The effect of simple metal (Al, Ga) addition on the crystallisation and density of amorphous Zr-Ni alloys

The effect of simple metal (Al, Ga) addition on the crystallisation and density of amorphous Zr–Ni alloys

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Abstract. Amorphous metal ribbons of $(Zr_{0.64}Ni_{0.36})_{1-x}M_x$ where M = Al, Ga and $(Zr_{0.5}Ni_{0.5})_{1-x}Al_x$ for values of x between 0 and 0.25 have been prepared by a rapid quenching technique of melt spinning. The effect of adding Al or Ga to $Zr_{0.64}Ni_{0.36}$ and $Zr_{0.5}Ni_{0.5}$ is to increase the crystallisation temperature of both host alloys. The effect of Al or Ga substitution on the thermal stability of $(Zr_{0.64}Ni_{0.36})_{1-x}M_x$ is very similar. At a composition between $x = 0.05$ and 0.10, the M component completely suppresses the transformation to intermediate phases that has been observed in the crystallisation process for amorphous Zr–Ni alloys in a small composition range near 64 at.% Zr. The density of $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$ and of $(Zr_{0.5}Ni_{0.5})_{1-x}Al_x$ decreases linearly while that of $(Zr_{0.64}Ni_{0.36})_{1-x}Ga_x$ remains almost constant with x. An extension to ternary and higher order alloys of the Buschow kinetic model predicting the crystallisation temperature of binary alloys is proposed.

1. Introduction

The amorphous phase of a metallic alloy is metastable. At high temperatures these metallic glasses revert to the equilibrium crystalline phase in one or more exothermic processes. One of the more widely studied families is the series $Zr_{1-y}Ni_y$ metallic glasses which may be prepared by rapid quenching techniques over a large range of compositions ($y = 0.2$–0.8). Recent studies indicate that a large number of ternary amorphous alloys of the type $(Zr_{1-y}Ni_y)_{1-x}M_x$ based on this family may be prepared by rapid quenching. Ternary alloys in which the component M is a simple element such as H, B, Al, P or Si (Yamada *et al* 1987, Jansson and Nygren 1988) and in which M is another transition metal such as Ti, V, Cr, Mn, Fe, Co or Cu have been reported (Yamada *et al* 1988).

The crystallisation process for rapidly quenched $Zr_{1-y}Ni_y$ alloys is particularly interesting in the neighbourhood of $y \simeq 0.36$. Except for a narrow concentration range just around this value, the process occurs in one step that is characterised by a single exothermic peak. For $y = 0.365$ (and values nearby) two or three exothermic peaks are observed in DSC thermograms (Dong *et al* 1981, Altounian *et al* 1983, Kroeger *et al* 1984a). The separation of two outermost peaks is observed to be $\simeq 60$ K. X-ray diffraction (Buschow *et al* 1981, Altounian *et al* 1983, McKamey *et al* 1986)

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indicates that the phase after the first DSC peak is also amorphous or microcrystalline. The transformation to the second phase leads to an increase in electrical resistivity (Altounian *et al* 1983, Schulz *et al* 1984), and the second phase remains ductile (Frahm 1983). After the second exothermic peak in the DSC trace the alloy is completely crystalline and brittle. X-ray absorption near-edge structure (XANES) and extended x-ray absorption fine-structure (EXAFS) comparisons between the amorphous phase and this second metastable phase indicate a qualitative difference between the two structures (Frahm *et al* 1989) with respect to the coordination numbers of Ni and Zr atoms.

We have prepared ternary alloys with a simple-metal third component (M = Al, Ga) at a fixed Zr/Ni ratio to investigate the influence of this third component on the crystallisation process and the intermediate second phase. The unusual changes in the electron transport coefficients, the resistivity, thermopower and Hall coefficient, produced by a simple-metal ternary component have been reported for some of these alloys (Bhatnagar *et al* 1989, Rhie *et al* 1990). We report here the crystallisation behaviour and density measurements of amorphous $(Zr_{0.64}Ni_{0.36})_{1-x}M_x$ (M = Al, Ga) and $(Zr_{0.5}Ni_{0.5})_{1-x}Al_x$ alloys. We propose an extension to ternary alloys of the Buschow kinetic model of the crystallisation process in binary alloys (Buschow and Beekmans 1980) which provides a qualitative description of the behaviour of the crystallisation temperature of ternary $(Zr_{1-y}Ni_y)_{1-x}Al_x$ glasses formed by the addition of Al to three binary $Zr_{1-y}Ni_y$ glasses, those with $y = 0.36, 0.5$ and 0.67.

2. Experimental Details

Master alloys of $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$, $(Zr_{0.64}Ni_{0.36})_{1-x}Ga_x$ and $(Zr_{0.5}Ni_{0.5})_{1-x}Al_x$ with x values between 0 and 0.25 were prepared by melting 99.9% Ni, 99.6% Zr and 99.999% Al or Ga in an argon-filled arc furnace. Each alloy was melted several times to ensure homogeneity of the alloy button. The weight loss after melting was found to be less than 0.1% in each case. The metallic glass ribbons were prepared in an argon atmosphere by induction melting the alloy ingot in a quartz crucible and ejecting it onto a single-roller melt spinner. The surface speed of the copper roller was 27 m s^{-1} or greater. The metallic glass ribbons were approximately 1–2 mm wide and 15–30 μm thick. The amorphous nature of the ribbons was confirmed by x-ray diffraction and differential scanning calorimetry (DSC). The density of the glassy alloys was determined from Archimedes' method by weighing them in toluene and in air. The accuracy of density measurement is 1%. The crystallisation processes were studied with a Perkin-Elmer DSC-2 or equivalent apparatus at a scan rate of 10 K min^{-1}. The temperature and energy scales of the DSC-2 were calibrated using standard procedures. The transformation temperatures T_a and T_x were determined by the intersection of the tangent drawn to the rapid-rise part of the exothermic peak and the base-line.

