Structural relaxation and embrittlement of $Fe_{74}Co_{10}B_{16}$ and $Fe_{74}Co_5Cr_5B_{16}$ metallic glasses

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Structural relaxation and annealing embrittlement behaviour of $Fe_{74}Co_{10}B_{16}$ and $Fe_{74}Co_5Cr_5B_{16}$ metallic glasses has been studied by differential scanning calorimetry (DSC) and bend ductility measurements. A pre-anneal technique was employed with DSC to determine activation energies of relaxation at various temperatures. Activation energies of embrittlement were derived from measurements of the embrittlement kinetics. The results obtained for both the alloys are compared to ascertain the effects of chromium addition. A spectrum of activation energies is obtained corresponding to structural relaxation and embrittlement. The activation energies of structural relaxation are found to be slightly higher for the chromium-containing alloy than for the ternary alloy. This observation is consistent with the higher crystallization temperature of the chromium-containing alloy as reported earlier. The ductile–brittle transition temperature of the $Fe_{74}Co_{10}B_{16}$ glass, however, decreases by ~50 K (for 15 min anneal) on addition of 5 at% chromium. Activation energies for embrittlement of the chromium-containing alloy are also considerably smaller than for the ternary alloy. It is concluded that despite increasing the thermal stability, chromium reduces the mechanical stability of $Fe_{74}Co_{10}B_{16}$ glass.

1. Introduction

Iron-based amorphous alloys possess a number of practically useful characteristics such as high strength and good soft ferro-magnetic properties [1]. These alloys therefore attract the most intense interest among the large number of amorphous alloy systems. Many of these glasses, however, possess poor thermal stability and it is desirable to identify glasses of higher crystallization temperature. Akhtar *et al.* [2] have recently shown that replacement of 5 at% cobalt by chromium in $Fe_{74}Co_{10}B_{16}$ amorphous alloy increases the crystallization temperature, T_x by ~45 K.

An as-quenched metallic glass is thermodynamically unstable; its free energy can decrease continuously by a series of structural changes towards the metastable equilibrium configuration. This phenomenon is called structural relaxation and is manifested by continuous changes in many physical and mechanical properties. An important precrystallization phenomenon which correlates with structural relaxation is the annealing embrittlement. Iron-based metallic glasses, in particular, often become brittle when annealed at temperatures well below the glass transition/crystallization temperature [1]. Measurement of structural relaxation/annealing embrittlement in iron-based amorphous alloys is, therefore, of considerable importance especially when technological applications of these alloys are being considered.

Although several models [3–12] for embrittlement in metallic glasses have been proposed, the origin of embrittlement is not well clarified at present. In general, embrittlement behaviour has been found to depend strongly on composition. In the present study, structural relaxation and annealing embrittlement behaviour of $Fe_{74}Co_{10}B_{16}$ and $Fe_{74}Co_5Cr_5B_{16}$ metallic glasses was investigated by differential scanning calorimetry and bend ductility measurements. The results obtained for both the alloys are compared to ascertain the effects of addition of chromium in $Fe_{74}Co_{10}B_{16}$ glass.

2. Experimental techniques

Alloys were prepared and homogenized by induction melting repeatedly over a water-cooled copper hearth in dynamic argon atmosphere. The ingots were cut into small pieces and melt-spun on to a rotating (~3000 r.p.m.) polished copper wheel (~225 mm diameter) after remelting under an argon atmosphere in a quartz nozzle of ~1 mm orifice diameter and employing an ejection pressure of ~10 psi (~68.9 × 10^{-3} N mm^{-2}). The ribbons thus obtained were ~2 to 3 mm wide and 35 to 40 μm thick. X-ray diffraction traces of the as-quenched ribbons did not reveal any trace of crystallinity.

