JOURNAL OF MATERIALS SCIENCE 19 (1984) 1391–1396

Effects of elemental additions and superheat on melt surface tension and metallic glass embrittlement

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Additions of antimony, selenium, tellurium and some other alloying elements to iron–nickel base alloys have been investigated with regard to effects on melt surface tension and resultant metallic glass formation and characteristics. Surface tension of the molten alloys has been measured as a function of composition and melt temperature using a variation of the maximum bubble pressure method. The density of molten $Fe_{40}Ni_{40}B_{20}$ alloy has been measured as a function of temperature. Attempts to chill block melt-spin and alloys of the present investigation into metallic glass ribbons were largely successful. A few compositions were partially crystalline in the as-cast state and even fewer were not castable at all. The amorphous structure of ribbons made was assessed by X-ray diffraction, differential scanning calorimetry, and embrittlement temperatures for one hour anneals. A correlation has been established between changes in melt surface tension and metallic glass embrittlement temperature with the addition of surface active elements.

1. Introduction

Alloys such as $Fe_{81.5}B_{14.5}Si_{14}$, $Fe_{40}Ni_{40}B_{20}$, and $Ni_{81.5}B_{14.5}Si_4$ are known to form metallic glasses on rapid solidification from the melt. The elements antimony, selenium and tellurium have been shown to be strongly surface active in iron and nickel base melts [1]. Chill block melt-spinning experiments using glass-forming alloys containing small quantities of antimony, selenium and tellurium were conducted. Characterization of the ribbons made showed no measurable effects of these surface active elements on ribbon casting and magnetic properties, even though substantial reductions in melt surface tension were apparent [2]. The lack of surfactant-dependent ribbon casting characteristics is presumably the result of turbulence in the low viscosity molten alloy puddle on the rapidly moving substrate wheel during casting. Such melt turbulence can be viewed as sweeping solute atoms away from the liquid surface and thereby causing them to have little effect on molten alloy surface tension [3]. Strong effects of surfactant element additions were noted on the embrittlement temperature, fracture strain, and stress relaxation of the amorphous alloy ribbons cast [4].

The present report describes the measurement of liquid–vapour interfacial tension and density in some glass-forming metallic melts. Both the effects of elemental additions and melt superheat are studied. Amorphous alloy ribbon embrittlement temperatures obtained in a previous study [4] are correlated with melt surface tension suppression when surface active elements are present in the melt.

2. Experimental techniques and procedures

The alloys investigated in the present study were prepared by pre-melting high purity elements in an alumina crucible under argon atmosphere and pouring the melt into a split copper mould. Samples from all master alloy ingots were subject to melt surface tension measurement by a variation of the maximum bubble presssure [5] technique: the argon gas overpressure required to cause melt ejection through an orifice of known size at the foot of a flat-bottomed clear fused quartz tube was measured. Melt surface tension

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was calculated by

$$\gamma_{\mathrm{LV}} = (P_{\mathrm{h}} + P_0)\phi/4 \qquad (1)$$

where γ_{LV} is the liquid–vapour interfacial tension, P_{h} the melt head pressure, P_0 the argon gas overpressure, and ϕ the orifice diameter in the base of the quartz tube. The reliability of this technique was checked by measuring the surface tension of molten copper, which fell within 2% of that appearing in the recent literature [6–8]. The density of molten $Fe_{40}Ni_{40}B_{20}$ alloy was measured by observing the volume change with temperature in a clear fused quartz tube.

Samples from most ingots were chill block melt-spun under vacuum into ribbons [9]. Transmission Laue X-ray diffraction was used to ascertain that most of the ribbons cast were amorphous. Differential scanning calorimetry (DSC) at 40 K min^{-1} has been used to characterize some of the metallic glass samples. Select compositional groups of the amorphous alloy ribbons cast were subject to one hour isochronal anneals at various temperatures in order to establish a one hour embrittlement temperature.

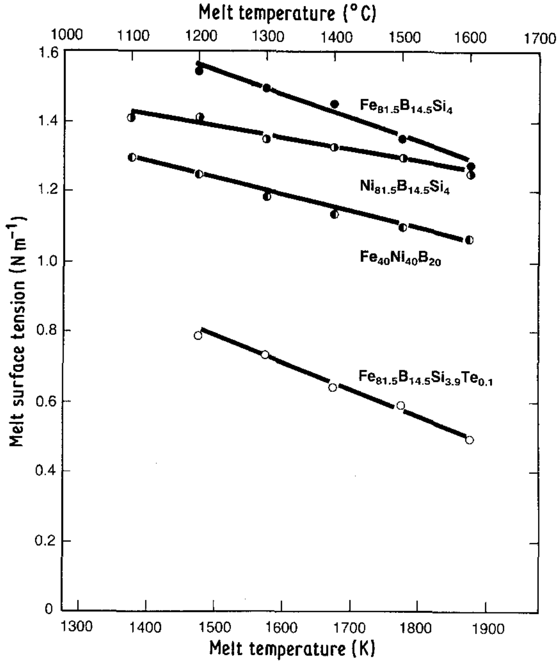

Figure 1 Melt surface tension dependence on superheat for three metallic glass-forming base alloy systems.

