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Influence of glass forming material on atomic and magnetic ordering of Fe-based metallic glass

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Abstract : Fe-based amorphous ribbons have been prepared by melt spinning technique with the general composition $Fe_{90-x}Si_xB_{10}$ [x = 6, 8, 10, 12 and 14]. Since atomic ordering, as manifested by crystallization temperature (T_x) and glass transition temperature (T_g), and the magnetic ordering as indicated by Curie temperature (T_c), are affected by the nature of the glass forming atoms in respect of atomic size and electronic structure, a series of amorphous ribbons have been prepared with the variation of silicon content from 6 to 14 At.%, while keeping the boron content fixed at 10 At.%. With increasing percentage of silicon the glass transition temperature increases, indicating an increase in the structural stability of the amorphous state. The glass transition temperature, however, tends to attain a saturation value around this percentage of the silicon content. The primary crystallization temperature (T_x) increases rather slowly with increasing amount of silicon while the secondary crystallization temperature (T_x') practically remains unchanged. The Curie temperatures of the ribbons for their different compositions, as determined by A.C. permeability, also shows an increase with increase in silicon content. The temperature *versus* A.C permeability curves shows that permeability increases to a maximum value at around the Curie temperature and falls very sharply at T_c to almost zero value. The increase of permeability around T_c is explained in terms of relaxation of the domain wall pinning due to Hopkinson effect.

Keywords : Fe-based metallic glass, magnetic ordering, glass transition

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1. Introduction

Amorphous magnetic alloys are metastable condensed matter, where no long range order exist because of the high rate of cooling of the melt through the glass transition temperature. The lack of long range order creates a deviation of the system from the minimum free energy configuration of the constituent atoms. Although these amorphous alloys are in metastable state, they maintain this state over a temperature range due to the energy barriers created locally due to both structural and kinetic factors. The structural stability of these materials are related to the arrangement of atoms, their size and bonding. The kinetic factors are the nucleation and crystal growth rate, and diffusion of atoms as described by Turnbull [1] and Spaepen and Turnbull [2]. It is important to find out the thermal stability of amorphous ribbons in respect of their operational temperature so that these materials can be used reliably and reproducibly in technological applications. This stability depends on the kinetic barriers to the formation and growth of stable nuclei. The structural barrier to crystallization can be controlled by the selection of the metalloids and their amounts in respect of their atomic size and their affinity to form bonds. The kinetic factors which are dominant in nucleation and crystal growth, although depend primarily on the cooling rate, are also affected by the nature of the metalloids and their contributions to the diffusion rate. It is important, therefore, to determine the effect of metalloid on the stability of amorphous alloys which is reflected in T_g, T_x and T'_x. The crystallization process in binary iron-boron glassy alloy is well known as described by Potocky *et al* [3], Tarnoczi *et al* [4], Kim *et al* [5] and Nunogaki *et al* [6]. It was found by Hasegawa and Roy [7] and Sikder *et al* [8] that the crystallization temperature depends on the boron content.

The magnetic characteristics of metallic glasses are also affected by the nature and the quantity of glass forming metalloids. In the present work Fe-based amorphous ribbons with composition $Fe_{90-x}Si_xB_{10}$ are prepared by melt spinning technique employed by Duwez and Willens [9], Pond and Maddin [10] and Asgar [11], where silicon was varied from 6 to 14 At.% while the fraction of the boron was kept fixed at 10 At.%. The addition of silicon in the iron-boron amorphous binary system is likely to affect the stability of the amorphous phase due to the introduction of kinetic barrier to the transformation of amorphous to crystalline state. The structural stability, as affected by the change in the silicon content and as reflected in the measured values of T_g, T_x and T'_x, are studied by differential thermal analysis which has been used by Chatelier [12], Hossain and Dollimor [13] and others. The effect of variation of silicon content on the magnetic ordering is also studied from the variation of T_c. In spite of chemical and structural disorder an amorphous ferromagnet demonstrates a well defined ferromagnetic ordering temperature, although T_c of a magnetic alloy in the crystalline state differ from that of its amorphous state. The T_c of amorphous transition metal-metalloid alloys are always found to be significantly lower than those of pure crystalline transition metals. The variation of T_c with transition metal content for a fixed metalloid composition may be systematised using a phenomenological model as described by Kouvel [14]. In our case the situation is a bit more complex, where metalloid composition is not kept fixed. The T_c, which is affected by exchange interaction between the magnetic atoms, is also very complicated in the case of amorphous Fe–B–Si system to be understood theoretically, and can only be found out experimentally.

