

# Effect of sharp concentration gradients on crystal nucleation in amorphous layers obtained by solid state reaction

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## Abstract

Using thermodynamic arguments it is shown that the sharp concentration gradient, occurring during diffusive mixing in multilayers, may reduce the absolute value of the Gibbs energy of crystallization, leading to cancellation of the driving force for homogeneous and heterogeneous nucleation of compounds in the amorphous interlayer. A thermodynamic critical concentration gradient is defined, above which there is no available driving force for nucleation. As the concentration gradient diminishes during growth of the amorphous layer, the driving force for nucleation is restored. This yields a thermodynamic critical maximum amorphous layer thickness, which has been observed experimentally. The cases of formation of a compositionally different compound embryo and of polymorphous (or partitionless) nucleation are both treated and discussed. The heterogeneous nucleation of compounds under a concentration gradient, which has been proven to be at the origin of the cessation of amorphization, is treated in more detail. The nucleus shape anisotropy and non-stoichiometry of the nucleating compound are taken into account. The results are applied to the NiZr system.

## 1. Introduction

Since its discovery [1], solid state amorphization has received much attention from the Materials Science community. The possibility of producing bulk amorphous alloys by such a method is of interest for applications and explains in part the numerous experimental studies conducted during the last seven years. In fact many of these works have been in search of a fundamental understanding of this amorphization process through thermodynamic and kinetic aspects. It is now established that in AB type multilayers, a large asymmetry in the atomic mobilities in solid solutions and a strong negative enthalpy of mixing of the liquid solution favour solid state amorphization reaction (SSAR). Vredenberg *et al.* [2] proved that the presence of grain boundaries in the crystalline layer of the less mobile atoms (A) is necessary in the first stage of the genesis of the amorphous phase. Thus the triple joints at contact zones of two A-grains and a grain of the fast diffusing B-element constitute privileged nucleation regions. Transmission electron microscopy [3] has also proved that, starting from such nucleation sites, glassy zones rapidly coalesce to form a continuous amorphous interlayer. The subsequent growth in thickness of the amorphous interlayer is a diffusion-controlled process. Consequently, sharp concentration gradients of the order of

$10^5$ – $10^6$  cm<sup>-1</sup> develop in the direction of growth. Such transient metastable amorphous interlayers have been observed experimentally to reach a maximum (critical) thickness prior to nucleation of more stable intermetallic compounds. Approaches based on kinetics of nucleation [4, 5] have been used to explain this effect. It has also been demonstrated from thermodynamics that a critical concentration gradient  $\nabla c_c$  can be defined [6]. Above such a critical gradient, the Gibbs energy for nucleation  $\Delta G_N$  is no longer negative whatever the nucleus size. This critical concentration gradient yields a thermodynamic critical thickness under the hypothesis of a linear variation in concentration with distance in the direction of growth of the amorphous interlayer. As the amorphous interlayer grows the concentration gradient flattens out and the thermodynamic driving force for nucleation is restored when  $\nabla c < \nabla c_c$ .

The aim of the present paper is to review and discuss the effects of sharp concentration gradients on the potentiality of homogeneous and heterogeneous nucleation of a compound in an amorphous layer.

## 2. Homogeneous nucleation of compounds in the amorphous interlayer

### 2.1. Simplified approach

First, the following simple case can be investigated. A strictly stoichiometric compound with mole fraction

$c=c^*$  is expected to form in the amorphous phase through the homogeneous nucleation process. The nucleus is supposed to be of cubic form of size  $2r$ . The concentration gradient is unidirectional in the direction OX of amorphous layer growth (Fig. 1). The amorphous layer thickness is thought of as divided into successive slices of uniform composition but with concentration varying with distance  $x$ :  $c(x)$ . It is considered that under the constraint given by the concentration gradient in the direction of growth, the probability of formation of an ordered structure of composition  $c^*$  is maximum in the amorphous zone where the composition is exactly  $c^*$ . It is obvious that the amorphous zone for which the driving force for homogeneous nucleation is optimal is symmetrically situated on the two sides of the plane where  $c=c^*$ . For simplicity the Gibbs free energy of the amorphous phase is supposed to be minimum for the composition  $c^*$ .