3. Results

The appearance of diffuse diffraction rings in the x-ray diffraction patterns and at least one exothermic peak in the DSC scans indicated that alloys with Al as the ternary element were amorphous for a concentration range $x = 0$–0.25, whereas the alloys with Ga could not be made amorphous for concentrations greater than $x = 0.20$ under the

preparation conditions mentioned above. The addition of Al or Ga in either Zr–Ni host alloy studied increased the brittleness of the amorphous alloy. Ga alloys were somewhat more brittle than Al alloys of the same composition.

The x-ray diffraction pattern of $Zr_{0.64}Ni_{0.36}$ showed a large and wide peak centred at $q \simeq 2.63$ Å^{-1} and another much smaller peak at $q \simeq 4.3$ Å^{-1}. The addition of Al up to 25 at.% shifted the peak only slightly to higher values. Values q_p of the peak location in the structure factor $qI(q)$ are given in table 1 for $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$ alloys.

Table 1. T_a, first peak in DSC scan; T_x, crystallisation temperature, the final peak in DSC scan; ΔH, total transformation enthalpies; q_p, first peak in structure factor $qI(q)$; ρ, mass density; $\bar{V}$, average atomic volume; $\bar{V}_m$; average volume of Zr–Ni ions; and η, the packing fraction of Zr–Ni ions, for amorphous $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$, $(Zr_{0.64}Ni_{0.36})_{1-x}Ga_x$ and $(Zr_{0.50}Ni_{0.50})_{1-x}Al_x$ alloys.

Alloy	T_a (K)	T_x (K)	ΔH (kJ mol^{-1})	q_p (Å^{-1})	ρ (g cm^{-3})	$\bar{V}$ (Å^3)	$\bar{V}_m$ (Å^3)	η
$(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$								
$x = 0.00$	688	748	4.61	2.63	7.24	18.2	18.2	0.73
$x = 0.05$	722	788	4.00	2.64	6.96	18.3	19.3	0.69
$x = 0.10$		767	4.27	2.65	6.73	18.3	20.4	0.65
$x = 0.15$		792	4.10	2.65	6.53	18.2	21.4	0.62
$x = 0.20$		806	4.04	2.66	6.21	18.4	23.1	0.54
$x = 0.25$		844		2.65	6.00	18.4	24.5	0.54
$(Zr_{0.64}Ni_{0.36})_{1-x}Ga_x$								
$x = 0.05$	740	777	4.48		7.15	18.3	19.3	0.69
$x = 0.10$		764	4.14		7.13	18.3	20.3	0.66
$x = 0.15$		778	4.39		7.13	18.2	21.4	0.62
$x = 0.20$		822	3.64		7.14	18.0	22.5	0.59
$(Zr_{0.50}Ni_{0.50})_{1-x}Al_x$								
$x = 0.00$		772	3.01		7.46	16.7	16.7	0.72
$x = 0.05$		793	3.34		7.37	16.3	17.2	0.70
$x = 0.10$		811	3.94		7.19	16.2	18.0	0.67
$x = 0.15$		822	4.51		6.93	16.5	19.4	0.62
$x = 0.20$		836	5.48		6.77	16.0	20.0	0.60

Typical DSC scans for $x = 0$ and for $x = 0.05$ with both Al and Ga alloys are shown in figure 1. For $x = 0$, two sharp exothermic peaks are observed separated by approximately 60 K with another small, broad peak between them. Samples prepared at different times showed the same behaviour. This result agrees with Dong *et al* (1981), Altounian *et al* (1983) and Kroeger *et al* (1984a) but does not agree with the observation of Buschow *et al* (1981) who reported only two peaks. For $x = 0.05$ of either Al or Ga there are only two sharp exothermic peaks that have both been displaced to higher temperatures with a smaller temperature separation between them. The small, broad peak present for $x = 0$ has disappeared. The second sharp, strong peak indicates the final and total crystallisation of the amorphous alloy, as no other exothermic peak is observed at higher temperature. Only a single peak in the DSC thermograms is observed for 10 at.% or higher of either Al or Ga in $Zr_{0.64}Ni_{0.36}$. Only one DSC peak was observed for the $(Zr_{0.5}Ni_{0.5})_{1-x}Al_x$ series. Values of the transformation temperatures, T_a (transformation to intermediate amorphous phase as indicated by the first peak in the DSC scan when more than one is present), T_x (crystallisation as indicated by the

final peak in the DSC scan), crystallisation enthalpies, ΔH, and mass densities ρ are also given in table 1.
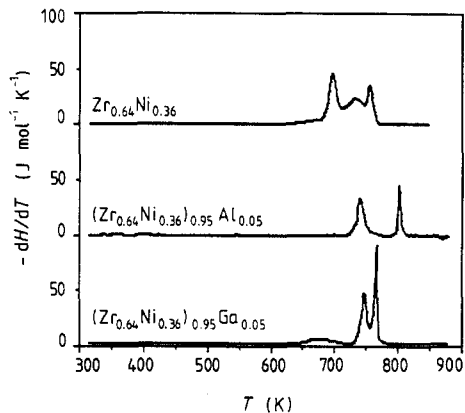

