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The influence of composition on the formation and stability of Ni-Si-B metallic glasses

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The influence of composition on the formation and stability of Ni-based glassy alloys containing Si and B has been investigated systematically. Depending on the Si:B ratio certain compositions, with total metalloid contents in the range 17 to 49 at % (a wider range than has hitherto been reported for metal–metalloid glasses), have been vitrified by melt–spinning to an average thickness of 17 μm. For metalloid concentrations greater than 36 to 40 at % the amorphous phase is brittle in the as-quenched state. The highest crystallization temperatures, T_x, occur at 32 to 38 at % metalloid, the actual value of T_x again depending on the Si:B ratio. It is shown that, over a wide composition range, the glass-forming boundary corresponds closely with a value for the reduced crystallization temperature isometric of 0.52. This value corresponds to a critical cooling rate for glass formation of about 10^6 K sec^{-1}, predicted from kinetic theories and assuming that T_x is a good estimate of the glass transition temperature, T_g. This agrees quite closely with the cooling rate for approximately 17 μm thick tape predicted from thermal studies of the melt-spinning process. Hence, T_x/T_{liq} usefully describes the glass-forming ability (GFA) for much of the composition range studied, although preliminary results suggest that near the centre of the glass-forming range the GFA may be over-estimated. Substitution of Si by other metalloid elements from Groups IIIb–Vb in $Ni_{78}Si_{10}B_{12}$ glassy alloy generally decreases the thermal-stability.

1. Introduction

The ease of formation and the thermal-stability of metallic glasses are strongly dependent on the composition. For instance, it is recognized that alloy compositions close to deep eutectics are often comparatively easy glass-formers [1–6] since they usually exhibit high reduced glass temperatures, T_g/T_{liq} (where T_g and T_{liq} are the glass transition and liquidus temperatures, respectively). It has also been established that glassy alloys based on refractory metals which have high cohesive energies exhibit the highest thermal-stability of metallic systems [3–6] with crystallization temperatures, T_x, in excess of 1200 K in some instances, e.g. $Ta_{55.5}Ir_{44.5}$ [7]. Recently, it has been shown that lower concentrations of refractory metals (i.e. less than 10 at %) can substantially improve the thermal-stability of melt-spun Fe- and Ni-based glassy alloys, particularly when the atomic size difference between solvent and solute metal species is large [8, 9].

There have, however, been relatively few detailed studies of the effects of metalloid species and concentrations on the formation and stability of Fe- and Ni-based glassy alloys [10–12]. In this paper, following an earlier preliminary report [13], the results of a comprehensive investigation of the formation and thermal-stability of Ni–Si–B metallic glasses prepared by chill-block melt-spinning are presented and discussed. Previous studies of this system [11] have concentrated on tape vitrified by twin roller-quenching for which the glass-forming concentration range is more restricted. In addition, the effects on thermal-stability of substituting Si in $Ni_{78}M_xSi_{10-x}B_{12}$ alloys by other metalloids, M, from Groups IIIb–Vb (B, Al, C, Ge, Sb or Bi) is briefly summarized.

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2. Experimental procedures

Alloy ingots of nominal composition $Ni_{100-(x+y)}Si_xB_y$ were prepared by melting mixtures of the appropriate high-purity elemental materials in a boron nitride crucible in flowing argon–5 vol% hydrogen. A small weight loss (between 0.1 wt% and 0.2 wt%) usually occurred on melting. The alloys were subsequently melt-spun in air to produce extended tapes 0.5 mm to 2.0 mm in width with an average thickness of 17 ± 3 μm. The details of this technique have been reported elsewhere [14, 15]. The amorphous structure of the tapes was established by X-ray diffraction methods (within the limits of detection of about 2% crystal). Thermal traces for crystallization of amorphous samples were obtained using a Perkin-Elmer DSC-2 differential scanning calorimeter at a heating rate of $80\,K\,min^{-1}$. In all instances, the crystallization temperature, T_x, was defined as the temperature at which deviation from the base-line first occurred. The high heating rate was employed in an attempt to resolve the glass-transition (the magnitude of the glass-transition temperature, T_g, being assumed to be a direct reflection of the glass-stability). However, only a few samples exhibited a well-defined glass-transition and, in the absence of the thermal manifestation of this transition, T_x was taken as a lower limiting estimate of T_g. Generally, in the present case, T_x measured at $80\,K\,min^{-1}$ is indeed a good estimate of T_g, though with notable exceptions; this is discussed in detail later.

