In situ hot stage transmission electron microscopy observations of nanocrystal formation in a Co$_{65}$Si$_{15}$B$_{14}$Fe$_{4}$Ni$_{2}$ amorphous magnetic alloy

H.F. Li, R.V. Ramanujan *

School of Materials Science and Engineering, Nanyang Technological University, Singapore, 639798, Singapore

Received 16 August 2005; received in revised form 14 February 2006; accepted 27 February 2006
Available online 31 March 2006

Abstract

Real time in situ hot stage transmission electron microscopy observations were carried out to characterize the crystallization behavior of a Co$_{65}$Si$_{15}$B$_{14}$Fe$_{4}$Ni$_{2}$ amorphous alloy. It was found that the crystallization in the thin foil was highly thickness dependent. The crystallization occurred quickly at 400 °C in the thin regions (∼ 80 nm) and slowly in thicker regions (∼ 250 nm). The crystallization product was found to be cobalt with either hexagonal closed packed or face centered cubic crystal structure. The crystal morphology was that of nanosized spheres, faulted elongated crystals and irregular highly faulted crystal clusters; the morphology varied with the local thickness. Quantitative analysis of the thickness dependence of precipitate size and nucleation density indicated that: the precipitate size increased continuously with an increase in thickness; the nucleation density decreased sharply with increasing thickness. The thickness dependence of the crystallization products was analyzed in terms of surface mobility and strain effects. Crystallization in thin foils and conventional samples was compared. © 2006 Elsevier B.V. All rights reserved.

Keywords: In situ TEM; Crystallization of thin films; Cobalt based amorphous magnetic alloy; Thickness dependence

1. Introduction

The investigation of crystallization behavior of amorphous soft magnetic precursors is a focus area of materials research [1–9], since commercial nanocrystalline soft magnetic materials (such as Finemet) have been successfully developed by crystallization from amorphous precursors [3,10]. These nanocrystalline materials typically possess a microstructure of nanocrystals about 10 nm in size embedded in an amorphous matrix; they exhibit soft magnetic properties superior to the counterpart amorphous and conventional crystalline magnetic alloys. Developing this type of microstructure in other alloy systems would be useful. Secondly, crystallization behavior of amorphous materials is of interest since there are several differences between crystallization of amorphous materials and conventional solidification from the melt. Crystallization from the amorphous phase has yielded a number of new metastable crystalline phases [8,11]. Crystallization can also lead to deterioration of the properties hence studies of the thermal stability of amorphous alloys are also important [12–14]. Investigations carried out so far on the crystallization of amorphous alloys include crystallization kinetics, composition effects, microstructure, surface effects, pressure effects etc [1,15–19].

In our previous work, crystallization behavior of Co$_{65}$Si$_{15}$B$_{14}$Fe$_{4}$Ni$_{2}$ amorphous ribbons produced by melt spinning was reported [20,21]. This material is a magnetic amorphous alloy used in several commercial applications; crystallization studies are of direct relevance to examining the temperature limits of use of this alloy. From dynamic differential scanning calorimetry and electrical resistivity measurements, the first crystallization event was found to occur at about 530 °C. The crystallization process was complex in this alloy; it included the crystallization of large crystals, precipitation at grain boundaries as well as within the crystals, formation of both a heterogeneous microstructure as well as equiaxed crystals. During this crystallization process induced by conventional annealing, an interesting highly modulated nanolamellar structure was also observed within the large grains [21].

* Corresponding author. Fax: +65 67909081.
E-mail address: ramanujan@ntu.edu.sg (R.V. Ramanujan).
In order to further understand the crystallization behavior of this amorphous alloy, in situ transmission electron microscopy (TEM) observation of the crystallization process was carried out. It was found that the local thickness of the thin foil of the sample had a significant effect on the crystallization products: the crystals formed could vary from nanosized to submicron size for different local thicknesses ranging from 80 nm to more than 250 nm. This work thus provides information on the modification of microstructures by thickness effects, which will be useful in the development of Co based thin films used e.g., in data storage. It can also provide information on how to form large crystals with the nanolamellar structure described earlier [21]; this nanolamellar structure is potentially useful in applications such as nanogratings, nanotemplates, catalysts and electronic devices.