3. Results and discussion

3.1. Temperature dependence of melt surface tension

Data showing the effect of temperature on melt surface tension are shown in Fig. 1 for three base alloy systems. As in the case for pure metals [7], melt surface tension is seen to decrease with increasing temperature. Thermodynamically, the derivative of surface tension with respect to temperature gives negative excess entropy, S_{xs}

$$\frac{\partial \gamma_{\mathrm{LV}}}{\partial T} = -S_{\mathrm{xs}}. \qquad (2)$$

Lauermann *et al.* [10], for example, physically define surface entropy as the tendency for material to be transported from the interior to the surface of a liquid. Alternatively, this thermodynamic quantity has also been described as a measure of surface disorder in specialized cases [11]. As discussed by Shimoji [12], a large negative excess entropy indicates a substantial deviation of a solution from ideal behaviour and suggests the likelihood of enhanced atomic short range order (SRO) in the melt surface. Since atomic clustering in the melt has been shown to favour metallic glass formation on rapid solidification [13], it appears that excess entropy of glass-forming melts may scale with the corresponding amorphous alloy stability (crystallization temperature). Table I gives a compartive listing of measured melt excess entropies (see Equation 2 and Fig. 1) and corresponding amorphous alloy crystallization peak temperature scales in the alloy composition sequence as the melt excess entropies. Note that while a small tellurium addition to the iron-base alloy significantly lowers melt surface tension, melt excess entropy and amorphous ribbon

TABLE I Amorphous alloy crystallization temperatures and corresponding melt excess entropies for three base alloy systems. Subscripts "X1" and "X2" indicate first the second crystallization exotherms; superscripts "s" and "p" indicate crystallization start and peak temperatures, respectively.

Alloy	$T^{\mathrm{s}}_{\mathrm{X1}}$ (K)	$T^{\mathrm{p}}_{\mathrm{X1}}$ (K)	$T^{\mathrm{s}}_{\mathrm{X2}}$ (K)	$T^{\mathrm{p}}_{\mathrm{X2}}$ (K)	$-10^4 S_{\mathrm{xs}}$ (N m^{-1} K^{-1})
$Ni_{81.5}B_{14.5}Si_4$	703	720	–	–	3.31
$Fe_{40}Ni_{40}B_{20}$	699	727	–	–	4.61
$Fe_{81.5}B_{14.5}Si_4$	784	799	820	833	6.89
$Fe_{81.5}B_{14.5}Si_{3.9}Te_{0.1}$	777	793	813	827	7.42

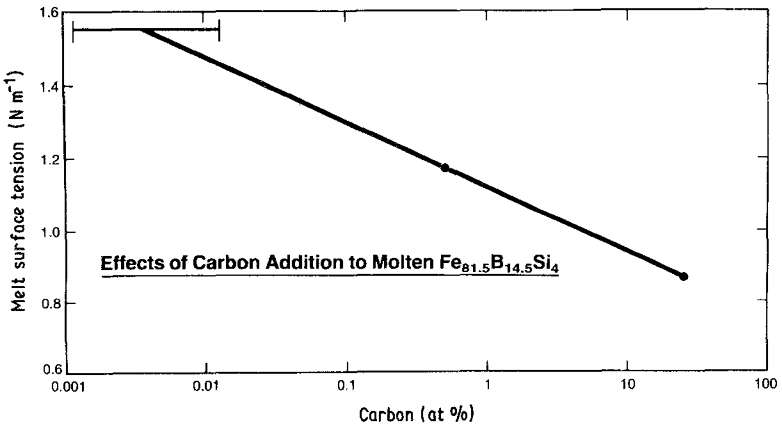

Figure 2 Melt surface tension dependence on carbon additions for a ferrous glass-forming alloy system.

crystallization temperature remain relatively unaffected.