Since the concentration gradient acts as a constraint, exchange of matter leading to homogenization (to the concentration  $c^*$ ) is forbidden in the  $\nabla c$  direction both through concentration fluctuations in the amorphous state at the nucleus scale and via atomic diffusion inside the zone of formation of the compound embryo. (In fact the first slice of the embryo of composition  $c^*$  constitutes a diffusion barrier preventing mixing in the  $\nabla c$  direction between amorphous slices that it separates.)

To apply the tangent rule, any exchange of matter to form the nucleus of concentration  $c^*$  must occur between each embryo slice and its surrounding in the plane perpendicular to  $\nabla c$ , acting as a reservoir. The classical tangent rule in the Gibbs energy diagram represented in Fig. 2 is used to calculate the driving force for crystallization. For a slice of concentration  $c$  the molar contribution to the global driving force for crystallization is

$$\Delta G_m = c^*[\mu_A^s(c^*) - \mu_A^a(c)] + (1 - c^*)[\mu_B^s(c^*) - \mu_B^a(c)]$$

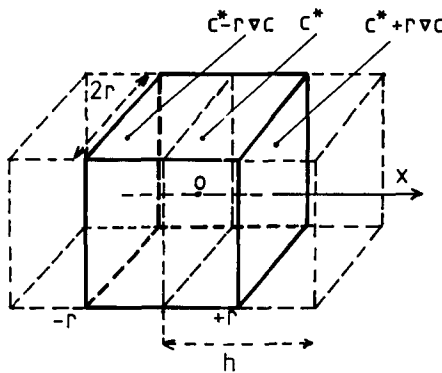


Fig. 1. The volume element of a cubic nucleus with dimensions  $2r$  cut into successive slices of different concentrations along the direction OX of the concentration gradient  $\nabla c$ .

where  $\mu_A^s(c^*)$ ,  $\mu_B^s(c^*)$ ,  $\mu_A^a(c)$ ,  $\mu_B^a(c)$  are respectively the chemical potentials in the compound (s) and in the amorphous slice (a). This contribution is represented by the segment EI in Fig. 2.

Adding the different contributions over the entire volume of the embryo and developing  $\Delta G_a$  to the second order in  $(c - c^*)$  around  $c = c^*$ , one obtains for the global driving force for crystallization [6]:

$$\Delta G_{ac} = 8\rho\Delta G_{pc}r^3 + \frac{4}{3}\rho\alpha(\nabla c)^2r^5 \quad (1)$$

where  $\rho$  is the number of moles of atoms per unit volume,  $\Delta G_{pc}$  is the polymorphous Gibbs energy of crystallization for the concentration  $c^*$  (Fig. 2), and  $\alpha = (\partial^2\Delta G_a/\partial c^2)_{c=c^*}$  is the Gibbs stability of the amorphous phase at  $c = c^*$ .

The Cahn correction term for the Gibbs energy of the amorphous phase due to the non-uniformity has been found to be negligible for the concentration gradients involved during solid state amorphization and consequently does not appear in eqn. (1). As no phase separation is allowed in the amorphous phase,  $\alpha$  is positive and the second term in  $r^5$  of eqn. (1) lowers the driving force for crystallization ( $\Delta G_{ac}$  becomes less negative).

It is interesting to note that calculation of  $\Delta G_{ac}$  from a mechanism which would allow mixing in the amorphous phase in the nucleation zone in the  $\nabla c$  direction prior to crystallization yields a negative second term in  $r^5$  of the same mathematical form as the second term in eqn. (1). However, such a mechanism would mean a local cancellation of the concentration gradient in the amorphous phase. This would contradict the initial condition of an imposed  $\nabla c$  in the amorphous layer.

Adding the interfacial term  $24\sigma r^2$  one obtains the Gibbs energy for nucleation of the cubic embryo of size  $2r$ :

$$\Delta G_N = 24\sigma r^2 + 8\rho\Delta G_{pc}r^3 + \frac{4}{3}\rho\alpha\nabla c^2r^5 \quad (2)$$

where  $\sigma$  is the interfacial energy between the amorphous phase and the compound.

