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Resistivity measurements and Crystallization of Phases in a Series of Co_{100-x}-B_x Metallic Glasses

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Abstract

A systematic study of electrical resistivity of a series of $Co_{100-x}B_x$, where x=30, 29, 27, 25, 24, 23, 21.5 and 20.5, amorphous alloys in the temperature range of 300 to1000 K was undertaken. The analysis of data established step-wise crystallization. It has been of particular interest to study the range of formation of different phases and their transformation to thermodynamically stable phases at higher temperatures.

Keywords: Phase Transformations; Electrical Resistivity; Co-B Alloys

INTRODUCTION

The crystallization behavior of $Co_{100-x}B_x$ metallic glasses have been studied [1-4]. The most interesting feature is the step-wise crystallization in these amorphous alloys [1-5]. Similar behavior has also been noted in Fe-B and other metallic glasses having different compositions [3,6-9]. The temperature at which crystallization starts and finishes are dependent upon a number of factors such as, alloy composition, rate of quenching/cooling during preparation [10] and heating rates during the crystallization [11]. In another of our work the differential thermal analysis for the four Co-B alloys were analyzed and compared with dynamic temperature X-ray diffraction (DTXRD) and electrical resistivity measurements [11]. The high order of accuracy achievable in this technique was the main reason of the measurements of anomalies in the crystallization temperatures of the alloys. Furthermore, the thermodynamic equilibrium was attained exactly at phase transformation where crystal structure changes from one type to the other, mainly due to the exact control of the heating rate. Present study undertakes determination of the onset, end and the intermediate stages of crystallization by measuring electrical resistivity during slow heating of the samples in the temperature range of 300 to 1000 K.

EXPERIMENTAL

A series of six alloys of alloys, $Co_{100-x}B_x$ were chosen for this work. Boron content was varied from 20.5 to 30. All the amorphous alloys were prepared under identical conditions using jet melt spinning method in helium atmosphere. Details are given elsewhere [12,13]. The thin ribbons formed were 2-3 mm wide and 3-4 µm thick.

For electrical resistivity measurements, four probe method was used. The pressure contacts were employed on the ribbon sample of 2 cm length placed on sample holder made of mica. For high temperature, the assembly was placed in a furnace. The heating rate of the furnace was carefully controlled to 60-75 K/hr. The equipments used for resistivity measurements were Kiethley multimeter -197, a constant-current source, Digistant-6426 and Fenwal digital thermometer with sensor. Resistance hence resistivity with change in temperature was calculated and plotted for each sample.

RESULTS and DISCUSSION

The changes in electrical resistivity (*ρ*) were noted against the rise in temperature (*T*) and were plotted for all the six alloys up to 1000 K. For one alloy $Co_{71}B_{29}$ data over 700 K could not be recorded.

The *ρ*-*T* curves bring out the general behavior in these alloys, i.e., stress relaxation of the amorphous matrix up to about 600 K; a well defined threshold temperature marking the onset of crystallization, diffusional coalescence and progress of crystallization leading to insulator-metal transition.

At temperatures below 700 K, the visible kinks in the *ρ* versus *T* curve (inset of Fig. 1) are due to thermal stress relaxation and progressive diffusional recovery processes in the quenched amorphous alloys of $Co_{70}B_{30}$. Around 730 K, the sudden changes in *ρ* values are indicative of the onset of phase transformation. At higher temperature insulator-metal transition is distinctly recorded by the peak values at 820 and 905 K (Fig. 1). This is also indicative of the stepwise crystallization as reported in earlier studies [5]. Values of *ρ* were recorded up to 700 K and *ρ*-*T* curve (Fig. 2) shows two stage thermal stress relaxation and diffusional recovery process for $Co_{71}B_{29}$.

