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LETTER TO THE EDITOR

The quantification of criteria for predicting glass formation of binary transition metals by mechanical alloying

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Abstract. A two-dimensional scheme is constructed in order to predict the possibility of amorphization of binary transition-metal systems by mechanical alloying. The two coordinates of the scheme are the size factor $(R_A - R_B)/R_A$, and the enthalpy of formation of the amorphous phase ΔH_f^a , which is calculated from the Miedema model. In this scheme amorphous and non-amorphous regions can be separated by the empirical line $\Delta R/R = 0.068 \Delta H_f^a + 0.716$. The investigation is an advance in the quantitative prediction of glass-forming ability using a mechanical alloying technique.

Mechanical alloying (MA) is a technique widely used for the formation of metastable alloys that are difficult to produce by conventional methods, and it is particularly attractive because it can be used to process bulk quantities of powdered material and appears to be applicable to many combinations of elements [1–3]. Recently, a large number of amorphous metal–metal and metal–metalloid alloys have been investigated. However a primary problem in the case of amorphous alloys is knowing which alloys can be formed. Therefore, the regularity of the formation of amorphous alloys by MA is of considerable interest because it can be used to explain the experimental data and to guide the investigation of new amorphous systems.

Some previous analyses [4,5] of the reaction process during MA reveal that glass formation of elemental powders occurs via an interdiffusion reaction similar to the solid-state amorphization reaction (SSAR) of layered compositions [6,7]. The criteria for the realization of amorphization by MA based on the mechanism of SSAR are a negative heat of formation, which provides the thermodynamic driving force that favours interdiffusion, and a system that exhibits fast diffusion in crystals resulting in characteristic reaction times for nucleation and growth of the amorphous phase that are shorter than those of the crystalline phase.

Weeber *et al* [2,8] introduced the above rule for TM_1 – TM_2 ($TM_1 = \text{Ti, Zr, Hf etc}$; $TM_2 = \text{Cu, Ni, Fe, Co etc}$) systems, and summarized the general criteria of SSAR by MA as:

- (i) the system must have a negative heat of mixing;
- (ii) the metal–host-atom volume ratio must be below a critical value, which depends on the host [2].

The first criterion can be investigated according to the Miedema model [9] and the second is based on the consideration that the larger the volume ratio, the slower the diffusion [10]. This rule is an advance in the prediction of glass-forming ability (GFA). The above work, however, is limited to selected TM_1 – TM_2 systems, and has not been quantitative;

for example, other than the criterion values of metal–host-atom volume ratio for Ti–TM₂ and Zr–TM₂, determined as 0.70 and 0.58 respectively [2], no other certain values have been determined for any other combinations. There are also reports that some systems with positive enthalpy can amorphize and some with negative enthalpy cannot. Hence this cannot be used as a general rule for predicting the GFA by MA. Obviously, further investigation into the regularity of GFA for TM–TM systems by MA is necessary and a more general rule would be welcomed.

We can construct a two-dimensional scheme based on the thermodynamic and kinetic criteria of SSAR and Weeber's view for TM₂–TM₁. The two thermochemical coordinates used to construct the glass formation diagram are the size factor and the heat of formation of the amorphous phase with short-range chemical order ΔH_f^a , at the equiatomic composition. ΔH_f^a was calculated using the Miedema–Weeber model [9, 11, 12]:

$$\Delta H_f^a(x_A, x_B) = x_A \Delta H_f^a \Delta V_A^{2/3} f_B^A \Delta H^{\text{amplitude}} \quad (1)$$

where x_A and x_B are the atomic concentrations; f_B^A is an empirical function of the cell surface area concentration C_A^S such that

$$f_B^A = (1 - C_A)(1 - 5[C_A^S(1 - C_A^S)]) \quad (2)$$

$$C_A^S = x_A V_A^{2/3} / \{x_A V_A^{2/3} + (1 - x_A) V_B^{2/3}\} \quad (3)$$

where V_A and V_B are atomic volumes. $\Delta H^{\text{amplitude}}$ can be written in terms of the electronegativities (ϕ) and electron densities (n) at the surface of atomic cells:

$$\Delta H^{\text{amplitude}} = 2\{-P(\Delta\phi)^2 + Q(\Delta n_{ws}^{1/3})^2 - R\} / \{(n_{ws}^A)^{1/2} + (n_{ws}^B)^{1/3}\} \quad (4)$$

where the electronegativities, electron densities, atomic volumes and constants P , Q and R are taken from [9] and [11]. The size factor is taken as half of the interatomic separation of the elements, R , in the crystal structure at room temperature because the amorphization by MA is usually realized near room temperature. Thus, we have

$$x = \Delta H_f^a \quad y = |(R_A - R_B)/R_B| \quad (5)$$

where R_A , R_B are the atomic radii of elements A and B, respectively, which are taken from the literature [13].

