section 5.8.3 and the general planar fault energy effect described in Section 5.5 [171]. A recently proposed “stimulated slip” model [241] was also used to explain the inverse-grain size effect on twinning [243], which is not appropriate because the deformation physics assumed in the model is consistent with coarse-grained metals, but not with nanocrystalline metals. In addition, the “stimulated slip” model cannot explain the grain size effect on the formation of stacking faults.

5.5. General planar fault energy effect

Traditionally, stacking fault energy is considered as the primary intrinsic material property that affects the twinning propensity [54]. It is well known that lower stacking fault energy promotes deformation twinning in coarse-grained fcc metals and alloys. The same trend has also been observed in nc fcc metals and alloy. For example, higher density of deformation twins was observed with decreasing stacking fault energy in nanostructured Cu–Al alloys subjected to dynamic plastic deformation [244], and in the Cu–Zn alloy system subjected to HPT processing [51,101,219,221,222,245].

Recent molecular dynamics (MD) simulations, phase field simulation, analytical modeling and experimental observations reveal that the stacking fault energy alone is not sufficient to explain the observed twinning behavior, and the generalized planar fault energies (GPFs) also significantly affect the partial-dislocation-mediated deformation processes in nc materials [10,29,188,246]. In fcc metals, the GPFE curves describe the energy change caused by rigidly shifting two semi-infinite crystals on a $\{1\ 1\ 1\}$ plane along a $\langle 1\ 1\ 2 \rangle$ direction [10]. The GPFE curves can be most accurately calculated using the *ab initio* approach [201], although some errors and variation could result from boundary conditions and simulation code.

The three most important energies on the GPFE curves are the stacking fault energy (γ_{sf}), unstable stacking fault energy (γ_{usf}), and unstable twin fault energy (γ_{utf}). As shown in Fig. 37, Ni has very high stacking fault energy, and therefore, by conventional wisdom, should not deform by the slip of partial dislocations, which generate stacking faults. However, MD simulations revealed stacking faults, and experiments revealed both stacking faults and deformation twins in nc Ni. These results were explained by the GPFs [10] and other factors [188,247]. Specifically, after a leading partial generates a stacking fault, the nucleation and gliding barrier for the trailing partial is a function of $\gamma_{usf} - \gamma_{sf}$, which is large for Ni and Cu, as compared to Al. This makes it possible for some first partials to slip without trailing partial following them, creating stacking faults. Also, since the unstable twin fault energy is not much higher than the unstable stacking fault energy, twins should be possible once a leading partial is emitted, thus making it possible to produce twins in nc Ni despite its high stacking fault energy. The GPFs have been used to explain the differences in deformation mechanisms of nc Al, Ni and Cu with a small grain size of 12 nm, which were investigated by MD simulations [10].

The GPFE curves can also help explain the grain size effect on twinning and stacking fault shown Fig. 36. The precondition for the nucleation of a deformation twin is to first form a stacking fault. In other words, a stacking fault was first formed by a leading partial, and then a twinning partial converted the stacking fault to a twin nucleus. This suggests that leading partials were first activated in grains with a wide range of grain sizes to create stacking faults, but twinning partials become more

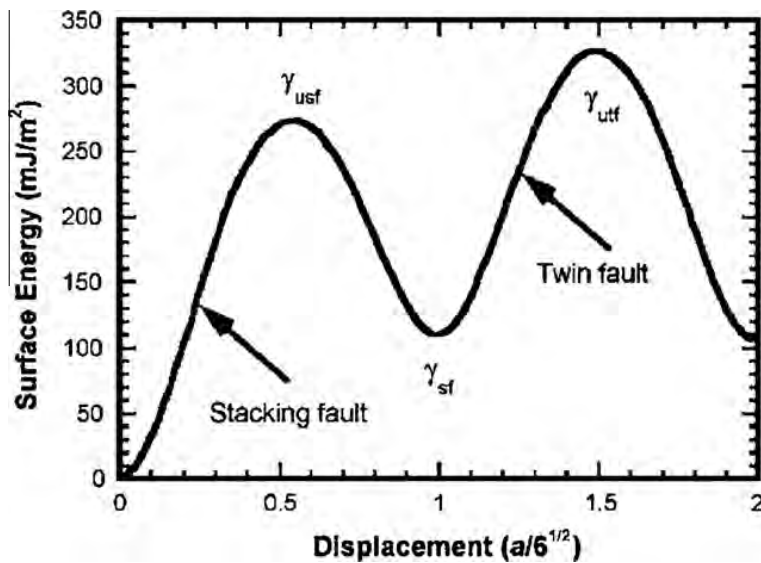


Fig. 37. Schematic of the generalized planar fault energy curves for Ni [201]. γ_{sf} is the stable stacking fault energy; γ_{usf} is the unstable stacking fault energy; γ_{uf} is the unstable twin fault energy; a is the lattice constant.

difficult to nucleate and slip with decreasing grain size if the inverse grain-size effect is operating. Therefore, it takes higher applied stress to emit a twinning partial than a leading partial that creates a stacking fault. This is consistent with the effect of GPFE energies on partial slip. As shown in Fig. 37, the unstable twin fault energy is higher than unstable stacking fault energy, which makes it more difficult to emit twinning partials. It has also been reported that higher stresses are required to emit partials in smaller grains [23,27]. One can envision that below a certain critical grain size the stress required to emit a twinning partial becomes higher than the applied stress, which stops twinning but still allows the emission of the leading partials to create extended stacking faults. Due to the variation in grain orientations and local stress states, this leads to a statistical decrease in twin density with decreasing grain size, i.e. the inverse grain-size effect on twinning. Since the stress is still high enough to emit leading partials, there is no inverse grain size effect on stacking fault.

Recently, an analytical model was proposed to quantitatively describe the twinning tendency of fcc metals basing on the GPFE curves [188]. It should be noted that the GPFE effect alone cannot explain the observed grain size effect on deformation twinning. Specifically, the grain size effect was not addressed in the reported GPFE models [10,188]. Also note that GPFE curves should be calculated using the *ab initio* method, which is much more accurate than the MD simulations in this case. The latter could lead to significantly different GPFE curves depending on the atom potentials used in the simulation [10,248]. It should be also noted that GPFE curves are not affected by grain size. MD simulations using a specific grain size can only represent that particular grain size and cannot be extrapolated to other grain sizes [171]. More discussions on the GPFE energy based models will be presented later in Section 5.8.4.

5.6. Non-equilibrium grain boundary

Nanocrystalline materials often have non-equilibrium grain boundaries with high densities of extrinsic (extra) dislocations [35,65,225,234,249,250]. This is especially true for those nc metals and alloys produced by severe plastic deformation [65]. A typical non-equilibrium grain boundary is shown in Fig. 38a, which is an HREM image of a low-angle grain boundary in a nc Cu [225]. The two grains are misoriented for about 9°. Fig. 38b is a structural model corresponding to the low-angle grain boundary. From this model, it is seen that two types of dislocations with Burgers vectors $\mathbf{b}_1$ and $\mathbf{b}_2$ are needed to accommodate the geometrical misorientation. In other words, these dislocations are geometrically necessary. Valiev et al. referred to these geometrically-necessary dislocations as intrinsic dislocations [251]. According to Fig. 38b, the spacing of type 1 dislocations is about 18 Å, which is

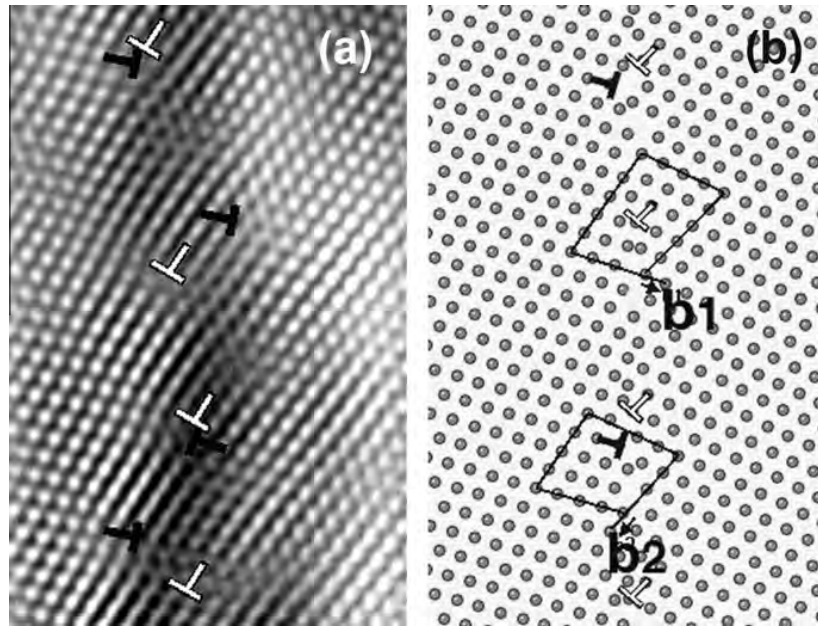


Fig. 38. (a) An HREM image of a non-equilibrium low-angle grain boundary and (b) its equilibrium structural model. Burgers vectors are $\mathbf{b}_1$ and $\mathbf{b}_2$ [225].

consistent with that measured from Fig. 38a. However, there are three more type 2 dislocations in Fig. 38a than in Fig. 38b, which indicates that three extrinsic (or non-geometrically-necessary) dislocations exist at the grain boundary shown in Fig. 38a. Therefore, this segment of low-angle grain boundary is in a high-energy configuration and should be called non-equilibrium grain boundary.

Dislocations on non-equilibrium grain boundaries may have unique structures. Fig. 15 shows an HREM image of a non-equilibrium low angle ($\sim 3^\circ$) grain boundary in nanocrystalline Ni formed by surface mechanical attrition treatment [187]. 60° dislocations with (1 1 1) half planes are marked on the grain boundary. Importantly, Fig. 15 shows dissociated 60° dislocations with wide stacking faults. The boundaries of two such wide stacking faults are marked by two pair of lines, respectively. The stacking fault widths are in the range of 1.22–3.66 nm.

The existence of dissociated dislocations on non-equilibrium grain boundaries has important consequences on the deformation twinning in nc Ni. First, the leading partial can simply slip into the grain interior under an external stress, becoming an extended partial and creating a stacking fault. In other words, the emission of the leading partial is affected by the stable stacking fault energy, but not by the much higher unstable stacking fault energy. Second, since the trailing partials already exist on the grain boundary, it could also slip into the grain interior, a process that does not have to overcome the high unstable SFE predicted by the GPFE curve. The easy emissions of the trailing partials effectively erase the stacking faults created by the leading partial, which lowers the density of stacking faults. In addition, if two dissociated dislocations on a grain boundary happen to be on adjacent planes, a twin nucleus forms. Such a twin nucleation process will not need to overcome the high unstable twin fault energy on the GPFE curves. Therefore, the non-equilibrium grain boundaries would make twinning easier.

5.7. Strain rate and temperature effect

The strain rate and temperature effect on deformation twinning in nc fcc metals and alloys is similar to their effect on coarse-grained fcc metals and alloys. Specifically, lower temperature and higher strain rate usually promote deformation twinning in nc fcc metals and alloys [103,104,252]. Zhao et al. [153] reported that nanostructured Cu did not deform by twinning at room temperature but produced large quantity of deformation twins at liquid nitrogen temperature, verifying that the low temperature indeed promote deformation twinning in nanostructured materials.

Wu and Zhu [171] statistically studied the strain rate and strain effect on deformation twinning in nc Ni. An electrodeposited nc-Ni foil with grains in the range of 10–75 nm and an average grain size of ~ 25 nm were deformed at liquid nitrogen temperature under three deformation modes with increasing strain rate and strain: (1) quasi-static tension at a strain rate of $3 \times 10^{-3} \text{ s}^{-1}$ to a strain of 5.5% and at a flow stress of 1.5 GPa, (2) rolling at a strain rate of $2 \times 10^{-2} \text{ s}^{-1}$ to a strain of 9.8%, and (3) split Hopkinson pressure bar (SHPB) test at a strain rate of $\sim 2.6 \times 10^3 \text{ s}^{-1}$ to a strain of 13.5% and a flow stress of ~ 2 GPa. About 130 grains for each sample were examined using HREM to obtain good statistics. Shown in Fig. 39 is the fractions of grains that contain at least one twin. The fraction of twinned grains increased from 28% under tension to 38% under rolling to 44% under SHPB. The strain rate effect is believed caused by the higher flow stress with higher strain rate [171]. The flow stress under tension was 1.5 GPa and this was increased to 2.0 GPa under SHPB [188,193]. Although the flow stress under rolling could not be measured, it should be between 1.5 GPa and 2.0 GPa, because higher strain rate usually leads to higher flow stress. This observation is somewhat different from that in a recent study using laser driven compression at an extremely high strain rate of $>10^7 \text{ s}^{-1}$ [189], but consistent with a recent MD simulation on strain rate effect [193,194].

