

## PREDICTION OF GLASS FORMATION BY SOLID STATE REACTION IN ALLOYS

L.J. GALLEGO, J.A. SOMOZA, H.M. FERNANDEZ and J.A. ALONSO\*

*Departamento de Física de la Materia Condensada, Facultad de Física,  
Universidad de Santiago, Santiago de Compostela, Spain*

*\*Departamento de Física Teórica, facultad de Ciencias, Universidad de  
Valladolid, Valladolid, Spain*

**Résumé** - On examine les aspects thermodynamiques de l'amorphisation des alliages par réaction en état solide; pour ce faire on utilise une démarche qui conjugue la théorie classique de l'élasticité avec le modèle de Miedema pour la chaleur de formation des alliages. La prédiction de l'intervalle de concentrations dans lequel on peut trouver des phases amorphes demande de construire les diagrammes d'énergie libre correspondants, qui, dans ce travail, sont présentés pour plusieurs alliages intéressants, qui montrent des comportements très différents.

**Abstract** - The thermodynamic aspects of the amorphization of alloys by solid state reaction are examined using a combination of classical elasticity theory and Miedema's model for the heat of formation of alloys. Prediction of the concentration range where amorphous phases can be found requires construction of the pertinent free energy diagrams. These are presented here for several alloys of interest with quite different behaviours.

## 1 - INTRODUCTION

In the past few years, several techniques have been developed to produce amorphous alloys by isothermal solid-state reaction (SSR) /1,2/. Examples are the amorphization of pure polycrystalline thin films by atomic interdiffusion /1-3/ and the mechanical alloying of elemental crystalline powders /4/. In contrast to the traditional methods of rapid quenching (RQ) from the melt or from the vapour phase, SSR is capable of producing bulk amorphous alloys, and thus has greater technological interest.

The basic requirements for successful SSR amorphization have in general been found to be a large negative heat of mixing in the liquid (or amorphous) phase, and fast diffusion of one of the elements into the other. The latter factor is linked to a large atomic size mismatch /5/. These two variables (heat of mixing and atomic volume ratio) have been used as coordinates by Weeber and Bakker /6/ in an attempt to separate glass-forming and non-glass-forming alloys in a two dimensional map. In addition, the amorphization process must occur in a time shorter than the time required for the nucleation and growth of any equilibrium intermetallic compounds whose formation might also be favoured by the SSR technique being used. An appropriate combination of thermodynamic and kinetic factors is thus the requisite for amorphization by SSR, a characteristic which is in fact common to the earlier RQ methods. The main difference between these two kinds of method lies in the fact that the formation of high-melting-point intermetallic compounds is difficult to avoid in RQ processes at the quenching rates currently achieved, which restricts the composition range over which amorphous alloys can be formed, whereas competition from such compounds appears to be less intense in SSR, which accordingly, in general, allows wider glass-forming ranges centred near equiatomic composition.

Although the maps presented by Weeber and Bakker are useful for predicting SSR amorphization, proper interpretation of the experimental results needs a more quantitative model. This paper examines the thermodynamic aspects of amorphization by SSR on the basis of a semi-empirical treatment which combines classical elasticity theory /7/ and Miedema's model for the heat of formation of alloys /8/. We first applied this kind of approach to the formation of

Zr-based amorphous alloys obtained by melt spinning /9/, and a similar scheme has also been employed by Miedema and coworkers /10,11/ (see also ref./4/). The aim of this paper is to show the usefulness of this treatment by comparing the predictions of the theory with available experimental SSR information for some systems of interest covering a wide range of different behaviours. We describe the model itself only briefly below; for more details, the reader is referred to ref./9/ and to the papers of Miedema and coworkers /10,11/.

## 2 - MODEL FOR THE ENTHALPIES OF FORMATION

In order to predict the possible glass-forming concentration range of a binary alloy, the free energies of the various competing phases have to be known to determine their relative stabilities. In general, entropy effects play only a secondary role, and the simple ideal solution model may be taken as a first approximation for both solid and amorphous phases. Enthalpies of mixing, however, have to be considered in detail.