Figure 3 displays the influence of increasingly sharp concentration gradients on  $\Delta G_N$  represented *vs.*  $r$  in the case of homogeneous nucleation of the compound  $Ni_{10}Zr_7$  in an amorphous layer of NiZr [6].

It appears that for  $\nabla c$  higher than  $5 \times 10^5 \text{ cm}^{-1}$ , no negative value of  $\Delta G_N$  is obtained whatever the value of  $r$ . This implies that for  $\nabla c$  higher than a critical concentration gradient  $\nabla c_c$ , no driving force is available for nucleation of  $Ni_{10}Zr_7$ . Some algebra leads to the following expression for  $\nabla c_c$ :

$$\nabla c_c = \frac{\rho}{9\sigma} \frac{(-2\Delta G_{pc})^{3/2}}{\alpha^{1/2}} \quad (3)$$

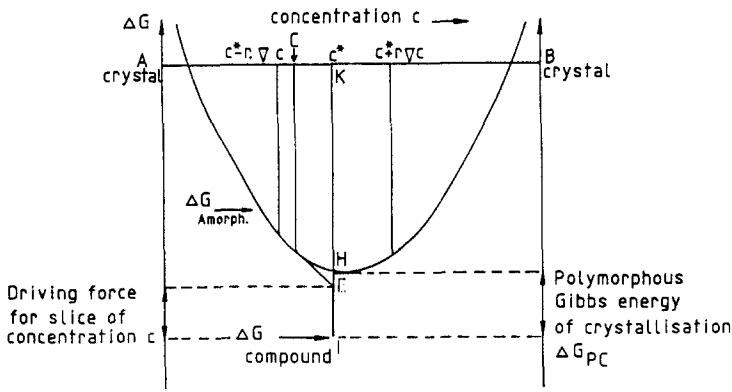


Fig. 2. Gibbs free energies of the amorphous phase under concentration gradient  $\nabla c$ , intermetallic compound at  $c^*$  and the classical tangent construction.

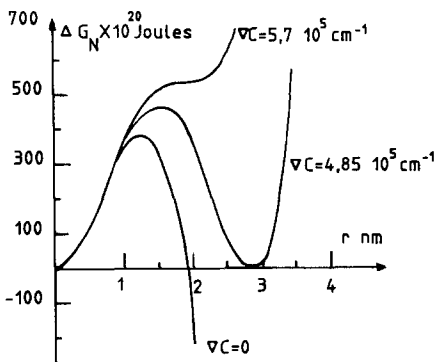


Fig. 3. Gibbs free energy  $\Delta G_N(r)$  of formation of crystal embryo of radius  $r$  with different concentration gradients  $\nabla c$ . For  $\nabla c$  above a critical value,  $\Delta G_N > 0$  and nucleation is disallowed.

Supposing a constant  $\nabla c$  vs.  $x$  in the amorphous layer,  $\nabla c_c$  yields a thermodynamic critical thickness  $e_c$  for a given nucleating compound such that

$$e_c = \Delta c / \nabla c_c$$

where  $\Delta c$  is the concentration range of existence of the amorphous phase. For a cubic nucleus of  $\text{Ni}_{10}\text{Zr}_7$  the critical thickness was found to be of the order of 12 nm.

### 2.2. Effect of the compound Gibbs stability on the critical concentration gradient

In the previous simplified approach, it was supposed that the nucleating compound was perfectly stoichiometric and that its Gibbs energy of formation was represented by a straight line (line compound). This approach has been extended [7] to the more realistic case where the Gibbs energy curve  $\Delta G_c$  associated with the formation of the compound has a definite Gibbs stability at  $c = c^*$  designated by  $\alpha' = (\partial^2 \Delta G_c / \partial c^2)_{c=c^*}$ .

