

STABILITY OF THE AMORPHOUS INTERLAYERS DURING S.S.A.R. AGAINST HOMOGENEOUS AND HETEROGENEOUS NUCLEATION

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Résumé - A partir d'arguments thermodynamiques simples, nous démontrons que les forts gradients de concentration ∇C présents dans les multicouches facilitent l'amorphisation par réaction en phase solide en réduisant ou supprimant le moteur thermodynamique ΔG_{ac} de la cristallisation. Lorsque ces gradients baissent avec la croissance de la couche amorphe, le moteur pour la cristallisation est rétabli ; ce qui donne une épaisseur critique maximum pour la couche amorphe comme on observe expérimentalement. Les mécanismes de nucléation homogène et hétérogène sont considérés. l'effet mis en évidence croît avec la courbure dans l'espace concentration de l'énergie libre ΔG de la formation de l'alliage amorphe. Dans le cas de la germination hétérogène de composés de concentration ayant un écart ΔC^* avec celle de l'amorphe à l'interface site de germination, nous traçons la région dans l'espace $(\Delta C^*, \nabla C)$ dans laquelle le moteur thermodynamique pour la cristallisation est nul. Le développement est appliqué au système modèle NiZr.

Abstract - Using simple thermodynamic arguments, it is shown that sharp concentration gradients ∇C occurring during diffusive mixing in multilayers facilitate amorphisation by solid state reaction by reducing or suppressing the driving force for crystallisation ΔG_{ac} . As the concentration gradients diminish during the amorphous layer growth, the driving force for crystallisation is restored. This evolution yields a critical maximum amorphous layer thickness as observed experimentally. Both homogeneous and heterogeneous nucleation of compounds are considered. It is shown that the effect increases with the second concentration derivation of the Gibbs free energy ΔG of formation of the amorphous phase. For heterogeneous nucleation of a compound of nominal concentration differing by ΔC^* for that of the amorphous phase at interface serving as nucleation site, the contours of the domain in $(\Delta C, \nabla C^*)$ space where no driving force for nucleation is available have been derived out and applied to the Ni-Zr system.

INTRODUCTION

Since the early results of R.B. Schwarz and J.W. Johnson /1/ amorphisation by solid state reaction (SSAR) has been observed in many binary multilayers systems. It is now admitted that amorphous phases form from bimetallic layers when chemical affinity between the two compounds is strong (highly negative enthalpy of mixing ΔH_{mix}) and when there is a significant asymmetry in the atomic mobilities. In thin film configurations certain metastable phases may grow at the expense of the thermodynamically more stable phases as the system attempts various paths toward equilibrium. Critical thicknesses for such transient amorphous phases have been observed experimentally. Several explanations and predictions for the existence of such critical thicknesses have been given. Approaches based on the kinetics of nucleation in the steady state /2/ and the incubation (transient) regime /3/ have shown that amorphous layers can grow to a critical thickness during the "crystal phase minimum nucleation time". On the base of kinetic stability analysis and principle of maximum degradation rate of the Gibbs energy /4/. U. Gosele and K.N. Tu /5/ proposed an approach which examines two different possible situations (represented on a Gibbs energy diagram) for the relative stability of the amorphous phase compare to the expected

nucleating compound. This attempt which does not account for the effect of creating new interfaces when nucleation proceeds leads to a lower limit for the critical thickness.

Using simple thermodynamic arguments it will be demonstrated in the present approach that the sharp concentration gradient set up within amorphous interlayer growing by solid state reaction, improves the metastability of the amorphous phase by eliminating or reducing the driving force ΔG_{ac} for nucleation of intermetallic compounds. This effect increases with increasingly negative ΔH_{mix} and Gibbs energy of alloying ΔG .

As diffusive mixing proceeds further, during amorphous layer growth, the concentration gradient flattens out and the thermodynamic driving force for crystalline phase formation is gradually restored. This evolution yields a thermodynamic critical thickness for compound nucleation /6/.

It has been shown experimentally that heterogeneous nucleation can take place at the interface of amorphous layer with the crystalline parent phase of the slow diffusing species. As such both homogeneous and heterogeneous compound nucleation in the amorphous layer, will be treated in this paper.

