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Four Approaches to Improve the Tensile Ductility of High-Strength Nanocrystalline Metals

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Until recently, the reported tensile ductility of high-strength nanocrystalline metals was disappointingly low. This article presents a brief overview of the latest encouraging progress in developing nanocrystalline metals that offer not only gigapascal strength but also decent ductility. Four different approaches have been identified in recent studies, including some of the author's experiments. These efforts are interesting extensions of previous/parallel success in optimizing the tensile properties of bulk nanostructured/ ultrafine-grained metals.

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

1. Introduction

Over the past two decades, bulk nanostructured metals have generated widespread interest. Because of their ultrahigh strength at room temperature, these metals have been heralded as potentially a new class of high-performance engineering materials. However, as summarized in a review by Carl Koch (Ref 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 regimen 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 the advantage in ultrahigh strength, typically above 1 GPa.

Partly due to these concerns, much of the research on the structural applications of bulk nanostructured materials shifted toward 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) below 100 nm, which contribute substantially to their properties 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, so porosity and contamination problems that ruin the ductility of nanocrystalline metals are completely avoided. An elongation to failure on the order of 10% is common, although the useful uniform ductility is still inadequate. Recently, Koch (Ref 2) and Ma (Ref 3) discussed the factors influencing the tensile ductility of these ultrafine grained materials. New approaches and strategies have also been devised to reach a good combination of strength and uniform ductility, e.g., the results from Valiev et al. (Ref 4) and Wang et al. (Ref 5). Wang and Ma, in particular, discussed three specific strategies to achieve uniform tensile elongation in such materials (Ref 6), as outlined in passing below.

The main idea of Ref 6 is to preserve uniform tensile deformation by invoking strain hardening and strain rate hardening mechanisms to suppress the instabilities from which these high-strength metals tend to suffer. The first approach uses an in situ formed composite-like microstructure, such as a bimodal grain-size distribution (or a grain-size distribution in general), to impart strain hardening to the material and attain significant uniform tensile strains while maintaining the majority of the strengthening brought forth by nanostructuring. In the second route, deformation is conducted at low temperatures, such as 77 K. The material regains the ability to work harden due to suppressed dynamic recovery. Uniform elongation is improved as a result, together with an elevated strength at the cryogenic temperature. The third method, rather than trying to attain strain hardening, takes advantage of the elevated strain rate sensitivity of the flow stress observed at the small grain sizes, especially at slow strain rates. Using the stabilizing effects of strain rate hardening on tensile elongation, nearly uniform strains can be acquired in the absence of strain hardening. Very recently, Ma et al. (Ref 7) added another strategy by designing and depositing a (multimodal) distribution of growth twins inside the submicron grains. The twin lamella structure is inherently bimodal and showed the ability to strain harden at high stress levels (Ref 7). To rephrase these four strategies, the central thought is to acquire strain hardening by designing micro/nano- structure or using favorable deformation conditions, or, when strain hardening is unavailable or inadequate, going for strain rate hardening, which is available in these face-centered-cubic ultrafine-grained materials to a moderate

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extent. For examples of model studies of the ductility behavior of ultrafine-grained metals, refer to several recent publications (Ref 1-9).

However, these ultrafine-grained metals, with strength typically a factor of ~5 of that of their coarse-grained counterpart, are not as impressively strong as the truly nanocrystalline metals, which (as mentioned above) are defined as those with grains <100 nm in size, separated by general high-angle grain boundaries. The latter group commonly has strength well over 1 GPa and hence is some 10-20 times stronger than conventional metals. Here in this short overview, there is an attempt to address their ductility issue. All the nanometals discussed in this article are considered to be bulk nanocrystalline materials, in the sense that they are considerably bulkier than nanocrystalline thin films and have obvious potential for scale-up. Whereas instability problems are more difficult to overcome in these superstrong materials, there has been encouraging news over the recent months that even at the gigapascal strength level, a respectable ductility useful for engineering applications can be derived at the same time. Four factors will be examined that have been in action so far for improving ductility. Some of them are parallels to those strategies mentioned above for ultrafine-grained nanostructured metals, and others are unique to the truly nanocrystalline metals.

