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ENHANCED DUCTILITY OF NANOCRYSTALLINE AND ULTRAFINE-GRAINED METALS

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Abstract. This article briefly summarizes the extensive information now available, from recent experiments and theoretical models, addressing the enhanced tensile ductility of nanocrystalline (NC) and ultrafine-grained (UFG) metals. Special attention is devoted to the key strategies and procedures developed to concurrently optimize both the strength and tensile ductility of NC and UFG metals with an emphasis on the effects of basic deformation mechanisms, crystallographic structure, chemical composition and the presence of second-phase precipitates.

1. INTRODUCTION

Metallic materials having NC and UFG structures exhibit superior mechanical properties that have attracted a rapidly growing research interest over the past decade [1–3]. Nevertheless, in spite of their excellent mechanical characteristics, and in particular their very high strength and hardness, NC and UFG metals generally exhibit a rather low tensile ductility and this places a severe limitation on their practical applications. At the same time, there are several examples of substantial tensile ductility [4-14] of superstrong NC and UFG metals at room temperature and even of superplastic elongations in UFG metals at elevated temperatures [15]. Such materials, with unique combinations of very high strength and good ductility at room temperature, represent ideal materials for a wide range of structural applications in the aerospace and automotive industries and for use in innovative application in fields as diverse as medicine, energy and the fabrication of sports products.

In order to develop these materials for advanced technological applications and to obtain progress in the fundamental science of nanostructures, it is important to understand the nature of this enhanced ductility and the effective strategies that are available to attain high ductilities in NC and UFG metallic structures. Thus, the objective of this article is to provide an overview of the key strategies and methods developed to optimize the strength and tensile ductility of NC and UFG metals, with special emphasis on the effects of structure, composition and phase content on their deformation behavior.

2. INSTABILITIES SUPPRESSING TENSILE DUCTILITY IN NANOCRYSTALLINE AND ULTRAFINE-GRAINED METALS

In general, the tensile ductility of a solid is controlled by a competition between plastic deformation and fracture processes as well as by the resis-

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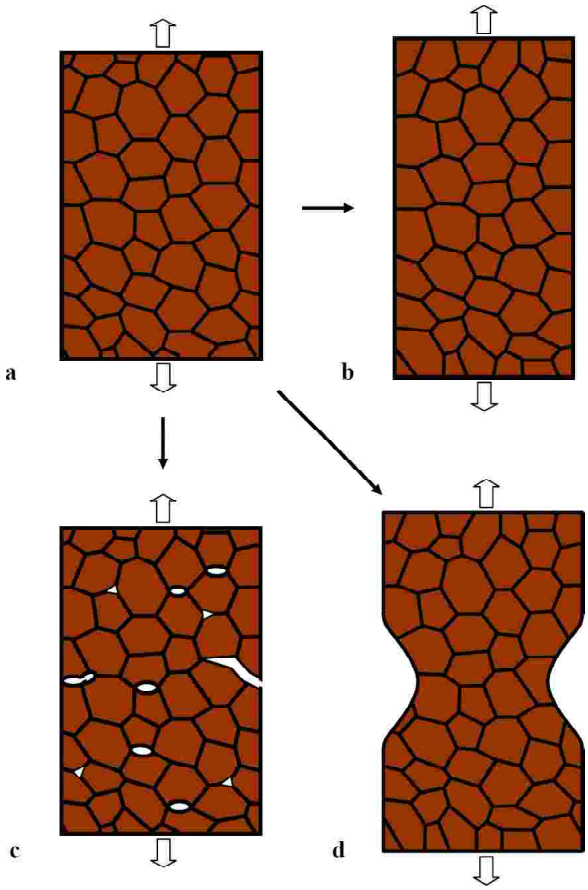

Fig. 1. (Color online) Key evolution routes of a NC specimen under tensile load. (a) Initial state of the NC specimen. (b) Homogeneous plastic deformation of the specimen corresponding to its enhanced ductility. (c) Brittle fracture in the NC specimen occurs through crack nucleation and growth instabilities, typically involving the fast nucleation of nanoscale cracks, their convergence and/or growth along the grain boundaries. (d) The specimen shows plastic strain instability with necking. Routes (c) and (d) correspond to low tensile ductilities.

tance to plastic flow localization (Fig. 1). Most NC and UFG metals fail to exhibit homogeneous plastic deformation in tensile testing (Fig. 1b) but instead they are characterized by low tensile ductility at room temperature because of two processes [2,3,7,16-18]: (i) brittle crack nucleation and propagation instabilities (Fig. 1c) and (ii) plastic strain instability in the form of a localization of plastic flow in shear bands and neck formation (Fig. 1d). The former process dominates in NC metals having the finest grains with grain sizes, d, lower than a critical value of $d_c \approx$ 10-30 nm depending on the material and structure characteristics. Alternatively, a plastic strain instability is the main factor causing low tensile ductility in NC metals with intermediate grain sizes up to 100 nm and in UFG metals with grain sizes from 100 to 1000 nm.

