Novel Properties of Nanostructured Metals

K. Lu

Shenyang National Laboratory for Materials Science, Institute of Metal Research
Chinese Academy of Sciences, Shenyang 110016, China
E-mail: lu@imr.ac.cn

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Due to the ultrafine grains (or domains or particles) and a high density of grain boundaries (or generally interfaces) in nanostructured materials, many properties and performance of the materials are expected to be significantly varied with respect to their coarse-grained counterparts. Extensive investigations over the past decades indicated that the nanostructured metals do possess some novel properties that may find technological applications in industry. In this talk, a brief survey of current status of investigations on properties of nanostructured metals will be summarized with emphasis on the following properties.

1. Strength and ductility

For nanostructured pure metals such as Cu and Ni, experimental data showed that their strength and hardness increase with a reduction of grain size down into the nanometer regime following the classical Hall-Petch relationship. Extremely high strength and hardness have been obtained experimentally for nanostructured pure metals, e.g., about 800 MPa strength was measured for a pure Cu with \( d=30 \) nm, which is one order or magnitude higher than that for conventional coarse-grained Cu. Early results on the reverse Hall-Petch relation in nanostructured pure metals can be attributed to the artifacts induced in the sample processing procedures including porosities and contaminations. Molecular dynamics simulations showed a maximum strengthen at a critical grain size beyond which a negative slope in the Hall-Petch plot appears. However, this has not yet been verified experimentally in pure metals, although similar phenomena were reported in nanostructured alloys and compounds.

Ductility of nanostructured metals is found to decrease at smaller grain sizes, even for those ductile metals in coarse-grained forms. The tensile elongation-to-failure of nanostructured Cu is only a few percent when \( d<30 \) nm [1]. The depressed ductility greatly of nanostructured metals limits their applications as structure materials. Improvement of ductility for nanostructured metals should be pursued in the future despite of some attempts have been made such as modifying the grain size distribution, addition of second phase, and adjusting grain boundary structures. Introduction of a high density of twin boundaries in ultrafine grained or nanocrystalline metals (as shown in Fig. 1), which can not only resist dislocation motion upon plastic deformation but also absorb dislocations at twin boundaries, may provide an effective approach to strengthen metals while keeping an impressive ductility.
2. Electrical conductivity

Electrical resistivity increases with a decreasing grain size for metals due to the large scattering of electrons at grain boundaries. Much elevated electrical resistivities have been measured for nanostructured metals especially with grain sizes less than 10 nm. Beside the grain size effect, the resistivity is also sensitive to the microstrain of the nano-metals which is related to the grain boundary structure. When the conventional grain boundaries in nanostructured metals are replaced by low-energy coherent twin boundaries, resistivity elevation can be minimized. Comparable electrical conductivity has been achieved for a pure Cu with nano-scale twins in comparison with the OFHC Cu [2]. The measurement results of tensile strength and room temperature electrical conductivity of the pure Cu with nano-scale twins are shown in Figure 1.

![Figure 1. Left: A typical TEM micrograph for an as-electrodeposited pure Cu sample with a high density of nano-scale twins in submicro-sized grains. Right: A plot of room-temperature electrical conductivity (1/ρ) versus ultimate tensile strength for several pure metals (Ag, Cu, and Al) and various Cu alloys. The measured data for the electrodeposited pure Cu with nano-scale twins are also included [2].](image)

3. Melting point

Melting point of a solid is dependent upon its dimension. For free-standing nano-sized particles, the melting point is considerably depressed relative to the equilibrium melting point of bulk solids ($T_m$), following the $d^{1.3}$ rule. However, when the nanoparticles are coated or embedded in a high-melting-point matrix with coherent or semi-coherent particle/matrix interfaces, the melting point can be elevated above its equilibrium $T_m$. And the degree of superheating increases with a reduction of particle size in the $d^{1.3}$ rule [3]. Such a superheating behavior is interesting not only for understanding the melting mechanism of solids but also for improvement of the thermal stability of nanostructured metals in practical applications.
Figure 2. Variation of melting point with the particle size for In nanoparticles embedded in Al matrix in two kinds of In/Al nanogranular samples prepared by means of melt-spinning and ball-milling. The remarkable different melting point variations in these two cases might be attributed to the In/Al interfacial structures. For the melt-spun sample a semi-coherent In/Al interface was formed as evidenced by the HRTEM image of the In particle and the electron diffraction pattern, and for the ball-milled sample, the In/Al interfaces are random (see inserted HRTEM image) [3].

4. Atomic diffusion
Due to the high density of grain boundaries in nanostructured metals, atomic diffusion is significantly enhanced with respect to the coarse-grained counterparts. Diffusion coefficients in nanostructured metals are found to be a few orders magnitude higher than the lattice diffusion. For example, diffusion coefficient of Cr in a nanocrystalline pure Fe is 7~9 orders of magnitude higher than that in Fe lattice diffusion [4], as shown in Figure 3. In addition, atomic diffusivity in nanostructured metals is also sensitive to the processing procedure which in turn affects the grain boundary structure. Higher diffusivities are detected in the nanostructured samples with non-equilibrium grain boundaries [4].

5. Chemical reactivity
Chemical reactivity of nanostructured metals is considerably enhanced due to the large number of grain boundaries. Several examples with obvious evidences will be showed to
support this argument. For example, the nitriding temperature of pure iron is reduced from about 500 °C to 300 °C after the nanocrystallization treatment [5]. The reduced nitriding temperature, indicative of an enhanced chemical reactivity, originates from the increased atomic diffusivity and nucleation site density in the nanostructured sample. This phenomenon is technically significant for expanding the scope of application of nitriding treatments and for reducing the distortion of treated samples and articles.

![Figure 3. Temperature dependence of the diffusion coefficient of Cr in the nanocrystalline (NC) and the coarse-grained (CG) Fe, in comparison with those for the lattice diffusion, the diffusion in Fe-Cr alloy and the grain boundary (GB) diffusion [4].](image-url)

**References**


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