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Recent Progress in Improving Ductility of Ultra-High Strength Nanostructured Metals

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Until very recently, the reported tensile ductility of ultra-high strength nanocrystalline metals was disappointingly low. This article presents a brief overview of recent progress in identifying a group of nanostructured bulk elemental metals that offer not only gigapascal strength but also decent ductility. These include electrodeposited nanocrystalline or nano-twinned metals, and consolidated full-density nanocrystalline metals. Our own recent studies of these interesting nanomaterials, extending our previous/parallel success in optimizing the properties of bulk nanostructured metals prepared via severe plastic deformation, also demonstrated unprecedented tensile plastic strains.

Keywords: nanocrystalline metals, nanostructure, strength, ductility, full-density consolidation

1. INTRODUCTION

Over the past two decades, nanostructured metals have generated widespread interest in many research laboratories worldwide. These metals, due to their ultra-high strength at room temperature, have been heralded as potentially a new class of high-performance engineering materials. However, as summarized in a review by Koch [1], it was found that virtually all the bulk nanocrystalline metals (defined as polycrystalline metals with grain size less than 100 nm) produced around the world suffer from the same problem: their ductility, or the ability to change shape without fracture under tensile stresses, was as disappointingly low as bordering brittle behavior. Many of them fail in the elastic regime without visible plastic deformation, others exhibit no more than 3 % elongation to failure. The utility of these exotic nanocrystalline materials is therefore called into question. It is doubtful that such dismal ductility would ever find use in forming or load-bearing structural applications, despite of the advantage in ultra-high strength typically above 1 GPa.

Partly because of these concerns, much of the research on the structural applications of bulk nanostructured materials shifted towards ultrafine-grained metals, for which the sizes of the grains separated by high-angle grain boundaries are above ~100 nm but well below 1 μm. These materials are often still categorized as nanostructured metals because they usually have extensive subgrain structures (such as low-angle grain boundaries and domain/mosaic structures) that are below 100 nm, which contribute to their properties substantially or even dominate their deformation behavior. For these materials the ductility is less of a problem, partly because they are usually processed through bulk processing routes such as severe plastic deformation such that porosity and contamination problems that ruin the ductility of nanocrystalline metals are completely avoided. An elongation to failure of the order of 10 % is common, although the useful uniform ductility is still inadequate. Recently, Koch [2] and Ma [3] discussed the factors influencing the tensile ductility of these ultra-fine grained materials. New approaches/strategies have also been devised to reach a good combination of strength and uniform ductility, e.g., the results from Valiev *et al.* [4] and Wang *et al.* [5]. For examples of model studies of the ductility behavior of ultrafine-grained metals, the readers are referred to several recent publications [1-8]. However, these ultrafine-grained metals, with a strength typically a factor of ~5 of that of their coarse-grained counterpart, are not as impressively strong as the truly nanocrystalline metals with grain sizes well below 100 nm, which are some 10~20 times stronger than conventional metals.

Here in this short overview, we make an attempt to address the ductility issue for the latter group, i.e., the ultra-high strength nanocrystalline metals with nanoscale general high-angle grain boundaries. All the nanometals discussed in this article are considered to be in bulk form, in the sense that they are considerably bulkier than nanocrystalline thin films and have obvious potentials for scale-up. We also include a recent nano-twinned Cu [9,10], because the coherent twin boundaries are a special type of high-angle grain boundaries,

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and also because the strength of this Cu reaches as high as ~1 GPa, similar to nanocrystalline Cu. There have been encouraging news over the recent months that even at such ultra-high strength levels, a ductility useful for engineering applications can be derived at the same time.

2. ELECTRODEPOSITED NANOCRYSTALLINE METALS

Several electrodeposited nanocrystalline metals are readily and even commercially available, notably nanocrystalline Ni. They can be made to have grain sizes as low as a few nanometers, and consequently ultra-high strengths in the 1 to 2 GPa range. The ductility in tension, however, was found to be of the order of 2 %, very low when compared to its coarse-grained or even the ultrafine-grained counterparts.