2. Four Routes Toward Improved Ductility of Nanocrystalline Metals

2.1 High-Quality Samples

Unlike the ultrafine-grained nanostructured metals mentioned above, which are often processed by bulk processes such as severe plastic deformation so that internal sample defects are not a pressing problem, truly nanocrystalline metals often require deposition or even consolidation to prepare them into bulk samples. Their ductility is therefore sensitively dependent on the processing flaws.

Truly nanocrystalline metals consolidated from powders never showed usable ductility before (Ref 10). Very recently, however, Youssef et al. used mechanical milling/in situ consolidation at both liquid-nitrogen and room temperature to produce artifact-free bulk nanocrystalline Cu (23 nm grain size) with a narrow grain size distribution (Ref 11). 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 (Ref 12), as predicted from a Hall-Petch extrapolation, along with good ductility.

Youssef et al. (Ref 11) used a miniature disk bend test (MDBT) to evaluate the strength and ductility. The shape of the MDBT curves is typical of ductile materials. Figures 1(a) and (b) are field-emission SEM images of surface morphology of their Cu specimens after MDBT. The two specimens have 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. 1(c) shows a dimpled rupture that extends thoroughly over the sample cross section with dimple size ranges from 100 to 400 nm. Considering the biaxial tensile stresses experienced by the sample in MDBT, this nanocrystalline Cu is believed to possess good ductility along with extraordinarily high yield strength (Ref 11). This was in fact the first time a consolidated truly nanocrystalline metal ever exhibited large ductility.

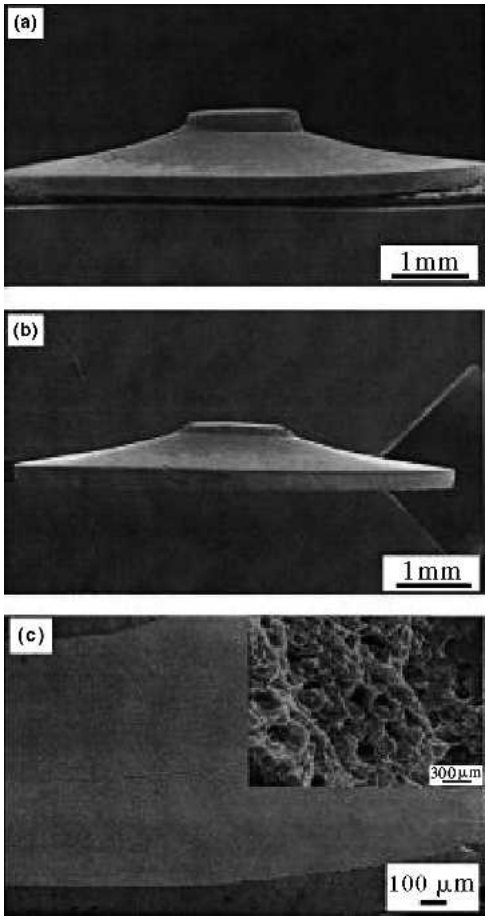

Fig. 1 Field-emission scanning electron micrographs of samples after MDBT (Ref 11): (b) shows a consolidated nanocrystalline Cu sample, in comparison with a cold-rolled and recrystallized ductile sample in (a). (c) is a higher magnification view of the nanocrystalline Cu sample in (b) near the fracture surface; the upper right inset shows the fracture surface of the nc Cu sample.

The authors of Ref 11 considered three main reasons for the good ductility:

- 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 increased only 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 detrimental effects of artifacts and flaws are eliminated.
- The MDBT tests suggested that there was strain hardening preventing plastic instability during the membrane-stretching regimen.
- The nanoscale grain size can inhibit crack nucleation and propagation, as would be suggested from the effect of grain size on ductility on conventional materials.