2. Experimental

Preparation of ribbons :

Amorphous $Fe_{90-x}Si_xB_{10}$ ribbons are prepared by melt spinning technique. In this method the molten alloy is injected through a nozzle onto a rotating drum, when it is subjected to a cooling rate of 10^6 °C/S to secure the amorphous state. The success of this technique depends on the thermal conductivity of the rotating drum and of the molten alloy, the linear speed of the drum, the injected volume and the viscosity of the molten alloy. The thickness of an amorphous ribbon depends on the linear speed of the roller and the gap between the nozzle and the rotating drum. Temperature of the melt and the stability of the drop on the surface of the drum are also important in the preparation of ribbons. The important parameters used in our preparation of the ribbons were as follows :

The surface velocity of the drum was 20 m/S, the angular velocity being 2000 rev./min. The gap between nozzle and the rotating copper drum was 100 to 150 μm with dynamic maximum displacement due to oscillation of the rotating drum varying between 1.5 and 5 μm which was estimated from the amplitude of the vertical component of vibration of the system. Pressure of the argon gas was 0.2 to 0.3 atmosphere and the temperature of the melt was ~1500°C, which was below the melting point of the quartztube.

Since a large number of variables are involved in the successful preparation of amorphous ribbons, the parameters were empirically chosen by trial and error. Although one should be able to produce amorphous materials of all compositions in principle, compositions close to the eutectic point are most convenient. We varied our composition around this eutectic point which corresponds to the maximum value of the reduced glass transition temperature and as such to the minimum cooling rate of the melt needed for producing amorphous ribbons. The ribbons produced were of average width 6 mm and thickness 22 to 26 μm.

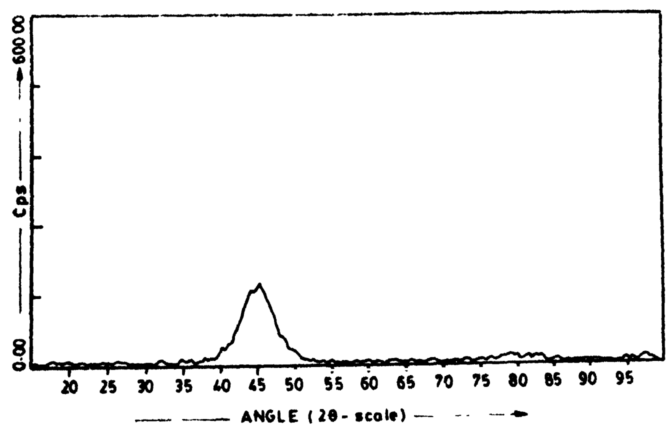

Figure 1. X-ray diffraction pattern of amorphous ribbon with composition $Fe_{80}Si_{10}B_{10}$.

The amorphousity of the ribbons have been confirmed by X-ray diffraction using Cu-K_α radiation. A representative picture is shown in Figure 1.

Differential thermal analysis :

The thermal characteristics of amorphous ribbons with composition $Fe_{90-x}Si_xB_{10}$ [x = 6, 8, 10, 12 and 14] were measured by DTA method at a heating rate of 10°C/min. For DTA measurements, a Shimadzu DTA system (model DT30), was used.

Measurement of T_c :

T_c is a measure of exchange interaction between the magnetic atoms and is quite complicated in the case of amorphous alloys and is very much an experimental parameter. Here theories can be helpful only as a guide in rationalising the results obtained experimentally. T_c of the amorphous samples of toroidal shapes have been measured from the temperature dependence of A.C. initial permeability by a laboratory built technique using a furnace in which a heating wire is wound bifillerly and two identical coils are wound in opposite directions such that the current induced flux in the two coils cancel each other. An alternating current i flowing through the primary of the toriadal ring shaped sample produces a magnetic field $H = \frac{0.4N_1 i\sqrt{2}}{d_{av.}}$ (oe), where N_1 is the total number of turns in the primary of the toriadal ring and $d_{av.}$ is the average diameter of the toriodal ring. The magnetic flux B is measured by a digital micro voltmeter connected to the secondary coil of turn N_2 on the toriodal ring of cross section S, and is given by $B = \frac{E\times 10^8}{4N_2 fS}$ (Gs). A constant frequency of 30 kHz was used for exciting current from a signal generator. The final permeability is then obtained from the relation $\mu = \frac{Ed_{av.} \times 10^8}{4fN_1N_2S \times 0.4i\sqrt{2}}$. The whole set-up was then introduced in the furnace, and by measuring the temperature dependence of the differential flux through the coils, T_c was determined. It is shown that for temperature below 100°C no noticeable effects in glassy materials are produced as described by Luborsky *et al* [15]. T_c has been estimated from μ *vs* T curve, where T_c corresponds to the temperature at which dM/dt attains a maximum value. It is interesting to note that the sharp fall of permeability at T_c enables us to determine this temperature unambiguously within 1°C. From the experience gained during the course of this work it is found out that the heating rate should preferably be above 10°C/min. To measure the temperature dependence of A.C. initial permeability, the samples were subjected to a heating rate of 12°C/min. A faster heating rate introduces error in the measurement of the differential temperature, while a slower heating rate introduces an effect of annealing on the specimen and tend to initiate nucleation and growth of the crystallites, deteriorating the glassy nature of the specimens.

