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Experimental studies of the amorphous to crystalline transition of $Fe_{79}B_{16}Si_5$, $Fe_{78}B_{13}Si_9$

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ABSTRACT

The transformation from the as quenched amorphous to the crystalline state of iron based metallic glasses with the following composition $Fe_{79}B_{16}Si_5$ and $Fe_{78}B_{13}Si_9$ has been investigated by electrical resistivity measurements and x-ray diffraction. Samples were continuously heated from room temperature up to beyond the crystallization temperature of these amorphous alloys using constant heating rates. The onset of crystallization was marked by a steep decrease in resistivity upon further increase in temperature. The final products of crystallization were found to be α Fe (Si) solid solution, Fe2B tetragonal and Fe_3B orthorhombic.

KEYWORDS

$Fe_{79}B_{16}Si_5$;
$Fe_{78}B_{13}Si_9$;
XRD;
Amorphous;
Crystalline.

1. INTRODUCTION

The research in the field of metallic glasses has been a topic of interest since (1960). Amorphous metals can be formed by retaining some of the disorder from a vapour or liquid state. This can be achieved by dissipating very quickly the heat generated by the kinetic energy thus inhibiting the migration of the atoms and preserving the disorder. Whichever way they are prepared amorphous metals are not in configurational equilibrium but are relaxing by a homogenous process towards an "ideal" metastable amorphous state.

The outstanding properties of metallic glasses, however, deteriorate rapidly during crystallization process.

Thus, understanding the process of crystallization is therefore a prerequisite for most applications, since the stability against crystallization determine their effective working limits. S.Thongmee et al.[1] reported that in the B-rich $Fe_{78}B_{16}Si_5$ ribbons, the crystallization is a two stage process: amorphous α-Fe(Si) nanocrystalline formation →(α-Fe, Fe_2B) nonocrystalline formation while the crystallization in the B-poor $Fe_{78}B_{13}Si_9$ ribbons is a three stage process: amorphous→Fe_3B nanocrystalline formation→α-Fe(Si) nanocrystalline formation→(α-Fe, Fe_2B) nanocrystalline formation..

2. EXPERIMENTAL

In order to investigate changes in electrical resistivity of metglass samples when subjected to heat treatments, a suitable sample holder was designed so that measurements could be made of the electrical resistivity up to about 820^0C,on 5 cm long ribbons using the four probe technique. The current and voltage leads were spot welded to the specimen. It was immediately evident

that any temperature-induced reactions between the sample and its chemical environment might produce adverse effects on sample resistivity. For this reason, the experiments were carried out in an Argon atmosphere.

The thermocouple junction was localized to within 1 to 2 mm below the sample (in between the sample and sample holder).the current through the specimen was measured by observing the potential drop across the standard four terminal resistor. Readings of the voltages were taken at one-minute intervals as the temperature rose and subsequently cooled down to room temperature (natural cooling).

3. RESULTS AND DISCUSSION

3.1 Electrical resistivity measurements

In many ways the amorphous alloy $Fe_{79}B_{16}Si_5$ appear similar to $Fe_{78}B_{13}Si_9$ with slight difference in the B/Si ratio. The x-ray data as discussed later for these two amorphous alloys showed that their crystalline products are the same. This inspired us to discuss their electrical resistivity during continuous heating at constant heating rates of 4^0C/min together. Plots of the electrical resistivity versus temperature of $Fe_{79}B_{16}Si_5$ and $Fe_{78}B_{13}Si_9$ are shown in figures 1-6 respectively.

In general, the curves were reproducible for other heating rates. The samples are amorphous in region 1 indicated in the figures. Crystallization starts at the steep

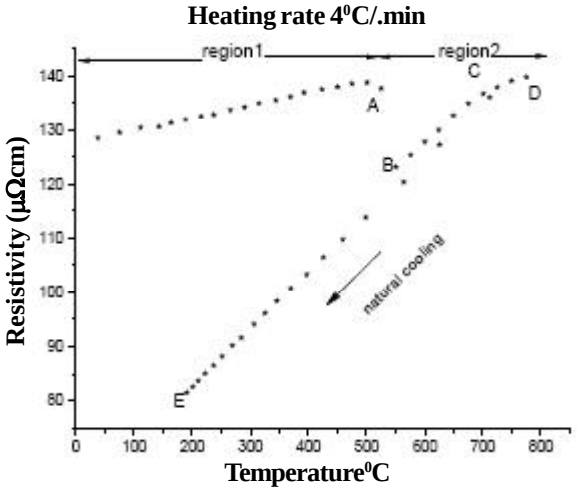

Figure 1: Plot of resistivity as a function of temperature for the alloy $Fe_{78}B_{13}Si_9$