Using a variation of their processing technique, in situ consolidated nanocrystalline Cu, centimeters in diameter and millimeters in thickness, was recently produced (Ref 13). TEM bright-field images of the Cu obtained after milling for 3 h at

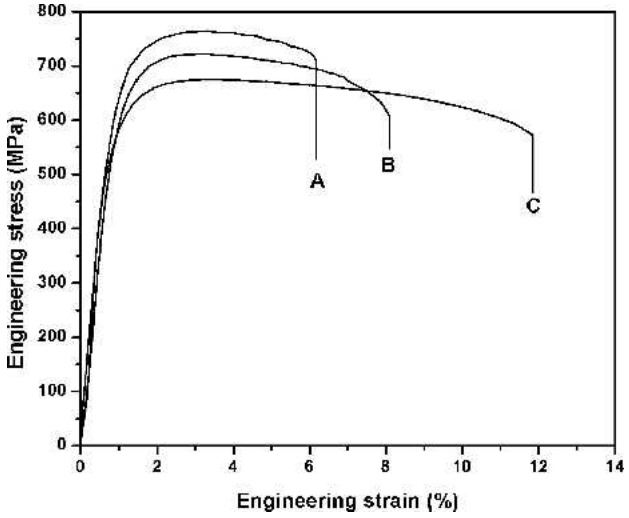

Fig. 2 Tensile test of in situ consolidated nanocrystalline Cu at RT with different strain rates (Ref 13): (a) $\dot{\varepsilon} = 10^{-2}$ s^{-1}; (b) $\dot{\varepsilon} = 10^{-3}$ s^{-1}; c) $\dot{\varepsilon} = 10^{-4}$ s^{-1}. The samples were ball milled at liquid nitrogen temperature for 3 h and consolidated in situ by room-temperature milling for 6 h.

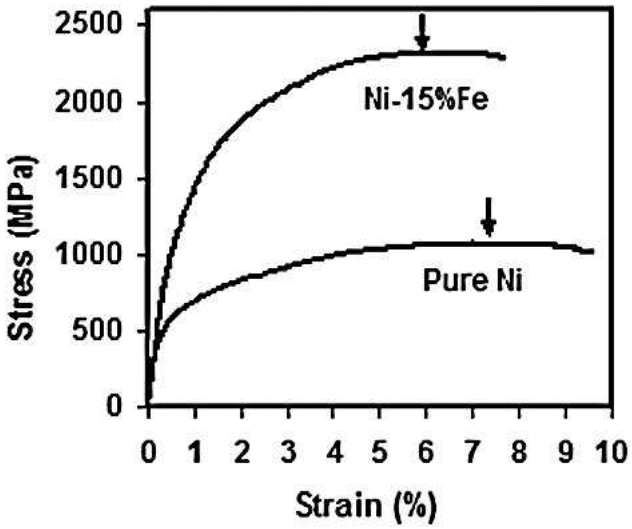

Fig. 3 Engineering stress-strain curves of electrodeposited nanocrystalline Ni (44 nm) and Ni-15%Fe alloy (9 nm) (Ref 15). Arrows indicate the maximum stress points, at which uniform elongation terminates.

liquid nitrogen temperature plus 6 h at room temperature indicated a wider grain size distribution than that of Youssef et al. (Ref 11), but with the vast majority of grains below 100 nm. Figure 2 displays the tensile engineering stress strain curves taken at three strain rates. Interestingly, such nanocrystalline Cu exhibits a strength approaching 800 MPa (higher than the tensile strength of most previous nanocrystalline Cu), and at the same time a sizable elongation to failure up to 12%.

There have been some very recent advances in such nanocrystalline Cu. Koch et al. showed (Ref 14) that their tensile test of their latest sample not only reached 1 GPa strength, but also exhibited apparent strain hardening and a tensile elongation of the order of 10%. Such exciting performance is likely to generate strong interest and motivate additional studies into the mechanisms.

Improvements have been made on electroplated truly nanocrystalline metals as well. Several electrodeposited nanocrystalline metals are readily and even commercially available, notably nanocrystalline Ni. They can be made to have grain sizes as small as a few nanometers, and consequently ultrahigh strengths in the 1-2 GPa range. The ductility in tension, however, used to be of the order of 2%, very low when compared with its coarse-grained or even the ultrafine-grained counterparts. Recently, however, Li and Ebrahimi (Ref 15) reported that without using plating additives that may degrade ductility, they can still electroplate metals and alloys with nanocrystalline grain sizes. Figure 3 shows their engineering stress-strain 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 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 (see Sec. 2.2 below), which would also explain its larger ductility than previous nanocrystalline Ni. However, Ni-Fe, which is much stronger due to its small grain size and the solute content that induces solution hardening, still had a respectable ductility that is in fact among the highest ever for such ultrahigh-strength nanocrystalline materials. A high strain hardening rate was cited (Fig. 3) as the reason the material is able to sustain the uniform deformation better than previous nanocrystalline metals (Ref 15).