The liquidus temperatures, T_{liq}, of powdered alloy samples contained in fused-silica or alumina crucibles were obtained by differential thermal analysis (DTA) (using a Stanton–Redcroft DTA 673/4) at heating rates of $10\,K\,min^{-1}$ and $20\,K\,min^{-1}$ in flowing argon. Significant undercooling of the small samples employed (occasionally as high as 150 K to 200 K for 200 mg samples) necessitated the use of heating rather than cooling programmes. Standard methods of determining T_{liq} from DTA traces were generally employed (for example [16]), but in some instances an empirical correction procedure utilizing DTA traces of alloys of accurately known T_{liq} (e.g. Cu–Ag) was necessary [9].

3. Results

The glass-forming range for Ni–Si–B alloys prepared by melt-spinning is shown in Fig. 1, together with the crystallization temperature isotherms. Depending on the Si:B ratio, alloys containing between 17 at% and 49 at% metalloid could be fully vitrified in a tape thickness of 17 ± 3 μm. Binary Ni–B alloys could however only be vitrified over a narrow composition range from 17 at% to 18.5 at% B and over the wider range from 31 at% to 41 at% B. Binary Ni–Si alloys could not be vitrified by melt-spinning. The highest crystallization temperatures, ($T_x > 800\,K$ measured at $80\,K\,min^{-1}$) occurred for B-rich alloys at relatively high total metalloid contents (between about 32 at% and 38 at%) the actual T_x depending on the Si:B ratio (e.g. for $Ni_{66}Si_8B_{26}$, $T_x = 834\,K$, whilst for $Ni_{66}Si_{18}B_{16}$, $T_x = 770\,K$). $Ni_{83}B_{17}$ exhibited the lowest stability of the fully amorphous binary alloys with $T_x = 547\,K$, whilst the ternary composition having the lowest stability was $Ni_{82}Si_4B_{14}$, with $T_x = 589\,K$.

Significantly, not all the glass-forming compositions yielded fully ductile tapes. Alloys situated to the high-metalloid side of the "ductile-brittle" boundary shown in Fig. 1 could not be bent through 180° without fracturing, although they were fully amorphous as resolved by X-ray diffraction. Using a simple bend test in which the radius of curvature of the tape at fracture was taken as an estimate of the brittleness of the material, it was noted that amorphous alloys generally became more brittle (i.e. the radius of curvature at fracture increased) as the metalloid content was further increased beyond this ductile–brittle boundary.

The thermal behaviour of the amorphous alloys, as resolved by the differential scanning calorimeter, was usually qualitatively similar for glasses situated along a given T_x isotherm. For instance, alloys coincident with the 660 K and 820 K isotherms exhibited two well-defined and well-separated exothermic peaks. On the other hand, alloys along the 780 K isotherm mostly exhibited either three well-defined peaks, or two peaks the first exhibiting a low-temperature shoulder; exceptions to the latter were alloys containing less than 2 at% Si which exhibited one or two peaks only. In contrast, the thermal behaviour of alloys along the 720 K isotherm varied markedly showing one to four exothermic peaks, depending on the composition.

The liquidus temperatures of many of the alloy compositions shown in Fig. 1 were measured by DTA in order to determine the corresponding re-

