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THE FORMATION AND STABILITIES OF Fe-, Ni- AND Co-BASED METALLIC GLASSES

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Abstract.- The influence of alloying substitutions from the 3d, 4d and 5d transition series on the thermal-stabilities of Fe-, Ni- and Co-based metallic glasses containing 10 at.% Si and 12 at.% B glass formers has been systematically investigated. The changes are interpreted in terms of variations in (s+d) electron concentration and of the size difference between solvent and solute metals. The effect of changes in metalloid ratios on the stabilities and formation of NiSiB alloys is also reported.

Introduction.- The ease of formation and the stability of metallic glasses are strongly influenced by the composition /1-6/. In this paper we report and discuss the results of a study of the effects of a wide range of alloying additions from Periods 4, 5 and 6 on the thermal-stability of Fe-, Ni- and Co-based materials containing Si and B. In addition, we discuss the effect of variations in metalloid content and ratio on the glass-forming ability and thermal-stability of Ni-based alloys.

Experimental.- Alloy ingots of nominal compositions, Ni_{100-(x+y)}B_xS_{12} and (Fe, Ni, or Co)_{78-x}M_{x}Si_{10}B_{12}, where M is a transition metal or Cu, were vitrified as thin ribbons ~20 µm thick and 0.5-2.0 mm wide by chill-block melt-spinning in air /7/. The amorphous structure of the tapes was established by X-ray diffraction. The thermal behaviour of the glassy alloys was established by DSC, scanning at a heating rate of 80 K/min. The high heating rate was employed in an attempt to resolve the glass transition. In the absence of a well-defined glass-transition, the crystallization temperature, T_c, was taken as a lower-limiting estimate of the glass-transition temperature, T_g, and hence of the glass stability. In all instances, T_c was defined as the temperature at which the calorimetric trace (i.e. the specific heat) first departs from the base line for the first exothermic peak in a DSC scan. Alloy liquidus temperatures, T_{liq}, were determined by differential thermal analysis (Stanton-Redcroft DTA 673-4) of powdered samples contained in alumina or fused silica crucibles.

Results.- The glass-forming range and crystallization temperature isotherms for Ni-Si-B alloys of average thickness 17 ± 3 µm are shown in fig. 1. Ternary alloys were fully vitrified over a wide composition range from 17-49 at.% metalloid, depending on the Si:B ratio. In addition, binary Ni-B alloys were vitrified in the composition ranges 17-18.5 at.% B and 31-41 at.% B. Not all the amorphous compositions were fully ductile. Alloys to the right of the boundary 'A-B' shown in fig. 1 could not be bent through 180°, in the as-cast state, without fracturing. Compositions close to the boundary exhibited some plastic deformation, although towards the high-metalloid extremity of the glass-forming range alloys were completely brittle and exhibited no macroscopic plastic deformation.

Fig. 1: Glass-forming boundary and crystallization temperature isotherms for 17 ± 3 µm thick melt-spun Ni-Si-B alloys. Glasses to the high-metalloid side of the boundary 'A-B' become progressively less ductile as the metalloid content is further increased.

In figure 2 are plotted the reduced crystallization temperature isometrics, T_c/T_{liq}. The glass-forming boundary is included for comparison, and it is notable that this generally corresponds closely to a T_c/T_{liq} isometric of 0.52. Exceptions are
found, however, centred around the low-boron binary eutectic and towards the high-metalloid extremity of the glass-forming region, and in these instances \( T_x \) is not a good estimate of \( T_y \). This is discussed later.

![Graph](image)

**Fig. 2:** Reduced crystallization temperature isometrics, \( T_x / T_{liq} \), as a function of composition for glassy Ni-Si-B alloys. The glass-forming boundary is shown for comparison with the 0.52 isometric.

The crystallization temperatures of alloys based on Fe or Ni with 10-12 at.% Si and containing transition metal or Cu additions, are plotted against the average outer \((d + s)\) electron concentration, \( e/a \), of the metallic components in fig. 3. It is seen that, with some exceptions, a well-defined non-linear trend of increasing \( T_x \) with decreasing \( e/a \) is obtained for Period 4 alloying additions, whilst for additions from Periods 5 and 6 significant deviation from the mean Period 4 curve occurs. The significance of these observations is discussed later.