3. Results and discussion

Iron-Silicon-Boron amorphous ribbons with composition $Fe_{90-x}Fe_xB_{10}$ [x = 6, 8, 10, 12 and 14] are potentially important candidates as soft magnetic materials for electromagnetic devices in power applications at high frequencies as referred by Horvat *et al* [16] and Sung Song and Ho [17]. This is because, ribbons of this composition have relatively higher structural stability and high Curie temperature. Studies of glass transition temperature (T_g) and crystallization temperature (T_x) are determined by DTA at a heating rate of 10°C/min. Structural relaxation in Fe–Si–B alloys is accompanied by a change in heat capacity which enables us to determine the ordering temperatures corresponding to glass transition and crystallization from the specific heat anomalies. The variation of T_g, T_x and T_x' in ferromagnetic glasses due to variation of the Si-content provide information regarding thermal stability of these glassy alloys.

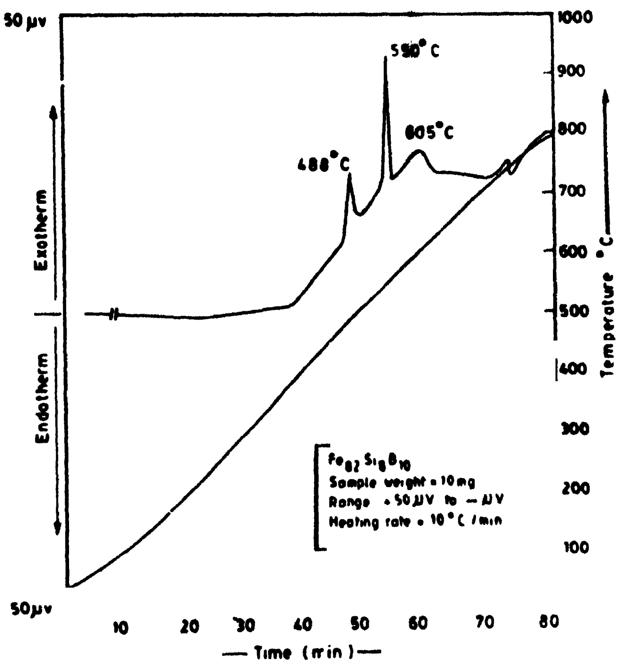

Figure 2. DTA graph of amorphous ribbon with composition $Fe_{82}Si_8B_{10}$.

The DTA traces of amorphous Fe–Si–B of composition $Fe_{82}Si_8B_{10}$ is shown in Figure 2. The three anomalies observed in the temperature *vs* time curve were at 448°C, 555°C and 605°C respectively. All the peaks which correspond to release of heat at these temperatures correspond to short range ordering, long range ordering at primary crystallization and secondary crystallization respectively. Figure 3 shows the DTA traces of the different amorphous ribbons with composition $Fe_{90-x}Si_xB_{10}$. For producing amorphous ribbons, the samples should have T_g well below T_x so that there is sufficient mobility of the atoms without the possibility of crystallization. The numerical values of T_g, T_x and T_x' for the different samples are shown in Table 1.

Figure 4 shows the dependence of T_g, T_x and T_x' on silicon content. T_g is found to increase with silicon content which reaches a saturation value at 12 At.% of silicon. T_x also

Table 1. Numerical values of T_g, T_x and T'_x for different samples.