1 - EFFECT OF SHARP CONCENTRATION GRADIENTS ON HOMOGENEOUS NUCLEATION OF COMPOUNDS IN THE AMORPHOUS LAYER.

Let us consider an amorphous layer of a binary AB alloy in which a concentration gradient is set up.

For a strictly stoichiometric $A_c \cdot B_{1-c}$ intermetallic compound to nucleate, embryos of the crystalline compound must attain a critical size r^* as determined by the classical theory of homogeneous nucleation. Figure 1 shows a schematic drawing of such cubic critical nucleus together with the unidirectional concentration gradient ∇C along x and the free energy $G_A(C)$ curves for the amorphous and the intermetallic phase. $C(-r^*)$ and $C(+r^*)$ indicate the concentrations in the amorphous phase at the two end of the critical nucleus of dimension $2r^*$ along ∇C . For the

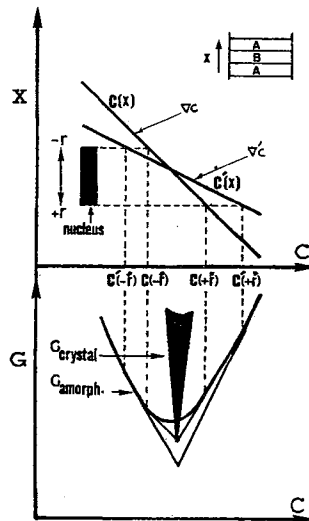


Fig. 1 - Gibbs free energy tangent constructions for compositions at the tips of the critical nucleus of intermetallic phase in an amorphous layer subject to concentration gradient ∇C .

nucleus to attain this critical size, the tangents to $G_a(C(-r^*))$ and $G_a(C(+r^*))$ of the amorphous phase free energy curve must touch the $G_{crystal}$ curve of the intermetallic compound. It can be seen that for a sufficiently sharp gradient ∇C , the tangents from $C(-r^*)$ and $C(+r^*)$ will miss the tip of the $G_{crystal}$ curve of the intermetallic compound and embryos of the latter will not attain the critical size. As long as the concentration gradient remains above a certain critical value the intermetallic phase will not be able to nucleate. On the base of a simple model of the crystalline embryo /6/, a quantitative approach of this effect is given in the following.

Using the thermodynamic approach of J.W. Cahn for non-uniform systems /7/, the Gibbs free energy of a volume v of the amorphous layer can be written as :

$$G_a(v) = \rho \int_v [G_0(C) + N_a \chi (\nabla C)^2] dv \quad \text{where } \rho \text{ is the number of moles of atoms per unit volume,}$$

N_a is Avagadro's number and χ is a constant. $G_0(C)$ is the Gibbs energy per mole of an amorphous phase of uniform composition c .

The driving force for crystallisation, at constant ρ , of a compound of composition C^* is then :

$$\Delta G_{ac}(v) = \rho \int_v \{ \Delta G_m - N_a \chi (\nabla C)^2 \} dv \quad (1)$$

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

$\mu_A^s(c^*)$, $\mu_B^s(c^*)$, $\mu_A^a(c)$, $\mu_B^a(c)$ are respectively the chemical potentials in the compound (s) and in the amorphous (a).

i) At first we treat the case of a **cubic nucleus** with cube edge equal to $2r$ ($h=r$ in figure 2). ∇C is supposed to be constant and unidirectional along x , normal to the A and B layers. In view of optimising the driving force for homogeneous nucleation, the plane parallel to the layers and passing through the center of the nucleus is taken to be at concentration C^* .

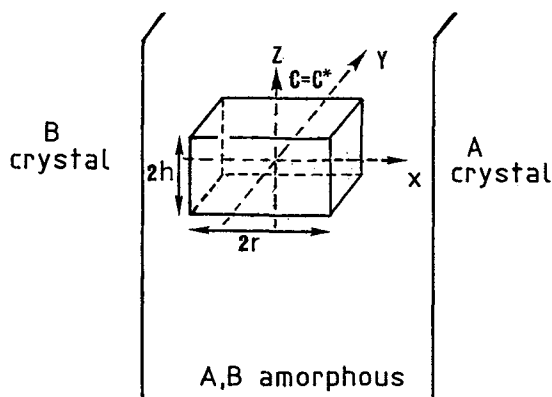


Fig. 2 - Parallel pipe or cube ($h=r$) shaped intermetallic phase nucleus in amorphous layer. r is parallel to concentration gradient ∇C along x .

