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Nitrogen as an alloying element in some metallic glasses

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Glassy alloy ribbons containing nitrogen as an alloying element have been produced by chill block melt-spinning master alloys which were specially pre-melted for enhanced nitrogen content. Alloying substantial amounts of Cr, a potent nitride former, has been found to greatly increase the amount of nitrogen in solution. In turn, thermal stability of the Cr-bearing metallic glasses has been found to increase as much as 31 K with only a 0.5 at% nitrogen addition. No analogous changes in glassy alloy embrittlement or Curie temperature have been observed. However, although weak, the response of Curie temperature to annealing in the Cr-bearing metallic glasses was found to be affected by the presence of nitrogen. Thus, nitrogen appears to be a viable alloying element in some metallic glasses and may have a potent effect on some properties.

1. Introduction

Nitrogen is widely used in the metallurgy of steels and is effective in the hardening of surfaces (in much the same way as carbon), in the stabilization of the austenitic structure in Mn-bearing steels, and in the formation of grain boundary precipitates for controlling grain size. This technologically useful element lies at the periphery of the group of elements on the periodic table typically used to stabilize transition metal–metalloid (TM–M) metallic glasses. Thus, it may be anticipated that nitrogen may act as a metalloid in TM–M metallic glasses if it could be retained in solution during pre-alloying and after subsequent rapid solidification from the melt. Although the effects of small amounts of nitrogen (< 0.1 at%) on some TM–M metallic glasses has already been disclosed [1], the present work involves substantially greater additions so that the nitrogen functions more as a significant alloying element rather than as a minor addition.

This initial investigation involves metallic glasses of nominal composition $Fe_{40}Ni_{40}B_{20}$, $Fe_{40}Ni_{40}B_{10}Si_{10}$ and $Fe_{65.2}Cr_{19.3}B_{12.9}Si_{2.6}$ pre-alloying under nitrogen gas. The Cr-bearing composition is particularly suited for the alloying of nitrogen because CrN may be used to supply all of the Cr in solution and because the addition of Cr to molten Fe promotes the dissolution of gaseous nitrogen [2, 3]. Thus, the Cr-bearing metallic glass is of primary interest because of the enhanced likelihood of nitrogen dissolution.

The addition of nitrogen in TM–M metallic glasses is anticipated to have a possible effect on crystallization, magnetic properties, and other properties affected by structural relaxation and atomic migration which occurs on annealing. The present investigation describes not only the extent to which nitrogen may be alloyed for the three base metallic glass-forming compositions, but also reports on how metallic glass properties are affected by the presence of nitrogen in solution. Besides the dependence of metallic glass nitrogen content on base alloy composition, the effects of chill block melt-spinning glassy alloy ribbon in vacuum and under nitrogen atmosphere are explored. With the results of the present work, it is anticipated that nitrogen may be incorporated in alloy design in order to obtain new, improved properties in some TM–M metallic glasses

2. Experimental procedure

Master alloys having analysed compositions of $Fe_{40}Ni_{40}B_{20}$, $Fe_{40}Ni_{40}B_{10}Si_{10}$ and $Fe_{65.2}Cr_{19.3}$-

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TABLE I Analysed alloy composition and processing atmospheres

Sample	Ribbon analysed composition	Atmosphere (kPa)		Nitrogen content (at%)	
		Pre-melt	Melt-spin	Master	Ribbon
A	$Fe_{40}Ni_{40}B_{20}$	100 Ar	vac.	0.002	0.006
B	$Fe_{40}Ni_{40}B_{20}$	200 N_2	vac.	0.005	0.015
C	$Fe_{40}Ni_{40}B_{10}Si_{10}$	100 Ar	vac.	0.001	0.009
D	$Fe_{40}Ni_{40}B_{10}Si_{10}$	200 N_2	vac.	0.012	0.006
E	$Fe_{65.2}Cr_{19.3}B_{12.9}Si_{2.6}$	100 Ar	vac.	0.019	0.027
F*	$Fe_{65.2}Cr_{19.3}B_{12.9}Si_{2.2}N_{0.4}$	200 N_2	vac	0.809	0.421
G	$Fe_{65.2}Cr_{19.3}B_{12.9}Si_{2.3}N_{0.3}$	100Ar	100 kPa N_2	0.019	0.251
H*	$Fe_{65.2}Cr_{19.3}B_{12.9}Si_{2.1}N_{0.5}$	200 N_2	100 kPa N_2	0.809	0.455

*Master alloys were made using CrN.