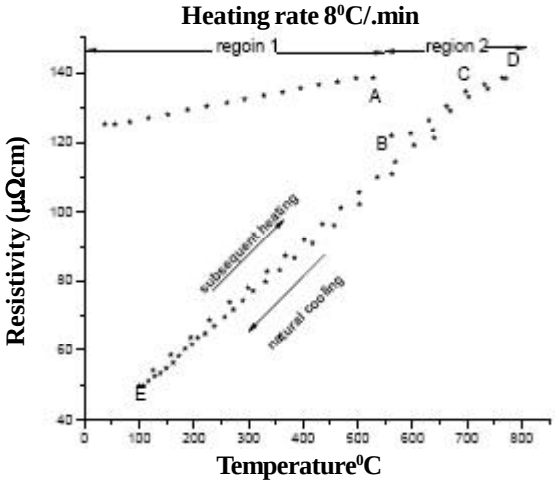

Figure 2 : Plot of resistivity as a function of temperature for the alloy $Fe_{78}B_{13}Si_9$

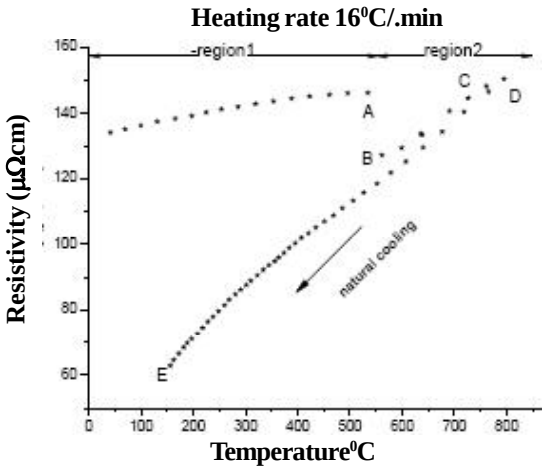

Figure 3 : Plot of resistivity as a function of temperature for the alloy $Fe_{78}B_{13}Si_9$

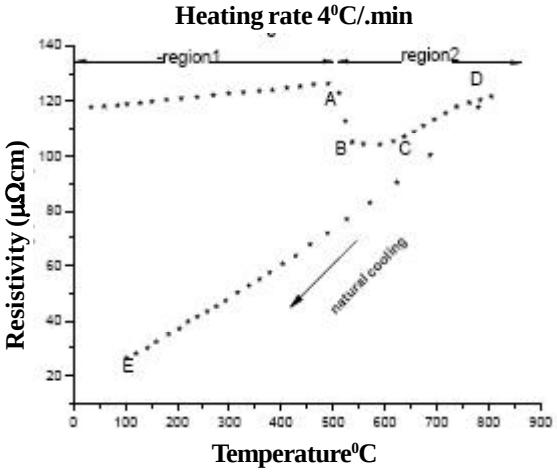

Figure 4 : Plot of resistivity as a funtion of temperature for the alloy $Fe_{79}B_{16}Si_5$

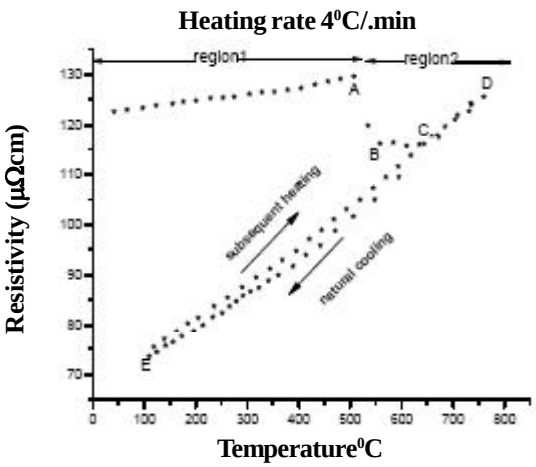

Figure 5 : Plot of ressitivity as a function of temperature for the alloy $Fe_{79}B_{16}Si_5$