These conditions lead to the more condensed form of (1) :

$$\Delta G_{ac}(v) = 4\rho r^2 \int_{-r}^{+r} \Delta G_m [c(x)] dx - 8\rho r^3 N_a \chi (\nabla C)^2 \quad (2)$$

Changing the integration variable from x to C , using $C(-r) = C^* - r \cdot \nabla C$ and $C(+r) = C^* + r \cdot \nabla C$ yields :

$$\Delta G_{ac}(v) = \frac{4\rho r^2}{\nabla C} \int_{C^*-r \cdot \nabla C}^{C^*+r \cdot \nabla C} \Delta G_m [c(x)] dC - 8\rho r^3 N_a \chi (\nabla C)^2 \quad (3)$$

Figure 3 represents the molar Gibbs free energies of formation of both amorphous phase and compound versus concentration.

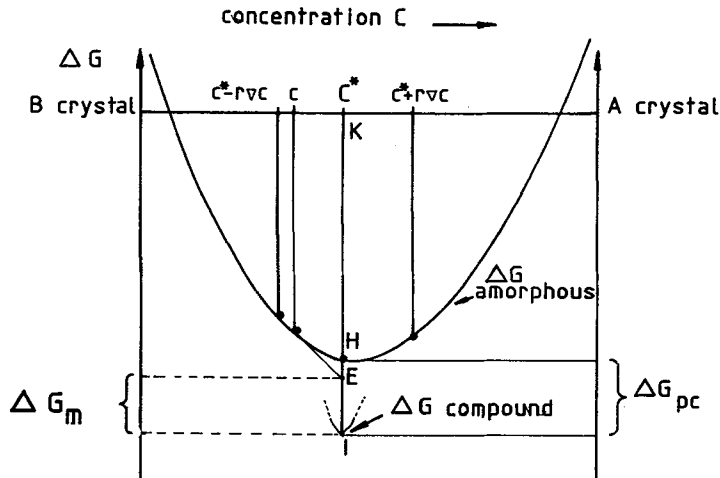


Fig. 3 - Gibbs free energies of formation of amorphous phase and intermetallic compound of composition C^* .

From the classical tangent rule, the segment $\overline{EI} = \Delta G_m$ is the molar driving force for crystallisation of an amorphous phase of composition C into the compound of composition C^* . \overline{EI} can be subdivided as $\overline{EI} = \overline{KI} - \overline{KE} = \overline{KI} - (\overline{KH} + \overline{HE}) = \overline{KI} - \overline{KH} + \overline{EH}$ where $\overline{KI} - \overline{KH} = \Delta G_{pc}$ is the Gibbs free energy for polymorphous crystallisation at $C = C^*$ and $\overline{EH} = \Delta G_{fl}$ is the molar Gibbs free energy associated with a concentration fluctuation $(C^* - C)/8$. A series development of ΔG_{fl} to second order in $(C - C^*)$ leads to :

$$\Delta G_{fl}(C) = \frac{1}{2} (C - C^*)^2 \left(\frac{\partial^2 \Delta G}{\partial C^2} \right) + \dots \quad (4)$$

as the first order term C^* in $(C - C^*)$ cancels from a straight forward application of thermodynamics and ΔG is the molar Gibbs free energy of formation of the amorphous alloy from pure crystalline A and B. It is assumed that no phase separation occurs in the composition range of the amorphous layer such that $(\partial^2 \Delta G / \partial C^2)$ is a positive quantity.

Using $\Delta G_m.[c(x)] = \Delta G_{pc} + \Delta G_{fl}$ to integrate (3), we obtain :

$$\Delta G_{ac}(v) = 8\rho[\Delta G_{pc}(C^*) - N_a \chi (\nabla C)^2].r^3 + \frac{4}{3}\rho\alpha(\nabla C)^2. r^5 \quad (5)$$

where $\alpha = (\partial^2\Delta G/\partial C^2)$ has been supposed to be constant in the range $C^* - r\nabla C < C < C^* + r\nabla C$.

