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Differential Thermal Analysis of Liquid Quenched Co-B Alloys

S. Dabir H. Rizvi Shabana Rizvi

Department of Physics, University of Karachi, Karachi-75270, Pakistan

Corresponding author
Email: srizvi2211@gmail.com

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Abstract

Differential Thermal Analysis (DTA) was performed on four samples of liquid quenched amorphous Co-B alloys, up to a temperature of 1000C, well above crystallization temperature of the four alloys. Phase transition study for the four samples were undertaken and the results were found in agreement with electrical resistivity.

Keywords: Differential Thermal Analysis; Liquid Quenched Amorphous Alloys; Co-B Alloys

INTRODUCTION

Alloy systems showing at equilibrium restricted terminal solubility together with a limited tendency to form intermediate phases are found to be specially susceptible to the formation of metastable phases by rapid quenching. The new phases formed cover a wide range of crystal structure and amorphous solid phases. The metastable phases like pure element are generally characterized by simple crystal structure, mainly cubic hexagonal and tetragonal. [1]

The concept of stable states as represented in the equilibrium diagrams are crucial in the study of physicochemical behavior of alloys. However, many practical applications we are encountered with metastable phases having higher free energy than corresponding stable states and tends towards the stable condition when supplied with the necessary thermal activation. The essential step in achieving metastability involves either direct supply or excess free energy by working or suppression of an equilibrium phase by quenching from higher temperature. During quenching if sufficient undercooling is achieved with none or negligible nucleation of equilibrium phases, one or more metastable phases may form at these lower temperatures. On subsequent ageing or annealing the metastable phase may revert back to form the equilibrium phase directly or through some intermediate phases.

Out of a number of liquid quenched amorphous alloys of Co_{100-x} B_x series, four were chosen for study of phase transition in these super cooled metallic glasses. Differential thermal analysis (DTA) was mainly used to measure glass transition temperature and progressive crystallization phenomenon. Results of DTA were compared and supplemented with Dynamic Temperature X-ray Diffraction (DTXRD) and Electrical Resistivity measurements reported in earlier works [2-4].

EXPERIMENTAL

All the four alloys, $Co_{79}B_{21}$, $Co_{78.5}B_{21.5}$, $Co_{77}B_{23}$ and $Co_{75}B_{25}$ were studied under identical conditions of controlled atmosphere. The constituents were taken in a water cooled quartz tube and melted in high frequency induction furnace. The final composition of the alloys were taken to be that of the weighted samples. The alloys were formed into 2-3 mm wide and 30-40 μm thick ribbons by jet-melt spinning under a helium gas pressure of about 250 mbar, using the outer surface of a rapidly rotating copper wheel as a substrate [5].

Differential thermal analysis (DTA) of $Co_{77}B_{23}$ and $Co_{75}B_{25}$ were carried out in a DTA apparatus under

nitrogen atmosphere at a heating rate of 10 C/min. DTA for samples $Co_{78.5}B_{21.5}$, $Co_{77}B_{23}$ and $Co_{75}B_{25}$ were also performed in a Shimadzu DT-30B apparatus controlled by DTA-TG cell type DGC-30 with analysis cell TMC 30. The specimens were heated in alumina crucible in open air (thermally shielded) at a rate of 10 C/min. DTA of $Co_{79}B_{21}$ were carried out in a Linseis DTA apparatus at a heating rate of 0.5 K/min [2].

The crystallization behavior of these alloys namely $Co_{79}B_{21}$, $Co_{77}B_{23}$ and $Co_{75}B_{25}$ were investigated by the Dynamic Temperature X-ray Diffraction (DTXRD) method [2,4]. Electrical Resistivity for two of the samples $Co_{77}B_{23}$ and $Co_{75}B_{25}$ were measured using four probe method [4].

All these measurements of DTXRD, DTA and Electrical resistivity were carried out to supplement the results obtained by any one single method.

