Small-Angle X-ray Scattering Study of Nanocrystalline and Amorphous States of the Fe$_{73.5}$CuNb$_3$Si$_{13.5}$B$_9$ Alloy

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Abstract

The structural evolution of the nanocrystalline material obtained from the amorphous compound Fe$_{73.5}$CuNb$_3$Si$_{13.5}$B$_9$ was investigated by small-angle X-ray scattering. Four sets of amorphous metallic ribbons were produced by melt spinning using different quenching rates. Samples of each set were annealed above the crystallization temperature; X-ray diffraction analysis showed the formation of an ordered Fe–Si solid solution with average grain sizes ranging from 9 to 11 nm. Small-angle scattering curves of the samples in the initial amorphous states revealed different intensities for different quenching rates, caused by the presence of heterogeneities with dimensions larger than those of the crystallites formed after thermal treatment. In addition, scattering measurements were carried out in situ during isothermal annealing showed an intensity evolution as a function of time, attributed to electron-density contrast variation caused by the atomic diffusion process that occurs during crystallization.

1. Introduction

Nanocrystalline materials have been considered a new class of materials, artificially produced, which consist mainly of very small crystallites (atomic domains spatially confined to less than 100 nm), randomly distributed in an amorphous matrix. Owing to their structural characteristics and to the interactions between the constituent crystallites, their properties are different from, and often superior to, those of conventional materials that have grain sizes on a coarser size scale (Gleiter, 1989). The controlled crystallization of certain metallic glasses, in particular the Fe–Si–B alloy containing small additions of Cu and Nb, is known to produce an ultrafine grain structure with very attractive soft magnetic properties, such as low magnetostriction and high magnetic permeability (Yoshizawa, Oguma & Yamauchi, 1988). After thermal treatment at 813 K for 60 min, the amorphous alloy of nominal composition Fe$_{73.5}$CuNb$_3$Si$_{13.5}$B$_9$ (at.%) becomes partially crystallized with the formation of Fe–Si grains about 10 nm in size. The formation of the nanocrystalline structure is attributed to the simultaneous addition of the elements Cu and Nb, since Cu increases the nucleation rate whereas Nb hinders the growth of the crystallites and enhances the thermal stability of the residual amorphous component (Yoshizawa & Yamauchi, 1990). The average size and the size-distribution function of the crystallites play the most important role in the magnetic behaviour of this material.

In recent years, several publications have dealt with the influence of atomic composition and annealing conditions on the formation of the nanocrystalline structure, as well as with the correlation between structural and magnetic properties of this material. Crystallization processes in the Fe–Cu–Nb–Si–B alloy have been studied using several techniques, such as differential thermal analysis, Mössbauer spectroscopy, X-ray diffraction and X-ray absorption spectroscopy (Herzer, 1990; Noh, Pi, Kim & Kang, 1991; Müller, Mattern & Illgen, 1991; Hampel, Pundt & Hesse, 1992; Knobel, dos Santos, Torriani & Turtelli, 1993; Ayers, Harris, Sprague & Elam, 1994; Danzig & Mattern, 1995). In the work described herein, we used small-angle X-ray scattering (SAXS) to perform structural investigations on this metallic alloy in different initial amorphous states and also during the annealing, which yields the state of the material that presents the best soft magnetic properties. Owing to its intrinsic characteristics, SAXS is a suitable technique to obtain reliable information on small clusters of atoms or compositional fluctuations and is, therefore, an important tool for testing theories of atomic diffusion or phase separation in inorganic materials. In addition, the high intensity of synchrotron radiation allows the evolution of the scattering intensity during a heat treatment to be studied by in situ SAXS measurements.

2. Experimental

Four series of Fe$_{73.5}$CuNb$_3$Si$_{13.5}$B$_9$ amorphous ribbons were produced by melt spinning in air using a rotating CuBe drum with peripheral velocities varying between 25 and 32 m s$^{-1}$. Each series corresponded to a different degree of amorphism, which was modified by changing the quenching rate to which the melt was submitted during the flow-casting procedure. The series, with thicknesses varying between 14 and 35 μm, were labelled A to D in decreasing order of quenching rate. Samples of
Table 1. Average radii of gyration $R_g$ obtained from the Guinier plot in each stage for heat treatment

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>$R_{g,1}$ (nm)</th>
<th>$R_{g,2}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>19.4 (1)</td>
<td>10.2 (2)</td>
</tr>
<tr>
<td>10</td>
<td>17.9 (2)</td>
<td>10.3 (2)</td>
</tr>
<tr>
<td>20</td>
<td>17.3 (1)</td>
<td>10.7 (1)</td>
</tr>
<tr>
<td>30</td>
<td>17.4 (3)</td>
<td>10.9 (1)</td>
</tr>
</tbody>
</table>