Recently, however, Li and Ebrahimi reported [11] that without using plating additives that may degrade ductility, they can still electroplate metals and alloys with nanocrystalline grain sizes. Fig. 1 shows their engineering stressstrain curves of nanocrystalline Ni (grain size 44 nm) and Ni-15%Fe alloy (9 nm). Arrows indicate the maximum stress points, at which uniform elongation terminates. The Ni showed a tensile strength of ~1080 MPa, an elongation to failure of ~9 %, a uniform ductility of 6~7 %, and strong work hardening. The Ni-15%Fe showed an impressive tensile strength of over 2300 MPa, an elongation to failure of ~6 %, a uniform ductility of 4~5 %, and very strong work hardening.

The nanocrystalline Ni seems to have a rather low yield strength (~500 MPa) for its grain size of 44 nm, judging from the Hall-Petch relationship known for nanocrystalline Ni. This observation suggests that the Ni sample may have had a grain size distribution wider than what the authors believed, which would also explain its larger ductility than previous nanocrystalline Ni. But for the Ni-Fe, which is much stronger due to its small grain size and the solute content that induces solution hardening, it still had a respectable ductility that is in fact among the highest ever for such ultra-high-strength nanocrystalline materials. A high strain hardening rate is cited as the cause for the ability of the material to better sustain the uniform deformation than all previous nanocrystalline metals.

Erb recently also tested Ni-Fe alloys prepared using electrodeposition [12]. Ductility similar to or even better than those reported by Li and Ebrahimi was also observed. They attribute the ductility to the relatively large thickness of their new samples that better meet the ASTM standards; their new samples are now millimeters thick, whereas those (such as nanocrystalline Ni) they tested earlier were much thinner than 1 mm. ASTM standards call for large samples, and thin samples may be susceptible to premature failure because of their increased sensitivity to the propagation of small surface cracks.

Karimpoor and Erb and their colleagues made nanocrystalline Co samples using electrodeposition [13]. The deposit was 0.2 mm thick but scale-up to bulkier thickness is presumably a straightforward extrapolation. The deposit exhibited an unusually faulted microstructure indicative of a high concentration of stacking faults/microtwins, which is consistent with the low stacking fault energy of cobalt [14]. The narrow grain size distribution based on measuring about 1000 grain diameters (including twins) on several dark field images showed a mean grain size of 12 nm. This nanocrystalline cobalt showed elongation to fracture values of up to 9 %, as shown in Fig. 2. Although these values are lower than those for polycrystalline samples tested at strain rates of 5×10^4 and $2.5\times10^{-3}(s^{-1})$, they are not much different from the values for polycrystalline samples tested at a strain rate of $1\times10^{-4}(s^{-1})$, and considerably higher (at any applied strain

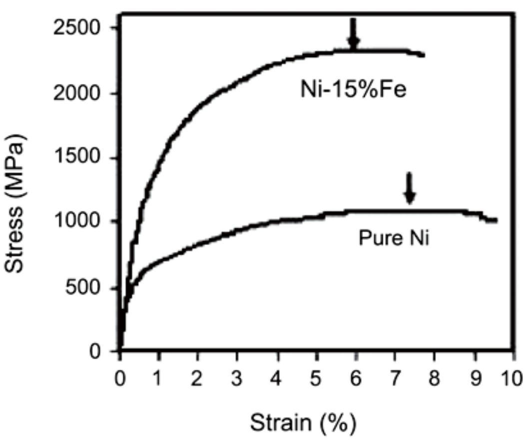

Fig. 1. The engineering stress-strain curves of electrodeposited nanocrystalline Ni (44 nm) and Ni-15%Fe alloy (9 nm) [11]. Arrows indicate the maximum stress points, at which uniform elongation terminates.

