

# ON THE ELASTIC MISMATCH IN THE ORDER-DISORDER TRANSFORMATION AND SOLID STATE AMORPHIZATION OF INTERMETALLIC COMPOUNDS—II. CRITERIA FOR THE SOLID-AMORPHOUS TRANSFORMATION IN INTERMETALLIC COMPOUNDS

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(Received 13 August 1990)

**Abstract**—Using simple thermodynamic considerations for the Gibbs-free energies of the crystalline and amorphous states a general condition for the solid-state amorphization of intermetallic compounds by irradiation or mechanical impact was derived. It was obtained that the amorphization is possible if the maximum elastic energy,  $\Delta H_{el}^m$ , stored during the (chemical) order-disorder transition is larger than  $\Delta H_{top}^a$ , the enthalpy of the topological change of amorphization. This condition can be rewritten into the form: the amorphization is not possible if the order-disorder temperature is less than the melting temperature,  $T_c < T_m$ , and if  $T_c > T_m$ —in contrast to Johnson's condition—the possibility of the amorphization depends on the relative magnitude of the elastic mismatch energy and the chemical energy of ordering. If their ratio is large enough the amorphization is possible. Detailed calculations, carried out for a large number of compounds, led to a satisfactory agreement with the experimental observations.

**Résumé**—En utilisant des considerations simples pour les énergies libres de GIBBS des états amorphe et cristallisé, on trouve une condition générale pour l'amorphisation à l'état solide des composés intermétalliques par irradiation ou par impact mécanique. On trouve que l'amorphisation est possible si l'énergie élastique maximale,  $\Delta H_{el}^m$ , stockée pendant la transition (chimique) ordre-désordre est plus grande que  $\Delta H_{top}^a$ , l'enthalpie du changement topologique d'amorphisation. Cette condition peut être réécrite sous la forme suivante: l'amorphisation n'est pas possible si la température ordre-désordre est inférieure à la température de fusion,  $T_c < T_f$ ; si  $T_c > T_f$ , contrairement à la condition de Johnson, la possibilité d'amorphisation dépend du rapport de l'énergie de désaccord élastique à l'énergie chimique de mise en ordre. Si ce rapport est assez grande, l'amorphisation est possible. Des calculs détaillés, effectués sur un grand nombre de composés, conduisent à un accord satisfaisant avec les observations expérimentales.

**Zusammenfassung**—Mit einfachen thermodynamischen Betrachtungen der freien Gibbs-Energien des kristallinen und amorphen Zustandes wird eine allgemeine Bedingung für die Amorphisierung einer intermetallischen Legierung im festen Zustand durch Bestrahlung oder mechanischen Einschlag abgeleitet. Es ergibt sich, daß Amorphisierung möglich ist, wenn die maximale, während des (chemischen) Ordnungs-Entordnungs-Überganges gespeicherte elastische Energie  $\Delta H_{el}^m$  höher ist als die Enthalpie  $\Delta H_{top}^a$  der topologischen Änderung bei der Amorphisierung. Diese Bedingung kann in die Form gebracht werden: Amorphisierung ist nicht möglich, wenn die Ordnungs-Entordnungs-Temperatur kleiner als die Schmelztemperatur ist,  $T_c < T_m$ ; für  $T_c > T_m$ —im Gegensatz zu der Bedingung von Johnson—hängt die Möglichkeit der Amorphisierung ab von der relativen Größe der elastischen Fehlpasungsenergie und der chemischen Energie der Ordnungseinstellung. Ist deren Verhältnis groß genug, dann ist Amorphisierung möglich. Ausführliche Rechnung werden für eine große Zahl von Legierungen durchgeführt; sie stimmen mit den experimentellen Beobachtungen zufriedenstellend überein.

## 1. INTRODUCTION

Crystal to glass transformations in the solid state are generally observed when crystalline solids are driven from equilibrium to an extent that the transformation to the glassy state becomes a thermodynamically

downhill process. If during this process certain kinetic constraints are also maintained (blocking the transformation to other more stable alternative crystalline phases) then the solid state amorphization proceeds. The type of the transition can be different in that respect that a transformation of type "nucleation and growth" or a massive transformation takes place [1–4].