The enthalpy of relaxation was monitored with a computerized differential scanning calorimeter (Du Pont 1090 Thermal Analyser). This instrument allows the data to be stored, processed and accurately compared. A set of specimens was sealed in quartz tubes under vacuum and preannealed for 15 min at various constant temperatures, T_a. Upon reheating in the differential scanning calorimeter, the apparent specific heat increases sharply at a temperature, T, which is in the vicinity of T_a. Variation of T with heating rate was monitored to obtain activation energy values at the various temperatures, T_a.

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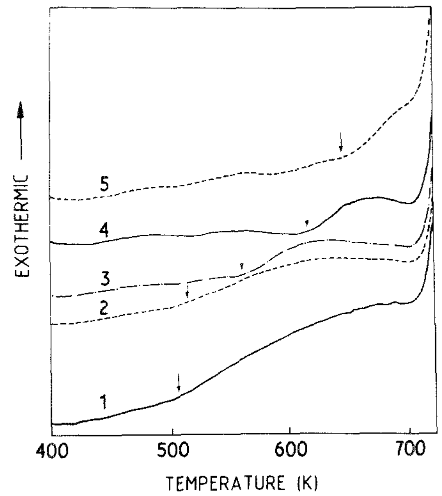

Figure 1 DSC thermograms of amorphous $Fe_{74}Co_{10}B_{16}$ at a heating rate of $100\,K\,min^{-1}$: (1) as-quenched, and preannealed for 15 min at (2) 473 K, (3) 523 K, (4) 573 K and (5) 623 K.

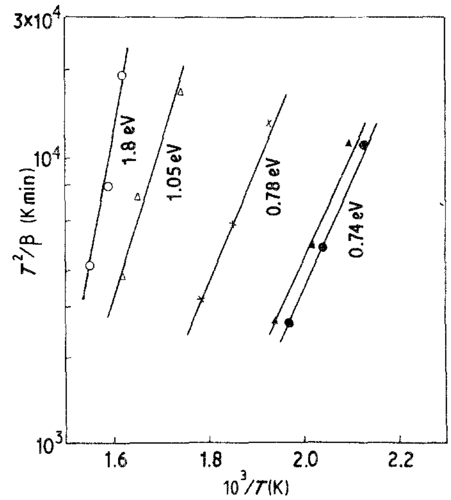

Figure 3 Kissinger plots of the structural relaxation of amorphous $Fe_{74}Co_{10}B_{16}$ preannealed for 15 min at (○) 623, (△) 573, (x) 523, (▲) 473 K and (●) as-quenched.

For annealing embrittlement studies, ribbon samples were annealed in sealed quartz tubes under vacuum. Ductility measurements on the as-quenched and annealed specimens were made by bending the samples into a U-shape between the plates of a micrometer. The plates were gradually brought closer to decrease radius of curvature of the U-shaped ribbon until the sample fractured. The relative maximum strain at fracture was then approximated to [3] $\varepsilon_f = t/(d - t)$ where d is the distance between the plates at fracture and t is the thickness of the ribbon.

3. Results

3.1. Structural relaxation

Fig. 1 shows DSC thermograms at a heating rate of $100\,K\,min^{-1}$ for $Fe_{74}Co_{10}B_{16}$ metallic glass samples preannealed isothermally for 15 min at temperatures, T_a, ranging from 473 to 623 K. For comparison, the thermogram of the as-quenched glass is also included. Note the onset of a well-defined exotherm corresponding to the further structural relaxation above the annealing temperature, T_a (onset temperature, T is marked by arrows). In curves 4 and 5 of the figure, small exotherms before the arrow marks are perhaps due to incomplete structural relaxation (in 15 min time) up to the temperature, T_a, in these samples. These exotherms are not considered as the calculation of activation energy remains unaffected.