$B_{12.9}Si_{2.1}N_{0.5}$ were pre-alloyed using high purity constituents in an alumina crucible and held under 200 kPa N_2 for 15 min in a pressure–vacuum furnace [4]. The chromium added to the last of these alloys was introduced as CrN in the alloy pre-melted under 200 kPa N_2 in order to maximize the nitrogen content of the melt. Nitrogen content of all master alloys and ribbons was measured using a Leco Model TC-36 Nitrogen-Oxygen Determinator and by inert gas fusion. Wet chemical analysis was used for determining percentages of the other elements. Control heats having composition $Fe_{40}Ni_{40}B_{20}$, $Fe_{40}Ni_{40}B_{10}Si_{10}$, and $Fe_{65.2}Cr_{19.3}B_{12.9}Si_{2.6}$ were prepared under 100 kPa Ar. While under the pre-melting atmosphere, the melts were poured into a split copper mould and allowed to freeze; the thermal arrests on solidification provided some alloy characterization. The chromium added to one of these alloys was introduced as CrN in the alloy pre-melted under 200 kPa N_2 in order to maximize the nitrogen content of the melt. Each ingot was crushed into pieces which were then used to fabricate rapidly-quenched ribbons from the melt by chill block melt-spinning in vacuum and under 100 kPa N_2 [5]. Samples thus formed had a typical cross-section of ~ 20 μm x 1 mm. The ribbons were subjected to bend ductility testing [6] in both the as-cast state and after one hour anneals. Samples able to sustain a 180° bend were designated as being ductile. The nature of glass alloy samples was further characterized using transmission Laue X-ray diffraction (with a Charles-Supper precession camera with a General Electric XRD-4 power generator), differential scanning calorimetry (using a Perkin Elmer DSC II) at a heating rate of 40 K min^{-1}, stress relaxation measurements [7], and by Curie temperature measurements from magnetization–temperature curves [8] for ribbon samples in both the as-cast and annealed states. Some of the as-cast ribbon samples which were fabricated were heated to the first and the second crystallization exotherms in the scanning calorimeter. The crystallized phases in these specimens were then analysed using X-ray power diffraction method. Some of the X-ray results were checked by transmission electron microscopy (TEM) (Hitachi Electron Microscope, Model 600-3) for microcrystallites not detectable by X-ray diffraction. TEM specimens were prepared by electrolytically thinning ribbons in a 1:4 volumetric ratio of perchloric acid–methanol solution immersed in liquid nitrogen. Chemical analysis of both the master alloys and rapidly-quenched ribbons was used to obtain exact compositions.

3. Results and discussion

3.1. Effects of alloy composition and processing on nitrogen content

All of the master alloy ingots were free of gas porosity. For the Cr-bearing alloy pre-melted under 200 kPa N_2, a light grey powder was observed to form on top of the melt. X-ray diffraction and chemical analysis was used to identify this powder as primarily boron nitrode with small amounts of iron and chromium oxides present. Chemically analysed compositions of all melt-spun ribbons are given in Table I. Although the nitrogen content of all the master alloys may be increased by pre-melting under gaseous nitrogen, substantially increased dissolution is achieved by the Cr-bearing heat pre-melted using CrN. This increased nitrogen content presumably results from the high propensity for gaseous nitrogen dissolution in the melt because of the substantial Cr content [2, 3] and also because of the additional nitrogen provided by the CrN used.

Only small, non-systematic variations in nitro-

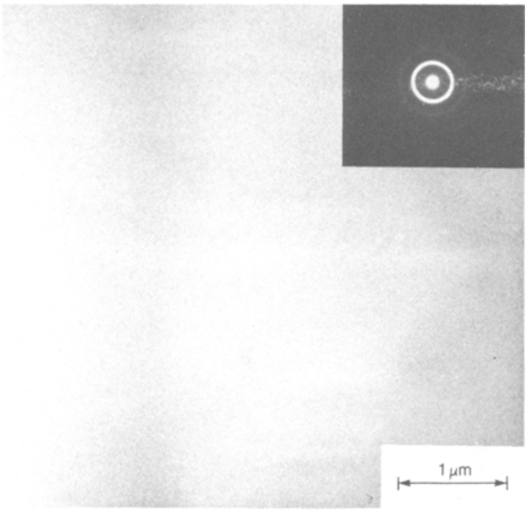

Figure 1 TEM micrograph and diffraction pattern showing no evidence for the presence of second phase regions in the glassy alloy $Fe_{65.2}Cr_{19.3}B_{12.9}Si_{2.2}N_{0.4}$.