The objective of this paper is to discuss the condition for the occurrence of above transformation in

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intermetallic compounds at stoichiometric compositions. We will try to explain why amorphization is possible rather than describe how it takes place. To answer this question we will investigate in which cases the energy of the crystal can be raised to higher values than the difference in energies of the crystalline and amorphous states. In practice there are two main ways to increase the energy of an initially ordered compound: irradiation [5] or mechanical deformation (ball-milling [6] or plastic deformation [7]). In both cases, during the attrition of the crystal, the increase in the energy is reached by the generation of (i) chemical disorder, (ii) point defects (vacancies and interstitials) and (iii) lattice defects (dislocations and other two or three dimensional defects). Obviously, depending on the way of the irradiation or mechanical deformation the relative amount of the above defects can be different and some differences in the transformation can be expected from case to case. However, there are both experimental and theoretical indications in the literature (see e.g. [8, 9] and [10, 11], respectively) that the most important factor is the production of chemical disorder. For example the energy stored by introducing dislocations and disclinations in heavily deformed crystals [12] is presumably less than the increase in the energy that result from the chemical disordering of the lattice [8]. Similarly, the fact that usually pure metals can not become amorphous under energetic particle irradiations or ball-milling indicate that the energy accompanied by the formation of extra point defects is also relatively small and can not be enough to shift the system above the energy of the amorphous state. Although, there are considerations in the literature where the importance of the above terms are emphasized (see e.g. [12] and [13]) we will first neglect the contribution of these defects. On the other hand, estimating the change in the Gibbs-free energy of the system during disordering we will make a clear distinction between the purely chemical and purely elastic terms accompanied with the production of the anti-site defects. The above terminologies will be used in that sense that the energy estimated from the usual Bragg-Williams approximation will be called pure chemical and the elastic mismatch energy will be considered as pure elastic term.

In our calculations the chemical energy will be estimated from the (slightly modified) Miedema expressions for the heat of formation of ordered alloys. The elastic energies will be taken from our previous paper [14] (hereafter Part I) where the elastic mismatch energy as the function of the (anti-site) defect concentration were derived and calculated for a set of compounds. With the help of thermodynamic considerations a general criterion for the amorphization will be derived. The results will be compared to the Johnson's condition [1] (according to which if the order-disorder temperature,  $T_c$ , is higher than the melting point,  $T_m$ , the amorphization is possible). It will be shown that, according to our model, amor-

phization is not possible if  $T_c < T_m$ , which is in agreement with Johnson's condition. If  $T_c > T_m$  a refinement is necessary. In this latter case detailed calculations were carried out and the results are compared with the experimental data for a large number of intermetallic compounds.

## 2. DERIVATION OF THE GENERAL CRITERIA FOR AMORPHIZATION

We will consider amorphization of an originally ordered phase (intermetallic compound at stoichiometric composition) in solid state. Since the amorphous state is metastable the Gibbs-free energies of the crystalline, liquid and amorphous phases can be schematically illustrated as it is shown in the Fig. 1.

The general condition for amorphization can be given as

$$\Delta G'_c > \Delta G_a \quad (1)$$

where  $\Delta G'_c$  is the change caused for example by irradiation, ball milling, etc. ( $\Delta G'_c \leq \Delta G_c$ ). Let us suppose that the temperature is low enough to avoid the thermally activated recovery processes and to neglect the entropy terms in (1)

$$\Delta H'_c > \Delta H_a \quad (2)$$

Since  $\Delta H'_c$  is mainly connected with the disordering of the ordered structure it can be written as

$$\Delta H'_c = \Delta H_{\text{chem}} + \Delta H_{\text{el}} + \Delta H_{\text{struct}} \quad (3)$$

where  $\Delta H_{\text{chem}}$  is the change caused by the *chemical* disorder (as it is given for example in the Bragg-Williams-model [15]),  $\Delta H_{\text{el}}$  arises from the size mismatch (which obviously increases with increasing disorder). Finally  $\Delta H_{\text{struct}}$  is connected with the change of the structure (topological change); this will be neglected because we will suppose that the structure remains crystalline. (By the same reason  $\Delta H_c > \Delta H'_c$ : see Fig. 1). Similarly, as it was already mentioned in Section 1, we will also neglect—in the right hand side of (3)—the energy stored during the plastic deformation or stored by producing extra point defects. It is worth mentioning that the presence of plastic deformation or extra point defects, at least partly, are also reflected in the first two terms in (3) since they are usually accompanied by the production of anti-state defects (as for example in the case of anti-phase boundaries).

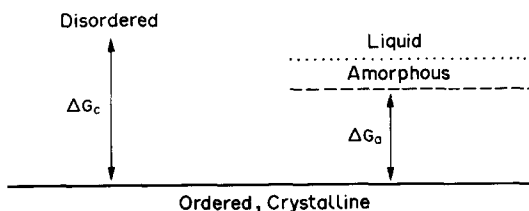


Fig. 1. Gibbs-free energies of crystalline, amorphous and liquid phases schematically.

