Journal of Alloys and Compounds, 189 (1992) 113–116
JALCOM 377

Calculation of formation enthalpies of both the amorphous phase and the solid solution of a transition metal and a non-transition element

H. Yang and H. Bakker
van der Waals–Zeeman Laboratorium, University of Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam (Netherlands)

(Received April 30, 1992)

Abstract

Based on Miedema's model, the formation enthalpies of both amorphous alloys and solid solutions composed of a transition metal and a non-transition element have been calculated as a function of composition. The results were drawn in an atlas. The outcomes for a number of alloy systems were used to predict phase transitions due to ball milling. These predictions are compared with experimental data.

1. Introduction

By Miedema's semiempirical model [1], various enthalpy effects in alloys and intermetallic compounds can be estimated. Some years ago the model was used to estimate the formation enthalpies of both amorphous alloys and random solid solutions of two transition metals [2]. Enthalpy diagrams were drawn for the whole composition range and the diagrams for many alloys were collected in an atlas [3].

In the present paper we extend the calculations to alloys consisting of a transition metal and a non-transition element. The results will be used to discuss phase transformations in intermetallic compounds under ball milling.

2. Details of the calculation

In order to obtain formation enthalpies, it was assumed in ref. 2 that for the solid solution there are three contributions to the total enthalpy:

$$\Delta H_{ss} = \Delta H_{chem} + \Delta H_{el}^{ss} + \Delta H_{struct} \tag{1}$$

The first contribution is of chemical nature: when element A is solved in an excess of element B, there will be an enthalpy effect by bringing element A into contact with element B. This enthalpy effect is denoted by $\Delta H_{A\text{ in }B}^{sol}$. According to ref. 2, the chemical contribution to the total enthalpy, as a function of composition, is given by

$$\Delta H_{chem} = c_A c_B (c_B^s \Delta H_{A\text{ in }B}^{sol} + c_A^s \Delta H_{B\text{ in }A}^{sol}) \tag{2}$$

where c_A is the atomic fraction of element A and c_B is the atomic fraction of element B. c_B^s is the degree to which A atoms are in contact with B atoms and c_A^s is the degree to which B atoms are in contact with A atoms in the random alloy, which can be expressed as

$$c_B^s = 1 - c_A^s = \frac{c_B V_B^{2/3}}{c_A V_A^{2/3} + c_B V_B^{2/3}} \tag{3}$$

Values for the enthalpies of solution ΔH^{sol} are tabulated in ref. 1.

The second contribution is the result of an elastic mismatch in the solid solution:

$$\Delta H_{el}^{ss} = c_A c_B (c_A E_{B\text{ in }A} + c_B E_{A\text{ in }B}) \tag{4}$$

The elastic mismatch energies $E_{A\text{ in }B}$ and $E_{B\text{ in }A}$ are calculated following Eshelby's [3] elastic continuum approach. So the elastic mismatch energy for a dilute solution of A atoms in a B matrix is

$$E_{A\text{ in }B} = \frac{2K_A \mu_B (W_B - W_A)^2}{3K_A W_B + 4\mu_B W_A} \tag{5}$$

where K_A is the bulk modulus of element A and μ_B is the shear modulus of element B. When a binary alloy is formed, the atomic volume is usually different from the volumes of the pure elements. W_A and W_B are the corrected volumes of A and B atoms respectively, following ref. 2.

For a random solid solution of two transition elements, apart from the chemical term and the elastic mismatch enthalpy, a third contribution is introduced, reflecting the preference for a solid solution to crystallize in one of the main crystal structures. However, the structural

0925-8388/92/$5.00

contribution has to do with alloying two transition metals and is absent in alloying a transition metal with a non-transition element. So, in the present case,

$$\Delta H_{ss} = \Delta H_{chem} + \Delta H_{el}^{ss} \qquad (6)$$

In the amorphous alloy, the atoms arrange themselves in such a way that elastic mismatch is avoided but, in addition to a chemical term identical with eqn. (2), there is a topological term due to the amorphous character. The total formation enthalpy for an amorphous alloy is estimated as [2]

$$\Delta H_a = \Delta H_{chem} + 3.5(c_A T_{m,\,A} + c_B T_{m,\,B}) \qquad (7)$$

where $T_{m,\,A}$ and $T_{m,\,B}$ are the melting temperature of elements A and B respectively.