**Discussion.** For the Ni-Si-B ternary alloys, a well-defined \( T_x \) is resolved (at 80 K min⁻¹) only for certain compositions lying near to the centre of the glass-forming range. However, \( T_x \) can be resolved thermally for many of the other compositions by heating at 320 K min⁻¹ which retards the onset of crystallization sufficiently to reveal the glass-transition. In these instances, \( T_x \) measured at 80 K min⁻¹ is a very good estimate of \( T_y \) (to within < 15 K). However, for alloys situated near to the low-boron binary eutectic, and also for alloys towards the extremity of the high-metalloid glass-forming range, \( T_x \) cannot be resolved even at 320 K min⁻¹. Hence, in these instances, \( T_x \) is >15 K above \( T_y \) measured at 80 K min⁻¹.

![Graph](image)

**Fig. 3:** Variation of crystallization temperature, \( T_x \), with the average outer \((d + s)\) electron concentration, \( e/a \), of the constituent metals for Fe- and Ni-based metallic glasses.

The glass-forming range shown in fig. 1 significantly extends the range of Ni-Si-B compositions vitrified by Inoue et al. /9/ by twin-roller quenching. Binary Ni-B alloys could not be vitrified by twin-roller quenching, although Inoue et al. /10/ later reported that alloys in the composition range 33-43 at.% B could be fully vitrified by melt-spinning.

The low-boron binary alloys have not been fully vitrified previously, although partially glassy Ni₈₁₈₁₈₅ has been reported /11/.

The dependence of \( T_x \) on composition is very high for the binary Ni-B alloys, being of the order of 190 K between 17 and 38 at.% B. A continuous increase in \( T_x \) is observed on increasing boron from 17 at.% (547 K) through to 38 at.% (737 K), after which \( T_x \) decreases.

In the present work for binary Ni-B, the eutectic compositions and temperatures derived by DTA are in closest agreement with the phase diagram given in reference 12. We find eutectics at \( \sim 18 \) at.% B (1374 ± 6 K), \( \sim 31.5 \) at.% B (1393 ± 6 K), and at \( \sim 39.5 \) at.% B (1300 K). The low-boron glass-forming range is centred narrowly around the eutectic at \( \sim 18 \) at.% B, whilst the high-boron glass-
The glass-forming range extends from the low-boron side of the eutectic at 31.5 at.%B to the high-boron side of the eutectic at 39.5 at.%B.

The $T_g$ isotherms shown in Fig. 1 lie approximately parallel to a line joining the two ternary eutectic compositions reported by Omori et al. at 12.9 at.%Si + 9.8 at.%B and 9.8 at.%Si + 20.3 at.%B, respectively. The highest crystallization temperatures occur toward the centre of the glass-forming range, but are displaced slightly to the high-metalloid side. The high values for the reduced crystallization temperatures (and by inference the glass-forming ability) in this range, are favoured more by increased $T_x$ and thus probably $T_g$, than by decreased $T_{liq}$.

Alloys containing $\geq 35-40$ at.% metalloid (depending on the Si:B ratio) are less ductile or brittle in the as-quenched state, possibly due to an increasing proportion of directional metalloid-metalloid covalent bonds. The structure of metalloid glassy alloys in the range $\sim 15-25$ at.% metalloid has been described by a dense random-packed metallic network, into which the smaller and softer metalloid atoms are situated interstitially /14/. This model cannot, however, describe the structure of the high metalloid alloys for which a proportion of the metalloid atoms must be accommodated substitutionally. The structure of these alloys is currently being examined by X-ray and neutron diffraction /15/, and also by EXAFS.

With the exception of alloys situated near to the Ni-B binary eutectic at $\sim 18$ at.%B and at the high-metalloid extremity of the glass-forming range, for which it has been shown that $T_g$ is not a good estimate of $T_{liq}$, the glass-forming boundary (Fig. 2) coincides remarkably closely to a value for the reduced crystallization temperature isometric, $T_x/T_{liq}$, of 0.52. This value corresponds to a critical cooling rate for glass formation of $\sim 10^6 \text{ K sec}^{-1}$ (2,16) (assuming $T_x$ is a good estimate of $T_g$, as generally appears to be the case), and studies of the melt-spinning process indicate that for 17 $\mu$m thick tape this is of the order of cooling rate obtained in practice for Ni-based alloys /16/. Hence, $T_x/T_{liq}$ usefully describes the glass forming range for the Ni-Si-B system. A more detailed study of the practical glass-forming ability is presently underway, and preliminary work has been reported elsewhere /17/.