Obviously in (3) the first two terms depend on the order parameter,  $\eta$ : the concrete forms of these functions will be discussed later. On the other hand,  $\Delta H_a$  in (2) is determined by the relation

$$\Delta H_a = \Delta H_{\text{chem}}^a + \Delta H_{\text{top}}^a \quad (4)$$

where  $\Delta H_{\text{chem}}^a$  has a similar meaning as the first term in (3), but since in the amorphous state there is no long range order, we will suppose that  $\Delta H_{\text{chem}}^a$  corresponds to the value taken at  $\eta = 0$ :  $\Delta H_{\text{chem}}^a = \Delta H_{\text{chem}}^m$ , where the index  $m$  refers to the maximal value of  $\Delta H_{\text{chem}}$ . The second term in (4) expresses the fact that the amorphous state is disordered not only chemically but topologically as well. Since there is no elastic mismatch energy in this case  $\Delta H_{\text{el}}$  is missing from (4).

If we look for a general condition for amorphization we can take the maximal values of  $\Delta H_{\text{chem}}$  and  $\Delta H_{\text{el}}$  (i.e. their limits at  $\eta = 0$ ) in equation (3) and we have from (1)

$$\Delta H_{\text{chem}}^m + \Delta H_{\text{el}}^m > \Delta H_{\text{chem}}^m + \Delta H_{\text{top}}^a \quad (5)$$

i.e.

$$\Delta H_{\text{el}}^m > \Delta H_{\text{top}}^a \quad (6)$$

Furthermore, since there is a relaxation in the amorphous state towards the crystalline one as compared to the liquid phase (see Fig. 1 and e.g. [16, 17])

$$\Delta H_{\text{top}}^a = \rho \Delta H_{\text{top}}^f \quad (7)$$

where  $\Delta H_{\text{top}}^f$  denotes the change in  $H$  accompanied with the topological change during fusion, and  $\rho = 0.7$  [16, 17]. Combining (6) and (7) we get

$$\Delta H_{\text{el}}^m > \rho \Delta H_{\text{top}}^f \quad (8)$$

According to this general condition, if  $\Delta H_{\text{el}}^m$  is zero it is not expected that the amorphization takes place i.e. equation (8) emphasizes the importance of the elastic mismatch in the amorphization of intermetallic compounds.

Equation (8) can be further rewritten if we express  $\Delta H_{\text{top}}^f$  in terms of the heats of fusion which are directly measurable quantities. If the order-disorder temperature,  $T_c$ , is less than the melting temperature,  $T_m$

$$\Delta H_{\text{ss}}^f = \Delta H_{\text{top}}^f - \Delta H_{\text{el}}^{\text{ss}} \quad (9)$$

where  $\Delta H_{\text{ss}}^f$  and  $\Delta H_{\text{el}}^{\text{ss}}$  are the heat of fusion and the elastic mismatch energy of the (disordered) solid solution. If  $T_c > T_m$

$$\Delta H_{\text{comp}}^f = \Delta H_{\text{top}}^f + \Delta H_{\text{chem}}^m \quad (10)$$

and here  $\Delta H_{\text{comp}}^f$  is the heat of fusion of the (ordered) compound. In accordance with the generally used supposition that there is no elastic mismatch energy in the ordered compound, and obviously neither in the amorphous state, the elastic term is missing from (10) (see Part I). Furthermore, according to Richard's-rule [18]

$$\Delta H_{\text{ss}}^f = \Delta S^f T_{\text{mean}} = 2kT_{\text{mean}} \quad (11a)$$

and

$$\Delta H_{\text{comp}}^f = 2kT_m \quad (11b)$$

where  $\Delta S^f$  is the entropy of fusion,  $k$  is the Boltzmann-constant and  $T_{\text{mean}}$  (the average value of the solidus and liquidus [19]) plays a role of  $T_m$  for disordered solid solutions. Now, defining the ordering energy as

$$\Delta H_{\text{ord}} = \Delta H_{\text{chem}}^m + \Delta H_{\text{el}}^m = \Delta H_{\text{chem}}^m \vartheta \quad (12)$$

where  $\vartheta$  is given by

$$\vartheta = 1 + \Delta H_{\text{el}}^m / \Delta H_{\text{chem}}^m \quad (13)$$

equation (8) can be rewritten as

$$\Delta H_{\text{el}}^m / \rho + \Delta H_{\text{chem}}^m > 2kT_m \quad (14a)$$

or

$$\Delta H_{\text{ord}} [\vartheta - 1 + \rho] / \rho \vartheta > 2kT_m \quad (14b)$$

if  $T_c > T_m$  and

$$\Delta H_{\text{el}}^m - \rho \Delta H_{\text{el}}^{\text{ss}} > 2k\rho T_{\text{mean}} \quad (15)$$

if  $T_c < T_{\text{mean}}$ . It can be seen from (14) that if there is no elastic mismatch i.e. when  $\Delta H_{\text{el}}^m = 0$  ( $\vartheta = 1$ )

$$\Delta H_{\text{ord}} = \Delta H_{\text{chem}}^m > 2kT_m.$$

But, according to equation (10) and (11b) this cannot be fulfilled because  $\Delta H_{\text{comp}}^f > \Delta H_{\text{chem}}^m$  always. Similarly, (15) never be fulfilled if  $\Delta H_{\text{el}}^m$  is zero.