Figure 1 is a plot of the thermochemical coordinates of known systems of binary transition metals treated by MA. The empirical straight line drawn in figure 1 is

$$y = 0.068x + 0.716 \quad (6)$$

separating amorphized and non-amorphized regions.

Of 37 amorphous alloys, 4 systems are located in the non-glass-forming (non-GF) region, and of the 14 non-GF alloys 4 systems are located in the glass-forming region. The accuracy of prediction of non-GF alloys is only 71.4%, but for GF alloys it is 89.2%. Therefore the thermochemical coordinate criteria are very successful in predicting glass formation by MA (average accuracy 84.3%); also the criteria are more effective for predicting amorphization than no amorphization.

Figure 1 shows that for $\Delta H_f^a \geq 0$, amorphization is not usually realized or it is very difficult to achieve: for instance, Cu–V and Cu–Cr require milling times of about 150 and

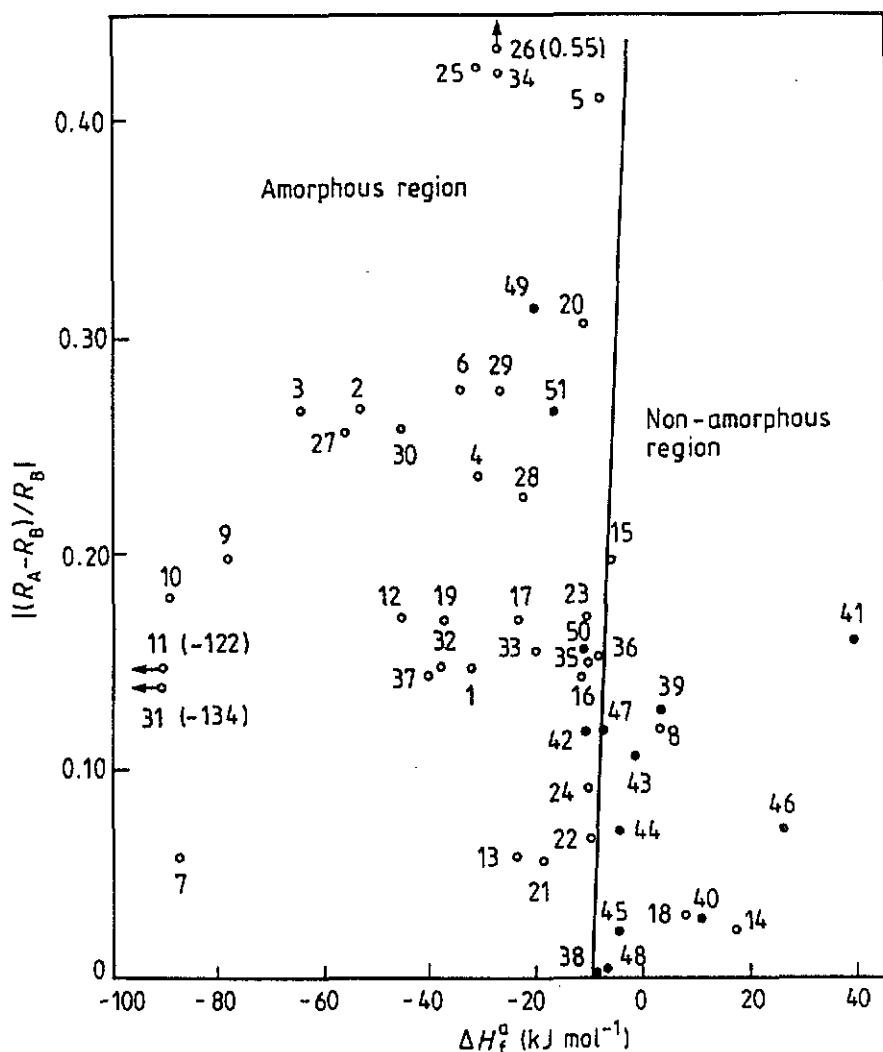


Figure 1. Description of thermochemical coordinates for the amorphous systems by mechanical alloying. ○, Formed amorphous alloys: 1, CoNb [14]; 2, CoZr [15]; 3, NiZr [15]; 4, CuZr [15]; 5, MnZr [15]; 6, FeZr [15]; 7, PdTi [2]; 8, CuTa [16]; 9, RuZr [17]; 10, RhZr [17]; 11, PdZr [18]; 12, NiTi [19]; 13, NiV [20]; 14, CuCr [21]; 15, VZr [18]; 16, CuTi [23]; 17, FeTi [23]; 18, CuV [24]; 19, CoTi [23]; 20, MnTi [23]; 21, CoV [25]; 22, FeV [26]; 23, CrTi [23]; 24, NiMo [27]; 25, CoY [28]; 26, CuEu [17]; 27, NiHf [3]; 28, CuHf [3]; 29, FeHf [17]; 30, CoHf [17]; 31, PtZr [29]; 32, NiTa [30]; 33, FeTa [31]; 34, CoGd [32]; 35, NbCr [33]; 36, TaZr [33]; 37, NiNb [1]. ●, Non-formed amorphous systems: 1, NiCr [35]; 2, CuAg [34]; 3, CuRu [36]; 4, FeAg [37]; 5, NiMn [35]; 6, VTi [19]; 7, TiMo [38]; 8, CuNi [9]; 9, CuW [40]; 10, CoMn [25]; 11, CoCr [25]; 12, FeNb [41]; 13, WZr [42]; 14, CrZr [2].