A crack nucleation instability (Fig. 1c) means that plastic flow is suppressed in a solid so that the applied stress rapidly reaches a level close to the critical stress needed to initiate cracks near local stress concentrations. These concentrations may occur either at fabrication-produced flaws or at defects generated due to the very limited local plastic deformation. The subsequent crack propagation is due to the suppression of conventional toughening mechanisms, such as lattice dislocation emission from crack tips, that are needed to provide a resistance to crack growth [19].

Plastic strain instability in a solid under tensile deformation (Fig. 1d) is controlled by its strain hardening θ and strain rate sensitivity m. These parameters are defined through the macroscopic characteristics (flow stress σ, plastic strain ε and plastic strain rate $\dot{\varepsilon}$) of the plastic deformation such that: $\theta = \sigma^{-1}(\partial\sigma/\partial\varepsilon)_{\dot{\varepsilon}}$ and $m = \{\partial\ln\sigma/\partial\ln\dot{\varepsilon}\}_{\varepsilon}$). The plastic strain instability is suppressed at sufficiently high values of strain hardening θ and/or strain rate sensitivity m. Thus, coarse-grained polycrystalline metals exhibit good tensile ductility due to high strain hardening associated with lattice dislocation storage in the grain interiors during plastic deformation. The superplasticity of microcrystalline metals with $d \approx$ 2-10 μm at elevated temperatures is due to a high strain rate sensitivity attributed to the role of diffusion-controlled intergranular sliding as the dominant deformation mode. By contrast, NC and UFG materials often have low values of θ and m so that they typically show plastic strain instability [4,18].

3. BASIC DEFORMATION MECHANISMS AND KEY STRATEGIES FOR TENSILE DUCTILITY ENHANCEMENT IN HIGH-STRENGTH METALS WITH ULTRAFINE-GRAINED AND NANOCRYSTALLINE STRUCTURES

In general, an enhancement of tensile ductility of UFG and NC metals without dramatic loss of their strength may be effectively attained if plastic strain instability as well as brittle crack nucleation and propagation instabilities are suppressed in these materials. In search for strategies for prevention of the instabilities in NC and UFG metals, of particular interest are plastic deformation mechanisms

operating in them. In NC metals having finest grains with $d < d_c$, amounts of grain boundaries (GBs) are extremely large, and GB deformation mechanisms are dominant [1-3]. These mechanisms – first of all, GB sliding, rotational deformation and stress-driven migration of GBs [1-3,20-22] - are characterized by very high flow stresses close to the stress level needed to initiate cracks. Besides, when plastic flow is conducted by GBs, it is typically hampered at GB junctions whose amounts are extremely large in NC metals with finest grains. Therefore, GB deformation in such metals rapidly creates local stress sources capable of initiating cracks at triple junctions [23].

In the light of these specific features of plastic flow mechanisms operating in NC metals with finest grains, the general strategies to enhance their ductility are in "smoothing" plastic strain non-homogeneities that serve as dangerous stress sources on the nanoscale level and/or fabricating structural composites consisting of NC and ductile, coarse-grained components of large scales. The first strategy (strategy I) aims at preventing or at least delaying crack generation at triple junctions during nanoscale plastic deformation. The second strategy (strategy II) is applicable to both NC and UFG metals, and its use allows one to enhance ductility and simultaneously provide high strength due to effects of ductile and NC/UFG components of large scales, respectively.

Now let us discuss plastic deformation modes in UFG metals and NC metallic materials having intermediate grains with d being in the range from d_c to 100 nm [1-3,7]. The lattice dislocation slip is dominant in these materials at room temperature [1-3,7]. At the same time, the lattice slip in UFG and NC metals has the specific features differentiating it from that dominating in coarse-grained polycrystals. So, the lattice slip in coarse-grained polycrystals is characterized by strain hardening due to intense generation and storage of lattice dislocations within grain interiors during plastic deformation. The dislocation annihilation through dislocation climb within grain interiors is not significant in polycrystals, because its rate is controlled by slow bulk diffusion. In contrast, the generation, storage and annihilation of dislocations at GBs (but not within grains) critically affects the lattice dislocation slip in UFG and NC metals where grain sizes are ultra small and amounts of GBs are large. After some initial stage of deformation, the considered processes in UFG and NC metals reach a dynamic equilibrium in which the dislocation generation and storage at GBs are completely compensated by the fast dislocation annihilation controlled by fast GB diffusion [7]. The dynamic equilibrium is specified by the absence of strain hardening. As a corollary, UFG metals and NC metallic materials with intermediate grains under tensile load typically tend to show plastic strain instability and thereby low ductility [7].