Enthalpy calculations were made on the basis of eqns. (6) and (7). The results for many alloy systems were collected in an atlas.

3. Comparison with ball-milling results of intermetallic compounds

Ball milling of an intermetallic compound may lead to a phase transformation either to an amorphous structure or to a different crystal structure, *e.g.* to a disordered solid solution. In this section we shall discuss the results of ball-milling experiments on a number of intermetallic compounds consisting of a transition metal and a non-transition element. First let us discuss the reason for such a transformation. Obviously the starting material (the intermetallic compound) in such experiments has a lower free energy than the final product.The question is how energy can be stored in the material by the ball-milling process. In the middle 1980s, it had already been postulated by Johnson [4] that the internal energy of the compound is raised by ball milling as a result of atomic (chemical) disordering in the compound. It is then suggested that, if the more or less disordered compound attains a state of higher energy than the amorphous state, a transformation to the amorphous state will take place. Disordering as a result of ball milling was assessed by a number of different techniques: by measuring the long-range order parameter by means of loss of intensity of superlattice reflections in the X-ray diffraction pattern for Nb_3Sn [5], for Ni_3Al [5, 6] and for Zr_3Al [7]; by measuring the degradation of the superconducting transition temperature of Nb_3Sn [8] and Nb_3Au [9]; by electron microscopy observation for $Mn_{54}Si_{46}$ etc. [10]; by measuring changes in the magnetic properties of CoGa [11] and CoAl [12]. In the two latter materials, so-called triple-defect disorder instead of the "normal" antisite disorder was observed. So evidently atomic (chemical) disorder is generated by ball milling. The next question is, however, whether or not the energy increase due to ball milling is high enough to drive the phase transformation. In a recent review, Koch [5] suggested a number of additional sources of energy increase, which may lead to amorphization: the formation of dislocations, the energy of which is estimated as 1–2 kJ mol^{-1} and the grain boundary energy, which should be considered when the crystallites are reduced to a nanometre size. Cahn [13] also discussed the problem in a recent review paper.

Let us now discuss the problem on the basis of concrete examples in the light of our calculations. Here we have to bear in mind the approximate character of the calculations: these calculations are only estimates but, nevertheless, let us examine what can be learned from these experimental results.

Let us first inspect the Ni–Sn diagram (Fig. 1(a)). In this diagram the upper curve gives the enthalpy for the solid solution, and the lower curve the enthalpy for the amorphous state. The energy of a compound such as Ni_3Sn has an enthalpy below the lower curve. Now let us introduce atomic disorder by ball milling. Then, following the idea of Johnson [4], the enthalpy of the intermetallic compound will increase until finally it may exceed the enthalpy of the amorphous state and then the material amorphizes. Amorphization of Ni_3Sn is really observed [14]. The second example is the A15 structure Nb_3Al compound. The diagram is given in Fig. 1(b). For this system, the enthalpy of the solid solution (completely disordered state) is below the enthalpy of the amorphous state for all compositions. Therefore a transformation to the solid solution of aluminium in niobium is expected by ball milling and this is found [15]. On the basis of the same arguments, $Mn_{54}Si_{46}$ should not amorphize (Fig. 1(c)), which is in agreement with experiment [10]. The V–Ga diagram is represented in Fig. 1(d). On the basis of this diagram, V_3Ga should transform to the solid solution and it does [16]. For the latter compound the enthalpy difference between the amorphous state and the solid solution is rather small. A difference of the same magnitude is found for the Zr–Al system (Fig. 1(e)). Electron irradiation is able to destroy the long-range order completely in Zr_3Al [17], but no amorphization occurs. This is in complete agreement with Fig. 1(e), where the enthalpy of the solid solution is (somewhat) below the enthalpy of the amorphous material. Ball-milling experiments [7] show a reduction in the long-range order parameter as well, but in contrast the material amorphizes after prolonged milling. Here it could well be that other sources of enthalpy increase as mentioned above supply additional energy high enough to drive the transformation. Even more convincing in this respect are the compounds Ni_3Al and Nb_3Sn. From Fig. 1(f) and Fig. 1(g) we observe a

