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## Glass formation in ternary transition metal alloys

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**Abstract.** We have recently used a combination of classical elasticity theory and Miedema's model for the heat of formation of alloys to predict the glass-forming ranges of binary transition metal systems. In this paper we extend this approach to study the glass-forming regions in the ternary case. The predictions of the theory are compared with available experimental information for some Co-based ternary alloys, and we relate our treatment to the empirical equation recently proposed by Ueno and Waseda to describe the minimum solute concentration for glass formation in ternary systems.

### 1. Introduction

Since the pioneering work by Buckel and Hilsch (1954) and Duwez and coworkers (Klement *et al* 1960), a wide variety of techniques have been developed to produce amorphous alloys by either liquid quenching, vapour quenching or solid-state reactions (see, e.g., Johnson 1986 and references therein). At the same time, various models have been proposed to predict the glass-forming ability (GFA) of metallic alloys (van der Kolk *et al* 1988), which depends on both alloy composition and cooling-rate conditions.

We have recently shown (López *et al* 1987, Alonso *et al* 1988, Gallego *et al* 1988; see also van der Kolk *et al* 1988 and Loeff *et al* 1988) that a treatment which combines classical elasticity theory and Miedema's model of heats of formation of alloys affords good predictions of the glass-forming ranges of binary transition metal systems. This approach takes into account the main factors that have been recognised empirically to be correlated with GFA, such as atomic size mismatch, the heat of formation of the liquid alloy, and differences in electronegativity and valence. Our treatment highlights the key role of atomic size mismatch in determining the composition range in which amorphous phases can be found. The importance of atomic size mismatch was also concluded by Egami and Waseda (1984), who have used an atomic elasticity theory to show that the minimum solute concentration necessary to obtain binary amorphous alloys by rapid quenching from the melt is inversely related to the atomic volume mismatch.

In this paper we use the same approach as for the binary case to predict the glass-forming regions of ternary transition metal systems. As will be shown, there is some relationship between our treatment and the equation suggested by Ueno and Waseda (1985) to describe the minimum solute concentration for glass formation in ternary alloys in terms of the relative size of the components, an extension of that proposed by

Egami and Waseda (1984) for binary alloys. In this paper we first introduce the main ingredients of the theory, and then compare its predictions with the experimental information reported by Nosé *et al* (1981) and Kim *et al* (1988) for a set of ternary Co-based alloys.

## 2. Method

The glass-forming region of a binary or multicomponent alloy is delimited both by the compositions at which the Gibbs free energies of competing crystalline phases (usually substitutional solid solutions) become more negative than that of the amorphous phase and, additionally, by the possible presence of structurally simple compounds (see, e.g., López *et al* 1987). Here we shall make the usual simplification of neglecting entropy effects (van der Kolk *et al* 1988, Loeff *et al* 1988) and compare only the enthalpies of formation of the different phases.

As in the case of binary alloys (López *et al* 1987, van der Kolk *et al* 1988, Loeff *et al* 1988), we write the enthalpy of formation of a ternary solid solution of transition metals A, B and C as

$$\Delta H_{ABC}^{\text{sol}} = \Delta H_{ABC}^{\text{c}} + \Delta H_{ABC}^{\text{e}} + \Delta H_{ABC}^{\text{s}} \quad (1)$$

where  $\Delta H_{ABC}^{\text{c}}$  is a chemical contribution due to electron redistribution when the alloy is formed,  $\Delta H_{ABC}^{\text{e}}$  is an elastic or atomic size mismatch contribution, and  $\Delta H_{ABC}^{\text{s}}$  is a structural contribution. In the amorphous state the elastic and structural contributions are absent, so that the enthalpy of formation can be written as

$$\Delta H_{ABC}^{\text{am}} = \Delta H_{ABC}^{\text{c}} + x_A \Delta H_A^{\text{a-s}} + x_B \Delta H_B^{\text{a-s}} + x_C \Delta H_C^{\text{a-s}} \quad (2)$$

where  $x_i$  is the concentration of component  $i$  and  $\Delta H_i^{\text{a-s}}$  is the enthalpy difference between the amorphous and crystalline states of the pure element  $i$ . According to van der Kolk *et al* (1988) this quantity is given by

$$\Delta H_i^{\text{a-s}} = \alpha T_{m,i} \quad (3)$$

where  $\alpha = 3.5 \text{ J mol}^{-1} \text{ K}^{-1}$  and  $T_{m,i}$  is the melting temperature of component  $i$ .