In the context discussed, an effective strategy (strategy III) to enhance tensile ductility in UFG and NC metals is in violating the balance between the dislocation storage and the dislocation annihilation at GBs. Typical methods within this strategy "shift" the dislocation storage process from GB regions to grain interiors where the dislocation annihilation is slow, as with coarse-grained polycrystals. Also, one can enhance ductility with another strategy (strategy IV) focused on simultaneous intensification of GB sliding and diffusion processes whose combined actions provide plastic flow with high strain rate sensitivity m, as with conventional superplasticity of microcrystalline alloys.

4. METHODS FOR TENSILE DUCTILITY ENHANCEMENT IN ULTRAFINE-GRAINED AND NANOCRYSTALLINE METALS

The discussed strategies may be realized through manipulation of the structure, chemical composition and phase content of the material and/or by adjusting the conditions of the mechanical load. The basic methods/approaches adopted to date to enhance the tensile ductility of UFG and NC metals are outlined briefly in this section. First, let us consider the approach A related to the strategy I.

(A) Enhanced intrinsic ductility of artifact-free NC metals with narrow grain size distributions. The experimental results [8-10] give evidence of enhanced tensile ductility in single-phase NC metallic materials having narrow grain size distributions and without artifacts. These results are of considerable interest because they are indicative of an intrinsic ductility of the "pure" NC structures in which extrinsic factors such as bimodal/multimodal grain size distributions or pre-existing pores and contaminations are not operative. In the experiments [8-10], an *in situ* consolidation mechanical alloying technique was used to fabricate artifact-free NC Cu and an Al-5%Mg alloy having mean grain sizes of ~23 and ~26 nm, respectively. These artifact-free NC materials gave both ultrahigh strength and good tensile ductility (Fig. 2) and they were characterized by moderate strain hardening and failure in a ductile fracture mechanism with ductile dimples at the frac-

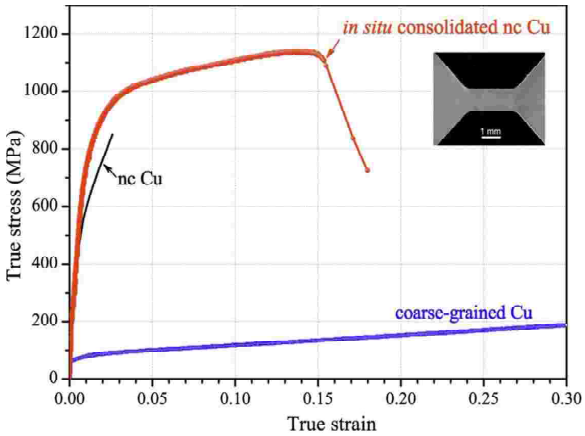

Fig. 2. (Color online) A typical tensile stress–strain curve for a bulk *in situ* consolidated nanocrystalline Cu sample compared with that of a coarse-grained polycrystalline Cu sample (an average grain size larger than 80 μm) and a nanocrystalline Cu sample prepared by an inert-gas condensation and compaction technique (with a mean grain size of 26 nm). Reprinted from [8]. Copyright 2005, with permission from American Institute of Physics.

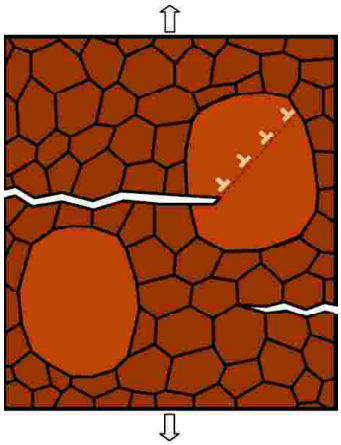

Fig. 3. (Color online) Deformation and fracture processes in a specimen with a bimodal structure. Large grains both suppress crack growth due to crack tip blunting associated with lattice dislocation emission and provide strain hardening related to lattice dislocation accumulation which is a necessary prerequisite for good ductility. In practice, the presence of the NC/UFG matrix leads to a high strength and hardness.

ture surfaces [8-10]. Lattice dislocation slip was reported active in the artifact-free NC Cu and Al-5%Mg alloy. Both the strain hardening and good ductility of the materials were attributed to lattice dislocation storage in the grain interiors.

The experimental data of simultaneous high strength and good tensile ductility [8-10] can be logically explained within the concept of the interaction of deformation modes in NC materials [2,23], with an optimization of the GB sliding, lattice slip and diffusion processes [23]. According to this concept associated with strategy I, various deformation modes mutually accommodate and enhance each other, producing a moderate strain hardening which acts in parallel with the suppression of crack nucleation.