3.2. Alloy composition dependence of melt surface tension

The reduction of liquid–vapour interfacial tension by the addition of surface active elements has been described in terms of a solute-rich layer on the liquid surface [1]. Thermodynamic models describing the effect of binary additions on the surface tension of molten metals have been discussed by Allen [8]. The reduction of molten iron and nickel surface tensions by solute additions has also been illustrated [1, 8]. A similar reduction of liquid–vapour interfacial tension for an iron-base glass-forming melt by the addition of carbon as a surfactant is shown in Fig. 2. Amorphous alloy ribbons were not castable for carbon additions above about 5 at%. As shown in Fig. 3, a substantially greater reduction of melt surface tension can be effected by adding tellurium, for example. rather than carbon. The potency of the three surfactant elements used scales as $Te > Se \gg Sb$. The data of Fig. 3 also show that surfactants (in addition to carbon) which are added to the melt have an effect on the reduction of liquid–vapour interfacial tension.

The increased melt surface tension observed with the addition of lanthanum presumably results from deoxidation of the melt by this element, as oxygen is surface active in ferrous melts. Fig. 4 shows melt surface tension trends for iron–nickel base glass-forming melts which are similar to those of the ferrous melts shown in, Fig. 3. Note that while the partial replacement of boron by silicon results in no measureable difference in the surface tension of the two melts, phosphorous does lower the melt surface tension. Fig. 5 shows the effect of some surfactant elements on the melt surface tension of a nickel-base glass-forming melt.

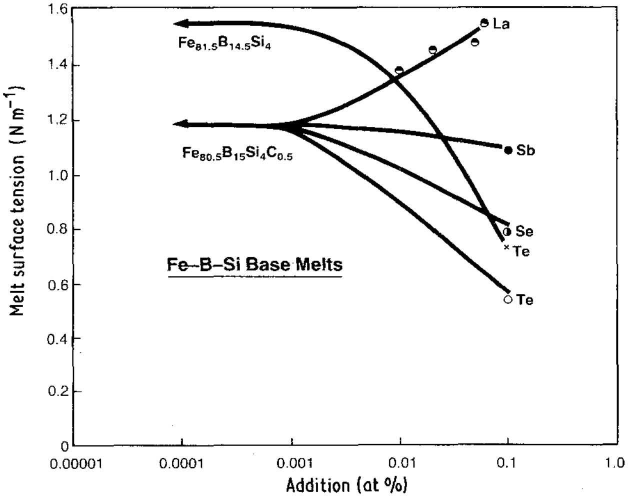

Figure 3 Effects of some elemental additions on the melt surface tension in some iron-based glass-forming alloys systems.

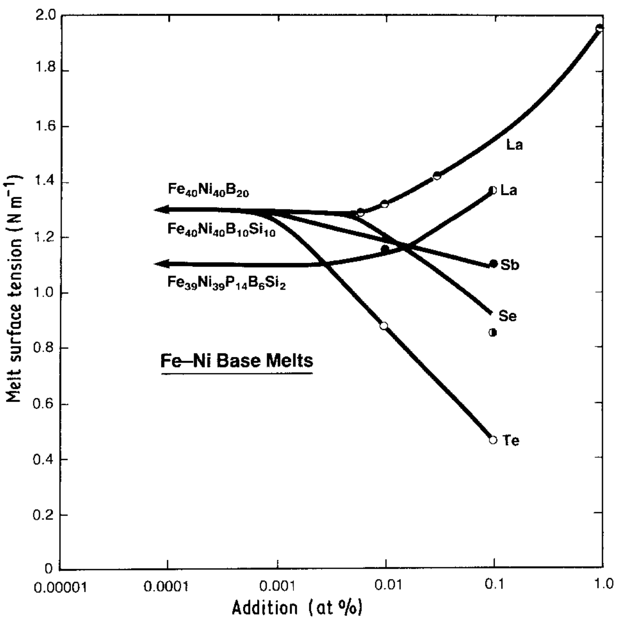

Figure 4 Effects of some elemental additions on the melt surface tension in same iron–nickel based glass-forming alloy systems.

3.3. Melt surface tension suppression and metallic glass embrittlement

The embrittlement temperatures of three base alloy compositions containing various amounts of surfactant elements are plotted against corresponding melt surface tensions in Fig. 6. The potency of the corresponding surface active elements for reducing melt surface tension scales in the same manner as that for the embrittlement of amorphous alloy ribbons [4]. An association between reduction of melt surface tension and amorphous alloy embrittlement by surfactant elements has, therefore, been established. A common atomic mechanism which could account for both the measured melt and amorphous alloy properly changes is not available.