In Miedema's model of binary alloys (Niessen and Miedema 1983), the chemical part of the heat solution of A in B is

$$\Delta h^{\text{c}}(\text{A in B}) = V_A^{2/3} F(\text{A}, \text{B}). \quad (4)$$

Here  $V_A$  is the atomic volume, and consequently  $V_A^{2/3}$  is proportional to the surface area of the atomic cell.  $F(\text{A}, \text{B})$  depends only on properties of the pure metals, namely the electronegativities  $\varphi_A$  and  $\varphi_B$ , and the electron densities  $n_A$  and  $n_B$  at the boundaries of bulk atomic cells. Specifically,

$$F(\text{A}, \text{B}) = [2/(n_A^{-1/3} + n_B^{-1/3})][ -P(\varphi_A - \varphi_B)^2 + Q(n_A^{1/3} - n_B^{1/3})^2 ] \quad (5)$$

where  $P$  and  $Q$  are constants.  $F(\text{A}, \text{B})$  is thus proportional to the interaction energy per unit area of contact between A and B cells. Extensive tables of  $\Delta h^{\text{c}}$  have been published (Niessen and Miedema 1983, de Boer *et al* 1988). The chemical contribution to the heat of formation of a random binary solid solution with concentrations  $x_A$  and  $x_B$  is (Loeff *et al* 1988)

$$\Delta H_{AB}^{\text{c}} = x_A x_B (x_B \Delta h^{\text{c}}(\text{A in B}) + x_A \Delta h^{\text{c}}(\text{B in A})) \quad (6)$$

which according to (4) can be expressed in the form

$$\Delta H_{AB}^{\text{c}} = x_A x_B (x_B V_A^{2/3} + x_A V_B^{2/3}) F(\text{A}, \text{B}). \quad (7)$$

The concentration-dependent factor  $(x_B V_A^{2/3} + x_A V_B^{2/3})$  takes account of the deviation

from regular solution behaviour, which in Miedema's model arises from the total interaction energy between the two components in the alloy being assumed to be proportional to the total surface area of contact between A and B atomic cells (equation (4)).

The extension of the above model to a ternary alloy with concentrations  $x_A$ ,  $x_B$  and  $x_C$  is

$$\Delta H_{ABC}^c = \Delta H_{AB}^c + \Delta H_{AC}^c + \Delta H_{BC}^c \quad (8)$$

with

$$\Delta H_{ij}^c = x_i x_j (x_j \Delta h^c(i \text{ in } j) + x_i \Delta h^c(j \text{ in } i)) \quad (9)$$

if one assumes that the chemical interaction per unit surface area of contact between A and B cells is not changed by the presence of a third component C. Work on some ternary compounds (de Boer *et al* 1988) appears to justify this assumption.

The expression for  $\Delta H_{AB}^c$  or  $\Delta H_{ABC}^c$  must be modified if evidence for chemical short-range order exists. In the case of a fully ordered binary intermetallic compound this can be taken into account (de Boer *et al* 1988) by multiplying the right-hand side of equation (6) by the factor  $[1 + \gamma(x_A^s x_B^s)^2]$ , which involves an empirical constant  $\gamma = 8$  and the cell surface concentrations  $x_A^s$  and  $x_B^s$  in the alloy:

$$x_A^s = x_A V_A^{2/3} / (x_A V_A^{2/3} + x_B V_B^{2/3}) \quad x_B^s = 1 - x_A^s \quad (10)$$

This factor takes account of the increased fraction of atomic cells of type A in contact with cells of type B. For the case of binary alloys with a partial degree of chemical order, Weeber (1987) has proposed using a reduced value of  $\gamma$  (note that  $\gamma = 0$  leads to complete disorder). Since little is known about chemical short-range order in binary solid solutions, and even less for ternary ones, we assume in this paper that the alloys are disordered.

