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Extreme glass forming range for amorphization by mechanical alloying

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Abstract

On the basis of metastable equilibrium between a binary amorphous phase and a crystalline phase of pure component, we deduced an analytic expression for the extreme glass forming range (extreme GFR) in mechanical alloying TM–TM systems. It is proposed that the extreme GFR can be predicted according to the thermodynamic parameter, *i.e.* the ratio of the enthalpy of solution at infinite dilution to the melting enthalpy of the components of a given system.

1. Introduction

An important part of thermodynamic analysis of amorphization by mechanical alloying (MA) is the prediction of the possibility and the glass forming range (GFR). There have been different models proposed to predict the GFR of TM–TM system. One of these uses the Miedema model to plot an enthalpy diagram and then uses the double-tangent rule to evaluate the GFR [1]. In principle, however, the GFR should be determined in terms of the metastable phase diagram which can be derived from the calculation of free energy of amorphous and crystalline phases which are in metastable equilibrium or competition with each other [2].

Calculation of the free energy involves the mixture enthalpy and entropy as well as the vibration enthalpy and entropy of the system. The competition phases may include amorphous phases, crystalline intermetallic compounds, solid solutions and pure crystalline components. Another problem in determining the free energy of the amorphous phase is whether to take the chemical short-range order into account or not. Owing to the shortage of some thermodynamic data, calculation of the free energy will be limited to the mixture enthalpy and entropy; furthermore, the metastable equilibrium can only be determined between the binary amorphous phase and the crystalline phase of the pure component.

The mixture enthalpy of the amorphous phase can be calculated on the basis of (1) statistical disorder, and (2) considering chemical short-range order in the system.

In spite of the simplification, it is practical to investigate the metastable equilibrium between the binary amorphous phase and the crystalline phases

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of pure components because the amorphous solubility limits obtained from this represent an extreme concentration range or extreme GFR. In addition, it is by means of the above idea that an analytical solution of the problem can be obtained, and a general discussion of the GFR of TM–TM systems can be given in this manner.

2. Equation of amorphous solubility limits

According to the prerequisites mentioned above, the amorphous solubility limit of B for an A–B binary system must comply with the equation as follows:

$$\frac{dG^a}{dx_B} = \frac{G^c_B - G^a}{1 - x_B} \tag{1}$$

where G^c_B, G^a are the free energies of the crystalline phase of pure B component and of the binary amorphous phase respectively. The free energy of the amorphous phase G^a is defined as

$$G^a = \Sigma G^a_i x_i + \Delta H^a_f - T\Delta S^a_f \tag{2}$$

where $\Sigma G^a_i x_i$ is the linear combination of free energies of the amorphous phases of the pure components; ΔH^a_f, ΔS^a_j are the formation enthalpy and entropy of the amorphous phase respectively.

In the binary system the following relation holds

$$\Sigma G^a_i x_i = G^a_A x_A + G^a_B x_B \tag{3}$$

calculating ΔS^a_f assuming an ideal mixture, we can obtain

$$\Delta S^a_f = -R(x_A \ln x_A + x_B \ln x_B) \tag{4}$$

On the basis of the statistical-disorder model (project 1), the formation enthalpy of the amorphous phase is calculated as [3]

$$\Delta H^a_f = x_A x_B (x_A \Delta\overline{H^0_{B(in\ A)}} + x_B \Delta\overline{H^0_{A(in\ B)}}) \tag{5}$$

where $\Delta\overline{H^0_{A(in\ B)}}$, $\Phi\overline{H^0_{B(in\ A)}}$ are the enthalpies of solution at infinite dilution for liquid metal, their values can be found in ref. 4.

If there is chemical short-range order in the amorphous phase (project 2), we have [5]

$$\Delta H^a_f = x_A x_B (f^B_A \overline{\Delta H^0_{B(in\ A)}} + f^A_B \overline{\Delta H^0_{A(in\ B)}}) \tag{6}$$

where

$$f^B_A = c_A[1 + 5(c_A c_B)^2] \tag{7}$$

$$f^A_B = c_B[1 + 5(c_A c_B)^2] \tag{8}$$

The physical meaning of $f^B_A(f^A_B)$ is the probability with which an atom of A(B) is found to be a nearest neighbor around an atom of B(A) in the amorphous phase; c_A, c_B are the surface concentrations defined in accordance with Miedema's semiempirical model [4]:

$$c_A = \frac{V_A^{2/3} x_A}{V_A^{2/3} x_A + V_B^{2/3} x_B} \tag{9}$$

$$c_B = \frac{V_B^{2/3} x_B}{V_A^{2/3} x_A + V_B^{2/3} x_B} \tag{10}$$

where parameters $V_A^{2/3}$, $V_B^{2/3}$ are equal to the surface areas in a Wigner–Seitz cell of components A and B respectively; they are also obtained from ref. 4:

For convenience, we use the notation

$$\Delta H_A \equiv \Delta\overline{H^0_{A(\text{in } B)}}, \quad \Delta H_B \equiv \Delta\overline{H^0_{B(\text{in } A)}}$$

then formulae (5) and (6) can be simply written as

$$\Delta H_f^a = x_A x_B (x_A \Delta H_B + x_B \Delta H_A) \tag{11}$$

$$\Delta H_f^a = x_A x_B (f_A^B \Delta H_B + f_B^A \Delta H_A) \tag{12}$$

The free energy of amorphous phases of the pure components can be expressed as

$$G_A^a = G_A^c + \Delta G_A^{c\to a}$$

$$G_B^a = G_B^c + \Delta G_B^{c\to a} \tag{13}$$

where $\Delta G_A^{c\to a}$, $\Delta G_B^{c\to a}$ are the changes in free energy from the crystalline to the amorphous phase of the pure components.