Equations (14) and (15) again give the conditions in terms of the elastic mismatch energies (and in the term of the  $\Delta H_{\text{chem}}^m$  if  $T_c > T_m$ ). Thus, in order to make estimations for different systems, we need estimations for the chemical part of the ordering energy and for the elastic mismatch energies as well.

### 3. ESTIMATION OF THE CHEMICAL ENERGY

The chemical energies of ordering can be estimated from the Miedema expressions for the heat of formation of ordered alloys. In the Miedema's model this quantity is given as [20]

$$\Delta H_{\text{ord}}^{\text{form}} = \{1 + 8[c_A^s c_B^s]^2\} \Delta H_{\text{liq}}^{\text{form}} \quad (16)$$

Here  $\Delta H_{\text{liq}}^{\text{form}}$  is the formation enthalpy of a liquid alloy and  $c_A^s$  and  $c_B^s$  are the surface concentrations [20]. The factor 8 was fixed empirically in [20] such a way that the model is in accordance with the experimental result that the enthalpy of ordering,  $\Delta H_{\text{ord}}$ , is about one third of  $\Delta H_{\text{ord}}^{\text{form}}$ . However, because during disordering in solid state there is an accumulation of elastic energy as well, not only the chemical but also the elastic terms are included in the experimentally observed  $\Delta H_{\text{ord}}$ . Consequently, the factor 8 is too high if we want to get the chemical term only.

Indeed, we can easily show that the use of the factor 5.3 instead of 8 is more appropriate. In a simple model taking into account nearest neighbor

interactions only, we can write for the formation enthalpy of a liquid alloy [18, 21, 22]

$$\Delta H_{\text{liq}}^{\text{form}} = z_1 v F_A \{1 - F_A\} = z_1 v / m. \quad (17)$$

Here  $z_1$  is the number of nearest neighbors,  $F_A$  is the atomic fraction of A atoms ( $F_A + F_B = 1$ ,  $F_A \leq F_B$ ,  $m = 1/F_A F_B$ ) and  $v$  is given by the interaction energies between different pairs of A and B atoms as [15]

$$v = v_{AB} - (v_{AA} + v_{BB})/2. \quad (18)$$

Furthermore, the heat of formation of an ordered AB alloy with f.c.c. structure, in the same approximation, is given as

$$v = 3\Delta H_{\text{ord}}^{\text{form}}/z$$

where  $z = 12$  and so

$$\Delta H_{\text{ord}}^{\text{form}} = z\Delta H_{\text{liq}}^{\text{form}}/3z_1 F_A [1 - F_A]. \quad (19)$$

The above relations were obtained in nearest neighbor approximation and there are suggestions in the literature for more realistic expressions including the interactions of not nearest neighbors and the size disparity effects as well [22, 23, 24]. However, for the sake of simplicity we will use (18) with  $z_1 = 12$  [22, 23]. Now, comparing (16) and (18) for  $F_A = 1/2$  and for equal atomic volumes (when  $c_A^s = c_B^s = 1/2$ ) we see that they will equal if we use a factor 5.3 instead of 8.

Finally, since  $\Delta H_{\text{chem}}^m$  can be expressed as the difference between the heat of formation of the compound,  $\Delta H_{\text{ord}}^{\text{form}}$ , and the liquid alloy,  $\Delta H_{\text{liq}}^{\text{form}}$ , at the same composition, we will use the relation

$$\Delta H_{\text{chem}}^m = 5.3[c_A^s c_B^s]^2 \Delta H_{\text{liq}}^{\text{form}} \quad (20)$$

in our calculations.  $\Delta H_{\text{liq}}^{\text{form}}$  are tabulated in [20] for equiatomic compositions and can be easily calculated for any  $F_A$  value.

