

Effect of sharp concentration gradients on the nucleation of intermetallics in disordered solids: influence of the embryo shape

By F. HODAJ†, A. M. GUSAK‡ and P. J. DESRÉ†

† Laboratoire de Thermodynamique et Physico-Chimie Métallurgiques, UMR, CNRS–Institut National Polytechnique de Grenoble–Université Joseph Fourier, BP 75, 38402 Saint Martin d'Hères, France

‡ Cherkassy State University, Department of Theoretical Physics, Shevchenko Street 81, Cherkassy 257017, Ukraine

[Received 7 August 1997 and accepted in revised form 14 October 1997]

ABSTRACT

This work, which concerns the effect of unidirectional sharp concentration gradients on the nucleation of intermetallics in amorphous layers or in supersaturated solid solutions, is focused on the embryo shape. The study leads to a new analysis of the critical concentration gradient beyond which the nucleation driving force is suppressed. Owing to the fluctuations in the embryo shape, it is shown that the minimization of the thermodynamic potential leading to the equilibrium aspect ratio of a parallelepiped-shaped embryo is only possible above a certain value of the concentration gradient. Beyond such a concentration gradient, the embryo aspect ratio is found to deviate significantly from that given by the Wulff conditions. Application is presented to the nucleation of the compounds Al_3Ni and $\text{Ni}_{10}\text{Zr}_7$ in a supersaturated Al–Ni solid solution and in a Ni–Zr amorphous layer respectively.

§ 1. INTRODUCTION

The effect of unidirectional sharp concentration gradients on the nucleation of intermetallic compounds either in amorphous layers obtained by solid-state reaction or in supersaturated solid solution has been studied and discussed since the beginning of the 1990s (Desré and Yavari 1990, Gusak 1990, Desré 1991, Hodaj and Desré 1996). Firstly it has been shown, from a pure thermodynamic approach that, under certain conditions, there is a critical concentration gradient beyond which intermetallic nucleation is suppressed. One of the conclusions of these studies is that the existence of such a critical gradient depends upon different possible mechanisms of formation of the embryos. These are as follows.

Mechanism I is polymorphic nucleation with frozen diffusion (Gusak 1990), which means that the expected intermetallic embryo would conserve the same concentration gradient as in the parent phase.

Mechanism II is nucleation by transverse diffusion (Desré 1991), where the embryo is fed by diffusion in a direction perpendicular to the unidirectional concentration gradient.

Mechanism III is nucleation by total mixing of atomic layers in the nucleation zone (Hodaj and Desré 1996).

Mechanism IV is nucleation by a combination of mixing mechanism and transverse diffusion (Hodaj and Desré 1996).

After some algebra and in the simple case where the embryo is of cubic shape of dimension $2r$, with no anisotropy of the interface energy, the Gibbs energy associated with the formation of an embryo is given by the following equation:

$$\Delta G_n = 8\rho \left(\Delta G_{pc} - \frac{p^{*2}}{2(\alpha - \alpha')} \right) r^3 + 24\sigma r^2 + \gamma_i (\nabla c)^2 r^5. \quad (1)$$

ΔG_{pc} is the polymorphic Gibbs energy associated with the transformation from parent phase to intermetallic. ρ is the number of moles of atoms per unit volume; σ is the interfacial free energy; $p^* = (\partial \Delta G_g / \partial c)_{c^*}$ is the slope of the tangent to the Gibbs energy of formation of the parent phase ΔG_g against concentration at $c = c^*$ where the Gibbs energy ΔG_c of formation of the compound is a minimum. $\alpha = (\partial^2 \Delta G_g / \partial c^2)_{c^*}$ and $\alpha' = (\partial^2 \Delta G_c / \partial c^2)_{c^*}$ are the Gibbs energy stabilities of the parent phase and of the compound respectively. γ_i is a coefficient whose expression differs according to the mechanism of the embryo formation: $\gamma_1 = \frac{4}{3}\rho(\alpha' - \alpha)$ for the mechanism I (Gusak 1990); $\gamma_2 = \frac{4}{3}\rho\alpha(1 - \alpha/\alpha')$ for mechanism II (Desré 1991); $\gamma_3 = -\frac{4}{3}\rho\alpha$ for mechanism III (Hodaj and Desré 1996); $\gamma_4 = \frac{4}{3}\rho\alpha[(1 - \alpha/\alpha')(1 - \delta) - \delta^2]$ for mechanism IV (Hodaj and Desré 1996). The parameter δ which appears in γ_4 is such that $2\delta r$ represents the distance over which the mixing effect by interdiffusion through the first-formed ordered atomic planes acts in the first stage of the nucleus formation.