2. Experimental details

In situ observations were carried out in a JEM-2000 V ultra high vacuum TEM (200 kV). The as melt-spun sample was slightly ground to about 10 μm and then ion-milled to electron transparency. The sample is then positioned on a 6×2 mm silicon slab which can be resistively heated. The temperature was held around 400 °C; the crystallization event started at the edge of the thin foil sample after dynamic heating. Micrographs were then taken every 5 s using CCD camera to record down the crystallization process. After holding at this temperature for about 8000 s, the sample was cooled to room temperature and characterized using conventional TEM (JEOL 2010 TEM, 200 kV). The thickness was estimated through energy dispersive X-ray technique [22] using a standard alloy with known thickness and composition as a reference.

3. Results

Fig. 1(a), (b) and (c) are micrographs from thin (close to the edge of the foil), thicker and thickest regions respectively, obtained from in situ TEM observations. In the regions of thickness less than 80 nm (called thin regions) (Fig. 1a), a high density of nanocrystals with a size of about 10 nm was observed after holding at 400 °C for about 150 s. These nanocrystals have a spherical shape and regularly spaced. In the thicker region...
(local thickness approx. 150 nm) (Fig. 1b), crystals about 40 nm were observed; many of the precipitates have an elongated shape and are faulted; and the density of the crystals is lower than in the thin regions. In the thickest region (local thickness more than 250 nm) (Fig. 1c), the crystals have a size of about 80 nm; the density of the crystals is lower than the thicker region; the crystals consisted of an irregular cluster of grains. On holding at 400 °C for longer time, the density of the crystals was found to increase (Fig. 1d, e); the crystals increased in size to about 15 nm after holding for 5900 s. Fig. 1(e) and (f) are from the same region held for 6800 and 7050 s respectively: the crystal density remained unaltered, minor differences in crystal shape and size were observed.

The thickness dependence of the crystallization product is shown in Fig. 2; this sample was observed in conventional TEM after the in situ TEM work was completed, i.e., after holding at 400 °C for about 8000 s. From the edge to the interior of the sample, the morphology of crystals varied from a regular shape to a highly faulted and irregular shape; the size increased from about 20 nm to more than 100 nm. Quantitative measurement of the average crystal size and nucleation density is provided in Fig. 3. The crystals increased in size from about 20 to 185 nm when the thickness varied from 80 to 320 nm. The nucleation density decreased sharply with increasing thickness from 80 to 150 nm; the nucleation density was nearly zero for thicknesses greater than 300 nm.

Fig. 2. Thickness dependence of crystalline size and density. From upper left to right and from lower right to left, the local thickness of the foil continuously increased, resulting in a variation of crystallization products.

Fig. 3. Crystal size and nucleation density as a function of thickness.
The crystal structure of the crystallization products was determined using selected area diffraction pattern (SADP) and convergent beam electron diffraction (CBED) (Figs. 4 and 5). The SADPs (ring pattern) from the thin region correspond to hexagonal closed packed (h.c.p.) Co phase (Fig. 4aa and db). Some weak diffraction spots were observed in samples characterized using conventional TEM (Fig. 4b); these weak spots correspond to the face centered cubic (f.c.c.) Co phase. The diffraction pattern from the regions with medium thickness (Fig. 4c) is consistent with the formation of the h.c.p crystal structure. F.c.c Co phase was formed in the thick region (Fig. 4d). The crystallization product in the thick region is a cluster of crystals consisting of twinned h.c.p Co phase and f.c.c Co phase (Fig. 5).

