Studies of crystallization of sputter-deposited Fe$_{82}$Si$_6$B$_{12}$ metallic glass film

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Abstract

In situ transmission electron microscopy observations have been undertaken to explore the nucleation and grain growth behaviour of a sputter-deposited Fe$_{82}$Si$_6$B$_{12}$ metallic glass film. The results show that the α-Fe crystals nucleated in a steady state homogeneous way. The initial growth of α-Fe crystals was diffusion controlled. When the crystals began to collide with each other, a more complex mechanism of grain growth was found. The final morphologies of the α-Fe crystals depend strongly on the heating procedures. Low energy electron irradiation substantially affected the crystallization of the Fe$_{82}$Si$_6$B$_{12}$ metallic glass film.

1. Introduction

The use of metallic glasses as precursors offers significant opportunities for microstructural design by controlled crystallization [1]. With suitable aging conditions, a series of new-structured materials containing various proportions of crystalline and metallic glass phases can be obtained.

Fe–Si–B-based metallic glasses are well noted for their outstanding magnetic properties [2, 3]. In the last decade, widespread investigations on the crystallization of Fe–Si–B-based metallic glasses have been initiated. However, the majority of the previous work has concentrated on melt-spun ribbons, and detailed studies of the microstructural evolution as a function of thermal annealing are lacking.

2. Experimental procedure

Thin film metallic glass Fe$_{82}$Si$_6$B$_{12}$ was prepared by d.c. sputter deposition; a melt-spun Fe$_{78}$Si$_9$B$_{13}$ metallic glass ribbon 50 mm wide and 70 mm long was used as target. The sputtering chamber was first pumped to 8 x 10$^{-6}$ Torr, then Ar gas was introduced to 5 x 10$^{-4}$ Torr. During sputtering the cathode voltage, anode voltage and tungsten filament current were 1 kV, 90 V and 50 mA respectively. Prior to formal deposition the metallic glass target was cleaned by sputtering to remove the contaminated surface layer. For the transmission electron microscopy (TEM) observations an Fe$_{82}$Si$_6$B$_{12}$ metallic glass overlayer 70 nm thick was deposited on an NaCl substrate. The TEM samples were collected by retrieving the floated Fe$_{82}$Si$_6$B$_{12}$ film in deionized water with Mo meshes. For electron microprobe analysis (EMPA) a layer 1000 nm was deposited on an Al substrate.

A JEM-100CX apparatus equipped with an electric resistance heating stage was used for crystallization studies; the vacuum was 10$^{-6}$ Torr and the acceleration voltage was 100 kV. First, dynamic heating at a rate of 20 °C min$^{-1}$ was performed from room temperature to 600 °C to detect the whole crystallization process. Second, isothermal annealing at various temperatures was performed on several samples to clarify the kinetics of crystallization of the Fe$_{82}$Si$_6$B$_{12}$ metallic glass.

3. Results and discussion

With a heating rate of 20 °C min$^{-1}$ the onset of crystallization occurred at about 400 °C; the primary crystallization product was α-Fe. Once the α-Fe crystals had formed, they quickly grew to larger sizes. The initially formed α-Fe crystals were sparsely scattered and had very distinctive dendritic morphologies even in the very early stages of growth. Figure 1 shows a TEM image after annealing to 450 °C. When the temperature was raised to 570 °C, a new Fe$_3$B phase was observed to grow along the arms of α-Fe dendritic crystals (see Fig. 2).
3.1. Nucleation kinetics of α-Fe

*In situ* TEM is a very effective method to explore the nucleation mechanism of the crystallization process. By counting the number of α-Fe crystals in the bright and dark field images under isothermal annealing, the nucleation kinetics of the as-deposited Fe₈₂Si₆B₁₂ metallic glass film can be obtained.

The variation in the number of crystals as a function of the isothermal annealing time is shown in Fig. 3, which represents a steady state homogeneous nucleation mechanism. In the initial period the number of α-Fe crystals increased linearly with the annealing time. Upon exhaustion of the activated nucleation sites this linear relationship levelled off and a new equilibrium was established. During further annealing the number of crystals remained unchanged.