Figure 1. DSC scans of $(Zr_{0.64}Ni_{0.36})_{1-x}M_x$ for $x = 0$, 0.05 and M = Al, Ga. The heating rate is 10 K min^{-1}.
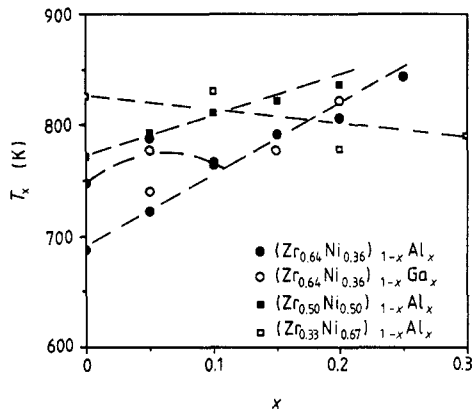
Figure 2. Transformation temperatures T_a, referred to the first sharp peak, and T_x, referred to the final peak in the DSC scans are plotted as a function of x for $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$, $(Zr_{0.64}Ni_{0.36})_{1-x}Ga_x$ and $(Zr_{0.5}Ni_{0.5})_{1-x}Al_x$. Data for $(Zr_{0.33}Ni_{0.67})_{1-x}Al_x$ are taken from resistance measurements by Mizutani *et al* (1990). The broken curves are guides to the eye.
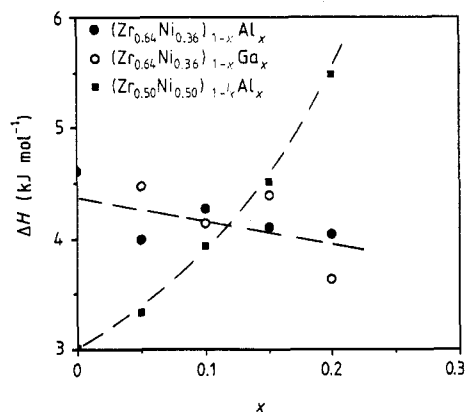

Figure 3. The enthalpies of the total transformation/crystallisation for $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$, $(Zr_{0.64}Ni_{0.36})_{1-x}Ga_x$ and $(Zr_{0.5}Ni_{0.5})_{1-x}Al_x$ are plotted as a function of x. The broken curves are guides to the eye.
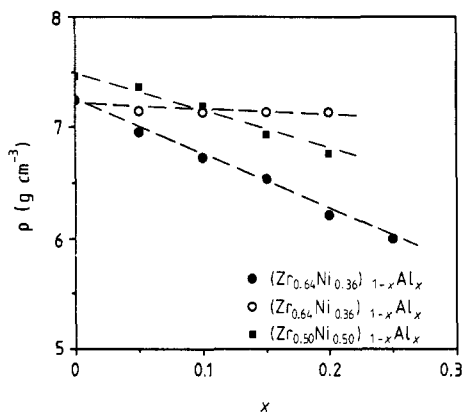
Figure 4. The densities of $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$, $(Zr_{0.64}Ni_{0.36})_{1-x}Ga_x$ and $(Zr_{0.5}Ni_{0.5})_{1-x}Al_x$ are plotted as a function of x. The broken curves are guides to the eye.

The transformation temperatures T_a and T_x are plotted in figure 2 as a function of concentration x for the alloys with both Al and Ga as the third component. The addition of either Al or Ga increases the transformation temperatures for amorphous $Zr_{0.64}Ni_{0.36}$ alloys. A surprising result is that, within experimental error, the effect of Al on the transformation temperature of the ternary alloys is practically the same as that of

Ga. The small difference could easily be explained by errors in the determination of the transformation temperatures and/or alloy concentrations. Addition of Al increases the crystallisation temperature of $Zr_{0.5}Ni_{0.5}$ alloys too, but not as much as for $Zr_{0.64}Ni_{0.36}$. The enthalpy changes in the transformation process are plotted in figure 3.

The density ρ is plotted in figure 4 as a function of x for $(Zr_{0.64}Ni_{0.36})_{1-x}M_x$ ($M =$ Al, Ga) and for $(Zr_{0.5}Ni_{0.5})_{1-x}Al_x$ ternary amorphous alloys. In the case of addition of Al, the density decreases linearly with increasing x, however, in the case of Ga addition, the density remains approximately unchanged.