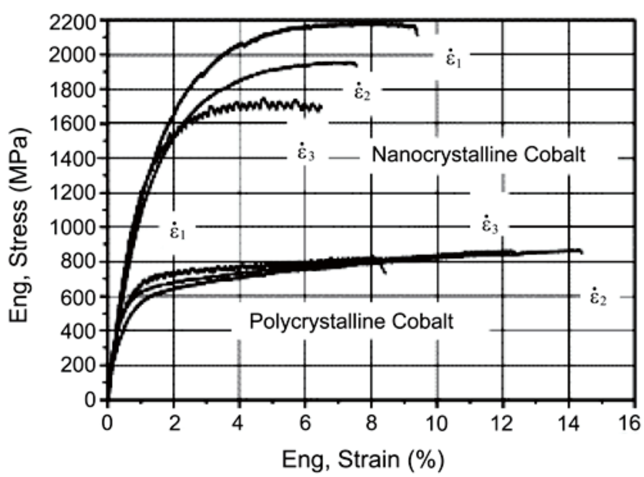

Fig. 2. Representative stress-strain curves for nanocrystalline cobalt and polycrystalline Co (annealed at 800 °C) at three different strain rates [13].

rate) than the ~1 % elongation to fracture observed previously for some nanocrystalline electrodeposits, such as one for Ni [15] with a similar grain size. The heavily twinned nanostructure, as seen in the high-resolution TEM micrograph we obtained recently on such a nanocrystalline Co, must have played an important role in its plasticity, but the exact effects are difficult to assess at present.

3. ELECTRODEPOSITED NANO-TWINNED Cu

An interesting finding very recently is that to achieve grain boundary strengthening, one could replace the general high-angle grain boundaries with a special type, namely, coherent twin boundaries. This can be done in Cu, for example, through pulse electrodeposition that induces high densities of growth twins. Lu *et al*. reported a twin lamella spacing as small as 15 nm (on average) in such a pulse electrodeposited pure Cu [9]. They found that the yield strength reached 900 MPa and the tensile strength was as high as 1068 MPa, as shown in Fig. 3(a), together with electrical conductivity similar to OFHC Cu (panel (b) in Fig. 3). What is perhaps more exciting is that such ultra-high strength Cu exhibited a tensile elongation to failure of 13.5 %. In other words, the nano-twinned material has not only a GPa strength but also a ductility significantly higher than those of nanocrystalline Cu prepared so far. An even more impressive ductility was reported for 77 K tests and an explanation to such high ductility was offered by Ma *et al*. recently [10]. The high efficacy of strengthening by the twin boundaries, on the other hand, has been discussed elsewhere [9,10], as well as for vacuum-deposited stainless steel films by Zhang *et al*. [16].

4. CONSOLIDATED NANOCRYSTALLINE Cu

Nanocrystalline metals consolidated from powders never showed usable ductility before [17]. Very recently, Youssef *et al.* used mechanical milling/*in situ* consolidation at both liquid-nitrogen and room temperature to produce artifact-free nanocrystalline Cu (23 nm) with a narrow grain size distribution [18]. This consolidated bulk nanocrystalline Cu exhibits a high yield strength (770 MPa, with a hardness of 2.3 GPa) similar to that found in a thin (11 μm) nanocrystalline (~30 nm) Cu foil prepared by surface mechanical attrition [19], as predicted from a Hall-Petch extrapolation, along with good ductility.

Youssef *et al.* used a miniature disk bend test (MDBT) to evaluate the strength and ductility. The shape of the MDBT curves is typical of ductile materials. Figs. 4(a) and (b) shows the field emission SEM images of surface morphology of their Cu specimens after MDBT. The two specimens have a hat-shaped disk morphology, which is an indication of significant plastic deformation. The punched out hat shows no indication of surface cracking. The fracture surface in Fig. 4(c) shows a dimpled rupture that extends thoroughly over the sample cross section with dimple size ranges from 100~400 nm. Considering the biaxial tensile stresses experienced by the sample in MDBT, this nanocrystalline Cu has been believed to possess good ductility along with an extraordinarily high yield strength [18]. This was in fact the first time a consolidated truly nanocrystalline metal ever exhibited reasonable tensile ductility, except for Zn for which room temperature is already a high homologous temperature [20].