Each series were submitted to isothermal annealing in an argon atmosphere at 813 K for 20, 40 and 60 min. Their X-ray diffraction profiles were measured using Cu Kα radiation from a Rigaku RU200 rotating-anode generator operating at 40 kV/80 mA. The Kα radiation was selected using an LiF curved-crystal diffracted-beam monochromator, which also eliminated the fluorescence from Fe in the samples. Small-angle scattering measurements were performed using synchrotron radiation. For the amorphous samples, SAXS measurements were performed using the D22 experimental station at LURE, Orsay, France. A linear position-sensitive detector was used, with a sample-to-detector distance, $D$, of 750 mm. The scattering vector, of magnitude $q = (4\pi \sin \theta)/\lambda$, where $\theta$ is half of the scattering angle and $\lambda = 0.984$ Å, was covered in the range $0.07 < q < 1.0$ nm$^{-1}$ with total acquisition times of the order of 3 h for each sample. In situ SAXS measurements were carried out during heat treatment at 813 K for a sample of the B series, using the D24 workstation (at LURE), with $\lambda = 1.488$ Å and $D = 1250$ mm. Because of the high flux available at this beamline, SAXS curves could be measured with acquisition times of 5 min, over the same range of scattering vectors.

3. Results and discussion

For the annealed samples, diffraction spectra confirmed the formation of an Fe–Si solid solution with $DO_3$ crystalline structure. The time evolution of the 220 peak can be observed in Fig. 1. The 220 and 440 diffraction profiles were corrected for instrumental broadening and analysed using the Fourier transform method, according to a procedure described in detail in a previous work (Knobel et al., 1993). This analysis revealed that for heat-treatment times between 20 and 60 min, the average grain size remains approximately constant, equal to 9 nm in the case of samples of the $B$ series, while the crystalline volume fraction increases from 60 to 90% (dos Santos, 1996).

The relative contrast of electronic density between the crystalline particles and the metallic matrix, estimated considering $\alpha$-Fe particles embedded in a matrix of the initial amorphous composition, is of the order of 8%. Consequently, a small-angle scattering effect is expected for these samples. Furthermore, Guinier plots for in situ measurements can be used to determine the time evolution of the grain size during the first stages of nucleation and growth.

The measured SAXS intensities were corrected for experimental effects, such as absorption, fluctuations of the incident intensity, parasitic scattering, background scattering and heterogeneity in the linear-detector response. The results of the in situ measurements are plotted in Fig. 2, where an increase in the scattering intensity as a function of the annealing time can be readily observed. Guinier plots, also presented in Fig. 2, indicate a bimodal system of scatterers. From the two linear regions shown in Fig. 2 we can extract two radii of gyration, designated $R_{g,1}$ and $R_{g,2}$ and presented in Table 1.

These values could be considered as the average radii of gyration of two distinct populations of scattering particles. Surprisingly, they do not show any significant size evolution as a function of annealing time. Furthermore, even the smallest value obtained for the radius of gyration of these scatterers is larger than the average dimension of the nanocrystals observed by X-ray diffraction. This suggests that the scattering particles

![Fig. 1. Intensity evolution of the 220 X-ray diffraction profile for samples of the $B$ series annealed at 813 K for different times.](image1)

![Fig. 2. Intensity evolution of the small-angle scattering curves as a function of annealing time for a sample of series $B$. The Guinier plots are shown in the insert.](image2)
Table 2. Average radii of gyration $\bar{R}_g$ obtained from the Guinier plot for amorphous samples produced with different quenching rates

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\bar{R}_{g,1}$ (nm)</th>
<th>$\bar{R}_{g,2}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>13.5 (1)</td>
<td>7.5 (1)</td>
</tr>
<tr>
<td>B</td>
<td>13.1 (1)</td>
<td>6.5 (1)</td>
</tr>
<tr>
<td>D</td>
<td>13.1 (1)</td>
<td>7.1 (2)</td>
</tr>
</tbody>
</table>

could be formed by aggregates of crystalline domains, but this hypothesis is not compatible with X-ray diffraction results, which do not show the presence of particles with crystalline order until 10 min of heat treatment (Knobel et al., 1993). Furthermore, real-space information obtained from transmission electron microscopy and reported for this material (Yoshizawa & Yamauchi, 1990) shows a highly concentrated homogeneous distribution of grains with an average diameter of 10 nm. These observations agree with diffraction results only if the particles are single-crystalline domains.

To interpret our SAXS results we should consider that in the last stages of crystallization the crystalline volume fraction reaches 90%, and the residual amorphous phase is the minority sample component. Thus, according to the Babinet principle, the system could be considered an ensemble of amorphous domains embedded in a crystalline matrix. In the first 2 min of heat treatment, however, the crystalline phase is not yet present and the scattering data seem to indicate the existence of demixing structures or compositional fluctuations constituting an amorphous two-phase system.