4. Discussion

The DSC thermogram shown in figure 1 clearly shows that the crystallisation process of amorphous $Zr_{0.64}Ni_{0.36}$ takes place in three steps. Two outermost exothermic peaks are relatively sharp compared to the middle one. On the other hand $Zr_{0.5}Ni_{0.5}$ shows only a single peak although a slight asymmetry can be seen at the lower temperature side indicating that this peak may be composed of two overlapping peaks. Three peaks in $Zr_{1-y}Ni_y$ near $y = 0.36$ have been reported earlier by Dong *et al* (1981), Kroeger *et al* (1984a) and Altounian *et al* (1983) although Buschow *et al* (1981) observed only two peaks. The general observation is that the first DSC peak in $Zr_{1-y}Ni_y$ for $y \simeq 0.36$ is narrower than the peaks or peak at higher temperatures, and the later two peaks may overlap or be distinct depending upon the preparation conditions and the DSC heating rate. Dong *et al* (1981) reported that $Zr_{0.64}Ni_{0.36}$ crystallised at the first peak. In contrast, Buschow *et al* (1981) observed no evidence of crystallisation of the sample when heated just beyond the first peak, and therefore, concluded that the sample remained amorphous after the first DSC peak. They interpreted the heat associated with the first peak arising due to a structural change in the original amorphous phase. Kroeger *et al* (1984b) reported an unusual temperature dependence of the density of states at the Fermi level and two superconducting transitions in amorphous $Zr_{1-y}Ni_y$ alloys with y between 45 and 26 at.% which they attributed to the presence of two amorphous phases in the alloys. Altounian *et al* (1984), looked carefully for the second amorphous phase in a Zr_2Ni amorphous alloy but could not find one. A study of $(Zr_{1-x}Hf_x)_{0.62}Ni_{0.38}$ and of $Zr_{0.62}Ni_{0.38}$ by Schulz *et al* (1984) concluded that the phase transformation occurring during the first exothermic peak was due to the precipitation of very small ordered clusters of 10–20 Å size which is too small to be detected by x-ray diffraction. Recent XANES and EXAFS measurements by Frahm *et al* (1989) on $Zr_{0.635}Ni_{0.365}$ amorphous alloys, as-cast and after heating just to the first DSC peak, indicated an increased number of or the growth of some kind of ordered structural units in the heated sample in comparison with as-cast alloy. In addition, they reported an increase in the Zr–Zr coordination number (from 5.97 to 8.91) and a slight decrease in the Zr–Ni coordination number (from 1.81 to 1.56) although the Zr–Zr and Zr–Ni bond distances remained unchanged. While we have not investigated the details of the changes taking place in the $Zr_{0.64}Ni_{0.36}$ amorphous alloy after the first exothermic peak, it is our opinion that the first peak is generally too sharp to represent a change in amorphous structure without any kind of growth of either ordered structural units or precipitate of extremely small crystallites not identifiable by x-ray diffraction. In a TEM investigation of $Zr_{0.65}Ni_{0.35}$ and $Zr_{0.61}Ni_{0.39}$ Dey and Banerjee (1985) claimed that the first exothermic transformation corresponded to the primary BCT crystals which showed closely spaced internal twining. Thus the status of the phase of $Zr_{1-y}Ni_y$ near

$y = 0.36$ after the first DSC peak still remains unsettled. Careful x-ray, TEM and neutron structural investigations on amorphous $Zr_{1-y}Ni_y$ alloys near $y = 0.36$ are required to resolve the question.

No one seems to have given any consideration to the broad second peak in the DSC thermogram of $Zr_{0.64}Ni_{0.36}$. We think that in this region some structural rearrangement, whether within amorphous or ordered structural units, is going on which extends over a larger temperature interval with a sluggish rate. The third peak, of course, indicates the final crystallisation of the alloy. The addition of only 5 at.% or less of the simple metal Ga or Al suppresses the broad second peak, and the addition of 10 at.% or less eliminates all intermediate phases. This third element serves to inhibit nucleation of the intermediate phase and its gradual structural rearrangement.

The variation of T_a and T_x with x is shown in figure 2 for the three amorphous alloys studied and for amorphous $(Zr_{0.33}Ni_{0.67})_{1-x}Al_x$ as reported by Mizutani *et al* (1990). The T_x values of $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$ and of $(Zr_{0.64}Ni_{0.36})_{1-x}Ga_x$ are approximately the same. The T_x values of amorphous $(Zr_{0.5}Ni_{0.5})_{1-x}Al_x$ alloys are higher than those of $(Zr_{0.64}Ni_{0.36})_{1-x}M_x$ (M = Al, Ga) alloys, but the increase in T_x as the Al concentration is increased is smaller than for the Zr-rich alloy. The trends suggest that the two curves could intersect in the region where $x = 0.3$ if the samples can be quenched rapidly enough to stabilise the amorphous phase at these higher concentrations of Al. For the Ni-rich alloy, $Zr_{0.33}Ni_{0.67}$, addition of Al appears to decrease T_x. It should be noted that the values of T_x for the Ni-rich alloy were determined by resistance measurements rather than by DSC measurements and are not directly comparable to our values determined by DSC measurements. Nevertheless, the trend for these Ni-rich alloys is clear. The values of T_x for the $Zr_{1-y}Ni_y$ alloys shown in figure 2 are in agreement with the general trend observed by Buschow and Beekmans (1979), but they do not agree with those reported by Altounian *et al* (1983) for $y = 0.5$ who reported a decreasing value of T_x for y between $y = 0.36$ and 0.50.

Two of the most interesting features of the crystallisation properties of Zr–Ni–M (M = Al, Ga) amorphous alloys are: (i) the apparent similarity between the influence of Al and Ga on T_x and (ii) the changing influence on T_x of the M-component on going from Zr-rich to Ni-rich. Although Al and Ga are essentially isoelectronic and have similar Goldschmidt radii (1.43 Å for Al and 1.39 Å for Ga (Pollack 1982)), other properties of the pure metals, such as the melting point and crystal structure, are quite different.