It must be pointed out that, in mechanisms I and II, γ_i is a positive quantity; this means that the Gibbs energy of formation is significantly increased by sharp concentration gradients (greater than 10^5 cm^{-1}). Beyond this critical concentration gradient, nucleation becomes thermodynamically impossible. In mechanism III where mixing is operating at the embryo scale, γ_3 is a negative quantity; consequently, the concentration gradient does not suppress the possibility of nucleation. Furthermore, the nucleation driving force is, in this case, increased by a sharp concentration gradient.

γ_4 can be either positive or negative depending on the extent of the mixing mechanism measured by δ . In the case of a cubic-shaped embryo, it has been shown that γ_4 remains positive provided that $D_s/D_c < 4\delta_0^2$ where D_s/D_c is the ratio of the diffusion coefficient D_s in the disordered parent phase to the diffusion coefficient D_c in the compound. δ_0 is the value of δ which gives $\gamma_4 = 0$. As in general the diffusivity in an ordered phase is expected to be significantly smaller than in a disordered phase the previous condition for $\gamma_4 > 0$ is not restrictive. Consequently a critical concentration gradient can be defined in mechanism IV. Let us recall that this latter case which results from a combination of mechanisms II and III is expected to be more representative, from a physical point of view, of the actual construction of the embryo. It can be added that the extent of the mixing process, measured by δ , does not influence significantly the value of the critical gradient. As an example, when δ varies from 0 to 0.5 this yields only an increase in the critical gradient of about 15% (for a cubic embryo).

As we are concerned with nucleation of intermetallics and in order to be more general and more rigorous, it is necessary to take into account the anisotropy of the interfacial energy and the eventual change in the embryo shape during its construction. A study of the effect of nucleus shape in a concentration gradient has already

been proposed (Gusak *et al.* 1991) but for particular conditions such as the case of frozen diffusion (mechanism I).

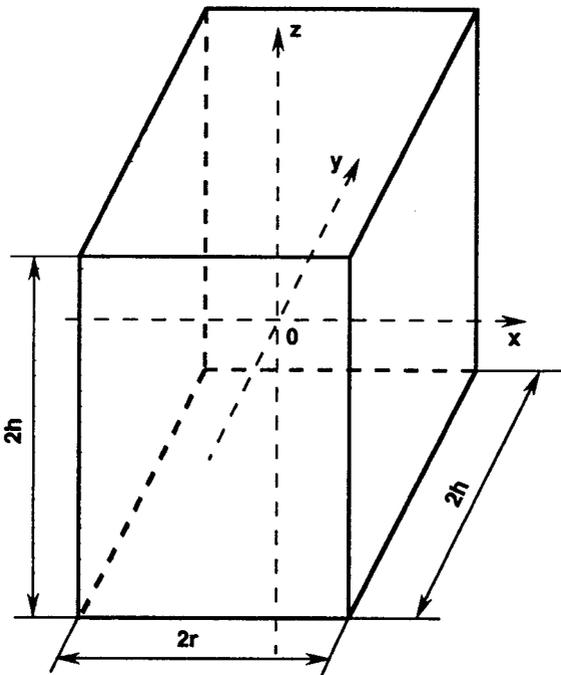
§ 2. EFFECT OF THE EMBRYO SHAPE ON NUCLEATION UNDER SHARP CONCENTRATION GRADIENTS

For simplicity and in order to study the specific effect of a unidirectional concentration gradient on intermetallic nucleation, a parallelepiped-shaped embryo of dimension $2r$ in the x direction and $2h$ in the y and z directions has been chosen (figure 1). The general form of the Gibbs energy associated with the formation of the nucleus of volume $v = 8rh^2$ in a concentration gradient denoted ∇c can be written

$$\Delta G_n = \rho \left(\Delta G_{pc} - \frac{p^{*2}}{2(\alpha - \alpha')} \right) v + 2(\sigma_x \varphi^{2/3} + 2\sigma_z \varphi^{-1/3}) v^{2/3} + \gamma_i \frac{(\nabla c)^2 \varphi^{-4/3}}{32} v^{5/3}. \quad (2)$$