According to Miedema /12/ (see also ref./13/), the enthalpy of mixing  $\Delta H$  of a substitutional solid solution of transition metals can be considered as the sum of three contributions: a chemical contribution,  $\Delta H^c$ , due to electron redistribution when the alloy is formed; an elastic or size-mismatch contribution,  $\Delta H^e$ , arising as a consequence of the elastic stresses generated when solvent atoms are substituted by solute atoms in the host lattice; and a structural contribution,  $\Delta H^s$ , which accounts for possible differences between the two metals as regards valence and crystal structure. For amorphous phases and intermetallic compounds, only the chemical contribution is present /9-11/. We give below the expressions for the different contributions to the enthalpy.

The chemical contribution is given by /14/

$$\Delta H^c = \Delta H^{\text{amp}} x_A V_A^{2/3} f_{AB} \quad (1)$$

where  $\Delta H^{\text{amp}}$  is an amplitude reflecting the magnitude of the chemical interaction,  $x_A$  is the atomic concentration of metal A,  $V_A$  is the atomic volume of A in the alloy, and  $f_{AB}$  is a function which accounts for the degree to which atoms of type A are  $AB$  surrounded by atoms of type B. For statistically disordered alloys  $f_{AB}$  is given by

$$f_{AB} = x_B^s \quad (2)$$

where  $x_B^s$  is the atomic cell surface area concentration of metal B in the alloy. For ordered intermetallic compounds Miedema and coworkers use the empirical relation /14/

$$f_{AB} = x_B^s [ 1 + \gamma (x_A^s x_B^s)^2 ] \quad (3)$$

with  $\gamma = 8$ . In the case of amorphous alloys, Weeber /15/ has suggested using equation (3) with  $\gamma = 5$  in order to take into account the existence of partial chemical short-range order. This value of  $\gamma$  has been used for both solid solutions and amorphous phases in calculating free energy diagrams in this paper.

The elastic contribution to the enthalpy of mixing of the solid solution can be derived from the interpolation equation /10,11/ (see also ref./16/)

$$\Delta H^e = x_A x_B [ x_B \Delta h^e(\text{A in B}) + x_A \Delta h^e(\text{B in A}) ] \quad (4)$$

where  $\Delta h^e(i \text{ in } j)$ , the elastic contribution to the heat of solution of i in j, is given by /12/

$$\Delta h^e(i \text{ in } j) = \frac{2 k_i \mu_j (V_j^* - V_i^*)^2}{3 k_i V_j^* + 4 \mu_j V_i^*} \quad (5)$$

In the later expression  $\mu_j$  is the shear modulus of the host,  $k_i$  is the bulk

modulus of the solute metal, and  $V_i^*$  and  $V_j^*$  represent effective volumes corrected for charge transfer effects. Room temperature values of  $\mu$  and  $k$  for the elements have been given by Gschneidner /17/. Finally, the structural contribution  $\Delta H^s$  can be calculated from the expression

$$\Delta H^s = E(\bar{Z}) - x_A E_A(Z_A) - x_B E_B(Z_B), \quad (6)$$

where  $\bar{Z}$  is the average number of valence electrons per atom, and  $E$ ,  $E_A$  and  $E_B$  are the lattice stabilities of the alloy and the pure components respectively. The dependence of lattice stability on  $Z$  for bcc, hcp and fcc structures has been derived by Niessen and Miedema /12/.

To compare the stabilities of the solid solution and amorphous phase we need to refer the enthalpy of the latter to the pure crystalline metals. Following the recent suggestion by Miedema and coworkers /10,11/, we write for the enthalpy of mixing of the amorphous phase

$$\Delta H(\text{amorphous}) = \Delta H^c + \alpha (x_A T_{m,A} + x_B T_{m,B}), \quad (7)$$

where  $\alpha$  is an empirical parameter equal to 3.5 J/(mol K) and  $T_{m,i}$  is the melting temperature of component  $i$ . In using the temperature-independent expression (7) to calculate the enthalpy of mixing of the amorphous phase at room temperature (see below), we are assuming additivity of the specific heat (Neumann-Kopp rule).