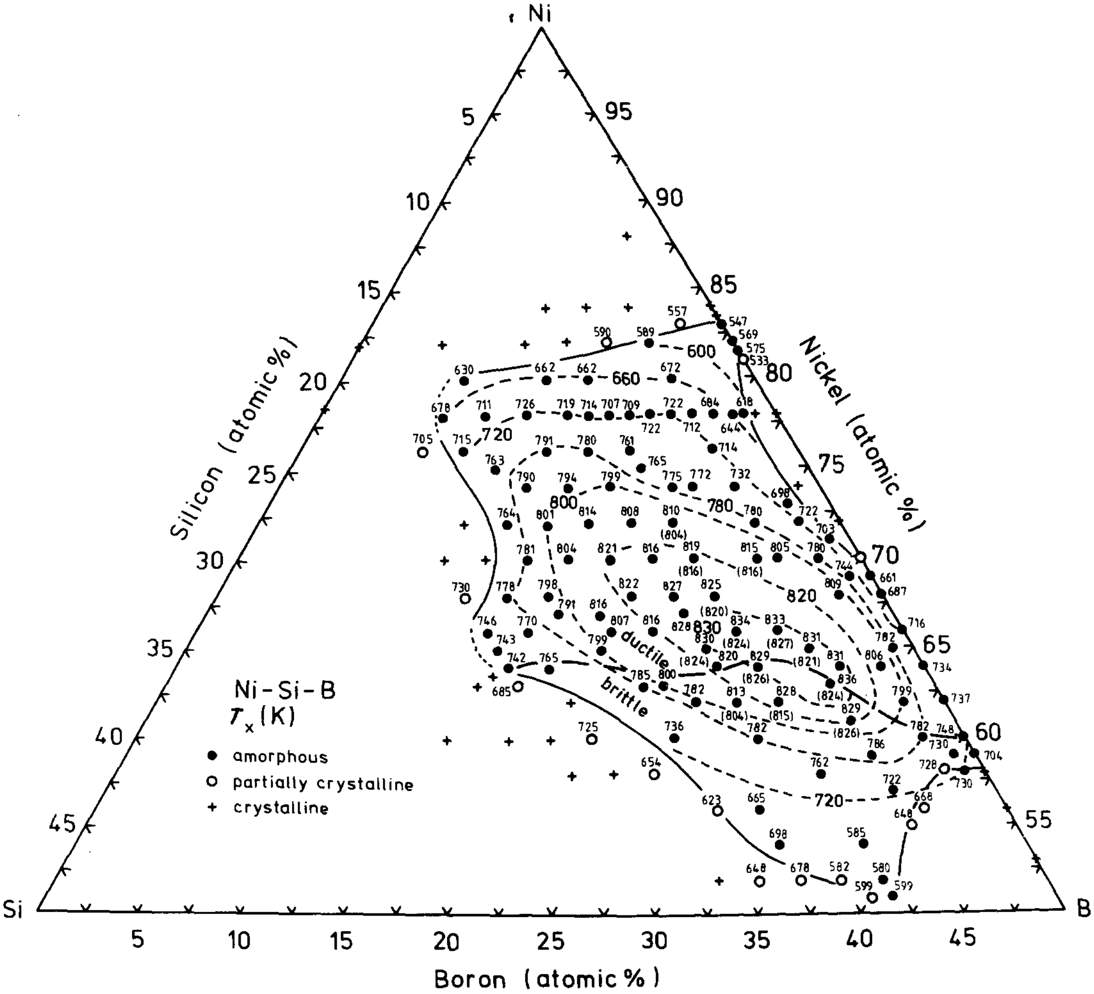

Figure 1 Glass-forming boundary and crystallization temperature isotherms (in K) for melt-spun Ni–Si–B alloys of thickness 17 ± 3 μm. Individual alloy compositions and crystallization temperatures (determined at a cooling rate of 80 K min^{-1}) are indicated. The glass transition temperature (mid-point) is also recorded (in brackets) for the limited number of alloys for which a *well-defined* glass-transition is thermally manifest at 80 K min^{-1}. Alloys situated to the high-metalloid side of the "ductile–brittle" boundary cannot be bent through 180° without fracturing.

duced crystallization temperatures, T_x/T_{liq}. It is appropriate, however, to briefly summarize and compare with the available published data some of the present results since they relate closely to the glass-forming ability within the system. In the binary Ni–B system, for instance, the following eutectic compositions and temperatures (T_{eut}) were obtained (the eutectic temperatures were calculated by averaging the values for solidus temperatures of alloys in the vicinity of the eutectic composition: (i) ~ 18 at % B, T_{eut} = 1374 ± 6 K; (ii) ~ 31.5 at % B, T_{eut} = 1393 ± 6 K; (iii) ~ 39.5 at % B, T_{eut} = 1306 ± 4 K. These results compare with a diverse range of published data [17, 18] reporting binary eutectics at (i) 18, 18.4 or 18.5 at % B with T_{eut} = 1353, 1366 or 1413 K respectively; (ii) 30, 30.8 or ~ 36 at % B with T_{eut} = 1368 or 1398 K respectively; (iii) 38 or ~ 44 at % B with T_{eut} = 1263 K.