Fig. 2 shows DSC thermograms at heating rates (β) of 20, 50 and $100\,K\,min^{-1}$ for $Fe_{74}Co_{10}B_{16}$ glass samples preannealed isothermally for 15 min at a temperature, T_a, of 523 K. It is clear that the onset temperature, T, for structural relaxation shifts with heating rate. The apparent activation energy of structural relaxation was determined using the method of Kissinger [13] from the slope of a plot of log (T^2/β) against $1/T$. Figs 3 and 4 show such plots for the $Fe_{74}Co_{10}B_{16}$ and $Fe_{74}Co_5Cr_5B_{16}$ glasses, respectively, at the various preannealing temperatures, T_a. Activation energy values thus obtained are depicted in these figures and plotted as a function of temperature in Fig. 5 for both alloys. Note that for a constant temperature the activation energy estimated for structural relaxation is slightly higher for $Fe_{74}Co_5Cr_5B_{16}$ glass as compared to $Fe_{74}Co_{10}B_{16}$ glass. It should be pointed out here that the temperature of the onset of relaxation, T_R, in the as-quenched state was almost the same for both alloys (~ 468 K at a heating rate of $20\,K\,min^{-1}$).

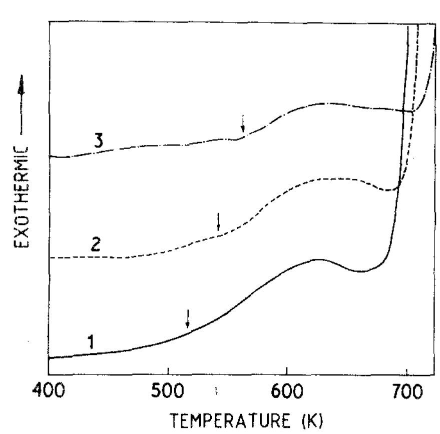

Figure 2 DSC thermograms of amorphous $Fe_{74}Co_{10}B_{16}$ (preannealed for 15 min at 523 K) at heating rates of (1) $20\,K\,min^{-1}$, (2) $50\,K\,min^{-1}$ and (3) $100\,K\,min^{-1}$.

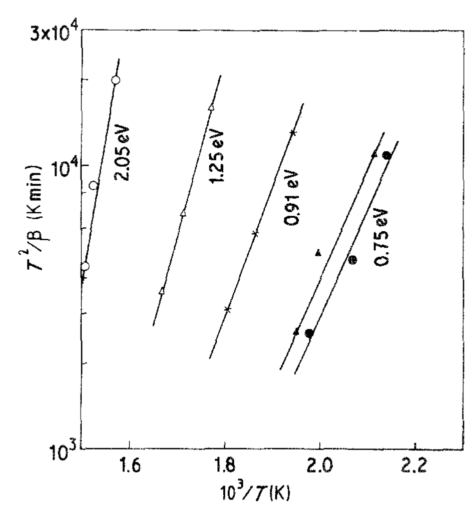

Figure 4 Kissinger plots of the structural relaxation of amorphous $Fe_{74}Co_5Cr_5B_{16}$ preannealed for 15 min at (○) 623, (△) 573, (x) 523, (▲) 473 K and (●) as-quenched.

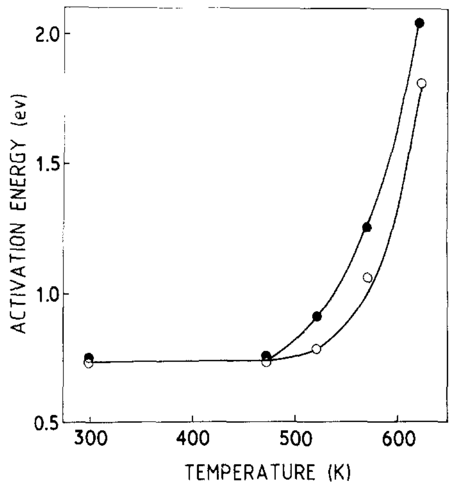

Figure 5 Activation energy for structural relaxation of amorphous (○) $Fe_{74}Co_{10}B_{16}$ and (●) $Fe_{74}Co_5Cr_5B_{16}$ as a function of preannealing temperature.