#### 4. ELASTIC MISMATCH ENERGY

In our previous paper (Part I), using a method similar to the theory of almost completely ordered alloys, an estimation for the elastic mismatch energy of ordered compounds was derived as the function of the long-range order parameter,  $\eta$ , from the continuum elastic theory. It was shown that, similar to  $\Delta H_{\text{chem}}^m$ , this has a simple  $(1 - \eta^2)$ -type dependence

$$\Delta H_{\text{el}} = \Delta H_{\text{el}}^m (1 - \eta^2) \quad (21)$$

where

$$\Delta H_{\text{el}}^m = E_0(0)/2m. \quad (22)$$

Here  $E_0(0)$  is the elastic energy of the system when a "pair" of anti-site defects (i.e. one A atom in the  $\beta$  and one B atom in the  $\alpha$  sublattice, respectively) is produced at  $T = 0$  K in an otherwise ideal, ordered crystal. Unfortunately the estimation of  $\Delta H_{\text{el}}^m$  is restricted by our knowledge on the volumes of atoms and holes in the compound. It was demonstrated in Part I, that the use of uncorrected volumes (i.e. the

atomic volumes of pure A and B, respectively) or corrected volumes following Miedema [20] (which takes into account the change in the atomic volumes caused by the change in their environment in the alloy) in the calculation of  $E_0(0)$  could result in a difference of about a factor of two in the  $\Delta H_{\text{el}}^m$  values.

#### 5. RESULTS

Before presenting and analyzing the results of the numerical calculations we can investigate the question: whether the conditions (14) and (15) are equivalent to the condition obtained by Johnson [1], or not. In deriving his relation Johnson, supposing that  $\rho \cong 1$  and neglecting the elastic mismatch energies, started from the relation

$$\Delta H_{\text{ord}} = \Delta H_{\text{chem}}^m > \Delta H_{\text{comp}}^f. \quad (23)$$

Using the Richard's rule ( $2k = \Delta S^f$ ) and a simplified relation between  $T_c$  and  $\Delta H_{\text{chem}}^m$  ( $\Delta H_{\text{chem}}^m \cong kT_c$ ) he got the condition for the amorphization as

$$T_c/T_m \geq 1. \quad (24)$$

Now, taking into account that  $\Delta H_{\text{el}}^m$  is usually equal to or less than  $\rho \Delta H_{\text{el}}^s$  ( $\rho = 0.7$  and see our calculations in Part I), we also get from (15) that the amorphization is not possible in solid state if  $T_c < T_m$ .

If  $T_c > T_m$  from (17) and (20) we have

$$v = m \Delta H_{\text{chem}}^m / 63.5 (c_A^s c_B^s)^2. \quad (25)$$

Now, neglecting the elastic mismatch in the theory of the order-disorder transition, from the  $\eta$ -dependence of the Gibbs-free energy usually a relation of type

$$v/kT_c = 1/q_c = \Delta H_{\text{chem}}^m / z F_A^2 kT_c \quad (26)$$

is obtained for the order-disorder temperature. Here  $z'$  is the number of unlike nearest neighbors (e.g.  $z' = 8$  and  $z' = 6$  for  $L2_0$  and  $DO_3$  structures, respectively [15]) and the value of  $q_c$  generally depends on the type of alloy and on the order of approximation used in the description of the system [25, 26]; its value lies between 1 and 3 for the most simple structures.

If there is also an elastic mismatch, using the fact that both the chemical and the elastic mismatch energies of ordering have the same  $(1 - \eta^2)$ -type dependence, it would be easily shown that the role of  $v/kT$  is played by the expression

$$v\{1 + [\vartheta - 1][1 - \lambda_z T/T_m]\}/kT \\ = v\vartheta\{1 + \lambda_z T[1 - \vartheta]/\vartheta T_m\}/kT. \quad (27)$$

Taking this quantity equal to  $1/q_c$ , we have

$$T_c = q_c v \vartheta / k [1 + q_c v (\vartheta - 1) \lambda_z / k T_m]. \quad (28)$$

In (27) the factor  $[1 - \lambda_z T/T_m]$  appears because of the temperature dependence of elastic moduli (see Part I).  $\lambda_z$  is the Zener constant ( $\lambda_z = 0.35$ ) and  $T = 300$  K was taken in our calculations because the elastic moduli are usually given at room temperature.