Now let us discuss the methods B and C associated with the strategy II operating with structural composites consisting of ductile and NC/UFG components of large scales.

(B) Enhanced ductility of single-phase metals with bimodal ("nano-micro") structures. One of the most effective methods for achieving a high strength in metals without a corresponding loss in tensile ductility is to fabricate single-phase metallic materials with bimodal structures composed of a mix of nanoscopic (or ultrafine) and comparatively large grains [4,7,24,25] (Fig. 3). Such nanomaterials have two peaks in their grain size distributions, one in the nanometer or ultrafine range and the other in the (sub)micrometer range. Although the micromechanisms responsible for a combination of high strength and good ductility in nanomaterials with bimodal structures are currently under debate [4,7,24,25], it is generally assumed that the presence of large grains suppresses crack propagation (Fig. 3) and provides the strain hardening required for good ductility whereas the NC matrix provides a combination of high strength and hardness.

(C) Enhanced ductility of graded nano-grained copper. A recent report [14] describes enhanced tensile ductility of graded nano-grained Cu specimens produced by surface mechanical grinding treatment of initially coarse-grained specimens. The graded material represents a structural film/substrate composite specified by a gradient grain size transition from nano- to coarse-grained structures. The graded Cu shows high tensile ductility controlled by its coarse-grained substrate structure, along with a high strength due to the effect of its NC film component [14].

The following approaches D - I are suggested within the strategy III, and they are focused on intensification of the dislocation storage in grain interiors where the dislocation annihilation controlled by bulk diffusion is too slow to compensate the storage.

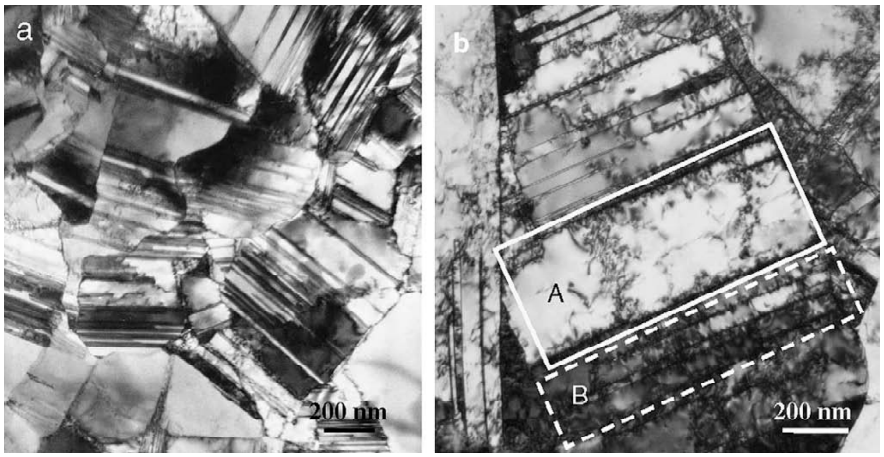

Fig. 4. Transmission electron microscopy images of nanotwinned Cu. (a) As-deposited sample showing that coherent twin boundaries are initially straight and defect-free. (b) Sample after a stress relaxation test showing the dislocation accumulation at twin boundaries (as shown in rectangle B), as well as dislocation tangles and networks within the wide twin lamellae (as shown in rectangle A). Reprinted from [26]. Copyright 2009, with permission from Elsevier.

(D) Enhanced ductility of UFG metals with nanotwinned structure. Recently, special attention was devoted to the unique combination of high strength and enhanced ductility that may be attained in nanotwinned copper having ultrafine grains with a high density of nanoscale growth twins [6,11,26,27] (Fig. 4a). Thus, the structure at the nanoscale level is composed of twins which are divided by coherent twin boundaries that serve as storage sites for lattice dislocations under mechanical load (Fig. 4b). Coherent twin boundaries have much lower energies and thus they are more stable against migration by comparison with high-angle grain boundaries [3,6,11,26,27]. In detailed experiments [3,6,11,26,27], it was found that nanotwinned Cu specimens have high strength and good ductility. For example, nanotwinned copper with an average twin lamella thickness of ~15 nm was reported to exhibit good tensile ductility with strains-to-failure of $\varepsilon_f \approx 0.14$, high values of the yield stress of ~900 MPa and ultimate tensile stresses of ~1068 MPa [11]. These stress values are at least one order of magnitude higher than those characterizing coarse-grained copper.

A similar approach has been developed in ductility enhancement through twin deformation in electroplated NC Co [12,28]. In this case, twins serve as both carriers of plastic flow and structural elements whose boundaries cause the lattice dislocation storage within grains.