The elastic contribution to the heat of solution in a binary system is given by (Niessen and Miedema 1983, de Boer *et al* 1988)

$$\Delta h^e(\text{A in B}) = 2K_A \mu_B (V_B^* - V_A^*)^2 / (3K_A V_B^* + 4\mu_B V_A^*) \quad (11)$$

where  $\mu_B$  is the shear modulus of the host,  $K_A$  is the compressibility of the solute metal and  $V_A^*$  and  $V_B^*$  are effective volumes corrected for charge transfer effects. An extension to the finite concentration case has been developed by López and Alonso (1984), but we have observed that similar results can be obtained for the elastic contribution to the heat of formation with a simple interpolation formula similar to equation (6) (Loeff *et al* 1988):

$$\Delta H_{ij}^e = x_i x_j (x_j \Delta h^e(i \text{ in } j) + x_i \Delta h^e(j \text{ in } i)). \quad (12)$$

For the ternary case we now assume

$$\Delta H_{ABC}^e = \Delta H_{AB}^e + \Delta H_{AC}^e + \Delta H_{BC}^e. \quad (13)$$

In the applications of the theory described in section 3 below we will focus on the A-rich region of the ternary phase diagram. Under these conditions, the work of Alonso *et al* (1985) on the interaction of impurities in ternary alloys indicates that the additivity approximation is reasonable when elements B and C are both oversized or both undersized with respect to the host A. On the other hand, an elastic contribution  $\Delta H_{ABC}^e$  smaller than that given by equation (13) is to be expected if  $V_B > V_A > V_C$ , in which case the size mismatch effects of B and C in A can partly cancel each other when B and C are nearest neighbours. Chemical short-range order must evidently contribute

to this effect, i.e. the cancellation effect increases if first-neighbour B–C pairs are found more often than for a random distribution.

The structural contribution  $\Delta H^s$  to the heat of formation of a solid solution arises from the well-known correlation between the number of valence ( $s + d$ ) electrons in transition metals and the observed crystal structure (Niessen and Miedema 1983). The addition of a second transition element with a different valence must in general modify the structural contribution that stabilises the known crystal structure of the pure host. Niessen and Miedema (1983) (see also López and Alonso 1985) have been able to quantify this effect for binary solid solutions:

$$\Delta H_{AB}^s = E_{\sigma(\text{alloy})}(\bar{Z}) - x_A E_{\sigma(A)}(Z_A) - x_B E_{\sigma(B)}(Z_B) \quad (14)$$

where  $\bar{Z}$  is the average number of valence electrons in the alloy, and the  $E_{\sigma}(Z)$  are lattice stabilities found by these authors as functions of the number  $Z$  of valence electrons for each crystal structure  $\sigma$  ( $\sigma = \text{BCC, HCP or FCC}$ ). This description of structural effects in alloys formed by two transition metals rests on the formation of a common  $d$  band on alloying, which is justified by band calculations (Pettifor 1987). Evidently there is no essential difference if there are two types of impurities instead of only one, so that in this case

$$\Delta H_{ABC}^s = E_{\sigma(\text{alloy})}(\bar{Z}) - x_A E_{\sigma(A)}(Z_A) - x_B E_{\sigma(B)}(Z_B) - x_C E_{\sigma(C)}(Z_C). \quad (15)$$

### 3. Results

By comparing the enthalpies of formation of the solid solution and the amorphous phase (equations (1) and (2)), an estimate of the glass-forming range of ternary transition metal alloys can be obtained. Contrary to the binary case (see, e.g., Egami and Waseda 1984), systematic experimental information on the glass-forming capacity of ternary transition metal systems is very scarce, so that we are not able to test the model on a wide range of systems. However, the comparison carried out below between the theoretical predictions and the experimental information reported by Nosé *et al* (1981) and Kim *et al* (1988) for a set of ternary Co-based alloys provides, in our opinion, good evidence for the reliability of our treatment.

In table 1 we show the calculated minimum concentration of Zr for glass formation in Co–Zr–M ( $M = \text{Nb, W, Mo, V and Cr}$ ) for several concentrations of M, together with the experimental data obtained for glasses formed by liquid quenching (Nosé *et al* 1981) and sputtering deposition (Kim *et al* 1988). All data are for the Co-rich region. The predicted values agree reasonably with the experimental results, especially with those obtained by liquid quenching. The differences between the two sets of experimental data are due to differences in cooling rates (Nishi *et al* 1981): in the case of glasses produced by rapid quenching from the melt, the cooling rate is within the range  $10^5$ – $10^6 \text{ K s}^{-1}$ ; for alloys formed by sputtering deposition the effective quenching rate is more difficult to assess, and depends upon the details of the experimental conditions. Note that all the five ternary systems considered satisfy the condition discussed above for additivity of the elastic part of the enthalpy,  $V_A < V_C < V_B$  (see, e.g., de Boer *et al* 1988).