Table 1

Compound	$\Delta H_{el}^m$	$\Delta H_{chem}^m$	$\vartheta$	$T_m$	c14	c'14	Exp.	Concl. c	c'
LaAu	13.10	20.34	1.64	1600	2348	3206	Y	Y	Y
La <sub>2</sub> Co <sub>3</sub>	46.26	4.97	10.30	1233	4273	5462	N	Y	Y
LaCu <sub>2</sub>	32.12	6.49	5.96	1103	3149	4424	N	Y	Y
LaNi	53.98	6.03	9.96	958	4999	6427	N	Y	Y
GdCo <sub>3</sub>	22.58	4.40	6.14	1566	2204	4902	Y	Y	Y
Gd <sub>2</sub> Co <sub>7</sub>	18.34	3.82	6.08	1723	1805	4515	Y	Y	Y
PdZr	4.08	28.56	1.14	1873	2068	2831	Y	Y	Y
PtZr	3.48	31.46	1.12	2377	2191	3014	Y	N	Y
PtZr <sub>2</sub>	5.96	17.69	1.34	2075	1576	2089	Y	N	Y
Zr <sub>7</sub> Cu <sub>10</sub>	16.08	7.45	3.16	1066	1829	2496	Y	Y	Y
ZrCu	16.40	6.77	4.42	1203	1816	2467	Y	Y	Y
NiZr <sub>2</sub>	21.46	6.67	4.22	1393	2245	2848	Y	Y	Y
NiZr	21.64	14.05	2.54	1533	2704	3824	Y	Y	Y
CoZr	21.62	11.73	2.84	1673	2563	3620	Y	Y	Y
Zr <sub>2</sub> Al	2.74	8.24	1.34	1583	731	927	Y	N	N
Zr <sub>3</sub> Al	2.48	4.64	1.54	1425	492	652	N	N	N
RuZr	13.42	18.00	1.74	2375	2235	3653	Y	N	Y
Cr <sub>2</sub> Zr	18.98	3.58	6.30	1946	1846	3023	N	N	Y
CuTi <sub>2</sub>	4.80	1.65	3.90	905	511	728	Y	N	N
CuTi	5.16	2.88	2.80	1218	616	867	Y	N	N
Ti <sub>3</sub> Cu <sub>4</sub>	5.14	2.97	2.74	1255	620	861	Y	N	N
Ti <sub>2</sub> Cu <sub>3</sub>	5.08	2.89	2.76	1320	610	840	Y	N	N
TiCu <sub>4</sub>	4.02	1.11	4.60	1200	412	522	N	N	N
NiTi	6.82	10.87	1.62	1583	1239	1810	Y	N	Y
NiTi <sub>2</sub>	7.18	5.92	2.22	1273	973	1328	Y	N	Y
Ni <sub>3</sub> Ti	4.64	6.68	1.70	1653	800	1343	N	N	N
Co <sub>2</sub> Ti	5.50	7.89	1.70	1510	947	1526	Y	N	Y
CoTi	6.82	8.91	1.76	1598	1122	1651	?	N	Y
Fe <sub>2</sub> Ti	4.36	4.61	1.94	1700	652	1191	Y	N	N
FeTi	5.46	5.37	2.02	1600	792	1209	?	N	N
Mn <sub>2</sub> Ti	4.24	2.22	2.92	1600	497	687	Y	N	N
RuTi	1.10	14.05	1.08	2403	939	1424	Y	N	N
AuZn	3.10	5.35	1.58	998	588	368	N	N	N
Ni <sub>6</sub> Nb	10.22	8.63	2.48	1595	1397	1921	Y	N	Y
NiMo	8.94	2.35	4.80	1836	909	1189	Y	N	N
Ni <sub>3</sub> Al	2.74	4.13	1.66	1675	484	872	N	N	N
NiAl	4.60	7.05	1.66	1911	819	1151	N	N	N
FeCo	0.12	0.17	1.74	1750	20	31	N	N	N
PdIn	6.40	9.37	1.68	1475	1113	1723	N	N	Y
CoGa	11.66	3.38	4.44	1325	1234	1720	N	N	Y
CoAl	4.64	5.93	1.78	1921	755	1054	N	N	N
Cu <sub>3</sub> Sn	22.48	0.26	6.56	970	1947	2186	N	Y	Y
Pd <sub>3</sub> Sn	6.20	7.13	1.86	1599	962	1850	N	N	Y

Inserting (25) into (28) and supposing that  $c_A^s c_B^s \cong 1/m$  (this is a good approximation if the volumes  $\Omega_{AinA}$  and  $\Omega_{BinB}$  are not so much different; see also [20]), we can express  $\Delta H_{ord}$  with the help of (12) as

$$\Delta H_{ord} = 63.6kT_c/q_c m^3 [1 - (T_c/T_m)\lambda_Z(\vartheta - 1)/\vartheta]. \quad (29)$$

Taking into account that  $\rho = 0.7$  and  $\lambda_Z = 0.35$  we obtain from (14)

$$T_c/T_m > M2q_c m^3/63.6 \quad (30)$$

where

$$M = 1/\{1.43 - 0.43/\vartheta + (1 - 1/\vartheta)0.35(2q_c m^3/63.6)\}. \quad (31)$$

At  $\vartheta = 1$ , i.e. when there is no elastic mismatch,  $M = 1$ . But in this case, although  $T_c/T_m > 1$ , the inequality (30) can not be fulfilled as it was discussed before after equations (14) and (15). Consequently the transition temperature, even if it is higher than  $T_m$ , always should be less than  $T_m 2q_c m^3/63.6$ , i.e. the value of  $T_c$  lies between  $T_m$  and  $2q_c T_m m^3/63.6$ . Thus condition (30) can be fulfilled only if  $\vartheta > 1$  ( $M < 1$ ). It is hard to conclude anything more from (30)

because we are not able to determine  $T_c$  experimentally, but it is clearly seen that the condition  $T_c > T_m$  is not a sufficient condition.