3.2. Annealing embrittlement

As-quenched ribbons of $Fe_{74}Co_{10}B_{16}$ and $Fe_{74}Co_5Cr_5B_{16}$ glassy alloys were ductile and could be bent completely back on to themselves without fracture. A series of samples were annealed for 15 min at different temperatures and subjected to a bend ductility test. Measured values of fracture strain are shown in Fig. 6, for both alloys. The data indicate a loss in ductility above temperatures of 523 and 573 K for $Fe_{74}Co_5Cr_5B_{16}$ and $Fe_{74}Co_{10}B_{16}$ alloys, respectively.

Kinetics of embrittlement was determined by isothermal annealings at different temperatures. The loss of ductility on isothermal annealing of $Fe_{74}Co_{10}B_{16}$ and $Fe_{74}Co_5Cr_5B_{16}$ glasses is shown in Figs 7 and 8, respectively. The ductility of $Fe_{74}Co_{10}B_{16}$ glass ribbons does not change on annealing at 573 K; however, a sharp decrease in ductility is observed on annealing at higher temperatures. $Fe_{74}Co_5Cr_5B_{16}$ glass ribbons become brittle on annealing at 573 K and higher temperatures; however, annealing at 523 K does not alter the ductility of this alloy.

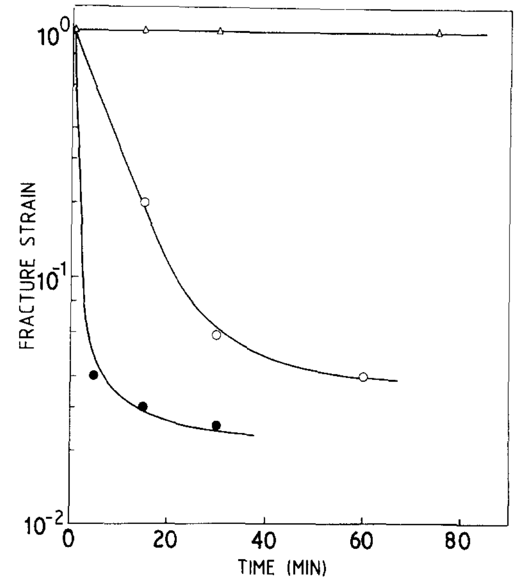

Figure 7 Variation of ductility of amorphous $Fe_{74}Co_{10}B_{16}$ with annealing time at temperatures of (△) 573, (○) 623 and (●) 673 K.

From Figs 7 and 8 the annealing times (t) required at various temperatures (T) to obtain a constant fracture strain, ε_f, were determined. Plots of log t against $1/T$ yielded straight lines and the activation energy of embrittlement was evaluated from the slope of these plots. Estimated values of activation energy are presented in Fig. 9 with respect to fracture strain for both alloys. It is apparent that the activation energy values obtained for embrittlement of $Fe_{74}Co_5Cr_5B_{16}$ glass are considerably lower as compared to $Fe_{74}Co_{10}B_{16}$ glass.

4. Discussion

Any model for relaxation must be based on some general property of materials that are in the amorphous state. It has been proposed [14, 15] that a supercooled liquid structure near T_g is inhomogeneous and consists of liquid-like regions of large free volume or high local free energy and solid-like regions with small free volume or low local free energy. The resulting

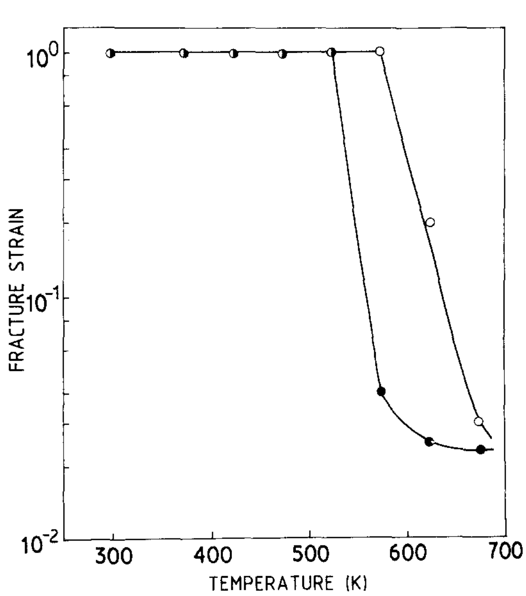

Figure 6 Effect of annealing (15 min at temperature) on ductility of amorphous (○) $Fe_{74}Co_{10}B_{16}$ and (●) $Fe_{74}Co_5Cr_5B_{16}$ as measured in the bend test.

