CRYSTALLIZATION MECHANISM AND CHARACTERIZATION OF NANOSTRUCTURES FROM AMORPHOUS ALLOYS

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Abstract -- Some recent results on the crystallization mechanism and structural characterization of nanostructures synthesized by completely crystallizing amorphous alloys are briefly reviewed. The morphologies, grain size, interfaces, defects, and nm-sized crystallites in the crystallized nanocrystalline samples are dealt with. Emphasis is placed on the features of interface structure and lattice structure of the nm-sized crystallites in these nanocrystalline materials.

INTRODUCTION

Nanocrystalline (NC) materials may be formed by completely crystallizing the amorphous solids under proper heat treatment conditions [1]. Among various methods of synthesizing this new class of materials, complete crystallization from amorphous solids possesses some unique advantages. (i) The synthesis is very simple and easy to control. Conventional annealing achieves nanocrystallization in most the alloy and element systems, which can be prepared with an amorphous structure, and can yield a large quantity of the NC samples. Also, variable grain sizes (from a few to several hundred nm) can be easily obtained in the as-crystallized NC specimens by modifying the annealing conditions. (ii) The complete crystallization method provides an efficient way to produce porosity-free NC samples [2]. As no artificial consolidation process is involved and the nm-crystallites as well as their boundaries are formed naturally during the crystallization, the NC sample is dense and clean in the internal interfaces. (iii) Nanocrystallization itself provides a unique opportunity to study the process of interface formation from the amorphous state, and, consequently, reveals some fundamental features of the NC interfaces [3].

In recent years, the amorphous-to-NC process has been investigated thoroughly and successfully applied to obtain NC materials in various alloy systems [4-7] as well as some pure elements [8]. In this paper, some recent results on the crystallization mechanism and structural characterization of some Fe- and Ni-base NC alloys are briefly reviewed.

NANOCRYSTALLIZATION MECHANISM

Similar to the conventional crystallization processes in amorphous alloys, three kinds of mechanism have been observed in the amorphous-to-NC transformation depending upon the composition of the glass and the thermodynamic properties of the corresponding crystalline phase(s): polymorphous, eutectic, and primary crystallization.
Typical eutectic nanocrystallization was observed in an amorphous Ni$_{80}$P$_{20}$ alloy upon isothermal annealing. Two nanophases of an Ni(P) solid solution (fcc structure) and an Ni$_3$P compound (bct) are formed simultaneously with the two phases growing in a coupled fashion. Both NC phases are in the form of anisotropically-shaped blocks with the Ni$_3$P nanophases separated by the Ni phases. A specified orientation relationship between the Ni phase and the Ni$_3$P compound was found to be: $\langle 001 \rangle_{\text{bct}}//\langle 110 \rangle_{\text{fcc}}$ and $\langle 110 \rangle_{\text{bct}}//\langle 111 \rangle_{\text{fcc}}$ [9].

Crystallization of an amorphous Ni$_{33}$Zr$_{67}$ alloy is a typical polymorphous transformation whose products consist of only one crystalline phase: an NiZr$_2$ intermetallic compound [10]. Under proper annealing conditions, the crystallization products are irregularly-shaped crystalline regions which are composed of NC lamellar domains (the thickness is 2–5 nm and length less than 100 nm). There is a coherent twin boundary between the neighboring lamellae, and the orientation relationship between the two grains is: $\langle 001 \rangle_1//\langle 111 \rangle_2$ and $\langle 110 \rangle_1//\langle 110 \rangle_2$. Crystallization of an amorphous (Fe$_{99}$Cu$_1$)$_7$Si$_9$B$_{13}$ alloy during isothermal annealing leads to the formation of NC $\alpha$-Fe(Si) as the primary phase; then the residual amorphous phase crystallizes completely into NC $\alpha$-Fe(Si) and Fe$_2$B phases [7]. The shapes of these two randomly-oriented nanophases are approximately isotropic and their grain sizes are uniform with a narrow size distribution.

The average grain size in the as-crystallized NC sample is found to increase in some cases (e.g., Ni-P [1], Fe-Co-Zr [11], etc.) at higher annealing temperature ($T_a$), whereas it decreases with an increase in $T_a$ in the nanocrystallization of CoZr$_2$ [4]. For some alloys (such as in NiZr$_2$ [10]), no significant variation in the grain size was observed within a wide $T_a$ range. The grain size distribution in the crystallized NC samples can be very narrow. From many experimental results of grain size dependence of the annealing temperature we noticed that the minimum grain sizes frequently appear if $T_a=0.5T_m$ (where $T_m$ is the melting temperature for the alloy) [12]. The grain size limit for the nanocrystallization process is found to be about 7–10 nm for polymorphous and eutectic crystallization, and is above 15 nm for primary nanocrystallization.