We note that the second term in (5) is positive and varies with the fifth power of the embryo size r . It also increases with the second derivative of the ΔG of alloying which measures the **Gibbs metastability** of the amorphous phase. Finally, the Gibbs free energy of formation of an embryo of the compound $A_{C^*}.B_{1-C^*}$ which includes the classical interfacial term is given by :

$$\Delta G_N = 24 \sigma_{pc}.r^2 + 8\rho[\Delta G_{pc}(C^*) - N_a \chi (\nabla C)^2].r^3 + \frac{4}{3}\rho\alpha (\nabla C)^2.r^5 \quad (6)$$

where the interfacial energy σ_{pc} at the polymorphous crystallisation front is at first supposed to be isotropic.

We take as example, the homogeneous nucleation of $Ni_{10}Zr_7$, which is the stable crystallisation product in glassy $Ni_{64}Zr_{36}/2/$, in an amorphous layer under a concentration gradient ∇C . The enthalpy of crystallisation of amorphous $Ni_{10}Zr_7$ obtained by calorimetric measurements /9/ is $\Delta H_{pc} = -4,5$ kJ/mole. Neglecting the entropic contribution by virtue of the Kauzmann argument /10,11/, we use : $\Delta G_{pc} \cong -4,5$ kJ/mole. A crude evaluation of Cahn's term, $N_a \chi (\nabla C)^2$ in relation (6) yields from the regular solution approximation $N_a \chi (\nabla C)^2 = \lambda(a^2/2) (\nabla C)^2$ where λ is the classical regular solution parameter and "a" is of the order of the interatomic distance /7/.

With $\lambda \cong -200$ kJ/mole for $NiZr$ /12/, $a = 3\text{\AA}$ and $\nabla C = 6 \times 10^5/\text{cm}$ (of the order of the gradients which will be considered later), we obtain $N_a \chi (\nabla C)^2 \cong -33$ J/mole which is less than 1 % of ΔG_{pc} . The interfacial energy σ_{pc} is not known experimentally. Skapski's model /13/ for liquid-solid alloy interfacial energy σ_{sl} , using a linear approximation from the pure component σ values, yields $\sigma_{pc} = 270$ mJ/m². Another possibility is to approximate σ_{pc} by σ_{sl} and following Waren /14/ to write $\sigma_{sl} \cong \sigma_{lv}/5.25$ where σ_{lv} is the pure component liquid surface energy at its melting temperature (relationship obtained when supposing perfect wetting condition of a pure solid by its melt). To obtain σ_{sl} at the amorphisation temperature $T \cong 560$ K, we use a temperature extrapolation with $d\sigma/dT = -0.1$ mJ/m²K for Zr (as the experimental value is not known /15/) and $d\sigma/dT = -0.3$ mJ/m²K for Ni /15/. This together with a linear extrapolation from the pure component values gives $\sigma_{pc} \cong 370$ mJ/m². We have used for the present application of equation (6), the value $\sigma_{pc} = 300$ mJ/m². The value of $\alpha = 468$ kJ/mole ($T = 560$ K) has been calculated from available thermodynamic data for liquid $NiZr$ /12/. With $\rho = 0.105$ moles of atoms per cm³ of $Ni_{10}Zr_7$, ΔG_N in (6) becomes :

$$10^{20} \Delta G_N (r) = 7.20 r^2 - 0.38 r^3 + 6.55 \times 10^{-16} (\nabla C)^2 .r^5 \quad (7)$$

where r in Angstroms (0.1nm) yields $\Delta G_N (r)$ in Joule units as given for three different ∇C values plotted versus r in figure 4. For a critical gradient $\nabla C_c = 4.85 \times 10^5/\text{cm}$, no negative value of ΔG_N is obtained and the minimum is attained at $\Delta G_N = 0$. This implies that for $\nabla C > \nabla C_c$, no driving force is available for nucleation of $Ni_{10}Zr_7$. Furthermore, the minimum in $\Delta G_N (r)$ versus r no longer occurs in the ∇C range greater than $5.7 \times 10^5/\text{cm}$.

