JOURNAL OF MATERIALS SCIENCE 21 (1986) 64–70

# Fast diffusion and metallic glass formation in zirconium–metal alloys

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In this work it was found for a range of zirconium–metal alloys that the differences in atomic size, electronegativity and valence of the metals with respect to zirconium, and the extent of the mutual solid solubility act as phenomenological connections between the fast diffusion of the metal in zirconium and the ability of the zirconium–metal alloy to form glasses. It was found that all the alloys of zirconium which exhibit fast diffusion are also able to form glasses. Only metallic glasses obtained by rapid quenching from the melt were considered. The analysis was performed using two criteria to evaluate the glass-forming ability of the alloy, the criteria to ascertain those metals that can behave as fast-diffusing solutes in zirconium and the data for heterodiffusion in zirconium.

## 1. Introduction

The fast diffusion of metallic solutes in metals [1] is a widely known phenomenon. It has been observed for the noble metals, zinc, beryllium and the later transition metals diffusing in high-valent metals (indium, thallium, tin and lead), in the early members of the d-transition groups (especially titanium and zirconium) or in some elements of the lanthanide and actinide series [1, 2]. The diffusion coefficient of the fast-diffusing solute is several orders of magnitude greater (the precise value depending on the solvent) than the solvent self-diffusion coefficient.

In earlier work [3] we have studied heterodiffusion in zirconium and the phenomenological criteria that allow potential fast solutes to be identified. The literature on metallic glasses reveals many binary metallic alloys that form glasses and are also fast-diffusing systems. A decade ago and for the first time Turnbull [4] pointed out this experimental fact for "systems composed mainly of noble or certain transition metals (A) alloyed with certain metalloidal or electropositive elements (B)". A phenomenological analysis of the effect of alloying a pure metal on its glass-forming ability (GFA) led Turnbull to the assumption that in these "elemental combinations AB the interatomic potential is least sensitive around its minimum to the AB separation and the local configuration". Such a weak interaction would favour both the tendency to glass formation and the tendency to the fast diffusion behaviour [4–6].

A metallic glass is an alloy supercooled below a particular temperature $T_g$, with its atomic configuration frozen so as not to change appreciably with temperature. $T_g$, the glass transition temperature, is conventionally defined as the temperature at which the viscosity is $10^{13}$ poise. The $T_g$ value is defined by the kinetics of the solidification process and it falls as the cooling rate decreases. Glassy metals (strictly, alloys) can be obtained in suitable systems by several methods, notably rapid quenching from the melt. The rate of cooling characterizes the quench and varies between $10^5$ and $10^8\,\mathrm{K\,sec^{-1}}$ when the quenching method used is one of those classified as "splat" [6, 7]. In this work we shall consider only glassy metals prepared by rapid quenching from the melt.

Much effort has been devoted to the search for universal criteria for identifying those binary, ternary or higher order alloys that readily form a glass on rapid quenching from the melt [8]. Using the classification of GFA alloys into categories [9], two of the criteria for the prediction of the GFA–the structural [9, 10] and the thermodynamic [11]–which had both been applied by their authors to the zirconium–metal systems, and working with the criteria for predicting fast diffusion [3], we have attempted in this paper to find the phenomenological connections between GFA and fast diffusion for zirconium–metal systems.

## 2. Previous studies

### 2.1. Fast diffusion in zirconium

In hcp α-zirconium, the volume diffusion coefficients of the fast-diffusing solutes manganese [12], chromium [13], beryllium [14], copper [15], iron [3, 16], nickel [16] and cobalt [17] at very high dilution are three to seven orders of magnitude larger than the zirconium self-diffusion coefficient measured in polycrystals [18]. At very high dilution, there are other solutes, predominantly substitutionals, that diffuse within one order of magnitude slower than (antimony [19], aluminium [19], yttrium [20], vanadium [21]) or faster than (cerium [22], niobium [18], cadmium [3], tantalum [23], silver [19, 24], gold [19]) or even at the same rate as (titanium, [19], tin [25], molybdenum [22]) self-diffusion in α-zirconium polycrystals.

Solute atoms form a mixed substitutional and interstitial solid solution in which the fast diffusion is due to migration of the interstitial atoms. Such a mixed solution is named a dissociative solution [1, 3]. In this

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dissociative solution, interstitial and substitutional solute atoms are in mutual equilibrium. The measured solute diffusion coefficients suggest [26] that the equilibrium atomic fraction of interstitials starts, increasing gradually from the slowest predominantly substitutional solutes, to become distinctly predominant for the fast-diffusing solutes.