5.8. Twin nucleation and growth models

Several models based on various assumptions have been proposed to describe the formation of deformation twins in nc fcc metals. The validity of a model is determined by how much deformation physics it is based on and it predicts. A model that is not based on the deformation physics observed by experiments or MD simulations is of little scientific value, although it sometimes can be used to fit the observed experimental data by adjusting the fitting parameters. Such a model can often mislead the scientific community. Below we discuss a few well-known models and their limitations.

5.8.1. Conventional dislocation model

Two similar models were proposed to explain the formation of deformation twins in nc metals [6,65]. In the model by Chen et al. [6], the stress needed to activate a lattice dislocation is described as

$$\tau_L = \frac{2\eta Gb}{d} \quad (13)$$

where η is a parameter that reflects the characteristics of the dislocation ($\eta = 0.5$ for an edge dislocation and $\eta = 1.5$ for a screw dislocation), G is the shear modulus, b is the magnitude of the Burgers vector of the lattice dislocation, d is the grain size. The stress to activate a partial dislocation is described as

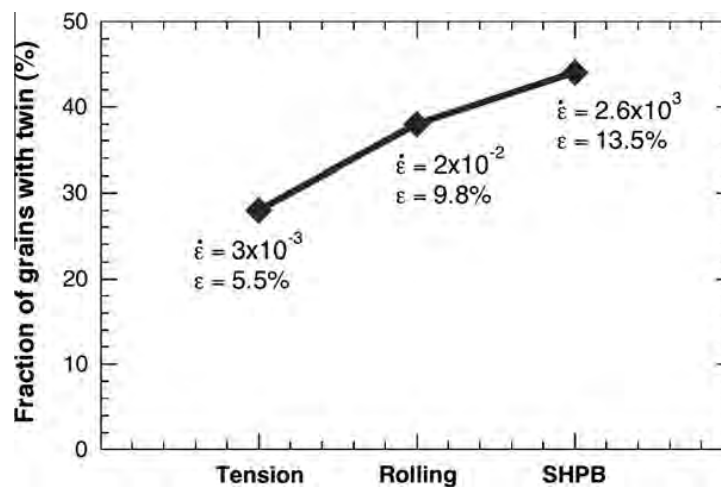


Fig. 39. The fraction of twinned grains in nc Ni deformed at liquid nitrogen temperature under tension, rolling and SHPB. Tension: strain rate = $3 \times 10^{-3} \text{ s}^{-1}$, strain = 5.5%, flow stress = 1.5 GPa; rolling: strain rate = $2 \times 10^{-2} \text{ s}^{-1}$, strain = 9.8%; SHPB: strain rate = $\sim 2.6 \times 10^3 \text{ s}^{-1}$, strain = 13.5%, flow stress = ~ 2 GPa [171].

$$\tau_p = \frac{2\eta G b_1}{d} + \frac{\gamma}{b_1} \quad (14)$$

where b_1 is the magnitude of the Burgers vector of the partial dislocation, and γ is the stacking fault energy. When $\eta = 0.5$, these two equations become identical to those in the work by Liao et al. [65].

Because $b > b_1$, τ_p will increase at a slower rate than τ_L , which means that it will be easier to activate a partial dislocation than a perfect dislocation when the grain is below a critical size. These two models seem very straightforward in explaining the activation of partial dislocations, which is a prerequisite of deformation twinning.

Unfortunately, experimental data show that smaller grain size hinders, not promotes, deformation twinning [11,81], which directly contradicts these two models [6,65]. It has been found that the critical stress for twinning follows a Hall–Petch relationship [11],

$$\sigma_t = \sigma_{t0} + \kappa_t d^{-1/2} \quad (15)$$

where σ_{t0} is a constant and κ_t is the Hall–Petch slope for twinning. Eq. (15) is similar to the well-known Hall–Petch relationship for the slip of a perfect dislocation:

$$\sigma_s = \sigma_{s0} + \kappa_s d^{-1/2} \quad (16)$$

where σ_{s0} is a constant and κ_s is the Hall–Petch slope for the slip of a perfect dislocation.

Table 1 lists the Hall–Petch slope for both twinning and for slip of lattice dislocations [11]. As shown, the Hall–Petch slope for twinning is higher than that for the slip of lattice dislocation for bcc, fcc, and hcp metals and alloys. Therefore, the models are not supported by experimental data. Moreover, these two models predict an unrealistically high critical stress for twinning [6], which reflects their problem. The models also made an inexplicit assumption that activation of partial dislocation equals formation of twinning, which, as shown later, is not correct. Another obvious evidence that this model cannot account for the deformation physics is that it cannot explain the experimentally observed inverse-grain size effect shown in Fig. 36.

The reason for the failure of this model is that Eqs. (13) and (14) are based on an early (1961) work by Venables [72], which did not account for the recently observed deformation physics of nc materials, i.e. the dislocation emission from grain boundaries, as discussed in Section 5.3.2. In other words, this model is not based on physics that prevails in nc materials, and therefore is not correct. However, unfortunately, due to its simplicity, this model has been used by many research groups to explain why deformation twinning occurs in nc materials [6,65,80].

Table 1
The Hall–Petch slopes for bcc, fcc and hcp metals and alloys [11].

Material	H–P slope for slip, κ_s (MPa mm ^{1/2})	H–P slope for twinning, κ_t (MPa mm ^{1/2})
<i>bcc</i>		
Fe–3 wt.% Si	12	100
Armco Fe	20	124
Fe–25 at.% Ni	33	100
Cr	10.08	67.75
Va	3.46 (20 K)	22.37
<i>fcc</i>		
Cu	5.4 (RT)	21.66 (77 K)
Cu–6 wt.% Sn	7.1	11.8 (77 K), 7.9 (RT)
Cu–9 wt.% Sn	8.2	15.77 (77 K)
Cu–10 wt.% Zn	7.1	11.8 (77 K)
Cu–15 wt.% Zn	8.4	16.7 (295 K)
<i>hcp</i>		
Zr	8.26	79.2
Ti	6 (78 K)	18 (4 K)

5.8.2. Partial emission from grain boundaries

A recent analytical dislocation model by Asaro et al. [253] considered the MD simulation and experimental results, which indicate partial dislocations emissions from boundaries of nanosized grains. The critical stress needed to move a lattice dislocation is described as

$$\tau_L = \frac{Gb}{d} \quad (17)$$

and the critical stress needed to move a partial dislocation is described as

$$\tau_P = \frac{Gb}{3d} + (1 - \delta) \frac{\gamma}{Gb} \quad (18)$$

where δ is the ratio of equilibrium stacking fault width to grain size.

This model predicts that below a certain critical grain size partial dislocations from GBs need a lower stress to move than lattice dislocations in nc metals. Most importantly, it predicts a realistic, low twinning stress that is obtainable under experimental conditions such as ball-milling. However, the model does not address one critical issue: as shown in Fig. 36, the emission of a partial dislocation does not guarantee the nucleation of a deformation twin because the trailing partial could easily follow to erase the stacking fault formed by the first partial.

5.8.3. Twinning partial from grain boundaries

To address the above issue in the above model, Zhu et al. recently developed an analytical model to describe the nucleation and growth of deformation twins in nc fcc metals [57,59]. This model is described below.

The model assumes a grain with a square (1 1 1) slip plane, as shown in Fig. 40, similar to that used in a previous study [253]. Under an external shear stress, τ , a 30° leading Shockley partial, $\mathbf{b}_1$, is emitted from grain boundary AB, depositing two segments of partial dislocation lines (Aa and Bb) on the grain boundaries. τ is oriented at an angle α with line ab. A trailing 30° partial, $\mathbf{b}_2$, is also emitted (line Aa'b'B). The two partials ab and a'b' are separated by a stacking fault (Fig. 40a). The two partials react to form two perfect dislocation segments, Aa' and Bb' at the GBs. This dislocation system is called a *Screw system* hereafter, because the two partials can form a perfect screw dislocation along the grain boundary AB.

To nucleate a deformation twin, a stacking fault needs to be first created. This can occur via: (1) emission of a 30° partial, $\mathbf{b}_1$, from grain boundary, (2) extending the stacking fault ribbon in Fig. 40a across the grain. Both scenarios may occur depending on the orientation of τ . In Fig. 40a, for the partial $\mathbf{b}_1$ to move, τ has to perform a work to overcome increases in both the stacking fault energy and dislocation energy from lengthening segments Aa and Bb [54]. The critical stress for moving partial $\mathbf{b}_1$ can be derived as [57]:

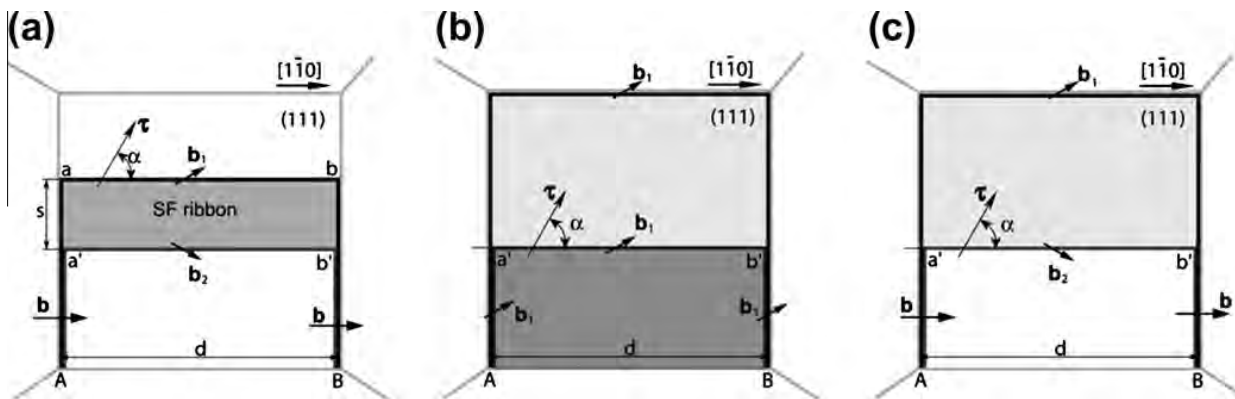


Fig. 40. A schematic illustration of the dislocation model for the nucleation of deformation twins. (a) a perfect screw dislocation dissociated into two partials $\mathbf{b}_1$ and $\mathbf{b}_2$; (b) the nucleation of a deformation twin via the emission of a twinning partial on a (1 1 1) plane adjacent to the stacking fault plane; (c) the emission of a trailing partial that removes the stacking fault [57,59].

$$\tau_p = \frac{1}{\cos(\alpha - 30^\circ)} \left[\frac{\sqrt{6}\gamma}{a} + \frac{Ga(4 - \nu)}{8\sqrt{6}\pi(1 - \nu)d} \ln \frac{\sqrt{2}d}{a} \right] \quad (19)$$

where γ is the stable stacking fault energy, a is the lattice parameter, ν is the Poisson's ratio, and d is the grain size defined in Fig. 40.

The τ needed to move the leading and trailing partials together is equivalent to τ for moving a screw lattice dislocation. τ has to overcome the work needed to lengthen the lattice dislocation segments Aa' and Bb', and can be derived as:

$$\tau_L = \frac{Ga}{2\sqrt{2}\pi(1 - \nu)d \cos \alpha} \ln \frac{\sqrt{2}d}{a} \quad (20)$$

After the stacking fault formation, a twin may nucleate via the emission of a second 30° partial, $\mathbf{b}_1$, from the grain boundary on a plane adjacent to the stacking fault (Fig. 40b). On the other hand, a trailing partial may also emit on the stacking fault plane and erase the stacking fault in its path (Fig. 40c). The critical twin nucleation stress can be derived as:

$$\tau_{twin} = \frac{Ga(4 - \nu)}{8\sqrt{6}\pi(1 - \nu)d \cos(\alpha - 30^\circ)} \ln \frac{\sqrt{2}d}{a} \quad (21)$$

The trailing partial requires a stress, τ_{trail} , to move, which can be derived as

$$\tau_{trail} = \frac{1}{\cos(\alpha + 30^\circ)} \left[\frac{\sqrt{6}(8 + \nu)Ga}{48\pi(1 - \nu)d} \ln \frac{\sqrt{2}d}{a} - \frac{\sqrt{6}\gamma}{a} \right] \quad (22)$$

Once a twin is nucleated, it may grow via the emission of more $\mathbf{b}_1$ twinning partials under stress τ_{twin} . It may also shrink via the emission of a shrinking partial, $\mathbf{b}_2$, on a plane adjacent to the twin boundary but on the twin side. The stress needed to move a shrinking partial can be derived as:

$$\tau_{shrink} = \frac{1}{\cos(\alpha + 30^\circ)} \frac{\sqrt{6}(8 + \nu)Ga}{48\pi(1 - \nu)d} \ln \frac{\sqrt{2}d}{a} \quad (23)$$

The stresses, τ_p , τ_L , τ_{twin} , τ_{trail} , and τ_{shrink} , determine the nucleation and growth of a deformation twin. For example, at $\tau_p < \tau_L$, partial dislocations will be emitted from the grain boundary, and at $\tau_{twin} < \tau_{trail}$, a twin may nucleate. In the following, Al is used as a model material to validate the model [57,59]. For Al, $G = 26.5$ GPa, $\nu = 0.345$, $a = 0.404$ nm, and $\gamma = 122$ mJ/m² [54,144]. In Fig. 41, the stresses, τ_p , τ_L , τ_{twin} , τ_{trail} , and τ_{shrink} , are plotted as a function of grain size d for $\alpha = 25^\circ$. The point B in Fig. 41 represents the critical grain size, d_B , below which a deformation twin nucleates because $\tau_{twin} < \tau_{trail}$.