4. Discussion

4.1. Thin foil crystallization process and their thickness dependence

In situ TEM provides real time observations of the morphological evolution at high temperatures [23–26]. For
this initially amorphous alloy, crystallization was fast in the thin region near the edge of the foil and a high density of 10 nm size nanocrystals was observed. With increasing holding time, the density of nanocrystals increased, however the growth of the nanocrystals was slow and even after 5900 s of holding time the precipitates had only increased by about 5 nm in diameter. Interestingly, crystal density decreased with increasing local thickness. The morphology of the crystalline precipitates also varied with local thickness: In the thin region, spheroidal crystals were observed; in the thicker region, twinned crystals with elongated shape were formed; in the thickest regions, irregular shaped faulted crystal clusters with a size of about 100 nm was observed. Differences in the shape and contrast of crystals suggested that in the later stage heterogeneous nucleation and growth dominate the crystallization of the remaining amorphous matrix. These observations indicated that (a) the crystallization of this alloy is a diffusional nucleation and growth process, (b) nanocrystallization can occur, (c) crystal growth was slow, and (d) in the later stages of crystallization, homogeneous nucleation and growth dominated in the thin region whereas heterogeneous nucleation dominated in the thick region.

The significant thickness dependence of the crystallization is also suggested in the crystallization product (Fig. 2). A
continuous increase of crystal size and decrease of nucleation density from the edge to the interior of the foil was observed. The morphology also changed with local thickness. Quantitative analysis of the crystalline size and nucleation density (Fig. 3) suggested that (a) nucleation density was high at thickness less than 150 nm; (b) nucleation was sparse when the thickness was larger than 300 nm and (c) the size of crystals increased continuously with thickness.

The crystallization product(s) of metallic glass depends on both intrinsic and extrinsic conditions, including composition, heat treatment, surface treatment etc [1, 2, 15–19]. The different crystallization behavior is due to thermodynamic driving forces and kinetic parameters. The thickness dependence of crystallization behavior can be attributed to both thin foil diffusion and strain. Surface diffusion may play a less significant role in the crystallization behavior can be attributed to both thin foil diffusion and strain.

The pressure induced can be expressed as

\[ P = \frac{\Delta G}{V} \]

Where \( \Delta G \) is the free energy change during crystallization of a crystal with volume \( V \), \( V \) is the total thickness, \( P \) is the pressure, \( E \) is Young’s modulus. The free energy change during crystallization of a crystal with volume \( V \) can be expressed as

\[ \Delta G = V \cdot \Delta G_{v,a-c} + S \cdot \gamma_{a-c} + \Delta \left( P \cdot \frac{V}{E} \right) \quad (1) \]

\[ \Delta G = V \cdot \Delta G_{v,a-c} + S \cdot \gamma_{a-c} + \frac{aE}{t} \cdot V \quad (2) \]

Where \( S \) is the surface of the crystalline phase, \( \Delta G_{v,a-c} \) is the volume free energy change from amorphous to crystal, \( \gamma_{a-c} \) is the interfacial area of the amorphous–crystalline interface.

Thus the free energy change can be seen to be inversely related to the local thickness due to strain effects.

If the critical size for nucleation of spherical crystals can be expressed as

\[ d^* = - \frac{3\gamma_{a-c}}{\Delta G_{v,a-c} + \frac{aE}{t}} \quad (3) \]

from Eq. (3), it can be seen that to form a smaller volume of crystals, \( a \) will be negative, i.e., the critical nucleus size will decrease in the thin region. From amorphous to crystalline phase, generally the molar volume will decrease. Therefore, smaller crystals are expected to form in the thin region. From Eq. (3), it can also be seen that with increasing thickness, this effect will be less important. This is consistent with our experimental observations that the crystal size remained at around 40 nm in the thick region although the crystal cluster size increased to more than 100 nm (Fig. 4).

The nucleation rate can be expressed as [27, 28]

\[ I = I_0 \exp \left( -\frac{\Delta G^* + Q_n}{kT} \right) \quad (4) \]

\( \Delta G^* \) is the thermodynamic barrier for nucleation, \( Q_n \) is the activation energy for the transport of an atom across the interface of an embryo, \( k \) is the Boltzmann’s constant. \( \Delta G^* \) will be significantly decreased when the critical nucleus size is decreased. This suggests that the nucleation rate in the thin region will be much larger than in thicker regions. The number density of crystals will increase significantly with longer holding time and this effect will decrease with increasing thickness, consistent with the experimental observations. In the thick region, the nucleation rate is low; heterogeneous nucleation was preferred.