In the ternary system, a well-defined eutectic was noted at approximately 10 at % Si/20 at % B with T_{eut} ~ 1275 K. This compares favourably with a value of 9.8 at % Si/20.3 at % B and T_{eut} = 1264 K reported by Omori *et al.* [18]. Other minimum melting point composition regions were noted in the present work, but there are insufficient data to specify these with sufficient accuracy.

The reduced crystallization temperature

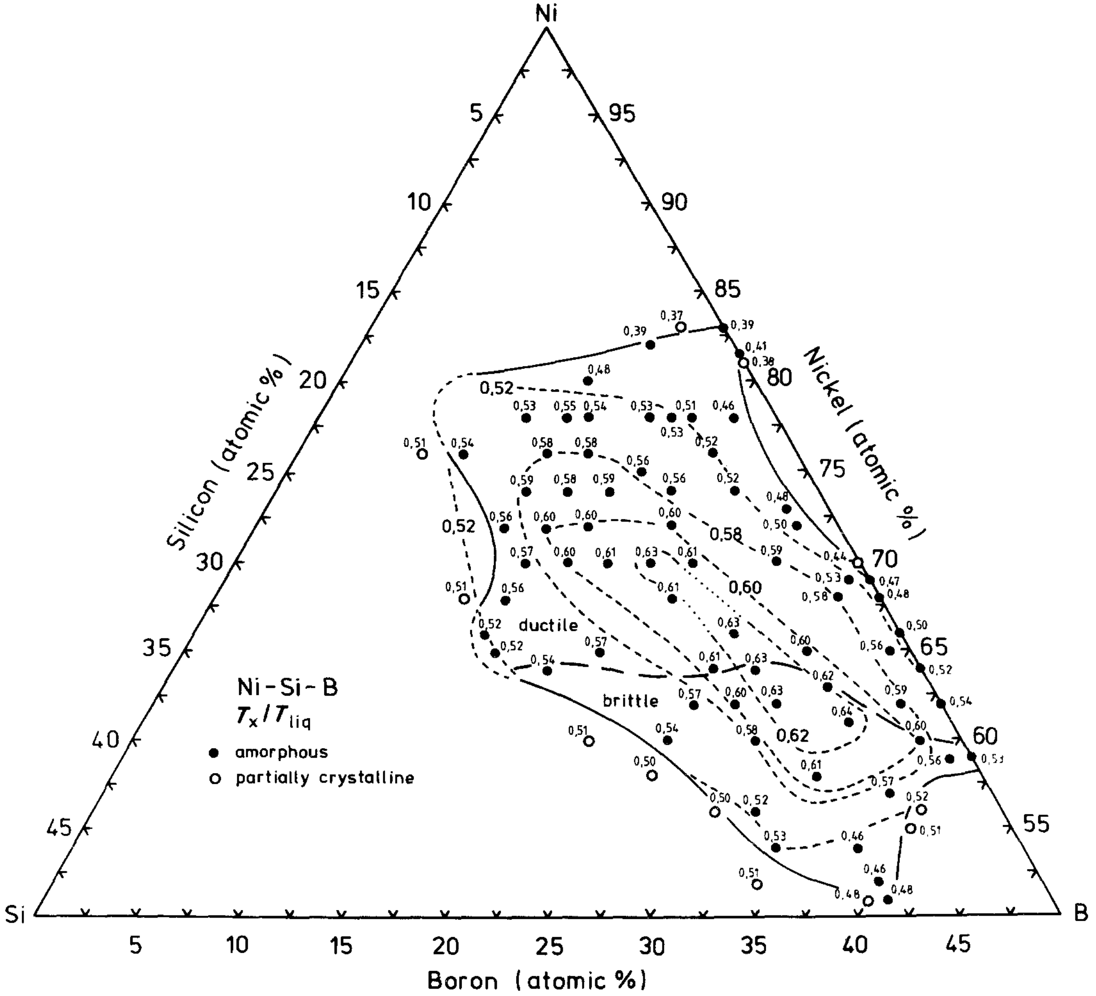

Figure 2 Reduced crystallization temperature (T_x/T_{liq}) isometrics as a function of composition for glassy Ni–Si–B alloys of mean thickness 17 μm. The glass-forming boundary is superimposed for comparison with the 0.52 isometric.

