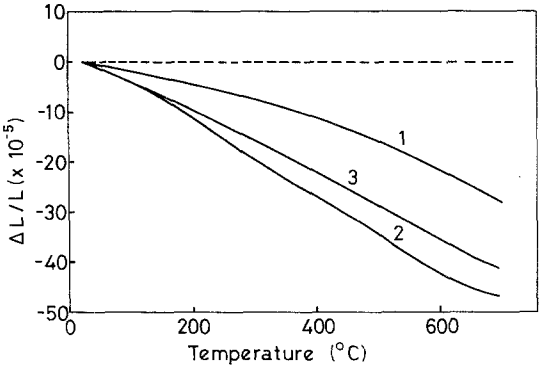

Figure 2 Thermal expansion of the TiO_2–SiO_2 glasses prepared from metal alkoxides. Fused silica is used as a reference.

sitions of the glasses agreed with the analysed ones for the TiO_2–SiO_2 system [11]. The densities of the present glasses are slightly lower than those prepared by melting method, which may be partly attributed to the inclusion of some small pores giving the foggy appearance seen in Fig. 1. The thermal expansion coefficients of the present glasses are as low as those prepared by melting method. In summary, the monolithic TiO_2–SiO_2 glasses of the ultra-low thermal expansion were made from metal alkoxides through hydrolysis and gelling processes.

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Ni–Si–B metallic glasses with high metalloid contents

The compositions of metal–metalloid glassy alloys prepared from the melt in thicknesses $\gtrsim 20\,\mu m$ have generally been limited to fairly narrow ranges centred around deep metal-rich eutectics, typically at ~ 20 at% metalloid [1, 2]. Over these composition ranges glass formation is kinetically favoured because the reduced glass temperature, T_g/T_{liq}, (where T_g and T_{liq} are the glass transition and liquidus temperatures, respectively) is usually $\gtrsim 0.5$ [3]. The structure of the metal–metalloid glasses has been described [4] as a dense random-packed metal network into which the generally smaller metalloid atoms are packed interstitially and it has also been proposed that this would promote glass formation specifically in the range of 15 to 25 at% metalloid. Recently, however, work on ternary systems based on Fe, Ni or Co with Si and B [5–7] has demonstrated that the glass-forming ranges can be extended well beyond 25 at% metalloid, up to ~ 35 at%. In this paper the results of a comprehensive investigation into the formation and properties of Ni–Si–B metallic

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glasses is reported, in which vitrification was achieved to even higher metalloid concentrations, up to 49 at% depending on the Si : B ratio.

Glassy alloy tapes of mean thickness 17 ± 3 μm and width 0.5 to 2.0 mm were prepared by melt-spinning in air. The details of this technique have been reported elsewhere [8]. The amorphous structure of the tapes was established by X-ray diffraction (within the limits of detection of ~ 2% crystal). Crystallization temperatures, T_x, were obtained from differential scanning calorimeter traces recorded at 80 K min^{-1}, and were defined in each case as the temperature at which deviation from the base-line first occurred.

The glass-forming range is shown in Fig. 1 together with the T_x isotherms. Depending on the Si : B ratio, glassy alloys have been prepared containing 17 to 49 at% metalloid. This is a much wider range of metalloid contents than hitherto reported for metal–metalloid glasses, and significantly extends the range of Ni–Si–B glassy alloys reported by Inoue *et al.* [6] for twin roller-quenched tape. In addition, glassy Ni–B alloys have been prepared (which could not be vitrified by twin roller-quenching) over a narrow composition range from about 17 to 18.5 at% B and over a wider range from 31 to 41 at% B. The latter composition range is similar to that reported