$Fe_{90-x}Si_xB_{10}$	T_c (°C)	T_g (°C)	T_x (°C)	T'_x (°C)	μ_i ($H = 0.11$ A/m)
$x = 6$	357	458	545	595	374
$x = 8$	387	488	555	605	666
$x = 10$	421	525	564	600	507
$x = 12$	434	545	568	600	457
$x = 14$	448	550	570	600	429

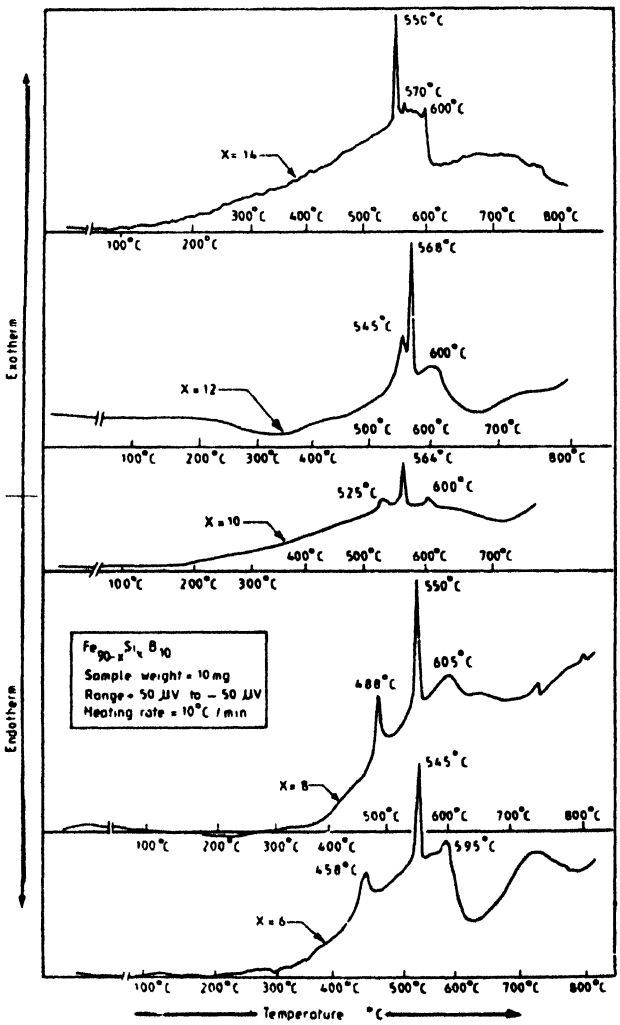

Figure 3. Determination of T_g, T_x and T'_x from DTA graph of amorphous ribbons with compositions $Fe_{90-x}Si_xB_{10}$ [$x = 14, 12, 10, 8$ and 6].

increases slightly with the increase of Si-content. The T'_x remains practically unchanged with the addition of Si-content.

Figure 5 shows that the A.C. initial permeability (μ_i) of Fe–Si–B amorphous system increases with decreasing silicon content and has the maximum value at 8 At.% of silicon.

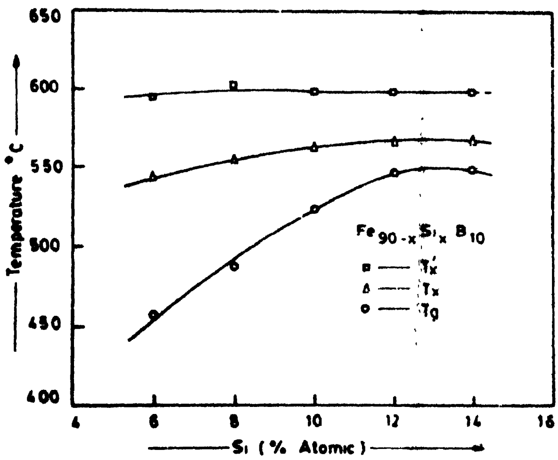

Figure 4. Variation of T_g, T_x and T'_x due to change in the silicon content in $Fe_{90-x}Si_xB_{10}$ amorphous ribbons.

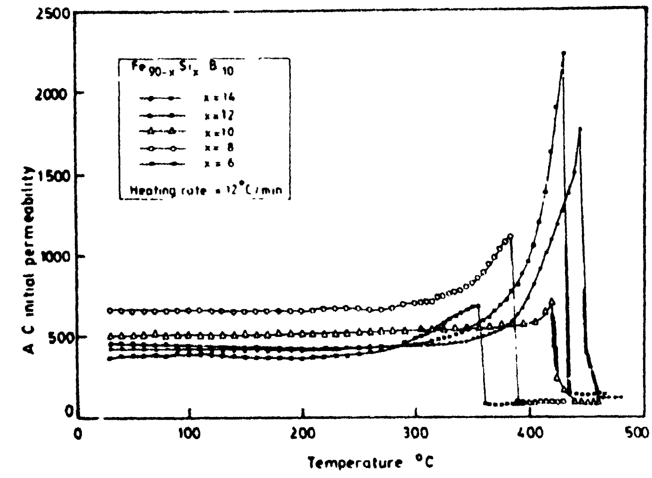

Figure 5. T_c determination from temperature dependence of A.C initial permeability of amorphous ribbon with compositions $Fe_{90-x}Si_xB_{10}$.