In table 1 we also give the calculated minimum solute concentration for glass formation obtained using the relation proposed by Ueno and Waseda (1985)

$$x_B^{\text{min}} = (\lambda_0 - |\Delta V_{AC}/V_A| x_C) / |\Delta V_{AB}/V_A| \quad (16)$$

where  $\lambda_0$  is an overall empirical parameter which depends on the kind of quenching

**Table 1.** Minimum concentrations of Zr for glass formation in Co–Zr–M (M = Nb, W, Mo, V and Cr) ternary alloys, in the Co-rich region. CAL: calculated in this work; UW: predicted from the Ueno–Waseda equation (16); LQ: liquid quenching results; SP: sputtering deposition data. Experimental data (LQ and SP) have been estimated from figures reported by Nosé *et al* (1981) and Kim *et al* (1988).

M	$x_M = 0.025$				$x_M = 0.050$			
	CAL	UW	LQ	SP	CAL	UW	LQ	SP
Nb	0.088	0.100	—	0.044	0.075	0.086	—	0.030
W	0.095	0.104	0.074	—	0.088	0.094	0.057	—
Mo	0.096	0.106	0.075	0.053	0.090	0.098	0.062	0.049
V	0.103	0.109	0.079	0.063	0.106	0.105	0.074	0.060
Cr	0.105	0.112	0.083	—	0.109	0.111	0.070	—

  

M	$x_M = 0.075$				$x_M = 0.100$			
	CAL	UW	LQ	SP	CAL	UW	LQ	SP
Nb	0.060	0.072	—	0.018	0.044	0.059	—	0.010
W	0.081	0.085	0.053	—	0.072	0.075	0.053	—
Mo	0.084	0.090	0.057	0.041	0.078	0.082	0.053	0.034
V	0.108	0.101	0.070	0.057	0.111	0.097	0.062	0.050
Cr	0.113	0.109	0.062	—	0.117	0.108	0.060	—

technique used (Kim *et al* 1988). Equation (16) emphasises the role of atomic size mismatch in determining the glass-forming concentration range, and is a generalisation of the equation proposed by Egami and Waseda (1984) for the binary case. In applying (16) to the systems of table 1 we have used the value  $\lambda_0 = 0.1$  suggested by Ueno and Waseda (1985) for liquid quenched alloys, and the volume mismatch effect has been evaluated from the atomic radii of the elements reported by these authors.

As table 1 shows, the values of the minimum solute concentration for glass formation derived from the Ueno–Waseda equation are close to those obtained with the model used in this paper. The reason is that the two approaches are related as follows. If we neglect the structural contribution in (1), and bear in mind that the chemical contributions in equations (1) and (2) are assumed to be the same, the glass-forming ranges of ternary alloys can be determined from the equation

$$\Delta H_{ABC}^e = x_A \Delta H_A^{a-s} + x_B \Delta H_B^{a-s} + x_C \Delta H_C^{a-s}. \quad (17)$$

The left-hand side of this expression is evaluated from equations (12) and (13). In the dilute region ( $x_A \rightarrow 1$ ), equation (17) becomes

$$x_B \Delta h^e(\text{B in A}) + x_C \Delta h^e(\text{C in A}) = \Delta H_A^{a-s} \quad (18)$$

so that, using equation (11), the minimum concentration of component B for glass formation will be given by

$$x_B^{\min} = \frac{\Delta H_A^{a-s} - [2K_C \mu_A (V_A^* - V_C^*)^2 / (3K_C V_A^* + 4\mu_A V_C^*)] x_C}{2K_B \mu_A (V_A^* - V_B^*)^2 / (3K_B V_A^* + 4\mu_A V_B^*)}. \quad (19)$$

The similarity in form of equations (16) and (19) is evident. Both expressions give the minimum solute concentration for glass formation in ternary alloys in terms of the relative atomic sizes of the components. It should be noted, however, that both these

equations are simple approximate expressions which strictly should be applicable only in the dilute region and when structural contributions can be neglected. The approach described in this paper points to a way of predicting the glass-forming ranges of ternary transition metal alloys under more general conditions.

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