gen content are observed between the $Fe_{40}Ni_{40}Si_{20}$ and $Fe_{40}Ni_{40}B_{10}Si_{10}$ glassy alloy ribbons and their respective master alloys. The relatively small nitrogen concentration changes observed on vacuum melt-spinning these compositions most likely stems from small differences in exact processing details from one run to the next. The rather significant 0.02 at% nitrogen content of the Cr-bearing alloy pre-melted in Ar atmosphere is the result of the up to 0.07 at% nitrogen content of the Cr used in pre-melting. The Cr-bearing master alloy pre-melted in nitrogen gas loses about half its nitrogen (about 0.5 at%) during melt-spinning of glassy alloy ribbons in either vacuum or in 100 kPa N_2. This loss occurs because pre-melting was conducted using a 200 kPa N_2 atmosphere and thus results in a supersaturation and subsequent release of nitrogen during melt-spinning in an ambient pressure less than the pre-melting pressure. Of course, the exact amount of nitrogen liberated is governed by kinetics and may therefore vary somewhat from one run to another. TEM has been used to verify that the nitrogen contained by the glassy alloy ribbons is truly in solution, not segregated or crystallized as second phase regions. Fig. 1 shows an electron micrograph and diffraction pattern in the $Fe_{65.2}Cr_{19.3}B_{12.9}Si_{2.2}N_{0.4}$ glassy alloy sample, showing a homogeneous, featureless image devoid of second phase regions. Thus, the nitrogen content derived by chemical analysis appears to be uniformly distributed throughout the sample volume.

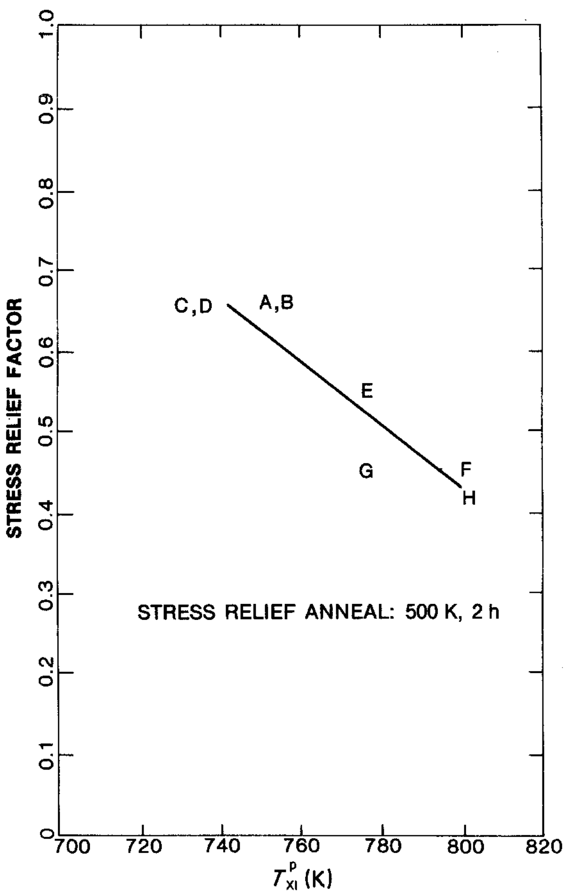

Figure 2 Stress relief dependence on the first crystallization peak temperature.

As shown in Table I, the nitrogen content measured for the Cr-bearing alloy (pre-melted without CrN) is raised significantly by simply melt-spinning in a nitrogen gas atmosphere. Thus, it may be inferred that this acquisiton of nitrogen is similar to that just discussed for master alloys pre-melted under N_2 atmosphere.

3.2. Stress relaxation and embrittlement

The relaxation of atoms in glassy alloys during annealing at temperatures well below those required to initiate crystallization results in an approach towards a "metastabilized" amorphous atomic configuration. The extent to which relaxation occurs in metallic glasses varies inversely with the degree to which spring-back is exhibited by a ribbon sample after being annealed in a toroidal container [7]. A summary of the ribbon stress relaxations measured after 500 K, 2 h anneal while constrained in a small diameter toroidal can is shown in Fig. 2. Note that while glassy alloy ribbon sets of base composition $Fe_{40}Ni_{40}B_{20}$ and