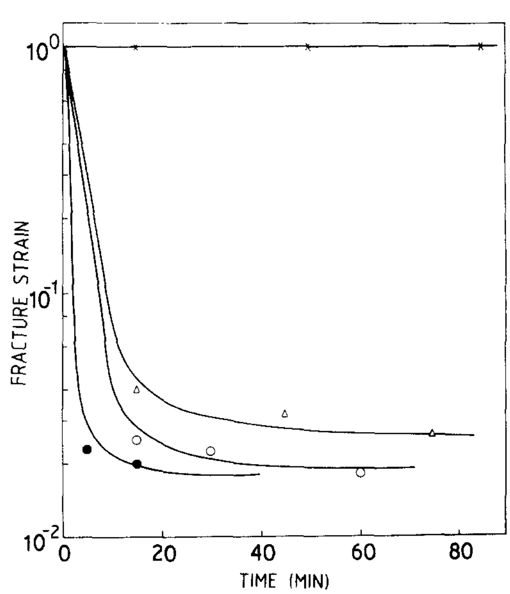

Figure 8 Variation of ductility of amorphous $Fe_{74}Co_5Cr_5B_{16}$ with annealing time at temperatures of (x) 523, (△) 573, (○) 623 and (●) 673 K.

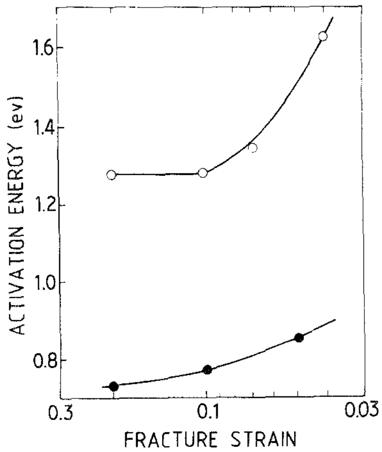

Figure 9 Activation energy for embrittlement as a function of fracture strain for isothermally annealed amorphous (○) $Fe_{74}Co_{10}B_{16}$ and (●) $Fe_{74}Co_5Cr_5B_{16}$.

amorphous solid prepared by melt-quenching contains a number of liquid-like regions with unrelaxed atomic configuration which are isolated from each other embedded in the solid-like matrix. The inhomogeneity for an alloy is considered to arise from fluctuations in concentration and density. When the amorphous solid is annealed, part of liquid-like regions undergoes configurational change to a relaxed state.

In the present investigations, a spectrum of activation energies is obtained for structural relaxation of $Fe_{74}Co_{10}B_{16}$ and $Fe_{74}Co_5Cr_5B_{16}$ glasses. The observed activation energies are slightly higher for the $Fe_{74}Co_5Cr_5B_{16}$ alloy, though the temperature of onset of relaxation, T_R, is almost the same for both alloys. Interestingly, the crystallization temperature, T_x, of $Fe_{74}Co_5Cr_5B_{16}$ glass is higher by ~ 45 K than that of $Fe_{74}Co_{10}B_{16}$ glass [2]. A correlation between crystallization and structural relaxation processes has indeed been proposed earlier [16].