Buschow and Beekmans (1980) in a kinetic approach to the stability of amorphous alloys have proposed that the crystallisation temperature of binary amorphous alloys $A_{1-y}B_y$ is controlled by the formation enthalpy ΔH_h^B of a hole the same size as the smaller atom B. With the hole enthalpy determined from Miedema's (Miedema 1979) semi-empirical model for monovacancies in metals and alloys they find an empirical correlation between T_x and ΔH_h^B for a large number of binary amorphous alloys, namely

$$T_x = 7.5 \, \Delta H_h^B \, . \tag{1}$$

The value of ΔH_h^B in Miedema's model is given by

$$\Delta H_h^B = (1 - f_A^B)\Delta H_{1V}^B + f_A^B (V_B/V_A)^{5/6}\Delta H_{1V}^A \tag{2}$$

where ΔH_{1V}^B and ΔH_{1V}^A are the formation enthalpies for a monovacancy in the pure metals, V_A and V_B are their molar volumes and f_A^B is the probability that the B atom

is surrounded by an A atom. For a random alloy, this would be the relative surface concentration of A atoms C_A^s,

$$C_A^s = \frac{(1-y)V_A^{2/3}}{(1-y)V_A^{2/3} + yV_B^{2/3}} \,. \tag{3}$$

Buschow and Beekmans assumed that the amorphous alloys were random alloys, but Weeber (1987) has determined empirically that a better description of f_A^B is given by

$$f_A^B = C_A^s[1 + 5(C_A^s C_B^s)^2] \tag{4}$$

which is indicative of some chemical short-range order. With values of ΔH_h^B calculated from (2), (3) and (4) he finds that the correlation between T_x and ΔH_h^B can be better described by

$$T_x = 5\Delta H_h^B + 275 \,. \tag{5}$$

Weeber interprets this observation as an indication that both a hole enthalpy for the viscosity coefficient and a migration enthalpy are needed in the kinetic approach to crystallisation of these alloys. Both relations, (1) and (5) qualitatively predict trends in T_x within many amorphous alloy series, e.g. the increase in T_x with Ni concentration for $Zr_{1-y}Ni_y$ alloys, but clearly (5) cannot be correct for the many amorphous alloys which have values of T_x below 275 K. The amorphous phase for these alloys can, of course, only be observed for samples which are quenched to cryogenic temperatures, e.g. alloys quenched from the vapour onto liquid helium or liquid nitrogen temperature substrates which frequently are amorphous with crystallisation temperatures as low as a few kelvin. For the Zr–Ni system of amorphous alloys and for many others, either Buschow's original formulation (1) with the assumption of random alloys or Weeber's modification (5) appears to provide an adequate description of T_x, however. A generalisation to ternary alloys may be helpful in understanding and predicting the crystallisation temperatures, or at least the trends, within alloy systems.

In a binary alloy system the crystallisation process can occur when the motion of one component is essentially frozen but when the mobility of the other is approaching a critical mobility. Buschow and Beekmans (1980) have proposed that the enthalpy governing this mobility is the enthalpy associated with the formation of a monovacancy. In the Miedema model, the enthalpy associated with formation of a monovacancy will be smaller for the smaller species B as shown in (2). Consequently, the crystallisation process is determined principally by ΔH_h^B. For a ternary alloy of the type $(A_{1-y}B_y)_{1-x}C_x$ where $V_A > V_C > V_B$, crystallisation cannot proceed if both species (A and C) are frozen. A first guess might be that the crystallisation process might be controlled by ΔH_h^C in a ternary alloy, but that cannot be the case since it would result in a large discontinuity in $T_x(x)$ near $x = 0$. We propose that, for ternary alloys, the appropriate enthalpy to use in the Buschow-Weeber model in equations (1) or (5) is