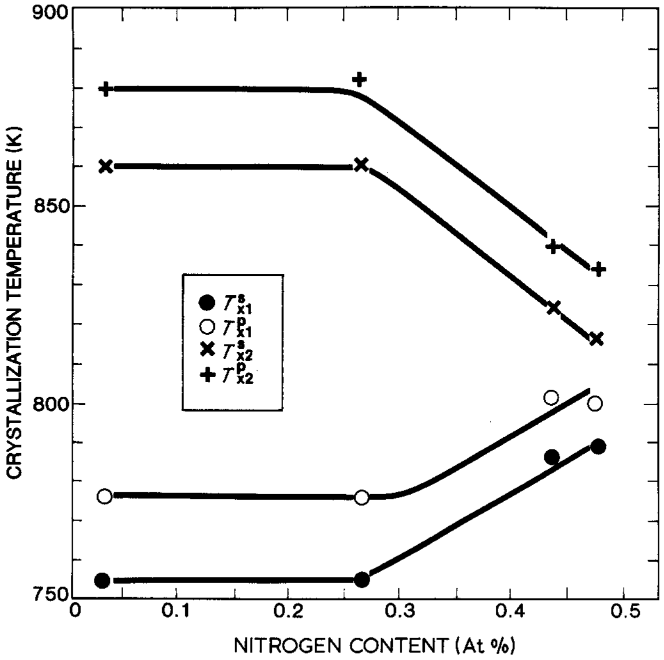

Figure 3 Crystallization start (T_x^s) and peak (T_x^p) temperatures as a function of metallic glass nitrogen content for the Cr-bearing alloys.

$Fe_{40}Ni_{40}B_{10}Si_{10}$ show undetectable differences in stress relief factor, the Cr-bearing glassy alloy data exhibits a trend: stress relief factor varies inversely with crystallization temperature of the various metallic glasses. This indicates a structural stabilization of the high nitrogen (high crystallization temperature, T_x) metallic glasses against the stress relief annealing treatment. Such an inverse variation of stress relaxation with glassy alloy composition (T_x) has already been reported for a similarly narrow range of relaxation factors [9]. Thus, the composition change caused by the presence of nitrogen is seen to increase thermal stability of the Cr-bearing metallic glasses.

Bend ductility testing [6] of all the glassy alloy ribbons has shown these samples to exhibit a precipitous drop in ductility between about 570 K and 630 K after one hour anneals. The 0.5 at% substitution of nitrogen for silicon in the two Cr-bearing alloys has no significant effect on the one hour embrittlement temperature. The embrittlement detected for all of the metallic glasses formed is due to incipient crystallization, as determined by X-ray diffraction.

3.3. Thermal stability and crystallization

Crystallization start and peak temperatures obtained by DSC are plotted in Fig. 3 for the Cr-bearing alloys. Note that the crystallization temperatures for the $Fe_{40}Ni_{40}B_{20}$ and $Fe_{40}Ni_{40}B_{10}Si_{10}$ base glassy alloy ribbon are insensitive to whether pre-melting is conducted in an Ar or a N_2 atmosphere. Apparently, the presence of both Si and B does not cause the start-of-crystallization temperature for the Cr-bearing metallic glass to differ significantly from that of an $(Fe-Cr)_{85}B_{15}$ alloy with the appropriate Fe–Cr ratio [10]. However, the $Fe_{65.2}Cr_{19.3}B_{12.9}Si_{2.1}N_{0.5}$ glassy alloy shows a 31 K increase in start-of-crystallization temperature over the $Fe_{65.2}Cr_{19.3}B_{12.9}Si_{2.6}$ control alloy. The DSC scans of the Cr-bearing metallic glasses shows two exothermic crystallization peaks (Fig. 3) and the substitution of nitrogen for silicon causes the lower peak to increase and the upper peak to decrease in temperature, thus resulting in enhanced overall thermal stability. From Fig. 3, it appears that some minimum nitrogen content (~ 0.25 at%) is required in the Cr-bearing metallic glasses in order to have an effect on thermal stability.