For the sake of an accurate description of diffusion in $\alpha$-zirconium, the solute diffusion coefficients have to be compared with the self-diffusion coefficients measured in $\alpha$-zirconium single crystals. Self-diffusion in $\alpha$-zirconium is still an open question [19, 27] far from being precisely understood. Self-diffusion coefficients in $\alpha$-zirconium single crystals [19, 27] are slower by up to two orders of magnitude than those measured in polycrystals. Owing to this shift, the predominantly substitutional solutes diffuse faster than zirconium single crystal self-diffusion [19, 27] by a factor ranging from around one order of magnitude (antimony) up to around three orders of magnitude (gold). On the other hand, the diffusion of the predominantly interstitial solutes mentioned above turns out to be even faster: five to nine orders of magnitude larger than self-diffusion. This description is based on solute and self-diffusion coefficients measured at 800 to 860° C.

In bcc $\beta$-zirconium the diffusion coefficient of the predominantly interstitial solutes is only one to two orders of magnitude larger than the zirconium self-diffusion coefficient [3]. Very dilute and predominantly substitutional solutes in $\beta$-zirconium have diffusion coefficients which do not differ by more than one order of magnitude from zirconium self-diffusion.

There are two models that predict significant interstitial dissolution (and fast diffusion) of metallic solutes in metallic solvents to occur. Both of them fit zirconium–metal (Zr–M) fast diffusion behaviour [3]. One of them, the atomic size criterion, was discussed when we analysed [3] the diffusion behaviour of Zr–M systems. Predominantly interstitial dissolution of metallic solutes in $\alpha$-zirconium is always related to a very restricted solid solubility. This experimental fact and the Hume–Rothery rules that control substitutional solubility [28] led to the criterion statement: "In very dilute metal–metal alloys a significant interstitial dissolution is expected when the Hume-Rothery 15% size rule prohibits extended solid solubility and when, at the same time, the atomic radius of the solute ($r$) is smaller than that of the solvent ($R$). For those solutes near the limit in which $r/R = 0.85$, both the criterion and the phase diagram have to be analysed together". The other model is the valency criterion [3, 29] and it specifies that:

1. the solvent must be high-valent or very electropositive. (Zirconium is a tetravalent metal and more electropositive than M in the studied systems);
2. the solute ion must be sufficiently small to be placed with little or no ion core overlap in the interstices formed by the solvent ions in the host lattice. This is a necessary condition. (When zirconium is the solvent the ionic radius of the solute must be smaller than 0.1 nm);
3. a low-valent solute is the condition that finally determines the fast diffusion behaviour. (Fast-diffusing solutes in zirconium have a valency less than or equal to one. Trivalent or higher valent solutes exhibit predominantly substitutional diffusion behaviour.)

## 2.2. Criteria for GFA prediction

### 2.2.1. *Structural criterion*

The structural criterion [9, 10] specifies that a binary metallic system has glass-forming ability when the atomic size of the components differ by more than 15% and when at the same time the heat of formation of the equiatomic liquid alloy ($\Delta H^{\mathrm{M}}$) is lower than $\sim -10\,\mathrm{kcal\,mol^{-1}}$. $\Delta H^{\mathrm{M}}$ is theoretically calculated [30] from the electronegativities and electron concentrations of the components by using a semi-empirical approximation. The heat of formation of the liquid alloy is negative owing to the electronegativity difference of the constituent metals.

Plotting $\Delta H^{\mathrm{M}}$ against $r/R$ for all the binary alloys of a selected metal, a GFA map can be constructed. It turns out that all the GFA alloys occupy a restricted area.

Giessen [10] drew a $\Delta H^{\mathrm{M}}$ against $r/R$ map for the Zr–M systems, considering principally those alloys that were previously tested concerning their GFA. He calculated $r/R$ using the atomic sizes obtained for co-ordination number 12 given by Pearson [31]. GFA alloys are in the lower left-hand corner of the plot, where $r/R < 0.85$ to $0.90$ and $\Delta H^{\mathrm{M}} < \sim -5\,\mathrm{kcal\,mol^{-1}}$. The boundary of this zone was drawn by taking into account those alloys which form glasses when the critical cooling rate is $\dot{T} = 10^5$ to $10^6\,\mathrm{K\,sec^{-1}}$.

A $\Delta H^{\mathrm{M}}$ against $r/R$ map was drawn in the present work (see Fig. 3) and will be discussed below (Sections 3.1 and 3.2).

### 2.2.2. *Thermodynamic criterion*

The reduced glass temperature ($T_{\mathrm{gr}}$) is the parameter that gives an evaluation of the glass-forming ability for any alloy. $T_{\mathrm{gr}} = T_{\mathrm{g}}/T_{\mathrm{L}}$, where $T_{\mathrm{g}}$ and $T_{\mathrm{L}}$ are the glass transition temperature and the liquidus temperature, respectively. As a general rule [9], a GFA alloy would be one for which $T_{\mathrm{gr}} > \sim 0.60$. Because there are only few systems with known values of $T_{\mathrm{g}}$ it is not possible to evaluate the GFA for a large number of systems calculating $T_{\mathrm{gr}}$. Nevertheless, in binary systems the GFA can be ascertained, because it appears around the eutectics. This is due to the fact that since $T_{\mathrm{g}}$ varies only slowly with composition, $T_{\mathrm{gr}}$ increases around the eutectics, where $T_{\mathrm{L}}$ decreases.