$$\Delta_h^* = \frac{y(1-x)\Delta H_h^B + x\Delta H_h^C}{x + y(1-x)} \tag{6}$$

where ΔH_h^B and ΔH_h^C are enthalpies associated with the creation of a hole the size of B and C atoms, respectively.
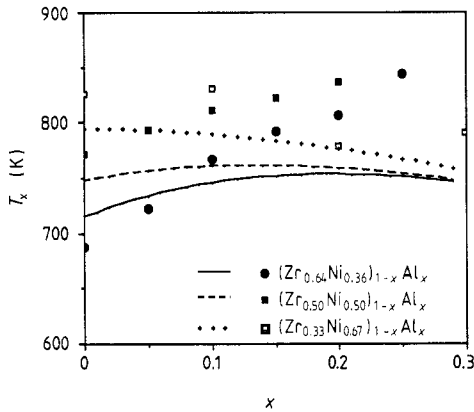
Figure 5. Experimental and calculated values of crystallisation temperature T_x for amorphous $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$, $(Zr_{0.5}Ni_{0.5})_{1-x}Al_x$ and $(Zr_{0.33}Ni_{0.67})_{1-x}Al_x$ alloys. For the Zr-rich alloy only the value of T_x for the first peak in the DSC scan is plotted in contrast to figure 2 where values for the two sharp peaks are plotted. Values for $(Zr_{0.33}Ni_{0.67})_{1-x}Al_x$ are taken from Mizutani *et al* (1990). The curves are calculated for the three amorphous alloy series based on the proposed extension of Buschow's model.
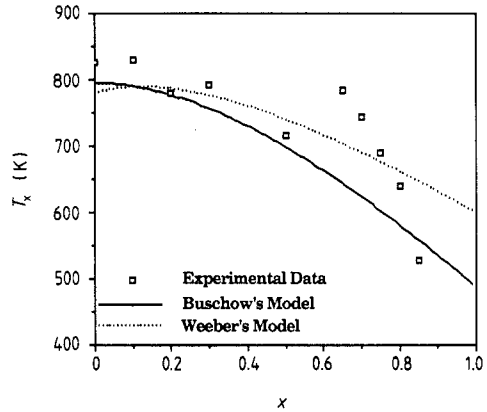
Figure 6. Experimental and calculated values of the crystallisation temperature for amorphous $(Zr_{0.33}Ni_{0.67})_{1-x}Al_x$. The experimental points are taken from Mizutani *et al* (1990). The solid curve is calculated from the proposed extension of Buschow's model (no short-range order for Ni-Zr). The dotted curve is calculated in a similar fashion but incorporating the modification proposed by Weeber to include short-range ordering.

We have calculated T_x for the Zr–Ni–Al (Ga) alloys for which experimental data are shown in figure 2 from both Buschow's model, equation (1), and Weeber's modification, equation (5), with the enthalpy given by equation (6). For the ternary alloy, ΔH_h^B and ΔH_h^C were calculated from (7) and (8)

$$\Delta H_h^B = (1 - f_A^B - f_C^B)\Delta H_{IV}^B + f_A^B(V_B/V_A)^{5/6}\Delta H_{IV}^A + f_C^B(V_B/V_C)^{5/6}\Delta H_{IV}^C \tag{7}$$

$$\Delta H_h^C = (1 - f_A^C - f_B^C)\Delta H_{IV}^C + f_A^C(V_C/V_A)^{5/6}\Delta H_{IV}^A + f_B^C(V_C/V_B)^{5/6}H_{IV}^B . \tag{8}$$

Here V_A, V_B, V_C are the appropriate molar volumes of the species and ΔH_{IV}^A, ΔH_{IV}^B, ΔH_{IV}^C are the enthalpies for a monovacancy in the pure metal species as tabulated by Miedema (1979). The short-range correlations between Zr and Ni (Weeber 1987) and the random distribution of Al(Ga) are included in the choice of f_j^i for Weeber's modification: $f_A^B = C_A^s[1+5(C_A^s C_B^s)^2]$, $f_C^B = C_C^s$, $f_A^C = C_A^s$, $f_B^C = C_B^s$ with C_A^s, C_B^s and C_C^s being the relative surface concentrations of the species, defined analogously to equation (3). For Buschow's model, the f_j^i are given by the relative surface concentrations, i.e. no short-range order. Results of this calculation (Buschow model) for $(Zr_{1-y}Ni_y)_{1-x}Al_x$ with $y = 0.36$, 0.5 and 0.67 are shown in figure 5 together with the experimental data from figure 2. For the two Zr-rich alloys with $x < 0.1$ only the values of T_x for the first peak in the DSC scans are shown. The values of T_x calculated from this generalisation of the Buschow model provide a good qualitative description of the experimental trends for the Zr–Ni–Al alloys including the increase in T_x with x for Zr-rich alloys and the decrease for Ni-rich alloys. If the curves were adjusted to fit the measured values of T_x for the binary Zr–Ni alloys, the variation with the concentration of the Al ternary component, x, would fit remarkably well for the Ni rich alloy where T_x decreases with x, but the predicted initial increase of T_x with x is appreciably smaller than that

observed for the Zr-rich alloy. Nevertheless, the model predicts a crossing of the T_x values for the Zr-rich and the 50:50 Zr–Ni alloy near $x = 0.3$ in excellent agreement with an extrapolation of the measured values of T_x. The generalisation to alloys with more than three components is tedious but straightforward.

Mizutani *et al* (1990) have reported values of T_x for $(Zr_{0.67}Ni_{0.33})_{1-x}Al_x$ over a very wide concentration range, Al poor to Al rich. The experimental values are compared with the calculated values over the entire composition range in figure 6. Curves for the extension of both the Buschow model and its modification by Weeber are shown. The simple Buschow model provides a significantly better description of the variation of T_x for $Zr_{1-y}Ni_y$ alloys as well as a somewhat better description for the variation with Al for all of the Zr–Ni–Al alloys shown in figure 5. We have performed these calculations with both sets of values for ΔH_{1V} given by Miedema (1979). Values from the rightmost column of table 1 give consistently better agreement. The predictions for $(Zr_{0.64}Ni_{0.36})_{1-x}Ga_x$ lie above those for $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$, actually in much better agreement with the experimental values of T_x. Consequently, the model does not predict the observed similarity between T_x values for the alloys with Al and Ga as the ternary component. The predictions are more sensitive to the value of the molar volume used for Ga and Al than to the value of ΔH_{1V}^C. We suspect that the value appropriate for Ga should be smaller than the measured value for pure Ga which corresponds to a more open cubic structure rather than the close-packed structure of Al. In the amorphous alloy, the Ga and Al most likely sit in equivalent locations and occupy volumes appropriate to their close-packed structures. If the molar volume of Ga is scaled from that given for Al by the ratio of the cube of their Goldschmidt radii, the predicted curve for the alloys with Ga lies below that for Al since the Goldschmidt radius for Al is larger than for Ga. We would expect more difficulty in application of the Buschow model in either the binary or ternary alloys when the elemental constituents include those elements with a more open structure such as Ga, In, Sn, Sb, Bi, B, Hg. Predictions of the model for $(Zr_{0.33}M_{0.67})_{1-x}Al_x$ where M = Ni, Ti and La were also compared with the experimental values of T_x reported by Mizutani *et al* (1990). The agreement for M = Ti was extremely good. That for M = Ni is shown in figure 6. For M = La, only experimental values for Al-rich alloys are available, and, like the values for M = Zr at the Al-rich side (figure 6), the experimental values are higher and decrease more rapidly with x than predicted.