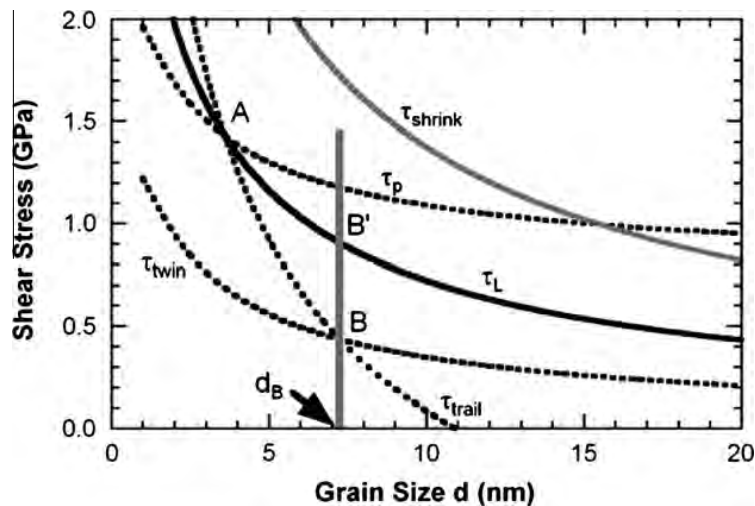


Fig. 41. The critical stresses, τ_p , τ_L , τ_{twin} , τ_{trail} , and τ_{shrink} , as a function of nc Al grain size d for a given α value of 25° [57].

However, a deformation twin can nucleate only after the formation of a stacking fault. As shown, at grain size d_B , $\tau_L < \tau_p$, i.e. the lattice dislocation is operating at point B'. It is also calculated that the stacking fault width at τ_L is far larger than d_B [57]. This means that a deformation twin nucleates after a stacking fault ribbon spreads across the grain. Interestingly, at point B' the grain size is larger and the critical stress is lower for twin nucleation than those for the partial dislocation emission at point A, because the stacking fault of a dissociated lattice dislocation would spread across the grain before a partial is emitted. In other words, a twin will nucleate at the critical grain size d_B under the stress of d_B at B'.

The above equations and analysis are for the *Screw* system only. There are two other possible dislocation systems: a $60^\circ I$ system with a leading 90° partial and a trailing 30° partial, and a $60^\circ II$ system with a leading 30° partial and a trailing 90° partial [57]. These two systems are amenable to the same procedure, and therefore we only present the final results. It is found that the $60^\circ II$ system does not operate because it requires much higher stress to nucleate a deformation twin. In a polycrystalline nc sample, grains are likely to orient in all orientations. Therefore, a deformation map linking stresses of deformation twin nucleation and growth with grain size is very useful and desirable. Such a map can be constructed by plotting the critical (the lowest) stresses against the critical grain sizes, without the stress orientation information (see Fig. 42).

The deformation map in Fig. 42 reveals that there are optimum grain sizes for deformation twin nucleation (the lowest stress point at cup bottom), which are 4.85 nm and 7.25 nm for the $60^\circ I$ and *Screw* systems respectively. The minimum stresses for the $60^\circ I$ and screw systems in Fig. 42 were derived and simplified as [59]

$$\tau_{min}^{60^\circ I} = \frac{1.72(4 - 3\nu)}{2.89 - \nu} \frac{\gamma}{a} \quad (24)$$

$$\tau_{min}^{screw} = \frac{12.21}{3.73 + \nu} \frac{\gamma}{a} \quad (25)$$

As shown in Fig. 42, these two minimum stresses are very close. For simplicity, we use their average as the critical stress for twinning, which can be derived as

$$\tau_m = \frac{\gamma}{2a} \left[\frac{1.72(4 - 3\nu)}{2.89 - \nu} + \frac{12.21}{3.73 + \nu} \right] \quad (26)$$

Eq. (26) can be approximated and simplified by assuming the value of ν in the denominators as 0.33, which yields

$$\tau_m = \frac{(5.69 - 2.02\nu)\gamma}{2a} \quad (27)$$

Calculation shows that the error in Eq. (27) caused by the approximation is less than 2% for a wide range of ν values from 0.25 to 0.45. Such a small error is negligible, considering the semi-quantitative nature of the model.

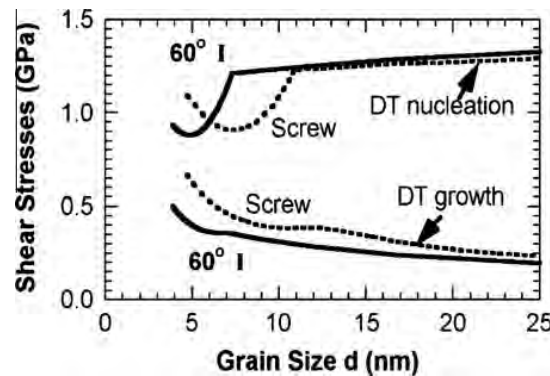


Fig. 42. A deformation map showing the critical stresses for deformation twin nucleation and growth in nc Al as a function of grain size for the $60^\circ I$ and the *Screw* dislocation systems [57].

The optimum grain size for twinning, or the grain size at which the twinning stress is lowest for the $60^\circ I$ and screw systems in Fig. 42 can be calculated from the following simplified equations [59]

$$\frac{d_m^{60^\circ I}}{\ln(\sqrt{2}d_m^{60^\circ I}/a)} = \frac{2.089 - \nu}{54.985(1 - \nu)} \frac{Ga^2}{\gamma} \quad (28)$$

$$\frac{d_m^{\text{screw}}}{\ln(\sqrt{2}d_m^{\text{screw}}/a)} = \frac{3.727 + \nu}{97.053(1 - \nu)} \frac{Ga^2}{\gamma} \quad (29)$$

For simplicity, we can use average of the Eqs. (28) and (29) as the critical grain size, d_m , for twinning:

$$\frac{d_m}{\ln(\sqrt{2}d_m/a)} = \frac{9.69 - \nu}{253.66(1 - \nu)} \frac{Ga^2}{\gamma} \quad (30)$$

The critical stress and optimum grain size for deformation twinning for Al, Cu and Ni calculated using Eqs. (27) and (30) are listed in Table 2. The predicted critical twinning stress is obtainable under experimental conditions and optimum grain size for twinning agrees well with experimental observations [57,59,171].

One of the most significant feature of this model is its successful prediction of normal and inverse grain size effect on deformation twinning [171]. However, it also has a major deficiency: it does not consider the effect of GPFE's, which affects the nucleation and gliding of the first and twinning partials. Consequently, this model cannot explain why no inverse grain size effect is observed for stacking faults (Fig. 36). In addition, this model treated dislocation lines as straight lines for simplicity, while they should be curved inside the grain in the real situation. Gu et al. recently developed a curved dislocation-line model to describe the partial emission from the grain boundary to form stacking faults [254], which is an improvement over the previous straight-line model [253]. Another modification and improvement is the incorporation of interactions between dislocations [255–257], which improved the accuracy of the equations, but also significantly increased the complexity of the mathematical equations.

Finally, the most significant contribution of this model is its successful description of the grain size effect on deformation mechanisms. As shown in Fig. 41, the critical stresses for moving all dislocations increase with decreasing grains size. However, the rate at which the critical stress increases with decreasing diameter varies with the type of the dislocation. For example, below a critical grain size the critical stress τ_p for the leading partial will be lower than that for the lattice dislocation τ_L . The physical reason for the grain size effect is the deposition of the dislocation lines (see Fig. 40) on the grain boundaries as a dislocation glides forward under an applied stress. The deposited dislocation lines add strain energy to the system and act to drag the gliding dislocation. The dragging force does not change with grain size d , while the driving force for the dislocation slip is proportional to the length of the gliding section of the dislocation, which is equal to the grain size d . The difference in grain size dependences of the dragging and driving forces makes it more difficult for dislocations to move in smaller grains.

Table 2

The critical stress and optimum grain size for the formation of deformation twinning in Ag, Al, Au, Cu and Ni, predicted by the twinning partial from the grain boundary model (Eqs. (27) and (30)) as well as parameters used for the calculation [54,57,59].

	G (GPa)	ν	γ (mJ m ⁻²)	a A (Å)	τ_m (GPa)	d_m (nm)
Ag	30	0.37	22	4.090	0.16	73
Al	26.5	0.345	122	4.04	0.89	6
Au	27	0.44	45	4.080	0.31	30
Cu	54.6	0.343	45	3.6146	0.37	46
Ni	94.7	0.312	125	3.5232	1.06	23

5.8.4. General-planar-fault-energy (GPFE) based models

It is generally agreed that GPFE curves have significant effect on the deformation twinning of materials [10,29,35,49,79,171,201,258–264]. However, how the GPFE curves affect the deformation twinning in nc materials have not been rigorously modeled. Most modeling works involving GPFEs have so far either focused on twinning at a crack tip in a single crystal [29,258] or using the GPFE concept to qualitatively explain MD modeling results [10]. The grain size, which has been experimentally observed to significantly affect the twinning, is conspicuously missing in these models. In other words, the GPFE models reported so far are not specific for nc materials and their validity for nc materials may be limited. For example, the GPFEs alone cannot explain the experimentally observed normal and inverse grain size effect shown in Fig. 36 and discussed in Section 5.4.

Using Rice's Peierls approach [30], Tadmor and Hai [258] derived an equation describing the twinning criterion:

$$T = \lambda_{crit} \sqrt{\frac{\gamma_{usf}}{\gamma_{utf}}} \quad (31)$$

where T is the twinning tendency, λ_{crit} is dimensionless factor that characterize the extra load to nucleate the trailing partial in comparison to the leading partial, γ_{usf} and γ_{utf} are the unstable stacking fault energy and the unstable twin fault energy, respectively, as defined in Fig. 37. The value of λ_{crit} depends on the materials parameters γ_{utf} , stable stacking fault energy γ_{sf} , ν , and geometric parameters. More details can be found in [258]. A two layer twin can nucleate if $T > 1$, and a trailing partial will nucleate if $T < 1$. It should be noted that grain size is not considered in the Eq. (31).

Asaro and Suresh [29] further explored Eq. (31) for a special case where the Burgers vector of the leading partial is orthogonal to the crack front, and applied shear stress is parallel to the Burgers vector of the leading partial. They developed Eq. (31) into the following equation

$$T = \sqrt{(1 + \beta) \frac{\gamma_{usf}}{\gamma_{utf}}} \quad (32)$$

where $\beta = 1 - \gamma_{sf}/\gamma_{usf}$. Therefore, T is only determined by the GPFEs.

Van Swygenhoven et al. [10] used the GPFE curves to explain the differences in deformation mechanisms of nc Al, Cu and Ni with a small grain size of 12 nm. Particularly, although both Al and Ni have similar high stacking fault energy, γ_{sf} , they deform via very different mechanisms. Al deforms via lattice dislocation slip because its γ_{sf}/γ_{usf} is very small, making the trailing partial easy to nucleate and emit, while Ni deforms via partial slip because γ_{sf}/γ_{usf} is very large, making the trailing partial difficult to nucleate and emit. In addition, twinning is rarely observed in three-dimensional nc Al, Ni and Cu because of their high unstable twin fault energy, γ_{utf} . However, these results from MD simulations cannot be extrapolated to nc materials with larger grain sizes, due to the grain size effect observed experimentally [171]. In other words, when the grain sizes become larger and near the optimum grain size for twinning, deformation twins were observed [59,171]. Therefore, there is a need to do MD simulations in which grain sizes are systematically varied.

Kibey et al. [79,260] recently developed a sequential, multi-scale approach to predict the twinning stress. GPFEs were incorporated into the model, and a closed-form expression for twinning stress was obtained, which was simplified into the following approximate form:

$$\tau_{crit} = \frac{2}{3Nb_{twin}} \left(\frac{3N}{4} - 1 \right) \left(\gamma_{utf} + \frac{2\gamma_{tsf} + \gamma_{sf}}{2} \right) - \frac{2}{3N} \frac{\gamma_{usf} + \gamma_{sf}}{b_{twin}} \quad (33)$$

where $N = 3$ represents a three-layer critical twin nucleus. γ_{tsf} is the energy of the twin boundary. γ_{tsf} can be approximated as half of the stacking fault energy γ_{tsf} , but this may not be obeyed by inhomogeneous alloys [261,265]. It is obvious from Eq. (33) that the grain size effect is not considered in this model.