(E) Transformation-induced enhancement of ductility in a UFG steel. A ductility enhancement method was proposed for UFG steels based on a martensitic transformation and the effects on plastic flow in UFG structures [29]. Thus, *in situ* observations revealed the formation of a martensitic phase which replaced the austenite during room temperature tensile loading of a UFG steel having a Fe-10%Cr-5%Ni-8%Mn-0.1%C composition. The transformation deformation dominated in the early loading stage specified by low θ. Both lattice dislocation slip and transformation deformation simultaneously operated in the main loading stage specified by high θ. For this result, it is reasonable to suggest that strain hardening and a suppression of the plastic strain instability are present due to dislocation storage at interphase boundaries in the UFG steel.

(F) Enhanced ductility of UFG metals due to tailoring of the stacking fault energy (SFE) via alloying. Several experiments have demonstrated the SFE may be effectively tailored to provide high strength and good tensile ductility. For example, tests were performed on pure Cu and bronze (Cu-10%Zn) where the SFEs are 78 and 35 mJ m^{-2}, respectively [30]. The results showed the bronze has both higher strength and higher ductility where the latter is due to the smaller grain size, higher twin and dislocation densities and solution hardening and the latter is due to the high strain hardening rate. Experiments on Cu and various Cu-Al alloys also confirmed the ability to tailor the SFE for an optimization of strength and ductility [31,32] (Fig. 5) and there are also similar results for two Ni-Co alloys [33]. It is important to note that the SFE has a major influence on the microstructural evolution and dislocation storage capability in UFG metals [34-36].

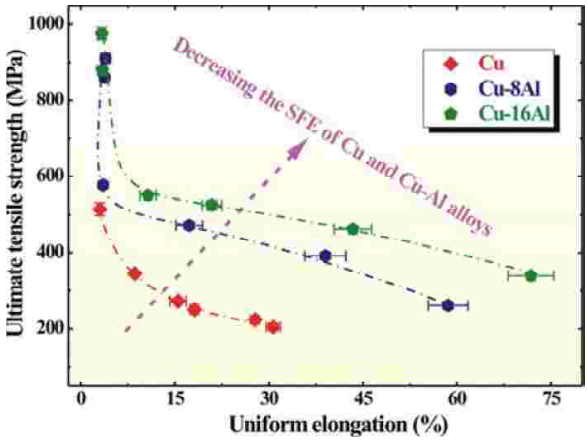

Fig. 5. (Color online) Variation in ultimate tensile strength with uniform elongation for Cu and Cu-Al alloys under different annealing conditions (for details, see [32]), showing the enhancing effect of a decrease in the stacking fault energy (SFE) on ductility. Reprinted from [32]. Copyright 2012, with permission from Elsevier.

(G) Enhanced ductility of UFG metals deformed at cryogenic temperatures. Experiments on Cu demonstrated the ability to achieve high strength and good ductility by initially processing using equal-channel angular pressing (ECAP) to achieve a UFG structure and then cryodrawing and cryorolling in liquid nitrogen at 77K to produce a minor reduction in grain size, from ~290 to ~230 nm, and a higher fraction of high-angle GBs [37]. The higher ductility after cryogenic processing was attributed primarily to a high density of pre-existing deformation twins but also to the change in the fraction of high-angle boundaries.

(H) Enhanced ductility in precipitation-hardened alloys. High strength and high ductility were achieved in a precipitation-hardened Al-10.8%Ag alloy by introducing an intermediate metastable phase [38]. In these experiments, a peak hardness was attained after processing by ECAP and aging for 100 h due to the precipitation within the grains of spherical particles with diameters of ~10 nm and elongated precipitates with lengths of ~20 nm. These spherical particles are expected to serve as dislocation storage centers within the ultrafine grains. The experiments demonstrated that, under optimum conditions for an aging of 100 h, there was a good tensile strength, an extensive region of uniform strain and a very good ductility.

A similar approach, with second-phase precipitation, was also exploited in the fabrication of a NC Al alloy with second-phase nanoparticles distributed within the grain interiors where these alloys showed high strength, strain hardening and enhanced tensile ductility [39].

(I) Enhanced ductility and fracture toughness in UFG steels with dispersed cementite and carbide particles. Experiments [40,41] have revealed that the formation of a UFG structure in steels processed by caliber rolling produces a technologically-attractive strength-ductility balance. For example, UFG steel specimens having Fe-0.3Si-1.5Mn-0.01P-0.002S-0.45C composition are characterized by a total elongation of around 20% at a tensile strength of 1000 MPa [41]. According to microstructural analysis [41], a warm caliber rolling treatment of coarse-grained steels with various carbon contents produces a structure consisting of ultrafine ferrite grains of equiaxed shape and dispersed cementite particles having sizes in the range from ~100 to 200 nm. The experimental data [40,41] are consistent with the proposal that the UFG ferrite structure of the steels is responsible for their high strength, whereas dislocation storage at the interfaces of second-phase cementite particles causes strain hardening that enhances ductility of the steel specimens.