RESULTS and DISCUSSION

For alloys $Co_{79}B_{21}$ [2] following observations were made:

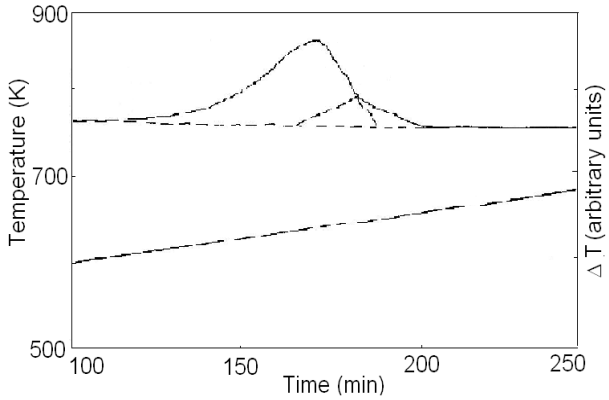

Figure 1a. DTA for $Co_{79}B_{21}$ [2]

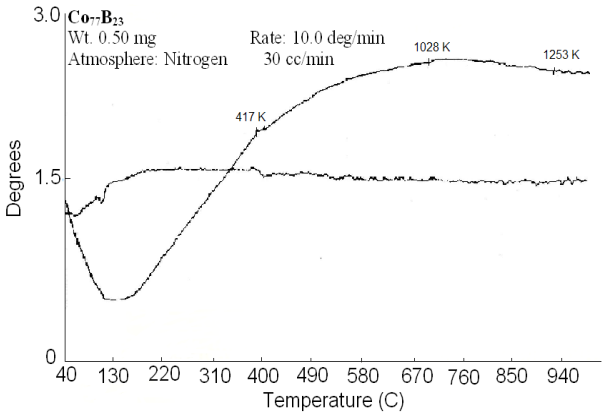

Figure 1b. DTA for $Co_{77}B_{23}$

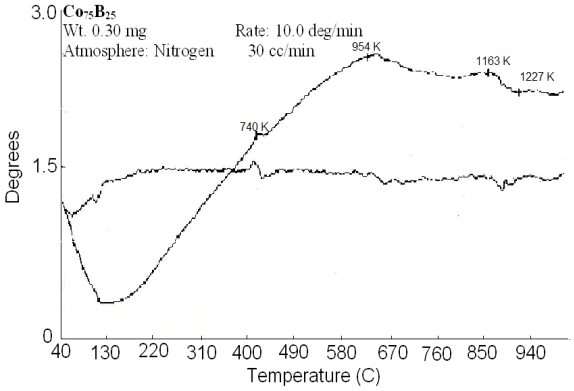

Figure 1c. DTA for $Co_{75}B_{25}$

DTXRD Data: Heating rate 50 K/hr ~ 1 C/min

Amorphous phase $\xrightarrow{620\,K}$ bct $Co_{3+x}B$ + Amorphous matrix

$\xrightarrow{650\,K}$ bct $Co_{3+x}B$ + O-Co_3B + Hex-Co

$\xrightarrow{620\,K}$ pt-$Co_{3+x}B$ + O-Co_3B + Hex-Co

$\xrightarrow{800\,K}$ O-Co_3B + fcc-Co

$\xrightarrow{1000K}$ bct-Co_2B + fcc-Co

Five steps of crystallization were recorded.