(T_x/T_{liq}) isometrics are plotted in Fig. 2 with the glass-forming boundary superimposed. It is notable that, with the exception of compositions centred around the low-boron eutectic, and around the high-metalloid extremity of the glass-forming range, the isometric corresponding to a value of 0.52 closely follows the glass-forming boundary. The significance of this is discussed later.

Substitution of Si by other metalloid elements, M = B, Al, C, Ge, Sb or Bi, in $Ni_{78}Si_{10-x}M_xB_{12}$ alloys decreased the stability (Fig. 3) with the exception of B for $x < 6$ at% which had minimal effect. Bismuth produced the maximum decrease (e.g. 5 at% Bi reduced T_x from 720 K to 590 K). The effect of the metalloid substitutions in reducing T_x falls in the series: Bi > C > Al > Sb > Ge > B (for B > 7 at%). As illustrated in Fig. 3, only Ge could be completely substituted for Si in the 10:12 ratio and still yield fully amorphous tape. Glassy alloys containing Bi or > 5 at% Sb were brittle as-quenched.

4. Discussion

As shown in Fig. 1, depending on the Si:B ratio, Ni–Si–B glassy alloys have been prepared containing 17 at% to 49 at% metalloid. This significantly extends the range reported by Inoue *et al.* [11] for twin roller-quenched tape and, in addition, covers a much wider range of metalloid contents than has hitherto been reported for metal–metalloid glasses. Binary Ni–B alloys have also been vitrified over a narrow composition range from about 17 at% to 18.5 at% B and over a wider range from 31 at% to 41 at% B. These binary compositions could not be vitrified by twin roller-quenching. The latter

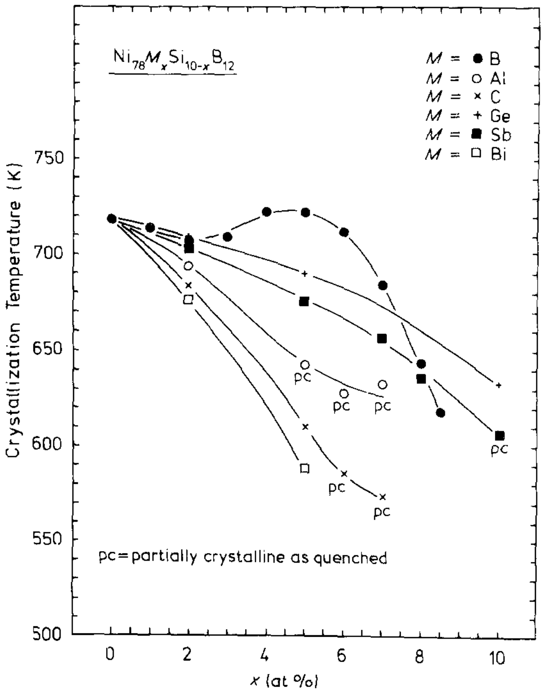

Figure 3 Crystallization temperature as a function of concentration, x, of metalloid elements, M, substituted for Si in $Ni_{78}M_xSi_{10-x}B_{12}$ alloy (where M can be either, B, Al, C, Ge, Sb or Bi).

B-composition range is similar to that reported recently by Inoue *et al.* [19] for melt-spun tape (33 at % to 43 at % B). Previously, high-boron (approximately 41 at %) Ni–B amorphous alloys had only been produced by electroless deposition [20]. Low concentrations of B yielded crystalline material by all these techniques, although Takahashi *et al.* [21] have reported partially amorphous melt-spun $Ni_{81.5}B_{18.5}$.

Alloys which are the most stable thermally are situated toward the metalloid-rich side of the glass-forming region (i.e. between 32 at % and 38 at % metalloid) and maximum crystallization temperatures, T_x, are obtained over a fairly wide composition range (Fig. 1). In contrast, the least stable alloys are situated around the low-B binary eutectic, with T_x values less than 600 K. The overall span of T_x is hence very high for the Ni–Si–B system, of the order of 290 K (for melt-spun Fe–Si–B [10] it is approximately 235 K). For Ni–B *binary* alloys the variation of T_x with composition is substantially larger than for other binary systems studied earlier, approximately 200 K between 17 at % and 40 at % B. This compares with about 80 K for Pd–Si [22] in the range 5 at % to 25 at % Si, and about 100 K for Fe–B [10], although here the composition range concerned is smaller, between 10 at % and 22 at % B.