3.2. Mechanism of grain growth for α-Fe crystals

3.2.1. Diffusion-controlled grain growth of α-Fe crystals

To investigate the grain growth behaviour of α-Fe crystals, isothermal annealing was employed; the annealing temperatures were chosen in the range 743 K to 673 K. At the beginning of grain growth the sparsely nucleated α-Fe crystals did not collide with each other; they grew in fourfold and threefold dendritic crystals. Figure 4 shows TEM images of the α-Fe crystals. Since the α-Fe crystals grew predominantly as fourfold symmetric dendritic crystals, only a few threefold symmetric dendritic crystals were observed. For both fourfold and threefold symmetric dendritic crystals the growth direction was along (110). This differs significantly from the situation with ribbon samples [4, 5], where the growth direction of the α-Fe crystals was along (100). Figure 5 shows the dependence of the grain size of α-Fe on the annealing time. The apparent linear relationship between the grain size and the square root of the annealing time reveals a typical diffusion-controlled grain growth process.
3.2.2. Multimorphology growth of α-Fe crystals

For steady state homogeneous crystallization the latter stage of crystallization is predominantly controlled by grain growth. As mentioned above, the initial period of grain growth for α-Fe crystals was diffusion controlled. The further growth of the α-Fe crystals depends strongly on the heating mode. Under a dynamic heating at a rate of 20 °C min⁻¹ the α-Fe crystals grew rapidly as the annealing proceeded. When the temperature was raised to about 570 °C, the Fe₃B phase formed close to the arms of α-Fe dendrites and both the α-Fe and Fe₃B grew quickly to large sizes (Fig. 2). Under isothermal annealing crystallization can lead to the formation of α-Fe crystals in various morphologies (see Fig. 6). Upon annealing at 480 °C, in the area where the unripe α-Fe crystals collided the α-Fe dendritic crystals split into many small crystals and a fine-grained structure was obtained (Figs. 6a and 6b). In the area where the fully grown α-Fe crystals collided the microstructural evolution of the α-Fe crystals can be classified into two categories: one is the formation of strip-shaped crystals (Figs. 6c and 6d) and the other is the formation of block-shaped crystals (Figs. 6e and 6f). Therefore for the thin film Fe₈₂Si₆B₁₂ metallic glass it is very hard to achieve a uniform microstructure with a single morphology of the α-Fe crystals by isothermal annealing.

3.3. Effects of low energy electron irradiation on the nucleation and growth of α-Fe crystals

Generally, low energy electron (100 keV) irradiation originating from TEM observation does not induce any structural changes in metallic glasses unless a high voltage electron beam is used to irradiate the sample. However, in the present experiment the evolution of microstructures of the Fe₈₂Si₆B₁₂ metallic glass during in situ annealing was significantly affected by electron irradiation.

With the TEM viewing field concentrated on a fixed area during in situ heating, continuous electron irradiation was realized. In this case, when the Fe₈₂Si₆B₁₂ metallic glass film was heated to about 350 °C at a heating rate of 20 °C min⁻¹, it began to crystalline; the primary crystallization product was α-Fe crystals in irregular network morphologies (Fig. 7). After continuous annealing at 350 °C for 15 min and 390 °C for 10 min the crystallization of the Fe₈₂Si₆B₁₂ metallic glass was completely finished; the product of crystallization was still α-Fe and its morphology remained unchanged. Subsequent isothermal annealing at 420 and 460 °C for 5 min each did not cause any change in
Fig. 8. Spherical α-Fe crystals induced from irregular net-shaped crystals by further annealing.

Fig. 9. Initial morphology of α-Fe in Fe₈₂Si₆B₁₂ metallic glass film heated at 20 °C min⁻¹ to 400 °C under electron irradiation.

the crystallized α-Fe structure apart from a slight grain growth. Only when the temperature was raised to about 470 °C did the initially formed irregular network α-Fe gradually change to spherical crystals with a grain size of about 20 nm (see Fig. 8). After final annealing at 500 °C for 45 min the grain size was about 45 nm.

When the metallic glass film was heated straight to 400 °C, the α-Fe crystals appeared in spherical morphologies (see Fig. 9) and grew relatively easy. After annealing at 400 °C for 40 min the mean α-Fe grain size was almost 50 nm. Electron irradiation enhanced the nucleation rate but not the growth rate. The crystal-

lized structure induced by electron irradiation at relatively low temperatures displayed better thermal stability than that at higher temperatures. As reported in a previous work, the initial morphology of α-Fe can only be affected by the composition [6], but in the present work the low energy electron irradiation could also alter the initial morphology of the α-Fe crystals and further affect their thermal stability.

4. Conclusions

In Fe₈₂Si₆B₁₂ metallic glass film, α-Fe crystals nucleate in a steady state homogeneous way and grow in fourfold and threefold symmetric dendritic crystals. The initial growth of the α-Fe crystals is diffusion controlled and along the direction (110). When the stage of crystal collision is approached, a more complex growth mechanism is found. The final morphologies of the α-Fe crystals depend strongly on the heating procedures. Low energy electron irradiation (100 eV) can affect the crystallization of the as-deposited Fe₈₂Si₆B₁₂ metallic glass by lowering the crystallization temperature and changing the morphology of the primary crystals. Low energy electron irradiation in combination with appropriate thermal annealing can induce nanograined structures which exhibit good thermal stabilities.

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References