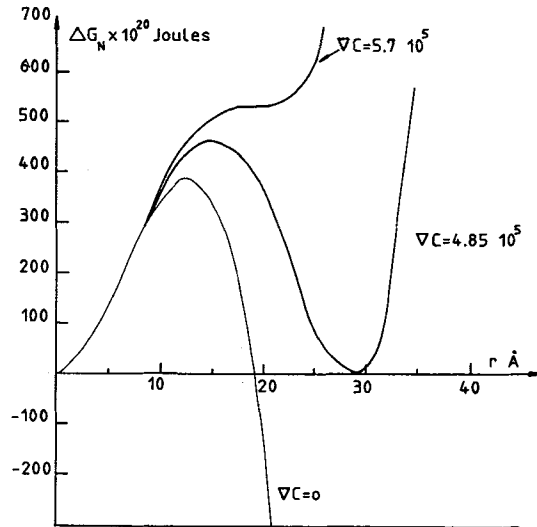


Fig. 4 : Gibbs free energy $\Delta G_N(r)$ of formation of crystalline embryo of radius r in amorphous phase with different concentration gradients ∇C . For ∇C above a critical value, $\Delta G_N > 0$ and nucleation is disallowed.

Since the total concentration variation across the amorphous layer is of the order of $\Delta C = 0.6$, the critical concentration gradient corresponds to a critical thickness $\epsilon_c \approx 0.6 / \nabla C_c$ of the amorphous phase forming by solid-state reaction across which crystallisation is thermodynamically disallowed. For $\nabla C_c \approx 5 \times 10^5 / \text{cm}$, we obtain a thermodynamic critical thickness $\epsilon_c \approx 120 \text{\AA}$ for the nucleation of a cubic nucleus.

The crystal structures of the NiZr intermetallic compounds are complex, often orthorhombic with highly asymmetric unit cells. The growth morphology of $\text{Ni}_{10}\text{Zr}_7$ from the amorphous phase is known to be anisotropic resulting in needle like crystals with aspect ratios greater than 100. This brings us to extend the previous analysis to anisotropic nucleation.

ii) We consider the effect of the nucleus shape anisotropy on the Gibbs energy of nucleation. The nucleus is represented by a parallel pipe as shown in figure 2 with aspect ratio $\phi = h/r < 1$ and the length $2r$ along ∇C . This shape has been chosen considering that the more rapid growth direction is expected to be oriented along the concentration gradient. In fact, the very small mobility of one of the species (Zr) at the relatively low temperature of experimentation does not help concentration redistribution even at the scale of a compound embryo. Consequently the embryo is expected to present an aspect ratio ($\phi = h/r$) which deviates from equilibrium conditions, for which ϕ would be equal to the interfacial anisotropy factor defined as $s = \sigma_{P,C}^{y,z} / \sigma_{P,C}^x$ ($\sigma_{P,C}^{y,z}$ et $\sigma_{P,C}^x$ are respectively the interfacial energies of the planes along and perpendicular to ∇C).

In addition to the anisotropy of the crystal structure itself the aspect ratio will be governed by the privileged growth direction of the embryo which is the ∇C direction : the most favorable conditions for growth of the embryo are those that do not require solute redistribution by keeping the growth tip at the nominal concentration C^* . As the interlayer amorphous phase thickness grows the gradient ∇C diminishes while simultaneously and the nominal growth tip concentration C^* can be kept constant in the ∇C direction. On the contrary for directions perpendicular to ∇C the concentration in the amorphous surroundings increasingly differs from C^* as the

interlayer amorphous phase thickness increases. These considerations lead us to distinguish, in the thermodynamic treatment of the nucleation under ∇C in the amorphous layer, the aspect ratio $\phi = h/r$ from the interfacial anisotropy factor : s.