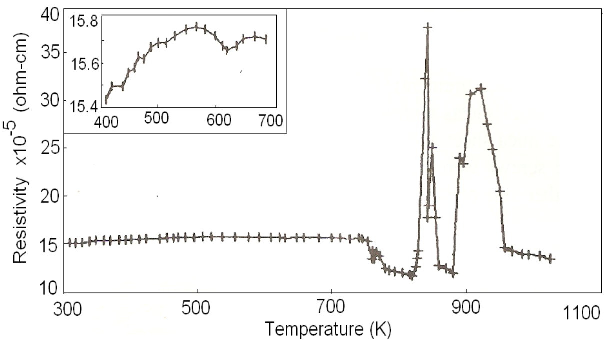

Figure 1. Electrical resistivity versus Temperature for amorphous alloy Co_{70} B_{30} in a temperature range of 300-1000 K.

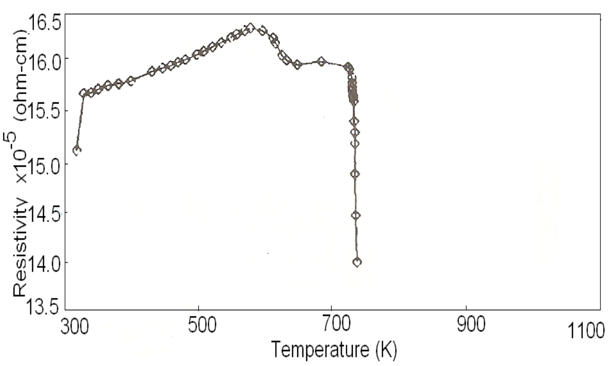

Figure 2. Electrical resistivity versus Temperature for amorphous alloy $Co_{71}B_{29}$ in a temperature range of 300-1000 K

In $Co_{73}B_{27}$ alloy, several thermal relaxations occurred up to about 700 K (inset of Fig. 3). Threshold phase transformation temperature is recorded at 740 K followed by two stage insulator-metal transition giving peak values of ρ at 760 K (Fig. 3). Several stages of diffusional recovery were recorded for $Co_{76}B_{24}$ below 700 K. Phase transformation starts around 700 K. The step fall of ρ in the temperature range 700 to 730 K, represents fast growth of crystallites and insulator-metal transition (Fig. 4). $Co_{78.5}B_{21.5}$ shows two stages of thermal stress relaxation prior to the onset of crystallization at 695 K. Arrhenius exponential function governs coalescence and crystal growth in the temperature range 675-740 K (Fig. 5).

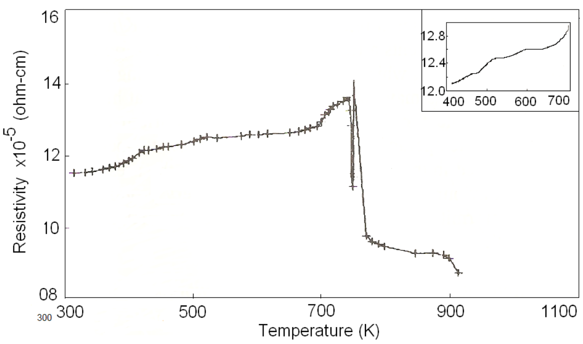

Figure 3. Electrical resistivity versus Temperature for amorphous alloy Co_{73} B_{27} in a temperature range of 300-1000 K

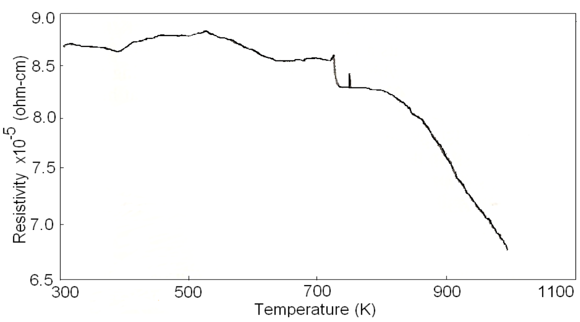

Figure 4. Electrical resistivity versus Temperature for amorphous alloy Co_{76} B_{24} in a temperature range of 300-1000 K