5.8.5. Future issues on modeling

As discussed above, both grain size and GPFs have significant effect on the formation of deformation twins and stacking faults. None of the current models has considered both factors. One possible approach is to incorporate the GPFs into the analytical model. However, this is not trivial and also needs experimental verification of any assumptions that are used in the analytical model. The GPFs can affect both the nucleation and glide of the dislocations.

Two fundamental issues need to be investigated. First, how do the GPFs affect the nucleation of first partials and twinning partials? This issue needs to be studied experimentally. One question that remains is if the GPF curves affect the nucleation of dislocations since the grain boundaries of nc materials may be in a non-equilibrium state with excess dislocations existing in them. Second, how do the GPFs affect the slip of the first and twinning partials. In other words, how the GPF curves affect the Peierls stresses for these partials. There have been several reports on calculating the Peierls stresses from GPFs [264,266–268]. However, a formula for calculating the Peierls stress from the GPFs remains to be derived.

It should be noted that any analytical descriptions of twinning models should be based on observed deformation physics instead of on convenient, arbitrary assumptions. The most important quality of an analytical model is to capture the deformation physics instead of fitting experimental data, because only such models can predict comprehensive experimental phenomena.

For MD simulations, it will be of great interest to systematically vary the grain size from 10 nm to 100 nm so that the experimentally observed effect of grain size on twinning can be studied. Ideally, MD simulations can investigate simultaneously the effects of both GPFs and grain sizes on deformation twinning. However, this could be currently difficult because the computational power available to most researchers may limit the grain sizes that can be practically investigated.

6. Deformation twinning in non-fcc metals

The study on deformation mechanisms of nc materials has been mostly focused on fcc metals. Nanomaterials with other crystal structures such as nc bcc and hcp metals have not been studied much, although such studies have recently been reported. In this section, we will give a brief overview on recent progress on the deformation twinning in nc bcc and hcp metals. It should be noted that studies on deformation mechanisms of nc bcc and hcp metals are at their very early stages, and many issues and controversies are to be investigated and resolved.

6.1. Deformation twinning in nanocrystalline bcc metals

Compared with the nc fcc metals, the deformation mechanisms of bcc metals are much less studied. Tang and Wang observed twin formation from crack tips in Mo in MD simulations [269]. Frederiksen et al. [270] did MD simulation studies of the deformation mechanisms of nc bcc Mo with a grain size of 12 nm, and observed deformation twinning. Although crack formations at grain boundaries were extensively observed, only some twins were emitted from cracks. Marian et al. [271] modeled single crystal bcc Fe using MD simulations and found that with increasing strain rate and shear stress, screw dislocation motion changed from smooth to rough and eventually twinning became the dominant deformation mechanism. Wang et al. [31] deformed nc bcc Ta with grain sizes of 10–30 nm by nano-indentation. Subsequent HREM investigation revealed extensive deformation twins in the nano-sized grains and some grains contain multiple twins with different twin orientations, indicating that twinning is a major deformation mechanism in nc Ta. These observations in nc bcc metals are consistent with observations in nc fcc metals and alloys.

6.2. Deformation twinning in nanocrystalline hcp metals

The twinning behavior of hcp materials is very different from that of fcc metals. As discussed earlier, for fcc metals, with decreasing grain size it becomes more difficult to deform by twinning in the coarse-grain size range [11], but twinning becomes easier once the grain size is smaller than 100 nm

[9], although twinning may become difficult again when the grain size is too small (inverse grain size effect) [171]. In contrast, coarse-grained hcp metals usually need twinning to accommodate plastic deformation in addition to dislocation slip [170,272,273], because there are not five independent deformation systems, as required by the von Mises criterion for compatibility [165]. However, twinning is rarely observed in nc hcp metals and alloys, with an exception of nc Zr processed by surface mechanical attrition [274]. It appears that the deformation twinning becomes more difficult with decreasing grain size and twinning is rarely observed below a certain grain size. The reason for the observed grain size effect on twinning in hcp materials is not clear.

The twinning mechanisms in hcp metals are still under intensive study. Capolungo and Beyerlein proposed a twin-nucleation model based on the nonplanar dissociation of the leading dislocation in a pileup of basal slip dislocations [163]. Wang et al. studied the nucleation of $[10\bar{1}2](\bar{1}012)$ twin in Mg by atomic simulations, and found that the twin nucleus consists of one $-50/107[10\bar{1}1]$ partial and multiple $1/15[10\bar{1}1]$ partials [159]. Kucherov and Tadmor revealed twin nucleation formed by partial emission at a crack tip in their MD simulation [275]. Li and Ma observed deformation twinning mediated by the nucleation and glide of zonal dislocations followed by atomic shuffling in hcp Mg in their MD simulation [164]. They also found that the most favorable zonal dislocation under compression has a Burgers vector of $\frac{1}{2}\frac{1}{2}\langle 10\bar{1}2 \rangle$, i.e. the twinning mode is $\{10\bar{1}1\}\langle 10\bar{1}2 \rangle$. This zonal dislocation involves two $(10\bar{1}1)$ planes, forming a two-layer step on the twin boundary. Tomé et al. studied another twinning mode, $\{10\bar{1}2\}\langle 10\bar{1}1 \rangle$, in hcp metals by means of *ab initio* (density function theory) and MD simulations [159,161,276]. Kim et al. recently studied the twinning mechanism in nc hcp Mg with $[11\bar{2}0]$ texture (2D columnar structure) [277]. However, no zonal dislocation is involved in the formation of the $\{10\bar{1}2\}\langle 10\bar{1}1 \rangle$ twin in their simulation results. It is expected that these issues and controversies will be further clarified and resolved by future investigations.

We have recently observed deformation twins in nc hcp Mg–10 at.% Ti alloy processed by ball milling [278]. Fig. 43 shows the HREM image of a deformation twin in the as-processed nc Mg–Ti alloy. The images are viewed from a $[11\bar{2}3]$ zone axis. Importantly, a two-atomic-layer step (marked by 2) and a one-layer step (marked by 1) on the coherent twin boundaries are shown. This is a $\{10\bar{1}1\}\langle 10\bar{1}2 \rangle$ deformation twin, which is consistent with the twinning mode observed in MD simulation of Mg under compression [164]. The two-layer step shown here is consistent with the zonal twinning dislocation predicted by the MD simulation. The MD simulation also predicted that the one-layer steps are immobile and the four-layer steps are unstable and can spontaneously dissociate into two two-layer steps [164]. The one-layer step is experimentally observed in Fig. 43, while no four-layer steps have been observed in our samples. Interestingly, this twinning system was also observed in hcp Ti and Zr processed by severe plastic deformation under pressure, although the twinning only happened in large grains [272,279].

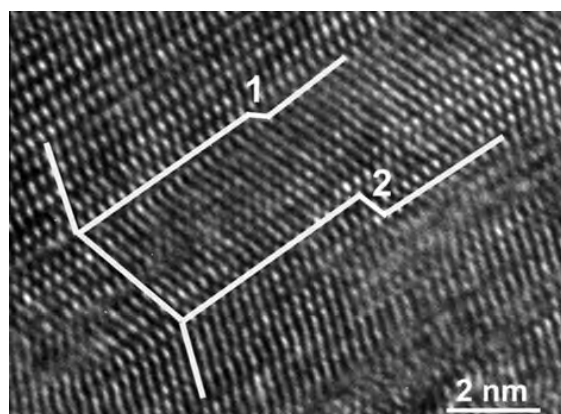


Fig. 43. HREM micrograph showing a deformation twin in the nc Mg–Ti alloy, viewed along a $[11\bar{2}3]$ zone axis. The twin system is $\{10\bar{1}1\}\langle 10\bar{1}2 \rangle$. A two-atomic-layer step and a one-layer step are on the twin boundary [278].

7. Interaction between dislocations and twin boundaries

Deformation twinning usually occurs simultaneously with the slip of perfect and partial dislocations, making it inevitable to have interactions between twins and gliding dislocations at twin boundaries, which have been observed both experimentally [40–44,218,280,281] and by molecular dynamics simulations [45–50,282]. These interactions are believed to make twins effective in simultaneously increasing the strength and ductility of nc materials [40,47,51,153,221,282,283]. When a dislocation glides on a slip plane and stops on a twin boundary, the dislocation line becomes parallel to the cross-line between the slip plane and the twin boundary before any dislocation reaction with the twin boundary occurs. Consequently, in fcc metals there are only four types possible dislocations to react with the twin boundary: 30° Shockley partial, 90° Shockley partial, screw perfect dislocation, and 60° perfect dislocation. To understand these dislocation-twin boundary reactions, we need to invoke the double Thompson tetrahedron [217,282,284], which is illustrated in Fig. 44. As shown, the Thompson tetrahedron above the (1 1 1) twin boundary represents slip systems in the matrix, while the bottom tetrahedron represents slip systems in the twin. The twin boundary plane is shared by the matrix above it and the twin below it. Therefore, the tetrahedron in the matrix and the tetrahedron in the twin should share the same base, which is ABC, as shown in Fig. 44. In other words, dislocations with Burgers vectors of $\mathbf{AB}$, $\mathbf{BC}$, $\mathbf{CA}$, $\mathbf{A}\delta$, $\mathbf{B}\delta$, and $\mathbf{C}\delta$ can slip both in the matrix and in the twin.

Below we will describe all possible reactions between dislocations and twin boundaries. Any reaction could happen provided that applied stress is high enough and in the right orientation. The energy barrier for dislocation reaction could be used to qualitatively measure how easy the reaction is. Nanocrystalline materials have much higher flow stress than their coarse-grained counterparts during plastic deformation, which should help overcome the energy barriers. Therefore, some dislocation reactions with relatively high energy barriers might happen in nc materials but not in coarse-grained materials.

7.1. Cross slip of a 30° partial [285]

When a 30° Shockley partial dislocation cross-slips into the ABC plane at the twin boundary (see Fig. 44), it can react at the twin boundary to grow the twin [42], or cause detwinning [285,286].

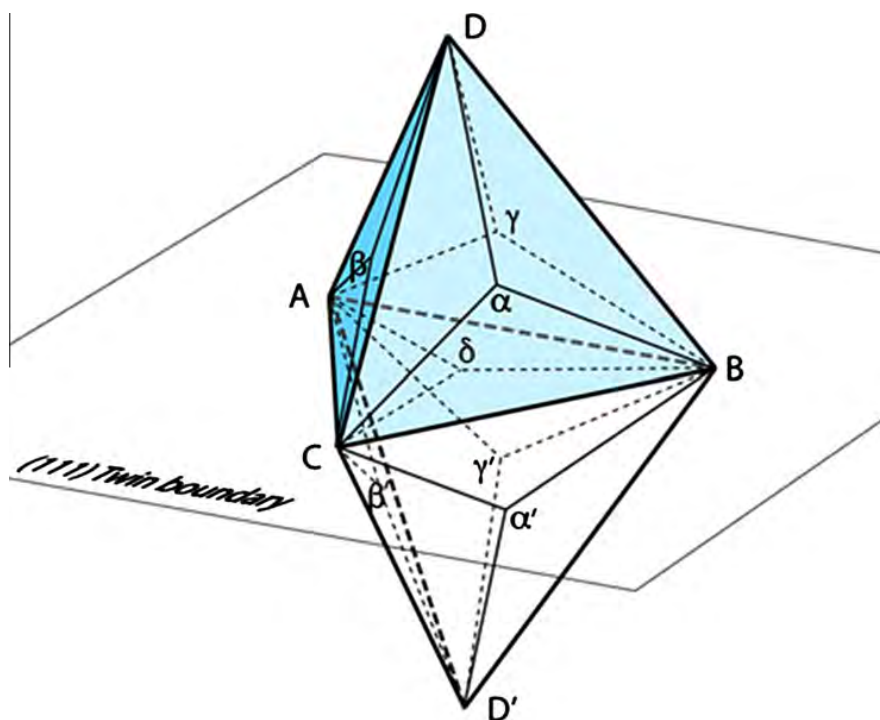


Fig. 44. Illustration of a double Thompson tetrahedron. The top tetrahedron above the (1 1 1) twin boundary represents slip systems in the matrix, while the bottom tetrahedron represents slip systems in the twin [159].

The detwinning process is very similar to the twin growth process, except that the partial glides toward the opposite direction after the cross-slip. Below we will describe the detwinning process only, since the twinning process has been described in Section 5.3.6.

As shown in Fig. 45, the 30° partial, $B\alpha$, glides on the BCD plane, leaving behind a stacking fault (SF), and stops at the twin boundary, TB. Under appropriate applied stress, the following dislocation reaction occurs (see Fig. 1 and 2):



$B\delta$ glides to the left to move the twin boundary toward the twin interior by one atomic plane. This also leaves a step on the twin boundary, and a stair-rod dislocation at the twin step, as shown in Fig. 45b.