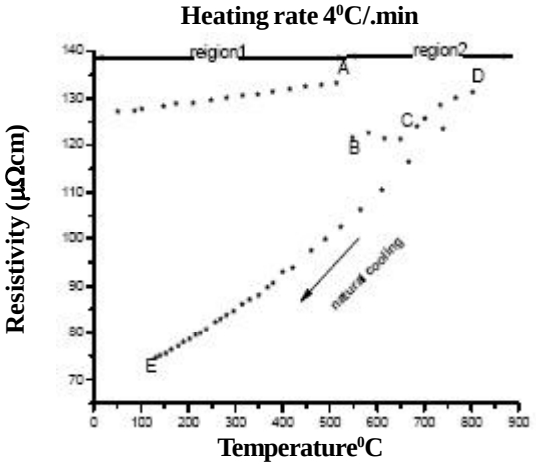

Figure 6 : Plot of resistivity as a function of temperature for the alloy $Fe_{79}B_{16}Si_5$

TABLE 1: Phases identified by x-ray analysis after heating the samples up to T at a constant heating rate of 4⁰C/min and cooled down in the furnace (natural cooling)

Alloy composition 4⁰C/min	Temperature treached at analysis	Phase identified by x-ray
$Fe_{79}B_{16}Si_5$	800	α-Fe(Si)+Fe_2B tetr.+Fe_3B orthorhombic
$Fe_{78}B_{13}Si_9$	780	α-Fe(Si)+Fe_2B tetr.+Fe_3B orth.

decrease at the beginning of region 2. In region one the temperature dependence of electrical resistivity is strictly linear, with a small positive slope $\alpha = 1.16\ 10^{-2}$ μΩcm/ ^{0}C and 2.0710^{-2} μΩcm/ ^{0}C respectively. The complete crystallization process led to a drop of 10 μΩcm for the alloy $Fe_{79}B_{16}Si_5$ and 6 μΩcm for the alloy $Fe_{78}B_{13}Si_9$. In region two, the electrical resistivity behaviour of $Fe_{79}B_{16}Si_5$ is quite different from that of $Fe_{78}B_{13}Si_9$. This suggests probably a different mode of crystallization in $Fe_{79}B_{16}Si_5$ to that in $Fe_{78}B_{13}Si_9$. Inflection points points A to C indicated in the figures are taken as an indication of microstructral changes occurring in the samples.

Unfortunately, no attempt whatsoever has been made to examine the samples at these points. Nevertheless, considering the work of Santiago et al.[2] who have investigated the crystallization process of $Fe_{78}B_{22-x}Si_x$ (x = 9, 10, 13) by x-ray diffraction, electron microscopy and differential scanning and the work by Quivy et al[3]. We can presume that the drop in resistivity at point A may be due to the precipitation of α Fe (Si) solid solution out of the glassy matrix. At point B the remaining amorphous matrix crystallizes and the alloy then contains a mixture of α Fe (Si) and Fe_3B or α Fe (Si), Fe_3B and Fe_2B.

The change in resistivity B to D may be taken as an indication of additional precipitation of α Fe (Si) and/ or transformation of one crystalline phase into another one (or more) like $Fe_3B \rightarrow Fe_2B$ +α Fe since Fe_3B is a metastable phase. On decreasing the temperature from about 800^{0}C (natural cooling), the electrical resistivity follows a linear temperature path. This behaviour is expected after the amorphous sample gets crystallized. There was no further indication of transformation of the crystalline phases during subsequent heating rate of 8^{0}C/ min up to about 800^{0}C, as shown in (figure 2 and figure 5). The portion of the curves labelled D to E (in figure 2 and figure 5),were found to be reversible.

3.2 X-ray diffraction studies

The results of the x-ray data analysis of these two samples were similar to a degree that merits their being discussed together. the as received samples were confirmed to be fully amorphous the x-ray diffractometer traces of these two samples showed only a broad halo centred on $\sin\theta/\lambda$=0.243,which is a characteristic of the glassy phase. The Fe-B-Si glass systems seem to crystallize in Fe_2B tetragonal and Fe(Si) solid solution (see TABLE 1), No α Fe has been detected as one of the crystalline products in $Fe_{82}B_{12}Si_6$[4] and , $Fe_{75.4}B_{14.2}Si_{10.4}$[5]. Furthermore, Santiago et al.[2] in their differential scanning calorimetry, transmission electron microscopy

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TABLE 2: X-ray diffraction data for the annealed $Fe_{78}B_{13}Si_9$