### 3 - FREE ENERGY DIAGRAMS AND AMORPHIZATION

We now concentrate on a set of four binary alloys, Zr-Ni, Ti-V, Zr-V and Hf-Ru, which illustrate well the diversity of the results obtained in SSR experiments. Table 1 lists the heats of mixing of the equi-atomic liquid alloys, as calculated using Miedema's theory (equations (1) and (2) with  $x_A = 0.5$ ), and the ratios of the effective volumes of impurity and host (this ratio is often different from the ratio of the pure metal volumes /18/). A large negative heat of formation favours the mixing of the elemental metals. A large atomic size mismatch also enhances mixing, through fast diffusion of the impurity into the host; additionally, the elastic stresses generated by size

Table 1. Heats of mixing  $\Delta H_M$  of equiatomic liquid alloys, and ratios between effective impurity volume and host atomic volume (from Weeber and Bakker/4,6/)

System A-B	$\Delta H_M$ (kJ/mol)	$V_B/V_A$
Zr-Ni	-49	0.38
Ti-V	-2	0.78
Zr-V	-4	0.56
Hf-Ru	-52	0.50

mismatch destabilize solid solutions, which are the main competitors of amorphous phases. On these grounds, Zr-Ni and Hf-Ru are good candidates for amorphization; Ti-V is not a good candidate; and finally Zr-V, with a significant atomic size mismatch, may be a borderline case. We now discuss the free energy diagrams of these four systems in detail.

Figures 1-4 show the free energy curves calculated for  $T = 300$  K using the model presented in Section 2. The amorphization of Zr-Ni by SSR is well documented /1,2,4/. Fig. 1 shows that the amorphous phase is indeed theoretically more stable than the solid solution phases over a wide range of composition. The free energy curves thus explain the observed ready amorphization of this system. The composition range of the homogeneous amorphous alloy, as estimated by the common tangent construction, is 0.18  $\leq$

$x_{Zr} \leq 0.71$ , which compares well with the experimental range of  $0.17 \leq x_{Zr} \leq 0.73$  reported by Eckert et al. /19/ for mechanical alloying of crystalline elemental Zr and Ni powders. This wide range of amorphization is possible because the formation of equilibrium intermetallic compounds /20/ can be bypassed kinetically, which cannot occur when the alloy is obtained by the melt-spinning technique (see ref./9/).

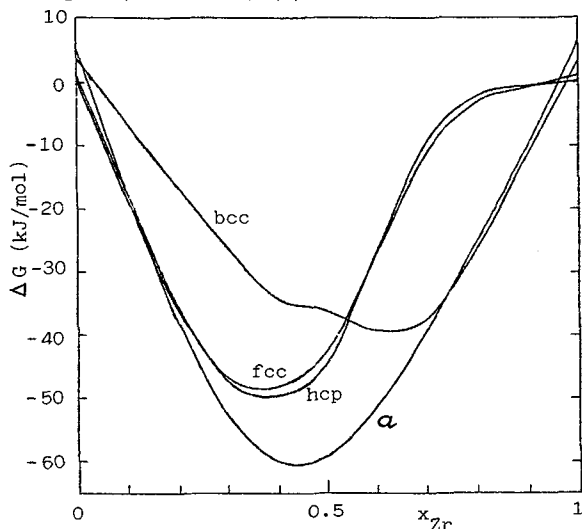


Fig. 1 - Free energy diagram of Zr-Ni at 300 K. *a* stands for the amorphous phase. The other curves correspond to crystalline solid solutions.

Turning now to a very different system, Figure 2 shows the free energy diagram of Ti-V. In this case the amorphous phase is unstable at room temperature, which is consistent with the non-amorphization reported for this alloy /21/. The predicted equilibrium states at room temperature (no intermetallic compounds have been found for this system /22/) are a bcc solid solution until around  $x_{Ti} = 0.2$ , and a two-phase mixture (bcc solid solution plus hcp(Ti)) at other compositions; these predictions agree with the results of extrapolating the reported equilibrium phase diagram /22/ to 300 K.

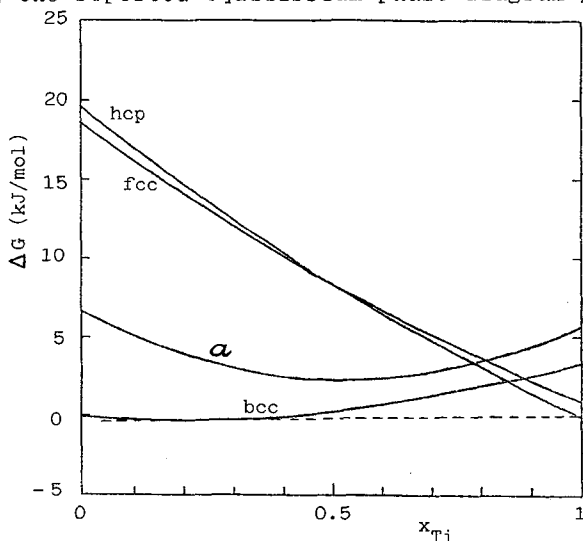


Fig. 2 - Free energy diagram of Ti-V at 300 K. *a* stands for the amorphous phase. The dashed line is the tangent common to the free energy curves of the bcc solid solution and the Ti-rich terminal solution.