The stair-rod dislocation $\delta\alpha$ could further dissociate into two partial dislocations according to the Thompson tetrahedron:



where the partial δB will glide on the twin boundary to the opposite direction of $B\delta$ under the same applied stress, because they represent partials with opposite Burgers vectors.

As shown in Fig. 45c, after the δB glides to the right, the twin thickness is reduced by one atomic plane, i.e. detwinning occurred during the above process. The partial $B\alpha$ advances to the new twin boundary under the original applied stress, and can repeat the above process to annihilate the whole twin.

The energy barrier, which is the energy increase for a dislocation reaction, for the dislocation reactions described in Eq. (34) can be described as [285]:

$$\Delta E_{Eq34} = \hat{E} + 2.0\tilde{E} \quad (36)$$

where $\hat{E} = \frac{Ga^2}{72\pi(1-\nu)} \ln \frac{\sqrt{2}d}{a}$ and $\tilde{E} = \frac{Ga^2}{72\pi(1-\nu)}$, a is the lattice parameter, d is the grain size, G is the shear modulus and ν is the Poisson's ratio, which is assumed to be 1/3, which is a reasonable approximation for most fcc metals. Note that energy barrier described in Eq. (36) and hereafter are based on the assumption of isotropic elasticity.

The energy barrier for the dislocation reaction in Eq. (35) is [285]

$$\Delta E_{Eq35} = 3.5\hat{E} + 5.5\tilde{E} \quad (37)$$

Eq. (37) indicates that the reaction in Eq. (35) requires much higher applied stress than the reaction in Eq. (34) to overcome the energy barrier. If the applied stress is high enough to activate the reaction described in Eq. (34) but not the reaction in Eq. (35), then a step will be produced on the twin boundary. Twin boundaries with steps have been extensively observed experimentally [65,218,281] and by MD simulations [45,22,157]. Some of these steps could be formed by the mechanism described here.

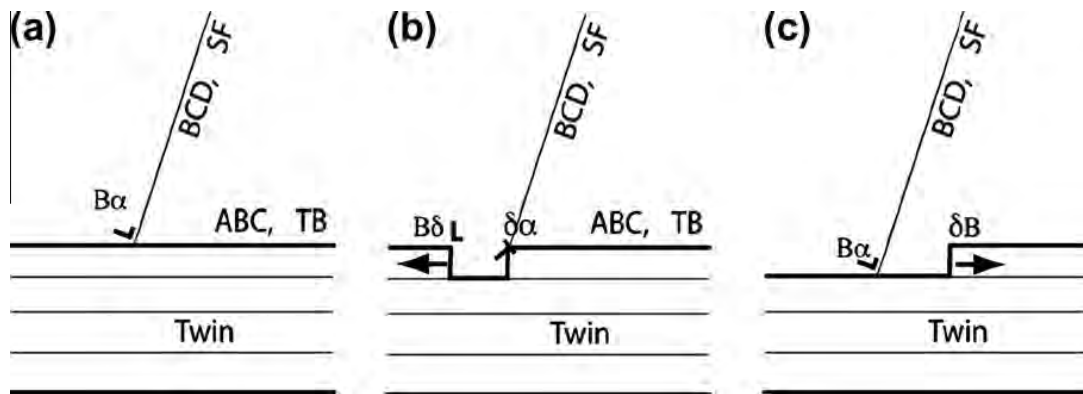


Fig. 45. Detwinning process caused by the interaction of a 30° partial, $B\alpha$, with the twin boundary. SF marks the stacking fault, TB marks the twin boundary (thick black lines). BCD and ABC represent the BCD and ABC slip planes in the Thompson tetrahedron, respectively [159].

7.2. Transmission of a 30° partial across twin boundary

As shown in the double Thompson tetrahedron (Fig. 44), the tetrahedron in the matrix and the tetrahedron in the twin share the same base, which is ABC, as shown in Fig. 44. In other words, dislocations with Burgers vectors of **AB**, **BC**, **CA**, **Aδ**, **Bδ**, and **Cδ** can slip both in the matrix and in the twin. The 30° partial, **Bα**, on the BCD slip plane in the matrix, can have the following dislocation reaction to release another partial in the twin:

$$\mathbf{B}\alpha \rightarrow \mathbf{B}\alpha' + \alpha'\alpha \quad (38)$$

where **Bα'** is a partial that can slip away in the twin from the twin boundary on the BCD plane, and **α'α** is a new type of stationary stair-rod dislocation across the twin boundary. The energy barrier of the dislocation reaction described in Eq. (38) can be calculated as

$$\Delta E_{Eq38} \approx 2.7\hat{E} + 4.1\tilde{E} \quad (39)$$

This indicates that the energy barrier for the 30° partial, **Bα**, to transmit across the twin boundary is energetically plausible under appropriate applied stress.

It can be seen from Fig. 44 that **α'α** is an edge dislocation with its Burgers vector perpendicular to both the dislocation line BC and the twin boundary (1 1 1). The dislocation configuration after the reaction is illustrated in Fig. 46, which shows two stacking faults from both sides of the twin boundary meeting at the twin boundary and connected by the stair-rod dislocation **α'α**.

7.3. Reaction of a 90° partial at twin boundary [285]

The cross-slip of 90° partials at the coherent twin boundary has been described in Section 5.3.5, and therefore won't be discussed here. The energy barrier for the cross-slip of the 90° partials is zero [285].

Below we will describe the transmission of 90° partial across the twin boundary. As shown in Fig. 44, the 90° partial **Dα** can dissociate as

$$\mathbf{D}\alpha \rightarrow \mathbf{D}\delta + \delta\alpha \quad (40)$$

The double Thompson tetrahedron indicates that the Burgers vector **Dδ** is identical to the **δD'** in the twin, i.e. **Dδ** = **δD'**, which can dissociate into a 90° partial **α'D'** and a stair-rod dislocation **δα'**, i.e.

$$\mathbf{D}\delta = \delta\mathbf{D}' \rightarrow \delta\alpha' + \alpha'\mathbf{D}' \quad (41)$$

Substituting Eq. (41) into Eq. (40) yields:

$$\mathbf{D}\alpha \rightarrow \delta\alpha + \delta\alpha' + \alpha'\mathbf{D}' \quad (42)$$

There are two stair-rod dislocations in Eq. (42). Both of them stay at the twin boundary and could react to form a dislocation structure with lower energy. With the help of the double Thompson tetrahedron, the stair-rod reactions can be described below

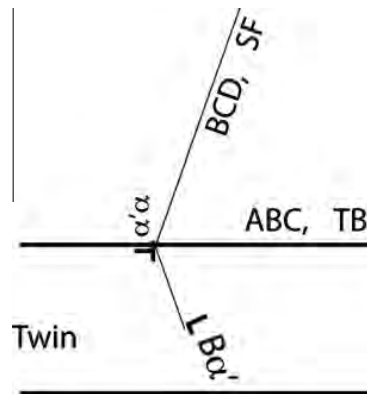


Fig. 46. The dislocation configuration after the partial **Bα** penetrates the twin boundary to release another partial **Bα'** on the BCD' plane inside the twin, leaving a stair-rod dislocation **α'α** on the twin boundary [285].

$$\delta\alpha + \delta\alpha' \rightarrow \frac{4}{9}\mathbf{A}\delta \quad (43)$$

Substituting Eq. (43) into the Eq. (42) yields

$$\mathbf{D}\alpha \rightarrow \frac{4}{9}\mathbf{A}\delta + \alpha'\mathbf{D}' \quad (44)$$

According to Eq. (44), a partial $\alpha'\mathbf{D}'$ will be emitted from the twin boundary to slip on the BCD' plane. The partial $\mathbf{D}\alpha$ can also transmit across the twin boundary to emit a partial on the ACD' plane or BAD' plane [285]:

$$\mathbf{D}\alpha \rightarrow \frac{2}{9}\delta\mathbf{C} + \beta'\mathbf{D}' \quad (45)$$

and

$$\mathbf{D}\alpha \rightarrow \frac{2}{9}\delta\mathbf{B} + \gamma'\mathbf{D}' \quad (46)$$

The energy barrier for reaction in Eq. (44) is

$$\Delta E_{\text{Eq44}} = 0.6\hat{E} + 1.4\tilde{E} \quad (47)$$

The energy barriers for the reactions in Eqs. (45) and (46) are

$$\Delta E_{\text{Eqs45,46}} = 0.1\hat{E} + 0.2\tilde{E} \quad (48)$$

Therefore, the energy barriers for dislocation reactions in Eqs. (44)–(46) are very low, which make it easy for the 90° partial $\mathbf{D}\alpha$ to transmit across the twin boundary to emit another 90° partial in the twin.

7.4. Reaction of a perfect screw dislocation at twin boundary

Assume that a perfect screw dislocation $\mathbf{BC}$ glides on the BCD plane toward the twin boundary (see Fig. 44.) It could dissociate into two 30° partials with a stacking fault in between, i.e.

$$\mathbf{BC} \rightarrow \mathbf{B}\alpha + \alpha\mathbf{C} \quad (49)$$

When this dissociated $\mathbf{BC}$ reaches the twin boundary, it could constrict to form a perfect dislocation again. Since $\mathbf{BC}$ is parallel to the dislocation line, it can either cross-slip into the $\mathbf{ABC}$ plane on the twin boundary, or onto the BCD' plane in the twin, depending on the orientation of the applied stress. Therefore, a screw dislocation can easily cross-slip on the twin boundary or transmit across the twin boundary.

If the stacking fault energy is very low, a scenario could occur where the leading partial cross-slips into the ABC plane while the trailing partial remains on the BCD plane, with a stair-rod dislocation at the twin boundary linking the stacking fault with the twin boundary.

7.5. Reaction of a perfect 60° dislocation at twin boundary

Assume that a perfect 60° dislocation $\mathbf{BD}$ glides on the BCD plane toward the twin boundary (see Fig. 44). It could dissociate into a 30° partial $\mathbf{B}\alpha$ and a 90° partial $\alpha\mathbf{D}$ with a stacking fault between them, i.e. $\mathbf{BD} \rightarrow \mathbf{B}\alpha + \alpha\mathbf{D}$. Partial $\mathbf{B}\alpha$ and $\alpha\mathbf{D}$ with a stacking fault ribbon between them glide together toward the twin boundary under applied stress. There are several plausible scenarios that could occur at the twin boundary, these are described below.

7.5.1. Partial first constrict to form a perfect 60° dislocation

The first scenario is where the partials are constricted to form the perfect dislocation $\mathbf{BD}$ first. Such a scenario can happen easily when the stacking fault energy is relatively high and the distance of the leading and trailing partials is small. It can be seen from the double Thompson tetrahedron (Fig. 44)

that **BD** has a 60° angle with the dislocation line BC. The dislocation reaction for **BD** to cross-slip onto the ABC plane is **BD** → **BC** + **CD**. The energy barrier for such a reaction is $6\hat{E}$, which is so high that such a cross-slip is almost impossible [285].

The perfect 60° dislocation **BD** can also transmit across the twin boundary to emit a perfect dislocation in the twin. The following analysis yields possible dislocation reactions. First, **BD** can dissociate according to

$$\mathbf{BD} \rightarrow \mathbf{B}\delta + \delta\mathbf{D} \quad (50)$$

where $\delta\mathbf{D}$ is equivalent to $\mathbf{D}'\delta$, which can further react to emit perfect dislocations in the twin according to

$$\delta\mathbf{D} = \mathbf{D}'\delta \rightarrow \mathbf{D}'\mathbf{B} + \mathbf{B}\delta \quad (51)$$

$$\delta\mathbf{D} = \mathbf{D}'\delta \rightarrow \mathbf{D}'\mathbf{A} + \mathbf{A}\delta \quad (52)$$

$$\delta\mathbf{D} = \mathbf{D}'\delta \rightarrow \mathbf{D}'\mathbf{C} + \mathbf{C}\delta \quad (53)$$

Substituting Eqs. (51)–(53) into Eq. (50), and also considering $\mathbf{B}\delta + \mathbf{A}\delta = \delta\mathbf{C}$, and $\mathbf{B}\delta + \mathbf{C}\delta = \delta\mathbf{A}$, we have

$$\mathbf{BD} \rightarrow 2\mathbf{B}\delta + \mathbf{D}'\mathbf{B} \quad (54)$$

$$\mathbf{BD} \rightarrow \delta\mathbf{C} + \mathbf{D}'\mathbf{A} \quad (55)$$

$$\mathbf{BD} \rightarrow \delta\mathbf{A} + \mathbf{D}'\mathbf{C} \quad (56)$$

The energy barrier is $\sim 4.5\hat{E}$ for the dislocation reaction in Eq. (54), and $3\hat{E}$ in Eqs. (55) and (56).

