Novel Electrodeposited Nanocrystalline Metals and Composites

NSF Functional Nanostructures Grant 9871980

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1. Research objectives and methodology

An important area of research on nanocrystalline materials is focused on their mechanical behavior. However, the inherent, often unique, mechanical properties of nanocrystalline materials are often masked by artifacts introduced during processing. The objective of this research project is to provide nanocrystalline materials free from processing artifacts such that inherent mechanical behavior can be probed.

Many nanocrystalline materials are made by "two-step" processes such as the gas condensation and compaction of nanoparticulates or the mechanical milling of powders (which attain a nanocrystalline grain structure) followed by compaction. It is the compaction step that often leads to residual porosity or incomplete bonding that can drastically affect the mechanical properties. We have chosen two "one-step" processes, that is, electrodeposition and laser ablation to provide nanocrystalline materials for study which avoid the compaction step and the likely artifacts it can produce. In addition, we have found that mechanical attrition of certain very ductile metals like Zn and Cu, can provide *in situ* consolidation of the powders during milling such that 3-6 or more mm balls, with nanocrystalline grain structures, are obtained that can be compressed into disks for mechanical testing.

The microstructures of the nanocrystalline materials prepared by the above methods are revealed by transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM). X-ray diffraction line broadening analysis was also used to provide estimates of the average grain size and lattice strain. Differential scanning calorimetry is used to determine the stability of the microstructure as well as to provide information on the formation of the nanocrystalline grain structure formed by mechanical milling. Mechanical behavior is probed by micro- and nano- hardness measurements.

2. Significant research accomplishments.

The discovery that nanocrystalline Zn could be made by mechanical attrition by milling at room temperature in the form of 3 to 6 mm diameter balls , that is, *in situ* consolidation provided samples free from artifacts. Zn milled at liquid nitrogen temperatures remained in power form. However, these cryomilled powders were also very ductile and could be consolidated to theoretical density and apparent complete particulate bonding at modest compaction temperatures such that grain growth during compaction was minimal. Large numbers of small grains (2 to 6 nm) have been found in the very early stages of milling[1]. The fact that a bimodal grain size distribution is observed in the early stages of milling with a range of grain sizes from less than 10 nm up to 100-200 nm casts doubt on the existing model for nanocrystalline grain formation during milling. The concept of dynamic crystallization is suggested to explain these results [2].

Laser ablation has been used to provide very narrow, uniform grain size distributions with a range of grain sizes in Zn, Cu, WC-Co, and TiN. The nanocrystalline grain sizes are obtained by favoring nucleation over growth during deposition by either adding monolayers of W (total less than 1%W) or varying the substrate temperature during deposition. While the mechanical attrition method limits the minimum average grain size to about 17 nm for cryomilled Zn, laser ablation was able to obtain average grain sizes in Zn as small as 6 nm. The ability to produce artifact free samples of the smallest grain sizes has allowed hardness testing over a large range of grain sizes. In both nanocrystalline Cu and Zn prepared by laser ablation, a clear inverse Hall-Petch phenomenon – that is softening with decreasing grain size – has been observed. This is obtained by nanoindentation hardness measurements on the thin films made by laser ablation. Figure 1 shows the Hall-Petch plot for nanocrystalline Zn including data from the laser ablation samples and from those prepared by mechanical attrition. Maximum hardness values about 5 times those for conventional grain size Zn are obtained.

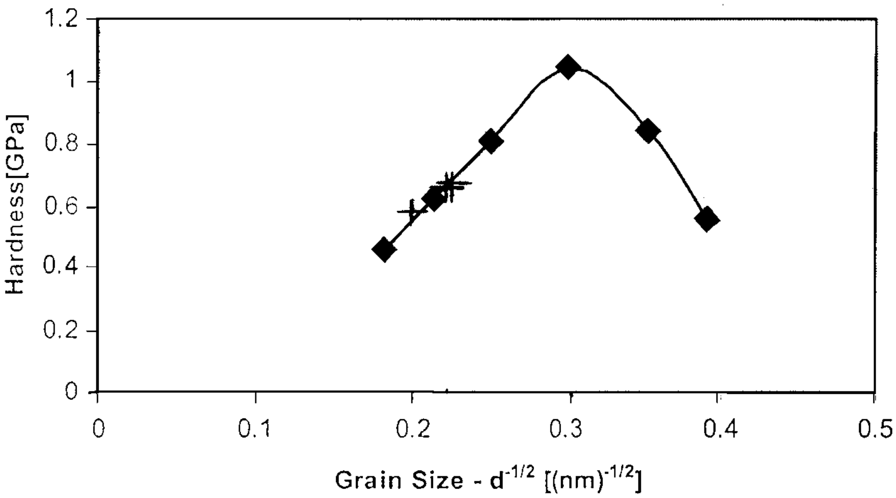

Figure 1. Hardness vs. grain size, $d^{-0.5}$ for nanocrystalline Zn made by laser ablation or mechanical attrition.

Pulse- and direct-current electrodeposition methods were applied to produce nc copper deposits containing grains of ~30 and ~10 nm, respectively, from acidic copper sulfate baths. In addition, direct current deposition was used to fabricate nanocomposites of alumina in a copper matrix. For example, 20 g/l of 50-nm alumina suspended in the copper sulfate bath yielded a composite with 70-nm copper grains. Additional grain-size reduction was achieved by addition of citric acid to the bath, which produced grains as small as 18 nm without affecting the amount of alumina co-deposited. In the absence of alumina, the citric acid additive effected copper grains ~10 nm under direct current control. The effects of citric acid in reducing grain size seemed to be independent of current density, and the grain size approached an asymptotic limit with increasing citric acid concentration. Comparison of hardness values for nc copper with and without alumina showed decreased hardness for the alumina-containing composites, although a Hall-Petch behavior was observed for the composite. Pulse plating was used to produce nc copper without additives present in the bath.

A multi-parameter study of pulse-plating conditions produced specimens with grain sizes below 50 nm. Processing conditions that yielded the highest electrode overpotentials seemed to favor nucleation and effect the smallest grain sizes.

3. Future directions and collaborations

The main goal of our research remains the production of artifact free nanocrystalline samples such that inherent mechanical properties can be measured. The data so obtained has/will provide the basis for understanding mechanical behavior of nanocrystalline materials. For example, J. Narayan has modeled the inverse Hall-Petch effect using grain boundary sliding as the controlling mechanism [3]. In addition to the hardness measurements already made, bend and small sample tensile tests are planned. In the latter case we have entered into a collaboration with Professor A. Mukherjee, University of California-Davis, to carry out miniature tensile sample testing on our nanocrystalline samples. We believe superplastic behavior at or near room temperature may be observed in out nanocrystalline Zn.

The focus of the electrodeposition studies is the preparation of nanoscale composites. Colloidal suspensions of nanoscale size dispersoids appear to produce like-size nanocrystalline electrodeposits. The mechanism for this result will be investigated.

Collaborative work with Drs. A. Cerezo and P. Warren at Oxford University, UK, will continue. The focus of this research is the identification of the grain boundary chemistry at the atomic level of our nanocrystalline samples using the Oxford three dimensional atom probe.

A complementary project, funded by the International Lead Zinc Research Organization (ILZRO) is exploring the processing, structure, and properties of nanocrystalline electrodeposited Zn coatings on automotive steel.

References:

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3. **J. Narayan, "Size and Interface Control of Novel Nanocrystalline Materials Using Pulsed Laser Deposition", J. Nanoparticle Research, 2 (2000) 91-96.**