The transformation enthalpies of these alloys are shown in figure 3. It is seen that the total enthalpies for $(Zr_{0.64}Ni_{0.36})_{1-x}M_x$ (M = Al, Ga) alloys decrease somewhat with x. On the other hand, enthalpy increases rapidly with x in $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$ alloys. The value of enthalpy for $Zr_{0.5}Ni_{0.5}$ is 3.0 kJ mol^{-1} which is a factor of two smaller than reported by Altounian *et al* (1983). We are unable to explain this difference. The similarity between values of the resistivity and Hall coefficient of our amorphous samples and those reported by other workers, and the absence of peaks in the x-ray diffraction scans indicate that our samples were completely amorphous. Consequently, this discrepancy cannot be explained as the result of significant partial crystallisation.

The variation of density ρ as a function of three amorphous alloys is shown in figure 4. The density of $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$ and $(Zr_{0.5}Ni_{0.5})_{1-x}Al_x$ decreases linearly with x. The density of $(Zr_{0.64}Ni_{0.36})_{1-x}Ga_x$ remains almost constant. These results are expected since Ga has an atomic weight comparable to those of Ni and Zr while Al is much lighter. The linear variation of density as a function of x in amorphous $M_{1-x}N_x$ or $(M_{1-y}P_y)_{1-x}N_x$ where M, P and N stand for metal, metal and metalloid atoms, has been observed by many workers (Gaskell 1981). The average atomic volume $\bar{V}$, the

average volume $\bar{V}_m$ occupied by Zr–Ni ions in these alloys, and the packing factor η for Zr–Ni are calculated as follows and tabulated in table 1:

$$\bar{V} = \bar{A}/N_A\,\rho \tag{9}$$

$$\bar{V}_m = \bar{V}/(1-x) \tag{10}$$

$$\eta = 4\pi(R_G)^3/3\,V_m \tag{11}$$

where R_G is the Goldschmidt radius of $(Zr_{0.64}Ni_{0.36})$ or $(Zr_{0.5}Ni_{0.5})$ obtained by the interpolation of the Goldschmidt radii of Zr and Ni, $\bar{A}$ is the average atomic weight, N_A is Avogadro's number and ρ is the density. The average volume is constant within experimental error. The packing factor η for metal ions Zr–Ni in amorphous $Zr_{0.64}Ni_{0.36}$ as well as $Zr_{0.5}Ni_{0.5}$ is almost equal to that of the crystalline close-packed structure (= 0.7405). The packing factor decreases with increasing x for all the three alloys. This indicates that the free volume in these amorphous alloys increases with x, i.e., the Al or Ga atoms are distorting the amorphous structure. Nevertheless, the Fourier transform of the structure factor $qI(q)$ used to obtain the radial distribution function $g(r)$ for $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$ amorphous alloys shows that the first peak in $g(r)$, like the first peak position q_p of the structure factor, is only slightly shifted to higher values for x up to 0.25.

Gaskell (1981) has examined the data on a large number of metal-metalloid amorphous systems and has found that their density can be calculated from a single equation relating ρ to the metalloid radius ratio and the atom fraction of the metalloid. For small metalloid atoms, which have $p = R_{metalloid}/R_{metal} < 0.53$, the metalloid fits within the trigonal prismatic cavities without distortion, leading to a decrease in the average atomic volume. This is true for amorphous alloys of transition metals with metalloids. However, for large metalloids having $p > 0.8$, each added metalloid atom results in large distortions of the trigonal prism, and for $p \geq 0.83$ the dilated volume is approximately equal to the atomic volume of the crystalline metal. The average atomic volumes of both metal and metalloid are thus nearly equal to the volume of the crystalline metal. If we assume that Al and Ga act as metalloids in these alloys, we find that $p \geq 0.8$ for all three alloys. The prediction of Gaskell that in such alloys the average atomic volume will be independent of the metalloid concentration is certainly borne out by the results. It may also be worthwhile to note that the average atomic volumes of amorphous $Zr_{0.64}Ni_{0.36}$ and $Zr_{0.5}Ni_{0.5}$ are approximately the same as those of their crystalline counterparts. The average atomic volumes of crystalline Zr_2Ni and ZrNi are 18.3 and 16.7 Å^3, respectively. The average atomic volume of crystalline $Zr_{0.64}Ni_{0.36}$, obtained by the intrapolation between these two values, is 18.1 Å^3. These values agree well with the values of average atomic volumes of amorphous $Zr_{0.64}Ni_{0.36}$ and $Zr_{0.5}Ni_{0.5}$ listed in table 1. Thus, Zr–Ni amorphous systems are much denser than other amorphous alloys. This was also noted by Dong *et al* (1981) and has been attributed to a strong Zr–Ni interaction within the glass resulting from charge transfer from Zr to Ni. It is expected that this kind of strong interaction would lead to some kind of short-range chemical ordering. However, Mizoguchi *et al* (1985) have concluded from their neutron diffraction measurements that there is poor chemical short-range ordering in the amorphous phase of $Zr_{0.64}Ni_{0.36}$ in comparison to that in crystalline Zr_2Ni. One may expect a better chemical short-range ordering in amorphous $Zr_{0.5}Ni_{0.5}$ as its composition corresponds to the crystalline compound ZrNi.