In reactions described by Eqs. (55) and (56), one partial will glide on the twin plane, which will grow or shrink the twin by one atomic plane and leave behind a step on the twin boundary depending on the gliding direction. At the same time a perfect 60° dislocation is emitted in the twin, which will also produce a step on the twin boundary. In comparison, the dislocation reaction in Eq. (54) will release two partials on the ABC plane to grow or shrink the twin by two atomic planes, which is why it has higher energy barrier.

7.5.2. 30° leading partial reacts first at twin boundary

The 60° dislocation **BD** glides on the BCD plane toward the twin boundary. It can dissociate as **BD** → **Bα** + **αD**, with the 30° partial **Bα** as the leading partial. The leading partial **Bα** could either cross-slip onto the twin boundary plane or transmit across the twin boundary. The reaction of the leading partial is identical to what are described in Sections 7.1 and 7.2. The trailing partials can either stay on the original slip plane in the matrix, cross-slip onto the twin boundary, or transmit across the twin boundary. We will discuss these scenarios below.

The first scenario is the cross-slip of leading 30° partial **Bα** onto the twin boundary plane, while the trailing 90° partial **αD** remains on the BCD plane, forming a dislocation structure with a stair-rod dislocation, as shown in Fig. 47a. Such a dislocation structure has been observed both experimentally and by MD simulations [46,47,77]. It has been assumed very effective in blocking other dislocations and consequently causes strain hardening [77].

As shown in Fig. 47a, under high applied stress, the trailing partial **αD** may be driven to the twin boundary to react with the stair-rod dislocation $\delta\alpha$:

$$\delta\alpha + \alpha\mathbf{D} \rightarrow \delta\mathbf{D} \quad (57)$$

From the double Thompson tetrahedron, $\delta\mathbf{D}$ is equivalent to $\mathbf{D}'\delta$. The latter can dissociate as $\mathbf{D}'\delta \rightarrow \mathbf{D}'\alpha' + \alpha'\delta$. Therefore, Eq. (57) can be rewritten as

$$\delta\alpha + \alpha\mathbf{D} \rightarrow \mathbf{D}'\alpha' + \alpha'\delta \quad (58)$$

The energy barrier for this reaction is 0. This scenario is schematically illustrated in Fig. 47b.

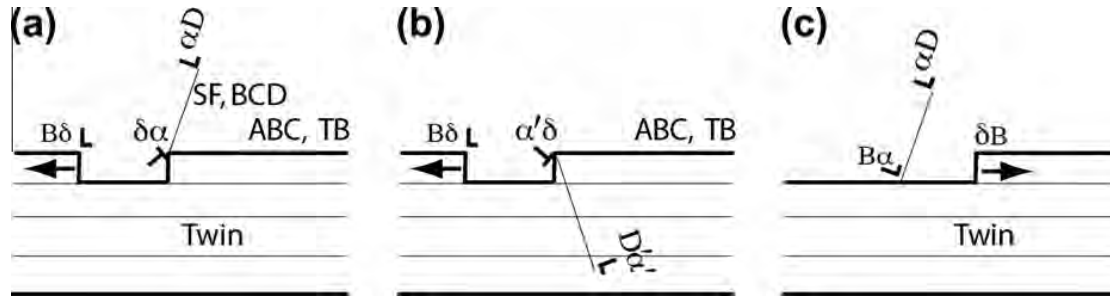


Fig. 47. Reaction of dissociated 60° dislocation $\mathbf{BD}$ with a 30° leading partial at the twin boundary. (a) The leading partial cross-slips onto the ABC twin boundary, leaving behind a stair-rod dislocation and the 90° trailing partial still on the original BCD slip plane. (b) After the trailing partial $\alpha\mathbf{D}$ reacts with the stair-rod dislocation $\delta\alpha$ and transmit across the twin boundary. (c) The stair-rod dislocation dissociates according to $\delta\alpha \rightarrow \delta\mathbf{B} + \mathbf{B}\alpha$ to reduce the twin by one atomic layer [285].

The second scenario is for the leading 30° partial $\mathbf{B}\alpha$ to transmit across the twin boundary. As discussed in Section 7.2, the 30° partial $\mathbf{B}\alpha$ may transmit across the twin boundary, leaving behind a large stair rod dislocation $\alpha\alpha'$. If the trailing partial $\alpha\mathbf{D}$ remains on the BCD plane, it will have a unique dislocation configuration where a stacking fault links the $\alpha\alpha'$ with partial $\mathbf{B}\alpha'$, and another stacking fault links the $\alpha\alpha'$ with the trailing partial $\alpha\mathbf{D}$, as shown in Fig. 48a. The trailing partial $\alpha\mathbf{D}$ can also cross-slip onto the twin boundary plane, becoming a partial $\delta\mathbf{A}$ to slip to the left to increase the twin by one atomic plane, as shown in Fig. 48b.

The third scenario is for the stair-rod dislocation $\delta\alpha$ in Fig. 47a to further dissociate into two partial dislocations, $\delta\alpha \rightarrow \delta\mathbf{B} + \mathbf{B}\alpha$, where the partial $\delta\mathbf{B}$ glides on the twin boundary to the opposite direction of $\mathbf{B}\delta$ to reduce the twin thickness by one atomic plane, as illustrated in Fig. 47c. Such a process can be repeated to reduce the twin, as described in Section 7.1. The energy barrier for such a reaction is about $3.5\hat{E}$, making it relatively difficult.

The trailing 90° partial $\alpha\mathbf{D}$ can also react with the stair-rod $\alpha\alpha'$ and transmit across the twin boundary [285]. However, the dislocation reactions have very high energy barriers, and are not likely to occur [285]. Therefore, the transmission of the trailing 90° partial will not be discussed in detail here.

7.5.3. 90° leading partial reacts first at twin boundary

If the 90° partial $\alpha\mathbf{D}$ is the leading partial, $\alpha\mathbf{D}$ could either cross-slip onto the twin boundary plane or transmit across the twin boundary. The first scenario is for the 90° leading partial to cross-slip onto the twin boundary plane ABC, as described in Section 7.3. The trailing partial $\mathbf{B}\alpha$ can also cross-slip onto the twin boundary to form $\mathbf{B}\delta$ on the ABC plane, following the procedure described in Section 7.1, leaving behind a stair-rod dislocation $\delta\alpha$. $\mathbf{B}\delta$ and $\delta\mathbf{A}$ can glide together on the twin boundary with a stacking fault between them. On the other hand, the trailing 30° partial $\mathbf{B}\alpha$ can also transmit across the twin boundary to emit a partial $\mathbf{B}\alpha'$ in the twin, as described in Section 7.2. This leaves behind a stair-rod $\alpha\alpha'$ at the twin boundary.

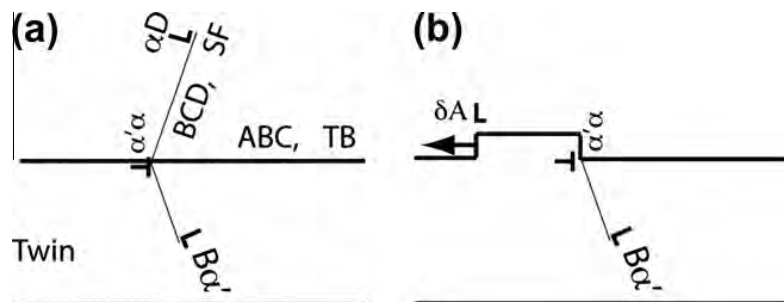


Fig. 48. (a) Dislocation configuration after the leading 30° partial $\mathbf{B}\alpha$ transmits across twin boundary and the trailing 90° partial $\alpha\mathbf{D}$ remains on the BCD plane. (b) After the trailing partial $\alpha\mathbf{D}$ cross-slips into the ABC plane to grow the twin by one atomic plane [285].

The second scenario is for the leading partial $\alpha\mathbf{D}$ to transmit across the twin boundary, as described in Section 7.3. The 90° partial $\alpha\mathbf{D}$ can transmit across the twin boundary after one of the following reactions:



and



where the partial dislocations $\mathbf{D}'\alpha'$, $\mathbf{D}'\beta'$, or $\mathbf{D}'\gamma'$ will glide away in the twin, leaving behind two stair rod dislocations at the twin boundary. When the trailing 30° partial $\mathbf{B}\alpha$ reaches the twin boundary, it can react with stair-rod dislocation, i.e.



This reaction is energetically favorable with an energy reduction of $-\hat{E}$. The $\mathbf{B}\delta$ can glide on the ABC plane, which either increase or reduce the twin thickness by one atomic plane, depending on its slip direction.

The trailing partial $\mathbf{B}\alpha$ can also react with stair-rod dislocations (as shown in Eqs. (59)–(61)) at the twin boundary to release a Shockley partial dislocation in the twin:



and



A first inspection suggests that the energy barrier should be zero for the reactions in Eqs. (63)–(65) because the number of partial dislocations and stair-rod dislocations does not change. However, the reacting stair-rod dislocation pairs on the left can combine to form a dislocation with lower energy, while the stair-rod dislocation pairs on the right form a dislocation with higher energy when they combine together [285]. This energy differences can be regarded as the energy barrier, which are about $3.4\hat{E}$ for Eq. (63) and $2.8\hat{E}$ for Eqs. (64) and (65). Therefore, the energy barrier for the trailing partial to transmit across the twin boundary is relatively high.

8. Effect of twinning on properties

The interaction between the twin boundary and dislocations will inevitably affect the mechanical and physical properties. The existence of twin boundaries significantly increases the dislocation storage capability in materials, and twin structure may also affect physical properties. These are discussed in the following sections. Since deformation twins and growth twins should have similar effect on the properties, no differentiation is made between them in the following discussion.

8.1. Strain rate sensitivity

Strain rate sensitivity (SRS) m is defined as $m = \frac{\partial \ln \sigma}{\partial \ln \dot{\epsilon}}|_{\epsilon, T}$, where σ is the flow stress and $\dot{\epsilon}$ is the strain rate [287]. By defining the activation volume, which is the rate of decrease of the activation enthalpy with respect to flow stress at a fixed temperature, $v^* = \sqrt{3}kT \left(\frac{\partial \ln \dot{\epsilon}}{\partial \ln \sigma} \right)$, where k is the Boltzmann constant and T is the absolute temperature, SRS can be re-written as $m = \frac{\sqrt{3}kT}{\sigma v^*}$ [287,288]. Experimental results have shown that nc materials are highly sensitive to strain rates and that the SRS of nominally defect-free nc Cu and Ni are several times higher than that of their coarse-grained counterparts [289–291]. The activation volume of nc materials is about two order of magnitude smaller than that of conventional coarse-grained materials [288].

Tensile strain rate jump tests of UFG copper with and without nanoscale twins over a wide range of strain rates indicated that twinned structures significantly increase the strain rate sensitivity [195]. Fig. 49 shows that increasing strain rate reduces moderately the SRS of twinned samples, while the SRS of the untwinned sample is independent of the strain rate. The SRS of nano-twinned Cu sample with a small twin boundary spacing of 15 nm is significantly higher than that of the nano-twinned Cu sample with a larger twin boundary spacing of 100 nm, while the SRS of the untwinned sample is the lowest among the three samples.

Lu et al. [292] carried out a series of systematic experiments of depth-sensing instrumented indentation with varying loading rates by three orders of magnitude, demonstrating that increasing the density of growth twins in UFG pure Cu leads to a significant increase in the strain rate-sensitivity. Fig. 50 shows nanoindentation hardness plotted as a function of loading rate for UFG Cu with different twin densities. By assuming indentation hardness and loading rate are equivalent to stress and strain rate, respectively, the SRS m for the three materials are calculated using the relationship of $\sigma \propto \dot{\epsilon}^m$. The results indicate that the SRS m for Cu with a lower twin density (average twin boundary spacing ~ 90 nm) and with a higher twin density (twin boundary spacing ~ 20 nm) is 0.025 ± 0.009 and 0.036 ± 0.009 , while the SRS for UFG Cu without twin, evaluated from tension tests instead of indentation because of the large scatter in the indentation response, is only 0.005 ± 0.001 . TEM microstructural investigation suggested that deformation-induced displacement of coherent twin boundaries (CTBs), formation of steps and jogs along CTBs, and blockage of dislocations at CTBs significantly

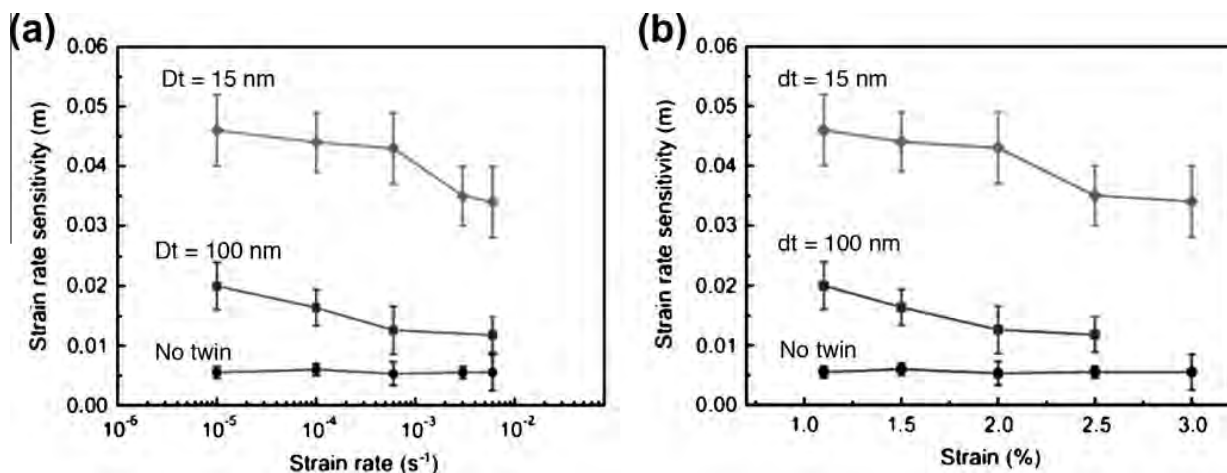


Fig. 49. The strain rate sensitivity as a function of (a) strain rate and (b) grain size for UFG coppers with no twin, twin boundary spacing is 100 ± 15 nm, and twin boundary spacing is 15 ± 7 nm [195].