The same procedure leading to (6) yields :

$$\Delta G_N(\phi, s) = 8\phi(\phi+2s) \cdot \sigma_{pc}^x \cdot r^2 + 8\rho \cdot \phi^2 \cdot \Delta G_{pc}(C^*) \cdot r^3 + \frac{4}{3} \rho \cdot \alpha \cdot \phi^2 \cdot \alpha \cdot \nabla C^2 \cdot r^5 \quad (8)$$

For metallic systems, the interfacial anisotropy factor is expected to vary between 0.7 and 1. When relation (8) applied to the nucleation of $Ni_{10}Zr_7$ with $\sigma_{pc}^x = 300 \text{ MJ/m}^2$ and $\phi = 0.2$, the critical concentration gradient is found to be $\nabla C_c = 1.8 \times 10^5$ for $s = 0.7$ and $\nabla C_c = 1.3 \times 10^5$ for $s = 1$ leading respectively to critical thicknesses (with $\Delta C = 0.6$) $\epsilon_c \cong 330 \text{ \AA}$ and 460 \AA which are somewhat lower than calculated previously /6/. We note that for $\phi = 1$ (cubic nucleus) the critical layer thickness is only 120 \AA (12nm). This is consistent with TEM observations /16/ of a thickness of $\cong 200 \text{ \AA}$ for the amorphous interlayer at a Pt/Al interface which crystallizes into cubic Al_2Pt /17/ and for which no shape anisotropy of nucleus is expected. Considering the results in figure 4 which indicate that the effect of the sharp concentration gradients persist at higher thicknesses (lower ∇C), in which the energy barrier to nucleation is nevertheless higher than in the absence of ∇C , the present predictions are consistent with the fact that homogenous nucleation of such compound crystals inside the NiZr (and similar) amorphous layers formed by solid-state reaction has never been experimentally detected. TEM observations indicate on the contrary, that crystallisation occurs by heterogeneous nucleation at the amorphous-pure Zr interface. Consequently, we are lead to study the influence of the concentration gradient on the heterogeneous nucleation of a compound at the amorphous layer parent crystal interface.

2. EFFECT OF SHARP CONCENTRATION GRADIENTS ON HETEROGENEOUS NUCLEATION OF COMPOUND IN AN AMORPHOUS LAYER.

When calculating the Gibbs energy of nucleation on a crystalline substrate of a 3-dimensional embryo (which is supposed to be cubic for simplicity).in an amorphous layer under concentration gradient ∇C , we have to take account of two additional factors :

i) the energy of the interface between the substrate (which can be the parent Zr-phase in the multilayer amorphisation process of NiZr) and the nucleating compound. Globally and following the classical theory of heterogeneous nucleation the relevant parameter is the contact angle θ formed by the compound on the substrate.

ii) the concentration difference $\Delta C^* = C^* - C_e$ between the nominal concentration of the compound C^* and the concentration C_e in the amorphous at the interface. Since the embryo is constrained to form at the interface it is easily understood that the concentration gradient ∇C will act on ΔG_N and that ΔC^* is the relevant parameter for describing such an effect.

The same procedure as used for homogeneous nucleation leads to the Gibbs energy of crystallization of the form :

$$\Delta G_{ac} = \frac{4\rho r^2}{\nabla c} \int_{C=C_e}^{C=C_e+2r\nabla c} \Delta G_m [c(x)] dC \quad (9)$$

where the Cahn's term has been neglected.

The classical procedure used for heterogeneous nucleation and applied to the present simple model with a cubic embryo leads to an effective $\sigma_{pc}(\theta) = \sigma_{pc}(5-\cos\theta)/6$ which can be substituted for σ_{pc} in the interfacial term of the Gibbs energy of nucleation given by (6).

The dependence of σ_{pc} on θ appears to be somewhat arbitrary for a cubic embryo placed on the substrate. But the present definition of the effective $\sigma_{pc}(\theta)$ results from an interfacial energy balance and its θ dependence comes indirectly from the application of the Young's relationship which relates the amorphous compound interfacial energy σ_{pc} to the difference between the compound-substrate and the amorphous-substrate interfacial energies.

The concentration limits for the integration are C_e , at the crystal amorphous interface and the concentration $C_e+2r\nabla c$ for the edge of a cubic embryo of size $2r$ placed in a concentration gradient ∇C (supposed to be constant between the concentration limits).