As indicated in Fig. 1, not all the amorphous compositions yield fully ductile tapes (i.e. tapes that can be bent plastically through 180° without fracturing). Alloys containing greater than 36 at % to 40 at % metalloid, depending on the Si : B ratio, are less ductile or brittle in the as-quenched state. It is interesting that over part of the composition range, at higher metalloid contents, the ductile–brittle boundary corresponds quite closely to the glass-forming boundary reported by Inoue *et al.* [11] for twin roller-quenched Ni–Si–B. Melt-spun amorphous Fe–Si–B alloys have also been reported to exhibit brittle behaviour in the high metalloid region of the system [23]. In contrast, certain low metalloid Fe–Si–B alloys are ductile as-quenched but are crystalline. This emphasizes the danger of using a simple bend–ductility test to establish whether or not a metal–metalloid alloy is glassy.

The structure of metal–metalloid glassy alloys has been described [24] as a dense random-packed (DRP) metallic network, into which the usually smaller metalloid atoms are packed interstitially, at least up to approximately 25 at %. Recent work on ternary systems based on Fe, Ni or Co with Si and B [10–13] has however demonstrated that glass-forming ranges can be extended well beyond 25 at % metalloid, and up to about 49 at % has been achieved in the present case for Ni–Si–B. Clearly, in these instances, not all the metalloid atoms can be accommodated interstitially and a proportion of the atoms, particularly the larger Si atoms, are presumably accommodated in the DRP network substitutionally, as proposed by Inoue *et al.* [11]. It is possible that the Ni–Si–B alloys become less ductile and brittle at high total metalloid contents due to an increasing proportion of directional metalloid–metalloid covalent bonds. As noted in Fig. 1, the ductile–brittle boundary starts at about 35 at % metalloid at the Si-rich end and increases to about 40 at % metalloid at the Ni–B binary. This would be expected since B is a significantly smaller atom than Si and hence more B could be accommodated before a sufficient number of metalloid–metalloid contacts are established to reduce the ductility. It is expected that the electrical resistivity of these glassy alloys will increase significantly as the metallic bonding component decreases in the very high metalloid range, and this aspect is presently under investigation. The structures of alloys containing both low and high metalloid concentrations are currently being compared using X-ray and neutron diffraction methods and these results will be reported shortly [25]. In addition, extended X-ray absorption fine structure (EXAFS) studies are also in preparation, from which an insight into the local atomic structure may be gained.

It has been proposed [1–6] that the critical cooling rate, R_c, required to vitrify a metallic material, and hence the glass-forming ability (GFA), is determined largely by the reduced glass temperature, T_g/T_{liq}. The glass-forming boundary shown in Fig. 1 for melt-spun tape of average thickness 17 μm corresponds closely with a reduced crystallization temperature (T_x/T_{liq}) isometric of 0.52 over the greater part of the composition range. Assuming T_x is close to T_g, this value of T_x/T_{liq} corresponds to a R_c value of about 10^6 K sec^{-1} [5]. Moreover, studies of the melt-spinning process indicate that the heat-transfer coefficient for the melt–roller interface for a range of materials including Ni-based alloys [5, 26] is about 10^5 W m^{-2} K^{-1}, for which 17 μm thickness tape also gives a cooling rate of about 10^6 K sec^{-1}. This suggests that the magnitude of T_x/T_{liq} gives a good estimate of the GFA over much of the boundary region. However, certain glass-forming compositions centred around the Ni–B eutectic (at ~ 18 at % B) exhibit anomalously low values for T_x/T_{liq}. On this basis, if T_x were close to T_g for these alloys they should require cooling rates of the order of 10^8 K sec^{-1} for vitrification, which is clearly not the case. Thus, in these instances, T_x is probably well below T_g, but the reason for this is unclear. As a test, some of the alloys not thermally manifesting a glass transition at a heating rate of 80 K min^{-1} were heated at 320 K min^{-1} in order to retard crystallization sufficiently to reveal T_g (transformation temperatures were corrected to a heating rate of 80 K min^{-1}). Alloys lying well within the glass-forming region exhibited well-defined T_g which agreed to within < 15 K of T_x when measured at 80 K min^{-1} (indicating that T_x is generally a good estimate of T_g). On the other hand, alloys close to the Ni–B eutectic did not manifest a glass-transition at this high heating rate, indicating that T_g for these alloys is greater than 15 K above T_x measured at a heating rate of 80 K min^{-1}. In addition, high-metalloid ternary compositions (> 45 at % B) situated at the extreme of the glass-forming range also exhibit anomalously low values for T_x/T_{liq}, and similarly these alloys do not manifest a T_g value at 320 K min^{-1}. On the other hand, however, most of the ternary alloys situated around the glass-forming boundary also do not exhibit a well-defined T_g at the high heating rate. The reasons for this are not clear and are currently being further investigated, but the close correspondence of much of the glass-forming boundary to the 0.52 isometric suggests that in these instances T_g is not much greater than 15 K