Equation (2) contains a volume term corresponding to the driving force of nucleation, a positive term containing the interfacial energies and a term owing to the gradient of concentration whose sign is given by γ_i . $\varphi = h/r$ is the aspect ratio of the embryo, σ_x is the interface free energy in the x direction and $\sigma_z = \sigma_y$ are the interface free energies in the y and z directions.

It must be pointed out that, when the subcritical embryo is constrained to be a Wulff crystal, the aspect ratio φ is given by the interfacial anisotropy factor s which in the case of the present model is $s = \sigma_z/\sigma_x$. According to the different cases of



Inhomogeneous solid solution under concentration gradient

Figure 1. Parallelepiped-shaped intermetallic phase nucleus in a solid-solution layer; r is parallel to concentration gradient along x .

application, it will be shown that thermodynamics suggest significant deviation from the value of the aspect ratio given by the Wulff condition.

In order to study from a pure thermodynamic approach the possible evolution of the aspect ratio of a growing embryo, we search for a minimum of ΔG_n against φ at constant volume. In the following the more probable case $\gamma_i > 0$ is considered (the less probable case $\gamma_i < 0$ is treated in another study (Gusak *et al.* 1998)). When $\gamma_i > 0$ a critical concentration gradient ∇c_c beyond which nucleation is suppressed can be defined. Furthermore a minimum of $\Delta G_n((\partial(\Delta G_n)/\partial\rho)_v = 0$ and $(\partial^2(\Delta G_n)/\partial\rho^2)_v > 0$) is obtained when $\varphi = \varphi_m$ with

$$\varphi_m = s \left[\frac{1}{2} + \left(\frac{1}{4} + \frac{v}{v^*} \right)^{1/2} \right], \quad (3)$$

where

$$v^* = \frac{32\sigma_x s^2}{\gamma_i} \frac{1}{(\nabla c)^2}. \quad (4)$$

For a given embryo volume, v/v^* increases with increasing ∇c . As a consequence, for sharp ∇c such as those considered in the following application, the approximation $v/v^* \gg 1$ is justified when $v > v_c$, where v_c is the critical volume of the embryo. This approximation leads to $\varphi_m = s(v/v^*)^{1/2}$. Substituting φ_m in equation (2), one obtains

$$\begin{aligned} \Delta G_n = & \left[\rho \left(\Delta G_{pc} - \frac{p^{*2}}{2(\alpha - \alpha')} \right) + \frac{3}{2} \left(\frac{\sigma_x}{2} \right)^{2/3} \gamma^{1/3} (\nabla c)^{2/3} \right] v \\ & + 8\sigma_z \left(\frac{\sigma_x}{2\gamma} \right)^{1/6} (\nabla c)^{-1/3} v^{1/2}. \end{aligned} \quad (5)$$

It can be shown that ΔG_n remains positive whatever the values of v when $\nabla c > \nabla c_c$ where

$$\nabla c_c = \frac{2}{\sigma_x} \left(\frac{2\rho \left[-\Delta G_{pc} + p^{*2}/2(\alpha - \alpha') \right]}{3\gamma^{1/3}} \right)^{3/2}. \quad (6)$$

This means that intermetallic nucleation is not thermodynamically possible for $\nabla c > \nabla c_c$. It is found that, when $\nabla c = \nabla c_c$, ΔG_n presents a maximum at $v = v_c = \infty$. Consequently and as v^* remains finite, equation (6) for ∇c_c can be considered as exact. It must be added that, when $\nabla c < \nabla c_c$, nucleation can still be suppressed from kinetic reasons.

It appears from equations (3) and (4) that, formally, when $\nabla c = 0$, one finds $\varphi_m = s$. This means that the absence of a concentration gradient leads to an aspect ratio independent of the volume of the embryo and equal to the anisotropy factor s . Starting from this formal result the following question arises: in what ∇c range is the aspect ratio expected to deviate significantly from the Wulff condition? On the basis of the previous results, a deeper insight into the meaning of the minimization of the thermodynamic potential ΔG_n against the aspect ratio at constant volume can be obtained from an evaluation of the fluctuations of the aspect ratio φ around s . Such a study is justified by the fact that, here, thermodynamics are applied to systems (the embryos) of nanometre scale dimensions.