The as-quenched ductility of $Fe_{74}Co_{10}B_{16}$ glass remains uneffected on addition of 5 at % chromium. However, for 15 min anneal, embrittlement of $Fe_{74}Co_5Cr_5B_{16}$ glass starts at temperatures beyond 523 K, whereas $Fe_{74}Co_{10}B_{16}$ glass remains ductile up to 573 K. If we define an embrittlement temperature, T_B, for 15 min anneal at which a detectable loss in ductility is observed, we find that the T_B value of $Fe_{74}Co_{10}B_{16}$ glass decreases by ~ 50 K on replacing 5 at % cobalt by chromium. Some other iron- and nickel-based metal–metalloid glasses containing phosphorous, boron and aluminium have also been reported to embrittle on addition of chromium or molybdenum [5]. Akhtar *et al.* [17] have recently shown that the embrittlement temperature of $Ni_{60}Nb_{40}$ glass decreases by more than 300 K on replacing 5 at % nickel by chromium. It appears that chromium embrittles metallic glasses irrespective of the presence of any metalloid.

A spectrum of activation energies is obtained for the annealing embrittlement process, and the activation energy values estimated for both alloys are comparable to the values obtained [7, 18] for some other metallic glasses. The activation energies for embrittlement of $Fe_{74}Co_5Cr_5B_{16}$ glass are, however, considerably lower (approximately half) than those for $Fe_{74}Co_{10}B_{16}$ glass. The activation energies have been found [8] to be correlated with the corresponding transformation temperatures, and smaller activation energy values obtained for embrittlement of $Fe_{74}Co_5Cr_5B_{16}$ glass are consistent with the lower ductile–brittle transition temperature of this alloy.

For some metal–metalloid glasses, embrittlement has been associated with rapid diffusion and clustering of the small metalloid elements [19]. This proposition is rather arbitrary, because annealing embrittlement has been observed in some glasses containing only metallic elements [17, 20–23]. Liebermann and Luborsky [24] have suggested that embrittlement by an individual species of atom in a metallic glass depends on a combination of aspects such as embrittler electronegativity and ionic size. The strong embrittlement behaviour of iron- and nickel-based metal–metalloid glasses on addition of chromium or molybdenum is attributed to incomplete filling of d-shell orbitals of chromium and molybdenum atoms [5]. It appears that embrittlement in metallic glasses is most likely based on the ability of embrittler atom to localize electrons from the matrix.

The structural relaxation and annealing embrittlement of $Fe_{74}Co_{10}B_{16}$ and $Fe_{74}Co_5Cr_5B_{16}$ glasses is found to be spread over a spectrum of activation energies. The activation energies of relaxation and temperature of onset of crystallization [2] are higher for $Fe_{74}Co_5Cr_5B_{16}$ glass as compared to $Fe_{74}Co_{10}B_{16}$ glass. On the other hand, activation energies of embrittlement and ductile–brittle transition temperature are considerably lower for the chromium-containing alloy. Thus no direct correlation is apparent between the structural relaxation and embrittlement processes as far as chromium-alloying is concerned. Although chromium enhances the thermal stability of $Fe_{74}Co_{10}B_{16}$ glass, it reduces the mechanical stability. Such a behaviour on alloying has also been observed [5, 21] earlier for a few other systems.

5. Conclusions

A spectrum of activation energies is obtained for structural relaxation and annealing embrittlement of $Fe_{74}Co_{10}B_{16}$ and $Fe_{74}Co_5Cr_5B_{16}$ glasses. The temperatures of onset of relaxation are almost similar for both alloys; however, activation energies of relaxation are slightly higher for $Fe_{74}Co_5Cr_5B_{16}$ glass compared to the $Fe_{74}Co_{10}B_{16}$ glass. For a 15 min anneal, the ductile–brittle transition temperature of the $Fe_{74}Co_{10}B_{16}$ glass is reduced by ~ 50 K on replacement of 5 at % cobalt by chromium and the activation energies of embrittlement decrease considerably. In the light of the present results and some earlier observations, it is concluded that addition of chromium in $Fe_{74}Co_{10}B_{16}$ glass enhances the thermal stability but reduces the mechanical stability.

Acknowledgements

We thank Mr V. N. Murthy for his help in preparation of the alloys, and Professor P. Rama Rao for encouragement and permission to publish this work.

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Received 4 August and accepted 16 October 1986