A similar approach was exploited in other experiments [42] documenting both ultrahigh strength and enhanced fracture toughness, together with a functional ductility, in steels with elongated ultrafine grains. (Note that, as with ductility, fracture toughness of superstrong NC materials is typically lower than that of their coarse-grained counterparts [2,43]. At the same time, there are examples of good fracture toughness of NC materials, and these can be explained in terms of specific toughening micromechanisms operating on the nanoscale level at certain conditions [43].)

Finally, let us discuss the approach K related to strategy IV.

(K) Enhanced ductility of UFG and NC metals with non-equilibrium grain boundaries. There are several examples of enhanced tensile ductility in UFG metals processed using severe plastic deformation methods [1,7,44-47]. The ductility enhancement is attributed to the operation of GB deformation modes specified by a high strain rate sensitivity *m*. In practice, lattice dislocation slip is hampered in UFG materials where the volume fractions of GBs are very high. As a corollary, GB-diffusion-controlled GB sliding can effectively operate as an alternative deformation mode in these materials provided the GB diffusivity is high. The latter condition is realized in UFG metals containing non-equilibrium boundaries defined as GBs with high-angle misorientations and highly defective and

disordered structures [1]. Non-equilibrium GBs with high diffusivity are effectively generated in UFG metals fabricated by severe plastic deformation [1] and these materials may show enhanced tensile ductility at room temperature [1,7,44-47] and even superplastic effects and evidence for GB sliding at relatively low temperatures [48].

5. ENHANCED DUCTILITY IN ULTRAFINE-GRAINED AND NANOCRYSTALLINE METALS UNDER COMPRESSION, COLD ROLLING AND HIGH-PRESSURE TORSION

Although the main topic of this review is concerned with tensile ductility in NC and UFG metals, methods for ductility enhancement in these materials under other schemes of mechanical loading are also interesting from both a fundamental and applied viewpoint. In particular, such methods may assist in developing strong NC and UFG metals having enhanced tensile ductility. In this section, we will briefly discuss methods for ductility enhancement in NC and UFG metals under compression, cold rolling and high-pressure torsion.

(L) Enhanced ductility of NC metallic composites with dendrite-like inclusions. Enhanced ductility was demonstrated in Ti-based NC alloys with large dendritic-like inclusions of the second phase under compressive loading [49,50]. Plastic flow was localized in shear bands propagating within the NC matrix in these metallic nanocomposites. Large dendrite-like inclusions of the second phase impeded the shear band propagation and caused strain hardening that prevented a dramatic localization of plastic flow. The experiments showed an enhanced compressive ductility up to strains-to-failure of ~14%. This approach is similar to methods (B) and (C) exploited within strategy II in enhancement of tensile ductility.

(M) Enhanced ductility of NC metallic composites with carbon nanotubes. A recent report describes enhanced ductility of NC Cu reinforced by multiwalled carbon nanotubes under compressive load [51]. The nanocomposite consisted of a NC Cu matrix with a mean grain size of ~22 nm and with 1% wt. carbon nanotubes located within the grain interiors and at the GBs. In compression loading, nanocomposite pillars showed good ductility with strains-to-failure of $\varepsilon_f \approx 0.28$, strain hardening and a high yield stress of ~1125 MPa. It was noted that lattice slip dominated in these nanocomposites, with the carbon nanotubes hampering the dislocation motion [51]. It appears that lattice dislocations tend to accumulate at interfaces between the NC Cu and the carbon nanotubes and thereby cause the strain hardening.

(N) Enhanced ductility of NC metallic composites with Lomer-Cottrell dislocation configurations. A microscopic approach to the enhancement of ductility in NC metals was developed by increasing the strain hardening θ [52,53]. In these experiments, strain hardening was revealed to occur in NC metals of Ni and a Ni-Fe alloy through the formation of Lomer-Cottrell locks that effectively pinned the lattice dislocations in the grain interiors and thereby increased the dislocation storage capacity of the NC structures. The dislocation storage during plastic deformation increased the strain hardening in NC metals in cold rolling [52] and in high-pressure torsion [53].

The methods (M) and (N) are similar to those exploited within strategy III in enhancement of tensile ductility in NC and UFG metals.