**INTERFACIAL STRUCTURES**

Microstructural analyses of the crystallized NC samples indicated that various types of interfaces can be formed in the nanocrystallization processes: interfaces with orientation relationship (coherent, semicoherent, or incoherent) and those with random orientations. By high resolution electron microscopy, different interfacial structures may be identified in various NC alloy samples. In the case of NC NiZr$_2$ which underwent polymorphous nanocrystallization, most grain boundaries are straight and well-fitted. They are coherent twin boundaries with a specific structure [10]. It can be expected that such kinds of boundaries are in a low energetic configuration with very small excess volumes.

In the primary nanocrystallization products of the Fe-based alloys, which are composed of randomly oriented NC crystallites, incoherent grain or interphase boundaries are always observed. HREM images of the $\alpha$-Fe(Si) grain boundary and the $\alpha$-Fe(Si)/Fe$_2$B interface in an NC (Fe$_{99}$Mo$_1$)$_7$Si$_9$B$_{13}$ alloy [13] show that the $\alpha$-Fe(Si) grain boundary is very flat and seems to be a typical high-angle grain boundary. And the interphase boundaries exhibit flat facets separated by steps. But in both interfaces no extended contrast effects caused by the "disordered boundaries" can be detected. As the orientations of the crystallites are random and no orientation relationship exists between the neighbouring grains in this sample, the
interfaces are expected to be in a higher state of energy with a relatively larger excess volume than the coherent or semicoherent ones as in the polymorphous nanocrystallization products.

Measurements of the interfacial energies in the eutectic crystallization products of NC Ni-P samples with different grain sizes [3] revealed that the average interfacial excess energy decreases significantly with a reduction of grain size in an approximate linear relation. In the sample with a grain size of a few nanometers, the interfacial energy is rather small, close to the energy of a small-angle grain boundary. The variation of the interfacial excess energy with the grain size is found to be correlated with that of the interfacial excess volume deduced from the experimental results [14]. These results suggest that the interfacial structure in the NC materials are susceptible of change and dependent on the grain size. Positron annihilation spectroscopy (PAS) studies on the defects in the crystallized NC Fe- and Ni-based alloy samples indicated that they have essentially the same types of defect as in the consolidated NC ones, except large voids: type-I of free volumes whose size is smaller than a monovacancy, and type-II of microvoids [2]. And with a decrease in grain size the interfacial density increases which agrees well with the results of calorimetric and density measurements.

It can be seen that the interfacial structures are susceptible of change in different alloy systems with different crystallization processes. For the polymorphous and the eutectic nanocrystallization products, comparatively, the interfaces seem to be in lower energetic configurations than those in the primary case. This feature can also be found from the PAS results [15].

NANOCRYSTALLITE LATTICE STRUCTURE

Quantitative XRD measurement of the lattice parameters of the nm-sized Ni₃P (bct) compound in the NC Ni-P alloy [16] and of the Fe₂B (bct) nanophase in the Fe-Cu-Si-B alloy [17] revealed that the lattice parameters of these two NC stoichiometric line compounds evidently deviated from the equilibrium values of the perfect crystal lattice. The value of a is always larger than the standard value of a₀ while c is smaller than c₀ for both nanophases, and with a reduction of the average grain size the value of a increases, but c decreases. The relative deviations attain as much as Δa=0.22%, Δc= -0.24% for the 25 nm-Fe₂B sample, Δa=0.21% and Δc= -0.13% for the 6 nm-Ni₃P. The unit cell volume of each compound, V=a²c, was found to be enlarged, relative to the corresponding equilibrium value, i.e., the nm-sized crystallite lattice is dilated relative to the perfect crystal structure. With decreasing grain size, lattice expansion increases for the both nanophases.

Mössbauer spectroscopy investigations of the microstructure of the Fe₂B nanophases [18] revealed that the isomer shift (IS) and the half-line width (HLW) for the Fe₂B subspectrum are increasing with the decrease of grain size. An increase in IS means that the density of s-electrons of Fe atoms in the Fe₂B phase decreases, which reflects a dilated lattice structure. While the increasing HLW value indicates that the distribution of the atomic coordination distances in the Fe₂B phase becomes less dense and the degree of disordering is enhanced. This result is in agreement with the XRD measurements that the distortion in the nanophase lattice is increasing with reducing grain size.

The intrinsic reason for the lattice distortion and expansion in the nanophase stoichiometric line compounds, which have no solubility of other elements in the equilibrium state, has not yet been found. This phenomenon may be qualitatively understood from considerations of the thermodynamics of the enhancements of solute (and/or vacancies) solubilities in the nm-crystallites [19]. But further intensive investigations are still highly needed.
CONCLUDING REMARKS

NC materials synthesized by complete crystallization from amorphous alloys possess some specific structural characteristics which might differ from those of the conventional NC materials made by consolidation of the ultrafine particles. However, some of their structural features might be intrinsic and representative of the nanostructured materials, which lead to the crystallized NC samples exhibit similar properties as other NC materials do.

The crystallized porosity-free NC samples should be very useful in thorough investigations of the microstructures and properties of the internal interfaces. More systematic experimental studies should concentrate on the simple systems (such as single phase or elements) with which the interface effects on the properties and the structure-property relationship in NC samples could be analyzed more easily.

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