Before analyzing the results of our calculations we note that qualitatively (8), (14) or (30) is in accordance with the conditions established empirically by Luzzi and Meshi [10] for solid state amorphization of compounds under electron irradiation. These conditions are:

- (1)  $T_c > T_m$
- (2)  $F_A \geq 1/3$  ( $F_A \leq F_B$ )
- (3) The constituents should be separated in the periodic table by more than two groups
- (4) Complex crystal structure of the compound.

The first condition is also confirmed by us [see our comment after (24)]. Furthermore, if the elastic mismatch energy is large [i.e.  $\vartheta$  is large and  $M$  is less than unity in (31)], the next two conditions are also expected to be fulfilled;  $m$  in  $\Delta H_{el}^m$  [see (22)] has a minimum for AB alloy and the size differences are large if the condition 3) is fulfilled, respectively.

In the first three columns of Table 1 the calculated  $\Delta H_{el}^m$ ,  $\Delta H_{chem}^m$  (in units kJ/mol) and  $\vartheta$  values are given,

respectively. The fourth column shows the melting points and the next three columns list the  $c14$  values (in units of temperature) calculated from condition (14)

$$c14 = \Delta H_{\text{ord}} \{9 - 1 + \rho\} / 2k\rho > T_m. \quad (32)$$

In order to illustrate the uncertainty accompanied with the unsatisfactory knowledge of the volumes of atoms and holes the  $c'14$  "temperatures" were also calculated using volumes without Miedema's corrections (see Part I) in  $E_0(0)$ .

The last two columns in Table 1 contain the experimental information on the amorphization investigated by irradiation [1, 5, 10] or by ball-milling (see references [28] to [35] and not yet published results from this laboratory) and the conclusions obtained from  $c14$  and  $c'14$  conditions, respectively. Here the letters Y (yes) and N (no) indicate that the amorphization is possible or not. For the CoTi and FeTi systems the question marks show that the experimental results are not unambiguous (see [1] and [10], respectively).

From the comparison of the last two columns of Table 1 we can conclude;

(i) The agreement is satisfactory in 28 cases from the 43 compounds: at least one of the  $c14$  or  $c'14$  values are in accordance with the experimental results.

(ii) In 13 cases there is a disagreement between the calculated and experimental data. For the  $\text{La}_2\text{Co}_3$ ,  $\text{LaCu}_2$ ,  $\text{LaNi}$  and  $\text{Cu}_3\text{Sn}$  compounds the melting point is relatively low and the effect of the dynamic recovery—which was neglected here—can be important. It is possible that more precise measurements at low temperatures could lead to amorphisation in these alloys.

(iii) In systems containing  $\text{Ti}$  (14 cases) the agreement is wrong; usually amorphisation was observed, but the calculations led to opposite results. The reason of this fact is not clear at present.

(iv) We have to take into account that condition (14) is a necessary condition and in the majority of cases where disagreement was obtained the increase of the temperature calculated from (32) would lead to a better agreement. For example if we estimate the energy stored by the accumulation of lattice defects (mainly dislocations) during plastic deformation according to [1] and [36], as 1–2 kJ/mol, than this would increase the right hand side of (14) (and consequently (32)) by about 150–200 K.

## 6. CONCLUSIONS

Our main results can be summarized as follows:

—Using simple thermodynamic considerations for the Gibbs-free energies of the crystalline and amorphous states a general condition of solid-state amorphization for intermetallic compounds was derived. This condition, using relations between the heat of fusion and the melting point as well as between the

critical temperature and the ordering energy, can be rewritten into the form of a relation between  $T_c$  and  $T_m$ . It was obtained that if  $T_c < T_m$  the amorphization is not possible. If  $T_c > T_m$ —in contrast to the Johnson's condition—the possibility of the amorphization depends on the relative magnitude of the elastic mismatch energy and the chemical energy.

—Detailed calculations for a large number of compounds (with  $T_c > T_m$ ) shows, in agreement with the experimental observations, that in these cases amorphization is not always possible. Our results emphasize the role of the elastic mismatch energy; if it is large enough (as compared to the chemical energy of ordering) than the amorphization is possible in solid state. The agreement between the calculated and experimental results—if we take into account the limits of the estimations of  $\Delta H_{\text{chem}}^m$  and  $\Delta H_{\text{el}}^m$ —is satisfactory.

—Our condition (14) or (32) is a *necessary* condition since we neglected the energies which can be stored by extra point defects and lattice defects (dislocations). Furthermore it was also supposed that—during the attrition of the crystal—the temperature is low enough to avoid the effects of dynamic recovery. In the investigation of the role of the above defects a comparative measurements on the same compound by irradiation and by ball-milling at low temperatures would be desirable (because probably the relative role of these defects is different during irradiation or ball-milling).