6. CONCLUDING REMARKS AND IMPORTANT UNRESOLVED QUESTIONS

In summary, NC and UFG metals typically exhibit high strength and low tensile ductility, but this deficiency may be addressed using several different experimental procedures that are outlined briefly in the preceding subsections (A) to (K). These procedures are focused on a suppression of plastic flow and fracture instabilities by specifically designing the fabrication of NC and UFG metals through the use of special methods including the manipulation of structural features, the composition of the material and the use of phase contents that suppress plastic strain and fracture instabilities. The procedures are based on ductility enhancement strategies exploiting current representations on fundamental deformation mechanisms operating in NC and UFG metals. At the same time, despite the evident progress in understanding the fundamental nature of ductility enhancement in NC and UFG metals as well as the fabrication of such metals characterized by a good strength-ductility balance, the systematic production of superstrong and simultaneously ductile metallic materials with UFG/NC structures and various chemical compositions remains an elusive and critical technological issue. The solution of this problem requires further focused research efforts involving considerations of the following key points: (i) search for new methods and optimization of the current methods for ductility en-

hancement in NC and UFG metals within the known strategies I – IV; (ii) experimental identification and theoretical description of new intrinsic mechanisms of plastic flow and fracture operating in NC and UFG structures; (iii) search for new strategies in ductility enhancement in NC and UFG metals, with point (ii) used as input. Success in treatment of these important unresolved questions will make a large impact on fundamental nanomaterials science and open new intriguing perspectives in fabrication of NC and UFG metals having simultaneously good ductility and superior strength with a wide range of technological applications.

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References

[1] R.Z. Valiev // *Nature Mater.* **3** (2004) 511.
[2] C.C. Koch, I.A. Ovid'ko, S. Seal and S. Veprek, *Structural Nanocrystalline Materials: Fundamentals and Applications*. (Cambridge University Press, Cambridge, 2007).
[3] M. Dao, L. Lu, R.J. Asaro, J.T.M. De Hosson and E. Ma // *Acta Mater.* **55** (2007) 4041.
[4] Y. Wang, M. Chen, F. Zhou and E. Ma // *Nature* **419** (2002) 912.
[5] Y. Champion, C. Langlois, S. Guerin-Mailly, P. Langlois, J.-L. Bonnentien and M. Hytch // *Science* **300** (2003) 310.
[6] L. Lu, Y. Shen, X. Chen, L. Qian and K. Lu **//** *Science* **304** (2004) 422.
[7] Y.M. Wang and E. Ma // *Acta Mater.* **52** (2004) 1699.
[8] K.M. Youssef, R.O. Scattergood, K.L. Murty, J.A. Horton and C.C. Koch // *Appl. Phys. Lett.* **87** (2005) 091904.
[9] S. Cheng, E. Ma, Y.M. Wang, L.J. Kecskes, K.M. Youssef, C.C. Koch, U.P. Trociewitz and K. Han // *Acta Mater.* **53** (2005) 1521.
[10] K.M. Youssef, R.O. Scattergood, K.L. Murty and C.C. Koch // *Scr. Mater*. **54** (2006) 251.
[11] L. Lu, X. Shen, X. Huang and K. Lu // *Science* **323** (2009) 607.
[12] Y.M. Wang, R.T. Ott, A.V. Hamza, M.F. Besser, J. Almer and M.J. Kramer // *Phys. Rev. Lett.* **105** (2010) 215502.
[13] G. Wang, Z. Jiang, H. Zhang and J. Lian // *J. Mater. Res*. **23** (2008) 2238.
[14] T.X. Fang, W.L. Li, N.R. Tao and K. Lu // *Science* **331** (2011) 1587.
[15] M. Kawasaki, N. Balasubramanian and T.G. Langdon // *Mater*. *Sci. Eng. A* **528** (2011) 6624.
[16] C.C. Koch // *Scr. Mater*. **49** (2003) 657.
[17] E. Ma // *Scr. Mater*. **49** (2003) 663.
[18] E. Ma // *JOM* **54** (2006) 49.
[19] I.A. Ovid'ko and A.G. Sheinerman // *Acta Mater.* **58** (2010) 5286.
[20] I. A. Ovid'ko // *Science* **295** (2002) 2386.
[21] Z. Shan, E.A. Stach, J.M.K. Wiezorek, J.A. Knapp, D.M. Follstaedt and S.X. Mao // *Science* **305** (2004) 654.
[22] T.J. Rupert, D.S. Gianola, Y. Gan and K.J. Hemker // *Science* **326** (2009) 1686.
[23] I.A. Ovid'ko and A.G. Sheinerman // *Acta Mater.* **57** (2009) 2217.
[24] V.L. Tellkamp, E.J. Lavernia and A. Melmed // *Metall. Mater. Trans. A* **32** (2001) 2335.
[25] A.V. Sergueeva, N.A. Mara and A.K. Mukherjee // *Rev. Adv. Mater. Sci*. **7** (2004) 67.
[26] L. Lu, T. Zhu, Y. Shen, M. Dao, K. Lu and S. Suresh // *Acta Mater.* **57** (2009) 5165.
[27] K. Lu, L. Lu and S. Suresh // *Science* **324** (2009) 349.
[28] A.A. Karimpoor, U. Erb, K.T. Aust and G. Palumbo // *Scr. Mater*. **49** (2003) 651.
[29] K. Tao, H. Choo, H. Li, B. Claussen, J.-E. Jin and Y.-K. Lee // *Appl. Phys. Lett.* **90** (2007) 101911.
[30] Y.-H. Zhao, Y.T. Zhu, X.-Z. Liao, Z. Horita and T.G. Langdon // *Appl. Phys. Lett.* **89** (2006) 212906.
[31] X.H. An, Q.Y. Lin, S.D. Wu, Z.F. Zhang, R.B. Figueiredo, N. Gao and T.G. Langdon // *Scr. Mater.* **64** (2011) 954.
[32] X.H. An, S.D. Wu, Z.F. Zhang, R.B. Figueiredo, N. Gao and T.G. Langdon // *Scr. Mater.* **66** (2012) 227.
[33] P.L. Sun, Y.H. Zhao, J.C. Cooley, M.E. Kassner, Z. Horita, T.G. Langdon, E.J. Lavernia and Y.T. Zhu // *Mater. Sci. Eng. A* **525** (2009) 83.
[34] Y.H. Zhao, X.Z. Liao, Y.T. Zhu, Z. Horita and T.G. Langdon // *Mater. Sci. Eng. A* **410-411** (2005) 188.