We have shown previously that the thermal-stability of a wide range of glassy alloys is broadly related to the cohesive energies of the constituents (3,4). However, in detail, the composition dependence of the thermal-stability for Fe- and Ni-based glassy alloys containing dilute concentrations (\textless 15 at.%) of refractory and other transition metals is a function of both the average outer (d+s) electron concentration, $g/a$, of the metallic components, and the atomic size difference between solvent and solute metal species /8/. Figure 3 shows the dependence of $T_x$ on $g/a$ for Period 4 additions (bottom curve) which, with the exception of Ti, Mn and V, have very similar atomic sizes to Fe and Ni. ($T_x$ measured at 80 K min$^{-1}$) is again taken as an acceptable estimate of $T_g$ studies at higher heating rates, up to 320 K min$^{-1}$, confirm that $T_x \approx T_g$ at 80 K min$^{-1}$ for these alloys). Also, in Fig. 3 (top curve) the effect of solute substitutions from Periods 5 and 6 which have significantly larger atomic sizes than Fe or Ni is shown. The increase in $T_x$ for these additions is greater than that obtained solely from an $g/a$ contribution, with Zr and Hf providing a greater increase than Mo and Ta which in turn give a greater increase than Nb and Tc, and this is also in the order of decreasing atomic size. Hence, if $\Delta T_x$ (defined as the actual $T_x$ minus the $g/a$ contribution computed from the mean Period 4 curve for which atomic size difference is negligible) is plotted against $\Delta a/a^2$, where $\Delta a/a$ is the fractional difference in Goldschmidt diameter between solvent and solute metal atoms, a well-defined linear relationship is obtained (Fig. 4), which is common to both the Fe- and Ni-based alloys. The introduction of solute atoms of larger size than Fe or Ni would be expected to increase the strain-energy associated with interdiffusion of the atoms and thus increase the thermal-stability (assuming the size of 'holes' in the structure did not increase).

The effects of Mn, Ti and V substitutions for Ni in Ni-Si-B deviate clearly from the main curve for the Period 4 metal substitutions (Fig.3). This can be explained on the basis of the significantly different atomic sizes. On the other hand, the anomalous effect of the Co-rich alloys cannot be explained on this basis, but seems to be associated with a crystallization behaviour signifi-

antly different from that of the other alloys, and this is also reflected in greatly reduced...
activation energies for crystallization /8/. The apparent continuous extension to the $T_x$ v. $\theta/a$ curve for Cu additions to Ni-Si-B is probably fortuitous, since additions of Cu to Fe-Si-B produce a catastrophic decrease in $T_x$, even for very small concentrations. The reasons for this are unclear, but Cu is not a transition metal and has a "softer" atom and a lower cohesive energy than members of the transition series.

Tentative data for more complex alloys containing Period 4 additions (FeNiCrV-Si$_{10}$B$_{12}$) indicate that the basic $T_x$ v. $\theta/a$ curve is followed, despite the greater alloy complexity. Further data suggest that the basic $T_x$ v. $\theta/a$ dependence for Period 4 alloying additions is generally reflected with other Si:B ratios (fig. 5). Hence, $T_x$ v. $\theta/a$ for Si - B concentrations of 0-17, 4-16, and 10-12 (at.%), all show a non-linear dependence with an initial steep rise in $T_x$ for $\theta/a < 10.0$ (Ni-Si-B) followed by a more gradual rise to an $\theta/a$ of $\approx 8.0$ (Fe-Si-B), again followed by a somewhat steeper rise. The initial steep rise in $T_x$ from Ni-Si-B is not however reflected in the data for alloys containing 10 at.%Si + 18 at.%B, for which $T_x$ is almost independent of $\theta/a$ in the range $\theta/a = 10.0 - 9.0$, after which a gradual increase in $T_x$ does occur. In calculating $\theta/a$ values, we have neglected any charge transfer from the metalloid to the metal atoms. The fact that the detailed $T_x$ v. $\theta/a$ dependence differs slightly, depending on the Si-B content, may reflect differing degrees of charge transfer, although for the low-metalloid alloys it could reflect also artificially low values for $T_x$ (we believe for instance that $T_x$ for Ni$_{0.8}$B$_{17}$ is substantially lower than, and thus not a good estimate of, $T_0$). Work in this field is continuing.

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