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Crystallization Mechanism of $Co_{77}B_{23}$ Amorphous Alloy

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Crystallization behavior of $Co_{77}B_{23}$ alloy at increasing temperature has been studied using resistivity measurements and auger-electron spectroscopy. The amorphous nature of the specimen ribbon was ascertained by X-ray diffraction analysis. The resistivity measurements showed a gradual increase of resistivity with temperature, which at about 600 K showed an abrupt fall in its value due to the onset of crystallization. As the heating continued, more peaks at different temperatures were detected in the resistivity–temperature distribution curve. These were identified as belonging to other phase changes in the crystallized alloy. Auger-electron analysis has been made to investigate chemical composition changes during heating. The results show a decrease in boron content on surface layers, which points to an inward diffusion of boron atoms. An excess of cobalt atoms is left on the surface, making the amorphous layers on the surface unstable, which leads to crystallization. © 2000 Academic Press

INTRODUCTION

Amorphous metallic alloys or noncrystallized solid metals are formed by rapid cooling of the melt. The glassy alloys based on third-transition metal borides possess an interesting combination of electrical, optical, magnetic, and mechanical properties due to their unique structure, in particular a lack of magneto-crystalline anisotropy and an absence of dislocation (1). This combination of remarkable properties are directly derived from their glassy state, e.g., soft ferromagnetism, relatively high electrical resistivity, very high fracture stress, better ductibility, and excellent corrosion behavior (1, 2). It is worth nothing that such a combination of properties is not found in any known crystalline material.

Fabrication and casting techniques of amorphous alloys are on the verge of yielding commercially applicable products such as wires and ribbons, which can be used as strengthening agents in aerospace composites and as transformer cores with great advantages.

Fabrication of glassy alloys depends entirely on the glass-forming ability criterion, comprising certain rules (1–4). There are a number of fabrication methods (1–7), but the samples studied in this work were prepared by rapid quenching (10^{-10} K/s) from the melt. This is recognized as the most versatile method for fabricating good quality glassy alloys.

Glassy metallic alloys lose their superior properties on crystallization. From an application point of view, the knowledge about crystallization temperature of an amorphous alloy is essential. A successful method is dynamic temperature X-ray diffraction (DTXD), which is a technique in which X-ray diffraction pattern is recorded on a photographic film that continuously runs in synchronization with the increasing temperature of the sample. Another useful technique is dynamic temperature resistivity measurement (DTRM) in which the resistivity measurement of the sample is made at an increasing temperature at a constant rate (8–12). This technique has been used to study the crystallization temperature of $Co_{77}B_{23}$ in this work. Another point of interest is to study the mechanism that leads to crystallization. For this study Auger electron spectroscopy has been used.

EXPERIMENTAL TECHNIQUE

The amorphous alloy $Co_{77}B_{23}$ was prepared at Ruhr University, Bochum, Germany by rapid quenching of the melt, using the free jet melt spinning technique (1–3). Metallic ribbons about 3 mm wide and 30 μm thick were prepared in this way. The amorphous or glassy nature of the ribbon specimen so obtained was ascertained by X-ray diffraction analysis. Such an alloy being in metastable state tends to settle to a stable crystallization state on heating at a certain minimum temperature called crystallization temperature.

The dynamic resistivity measurement technique (8, 9) was used to determine the crystallization temperature of the ribbon sample. A 15-cm-long ribbon piece was fixed onto a small and thin unglazed ceramic slab with four thin tungston wire springs along a straight line. The whole assembly was put in a Gallenkamp tube furnace and heated at a constant rate of 50 K/h in an inert atmosphere of argon. The four tungston wire springs also served as electrical contacts with the sample, whose resistivity was determined by the potential probe method using the apparatus shown in Fig. 1.

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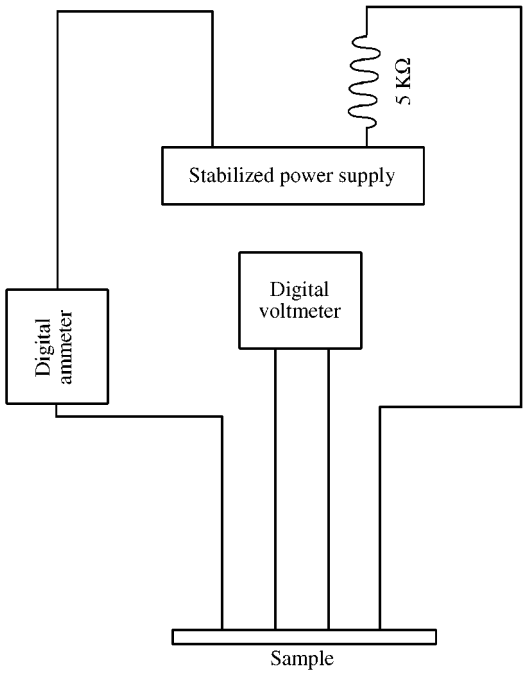

FIG. 1. Potential probe circuit used to measure resistivity.

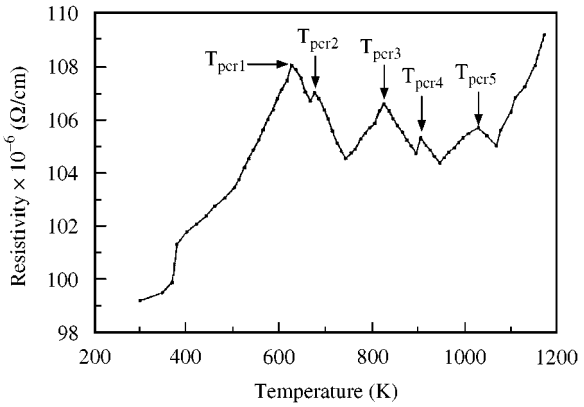

FIG. 2. Variation of resistivity with temperature of $Co_{77}B_{23}$ amorphous alloy.