[35] Z.W. Wang, Y.B. Wang, X.Z. Liao, Y.N. Zhao, E.J. Lavernia, Y.T. Zhu, Z. Horita and T.G. Langdon // *Scr. Mater.* **60** (2009) 52.
[36] X.H. An, Q.Y. Lin, S.D. Wu, Z.F. Zhang, R.B. Figueiredo, N. Gao and T.G. Langdon // *Philos. Mag.* **91** (2011) 3307.
[37] Y.H. Zhao, J.F. Bingert, X.Z. Liao, B.-Z. Cui, K. Han, A.V. Sergueeva, A.K. Mukherjee, R.Z. Valiev, T.G. Langdon and Y.T. Zhu // *Adv. Mater*. **18** (2006) 2949.
[38] Z. Horita, K. Ohashi, T. Fujita, K. Kaneko and T.G. Langdon // *Adv. Mater.* **17** (2005) 1599.
[39] Y.H. Zhao, X.Z. Liao, S. Cheng, E. Ma and Y.T. Zhu // *Adv. Mater.* **18** (2006) 2280.
[40] K. Nagai // *J. Mater. Proc. Technol.* **117** (2001) 329.
[41] S. Torizuka, E. Muramatsu, S.V.S.N. Murty and K. Nagai // *Scr. Mater.* **55** (2006) 751.
[42] Y. Kimura, T. Inoue, F. Yin and K. Tsuzaki // *Science* **320** (2008) 1057.
[43] I.A. Ovid'ko and A.G. Sheinerman // *Rev. Adv. Mater. Sci*. **29** (2011) 104.
[44] R.Z. Valiev, I.V. Alexandrov, Y.T. Zhu and T.C. Lowe // *J. Mater*. *Res.* **17** (2002) 5.
[45] P. Kumar, C. Xu and T.G. Langdon // *J. Mater*. *Sci*. **44** (2009) 3913.
[46] R.Z. Valiev, M.Yu. Murashkin, A. Kilmametov, B. Straumal, N.Q. Shinh and T.G. Langdon // *J. Mater*. *Sci*. **45** (2010) 4718.
[47] K. Hockauf, L.W. Meyer, M. Hockauf and T. Halle // *J. Mater*. *Sci*. **45** (2010) 4754.
[48] N.Q. Chinh, P. Szommer, Z. Horita and T.G. Langdon // *Adv. Mater.* **18** (2006) 34.
[49] G. He, J. Eckert, W. Loeser and L. Schultz // *Nature Mater*. **2** (2003) 33.
[50] G. He, M. Hagiwara, J. Eckert and W. Loeser // *Philos. Mag. Lett*. **84** (2004) 365.
[51] H. Li, A. Misra, Z. Horita, C.C. Koch, N.A. Mara, P.O. Dickerson and Y.T. Zhu // *Appl. Phys. Lett.* **95** (2009) 071907.
[52] X.L. Wu, Y.T. Zhu, Y.G. Wei and Q. Wei // *Phys. Rev. Lett.* **103** (2009) 205504.
[53] S. Ni, Y.B. Wang, X.Z. Liao, S.N. Alhajeri, H.Q. Li, Y.H. Zhao, E.J. Lavernia, S.P. Ringer, T.G. Langdon and Y.T. Zhu // *Scr. Mater.* **64** (2011) 327.