A wider comparison of the observed glass-forming abilities with the theoretical predictions based on kinetic theories is currently being made. Preliminary experiments have been performed in which the thickness of glassy alloy tapes has been varied (by controlling the roll speed) in order to determine the limiting thickness greater than which the material can no longer be fully vitrified. For a material of given T_x/T_{liq}, the theoretical critical cooling rate can be roughly estimated from a plot of R_c against T_g/T_{liq} which has been compiled from alloys of known T_g/T_{liq} [5]. From a knowledge of R_c values, the maximum thickness, x, that can be vitrified in one operation can then be estimated from a plot of cooling rate against x [5]. Close to the glass-forming boundary, it appears that alloys can be vitrified in thicknesses slightly greater than those predicted, whilst near the centre of the glass-forming range the predicted thicknesses are an over-estimation. The detailed results of this investigation will be reported in a later publication.

The effect on the thermal-stability of substituting other metalloid elements, M, for Si in $Ni_{78}M_xSi_{10-x}B_{12}$ alloys (Fig. 3) cannot be adequately explained on the basis of cohesive energy, atomic size or outer electron configuration of the element M. The closest qualitative approximation is found with the melting temperatures, T_m, of the Ni_3M compound, which in order of decreasing T_m is: Al > Si > Ge/B > Sb (C and Bi do not form stable compounds with Ni). The increase in stability on alloying with Al predicted on this basis is not however realized. The small size of the C-atom would give rise to a lower activation barrier for diffusion which would decrease the thermal stability. Germanium is the only metalloid of this series that can be completely substituted for Si (in the 10:12 ratio) and still yield fully amorphous alloy, although this may not be surprising in view of the chemical similarity between Si and Ge.

5. Conclusions

(a) Ni–Si–B alloys have been vitrified by melt-spinning to an average thickness of $17\,\mu m$ over a wider composition range (between about 17 at % and 49 at % metalloid) than has hitherto been reported for metal–metalloid systems. Binary Ni–B alloys have also been vitrified over the composition ranges 17 to 18.5 at % B (not previously reported) and between 31 at % and 41 at % B.

(b) The highest crystallization temperatures, T_x, occur at relatively high total metalloid contents, between 32 at % and 38 at %, the actual value of T_x depending on the Si : B ratio.

(c) The variation of T_x with composition is larger than that observed previously for other systems, approximately 290 K for Ni–Si–B over the range 17 at % to 49 at % metalloid and approximately 200 K for binary Ni–B between 17 at % and 40 at % B.

(d) At high metalloid concentrations (> 36 at % to 40 at %, depending on the Si : B ratio) the glassy alloys are less ductile or brittle in the as-quenched state, probably due to the existence of super critical proportions of directional metalloid–metalloid bonds. This emphasizes the unreliability of a simple bend-ductility test to establish whether or not a metallic alloy is glassy.

(e) The glass-forming boundary corresponds closely to a value of 0.52 for the reduced crystallization temperature (T_x/T_{liq}) isometric over much of the composition range studied. This value corresponds to a critical cooling rate for glass-formation of about 10^6 K sec^{-1} and agrees well with the experimentally estimated cooling rate for $17\,\mu m$ ribbon for the chill-block melt-spinning process.

(f) Substitution of Si by other metalloid elements, M, in the $Ni_{78}M_xSi_{10-x}B_{12}$ alloy decreases the thermal-stability for a given concentration, x, in the order: Bi > C > Al > Sb > Ge > B (for B greater than 7 at %).

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