By using the classical tangent rule and optimizing the global driving force for homogeneous crystallization within the amorphous layer, the following expression for the critical gradient is obtained:

$$\nabla c_c = \frac{\rho}{9\sigma_{pc}} \frac{[p^{*2}/\alpha(k-1) - 2\Delta G_{pc}]^{3/2}}{\alpha^{1/2}[(1-1/k)]^{1/2}} \quad (4)$$

where  $k = \alpha'/\alpha$  is the Gibbs stability of the compound over that of the amorphous phase for  $c = c^*$ , and  $p^* = (\partial \Delta G_a / \partial c)_{c=c^*}$  is the slope of the Gibbs energy of the amorphous phase  $\Delta G_a$  at  $c = c^*$ .

It appears clearly from eqn. (4) that a relatively small value of  $k$  or a low Gibbs stability of the compound allowing significant deviations from stoichiometry, as displayed in the phase diagram, increases  $\nabla c_c$  and lowers the critical thickness.

More quantitative analysis of the effect of non-stoichiometry of the compound on the critical concentration gradient has been given elsewhere [7]. Experience proves that binary multilayer systems which have been amorphized by SSR form at higher temperatures, intermetallic compounds which present very small deviations from stoichiometry. This situation is consistent with the previous thermodynamic approach predicting a reduced potential for amorphization of multilayers of binary systems with non-stoichiometric intermetallic crystalline phases.

### 2.3. Compound embryo formation through polymorphous transformation

We have also considered the case when compound embryos are formed from the amorphous phase under  $\nabla c$  without a change in composition. It can be seen in the schematic drawing of Fig. 4 that the free energy for crystallization  $\Delta G_{ac}(c)$  disappears when the sum of the areas with opposing signs between the free energy curves of crystalline and amorphous phases is zero in the composition range of embryo volume. Referring to the previous analysis this means that each slice of amorphous phase of concentration  $c$  in the homogeneous nucleation zone will give a slice of compound of the same composition  $c$ . Starting from the same basic hypothesis mentioned previously, it follows that the

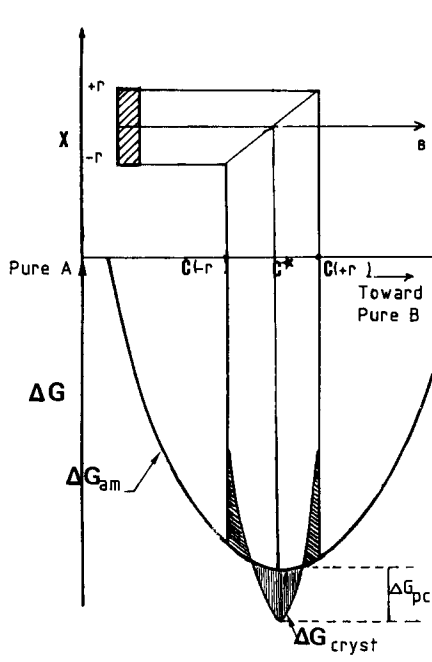


Fig. 4. Schematic drawing of a critical sized nucleus extending along the concentration gradient  $\nabla c$  from  $-r$  to  $+r$ . Polymorphous crystallization may occur only when  $\nabla c$  is low enough so that the shaded area below the  $\Delta G$  curve of the amorphous phase is larger than those above it.

Gibbs energy for the nucleation of a cubic compound embryo is

$$\Delta G'_N = 24\sigma r^2 + 8\rho\Delta G_{pc}r^3 + \frac{4}{3}\rho(\alpha' - \alpha)(\nabla c)^2 r^5 \quad (5)$$

This leads to the following critical concentration gradient:

$$\nabla c_c^{(p)} = \frac{\rho}{9\sigma} \frac{(-2\Delta G_{pc})^{3/2}}{(\alpha' - \alpha)^{1/2}} \quad \text{with } \alpha' > \alpha \quad (6)$$

where (p) indicates polymorphous nucleation.

The greater the Gibbs stability of the compound over the Gibbs stability of the amorphous phase, the smaller the critical concentration gradient. A very similar approach for the polymorphous homogeneous nucleation of a compound in a solid solution under  $\nabla c$  has been developed independently by Gusak [8].