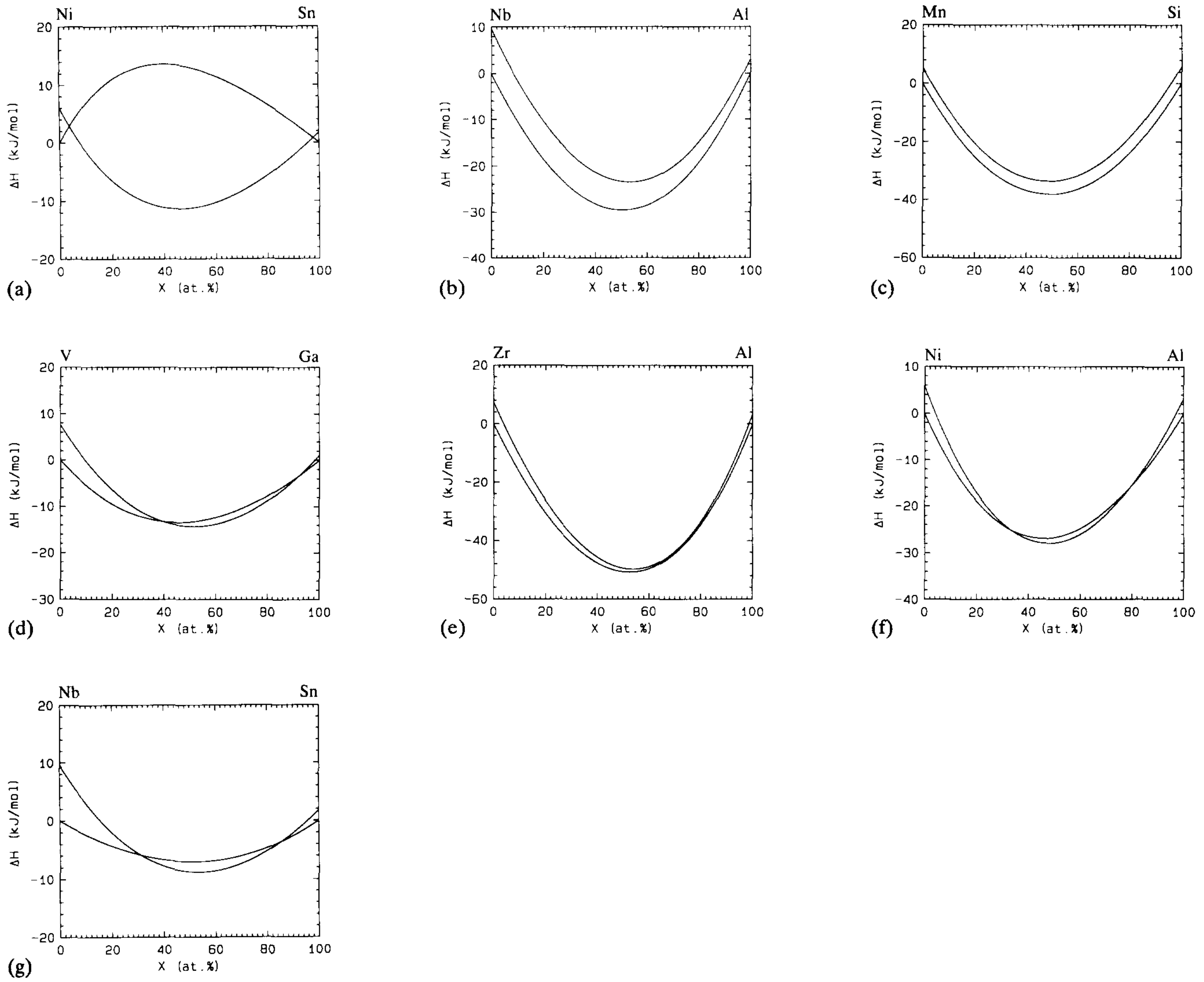

Fig. 1. The formation enthalpy of both amorphous alloys and solid solutions *vs.* composition in the (a) Ni–Sn, (b) Nb–Al, (c) Mn–Si, (d) V–Ga, (e) Zr–Al, (f) Ni–Al and (g) Nb–Sn systems. The curves of the solid solution are those which start at (0, 0) and end at (100, 0).

difference in enthalpy between the completely disordered state and the amorphous state of only about 1 kJ mol^{-1}, where the amorphous state has a somewhat higher energy. Both compounds are reported first to disorder completely [5, 6]— as they should on the basis of the diagrams—and then to amorphize. In fact, such a behaviour is not surprising, because it is very probable that such a small enthalpy difference between both states can be overcome by the additional energy contributions discussed above.

The above conclusions seem reasonable. Nevertheless they should be considered with some caution. In the first place there is the approximate character of the present calculations. However, experimental circumstance may also play an important role in the outcome of the investigations; the type of ball mill, the purity of the atmosphere during the experiment and the ball-milling periods may also be important factors and it is imaginable that different investigators could obtain different results, although the experiments cited above seem rather decisive.

Acknowledgment

Financial support by the Dutch Foundation for Fundamental Research on Matter (FOM) is gratefully acknowledged.