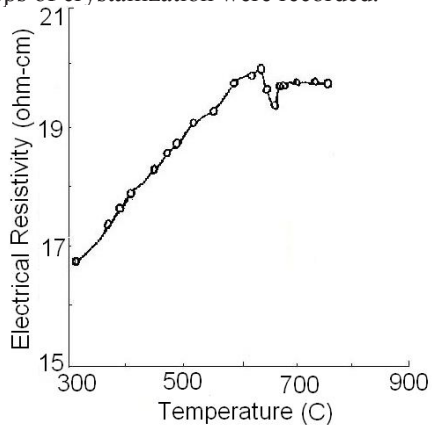

Figure 2a. Electrical Resistivity of $Co_{77}B_{23}$

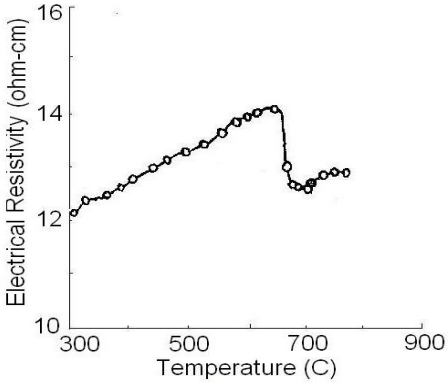

Figure 2a. Electrical Resistivity of $Co_{75}B_{25}$

DTA Data: Heating rate 0.5 K/min ~ 0.5 C/min (Fig. 1a)

LQA $Co_{79}B_{21}$ crystallizes in two steps.
First crystallization occurs at 610 K and second stage of crystallization is recorded at 640 K.
For alloys $Co_{77}B_{23}$ and $Co_{75}B_{25}$ DTXRD, Electrical Resistivity and DTA measurements [4] were recorded as:

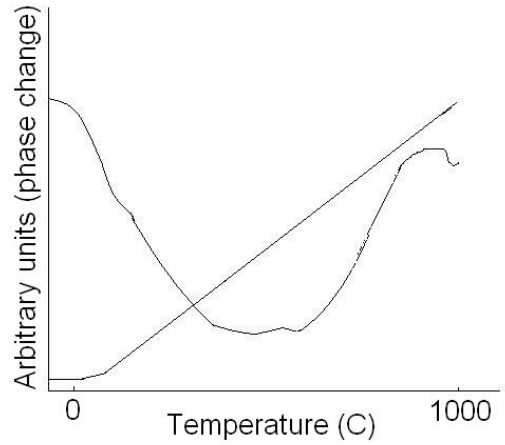

Figure 3a. DTA for $Co_{78.5}B_{21.5}$

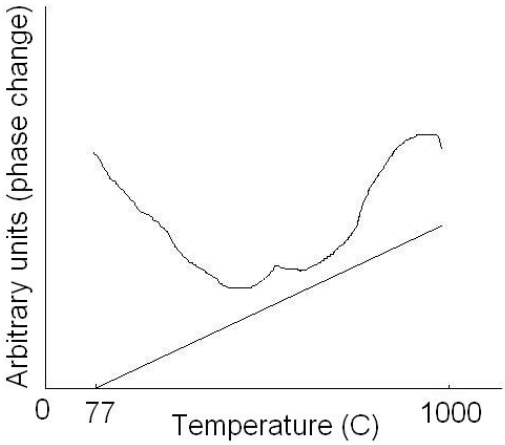

Figure 3b. DTA for $Co_{77}B_{23}$

DTXRD Data for $Co_{77}B_{23}$: Heating rate ~ 1 C/min

Amorphous matrix $\xrightarrow{620\,K}$ bct- Co_3B + Amorphous matrix

$\xrightarrow{670\,K}$ bct- Co_3B + Hex-Co

$\xrightarrow{820\,K}$ bct-Co_2B + Hex-Co + O-Co_3B

$\xrightarrow{900\,K}$ bct-Co_3B + fcc-Co

$\xrightarrow{1020\,K}$ bct-Co_2B

Five steps of crystallization were recorded.