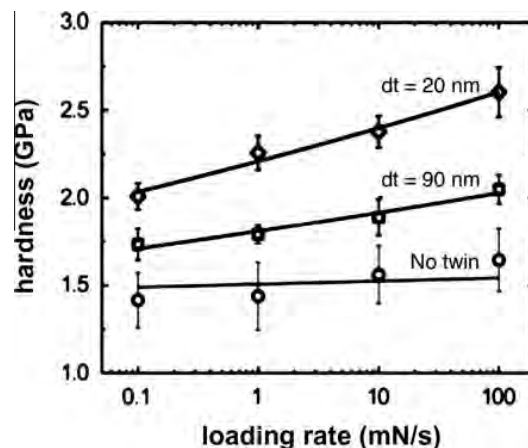


Fig. 50. The hardness as a function of loading for UFG coppers with no twin, twin boundary spacing is 90 nm, and twin boundary spacing is 20 nm [292].

influence the evolution of thermal activation volume for plastic flow, which is some three orders of magnitude smaller than that known for microcrystalline Cu.

Lu et al. [293] summarized the experimental results on the effect of twin lamellar thickness d (or λ) on the strain rate sensitivity m of nano-twinned copper, as shown in Fig. 51. They reported that m can be one order of magnitude higher than conventional coarse-grained materials when λ is reduced down to about 15 nm. For comparison purpose, the m values of nanocrystalline copper, with grain size d replacing twin lamellar thickness λ , are also plotted in the figure. It is very clear that the dependence of m on λ and d are very similar.

Asaro and Suresh [29] proposed that the rate-controlling mechanism for nc materials is grain boundary mediated dislocation activity, which is different from the bulk dislocation–dislocation interaction (forest hardening) in coarse-grained materials [294]. They developed mechanism-based models that rationalize the distinct deformation characteristics of fcc metals with grain size and twin dimensions in the nanometer regime. They developed estimates of flow stress as a function of strain rate and activation volume by exploring the roles of crystal stacking energies, such as the intrinsic stacking fault and the unstable stacking fault energy, in the process of initiating deformation via the emission of either partial dislocations or perfect dislocations from the grain or twin boundaries of nc FCC metals. Results obtained from their models are consistent with available experimental data on activation volumes and rate sensitivity in both a quantitative and qualitative manner.

8.2. Strain hardening rate

For coarse-grained materials, twinning has been known to contribute significantly to plastic deformation in materials with low SFE [295,296]. Higher rates of strain hardening have been reported in low SFE alloys due to deformation twinning that acts as strong barriers to dislocation motion, which consequently resulted in higher tensile ductility [297–302]. Through the analysis of the barriers to slip caused by twinning in an fcc crystal, Mahajan and Chin [74] predicted that the strain-hardening rate should be increased by the formation of twins. The prediction was supported by experimental results on polycrystalline coarse-grained FCC 70/30 brass and MP35 N with low stacking fault energies [81,303]. Ma et al. reported that the strain hardening rate of nano-twinned copper is much higher than that of UFG Cu [304].

Chen and Lu [305] measured the strain hardening rates of four UFG Cu samples – nt-Cu-20 with twin spacing of $\sim 20 \pm 4$ nm (nt = nanotwin), nt-Cu-36 with twin spacing of $\sim 36 \pm 7$ nm, nt-Cu-90 with twin spacing of 90 ± 26 nm, and UFG-Cu without twin, using uniaxial tensile tests. Fig. 52 shows strain hardening rates plotted against the true strain for the four samples. As shown, the strain-hardening rate is achieved in nt-Cu-20 at stresses that is higher than that of the other three samples. The highest strain-hardening rate is also seen in nt-Cu-20 over a range of strains. Comparison of the values of the strain hardening rates obtained from the three nt-Cu specimens leads to the conclusion that introducing nanoscale twins into UFG grains enhances strain hardening rate significantly.

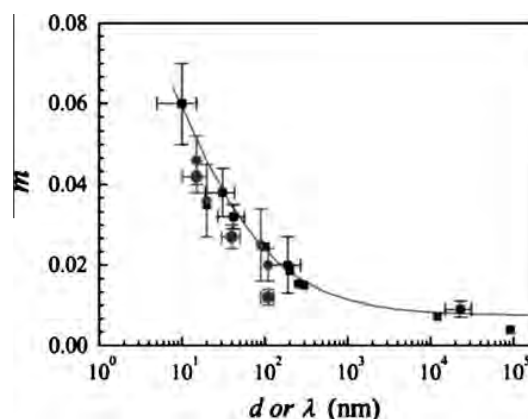


Fig. 51. The effect of the twin lamellar thickness d (or λ) on the strain rate sensitivity m [283].

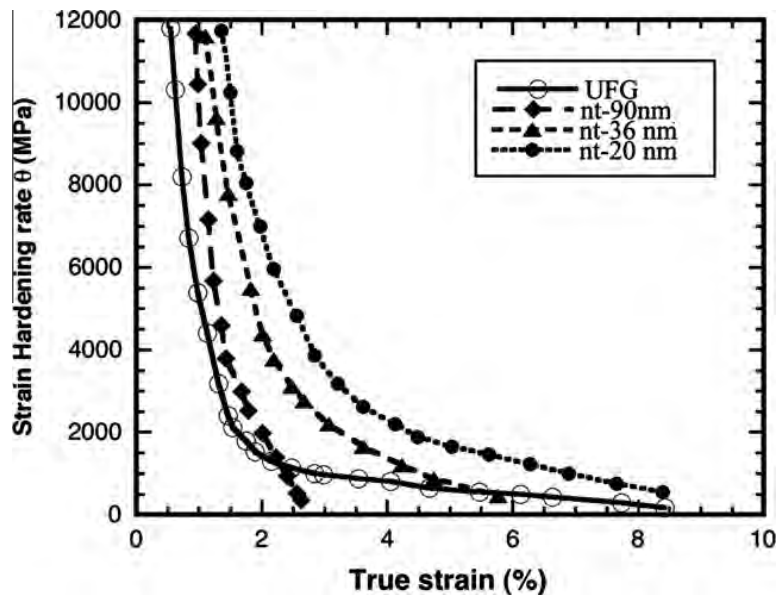


Fig. 52. The strain hardening rates of four copper samples measured by tensile tests: nano twinned sample with a twin spacing of 20 nm (nt-20 nm), nano twinned sample with a twin spacing of 36 nm (nt-36 nm), nano twinned sample with a twin spacing of 90 nm (nt-90 nm), and UFG sample without twin [305].

8.3. Strength and ductility

It has been well accepted that twin boundaries are equivalent to conventional grain boundaries with respect to the H–P effect [306–312], i.e., the same H–P slope for both twin boundaries and grain boundaries [290], because twin boundaries are strong barriers for dislocation motion [310–313]. Significant enhancement of tensile strength in copper [40,314] and hardness in fcc γ phase 330 stainless steel thin films [315] as well as fcc Cu/330 stainless steel multilayer films [316,317] was achieved by nano twins. Growth twins in Copper [291] and Nickel [195] and deformation twins in steel [292] with twin boundary spacing of tens to hundreds of nanometers show H–P behavior.

Nano-twinned FCC 330 stainless steel [294] with an average columnar grain size of ~ 30 nm and an average twin spacing of ~ 4 nm is observed to have a hardness of ~ 6.5 GPa, while the hardness of bulk conventional 330 SS is only ~ 200 MPa. However, the hardness value cannot be explained using the H–P relationship extrapolated from data of other similar steels [294]. This phenomenon is explained as that, instead of dislocation pile-ups at twin boundaries, materials with this extremely fine twin spacing are strengthened via single dislocations transmission across twin boundaries, in which the twin boundaries act as strong barriers for the transmission of dislocations. The mechanism has also been used to explain the observed phenomena that in FCC Cu/330 stainless steel multilayer films with high densities of twins in the nano Cu and 330 SS layers, the increase of hardness with decreasing layer thickness follows the Hall–Petch law for layer thickness greater than about 50 nm, but at lower layer thickness the hardness saturates to a value of about 5 GPa [296].

Lu et al. [41] reported that reducing the thickness of twins down to 15 nm in nano-twinned (nt) Cu samples resulted in continuous increase in strength. However, further reducing the thickness resulted in softening accompanied by enhanced strain hardening and tensile ductility, i.e., the maximum strength of nt-Cu samples exists at a twin thickness of 15 nm (see Fig. 53). They suggested that the strongest twin thickness originates from a transition in the yielding mechanism from the slip transfer across twin boundaries to the activity of preexisting easy dislocation sources. Curves for a twin-free UFG-Cu with a mean grain size of 500 nm and for a coarse-grained-Cu with a mean grain size of 10 μ m are included for the comparison purpose.

The maximum strength observed by Lu et al. [41] is consistent with an MD simulation [50], and was further investigated using large-scale MD simulations and a kinetic theory of dislocation nucleation by Li et al. [318]. They proposed a dislocation–nucleation-controlled mechanism in

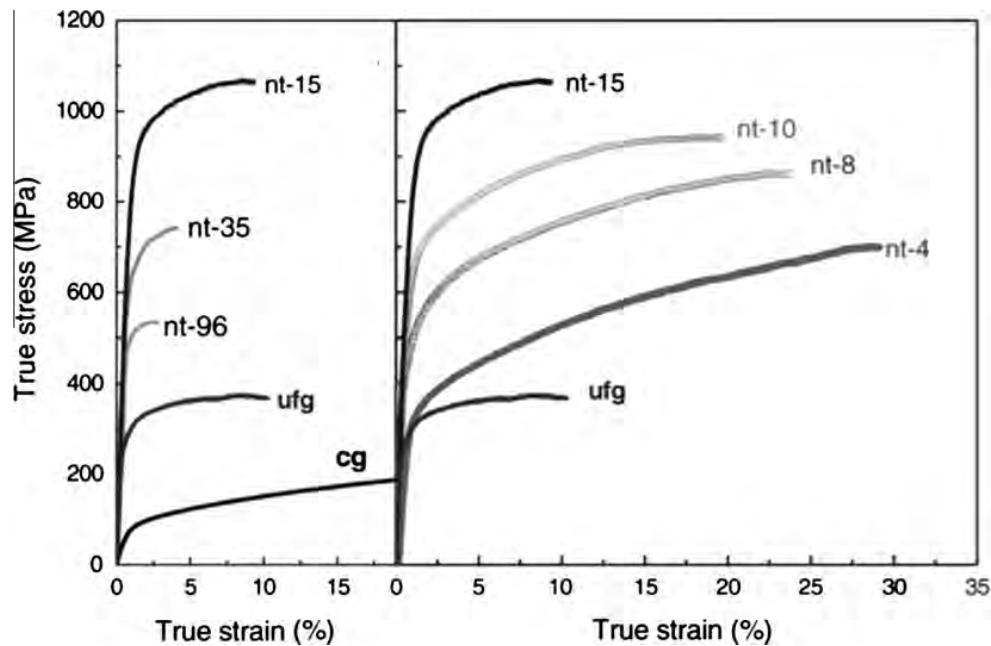


Fig. 53. Tensile true stress–strain curves of nano twinned copper tested at a strain rate of $6 \times 10^{-2} \text{ s}^{-1}$ [41].

nano-twinned metals, in which there are plenty of dislocation nucleation sites but dislocation motion is not confined. They showed that dislocation nucleation governs the strength of such materials, resulting in the softening of the materials below a critical twin thickness. They found that there exists a transition in deformation mechanism, occurring at a critical twin-boundary spacing for which strength is maximized. At this point, the classical Hall–Petch type of strengthening due to dislocation pile-up and cutting through twin planes switches to a dislocation–nucleation-controlled softening mechanism with twin-boundary migration resulting from nucleation and motion of partial dislocations parallel to the twin planes.