Marcus and Turnbull [32] have pointed out that the greatest GFA would correspond to the abnormally deep eutectics, i.e. those for which $T_{\mathrm{L}}$ is much smaller than the liquidus temperature of the ideal liquid solution, $T_{\mathrm{L}}^0$. They noted that in alloys where the primary solid solubility is very small, the GFA correlates with the parameter $(T_{\mathrm{L}}^0 - T_{\mathrm{L}})/T_{\mathrm{L}}^0$. They found that a binary alloy of 0.15 atom fraction concentration of its minor constituent would form a glass by quenching from the melt at $10^6\,\mathrm{K\,sec^{-1}}$, when $(T_{\mathrm{L}}^0 - T_{\mathrm{L}})/T_{\mathrm{L}}^0 \geqslant 0.1$.

TABLE I $T_{0r}$ for Zr–M (and non–M) systems

| Eutectic composition (at %) [11] | $T_{0r}$ (from Equation 1) | Structure* |
|---|---|---|
| $Zr_{65.2}Be_{34.8}$ | 0.28 | G |
| $Zr_{75.9}Ni_{24.1}$ | 0.43 | G |
| $Zr_{78}Co_{22}$ | 0.54 | G |
| $Zr_{62.5}Cu_{37.5}$ | 0.56 | G |
| $Zr_{76}Fe_{24}$ | 0.58 | G |
| $Zr_{75}Rh_{25}$ | 0.72 | G |
| $Zr_{67.5}Mn_{32.5}$ | 0.73 | G |
| $Zr_{79}Pt_{21}$ | 0.77 | G |
| $Zr_{75.5}Pd_{24.5}$ | 0.77 | G |
| $Zr_{56.5}V_{43.5}$ | 0.81 | G |
| $Zr_{72}Cr_{28}$ | 0.84 | G |
| $Zr_{91}Si_9$ | 0.87 | G |
| $Zr_{79}Ga_{21}$ | 0.87 | C |
| $Zr_{79}Ru_{21}$ | 0.87 | G |
| $Zr_{80}Os_{20}$ | 0.88 | G |
| $Zr_{89.7}Ag_{10.3}$ | 0.91 | C |
| $Zr_{75}Bi_{25}$ | 0.91 | C |
| $Zr_{88}B_{12}$ | 0.92 | C |
| $Zr_{86}Re_{14}$ | 0.97 | C |
| $Zr_{70.5}Al_{29.5}$ | 0.98 | C |

*G: glass formation, not necessarily at the eutectic composition.
C: crystallization.

This correlation fails when appreciable solid solubility or compound formation occurs [32]. Another approach including these systems was reported by Donald and Davies [33]. Instead of $T_L^0$, they utilize the ideal melting point of the mixture defined as $\bar{T}_L^0 = T_m^A f_A + T_m^B f_B$, where $T_m^A$ and $T_m^B$ are the melting points of the pure A and pure B components in their normal isolated state, and $f_A$ and $f_B$ are the atom fractions. $\bar{T}_L^0$ is calculated for a simple binary eutectic mixture, $A_{f_A}B_{f_B}$. For the melt-quenched GFA alloys the parameter $(\bar{T}_L^0 - T_L)/\bar{T}_L^0$ turns out to be larger than 0.2.

An even more general approach was developed by Whang [11]. It is also suitable for alloys for which the eutectic compositions are associated with extensive solid solution. This model is based on the comparison between $T_g$ and a parameter $T_0$: if around the eutectic composition $T_g > T_0$, the alloy will transform into a glass by rapid quenching from the melt. $T_0$ is a composition-dependent temperature [7], and for an alloy of a given composition is the temperature at which solid and liquid each of this composition have the same free energy. $T_0$ has been theoretically shown [7] as being the maximum temperature of the solid–liquid interface at which an alloy solidifies without solute segregation.

Whang related the value of the reduced variable at the eutectic composition, $T_{0r} = T_0(C_e)/T_e$, to the reduced eutectic composition, $C_{er} = (C_e - C_s)/C_e$, and to $\Delta T_m/T_e = (T_m^A - T_e)/T_e$ by:

$$T_{0r} = 1 - \frac{\Delta T_m}{T_e}\left(\frac{2}{2 - C_{er}} - 1\right) \qquad (1)$$

where $C_e$ is the eutectic composition, $T_e$ the eutectic temperature, $T_0(C_e)$ the value of $T_0$ at $C_e$, and $C_s$ the maximum value of the solid solubility of the minor eutectic constituent (B) in the major one (A).