It is of interest to connect the polymorphous critical gradient  $\nabla c_c^{(p)}$  with the value of  $\nabla c_c$  obtained when exchange of matter during nucleation is allowed in the direction perpendicular to the constraint  $\nabla c$ . Taking for simplicity the particular case  $p^* = 0$ , the combination of eqns. (4) and (6) yields:

$$\frac{\nabla c_c^{(p)}}{\nabla c_c} = \left(\frac{\alpha}{\alpha'}\right)^{1/2} \quad (7)$$

a simple relationship which shows in particular that the critical concentration gradient for polymorphous

nucleation is always lower than the critical concentration gradient associated with a nucleation process allowing diffusion perpendicular to the growth direction. Values of  $p^* \neq 0$  will contribute to diminish the difference between  $\nabla c_c^{(p)}$  and  $\nabla c_c$ . For a given value of  $p^* \neq 0$ , the smaller the correction to formula (7) the greater the difference between the Gibbs stability of the compound and the amorphous phase  $\alpha' - \alpha$ .

### 3. Suppression of heterogeneous nucleation of a compound under $\nabla c$ at the amorphous crystal interface

#### 3.1. Case of a cubic nucleus of a perfectly stoichiometric compound

Experimental evidence indicates that compounds nucleate at the parent crystal–amorphous layer interface within the latter phase. Thus it is important to study the influence of the concentration gradient on heterogeneous nucleation of compounds.

When calculating the Gibbs free energy of nucleation on a crystalline substrate of a three-dimensional embryo in an amorphous layer under  $\nabla c$ , two additional factors must be considered:

- (i) the energy of the interface between the substrate and the nucleating compound; globally and following the classical theory of heterogeneous nucleation, the relevant parameter is the contact angle  $\theta$  formed by the compound on the substrate;
- (ii) the concentration difference  $c^* - c_e$  between the nominal concentration of the compound  $c^*$  and the amorphous phase concentration  $c_e$  at the interface.

The same procedure as used for homogeneous nucleation leads [9] to the Gibbs free energy of nucleation of the form:

$$\Delta G_N = 24\sigma(\theta)r^2 + \Delta G_{ac}$$

with

$$\Delta G_{ac} = 4\rho[2\Delta G_{pc} + \alpha(c^* - c_e)^2]r^3 - 8\rho\alpha(c^* - c_e)\nabla c r^4 + \frac{16}{3}\rho\alpha(\nabla c)^2 r^5 \quad (8)$$

Owing to the parameter  $(c^* - c_e)$ , it appears that  $\Delta G_{ac}$  can be positive (no driving force for crystallization) whatever the concentration gradient  $\nabla c$ . This happens when  $(c^* - c_e) < -(2|\Delta G_{pc}|/\alpha)^{1/2}$  and  $(c^* - c_e) > (8|\Delta G_{pc}|/\alpha)^{1/2}$ .

Consequently, it is only in the range  $-(2|\Delta G_{pc}|/\alpha)^{1/2} < (c^* - c_e) < (8|\Delta G_{pc}|/\alpha)^{1/2}$  that a critical gradient  $\nabla c_c$  can be defined. Some algebra leads to the following expression for  $\nabla c_c$ :

$$\nabla c_c = \frac{\rho}{12\sigma(\theta)} \left( \frac{2(-2\Delta G_{pc})^{3/2}}{\alpha^{1/2}} - 2\Delta G_{pc}(c^* - c_e) - \left(\frac{\alpha}{3}\right)(c^* - c_e)^3 \right) \quad (9)$$

This treatment was applied to the nucleation of  $Zr_2Ni$  at the amorphous phase–zirconium crystal interface. Though  $(c^* - c_e)$  is theoretically fully determined by the nominal composition of the compound  $c^*$  and the equilibrium concentration  $c_e$  in the amorphous layer at the interface, it was treated as a parameter because the concentration  $c_e$  is not known accurately.

The results are condensed in Fig. 5 as a diagram of  $\nabla c_c$  vs.  $(c^* - c_e)$ . Since a low energy coherent interface is not expected between  $Zr_2Ni$  and zirconium, we have performed the application for a large contact angle  $\theta = 120^\circ$  with  $\rho(\theta) = \rho(5 - \cos \theta)/6$  for a cubic nucleus.