The phases formed during the in situ crystallization were h.c.p. Co and f.c.c Co. In the thin region, in situ SADP characterization showed only h.c.p Co formation (Fig. 4a) while, at room temperature after cooling the sample, f.c.c Co phase was detected. This indicated that f.c.c Co phase formed during the cooling. The nanocrystals in the thin region were equixed crystals, twinning or stacking faults were seldom observed. In the thicker region, crystals had an elongated shape with lamellar faults along the short width direction. The faulted Co phase was also observed in Kim [13] and Byeon [29]’s investigation of Co_{95}Fe_{4}(BSi)_{x} amorphous alloy; it was considered to be induced by oxidation. However, the thickness dependence of morphology in the in situ crystallization of Co_{95}Si_{15}B_{14}Fe_{4}Ni_{2} metallic glass indicated that oxidation may not play a significant role in the formation of these faults. The faults in the crystals are mainly induced by the stress. Kulik has reported that a similar microstructure was observed in a Co_{78}Si_{11}B_{11} amorphous alloy after isothermal heat treatment at 472 °C for 30 min [1].

4.2. Comparison of in situ crystallization with conventional crystallization

During the conventional heat treatment, heat treatment at around 400 °C for 3 h is not sufficient to crystallize the
amorphous alloy. During in situ annealing, crystallization was not observed in the very thick region, which is consistent with the conventional annealing results. The occurrence of crystallization in the thin region at 400 °C suggested that surface diffusion and strain could be important factors. That nanolamellar structure was not formed during thin foil crystallization because (a) the crystal with the nanolamellar structure is metastable and (b) the mobility of atoms was higher in the thin foil. Equilibrium phases Co₂Si and Co₃B were not formed during in situ crystallization because the solid solubility of these crystals is small and formation of these two phases needs long range diffusion.

The strong thickness dependence of the crystallization products suggested that pressure may affect the crystallization process. Pressure has two aspects of effects on the crystallization [27]: promoting crystallization by decreasing the critical nucleus size and retarding the crystallization by reducing the atomic mobility. Applying pressure during the crystallization of this alloy may aid in the formation of large grains with nanolamellar structure [21].

5. Conclusions

In situ TEM observations of crystallization of a Co₆8Si₁₅B₁₄Fe₄Ni₂ amorphous alloy was carried out. The crystallization was found to be highly thickness dependent. The conclusions are:

(a) Crystallization occurred at around 400 °C in the thin region during in situ crystallization. The crystallization in the thin regions was faster than in the thick regions.

(b) High density spherical h.c.p. Co precipitates with a size about 10 nm were formed after holding at 400 °C for 150 s in the thin region of foil thickness less than 100 nm. The density of the crystalline precipitates increased with increasing holding time and the grain growth was slow at 400 °C.

(c) The thicker region slowly crystallized into highly faulted h.c.p. and f.c.c Co phases during the holding; these crystals were tens of nanometers in size and many of them had an elongated shape. The grains in the very thick regions were clustered and formed triangular irregular shapes.

(d) Quantitative analysis of the thickness dependence of the crystallization products showed that the size of the precipitates increased continuously with increasing local thickness: the precipitates have a size of less than 20 nm in the region with thickness of about 80 nm and a size of more than 180 nm in the region of 320 nm thickness. The nucleation density sharply decreased with increasing foil thickness for local foil thickness less than 160 nm.

(e) In addition to the enhanced effect of surface diffusion in thin regions, the thickness dependence of the crystallization behavior could also be due to the strain induced by the volume change during crystallization.

(f) The product of in situ thin foil crystallization differed significantly from that of conventional crystallization of ribbon amorphous sample of the same composition.

Acknowledgements

We would like to thank Dr.Y.L. Foo of Institute of Materials Research and Engineering, Singapore for his kind cooperation and help.

References