Table I contains $T_{0r}$ for Zr–M (and non-M) alloys calculated with $\Delta T_m/T_e$ and $C_{er}$ values taken from Whang [11]. In this table the alloys are arranged according to increasing $T_{0r}$ values.

$\Delta T_m/T_e$ and $C_{er}$ for Zr–M (and non-M) systems represented in a two-dimensional plot give the GFA map shown in Fig. 1. The boundary line that separates the GFA from the non-GFA alloys is the curve represented by Equation 1 when $T_{0r} = 0.87$. This value comes from Table I and from Fig. 1, where Zr–Si,

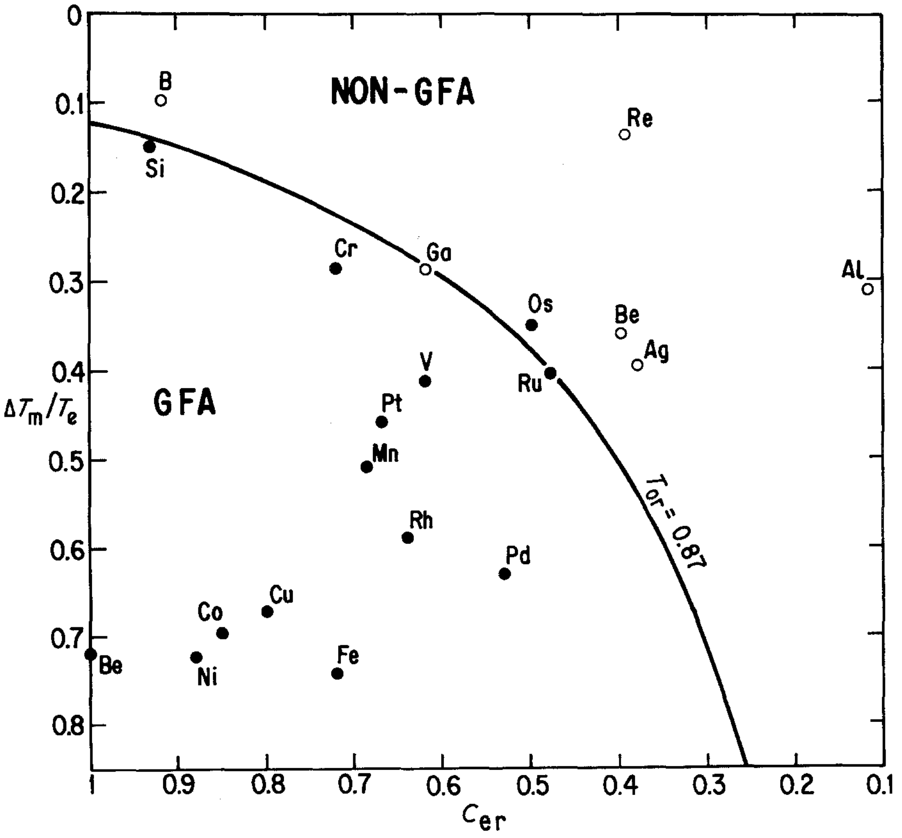

*Figure 1* Zr–M systems; GFA map of $\Delta T_m/T_e$ against $C_{er}$. ● GFA alloy, ○ non-GFA alloy.