As shown in Fig. 5,  $\nabla c_c$  presents a maximum  $\nabla c_{cmax}$  for  $(c^* - c_e) = (2|\Delta G_{pc}|/\alpha)^{1/2}$ . This behaviour can be understood as a compensation effect between the concentration gradient and  $(c^* - c_e)$  on the driving force for crystallization. For a given  $\nabla c_c$ , such that  $\nabla c_c$  (for  $c^* - c_e = 0 < \nabla c < \nabla c_{cmax}$ , we can state the following.

- (i) In the range of small  $(c^* - c_e)$ ,  $\nabla c$  yields an average concentration  $\langle c \rangle$  in the amorphous embryo zone at the interface which is too far from the nominal composition  $c^*$ . The driving force for crystallization is thus lowered and the driving force for nucleation cancelled.
- (ii) For higher values of  $(c^* - c_e)$  the average concentration  $\langle c \rangle$  in the embryo zone becomes closer to the nominal concentration  $c^*$  and the driving force for nucleation is restored.
- (iii) Finally, an additional increase in  $(c^* - c_e)$  leads to the limit  $(c^* - c_e) = [8|\Delta G_{pc}|/\alpha]^{1/2}$  above which there is no driving force for crystallization and *a fortiori* no driving force for nucleation.

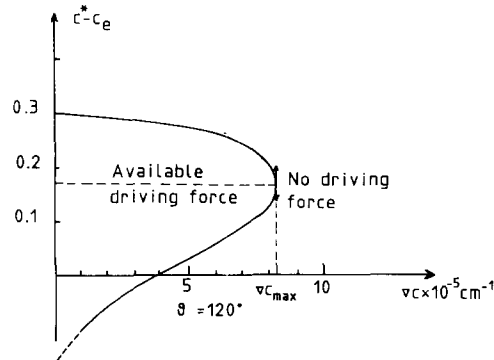


Fig. 5. Locus of points with driving force  $\Delta G_N = 0$  for heterogeneous nucleation in an amorphous phase of concentration  $c_e$ . The curve separates the negative and positive (no) driving force ranges on the  $(c^* - c_e)$  vs.  $\nabla c$  plane.

### 3.2. Generalization to the case of nucleus shape anisotropy and non-stoichiometry of the expected nucleating compound

Most of the intermetallic compounds in binary systems presenting solid state amorphization are complex with highly asymmetric unit cells. Owing to the small atomic mobility of one of the species and the relatively low temperature of experimentation, the complete redistribution of atoms even at the scale of a compound embryo is impeded during SSA. Consequently, in the framework of the present model, the embryo represented by a parallel pipe (see Fig. 1) is expected to present an aspect ratio  $\phi = h/r$  which deviates from equilibrium conditions, for which  $\phi$  would be equal to the interfacial anisotropy:  $s = \sigma^{yz}/\sigma^x$  where  $\sigma^{yz}$  and  $\sigma^x$  are the interfacial energies of the respective planes.

Distinguishing the aspect ratio  $\phi$  from the interfacial anisotropy and including the effect of non-stoichiometry, some algebra leads to the following expression for  $\nabla c_c$ :

$$\nabla c_c = \frac{\rho\phi}{2\sigma^x[\phi(1 - \cos \theta) + 4s]} \left( \left( \frac{p^{*2}}{\alpha'} - 2\Delta G_{pc} \right) (c^* - c_e) - \frac{4\Delta G_{pc}(1 - \alpha/\alpha') + p^{*2}/\alpha'}{3(1 - \alpha/\alpha')^2} \left[ \frac{p^{*2}}{\alpha\alpha'} - \frac{2(1 - \alpha/\alpha')\Delta G_{pc}}{\alpha} \right]^{1/2} - \frac{\alpha}{3} \left( 1 - \frac{\alpha}{\alpha'} \right) (c^* - c_e)^3 - p^* \frac{\alpha}{\alpha'} (c^* - c_e)^2 - \frac{p^*}{(1 - \alpha/\alpha')^2 \alpha'} \left\{ 2\Delta G_{pc}(1 - \alpha/\alpha') - p^* \times \left[ \frac{p^{*2}}{\alpha\alpha'} - \frac{2(1 - \alpha/\alpha')\Delta G_{pc}}{\alpha} \right]^{1/2} - \frac{p^{*2}}{\alpha'} \left( 1 + \frac{\alpha}{3\alpha'} \right) \right\} \right) \quad (10)$$