As discussed above, the ability to work harden is important for keeping the tensile deformation stable. All previous nanocrystalline or ultrafine-grained metals showed appreciable strain hardening rate only during the initial stage of plastic deformation (over a couple of percent of plastic strain). In this context, one could rephrase the idea behind this first approach as follows: high-quality samples recently prepared seem to allow one to take advantage of the intrinsic work hardening capability of the nanocrystalline grain structure in certain metals. In other words, the advent of high-quality samples may have revealed an important secret of nanocrystalline metals: intrinsically they may have mechanisms for strain hardening sustainable over a range of strains. The exact origins of such work hardening, however, require future studies because it is unlikely that the hardening comes from the conventional dislocation storage mechanism, given the tiny grains of these nanocrystalline materials.

Erb et al. also recently tested Ni-Fe alloys prepared using electrodeposition (Ref 16). Ductility similar to, or even better than, those reported by Li and Ebrahimi (Ref 15) 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 very thin samples may be susceptible to instability and premature failure due to, for example, their increased sensitivity to the propagation of small surface cracks.

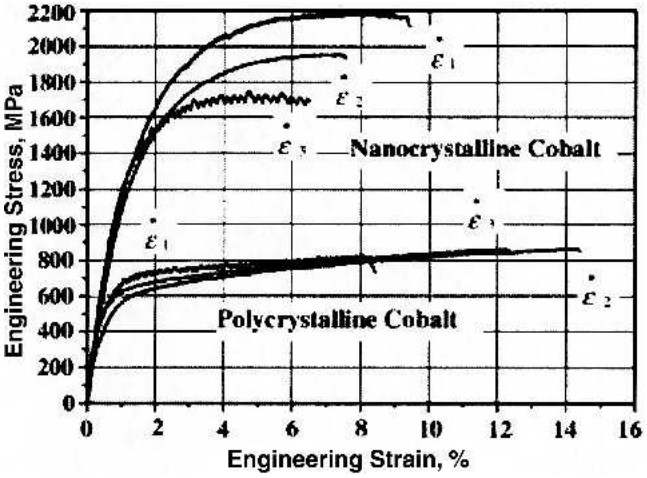

Fig. 4 Representative engineering stress-strain curves for nanocrystalline cobalt and conventional polycrystalline Co (annealed at 800 °C) tested at three different strain rates (Ref 20).

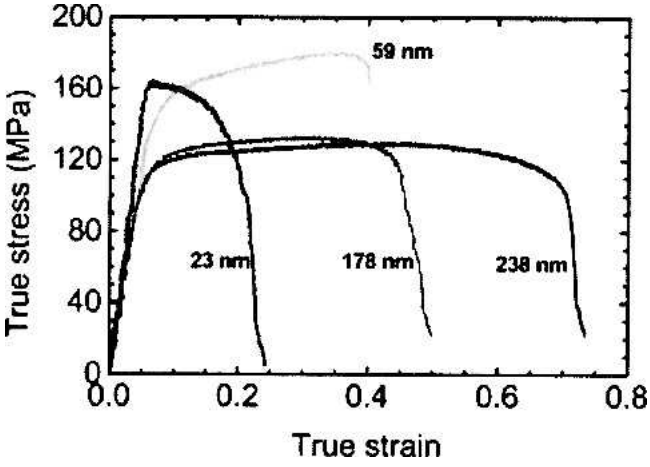

Fig. 5 Tensile stress-strain curves for Zn (with an average grain size of 240, 180, 60, and 23 nm, respectively) tested at a constant strain rate of 10^{-4} to 10^{-3} s^{-1} at room temperature (Ref 26)

2.2 Grain Size Distribution

This approach of using a grain-size distribution is similar to that discussed for ultrafine-grained nanostructured metals [bimodal nanostructured Cu (Ref 5, 6), for example]. The difference is that a grain-size distribution can result from stress-assisted grain growth, in situ during the tensile test. This occurs because the truly nanocrystalline metals have grain sizes so small that there is a very large driving force for grain growth, and the assisting applied stresses during the plastic flow is very high. In addition, the nanocrystalline grains are often prepared via vapor deposition. In such processing, the content of impurities that could pin the grain boundaries can be kept very low. Grain growth during tensile deformation was observed by several groups (Ref 17-19). The resulting grain structure can be bimodal or have a wide grain-size distribution. Tensile ductility was found for otherwise brittle nanocrystalline thin films, e.g., in vapor deposited Al (Ref 17).

