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Introductory Chapter: Nanocrystalline Materials

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1. Introduction

Nanocrystalline materials have been a hot research topic over the past 30 years. These materials abound in industry, bridging the gap between molecular and macroscale objects. Nanocrystalline materials are ultrafine-grained single-phase or multiphase polycrystals with grain sizes in the range of 1–100 nm, as depicted in **Figure 1**, the transmission electron microscopy (TEM) image of Fe-based nanocrystalline coating. In fact, the extremely small sizes and a large volume fraction of the atoms are located at the grain boundaries; on the other hand, these materials consist of about 50 vol.% crystalline component and 50 vol.% interfacial component.

It is recognizable that the nanocrystals are typically specified as anything, such as small grain polycrystalline materials, nanosynthesized surfaces, nanoparticles, and polymer micelles; each of them has varied usages, from drug delivery, to super capacitors, catalysts, and sensors. These materials are of interest for the following reasons:

1. The properties of nanocrystalline materials differ from the properties of single crystals and coarse-grained polycrystals and are amorphous with the same chemical composition. This deviation is strongly related to the reduced crystallites size as well as the large amount of grain boundaries between adjacent crystallites.
2. The concept of nanocrystalline materials seems to authorize the alloying of components which are immiscible in the solid or molten state. These fabricated alloys could be good candidates for advanced and technologically marvelous properties.

It is clearly seen that at a nanometric scale, the nanocrystalline materials contain a high grain boundary volume fraction; therefore grain boundaries and their interactions with crystal play a remarkable role in the different properties. It is important to point out that those nanocrystalline materials, as a new generation of advanced materials, have superior properties to conventional coarse-grained polycrystalline materials. They exhibit outstanding mechanical and physical properties such as high strength and hardness, low elastic modulus, improved ductility/toughness, excellent fatigue and wear resistance, increased diffusivity, higher electrical resistivity, reduced density, higher thermal expansion coefficient, enhanced specific heat, lower thermal conductivity, and better soft magnetic properties.

Nanocrystalline materials can be fabricated by gas condensation, plasma deposition, spray conversion technique, mechanical alloying, and some other methods.

Figure 1.
TEM image of Fe-based nanocrystalline coating (unpublished image).

Obviously, there are two approaches to fabricate the nanocrystalline materials: “top-down” and “bottom-up.” Both approaches play significant roles in industry and have some advantages and disadvantages. Bottom-up approach is nothing new in material synthesis and often emphasized in nanotechnology literature. As a matter of fact, the typical synthesis of materials is to build atom by atom on a large scale and has been used for over a century in industrial applications. Bottom-up approach mentions the buildup of a material from the bottom as molecule by molecule, atom by atom, or cluster by cluster. In the process of crystal growth, the growth species such as atoms, molecules, and ions assemble into crystal structure one after another after impinging onto the growth surface. Bottom-up approach also promises a preferable chance to get nanocrystalline materials with less defects, more homogeneous chemical composition, and higher short- and long-range ordering. It is recognizable that the bottom-up approach is driven mostly by the reduction of Gibbs free energy (ΔG), so that the nanocrystalline materials are in a state closer to a thermodynamic equilibrium state. In contrast to this, top-down approach most likely insets internal stress, in addition to contaminations and surface defects. Attrition or ball milling is a generic top-down method in making nanostructures, whereas the colloidal dispersion or gas-based reduction is a usual example of bottom-up approach. The former produces polycrystalline structures with irreproducible crystallography and poorly controlled grain orientation. The latter has generated a reproducible collection of structures and architectures, including alloys, pure metals, anisotropic nanostructures, and core-shell. In lithography, the process may be assumed as a hybrid approach, since the thin film growth is bottom-up and etching is top-down, while nanolithography is generally a bottom-up approach.

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