Figure 3 shows that, for Zr-V, the free energy of the amorphous phase at intermediate concentrations is close to the dashed line representing the unreacted crystalline elements. This indicates that the relative stability of these two states must be highly sensitive to the working temperature. Zr-V is thus a borderline case in which the possibility of amorphization is expected to depend on fine details of experimental conditions. In agreement with this expectation, Hellstern and Shultz /23/ failed to achieve amorphization of Zr-V (see also ref./19/), while Weeber and Bakker /6/ have obtained amorphous alloys by mechanical alloying at certain compositions.

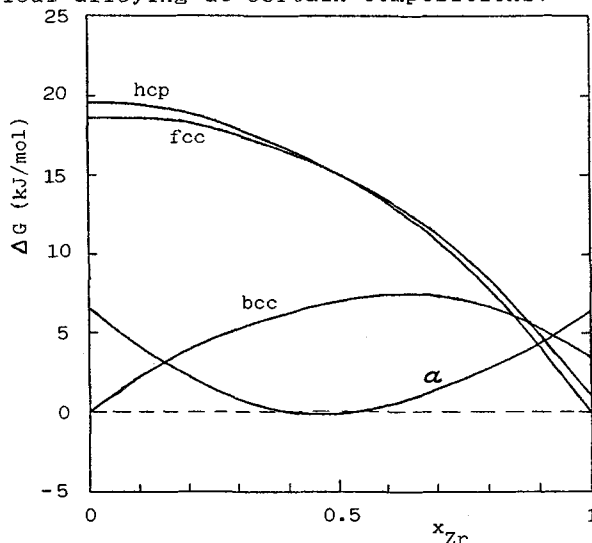


Fig. 3 - Free energy diagram of Zr-V at 300 K.  $\alpha$  stands for the amorphous phase. The dashed line represents the unreacted crystalline elements.

Finally, the diagram for the Hf-Ru system is shown in Figure 4. The amorphous phase is more stable than the solid solution phases over a wide

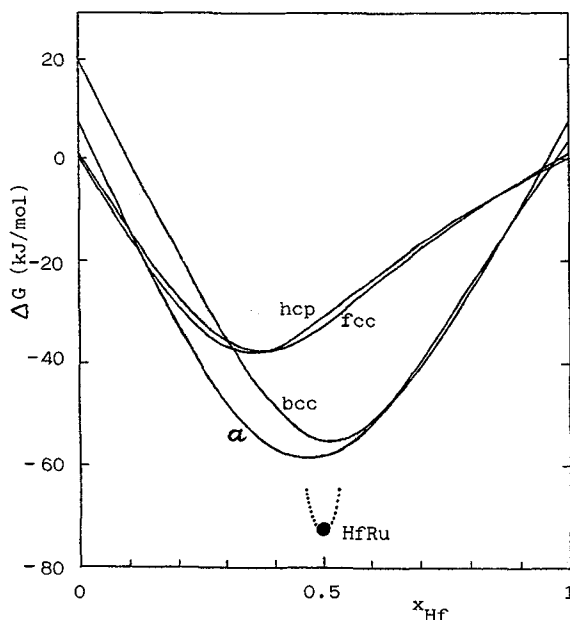


Fig. 4 - Free energy diagram of Hf-Ru at 300 K.  $\alpha$  stands for the amorphous phase. The dotted line for the HfRu compound is schematic.

range of composition, which leads one to expect SSR amorphization. Thompson et al. /24/, however, failed to achieve amorphization at the specific composition  $x_{\text{Hf}} = 0.5$ . As Thompson et al. themselves suggest, this failure must be blamed<sup>Hf</sup> on the formation of the equilibrium intermetallic compound HfRu, which has a simple cubic CsCl structure and a relatively broad homogeneity range. The free energy of this compound, as calculated using Miedema's theory, is represented in Figure 4 by a solid circle and a schematic curve indicating that its free energy changes relatively rapidly around the equiatomic composition, though less rapidly than for the usual line compounds. The broad homogeneity range is, in our view, the main reason why this compound becomes a competitive phase in SSR. This contrasts, for instance, with the situation in Zr-Ni, whose several equilibrium intermetallic compounds have such narrow homogeneity ranges that they can be easily bypassed in SSR.