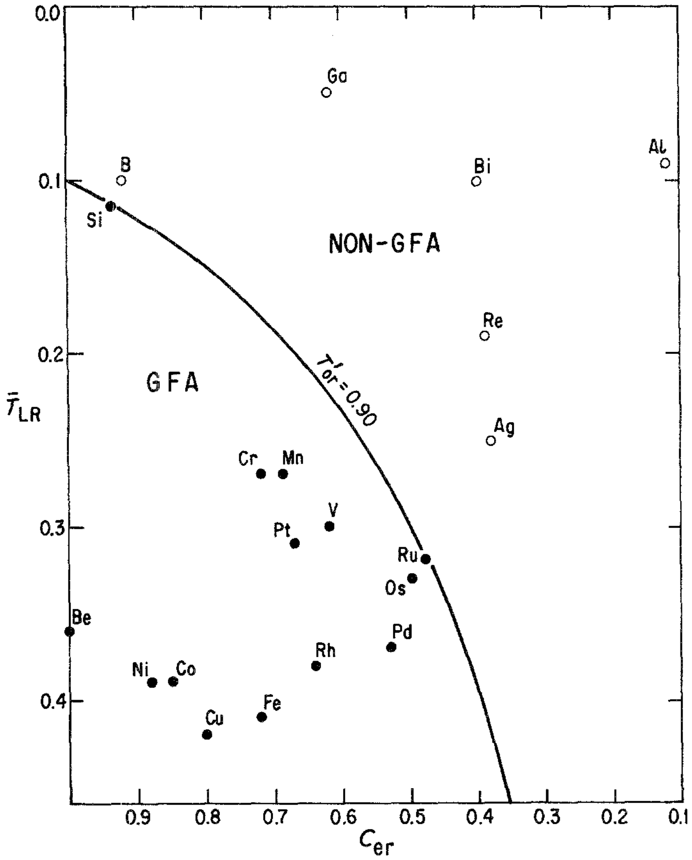

*Figure 2* Zr–M systems; GFA map of $\bar{T}_{LR}$ against $C_{er}$. ● GFA alloy, ○ non-GFA alloy.

Zr–Ga, Zr–Ru and Zr–Os appear as the limiting cases between glass formation and crystallization.

Whang [11], using $\bar{T}_L^0$ in place of $T_e$ and $\bar{T}_L^0 - T_L$ in place of $\Delta T_m = T_m^A - T_e$, obtained the liquidus reduced temperature $\bar{T}_{LR} = (\bar{T}_L^0 - T_L)/\bar{T}_L^0$ and used it instead of $\Delta T_m/T_e$ to construct the GFA map. He pointed out that $\bar{T}_{LR}$ is of "broader application" than $\Delta T_m/T_e$, because it permits the analysis of any alloy composition. The $\bar{T}_{LR}$ against $C_{er}$ map for Zr–M (and non-M) alloys from Whang [11] is shown in Fig. 2, except for the boundary line. In Whang's paper this line was calculated for Ti–M (and non-M) systems and used for the other systems studied there. In the present work it was specifically calculated for the Zr–M systems, using in Equation 1 the $\bar{T}_{LR}$ value for Zr–Si and Zr–Ru, the alloys which appear in Fig. 2 as the limiting cases of GFA. This gave $T'_{0r} = 0.90$ (the line drawn in Fig. 2). Note that we now denote the variable of Equation 1 as $T'_{0r}$ because $\bar{T}_{LR}$ was used instead of $\Delta T_m/T_e$.

## 3. Discussion

The following discussion will be developed in terms of the GFA maps, using the data of heterodiffusion in zirconium and the criteria for the prediction of fast diffusion, in order to reveal the phenomenological connections between glass-forming ability and fast diffusion in Zr–M systems.

### 3.1. The GFA map of $\Delta H^M$ against atomic size, and the measured fast diffusion

The $\Delta H^M$ against $r/R$ map drawn in the present work is shown in Fig. 3. In this map the abscissae represent the closest distances of approach of the atoms in the crystal structure of the metallic elements [28], and the ordinates represent the values of $\Delta H^M$ for Zr–M systems. The abscissae of the plot also show the positions of the metals with respect to Hume-Rothery's atomic size condition applied to the substitutional solubility of M in zirconium. In this plot the GFA zone is bordered by the ordinate $\Delta H^M = 0\ \text{kcal mol}^{-1}$ and the abscissa $r/R = 0.85$ ($R$ being the $\alpha$ and $\beta$-zirconium interatomic distances).

The alloy Zr–Au is an exception. It is outside the GFA zone although Giessen marked it as a GFA alloy [10]. The filled circle for manganese in the non-GFA zone does not constitute an exception, since there is another point for manganese well inside the GFA zone [28].

Although not reported in [10], metallic glasses of Zr–V and Zr–Cr alloys have recently been obtained by rapid quenching from the melt [11, 34].

The main observation, in conclusion, is that all the Zr–M systems of measured fast diffusion, M = chromium, manganese, iron, cobalt, nickel, copper and beryllium, are inside the GFA zone (Fig. 3).

### 3.2. Glass-forming alloys near the $r/R = 0.85$ limit and the prediction of their diffusion behaviour: Zr–V and Zr–Au systems

Around the limit $r/R = 0.85$ of the GFA zone there are glass-forming systems for which diffusion parameters have not been measured. They are the Zr–M systems with M = ruthenium, rhenium, lead, osmium, and platinum. We applied to them the criteria to predict fast diffusion, by using the data shown in Table II, with the following results.