*Acknowledgements*—Financial support by the Dutch Foundation for Fundamental Research on Matter (FOM) is gratefully acknowledged. One of us (D. L. Beke) partly performed this work under contract with the Hungarian Academy of Sciences No. 179/2.

## REFERENCES

1. W. L. Johnson, *Prog. Mater. Sci.* **30**, 81 (1986).
2. W. L. Johnson and H. Fecht, *J. less-common Metals* **145**, 63 (1988).
3. W. L. Johnson, *Trans. Japan Inst. Metals, Suppl.* **29**, 19 (1988).
4. K. Samwer, *J. less-common Metals* **140**, 25 (1988).
5. K. C. Russel, *Prog. Mater. Sci.* **28**, 229 (1984).
6. A. W. Weeber and H. Bakker, *Physica* **B153**, 93 (1988).
7. P. D. Askenazy, E. A. Kamenetzky, L. E. Tanner W. L. Johnson, *J. less-common Metals* **140**, 149 (1988).
8. R. B. Schwarz and R. R. Petrich, *J. less-common Metals* **140**, 171 (1988).
9. P. R. Okamoto, L. E. Rehn, J. Pearson, R. Bhadra and M. Grimsditch, *J. less-common Metals* **140**, 231 (1988).
10. D. E. Luzzi and M. Meshii, *Scripta metals* **20**, 943 (1986).
11. D. E. Luzzi and M. Meshii, *J. less-common Metals* **140**, 193 (1988).
12. V. A. Pavlov, *Physica Metals Metallov.* **59**, 1 (1985).
13. D. F. Pedraza, *J. less-common Metals* **140**, 219 (1988).
14. D. L. Beke, P. I. Loeff and H. Bakker, *Acta metall. mater.* **39** (1990). In press.
15. T. Muto and Y. Takagi, *Solid St. Phys.* **1**, 31 (1955).
16. T. Egami and Aur, *J. non-cryst. Solids* **89**, 60 (1987).
17. T. Egami, *Rep. Prog. Phys.* **47**, 1601 (1984).
18. R. A. Swalin, *Thermodynamics of Solids*, p. 60. Wiley, New York (1976).

19. D. L. Beke, G. Erdélyi and F. J. Kedves, *J. Phys. Chem Solids* (1979).
20. F. R. de Boer, R. Boom, W. C. M. Mattens, A. R. Miedema and A. K. Niessen, *Cohesion in Metals. Transition Alloys* North-Holland, Amsterdam (1988).
21. J. Lumsden, *Thermodynamics of Alloys* Inst. Metals Monogr. Rep. Ser. No. 11, p. 325. Grosvenor Gardens, London (1952).
22. I. Prigogine, A. Bellemans and V. Mathot, *The Molecular Theory of Solutions*. North-Holland, Amsterdam (1957).
23. M. Shimoji and K. Niwa, *Acta metall.* **5**, 496 (1957).
24. J. W. Christian, *The Theory of Transformations in Metals and Alloys* pp. 188. Pergamon Press, Oxford (1965).
25. M. A. Krivoglaz and A. Smirnov *Theory of Order-Disorder in Alloys*, p. 121. Macdonald, New York (1964).
26. R. Kikuchi and H. Sato, *Acta metall.* **22**, 1099 (1974).
27. L. Guillet and R. Le Roux, *Intermetallic Compounds* (edited by J. H. Westbrook), p. 217. Wiley, New York (1967).
28. P. I. Loeff and H. Bakker, *Scripta metall.* **22**, 401 (1988).
29. A. Ye. Yermakov, V. A. Barinov and Ye. Ye. Yurchikov, *Physics Metals Metallov.* **54**, 90 (1982).
30. A. Ye. Yermakov, Ye. Ye. Yurchikov and V. A. Barinov, *Physics Metals i Metallov.* **52**, 50 (1981).
31. F. H. M. Spit, P. I. Loeff and H. Bakker, *J. non-cryst. Solids* **108**, 233 (1988).
32. P. I. Loeff, F. H. M. Spit and H. Bakker, *J. less-common Metals* **145**, 271 (1988).
33. A. W. Weeber, H. Bakker and F. R. de Boer, *Europhys Lett.* **2**, 445 (1986).
34. T. J. Tiainen and R. B. Schwarz, *J. less-common. Metals* **140**, 99 (1988).
35. A. W. Weeber and H. Bakker, *Z. Phys. Chem. Neue Folge* **157**, 221 (1988).
36. M. B. Bever, D. L. Holt and A. L. Titchener, *Prog. Mater. Sci.* **17**, 1 (1973).