From this in situ annealing experiment we conclude that after 2 min of heat treatment the scattering centres do not grow in size, whereas the intensity increases continuously with annealing time. The intensity increase can thus be attributed to a density contrast evolution caused by the development of the nanocrystalline state. Our picture of the formation of the nanocrystals with annealing is that it takes place in Fe-rich regions in the quenched material. The crystallization process evolves within these regions without an increase in their dimensions but with a change in composition by atomic diffusion: Si atoms are incorporated while Cu, Nb and B atoms are displaced to the amorphous matrix. This leads to the interpretation of the intensity evolution as an increase in the density contrast between the Fe-Si nanocrystals and the residual amorphous matrix.

These conclusions are supported by the small-angle scattering curves of the amorphous samples (Fig. 3), which reveal the presence of heterogeneities in the electronic density even before the thermal treatments. The quenching procedure was therefore fast enough to avoid crystallization, but allowed the formation of compositional fluctuations with electron-density contrast in the amorphous samples. For these samples, the Guinier plots again show two linear regions; the corresponding radii of gyration are presented in Table 2. These values show that, though being fully amorphous for diffraction purposes, the as-quenched samples present heterogeneities with dimensions of the same order of magnitude as those observed during thermal treatment.

![Fig. 4. Volumetric radii distribution obtained assuming a polydisperse system of homogeneous spheres of radii $R$.](image1)

![Fig. 3. Scattering curves of amorphous samples produced with different quenching rates and the corresponding Guinier plots.](image2)

![Fig. 5. Experimental scattering curves (symbols) and theoretical curves calculated for the model of solid spheres (lines).](image3)
Small-angle scattering results reported for transition metal–metalloid glasses assign the small-angle scattering signals to heterogeneities located in regions adjacent to the edges of the melt-spun ribbons, where devitrification phenomena might have preferably occurred (Kranold, Walter & Stubicar, 1993). Our measurements were performed with point collimation, using a beam cross section of about 0.4 x 1 mm and samples of 5 mm width. Since only the central portion of the samples was irradiated, we believe that the demixing structures observed are uniformly distributed across the amorphous samples.

Moreover, amorphous samples produced with different quenching rates show different scattering intensities and different radii of gyration. The average radius of gyration corresponding to the larger particles, $R_{g,1}$, is approximately independent of the quenching rate, while for the smaller particles the values of $R_{g,2}$ show considerable differences. In order to expose these differences further, the size-distribution function of the atomic aggregates was determined. Assuming a dilute polydisperse system of homogeneous spherical particles of radii $R$, we used the GNOM program package (Semenyuk & Svergun, 1991) to calculate the volumetric radius distribution function $D_2(R)$, shown in Fig. 4. In Fig. 5, the corresponding theoretical scattering curves are presented together with the experimental data. The average radii of gyration obtained from the solid-spheres model in the real and reciprocal spaces are consistent with the values obtained directly from the experimental Guinier plots.

Fig. 4 shows approximately bimodal size distributions, with most of the scattering centres distributed according to the main peaks in the smaller radius region. From Fig. 4 we can clearly see that different quenching rates correspond to different size distributions, each one with an average size larger than those of the crystallites formed after thermal treatment. On account of the similarity with the results of the in situ measurements, these results suggest that the heterogeneities present in the amorphous samples are the regions which will preferably crystallize after the appropriate thermal treatment.

From the point of view of applications, these are important results, since the crystalline volume fraction and average crystallite dimension, as well as lattice parameter, lattice distortions and silicon content of the nanocrystals, are structural parameters of the final nanocrystalline state which are related in a reproducible manner to the initial amorphism (dos Santos, 1996).

4. Summary

We have used small-angle scattering to study amorphous metallic ribbons of nominal composition Fe$_{73.5}$CuNb$_3$, Si$_{13.5}$B$_9$ (at.%), produced by rapid quenching from the melt, and the structural evolution of this material during the annealing that yields the nanocrystalline state. After 2 min of heat treatment, the scattering centres do not grow in size, whereas the scattering intensity increases continuously with annealing time. The intensity increase was attributed to a density contrast evolution, caused by the atomic diffusion process that results in the formation of the nanocrystalline state.

Considering the very large volumetric concentration of crystalline particles formed in this sample and the large sizes observed for the scattering centres, we conclude that the scattering is caused by the residual amorphous component and not by the crystalline particles. This result is substantiated by the study of the different amorphous samples.

It is evident that the quenching procedure was fast enough to avoid crystallization but allowed the formation of compositional fluctuations in the as-quenched samples, with dimensions of the same order of magnitude as those observed by in situ measurements during thermal treatment. Different quenching rates corresponded to different size distributions for the scattering centres, with an average dimension larger than that of the crystallites formed after thermal treatment. Our results suggest that the demixing structures present in amorphous samples are Fe-rich regions which will preferably crystallize after the appropriate thermal treatment.

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References