X-ray diffraction of glassy alloy ribbons containing small or moderate amounts of nitrogen, Samples E and G, respectively, shows a poorly-defined α-iron phase when heating the samples tc the first crystallization exotherm. On heating to the second crystallization peak, these samples are characterized by a well-defined α-iron structure plus two or three lines belonging to an unknown but apparently simple structure. This second phase is more developed in the moderate nitrogen content ribbon than in the low nitrogen level sample. The high nitrogen content ribbon, Sample H, shows a complicated structure after heating to either the first or the second crystallization exotherm. As in the other two samples investigated, this structure is more developed for the ribbon heated to the second crystallization peak. The resulting X-ray diffraction pattern gives fairly good agreement with a sigma phase structure (e.g. FeCr and CoCr) plus α-iron, although this leaves several lines unidentified. This identification must be viewed with caution because sigma phase has only tetrahedral interstices which could not possibly accommodate nitrogen atoms, although sigma phase formation on crystallization could be induced by the presence of substantial amounts of nitrogen in the metallic glasses. All that can be said with confidence is that the crystallized structure is complicated and cannot be determined from X-ray powder diffraction data. Nevertheless, the crystallization of metallic glasses containing substantial amounts of nitrogen is different from and occurs at higher temperature than that of control samples having relatively low nitrogen contents. This difference in crystallization behaviour imparts enhanced thermal stability to the high nitrogen content alloys, as shown in Fig. 3.

3.4. Curie temperature measurements

The Cr-bearing metallic glasses of the present investigation have Curie temperatures, T_c, very close to that of $Fe_{66}Cr_{19}B_{15}$ glassy alloy [10]. While the 0.5 at% substitution of nitrogen for Si has been shown to cause a substantial increase in crystallization temperature, the effect of this alloying substitution on as-cast sample T_c is relatively minor. The variation in Curie temperature with one hour annealing temperature are plotted in Fig. 4. The effect of isochronal annealing on T_c for various metallic glasses typically shows an initial positive variation [11, 12] which may change to a negative variation at higher annealing temperatures. Therefore, the initially negative slope of the low nitrogen alloy shown in Fig. 4 is somewhat of an unexpected trend. Furthermore, the opposite sense of the T_c dependence on annealing with the 0.5 at% substitution of nitrogen and Si is also remarkable. Thus, while the addition of small amounts of nitrogen to the Cr-bearing alloy has no drastic effect on as-cast sample Curie temperature, the T_c annealing response is not yet understood.

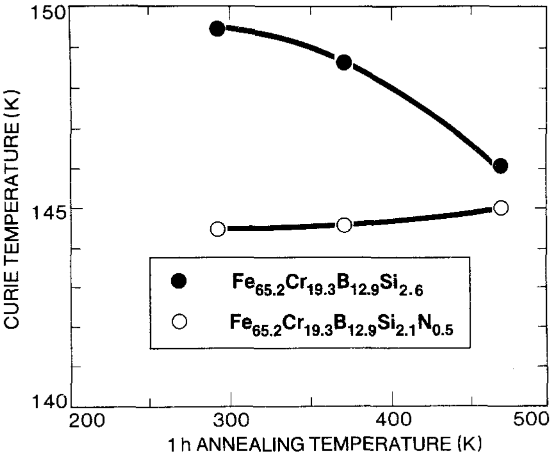

Figure 4 Cr-bearing metallic glass Curie temperature as a function of one hour anneal temperature.

4. Concluding remarks

Metallic glasses containing nitrogen as an alloying element have been fabricated using selective master alloy pre-melting and ribbon melt-spinning procedures. Furthermore, nitrogen has been demonstrated to be a desirable metalloid in the Cr-bearing composition investigated, raising the start-of-crystallization temperature by 31 K with only a 0.5 at% addition. In order to obtain a master alloy containing a substantial level of nitrogen, the composition should include a strong nitride former which promotes dissolution of gaseous nitrogen in the melt. Chromium is a preferred nitrode former because additional nitrogen may be added to the melt by using CrN during premelting. While melt-spinning in 100 kPa nitrogen atmosphere yields a glassy alloy ribbon containing more nitrogen than a control sample case in vacuum, the nitrogen level difference between the two metallic glasses differs by only a small amount.

While the as-cast Cr-bearing glassy alloy ribbons which were studied exhibited a dramatic increase in crystallization temperature with the addition of small amounts of nitrogen, embrittlement and Curie temperature are not as strongly affected. As shown by the data in Fig. 3, no change in crystallization temperatures is apparent until a nitrogen content of approximately 0.25 at% is exceeded. The shift in crystallization temperature observed is the result of nitrogen-induced changes in the precipitating crystalline phases. Thus, at low nitrogen contents, the dilution of this element in the metallic glass is believed to be great enough so that crystallization of a low nitrogen metallic glass is indistinguishable from that of a virtually nitrogen-free specimen. Perhaps it was the low nitrogen contents used (< 0.1 at%) which resulted in no mention of a nitrogen-induced effect on crystallization temperature by Shimada [1].

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