Using the classical tangent rule for the crystallization driving force and the quadratic form (4) for the Gibbs energy associated with the concentration fluctuation, the following expression for ΔG_N is obtained :

$$\Delta G_N = 24 \sigma_{pc}(\theta) r^2 + 4\rho[2\Delta G_{pc} + \alpha(\Delta C^*)^2].r^3 - 8\rho\alpha\Delta C^*.\nabla C .r^4 + \frac{16}{3}\rho\alpha (\nabla C)^2.r^5 \quad (10)$$

It is noteworthy that the r^3 term for ΔG_N can be either negative or positive according to the sign of the $2\Delta G_{pc} + \alpha(\Delta C^*)^2$. The particular case where $\Delta C^* = [2\Delta G_{pc}/\alpha]^{1/2}$ which cancels this r^3 term will be discussed later. Note also that only the r^4 and r^5 term in (10) are ∇C dependant.

This formulation has been applied to the nucleation of Zr_2Ni (Tetragonal Al_2Cu type) at the amorphous-Zr crystal interface. As the concentration $C_{Ni} = C_e$ at the interface is not known accurately ΔC^* has been treated as a parameter.

The same data sources as for homogeneous nucleation have been used for this application.

As a low energy coherent interface is not expected between the compound Zr_2Ni and the parent phase Zr, we have performed the application for a large contact angle $\theta = 130^\circ$. The results are condensed in a diagram ΔC^* versus concentration gradient ∇C represented in figure 5. The curve $\Delta C^*=f(\nabla C)$ is the locus of points for which the Gibbs energy of nucleation $\Delta G_N(r)$ has the feature represented in the inset of figure 5. Such curve delimits the contour of the domain, in the $(\Delta C^*, \nabla C)$ space, where there is no driving force for nucleation. It is noteworthy that this contour curve presents a "nose" (a maximum in ∇C) which corresponds to the particular value $\Delta C_c^* = [2\Delta G_{pc}/(\partial^2\Delta G/\partial C^2)]^{1/2}$ which as previously mentioned, cancels the r^3 term coefficient in the expression of ΔG_N (10).

The following explanation can be given for the features of the curve $\Delta C^*=f(\nabla C)$. Suppose that ∇C has the constant value represented by the arrow in the figure 5 and that the embryo size is fixed. Consequently the average concentration $\langle C \rangle$ in the corresponding volume of the amorphous phase is imposed. Let us vary ΔC^* (or C^* considering C_e constant for the present purpose) starting from zero. For small C^* , the as-fixed average

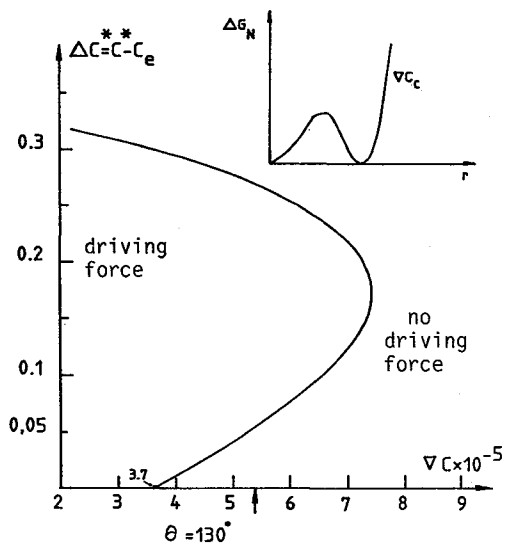


Fig. 5 - Locus of points $\Delta C^* = f(\nabla C)$ where the Gibbs energy of nucleation $\Delta G_N(r)$ has the feature represented in the upper part (no driving force for nucleation).

concentration $\langle C \rangle$ is much greater than the nominal concentration C^* for driving force to be available (very few tangents to the Gibbs energy of the amorphous phase touch the tip of $G_{crystal}$). For higher C^* the average concentration $\langle C \rangle$ becomes closer to the nominal composition and the driving force is restored. After more increase in C^* , $\langle C \rangle$ becomes too small and again there is no global driving force.

When ∇C becomes greater than the maximum value in ∇C versus ΔC , the average concentration $\langle C \rangle$ will always deviate too much from any possible nominal composition and there is no more driving force.