The authors considered the three main reasons for limita-

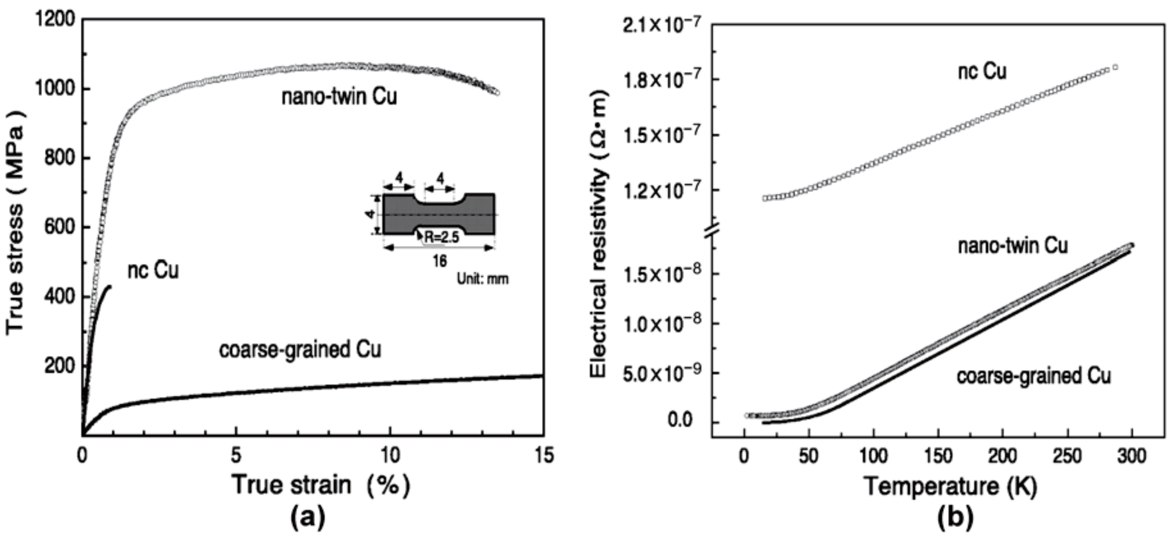

Fig. 3. (a) A typical tensile stress-strain curve for the as-deposited Cu sample with nano-twins in comparison with that for a coarse-grained polycrystalline Cu sample (with an average grain size larger than 100 μm) and a consolidated nanocrystalline (nc) Cu sample (mean grain size ~30 nm) [9]. The inset shows the geometry of the tensile sample. (b) The measured temperature dependence of electrical resistivity for the as-deposited nano-twinned Cu sample and the coarsegrained sample in a temperature range from 2 to 296 K. For comparison, electrical resistivity measurement results of a nc Cu sample with a mean grain size of 15 nm are also included.

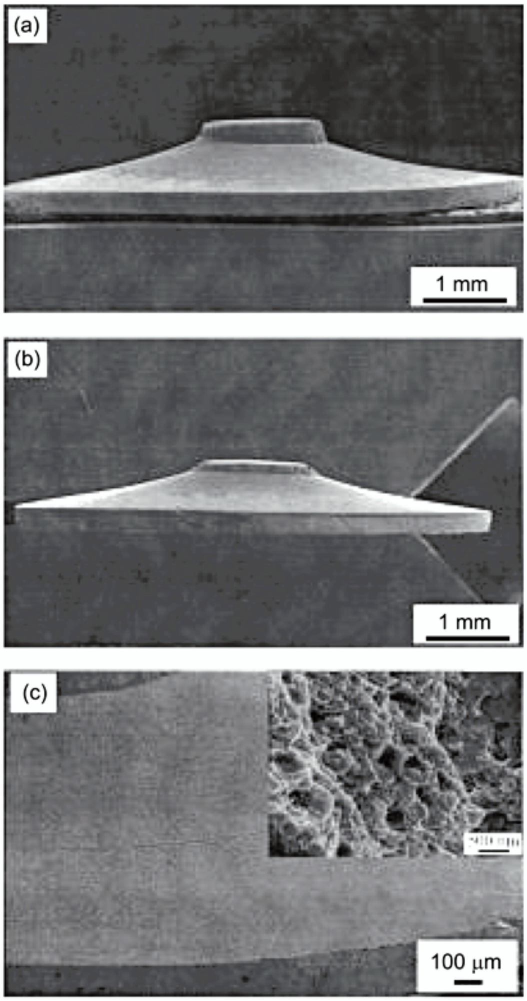

Fig. 4. Field emission scanning electron micrographs of samples after MDBT [18]: (b) shows a consolidated nanocrystalline Cu sample in comparison with a cold-rolled and recrystallized sample in (a). (c) is a higher magnification view of the nc Cu sample near the fracture surface, the upper right inset shows the fracture surface of the nc Cu sample.