Electrical Resistivity for $Co_{77}B_{23}$: Heating rate > 5 C/ min

(Fig. 2a)

Two stage transformation recorded
First stage occurred around 640 K
Second stage occurred around 690 K

Table 1: Data using Shimadzu DTA

Alloys composition	1st stage	2nd stage	3rd stage	4th stage
$Co_{78.5}B_{21.5}$	645K	837K	1033K	1233K
$Co_{77}B_{23}$	665K	857K	1049K	1241K
$Co_{75}B_{25}$	657K	857K	1049K	1225K

DTA Data for $Co_{77}B_{23}$: Heating rate 10 C/min (Fig. 1b)

Three stages were observed.
1st stage was very prominent at 717 K.
2nd stage at 1028 K and 3rd stage at 1253 K were not very clearly shown.

DTXRD Data for $Co_{75}B_{25}$: Heating rate ~ 1 C/min [4]

Amorphous $Co_{75}B_{25}$ $\xrightarrow{640\,K}$ bct- Co_3B + O-Co_3B

$\xrightarrow{930K}$ bct- Co_2B + Co_3B

Only two stages of crystallization were recorded as compared to five stages in the alloys $Co_{79}B_{21}$ and $Co_{77}B_{23}$.

Electrical Resistivity for $Co_{75}B_{25}$: Heating rate > 5 C/ min

(Fig. 2b)

As for alloy $Co_{77}B_{23}$, two stages of transformation was noted

1st stage occurred at 640 K
2nd stage occurred at 670 K

DTA Data for $Co_{75}B_{25}$: Heating rate 10 C/min (Fig. 1c)

Four stage transformation was recorded.

1st change occurred at 740 K
2nd change occurred at 954 K
3rd change occurred at 1163 K
4th change occurred at 12294 K

DTA data for three of the alloys using Shimadzu DTA apparatus DT-30B at a heating of 10C/min is given in table 1. See also Fig. 3a and 3b. In each of the three alloys

four stages of crystallization has been identified.

The data obtained by DTA, DTXRD and Electrical Resistivity for the four Co-B metallic glasses are all indicative of the stepwise crystallization process, transforming the amorphous matrix to the crystallized structure is given in table 2. However, the number of steps rather the number of intermediate metastable phases formed seems to be changing with the method of analysis used.

Table 2. Comparison of data

Alloys	DTXRD	Electrical Resistivity	DTA Linseis	DTA	DTA Shimadzu
$Co_{79}B_{21}$	5 stages	-	2 stages	-	-
$Co_{78.5}B_{21.5}$	-	-	-	-	4 stages
$Co_{77}B_{23}$	5 stages	2 stages	-	3 stages	4 stages
$Co_{75}B_{25}$	2 stages	2 stages	-	4 stages	4 stages

DTXRD has very clearly depicted the gradual crystallization process in all the four alloys. In two of the alloys; $Co_{79}B_{21}$ and $Co_{77}B_{23}$, the final crystallized state is reached through five intermediate phase transformations. In the alloy $Co_{75}B_{25}$, however, only two step crystallization is recorded [4].

Electrical Resistivity measurements carried out for two of the alloys namely $Co_{77}B_{23}$ and $Co_{75}B_{25}$ indicate two stage process of crystallization.

Interesting results were obtained using DT analysis. Three different dialatometers were used by three group of workers. Each set of data obtained differs from the others. The discrepancies in DTA results is mainly attributed to the different rates of heating used with the three dialato meters and also due to the attainable accuracy in the measurement of volume change in each case.

It is noted that when the heating rate was low of the order of 0.5-1 C/min, the volume change occurring during intermediate phase transformations was well marked, whereas, at higher rates of heating $\geq$ 10 C/min, changes occurring due to metastable phases were obscured. This is in total agreement with the kinetics of phase change when and where the magnitude of transformation from one phase to other is relatively small and/or thermodynamic equilibrium is gained in longer times. In the light of the above discussion it seems proper to stress the point that in all phase transformation studies, heating or cooling should be at a rate as nearer to the equilibrium state of the system as possible and more so if a record of metastable phases are to be obtained. This is more true in the case of crystallization of metallic glasses where the quenched in vacancies and quasi-nuclei both play a very important role.

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