In order to investigate the mechanism of crystallization of the amorphous $Co_{77}B_{23}$, a ribbon sample 1.0 cm long was taken and cleaned in acetone in an ultrasonic cleaner. The sample was then mounted on the heating stage of the Auger electron microprobe (Jeol Jamp 10-S). The microprobe has the built-in facility to sputter the sample with argon ions (Ag^+) at 3.0 keV energy. The Auger analysis was carried out in vacuum on the order of 5×10^{-10} torr. The Auger spectrum was recorded in differential mode.

RESULTS AND DISCUSSION

The resistivity as a function of temperature T is plotted in Fig. 2. Discrete peaks can be seen at different temperatures. At these temperatures, the rate of change of resistivity with temperature ($d\rho/dT$) changes sign due to a phase change (13). These peaks are marked as T_{pc1}, T_{pc2}, T_{pc3}, T_{pc4}, and T_{pc5}. The first peak at T_{pc1} occurs at crystallization temperature 600 K. X-ray diffraction of the specimen carried out at 850 K revealed the crystalline structure of the sample as orthogonal Co_3B. Because of low hysteresis losses in cobalt–boron amorphous alloys, they are being considered for making transformer cores. The crystallization temperature of 600 K found in this work is quite higher than the maximum working temperature found in transformers, including the large distribution transformers. A cobalt–boron amorphous transformer core would further decrease the working temperature because of low hysteresis losses.

The Auger spectrum of as received $Co_{77}B_{23}$ amorphous sample contained only peaks of oxygen and carbon with no visible peaks of cobalt or boron. A layer of carbon and oxygen completely covered the sample surface. This difficulty was resolved by a 11-min. sputtering with Ar^+. The new spectrum after sputtering is presented in Fig. 3A, where

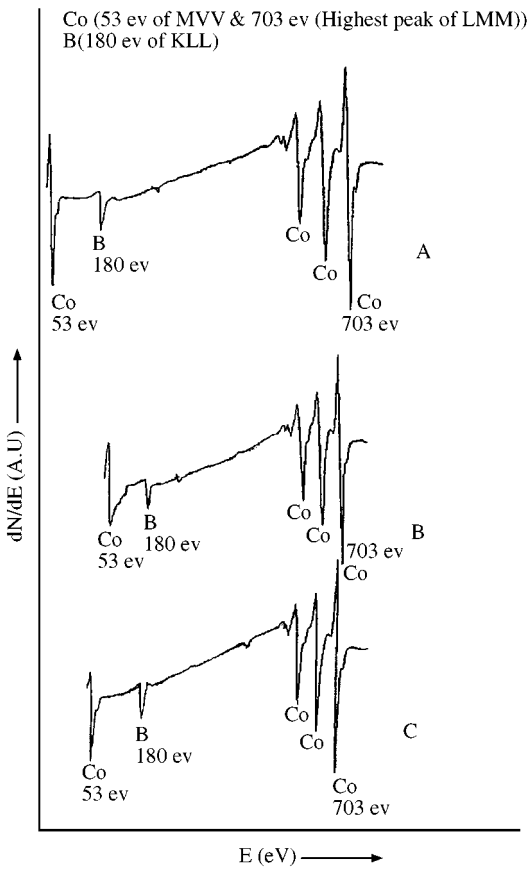

FIG. 3. Auger spectra during dynamic heating: (A) as received without heating, and heating for 1 min, at (B) 573 K and at (C) 973 K.

TABLE 1
Cobalt and Boron Auger Peak Ratios

	Room temperature	After heating to 573 K	After heating to 973 K
Co peak/B peak	1.65	2.69	2.46

the low-energy Co peak at 270 eV and high energy triplet peaks, with highest energy peak at 703 eV, can be seen. The B peak at 510 eV can also be seen in the same figure. C and O peaks are almost completely eliminated.

The sample was heated for 1 min. and afterward its Auger spectrum was obtained as shown in Fig. 3B. Later the sample's temperature was raised to 973 K. The temperature was held at that value for 1 min. and its Auger spectrum was obtained. This spectrum is presented in Fig. 3C.

The Co and B Auger peak ratio (Co peak at 703 eV) is determined at room temperature (after 11 min. sputtering), and at 573 and 973 K. The results are presented in Table 1. This ratio is higher after heating, suggesting an inward diffusion of light boron atoms. This causes an excess of cobalt atoms on the amorphous surface and makes it more unstable. This leads to crystallization. The lower Auger peak ratio at 973 K is probably due to reverse diffusion of boron atoms. Co_2B crystals have been formed upon heating the sample at 973 K. These have been detected through X-ray diffraction analysis. Co_2B has a greater proportion of B than that in amorphous $Co_{77}B_{23}$ alloy. This may be responsible for the reverse diffusion.

CONCLUSION

The crystallization temperature of $Co_{77}B_{23}$ amorphous alloy was measured by the well-tried resistivity-measurement method and found to be 600 K. The first peak in the resistivity versus temperature curve indicates the onset of crystallization and hence gives a crystallization temperature of the specimen that is higher than the working temperature in a transformer. Hence $Co_{77}B_{23}$ amorphous alloy can be used for making transformer cores.

The mechanism of crystallization was studied by observing the changes in chemical composition of the specimen on heating, using Auger microprobe. The first heating temperature of 573 K, a little below the crystallization temperature of 600 K, causes an inward diffusion of B atoms, leaving an excess of Co atoms on the surface, which leads to the onset of crystallization. The lower Auger peak ratio at 973 K is probably due to reverse diffusion of boron atoms.

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