200 h with ΔH_f^0 values of 7 and 17 kJ mol⁻¹ [21, 24]. The region $0 \leq \Delta H_f^0 \leq -16$ kJ mol⁻¹ is a borderline region, however. The first thermodynamic criterion of amorphization, based on a large negative enthalpy of formation, is not quantitative; however from our figure 1, the enthalpy of formation of the amorphous phase is estimated to be about -16 kJ mol⁻¹. If

we consider only the thermodynamic condition of SSAR by MA, out of 37 systems forming amorphous phases, 34 possess negative enthalpy and only three systems are exceptions. However, of 14 non-amorphous systems, only 6 have positive enthalpies of formation. Thus the accuracy of predicting the GFA by MA is only about 76.5%.

On the other hand, systems with atomic volume differences greater than 10% account for 30 out of 37 glass-forming systems, whereas of 14 non-amorphous systems, only 6 have a difference less than 10%. Therefore the accuracy of predicting glass formation using the criterion that the size factor must be larger than 10% from melt spinning [44] is only about 70.6%. This means that the size factor is less important than in the case of alloys quenched from the melt. However, its effect is not negligible; this is demonstrated by the fact that the empirical straight line of figure 1 is not perpendicular to the ΔH_f^a axis. Furthermore, taking the size factor into account, the accuracy of predicting the glass formation using the $\Delta H_f^a - \Delta R/R$ criteria increases from 76.5% for the ΔH_f^a criterion to 84.3%.

According to the amorphization mechanism of MA, the interdiffusion reaction can occur because of the difference between the free energy of the pure element and that of its amorphous phase. The difference in Gibbs free energy for solid-state amorphization can be presented as

$$\Delta G = G_0 - G_a = G_0 - \left(\sum_i x_i G_i^a + \Delta H_f^a - T \Delta S_f^a \right) \quad (7)$$

where G_0 [45] is the free energy of the initial crystalline state which can be achieved by the formation of layered microstructures during the early stages of milling; $\sum_i x_i G_i^a$ is a linear combination of amorphous free energies of pure elements; and ΔH_f^a is the enthalpy of formation of the amorphous phase.

From (7), it is easy to understand why a system with large negative enthalpy of formation can amorphize easily. Indeed in most cases, amorphous phases form in systems with negative enthalpy; in the cases of slightly negative, or even slightly positive enthalpies of formation, amorphization is still possible if the free energy of the initial crystalline state, G_0 , can be raised to a level at which it offsets the excess free energy of the amorphous phase G_a . However, the development of energy storage during milling is related to the atomic characteristics of constituent elements, crystalline structure [43], milling equipment and local conditions during milling. If the system is convenient for energy storage during milling, amorphization is still possible, although the enthalpy of formation is near zero. Amorphization may, however, require a much longer milling time. For example, the milling times for the Cu-V and Cu-Cr systems are 150 and 200 h, respectively [21, 24]. In the case of amorphization of liquid quenching (LQ), the size factor is large, the difference between the two atomic sizes is large, the two dissimilar atoms in the liquid are combined more tightly together and the atomic group is more stable. Therefore, it is more difficult for the atoms in the liquid to move any distance or to rearrange cooperatively. Crystallization in LQ of alloys is impeded and thereby leads to easy formation of amorphous alloys. In addition, the size factor plays an important part in the kinetic conditions of SSAR. As discussed previously, in many cases the atomic diffusion coefficient is inversely proportional to the ratio V_{imp}/V [10]. Obviously, with the increase in $\Delta R/R$, the diffusion coefficient will increase. This is favourable for the fast diffusion of the solute atom, which gives a characteristic reaction time for nucleation and growth of the amorphous phase shorter than that of the crystalline phase. Hence, the increase in $\Delta R/R$ leads to the glass formation being easy.

With the help of the $\Delta H_f^a - \Delta R/R$ map, the likelihood of amorphization of all binary TM-TM alloy systems by MA can now be predicted quantitatively. Figure 1 can be used

to predict whether unstudied alloy systems can be amorphized. For instance, the Ni-Pr and Ti-La systems with ΔH_f^a values of -35.1 and 25.3 kJ mol $^{-1}$ have values of $\Delta R/R$ equal to 0.3132 and 0.0685 respectively. Thus, the former is placed in the amorphous region, but the latter is placed in the non-amorphous region of figure 1. Further investigations into these systems should be very significant and interesting.

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