2.3 Use of Growth Twins

This approach is also a parallel to the strategies used for ultrafine-grained nanostructured metals (Ref 7), see discussion in Sec. 1. A large number of growth twins can be incorporated in nanocrystalline grains as well. Karimpoor and Erb and their colleagues made nanocrystalline Co samples using electrodeposition (Ref 20). 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 (Ref 21). 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. 4. At the three strain rates (5×10^{-4} to 2.5×10^{-3} s^{-1}) tested, the elongation to failure values of nanocrystalline Co are not much different from those for polycrystalline samples tested at similar strain rates and considerably higher (at any applied strain rate) than the elongation to fracture observed previously for some nanocrystalline electrodeposits. The heavily twinned nanostructure, as recently observed in the high-resolution TEM micrograph of nanocrystalline Co, must have played an important role in its plasticity, but the exact effects are difficult to assess at present. One could think of twinning induced plasticity (TWIP) or transformation induced plasticity (TRIP) [martensitic transformation between face-centered cubic (fcc) and hexagonal close-packed (hcp) Co, for example].

2.4 Strain Rate Hardening

This is also a strategy used for ultrafine-grained/nanostructured metals (Ref 6). The rate sensitivity of a material, according to Hart's criterion, would delay the plastic instability and prolong the uniform tensile deformation (Ref 6). Recently the strain rate sensitivity (m) for nanocrystalline Cu and Ni has been measured (e.g., Ref 13, 22-24). The m value is larger than that of coarse-grained Cu and Ni. However, at room temperature its magnitude is of the order of 0.03 and not sufficiently high to extend uniform tensile deformation to large elongations. This is true, in particular, because the nanocrystalline materials have very high flow stresses such that instability conditions would be easier to reach (Ref 6). Until the recent discoveries discussed in Sec. 2.1, one would not have expected the strain hardening rate (even when at low temperatures) or strain hardening rate in nanocrystalline metals to be high enough and sustainable to large strains, such that instabilities like as necking or shear banding could be prevented to give extensive uniform elongations. However, for nanocrystalline metals with relatively low melting temperatures, such as Al and especially Zn, for which room temperature is already a relatively high homologous temperature (Ref 25), m can be rather high and large tensile elongation has been reported (Ref 17, 26). For example, Zhang et al. (Ref 26) observed an m of at least 0.15 for ultrafine-grained and nanocrystalline Zn, and large tensile elongations even when grain size is well below 100 nm (Fig. 5). Note that in some of these Zn samples consolidated by ball milling, there is also a grain-size distribution and possibly grain growth during the tensile test, which are likely to contribute to ductility. In addition, the ability to consolidate these samples to full density is obviously a prerequisite for good mechanical properties. In other words, the other three factors discussed above from Sec. 2.1-2.3 may also be at work in this particular case.

3. Conclusions

In addition to examples of ductile ultrafine-grained metals that have been documented in recent years (e.g., Ref 1-9), there are now quite a few demonstrations of ductile behavior (elongation to failure well above 3%, similar to many materials usable in engineering) for truly nanocrystalline metals with general high-angle boundaries; these metals have strengths at least a factor of ten higher than their conventional coarse-grained counterparts. This is, obviously, cause for optimism: high strength nanocrystalline metals are joining ultrafine-grained metals to become potentially useful for structural applications, such as those in microelectromechanical systems. The approaches and mechanisms used to achieve decent ductility are often similar to those used for ultrafine-grained metals but can also be unique to truly nanocrystalline grains. The effective measures discovered so far were not all by design a priori, but they surely would provide useful guidelines for future developments in this field. It remains a challenge to understand the mechanisms underlying the strain hardening and strain rate hardening behavior of truly nanocrystalline metals and alloys.

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