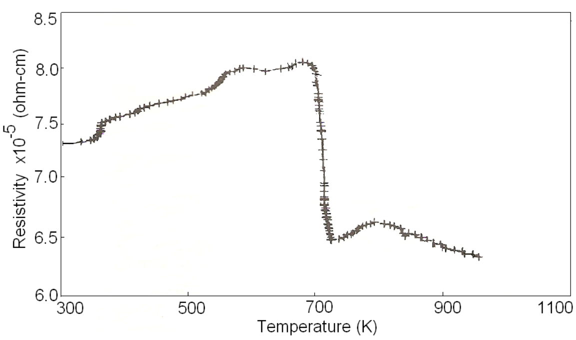

Figure 5. Electrical resistivity versus Temperature for amorphous alloy $Co_{78.5}B_{21.5}$ in a temperature range of 300-1000

K

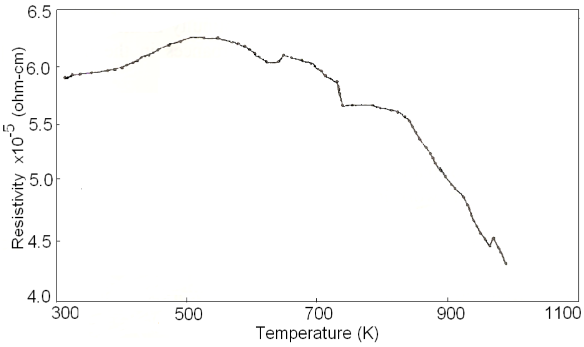

Figure 6. Electrical resistivity versus Temperature for amorphous alloy $Co_{79.5}$ $B_{20.5}$ in a temperature range of 300-1000 K

In the $Co_{79.5}B_{20.5}$ amorphous glassy matrix undergoes stabilization by diffusional recovery in three stages. Onset of crystallization occurs at 690 K (Fig. 6). Following Arrhenius law, natural exponential growth of the crystalline phase occurs leading to insulator-metal transition which is followed by change in crystal structure at higher temperature.

In the six samples heated at relatively slow rate of 1-1.4 K/min, the ρ-T curves show several peaks, each represents a transition stage of crystallization. However, in the two samples $Co_{77}B_{23}$ and $Co_{75}B_{25}$; heated at rates exceeding 5 K/min, the peaks were not very sharp. This may be attributed to the fact that at higher heating rates, enough time is not available for the system to reach equilibrium at the intermediate transition stages and high temperature phase competes the low temperature phase; thereby only hump is registered in the curve plotted. However, in the present work, the step-wise crystallization behavior of these metallic glasses is very prominently displayed in the *ρ-T* curves, in conformity with results so far obtained by dialatometry and DTXRD measurements [4,5,11].

DTA measurements were performed by several workers using different equipments and heating rates varying from 0.5 to 10 C/min [11]. The resistivity measurement for Co-B series are in agreement with DTA and DTXRD results [11]. They support step-wise crystallization for alloys containing 20.5 to 30 at. % boron.

The linear behavior of *ρ-T* curves up to about 600 K is suggestive of the fact that thermal excitation and diffusion of atoms is not optimum to form stabilized nuclei leading to growth of crystalline phase. Any discontinuity in the curves below 600 K is mainly due to the stress relaxation and thermal disturbances in the matrix and not a manifestation of phase changes.

CONCLUSION

Summing up the information from the resistivity measurements of Co-B alloys and their analysis in the light of this work leads to the following conclusion.

- Liquid quenched amorphous Co-B alloys undergo stress relaxation up to a temperature of about 600 K. As depicted by the variation in *ρ-T* curves; the diffusional recovery process takes place in several stages thereby helping the quenched in nuclei to attain critical size. A further rise in temperature sets in phase transformation.
- In alloys containing 20-30 at. % boron, the onset of phase transformation is well above 600 K, which is in agreement with the results obtained by DTA measurements [11].
- Once the threshold temperature of phase transformation is crossed, *ρ-T* curve registers a step fall reflecting natural exponential growth of crystallites.
- In B-rich alloys like $Co_{70}B_{30}$ and $Co_{73}B_{27}$ step-wise crystallization of metastable phase is distinctly observed while in alloys with decreasing amount of boron the metastable crystalline phases overlap each other and the *ρ-T* curve does not register any sharp peak.

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