3.4. Density of molten $Fe_{40}Ni_{40}B_{20}$ alloy

Experimental $Fe_{40}Ni_{40}B_{20}$ melt density data are given in Table II. A least-squares fit of the numbers shown gives

$$\frac{\partial \rho_L}{\partial T} = -1.37 \times 10^{-3}\ (\mathrm{g\,cm^{-3}\,K^{-1}}) \qquad (3)$$

with $r^2 = 0.99$.

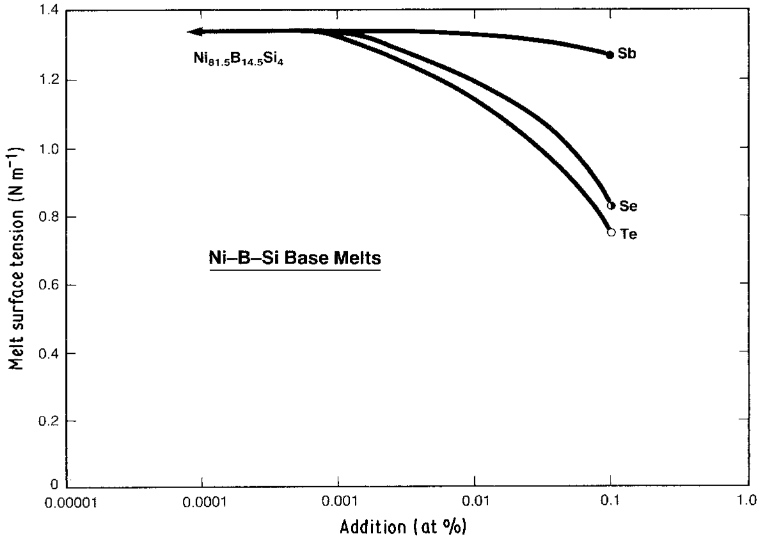

Figure 5 Effects of some elemental additions on the melt surface tension in a nickel-based glass-forming alloy system.

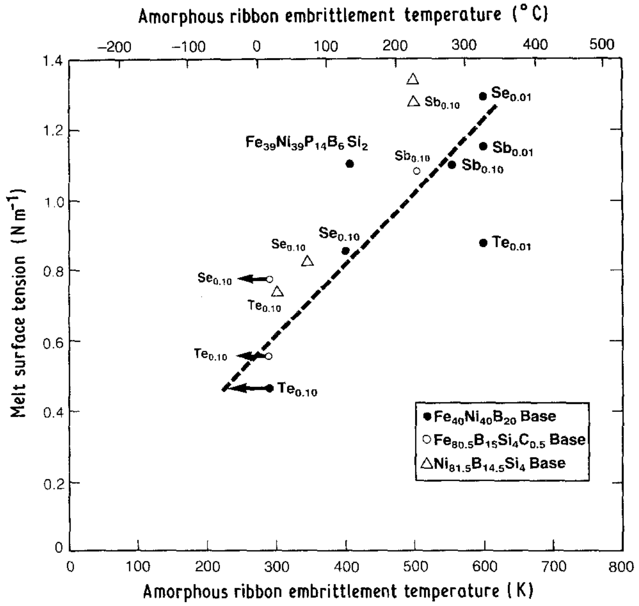

Figure 6 Correlation between molten alloy surface tension and corresponding amorphous alloy embrittlement temperature for various base alloys and surfactant additions.

4. Concluding remarks

The present report has considered the liquid–vapour interfacial tension of glass-forming metallic melts. It is interesting that while the addition of surfactant elements to the molten alloy lowers the melt surface tension (a surface-controlled effect), the chill block melt-spinning of amorphous alloy ribbon, for example, apparently disperses the surfactant atoms to the extent where they become distributed throughout the bulk. As has been discussed, this redistribution of solute surfactant atoms can result in metallic glass embrittlement [4] and other changes in bulk properties. While this very different distribution (surface as opposed to bulk) distribution of surfactant atoms can be explained in terms of liquid turbulence [3], it is worth noting that such a significant change in material behaviour can be effected by simply controlling liquid turbulence. While surface and bulk properties of materials are not obviously related, those of some simple substances have been reported [14].

TABLE II Molten $Fe_{40}Ni_{40}B_{20}$ alloy density at various melt temperatures.

T(K)	ρ_L(g cm^{-3})
1423	7.31
1513	7.21
1598	7.09
1703	6.93

Acknowledgement

All experimental work was conducted while the author was with General Electric Corporate Research and Development, Schenectady, NY, USA.

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*Received 5 July
and accepted 26 July 1983*