The valency criterion indicates that the fast diffusion of all these metallic solutes in zirconium is possible. They are more electronegative than

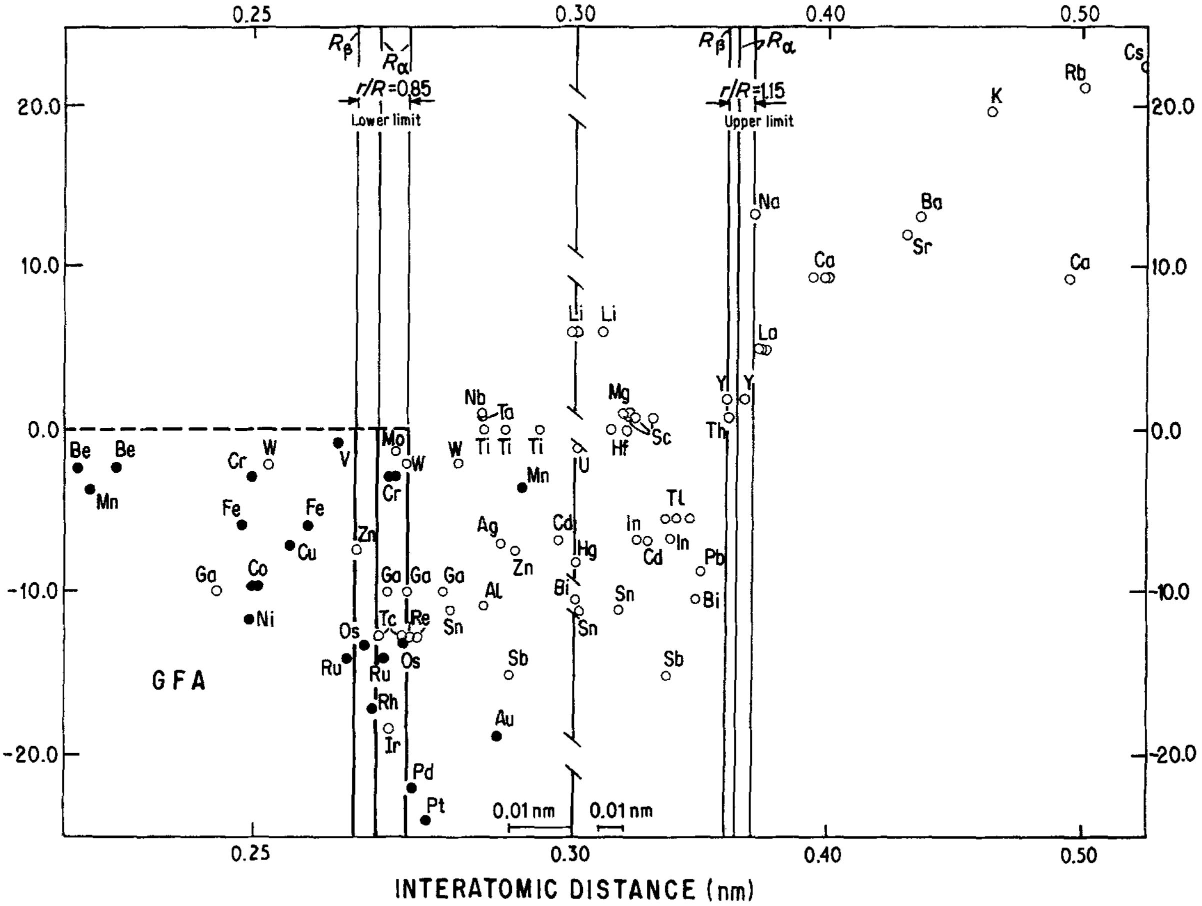

*Figure 3* Zr–M systems; GFA map of $\Delta H^M$ against interatomic distance. Interatomic distance: closest distance of approach of the atoms in the crystal structure of the metal. When a metal exists in different crystal structures or when there are two or more series of nearest neighbours of each atom, all these values are drawn [28]. $R$: Zr, $r$: the other metals. —— Hume-Rothery's atomic size condition; limits of the extensive substitutional solubility zone in $\alpha$ and in $\beta$-Zr. --- Enthalpy limiting value of the GFA zone. ● GFA alloy, ○ non-GFA alloy.

zirconium, their ionic radii are smaller than 0.1 nm (Table IIa) and their valency is 0 [29].

The Zr–Ru phase diagram [37–39] shows at both extreme compositions restricted solid solubilities (Table IIb). This system presents only two intermetallic compounds that exist over a range of compositions. Therefore, the solid solubilities do not seem to be restricted by the influence of the large electronegativity difference between zirconium and ruthenium (Table IIa). This difference would induce the formation of compounds more ionic in character and would preferentially reduce the solubility of ruthenium in zirconium. Then the difference in atomic sizes (Fig. 3) must be the reason for the restricted solid solubility.

In Fig. 3, where the abscissa represents Hume-Rothery's rule for substitutional solubility in zirconium, platinum is within the zone where solid solubility is favoured, though very near to the $r/R = 0.85$ limit. The Zr–Pt phase diagram shows restricted solid solubility at both extreme compositions [38]. Nevertheless, it has several intermetallic compounds that exist at stoichiometric compositions [37–39]. Therefore, the electronegativity difference seems to have an influence on the Zr–Pt diagram, restricting the solid solubilities. This influence is opposed to the significant partial interstitial dissolution of platinum in zirconium.

