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A STUDY OF CRYSTALLIZATION BEHAVIOUR OF GLASSY $Co_{79.5}B_{20.5}$ ALLOY USING DYNAMIC TEMPERATURE X-RAY DIFFRACTION AND RESISTIVITY MEASUREMENTS

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In this paper results of a study on the crystallization behaviour of glassy $Co_{79.5}B_{20.5}$ alloy resistivity measurements are presented. Results are also presented of measurements of transition temperatures after crystallization.

1. Introduction

Amorphous alloys, since their first fabrication in 1960 by Klement et al.[1] have attracted world wide interest as materials for scientific study and technological applications. An important property of these alloys is their crystallization on heating. This property has been studied using differential thermal analysis (DTA), differential scanning calorimetry (DSC), dynamic temperature X-ray diffraction (DTXD) by a number of workers[2-16].

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It has now been generally accepted that amorphous alloys contain quenched in nuclei[17]. These nuclei determine the phase that will be formed on crystallization. Continuous monitoring of phase changes with increasing temperature is, therefore, helpful for an understanding of crystallization in these materials. This paper presents the results of crystallization behaviour of an amorphous $Co_{79.5}B_{20.5}$ alloy using both dynamic temperature X-ray diffraction method and resistivity measurements.

2. *Experimental work*

Fabrication details of this alloy are given elsewhere[18]. Amorphous ribbons of the $Co_{79.5}B_{20.5}$ alloy of about 2 mm in width and 35 μm in thickness were used in this work.

For the DTXD modified Enraf- Nonius Guinier Lenne type high temperature X-ray camera was used[19]. For the X-ray source a Philips cobalt anode 1200 W fine focus X-ray tube was used. Nine pieces of ribbon, about 14 mm long were placed side by side on their flat surfaces and heated from 300 to about 1000 K, in the DTXD chamber in a vacuum which was better than 10^{-4} Pa. The heating was lcarried out at a constant rate of 50 K/hr.

The phase transition temperature can also be detected by measuring the variation of resistivity temperature[20-22]. For this purpose a 6 cm long ribbon of the specimen was chosen. As the resistivity of this specimen was only of the order of $10^{-4}\Omega \cdot$ cm, the contact resistance could introduce uncertainties in direct resistivity measurements. The potential probe method was, therefore adopted[23]. This method required four contacts with the specimen. Use of soldered and spot welded contacts were ruled out as the heating would change the physical nature of the sample in the vicinity of the contacts. Painted and plated contacts could not stand high temperature. The only alternative left was to use pressure contacts. This method was selected and successfully used in this work and is described in detail elsewhere[20,21]. The outer contacts were used as current contacts and the middle two as potential contacts ceramic beads were slipped over tungsten wire leads to avoid short circuiting. The specimen was heated in a Gallenkamp tube furnace No.4B-6432-1 in an inert atmosphere of argon to avoid oxidation of the specimen and the leads. A constant current of 5.0 mA was supplied with a stabilized power supply. The current was measured with a digital multimeter and the potential difference with a digital voltmeter (Hewlett Packard 3465 A). The heating rate was kept at 40 K/hr.

3. *Results and discussions*

Fig. 1. shows the DTXD pattern of the amorphous $Co_{79.5}B_{20.5}$ alloy in the temperature range 300 to 1000 K. It is seen from the pattern that the amorphous alloy crystallizes at about 625 K. This is the temperature at which the diffraction halo due to the amorphous state starts disappearing and relatively sharp X-ray diffraction lines begin to appear. All these reflections can be indexed on the basis of a body centred tetragonal (bct) unit cell of the Fe_3P-type. However, a fraction of the material still remains amorphous at this stage. At about 655 K the halo disappears completely showing that the whole of the amorphous material has

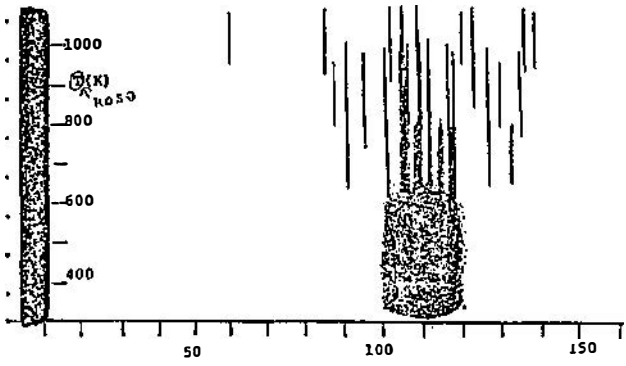

Fig. 1. Dynamic temperature X-ray diffraction (DTXD) pattern of $Co_{79.5}B_{20.5}$.