In order to display the possible competition between homogeneous and heterogeneous nucleation of the same compound Zr_2Ni we have reported in figure 6 the Gibbs energy barrier versus ∇C for the two mechanisms with

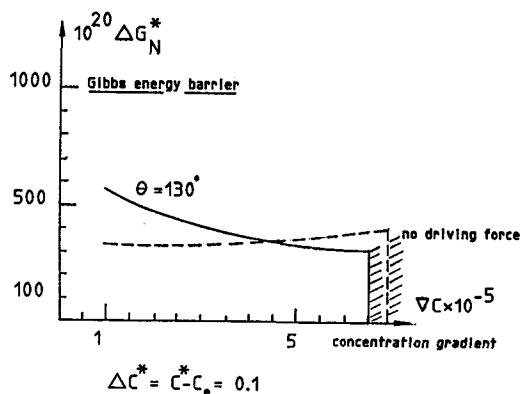


Fig. 6 - ——— Gibbs energy barrier for heterogeneous nucleation $\theta = 130^\circ$ (Zr_2Ni).
 - - - - - Gibbs energy barrier for homogeneous nucleation (Zr_2Ni).

$\theta = 130^\circ\text{C}$ and $\Delta C^* = 0,1$. (As the concentration in the amorphous phase at the amorphous-parent phase interface is not accurately known the value $\Delta C^* = 0,1$ has been chosen from the application of the Egami criterion [18] which gives the concentration limits for the metastability of the amorphous phase).

Figure 6 shows that, under the previously defined conditions for heterogeneous nucleation of Zr_2Ni , the energy barriers corresponding to the two mechanisms are comparable and that the driving force disappears approximatively for the same concentration gradient. Also, the reverse sense of the variation of the energy barrier with ∇C for homogeneous and heterogeneous nucleation has to be noted. More generally, a complete analysis of the heterogenous nucleation, lead on the base of relation (10), allows to state that for $\Delta C^* \neq 0$ the concentration gradient enhance heterogeneous nucleation by lowering the energy barrier until the critical concentration gradient is attained, the greater ΔC^* the higher this effect.

In conclusion it has been established that the concentration gradients set up in the amorphous layer affect sensitively the thermodynamic conditions for nucleation.

For the homogeneous nucleation mechanism there is a critical concentration gradient ∇C_c above which there is no driving force for nucleation of a compound. For different compounds the smaller the ratio $\Delta G_{pc}/(\partial^2 \Delta G/\partial C^2)$, the smaller the critical gradient and the higher the thermodynamic critical thickness.

For heterogeneous nucleation of a given compound, a domain can be delimited in the $(\Delta C^*, \nabla C)$ space where a driving force is available. The contour of this domain presents a nose at $\Delta C_c^* = [2|\Delta G_{pc}|/(\partial^2 \Delta G/\partial C^2)]^{1/2}$. Again it is found that the smaller $(\Delta G_{pc}/\partial^2 \Delta G/\partial C^2)$ the smaller the domain of a non zero driving force.

It is commonly admitted that binary systems with strongly negative enthalpies of mixing are better candidates for multilayers amorphisation. This property constitutes the classical thermodynamic criterion for solid state amorphisation. Strongly negative ΔH_{mix} means also highly positive value for $\partial^2 \Delta G/\partial C^2$ (as it can be seen in the simple case of regular solutions where $\partial^2 \Delta G/\partial C^2 = [RT/C(1-C)].[1-2\Delta H_{\text{mix}}/RT]$). Consequently the present approach demonstrates that the criterion $\Delta H_{\text{mix}} \ll 0$ is not only significant for glass forming ability but also for the amorphous phase metastability during growth under a concentration gradient. More specifically the greatest amorphous phase metastability is obtained when the Gibbs energy associated with establishment of long range order $|\Delta G_{pc}|$ is small compared with the second derivative versus concentration of the Gibbs energy of formation of the amorphous $\partial^2 \Delta G/\partial C^2$ which measures the intrinsic stability of the amorphous and reflects, in a sort, the importance of the chemical short range order in the amorphous phase.

Obviously the present approach does not contradict the kinetic treatments leading to effective critical thicknesses in the multilayer amorphisation process and connected with the low atomic mobility of one of the parent phase.

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