To sum up, the semiempirical treatment used in this paper, which combines classical elasticity theory and Miedema's model of heats of formation of alloys, provides a useful means of describing the thermodynamic aspects of amorphization by SSR, and is thus to be borne in mind as an alternative to other thermodynamic models of glass formation (see e.g./11/ and refs. therein) such as the CALPHAD approach developed by Saunders and Miodownik /25/ and Bormann et al. /26/. Although no attempt at extensive comparison between the predictions of these two models is made here, we note that they are often similar. As an example, the predicted glass forming range for Zr-Ni using the CALPHAD approach is  $0.17 \leq x_{\text{Zr}} \leq 0.77$  /26/, which is very close to that obtained in this paper. The advantage of the treatment developed here is its ease of application, which derives from its explicit use of the factors that have been recognized empirically as being most closely correlated with glass forming ability: valence, electronegativity, crystalline structure and atomic size mismatch.

**Acknowledgements** This paper has been supported by DGICYT of Spain (Grant PB86-0654-CO2), Junta de Castilla y León and Universidad de Valladolid (Consejo Social).

#### REFERENCES

- /1/ Johnson, W.L., Prog. Mat. Sci. 30 (1986) 81.
- /2/ Samwer, K., Phys. Rep. 161 (1988) 1.
- /3/ Schwarz, R.B. and Johnson, W.L., Phys. Rev. Lett. 51 (1983) 415.
- /4/ Weeber, A.W., and H. Bakker, Physica 153B (1988) 93.
- /5/ Bakker, H., J. Less-Common Met. 105 (1985) 129.
- /6/ Weeber, A.W. and Bakker, H., Z. Phys. Chem. 157 (1988) 221.
- /7/ Eshelby, J.D., Solid State Phys. 3 (1956) 79.
- /8/ de Boer, F.R., Boom, R., Mattens, W.C.M., Miedema, A.R. and Niessen, A.K., Cohesion in Metals, North-Holland, Amsterdam 1988.
- /9/ López, J.M., Alonso, J.A. and Gallego, L.J., Phys. Rev. B36 (1987) 3716.
- /10/ Loeff, P.I., Weeber, A.W. and Miedema, A.R., J. Less-Common Met. 140 (1988) 299.
- /11/ Van der Kolk, G.J., Miedema, A.R. and Niessen, A.K., J. Less-Common Met. 145 (1988) 1.
- /12/ Niessen, A.K. and Miedema, A.R., Ber. Bunsenges. Phys. Chem. 87 (1983) 717.
- /13/ López, J.M. and Alonso, J.A., Z. Naturforsch. 40A (1985) 1199.
- /14/ Niessen, A.K., de Boer, F.R., Boom, R., de Châtel, P.F., Mattens, W.C.M. and Miedema, A.R., CALPHAD 7 (1983) 51.
- /15/ Weeber, A.W., J. Phys. F 17 (1987) 809.
- /16/ López, J.M. and Alonso, J.A., Phys. Stat. Solidi A 85 (1984) 423.
- /17/ Gschneidner, K.A., Jr., Solid State Phys. 16 (1964) 275.
- /18/ Miedema, A.R. and Niessen, A.K., Physica 114B (1982) 367.
- /19/ Eckert, J., Schultz, L. and Urban, K., J. Less-Common Met. 145 (1988) 283.
- /20/ Elliot, R.P., Constitution of Binary Alloys, First Supplement, Genium, Schenectady, New York 1986.
- /21/ Hellstern, E. and Schultz, L., Mat. Sci. Eng. 93 (1987) 213.

- /22/ Hansen, M. and Anderko, K., Constitution of Binary Alloys, 2nd edn.,  
Genium, Schenectady, New York 1986.
- /23/ Hellstern, E. and Schultz, L., Phil. Mag. 56B (1987) 443.
- /24/ Thompson, J.R., Politis, C. and Kim, Y.C., Mat. Sci. Eng. 97 (1988) 31.
- /25/ Saunders, N. and Miodownik, A.P., J. Mat. Res. 1 (1986) 38.
- /26/ Bormann, R., Gärtner, F. and Zöltzer, K., J. Less-Common Met. 145 (1988)  
19.