Substituting the above formula into eqn. (1), the amorphous solubility limit for the B side of the A–B binary system can be found:

$$\Delta H - \Delta G_B^{c\to a} = RT \ln x_B \tag{14}$$

$$\Delta H = \begin{cases} \Delta H_1 = x_A^2[-2x_A \Delta H_A + (2x_B - 1)\Delta H_B] & (15) \\ \Delta H_2 = x_A^2\left(-\left\{ f_B^A + x_B[1 + 5c_B^2 c_A(3 - 5c_B)] \dfrac{dc_B}{dx_B} \right\} \Delta H_A \right. & \\ \qquad \left. + \left\{ x_B[1 - 5c_B c_A^2(2 - 5c_B)] \dfrac{dc_B}{dx_B} - f_A^B \right\} \Delta H_B \right) & (16) \end{cases}$$

where ΔH_1, ΔH_2 are the formation enthalpies of the amorphous phase calculated by projects 1 and 2 respectively. In addition, dc_B/dx_B can be deduced from eqn. (10) as follows:

$$\frac{dc_B}{dx_B} = \frac{V_A V_B}{(V_A x_A + V_B x_B)^2} \tag{17}$$

To solve eqns. (14)–(16), the value of $\Delta G_B^{c\to a}$ must be first determined, usually according to linear and singh-Holtz approximation [6]. The formula is deduced from eqn. (5) in ref. 16 under the condition $T<0.5T_B^f$.

$$\Delta G_B^{c\to a}=\Delta H_B^f - T\Delta S_B^f \tag{18}$$

$$\Delta G_B^{c\to a}=0.9375\Delta H_B^f - T\Delta S_B^f \tag{19}$$

where ΔH_B^f, ΔS_B^f are the melting enthalpy and entropy respectively. The above two formulae can be rewritten as follows:

$$\Delta G_B^{c\to a}=\eta\Delta H_B^f - T\Delta S_B^f \tag{20}$$

where η is a coefficient equal to unity or smaller.

Substituting eqn. (20) into eqn. (14) and finding T, we have the amorphous solubility limit expression for the B side of the A–B binary system.

$$T_B=\frac{\Delta H-\eta\Delta H_B^f}{R\ln x_B-\Delta S_B^f} \tag{21}$$

replacing the subscript B with A, the expression for the A side can also be given.

3. Calculations

The amorphous solubility limits of the Fe–Zr and Ni–Zr systems were computed on the basis of project 1. The results are shown in Figs. 1 and 2.

Figures 3 and 4 show the results for seven systems, calculated according to projects 1 and 2 when $\eta=0.5$.

4. Discussion

(1) In Table 1, we compare the results given in Figs. 3 and 4 with the experiment data in refs. 1 and 7. It is seen from Table 1 that the calculation

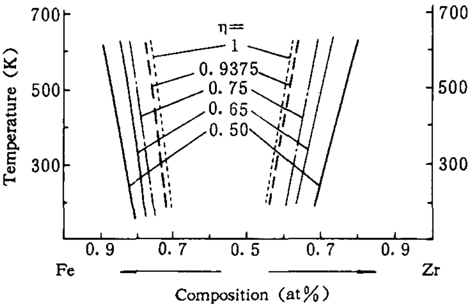

Fig. 1. The amorphous solubility limits of the Fe–Zr system according to project 1.

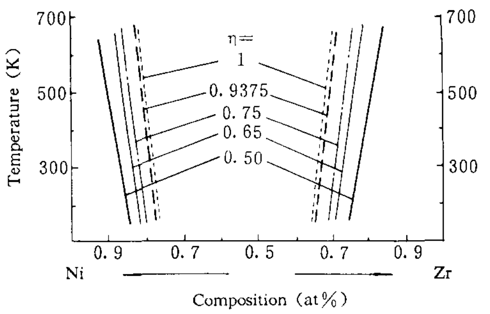

Fig. 2. The amorphous solubility limits of the Ni–Zr system according to project 1.

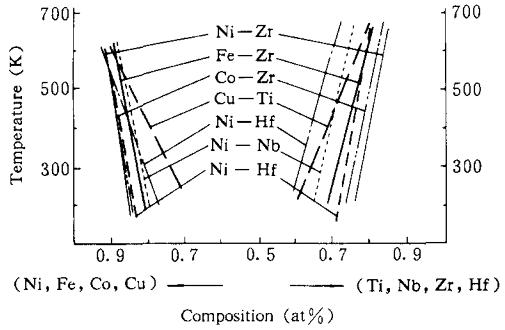

Fig. 3. The amorphous solubility limits of seven systems according to project 1.

