Research News

Synthesis of Nanocrystalline Materials from Amorphous Solids**

By Ke Lu*

1. Introduction

Nanocrystalline (NC) materials are single- or multi-phase solids with grain sizes in the nanometer region (typically, with at least one dimension less than 100 nm). Because of their extremely small dimensions, NC materials are structurally characterized by a large volume fraction of grain boundaries or interphase boundaries (generally called interfaces), which may significantly alter their physical, chemical, and mechanical properties with respect to the conventional coarse-grained polycrystalline materials. In fact, many properties of NC samples are found to be completely different from, and often superior to, those of the conventional polycrystalline or amorphous solids. For example, a NC material may exhibit an increased strength/hardness, an improved ductility/toughness, an enhanced diffusivity, a higher specific heat, a high thermal expansion coefficient, and a superior soft magnetic property in comparison with conventional polycrystalline materials.

The basic idea of nanocrystalline materials was proposed by Gleiter in the early 1980s. He envisioned that a new class of material could be generated by introducing such a high density of grain boundaries that 50% or more of the atoms are situated in the grain boundaries. Pioneer explorations to synthesize NC samples were performed by Gleiter et al. in early 1980s. They synthesized ultrafine (nanometer-sized) metallic particles using an inert gas condensation technique and consolidated these particles in situ into small disks under ultra-high vacuum conditions. Later, a number of different synthetic methods for NC materials were developed, with the starting materials in the solid, liquid, or gaseous states. These methods included mechanical attrition (or mechanical alloying), spray conversion processing, severe plastic deformation, sputtering, and the complete crystallization of amorphous solids. Amongst all these synthetic routes, the gas condensation, mechanical attrition, spray conversion processing, and crystallization from amorphous solids have been most commonly employed to produce large quantities of NC samples.

2. Preparation of NC Materials from Amorphous Samples

The basic principle for the crystallization method is to control the crystallization kinetics of amorphous solids by optimizing the heat treatment conditions (for example, annealing temperature, time, and heating rate), so that the amorphous phase crystallizes completely into a polycrystalline material with ultrafine crystallites. The key to the formation of nanocrystallites in an amorphous solid is to control the annealing temperature such that the nucleation rate is high while the growth rate is small. The amorphous solids can be prepared by means of a number of existing routes, such as rapid quenching and other non-equilibrium processing. Crystallization of amorphous solids has been successfully applied to the production of NC materials in various systems: for example, Fe-, Ni-, and Co-based alloys; and pure elements such as Se and Si. As a route to NC materials, the crystallization method has the following attractive features:

1) It is simple, convenient, and capable of producing large quantities of NC samples. It can be applied to most alloy and pure element systems as long as these materials can be prepared in the amorphous state.
2) It can change the grain sizes over a wide range. Grain size ranging from a few nanometers to several micrometers can be easily obtained by simply modifying the heat treatment conditions (such as annealing temperature and time). Figure 1 shows the variation of the mean grain size with the isothermal annealing temperature in several alloy sys-

---

[*] Prof. K. Lu
State Key Laboratory for RSA
Institute of Metal Research
Chinese Academy of Sciences, Shenyang
Liaoning 110015 (P. R. China)

[**] This work was financially supported by the Chinese Academy of Sciences and the National Science Foundation of China under grants No. 59431022, 59625101, and 59771019.
tems. This result also indicates that the annealing temperature dependence of grain size is quite different from system to system, but the minimum grain sizes usually appear when the annealing temperature is close to approximately 0.5T_m (where T_m is the melting temperature of the alloy).

3) It provides an efficient route to porosity-free NC materials that is necessary for studying their intrinsic structure and properties.\[10\] The NC samples are also clean at the interfaces because no artificial consolidation process is involved and the nanocrystallites and their boundaries are formed via a solid-state phase transformation.

4) Crystallization can produce various kinds (for example, coherent, semicoherent, and complete incoherent) of interfacial structures in the NC samples.\[7\] In comparison, other synthetic methods can only generate randomly oriented interfacial structures.

5) By use of the crystallization method, functional NC materials such as intermetallics, supersaturated metallic solid solutions and composites can be easily synthesized.

6) The nanocrystallization itself provides us a good chance to experimentally study the formation of interfaces from the amorphous state. The kinetics and thermodynamics of nanocrystallization are strongly affected by the presence of plenty of interfaces in the crystallization product.\[9\] Consequently, it is possible to reveal some fundamental features of interfaces in the NC materials from the transformation kinetic and thermodynamic signals.\[10\]

Because of these advantages, complete nanocrystallization from amorphous solids, and the crystallized NC materials, have been intensively investigated in the past few years. A comprehensive review describing the nanocrystallization from amorphous solids, their microstructural characteristics, thermal stabilities, and their properties was published in Materials Science & Engineering Reports.\[7\]

Controlled crystallization of amorphous alloys can also be used to obtain partially crystallized materials with nanometer-sized crystallites embedded in the residual amorphous matrix. This particular composite structure consisting of nanocrystalline and amorphous domains with appropriate compositions gives the material excellent mechanical or magnetic properties.\[11,12\]

3. Properties of NC Materials Prepared by Nanocrystallization

The structure and properties of the porosity-free NC materials crystallized from amorphous solids have been extensively investigated in different systems. Experimental observations revealed that the microstructural features of both the interface and the crystallites in NC materials are altered with respect to their corresponding coarse-grained counterparts. With a decrease of the grain size, the grain boundary energy is found to diminish in Ni-P and Se NC samples,\[10,13\] the lattice parameters, the Debye–Wallner parameters, as well as the Debye temperature are also dramatically changed, indicating a distorted lattice structure for the nm-sized crystallites.\[14\] Although the intrinsic reason for the evident lattice distortion in NC samples is not yet clear, its effect on the property changes should not be ignored. Mechanical property measurements on the porosity-free NC samples showed that the classical Hall-Petch relationship relating the hardness/strength and the grain size for polycrystalline materials is no longer valid for NC samples.\[15\] The Hall-Petch plots in several NC samples, as shown in Fig. 2, exhibit rather different trends. It implies the hardening mechanism for NC materials differs from the traditional hardening mechanism for polycrystalline materials. To get a deeper understanding on the mechanical behaviors of NC materials, more systematic experimental studies on 3D bulk, porosity-free, and clean NC samples are still needed.

Fig. 1. Plots of the measured mean grain size versus the annealing temperature (divided by T_m) for different nanocrystallization products from amorphous solids.

Fig. 2. Hall–Petch plots for different nanocrystalline samples crystallized from amorphous solids (Hv is Vickers hardness and d is particle size).