crystallized. At the same time new X-ray diffraction lines appear in the DTXD pattern, which can be indexed on the basis of an orthorhombic structure (*O*) of the type Fe_3 C-type and a hexagonal structure of A_3-type. A comparison of the observed relative intensities of the diffraction lines due to the orthorhombic phase with those due to the bct phase has revealed that the orthorhombic phase amounts to only about 15% of the total. This shows that the major phase crystallizing from the amorphous $Co_{79.5}B_{20.5}$ alloy is the bct phase. It is, therefore, suggested that the first crystallization product of amorphous $Co_{79.5}B_{20.5}$ is polymorphic. With further increase in temperature the bct transforms into the primitive tetragonal

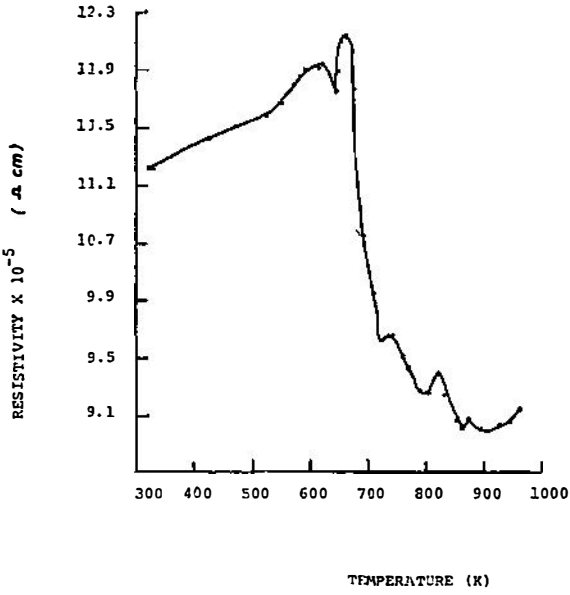

Fig. 2. Variation of resistivity of $Co_{79.5}B_{20.5}$ with temperature.

(pt) phase at 745 K. Finally, at 825 K a further transformation into the orthorhombic phase and the face centred cubic (fcc) cobalt takes place. The orthorhombic phase undergoes a further transformation into fcc cobalt, at about 880 K.

During this transformation excess of boron probably diffuses to the grain boundaries, forming an amorphous phase, which cannot be detected with X-ray diffraction. Babić et al.[24] have reported similar phenomenon in $Fe_{40}N_{40}B_{20}$ alloy.

Generally, the resistivity of a material increases with temperature. However, when a phase change occurs in the material, the slope of the resistivity versus temperature curve becomes zero[25]. Thus the curve has a peak at a phase transition. Fig. 2 shows the variation of resistivity of amorphous $Co_{79.5}B_{20.5}$ alloy. The first peak at A is produced by an amorphous to first crystalline phase- change. Peaks at B, C, D and E correspond to subsequent phase changes. The phase transition temperatures, T_{cr}, T_1, T_2, T_3 and T_4 corresponding to peaks at A, B, C, D and E respectively are compared with their corresponding values obtained with the DTXD technique in Table 1. DTXD values, in general are higher than their corresponding values obtained with resistivity measurements. The last row of the table shows a percentage difference between the DTXD and the corresponding resistivity measurements. A +ve sign means a higher and −ve sign a lower DTXD value.

TABLE 1.

	T_{cr}	T_{p1}	T_{p2}	T_{p3}	T_{p4}
I. DTXD results	625	655	745	825	880
II. Present work	621	663	743	823	867
% age difference between I & II	+0.64	−1.22	+0.27	+0.24	+1.48

A comparison of Figs. 1 and 2 show that resistivity measurements define the phase transition temperatures more precisely as the resistivity distribution peaks are fairly sharp. The diffraction lines at the start of a new phase are weak in intensity. The intensity increases to a maximum as the temperature is increased. This introduces a considerable uncertainly in the determination of phase transition temperature. However, the structural information can only be obtained with X-ray diffraction. Thus the resitivity method can be used to supplement the X-ray diffraction analysis.

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ISTRAŽIVANJE KRISTALIZACIJE AMORFNE SLITINE $Co_{79,5}B_{20,5}$ POMOĆU DINAMIČKE VISOKOTEMPERATURNE DIFRAKCIJE RENDGENSKIH ZRAKA I MJERENJA OTPORA

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Istraživana je kristalizacija amorfne slitine $Co_{79,5}B_{20,5}$. Korištena su dinamička visokotemperaturna difrakcija rendgenskih zraka i mjerenje električnog otpora. Kristalizacija koja počinje oko 625 K odvija se kroz više metastabilnih kristalnih faza te završava izlučivanjem kubičnog plošno centriranog kobalta oko 880 K. Simultana mjerenja električnog otpora dobro se slažu sa rezultatima rendgenske difrakcije te omogućavaju točnije određivanje temperatura promjena faza.