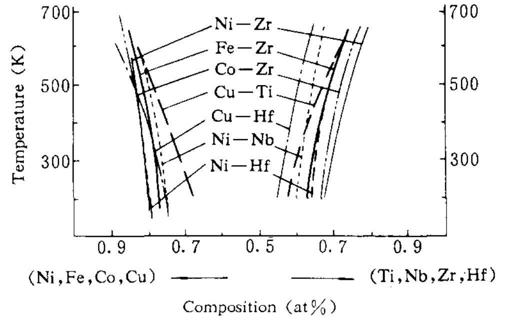

Fig. 4. The amorphous solubility limits of seven systems according to project 2 when $\eta = 0.5$.

is in agreement with experimental data at temperatures of 400–500 K. Project 2 seems better than project 1.

(2) The extreme GFR is extended with the rise in temperature investigated; this conforms to the explanation for solid state amorphization by means of a metastable phase diagram [2].

(3) It can be seen from eqn. (21) that the extreme GFR depends only on the enthalpy of solution at infinite dilution and the melting enthalpy of both components as well as the temperature, but is independent of the enthalpy of the crystalline phase of the pure component itself.

TABLE 1

Comparison of calculations with experimental data

Systems	Experiment data	Temperature (K)							
		Project A1				Project A2			
		300	400	500	600	300	400	500	600
Ni	80	87	88	90	92	81	82	83	85
Zr	80	78	80	81	83	70	72	75	78
Co	91	86	88	89	91	81	82	84	86
Zr	80	76	78	80	82	68	70	73	76
Fe	78	83	85	87	92	78	80	82	84
Zr	70	71	74	76	79	64	66	69	72
Ni	80	82	84	86	89	76	78	80	83
Nb	80	67	69	71	74	62	63	65	67
Ni	65	86	87	89	91	81	82	83	84
Hf	85	74	75	77	79	65	67	69	71
Cu	87	74	80	85	90	71	75	79	83
Ti	90	64	68	73	77	60	63	67	72
Cu	> 70	81	85	89	93	78	80	84	89
Hf	70	61	64	67	70	57	59	61	64

(4) Since the results obtained using the project 1 conform roughly with the experimental data, we will discuss factors or rules which affect the extreme GFR in the following way.

Now that we have found that the amorphous range extends with the rise in temperature, we can discuss the relation of the amorphous solubility limit with the thermodynamic parameters in terms of eqn. (21) at $T=0$ K.

$$x_A^2[-2x_B\Delta H_A+(2x_B-1)\Delta H_B]-\eta\Delta H_B^f=0 \qquad (22)$$

Transforming the equation we obtain

$$\frac{1}{(1-x_B)^2}=\frac{2(\Delta H_B-\Delta H_A)}{\eta\Delta H_B^f}x_B-\frac{\Delta H_B}{\eta\Delta H_B^f}$$

Using the following notation

$$a=-\frac{\Delta H_B}{\eta\Delta H_B^f},\ b=\frac{2(\Delta H_B-\Delta H_A)}{\eta\Delta H_B^f}$$

We have

$$\frac{1}{(1-x_B)^2}=a+bx_B \qquad (23)$$

According to the above relation, the amorphous solability limit is the intersection of the curve $1/(1-x_B)^2$ and the line $a+bx_B$, shown in Fig. 5. The following conclusions can be obtained from the above.

(i) The more negative the dissolution enthalpy of component B in A (ΔH_B) and the smaller the melting enthalpy of component $B(\Delta H_B^f)$, the larger the amorphous solubility limit of the B side in the A–B binary system.

(ii) The larger the difference in melting enthalpies of the two components, the larger the deviation of the amorphous region from the concentration $x_B=0.5$.

For the above we propose the following parameter

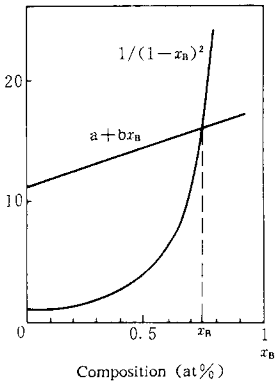

Fig. 5. Illustration of the amorphous solubility limit.

$$\xi = \frac{1}{2}\left(\frac{|\Delta H_A|}{\Delta H_A^f} + \frac{|\Delta H_B|}{\Delta H_B^f}\right) \tag{24}$$

to be used as the thermodynamic parameter with which the extreme GFR can be prejudged approximately. The larger the parameter ξ, the wider the extreme GFR. Speaking in a physical sense, the parameter ξ represents the comparative thermodynamic stability of an amorphous phase with its corresponding crystalline phase to a certain extent.

5. Conclusion

The extreme GFR formed by MA is only determined by the enthalpy of solution at infinite dilution and the melting enthalpy of both components as well as the temperature investigated. The accordance of the calculated results with the documented experimental data in the literature is satisfactory.

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