TABLE IIa Pauling electronegativities (EN) and ionic radii ($r_i$) of M = Ru, Rh, Pd, Os and Pt

| M | EN [35] | $r_i$ (nm) [36] |
|---|---|---|
| Ru | 2.2 | $Ru^{4+}$ 0.065 |
| Rh | 2.2 | $Rh^{3+}$ 0.068 |
| Pd | 2.2 | $Pd^{2+}$ 0.050 |
| Os | 2.2 | $Os^{4+}$ 0.067 |
| Pt | 2.2 | $Pt^{2+}$ 0.052 |

The solubilities of M = rhodium, lead and osmium in zirconium (Table IIb) are smaller than or very near to the characteristic solubility values of the interstitial metal solutes in zirconium. Instead, there is an extensive solubility of zirconium in M. In addition, Zr–Os [37, 38, 40] shows two and Zr–Rh [40] shows three intermetallic compounds and for both systems only one of these compounds, that which is richer in zirconium, appears as a line in the phase diagrams. Zr–Pd has four intermetallic compounds, all of them at stoichiometric compositions [38–40]. Therefore, in these systems substitutional solubility seems to be favoured by the electronegative and low-valent solvent (M) and would be restricted in the electropositive, high-valent solvent (zirconium). As the interatomic distances of rhodium, palladium and osmium are just near the limit $r/R = 0.85$, their substitutional solubilities in zirconium would not be restricted by the atomic size effect, but by their differences in valencies and electronegativities with respect to zirconium (Fig. 3 and Table IIa and b).

Summarizing, it can be said that the atomic size criterion combined with the judicious observation of some aspects of their phase diagrams predict

TABLE IIb Maximum of the solid solubility of M in α-Zr ($C_s^\alpha$) and β-Zr ($C_s^\beta$) and maximum of the solid solubility of Zr in M ($C_s^M$). M = Ru, Rh, Pd, Os and Pt

| M | $C_s^\alpha$ (at % of M) | Reference | $C_s^\beta$ (at % of M) | Reference | $C_s^M$ (at % of Zr) | Reference |
|---|---|---|---|---|---|---|
| Ru | 0.5 | [39] | 11 | [39] | 0.35 ss†<br>0.5 tp‡ | [37] |
| Rh | 1* (700° C) | [39] | 9 | [40] | 10 | [40] |
| Pd | 0.1* (700° C) | [39] | 11.5 | [38, 40] | 20* (700° C) | [39] |
|  | 0.2* (800° C) | [39] |  |  | 20* (1000° C) | [39] |
|  | Very small | [38, 40] |  |  | 14 | [40] |
| Os | 1.6 | [40] | 10 | [40] | 8 | [40] |
| Pt | 0.5 | [38] | 7 | [38] | 0.5 | [38] |

*Isolated values of solid solubility; the maximum values does not appear in [37–40].
†ss: solid solution.
‡tp: two-phase alloy.

predominant substitutional diffusion behaviour for rhodium, palladium and osmium in zirconium; and fast diffusion for ruthenium in zirconium. For platinum neither substitutional nor interstitial predominant diffusion behaviour can be predicted.

The Zr–V system forms metallic glasses and it is within the GFA zone in the map of Fig. 3, the ratio $r/R$ for vanadium being smaller than 0.85. Nevertheless its diffusion in zirconium is slow, substitutional and because of that, vanadium was previously marked as an exception to the atomic size criterion for fast diffusion prediction [41].

The ionic radius of $Au^+$ is larger than 0.1 nm [36] and for the Au–Zr system $r/R > 0.85$ (Fig. 3). The gold ionic size therefore prohibits its interstitial dissolution in zirconium and the atomic size criterion predicts its substitutional dissolution in zirconium. These predictions are confirmed experimentally, since diffusion of gold in zirconium is slow [19] and the solubility of zirconium in gold is extensive [37–40].

We conclude that the Zr–M glass-forming systems with $\Delta H^M < 0\,\text{kcal mol}^{-1}$ and placed in the limit $r/R \approx 0.85$ of the $\Delta H^M$ against interatomic distance plot, are not necessarily fast-diffusion systems.

## 3.3. GFA maps of $\bar{T}_{LR}$ (or $\Delta T_m/T_e$) against $C_{er}$, solid solubility in β-zirconium and fast-diffusion

An important characteristic of the thermodynamic criterion for GFA prediction [11] is that it relates through the variable $C_{er}$ the GFA of the alloys to the solid solubility of its minor constituent in the major one. In the thermodynamic criterion, $C_{er}$ is introduced as a variable, in addition to $\bar{T}_{LR}$ [31, 32] (see the expression for $C_{er}$ and Equation 1 in Section 2.2.2 and the maps in Figs. 1 and 2).