Beyond this point there is a decrease in the permeability with a decrease in Si content. The sharp fall of the A.C. initial permeability at T_c indicates that the material is quite homogeneous from the point of view of amorphousity. It is also observed from this curve that the permeability increases with temperature and attains the maximum value just before T_c, which we consider to be due to Hopkinson effect, as described by Kersten and Angew [18]. Figure 6 shows the dependence of T_c on the silicon content. It is noticed that T_c increases with increasing silicon content. The effect of silicon in bringing about an increase of T_g can be explained as follows :

In the first place, the addition of silicon as a third element, makes the alloy system more complex. This complexity of the chemical bonds between the constituent atoms should increase the relaxation time for the transformation from amorphous to crystalline state. Secondly, the diffusion of the silicon atoms into the interstitial positions bring about an increase in density.

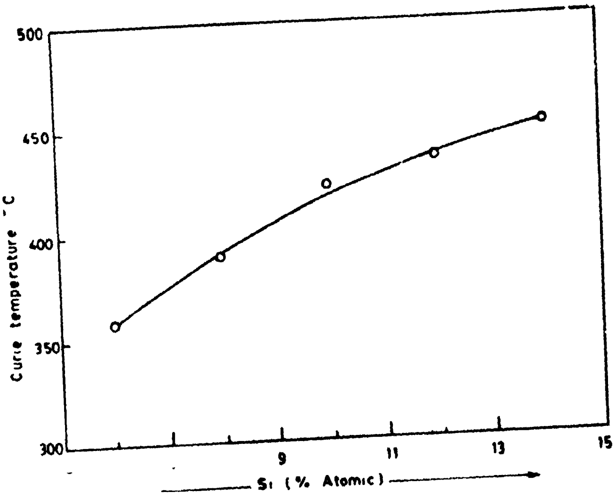

Figure 6. Variation of T_c due to change in the silicon content in $Fe_{90-x}Si_xB_{10}$ amorphous ribbons.

Unambiguous and sharp values of T_c, obtained from our measurements, support the fact that, in spite of chemical and structural disorder, ferromagnetic glass have well defined magnetic ordering temperature. This is in conformity with other results on magnetization *vs* temperature, Mössbauer and specific heat measurements by Wright [19], Luborsky and Walter [20] and Yamada and Wohlfarth [21]. A quantitative understanding of magnetism in amorphous solids is very difficult and is as yet an unsolved problem, because, the chemical and structural disorders change all the important parameter like magnetic moment, exchange interaction and single ion anisotropy of the system. However, the coupling of the moments in an amorphous system arising from single site exchange, which takes place by the inter site hoping electrons, produces a correlation between the moments at different magnetic atoms. Since the exchange interaction in the amorphous transition metal-metalloid alloys is assumed to be of RKKY type, the magnitude of the exchange integral is quite likely to depend on the interatomic distance between the magnetic atoms. Our observed increase of T_c with increasing silicon content can be understood, in principle, as arising from the dependence of J_{ij} on r_{ij}. The equation guiding the mechanism can be written as

$$T_c = [2S(S+1)/3K] \sum J_{ij}(r_{ij}),$$

assuming a molecular field approximation, where S is the spin number, K is Boltzmann constant and J_{ij} is exchange integral between atoms at position r_i and r_j. The results reported by Durand and Yung [22] on the Fe–P–B alloys show that with fixed concentrations of *P*, there is an increase of T_c with increasing Boron. This is quite in keeping with our results, where we found an increase in T_c when iron atoms are replaced by silicon atoms with the number of boron atoms remaining fixed.

4. Conclusions

Iron-boron amorphous system, which is a very well studied material with potential applications as a soft magnetic material, can be improved upon by adding silicon as a third element in respect of structural stability and magnetic ordering. When silicon atoms replace iron atoms in the $Fe_{90-x}Si_xB_{10}$ system, highest T_g of value 550°C is observed for $x = 14$. It is interesting that the maximum value of T_c which is 448°C also corresponds to this composition. This composition is, therefore, most suitable for Fe–Si–B ribbons as a soft magnetic material at an elevated temperature.

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