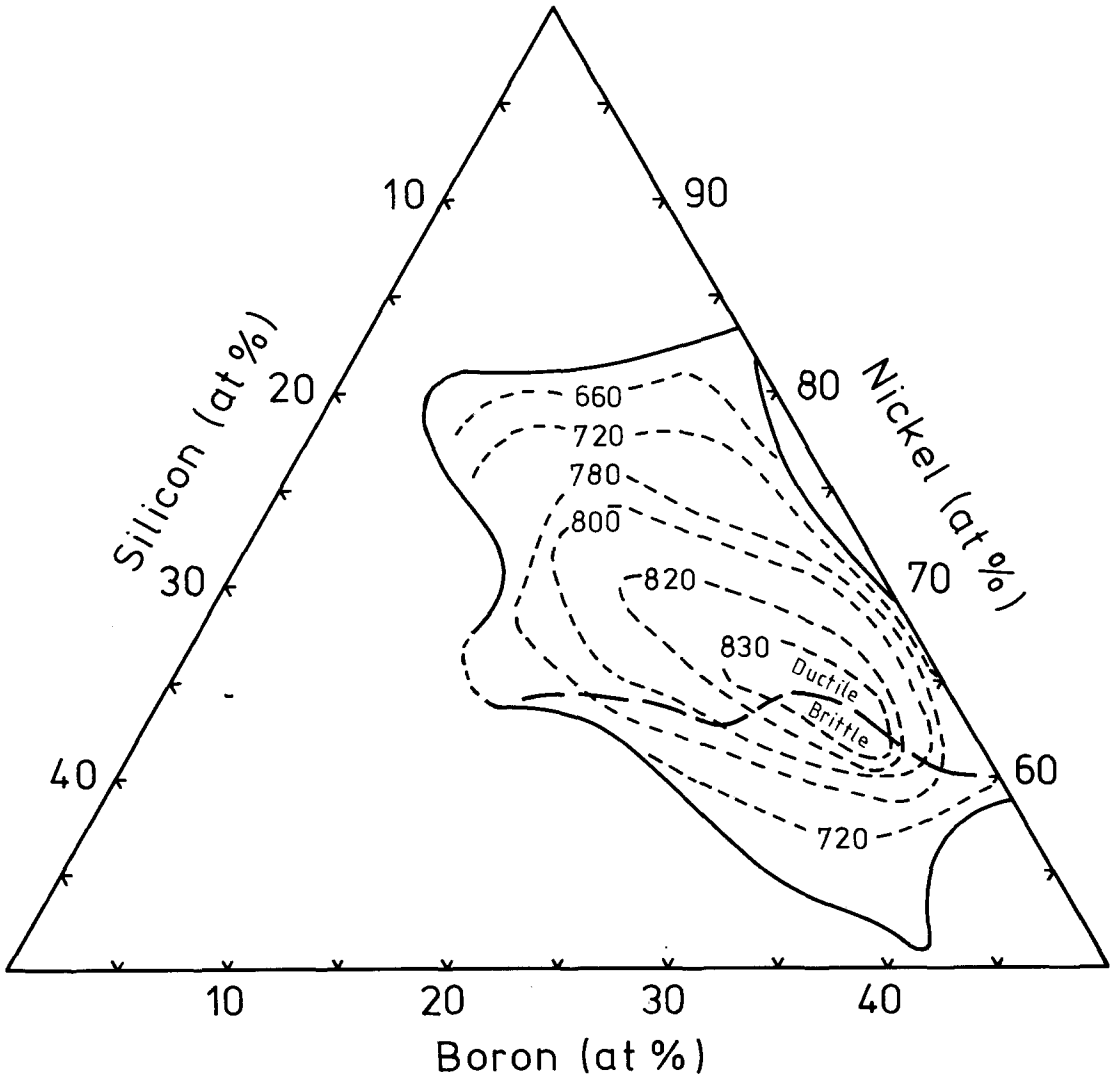

Figure 1 Glass-forming range and crystallization temperature isotherms (in K) for 17 ± 3 μm thick melt-spun Ni–Si–B alloys. The ductile–brittle boundary is also shown (see text for details).

recently by Inoue *et al.* [9] for melt-spun tape (33 to 43 at% B), but $Ni_{82}B_{18}$ was reported to be fully crystalline as quenched. Hence, to our knowledge, this is the first reported instance of fully amorphous binary Ni–$B_{17\ to\ 18.5}$, although partially glassy $Ni_{81.5}B_{18.5}$ has been previously reported [10]. Binary Ni–Si alloys have not been vitrified.

The highest crystallization temperatures are obtained at relatively high total metalloid contents, ~ 32 to 36 at% (e.g. for $Ni_{66}Si_8B_{26}$, T_x = 834 K), the actual T_x depending on the Si : B ratio. Binary $Ni_{83}B_{17}$ has the lowest stability, with T_x = 547 K. This gives a very wide range of T_x for the Ni–Si–B system (~ 287 K, compared with ~ 235 K for melt-spun Fe–Si–B [5]). As shown in Fig. 1, however, not all the amorphous compositions yield fully ductile tapes. Significantly, alloys containing greater than about 36 to 40 at% metalloid, depending on the Si : B ratio, are brittle in the as-quenched state (i.e. cannot be bent through 180° without fracturing). In addition, alloys become progressively more brittle (i.e. the radius of curvature at fracture in a simple bend test increases) as the metalloid content is further increased, presumably resulting from an increasing proportion of directional metalloid–metalloid covalent bonds. This emphasizes the danger of using a simple bend-ductility test to establish whether or not a metal–metalloid alloy is glassy.

These results indicate that glass formation in a metal–metalloid system is not confined to alloys in which the metalloid atoms are all interstitially sited. The structures of both the high and low metalloid Ni–Si–B alloys are currently being investigated by X-ray and neutron diffraction, and Extended X-ray Absorption Fine Structure (EXAFS) studies are also in preparation. A more detailed description and discussion of the Ni–Si–B system, including a study and comparison of the empirical and theoretical glass forming ability will be reported later.

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