TABLE IIc Maximum of the solid solubility of M = Cu to V in the first long period in β-Zr ($C_s^\beta$)

| M | $C_s^\beta$ (at % of M) | Reference |
|---|---|---|
| V | 16.5 | [37] |
| Cr | 10.4 | [37] |
|  | 7.8 |  |
|  | 7.5 | [39] |
| Mn | 10.2 | [37] |
| Fe | 6.75 | [38] |
| Cu | 5.3 | [37] |
| Co | 3.37 | [39] |
| Ni | 2.9 | [37] |
|  | 3 | [38] |

Table I contains the $T_{0r}$ values of Zr–M (and non-M) alloys and Table IIc shows the values of the maximum solid solubility of M in β-zirconium ($C_s^\beta$) for M = vanadium, copper and the later transition elements of the first long period. In this table, the elements are arranged according to decreasing $C_s^\beta$. From these and from Figs. 1 and 2, it can be seen [11] that as $C_s^\beta$ decreases, the point representing the alloy and its corresponding $T_{0r}$ value go further into the GFA zone, suggesting a tendency of the GFA to increase as $C_s^\beta$ decreases.

Thus, $C_s^\beta$ appears as a link between GFA and fast diffusion in zirconium, when it is remembered [3] that the extent of $C_s^\beta$ also characterizes the nature of the primary solid solution (and the diffusion behaviour) in zirconium. $C_s^\beta$ is always more restricted (less than 11 at %) for the predominantly interstitial solutes than for substitutional solutes; in the latter case it is significantly larger than 11 at % and in many cases reaches 100 at %. For the metals considered in Table IIc, the more soluble vanadium is a slow, substitutional diffusing solute whereas the less soluble copper and later transition metals are predominantly interstitial, fast-diffusing solutes.

## 3.4. Zr–M fast-diffusing systems in the classification of metallic glasses

The metallic glasses that can be obtained by rapid quenching from the melt were classified by Giessen [9],

TABLE III Classification of the metallic glasses (GFA alloys) according to the chemical nature of their components [9]

| Groups* | Representative systems |
|---|---|
| *Major systems* |  |
| $T^2$ (or noble) metal + metalloid (X) | Pd–Si, Co–P, Fe–P–C, Ni–P–B |
| $T^1$ metal + $T^2$ metal (or Cu) | Zr–Cu, Ti–Ni, Nb–Ni |
| A metal + B metal | Ca–Al, Mg–Zn |
| Lanthanide + $T^2$ or B metal | La–Ni, Ce–Al |
| Actinide + $T^2$ metal | U–Fe, Pu–Ni |
| *Miscellaneous systems* |  |
| $T^1$ metal + A metal | (Ti–Zr)–Be |
| Actinide + $T^1$ metal | U–Cr |
| A metal + $T^2$ metal | Ca–Ni, Ca–Pd |

*A metal = Li, Mg groups; $T^1$ metal = early transition metal (Sc, Ti, V groups); $T^2$ metal = late transition metal (Mn, Fe, Co, Ni groups); B metal = Cu, Zn, Al groups; metalloid = B, C, Si, Ge, P.

according to the chemical nature of their components. This classification consists of two categories: "major systems" and "miscellaneous systems". It is shown in Table III.

It is to be noted that the Zr–M glass-forming alloys that exhibit fast diffusion of M in zirconium, except Zr–Be, are found in the second group of the "major systems" category (i.e. $T^1$ metal + $T^2$metal (or copper)). Zr–Cr glasses [34] also appear in this group and category if chromium is considered as a late transition metal. Zr–Be glasses are found in the "miscellaneous systems" category.

## 4. Conclusions

Those binary alloys Zr–M in which there is fast diffusion of M in zirconium are easy glass-forming systems. In the framework of some semi-empirical criteria the same physical properties allow the prediction of both forms of behaviour. These experimental facts would confirm Turnbull's suggestion [4] that these two apparently unrelated phenomena have to be governed by the same kind of atomic properties.

## Acknowledgements

The author is indebted to Dr A. D. Le Claire, Professor R. W. Cahn and Dr J. P. Abriata for invaluable encouragement, discussion and critical review of the manuscript. Thanks are also given to Dr D. Kurlat for the first suggestions concerning metallic glasses, to Lic. S. N. Balart for the critical reading of the manuscript, and to Lic. S. Kurokawa for discussing some aspects of Section 2.

This work was partially supported by the Proyecto Multinacional de Tecnología de Materiales (Organización de Estados Americanos-Comisión Nacional de Energía Atómica, Argentina).

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*Received 28 December 1984*
*and accepted 31 January 1985*