Deformation twins produced by plastic deformation can also significantly improve the strength and ductility of nanostructured materials [51,153,221,319,320]. It has been reported that lowering SFE can simultaneously increase the strength and ductility of nanostructured materials [51]. Zhao et al. produced nanostructured Cu, Cu–10 wt.% Zn, and Cu–30 wt.% Zn alloys using HPT to study their mechanical properties. Their stacking fault energies decrease with increasing Zn content and are 41 mJ/m^2 , 22 mJ/m^2 , and 7 mJ/m^2 , respectively [221,321]. TEM and X-ray analysis revealed that as the stacking fault energy decreased from 41 mJ/m^2 to 7 mJ/m^2 , the grain size decreased from 180 nm to 10 nm , the dislocation density increased from $0.23 \times 10^{15} \text{ m}^{-2}$ to $3.10 \times 10^{15} \text{ m}^{-2}$, and twin density, defined as the probability of finding a twin boundary between any two adjacent $\{111\}$ planes, increased from 0.1% to 8.0% [221].

Fig. 54 shows the engineering stress–strain curves of the three samples. As shown, the strength increases monotonically with decreasing stacking fault energy. However, the ductility first increases (the Cu–10 wt.% Zn sample) and then decreases, indicating an optimum stacking fault energy for the best ductility. X-ray analysis revealed that the Cu–10 wt.% Zn sample has the best capability to accumulate dislocations, twins and stacking faults, and therefore has the highest hardening capability during the tensile testing. On the other hand, the Cu–30 wt.% Zn sample has the highest densities of twins and dislocations, which are already saturated before the tensile testing, making it impossible to further accumulate these crystalline defects during the tensile testing. This leads to very low strain hardening rate and consequently low ductility. It will be interesting to see if a controlled annealing of the sample could reduce the initial defect density and recover the strain hardening.

Note that the strength increase shown in Fig. 54 is partially caused by the solution hardening of the Zn solute. To isolate the effect of stacking fault energy, Sun et al. recently investigated the Co–Ni alloy, which has a systematic decrease in stacking fault energy with increasing Co content, but very little solution hardening [319]. The results confirmed that lower stacking fault energy improves both

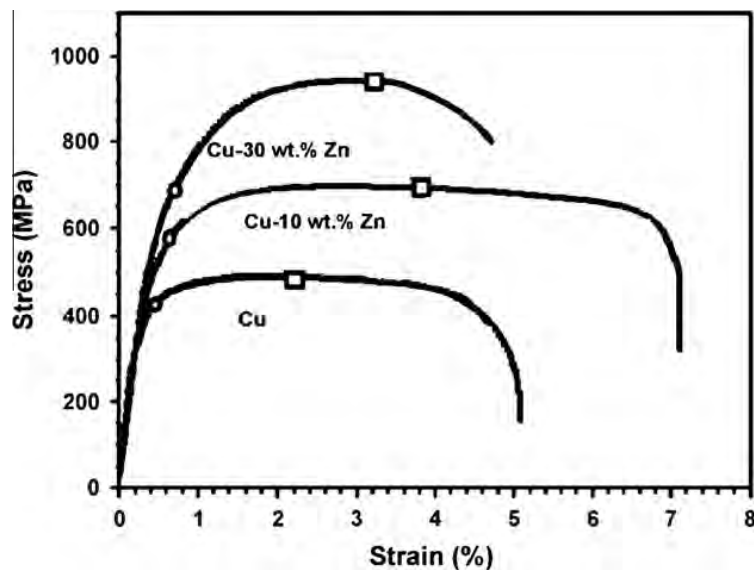


Fig. 54. The engineering stress–strain curves Cu, Cu–10 wt.% Zn, and Cu–30 wt.% Zn samples processed by HPT [221]. The gage dimension is 0.15 mm × 2 mm × 10 mm.

strength and ductility of NS materials. These data are very preliminary and further study is needed to probe this issue, especially when the stacking fault energy is very low.

8.4. Fatigue

This has not been extensively studied. A study on the effect of cyclic deformation on multilayer Cu/Cu samples with nanoscale twinning showed that (1) nano-twinned Cu is much more stable under cyclic deformation than equiaxed nanocrystalline Cu and (2) the fatigue of nano-twinned Cu is improved significantly over that of coarse-grained Cu [322]. However, although twin boundaries are strong in resisting fatigue cracking, it is also observed that some fatigue cracks could propagate along the twin boundary [323]. Another recent study found that detwinning happened during the cyclic deformation of nanocrystalline NiFe [324].

8.5. Conductivity

It is desirable for conducting metals to have both high strength and high electrical conductivity for many applications. However, many strengthening mechanisms including grain size refinement, cold working and alloying produce crystalline imperfections that serve as the scattering centers for conduction electrons in metals and therefore lower the conductivity. On the other hand, coherent twin boundaries, which are very effective in increasing strength, have an electron scattering coefficient that is an order of magnitude lower than that of conventional high-angle grain boundaries. Indeed, Anderoglu et al. reported that single-crystal-like nano-twinned copper films with average twin lamella thickness of 7–16 nm produced by magnetron sputtering exhibited much higher ratio of conductivity to strength as compared to nc columnar, textured, nano-twinned copper [325].

Lu et al. synthesized pure copper samples with a high density of nanoscale growth twins [40]. They showed a tensile strength about 10 times higher than that of conventional coarse-grained copper, while retaining an electrical conductivity comparable to that of pure copper. In comparison, the electrical conductivity values of the nc Cu foil without twins were at least one order of magnitude lower. The electrical resistivity can be described using the empirical Matthiessen's Rule, $\rho_{\text{total}} = \rho_t + \rho_i + \rho_d$, where ρ_{total} is the total resistivity of a metal, ρ_t , ρ_i , and ρ_d are the contributions from vibrations, impurities, and lattice defects such as dislocations and grain boundaries, respectively. The difference in the lattice dislocation density among the samples could be ignored, the major factor that contributes to the difference in electrical resistivity should be grain boundaries and twin boundaries. It has been

known that electrical resistivity of grain boundaries [326] and twin boundaries [327] in Cu at 295 K is about $3.6 \times 10^{-16} \Omega \text{ m}^2$ and about $1.7 \times 10^{-17} \Omega \text{ m}^2$, respectively. Therefore, the contribution to electrical conductivity from twin boundaries is much smaller than that from grain boundaries. This explains why the nano-twinned samples have conductivity that is close to that of the coarse-grained Cu.

9. Outstanding issues

There are still many outstanding issues for the materials community to solve. Most studies on deformation twinning in nc metals have focused on the fcc systems, while very few studies have concerned the nc bcc and hcp metals and alloys. Furthermore, the mechanisms for the formation of deformation twins are not very well studied even for coarse-grained bcc and hcp metals and alloys. Although the twinning mechanisms for coarse-grained and nc hcp metals are already under investigation [159–161,163,166,170,241,273,277,328–333], it is not clear if the twinning phenomena and mechanisms observed in nc fcc metals also occur in nc bcc and fcc systems. For example, it is unknown if the grain size effect on deformation twinning observed in nc fcc metals also exists in nc bcc and hcp metals. In fact, as discussed in Section 6.2, deformation twinning is rarely observed in nc hcp systems. It will take significant efforts by researchers using both MD simulation and experimental observations to establish the basic understanding of deformation twinning in nc bcc and hcp metals and alloys.

Even for nc fcc metals and alloys, there are still issues that need further study. As discussed in Section 5.8.5, to establish a comprehensive model to describe the twinning behavior of nc fcc metals, we need to understand how the GPFs affect the nucleation of first partials and twinning partials. Currently, it is not clear if the GPFE curves affect the nucleation of dislocations since non-equilibrium grain boundaries existing in nc metals can also act as a dislocation source. More experimental studies are needed to clarify this issue. In addition, the GPFs may also affect the slip of the first and twinning partials. Theoretical modeling is needed to develop a formula for calculating the Peierls stress for the slip of these partials from the GPFs.

Another outstanding issue is the grain size effect on the detwinning in nc metals and alloys. Almost all studies so far have focused on the formation of deformation twins. There have been recent studies on the detwinning process in nc materials also occurs in the nc fcc metals [131,156,227,246,285,286,334,335]. However, issues that are of interest for future studies include: (a) more experimental observations on the de-twinning process to compare with the proposed mechanisms [285,335], (b) the grain size effect of de-twinning, and (c) the existence of an equilibrium twin density and thickness.

10. Implications of deformation twinning within materials science

The discovery of new mechanisms for the formation of deformation twins in nc fcc metals has significantly extended our understanding of the deformation physics of metals and alloys as well as the role of grain boundaries in the deformation of fcc metals. It gives us a more complete picture on how the deformation mechanisms change with grain size [3]. As the grains of an fcc metal become smaller, dislocation sources that are active in coarse-grains, such as the Frank-Reed dislocation source, become inactive or more and more marginalized. Concurrently, grain boundary-mediated deformation mechanisms become active and eventually dominant [336]. In grain size range of a few tens to above 100 nm, grain boundaries become the source and sink of dislocations. Particularly, the emission of partial dislocations from grain boundaries becomes significant in nc fcc metals, even in systems with medium to high stacking fault energies. This leads to the formation stacking faults and deformation twins, which also shows grain size dependence. When the grain sizes decrease further, grain rotation and grain boundary sliding becomes dominant, which may also be assisted by diffusion and dislocation activities.

The new deformation mechanisms and deformation twinning discussed in this paper also provide fundamental physics for materials scientists to model the mechanical behavior of nc materials. For example, the strength of nc materials have been observed to deviate from the Hall–Petch relationship,

and even exhibit an inverse Hall–Petch relationship in some cases. Numerous analytical models and computational simulations have been carried out to describe and investigate this phenomenon [336–355]. The analytical Hall–Petch models are based on various assumptions and all of them can qualitatively describe the inverse grain size effect on strength. This makes it difficult to judge which models are physically better and more valuable. Any valuable analytical model or computer simulation on the mechanical properties must be based on real deformation physics. It is hoped that the deformation physics and deformation twinning of nc materials discussed in this review will be useful for future modeling of mechanical properties.

The deformation twinning also provides an effective approach for simultaneously improve the strength and ductility of nc materials, as discussed in Section 8.3. Due to the lack of dislocation accumulation in the interior of grains, nc materials usually have low tensile ductility. The twins could act as the barrier to dislocation slip and to enable dislocation accumulation, which increases both the strength and ductility. However, the effect of twins and deformation twinning on many other mechanical and physical properties needs to be further studied.

11. Summary and concluding remarks

In summary, nanocrystalline fcc metals deform by twinning more readily than their coarse-grained counterparts. Deformation twins in nanocrystalline fcc metals are largely formed by the emissions of Shockley partial dislocations from grain boundaries of nano-sized grains. In other words, the grain boundary acts as the source of partial dislocations in most cases. Another important source for partial dislocations is the dislocation reactions at the twin boundaries, which is the primary mechanism for the formation of multiple twins. Non-equilibrium grain boundaries play an important role in the deformation twinning because they may provide ready partials for the nucleation of stacking faults and twins. The partials emitted from grain boundaries may not have the same Burgers vector, which leads to twins with reduced or even zero shape change in the twinned grain. This is in sharp contrast to twins formed by mechanisms in coarse-grained metals, which have the same Burgers vector.

Both grain size and generalized stacking fault energy influences the formation of deformation twins in nanocrystalline fcc metals. There is an optimum grain size in nanocrystalline fcc metals at which the twinning is easiest, and this optimum grain size can be estimated from an analytical equation. Factors that affect the optimum grain size for twinning include the stacking fault energy and the shear modulus. When grains are smaller than the optimized grain size for twinning, an inverse grain size effect exists, where the twinning becomes more difficult with decreasing grain size. However, no inverse grain size effect on stacking fault formation exists. This difference is explained by the generalized planar fault energy effect, where the unstable twin fault energy is higher than unstable stacking fault energy. Therefore, both grain size effect and the generalized planar fault energy effect need to be considered in an analytical model to describe more accurately the twinning mechanisms in nanocrystalline fcc metals. Such a model is yet to be developed.

Deformation twinning and dislocation slip usually occur simultaneously during the deformation of nanocrystalline metals. The interactions of the dislocations with twins are very complex and the proposed interactions need to be further verified experimentally. Twin boundaries are effective barriers to dislocation slip, and consequently twins can increase the strength of nanocrystalline and nanostructured materials. Twins are also found to increase the strain hardening rate and the strain rate sensitivity, which leads to increase in ductility. Therefore, twinning is a mechanism that can simultaneously increase the strength and ductility. In the design of new nanocrystalline alloys for high strength, ductility and toughness, stacking fault energy can be adjusted by alloying to promote deformation winning.

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