Hkl	2θ	Dobs	Dcal	Peak characteristics	Phases
110	28.7	3.612	3.61	W	Fe_2B
	31.6	3.287		VW	
	36.6	2.851	2.869	VW	Fe_3B
200	41.1	2.550	2.56	M	Fe_2B
	47.4	2.122		VW	
002	49.9	2.013	2.12	M	
110	52.8	1.829	2.027	VS	α-Fe
112-220	58.6	1.807	1.83	W	Fe_2B
	59.4	1.714		VW	
	62.9	1.631	1.69	VW	Fe_3B
202-130	66.5	1.616	1.63	W	Fe_2B
	67.2		1.602	W	Fe_3B

VW: very weak W: weak M: medium VS: very strong

TABLE 3: X-ray diffraction data for the annealed $Fe_{79}B_{16}Si_5$

Hkl	2θ	Dobs	Dcal	Peak characteristics	Phases
110	28.7	3.612	3.61	W	Fe_2B
	29.5	3.516		W	
	32.7	3.180		S	
200	41.0	2.556	2.56	W	Fe_2B
	47.2	2.236		W	
	49.0	2.158	2.150	VW	Fe_3B
022	50.1	2.114	2.12	M	Fe_2B
110	52.6	2.020	2.027	VS	
112-220	58.7	1.826	1.83	VW	Fe_2B
	59.3	1.809		VW	
202	66.5	1.631	1.63	W	
	67.2	1.616	1.602	W	Fe_3B
200	77.4	1.430	1.433	S	α-Fe

VW: very weak W: weak M: medium VS: very strong

and X-ray diffraction studies on metallic glass $Fe_{78}B_{22-x}Si_6$ (X= 9,10,13) reported that the first crystallization step was always characterized by the formation of α Fe(Si) alloy.

In our continuously heated alloy specimen $Fe_{78}B_{13}Si_9$ at a constant heating rate of 4^0C/min (up to about 740^0C),the X-ray diffraction pattern showed very strong Bcc lines, whose lattice parameter is a_0=2.8468Å(see TABLE 2),this lattice parameter is about 0.7% Smaller than the literature value for the pure substance. Since the solubility of boron in bcc iron lattice is very small, only 0.0002% at 983 °K. It may be concluded that the bcc line is a Fe-Si alloy. The value a_0 = 2.8468 for the lattice parameter corresponds approximately to Fe 13 at % Si[6].

In the case of $Fe_{79}B_{16}Si_5$ the X-ray diffraction pattern also showed very strong bcc lines (see TABLE 3) whose lattice parameter is a_0 = 2.856Å, This value is about 0.36% smaller than the literature value for the pure substance. For the same reason cited above, we can conclude that the bcc lattice is a Fe-Si alloy. the value a_0 = 2.856Å correspond approximately to Fe 10 at% Si[6].

The other peaks in the X-ray diffraction analysis, suggested the presence of Fe_2B tetragonal and Fe_3B orthorhombic for both samples. however taking into account the presence of Si,it can be presumed that the slight difference of the d-spacings between those observed and calculated are accounted for, in that the Fe_2B and Fe_3B phases are more complex and rather of $(Fe, Si)_2$ B and $(Fe,Si)_3B$. By comparison with earlier work of Quivy et al[3], we may attribute the drop in resistivity labelled A in all figures to a primary crystallization of α Fe(Si),presumably followed by a polymorphous crystallization of Fe_3B which could have transformed to Fe_2B and α Fe(Si) at higher temperatures. Finally, it has to be mentioned that it has proved impossible to index some of the lines on the basis of known Fe-B-Si structure.

CONCLUSION

This work was aimed to get a better understanding of the amorphous to crystalline transition of series of commercially available metallic glasses by documenting the effects of annealing on the electrical resistivity and examining the x-ray diffraction patterns of the annealed samples. This research provided some interesting and reproducible results concerning the temperature dependence of the electrical resistivity.this was characterized by a drop in the first heating cycle by all samples studied and reversible change during subsequent heating after the crystallization has been completed. the results of this investigation also showed that, the amorphous to crystalline transformation temperature (T_1) greatly depend on the heating rate. in contrast the "overall" temperature spread of crystallization $\Delta T=T_2-T_1$remained unaffected by the heating rate.

Throughout the discussion, inflection points in the resistivity versus temperature plots were taken as an indication of micro structural changes occurring in the samples. A better understanding of phase transformation taking place at these points could be gained by making isothermal aging experiments and studying the process

of crystallization over long periods of time..

The x-ray data analysis showed that the phases present after crystallization seem to correspond to the equilibrium ones.

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