References

1 F. R. de Boer, R. Boom, W. C. M. Mattens, A. R. Miedema and A. K. Niessen, in F. R. de Boer and D. G. Pettifor (eds.), *Cohesion In Metals,* North-Holland, Amsterdam, 1988, p. 63.

2 P. I. Loeff, A. W. Weeber and A. R. Miedema, *J. Less-Common Met., 140* (1988) 299.

3 D. J. Eshelby, *Solid State Phys., 3* (1956) 79.

4 W. L. Johnson, *Prog. Mater. Sci., 30* (1986) 81.

5 C. C. Koch, *Mat. Sci. Forum, 88–90* (1992) 243.

6 S. Gialanella, S. B. Newcomb and R. W. Cahn, in A. R. Yavari (ed.), *Ordering and Disordering in Alloys,* Elsevier Applied Science, London, 1992, p. 67.

7 S. Gialanella, A. R. Yavari and R. W. Cahn, *Scripta Metall. Mater., 26* (1992) 1233.

8 L. M. Di, P. I. Loeff and H. Bakker, *J. Less-Common Met., 168* (1991) 183.

9 L. M. Di and H. Bakker, *J. Phys.: Condens. Matter, 3* (1991) 9319.

10 P. Y. Lee, J. Jang and C. C. Koch, *J. Less-Common Met., 140* (1988) 73.

11 L. M. Di, H. Bakker, Y. Tamminga and F. R. de Boer, *Phys. Rev. B, 44* (1991) 2444.

12 L. M. Di, H. Bakker and F. R. de Boer, *Physica B,* in the press.

13 R. W. Cahn, Mechanical amorphisation of ordered intermetallic phases, *World Scientific,* Singapore, submitted for publication.

14 L. M. Di, P. I. Loeff and H. Bakker, *Phys. Status Solidi A, 117* (1990) K99.

15 M. Oehring and R. Bormann, *J. Phys. Coll., 14* (1990) 169.

16 L. M. Di and H. Bakker, *J. Phys.: Condens. Matter, 3* (1991) 3427.

17 H. Mori, H. Fujita, M. Tendo and M. Fujita, *Scr. Metall., 18* (1984) 783.