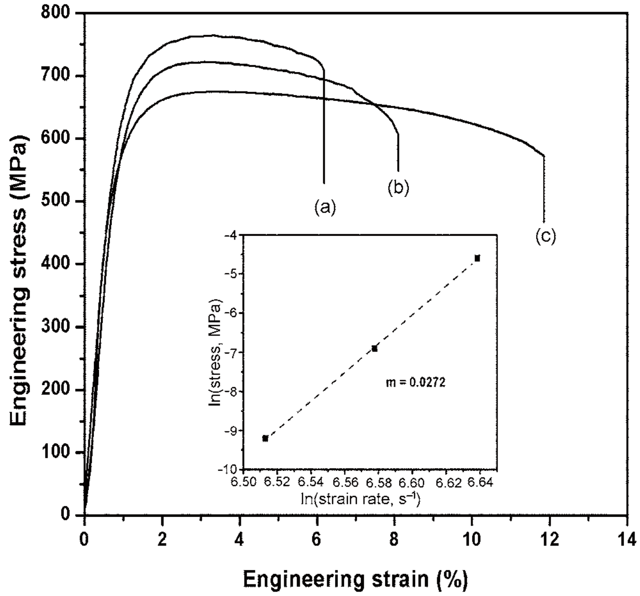

Fig. 5. Tensile test of *in situ* consolidated nanocrystalline Cu at RT with different strain rates [21]: (a) $\dot{\varepsilon}=10^{-2}$ s^{-1}, (b) $\dot{\varepsilon}=10^{-3}$ s^{-1}, and (c) $\dot{\varepsilon}=10^{-4}$ s^{-1}. The inset is used to estimate the strain rate sensitivity, *m*. The samples were ball milled at LN_2T for 3 h and RT for 6 h.

tions on ductility: (1) Density measurements and SEM observations show that no porosity was left after *in situ* consolidation of the nanocrystalline Cu powder. Also, the contamination during milling has no effect on the ductility because the oxygen content only increased from 0.10 at.% in the starting Cu powder to 0.29 at.% in the final bulk sample. The measured iron contamination was negligible. Therefore, the artifacts effect is eliminated. (2) Mechanical instabilitythe MDBT results suggested strain hardening that prevents plastic instability during the membrane-stretching regime. (3) Crack nucleation and propagation-the nanoscale grain size can inhibit these processes, as would be suggested from the effect of grain size on ductility in conventional grain size materials.

Using a variation of their processing technique, we recently also produced in situ consolidated nanocrystalline Cu centimeters in diameter and millimeters in thickness [21]. TEM bright-field images of the Cu obtained after milling for 3 h at liquid nitrogen temperature plus 6 h at room temperature indicated a wider grain size distribution than that of Yousssef *et al.*, but with the vast majority of grains below 100 nm. Fig. 5 displays the tensile engineering stress strain curves taken at three strain rates. Interestingly, such nanocrystalline Cu exhibits a strength approaching 800 MPa (much higher than the tensile strength of most previous nanocrystalline Cu such as the one in Fig. 3(a)), and at the same time a sizable elongation to failure up to 12 %.

5. CONCLUDING REMARKS

In addition to instances of ductile ultrafine-grained metals that have been demonstrated in recent years [1-8], there are now quite a few example of ductile behavior (elongation to failure well above 3 %) for truly nanometals (with general high-angle or special twin boundaries) that have strengths at least a factor of ten higher than their conventional counterpart [9-13,18,21]. This is obviously cause for optimism: ultrahigh strength nanostructured metals are joining ultrafine-grained metals to have the potential to be useful for structural applications, such as those in microelectromechanical systems.

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