Such a complicated expression reduces simply to relation (9) for  $\phi = 1$ ,  $s = 1$  and  $\alpha' = \infty$ . Let us focus application of the general expression (10) for  $\nabla c_c$  on the effect of anisotropy for the heterogeneous nucleation of  $Ni_{10}Zr_7$  at the amorphous phase–zirconium layer interface. With  $\phi = 0.2$  (needle-like crystals of  $Ni_{10}Zr_7$  have been observed during crystallization of an amorphous phase [6]) and  $s \approx 1$ , the thermodynamic critical thickness is of the order of four times its value for the equilibrium condition  $\phi = s$ .

A full application of relationship (10) to a practical example is hardly possible owing to inaccuracy in the knowledge of the different parameters contained in this expression. However, analysis of the influence of  $c^* - c_e$  on  $\nabla c_c$  would yield  $\nabla c_c$  vs.  $(c^* - c_e)$  with the same shape as given in Fig. 5 with a maximum in  $\nabla c_c$  and a limited range of  $(c^* - c_e)$  in which  $\nabla c_c$  can be defined. Furthermore, relation (10) shows that deviations from

stoichiometry increase the critical concentration gradient.

#### 4. Discussion and conclusion

It has been established that concentration gradients developing in amorphous interlayers during solid state amorphization of binary AB type multilayers increase the stability of amorphous phases against homogeneous and heterogeneous nucleation of intermetallic compounds. This yields a thermodynamic critical thickness for the amorphous layer below which nucleation is not possible. From a general point of view, the greatest amorphous phase stability is obtained when the Gibbs energy associated with the establishment of long-range order ( $|\Delta G_{pc}|$ ) is small compared with the Gibbs stability  $\partial^2 G_a / \partial c^2$  which reflects globally the importance of the chemical short-range order (CSRO). Such an approach demonstrates that the classical criterion  $\Delta H_{mix} \ll 0$  is not only significant for glass forming ability but also for amorphous phase metastability during growth under a concentration gradient by solid state reaction in thin film configuration. Mechanical alloying experiments have shown that amorphization of mixtures of some pure metals becomes possible even for systems with small enthalpies of mixing ( $\Delta H_{mix} \approx 0$ ). In this case, the entropy contribution to the Gibbs stability of the amorphous phase gives a small thermodynamic critical thickness (of the order of 2 nm). On the basis of this critical concentration gradient effect, it has been proposed [10] that simultaneous diffusive layer growth and thickness reduction during deformation cycles by mechanical alloying can result in amorphization in near constant and small layer thicknesses.

The effect of sharp concentration gradients in an amorphous layer on the driving force for crystallization has been extended recently [11] to ternary systems from the same thermodynamic approach used for binary systems. A critical concentration gradient was defined

along the diffusion path in the ternary amorphous layer. Under certain conditions connected with the strength of heteroatomic bonding of the constituent atoms of the binary systems it was foreseen that a ternary effect may lower the critical concentration gradient, thus increasing the metastability of the amorphous layer. In order to demonstrate this effect, solid state amorphization was induced in cold rolled multilayers of Cu<sub>50</sub>Ni<sub>50</sub> (at.%) and zirconium [11]. The results were compared with those obtained with binary NiZr interlayers. The initial thicknesses of the crystalline layers in both cases were similar. All of the initial unmixed layers were amorphized before the onset of crystallization in the ternary system but not in the binary configuration.

These latest results are consistent with the model's thermodynamic predictions and implicitly strengthen the validity of the general thermodynamic approach presented here which is the suppression of compound nucleation in amorphous layers under sufficiently sharp concentration gradients.

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