5. Conclusion

The effect of the substitution of Al in $Zr_{0.64}Ni_{0.36}$ and $Zr_{0.5}Ni_{0.5}$, and that of Ga in $Zr_{0.64}Ni_{0.36}$ on the crystallisation of these amorphous alloys is to increase the crystallisation temperature T_x. T_x in each alloy increases almost linearly with the Al or Ga concentration for concentrations less than $x \simeq 0.25$. A generalisation to ternary alloys of the Buschow model for crystallisation of amorphous alloys which qualitatively describes the experimental trends for T_x is proposed. The modification of Buschow's model by Weeber to incorporate short-range ordering does not describe the experimental results as well for either the Zr–Ni binary alloys or the ternary alloys with addition of Al or Ga as that of the original model proposed by Buschow. The presence of 10 at.% of Al or Ga in $(Zr_{0.64}Ni_{0.36})_{1-x}M_x$ restricts the multi-step exothermic process of crystallisation in the binary alloy to a single step process. The density of $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$ and $(Zr_{0.5}Ni_{0.5})_{1-x}Al_x$ decreases linearly with x while that of $(Zr_{0.64}Ni_{0.36})_{1-x}Ga_x$ remains constant. The average atomic volumes are found to be nearly constant as a function of x in $(Zr_{0.64}Ni_{0.36})_{1-x}M_x$ and $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$ alloys. The packing fraction η of the metal ions Zr–Ni is high and close to that of a crystalline close packed structure. The packing fraction η decreases with the Al or Ga concentration suggesting that the Al or Ga distorts the amorphous Zr–Ni structure, but the small shifts in q_p for $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$ with x indicate that the nearest-neighbour distance is only slightly increased.

References

Altounian Z, Strom-Olsen J O and Walter J L 1984 *J. Appl. Phys.* **55** 1566
Altounian Z, Tu G-H and Strom-Olsen J O 1983 *J. Appl. Phys.* **54** 3111
Bhatnagar A K, Pan R and Naugle D G 1989 *Phys. Rev.* B **39** 12460
Buschow K H J and Beekmans N M 1979 *Phys. Rev.* B **19** 3843
—— 1980 *Solid State Commun.* **35** 233
Buschow K H J, Verbeek B H and Dirks A G 1981 *J. Phys. D: Appl. Phys.* **14** 1087
Dey G K and Banerjee S 1985 *Rapidly Quenched Metals* ed S Steeb and H Warlimont (Amsterdam: Elsevier) p 343
Dong Y D, Gregan G and Scott M G 1981 *J. Non-Cryst. Solids* **43** 403
Frahm R 1983 *J. Non-Cryst. Solids* **56** 255
Frahm R, Haensel R and Rabe 1989 *J. Phys.: Condens. Matter* **1** 1521
Gaskell P H 1981 *Acta Metall.* **29** 1203
Jansson K and Nygren M 1988 *Mater. Sci. Eng.* **97** 373
Kroeger D M, Koch C C, McKamey C G and Scarbrough J O 1984a *J. Non-Cryst. Solids* **61–62** 937
Kroeger D M, Koch C C, Scarbrough J O and McKamey C G 1984b *Phys. Rev.* B **29** 1199
McKamey C G, Kroeger D M, Easton D S and Scarbrough J O 1986 *J. Mater. Sci.* **21** 3863
Miedema R A 1979 *Z. Metallk.* **70** 345

Mizoguchi T, Yoda S, Akutsu N, Yamada S, Nishioka J, Suemasa T and Watanabe N 1985 *Rapidly Quenched Metals* ed S Steeb and H Warlimont (Amsterdam: Elsevier) p 483

Mizutani U, Ohashi S, Matsuda T, Fukamichi K and Tanaka K 1990 *J. Phys.: Condens. Matter* **2** 541–57

Pollack D D 1982 *Physical Properties of Materials for Engineers* vol III (Boca Raton, FL: Chemical Rubber Company) p 10

Rhie K W, Bhatnagar A K and Naugle D G 1990 *Z. Phys.* B at press

Schulz R, Matijasevic V and Johnson W L 1984 *Phys. Rev.* B **30** 6856

Weeber A W 1987 *J. Phys. F: Met. Phys.* **17** 809

Yamada Y, Itoh Y, Matsuda T and Mizutani U 1987 *J. Phys. F: Met. Phys.* **17** 2303

Yamada Y, Itoh Y and Mizutani U 1988 *Mater. Sci. Eng.* **89** 289