Considering that the Wulff condition $\varphi = s$ corresponds to a minimum of the total interface free energy of the parallelepiped embryo, for a given volume, the calculation of the mean square deviation of $\varphi - s$, whose details are given in appendix A, leads to

$$f = \frac{[\langle(\varphi - s)^2\rangle]^{1/2}}{s} = \frac{(3kT/4\sigma_x)^{1/2}}{(sv)^{1/3}}. \quad (7)$$

Applying equation (7) with $T = 600$ K, $\sigma_x = 0.2$ J m⁻², $s = 1.5$ and $v = 10^{-21}$ cm³, one obtains $f = 0.15$.

As mentioned before, such a significant relative amount of aspect ratio fluctuation of 15% is not surprising owing to the smallness of the system constituted by the embryo. Note that, formally, these fluctuations become negligible for large embryo volumes ($v \gg v^*$).

This previous evaluation of the aspect ratio fluctuations allows us to define under what conditions the value of $\varphi = \varphi_m$ which minimizes ΔG_n , for a given embryo volume, is such that $(\varphi_m - s)/s$ is smaller than $[\langle(\varphi - s)^2\rangle]^{1/2}/s$. In fact, when

$$\frac{\varphi_m - s}{s} < \frac{[\langle(\varphi - s)^2\rangle]^{1/2}}{s}, \quad (8)$$

the corresponding value of φ_m , resulting from the minimization of the thermodynamic potential ΔG_n is not significant since such a value must be counted among the fluctuation states around s . From equations (3), (7) and (8), the condition expressing the validity of the thermodynamic potential minimization is given by

$$\frac{v}{v^*} > \frac{(3kT/4\sigma_x)^{1/2}}{(sv)^{1/3}} \left(1 + \frac{(3kT/4\sigma_x)^{1/2}}{(sv)^{1/3}} \right). \quad (9)$$

Taking account of equation (4) the previous condition can be expressed by making explicit the concentration gradient

$$\nabla c > \nabla c^*, \quad (10)$$

with

$$\nabla c^* = \left[\frac{32\sigma_x}{\gamma} \frac{(3kT/4\sigma_x)^{1/2} s^{5/3}}{v^{4/3}} \left(1 + \frac{(3kT/4\sigma_x)^{1/2}}{(sv)^{1/3}} \right) \right]^{1/2}. \quad (11)$$

The condition (10) means that, when the concentration gradient is such that $\nabla c < \nabla c^*$, the minimization of the thermodynamic potential in order to determine the aspect ratio φ_m becomes insignificant. In other words, when $\nabla c < \nabla c^*$, the aspect ratio can be considered as given by the Wulff condition. Two examples of application of the previous approach are presented in the following. They concern firstly the nucleation of intermetallics in a supersaturated Al-Ni solid solution and secondly the nucleation of intermetallics in an amorphous layer of Ni-Zr obtained by solid-state reaction.

§ 3. APPLICATION

Recent work on kinetic reactions in polycrystalline Al-Ni multilayers has demonstrated that interdiffusion between layers leads to supersaturated solid solutions with sharp concentration gradients (Edelstein *et al.* 1994). In the framework of

the previous model, where the embryo is parallelepiped shaped, the Gibbs energy associated with the nucleation of the compound Al_3Ni in the concentration gradient ∇c , which is supposed to be constant and unidirectional, is found to have the form

$$10^{19} \Delta G_n = -16.8v + 6(\varphi_m^{2/3} + 2\varphi_m^{-1/3})v^{2/3} + 6.2 \times 10^{-18} \varphi_m^{-4/3} v^{5/3} (\nabla c)^2, \quad (12)$$

with

$$\varphi_m = 0.5 + [0.25 + 2.1 \times 10^{-18} v (\nabla c)^2]^{1/2},$$

where ΔG_n is in joules, ∇c in reciprocal metres and v in cubic nanometres. Equation (12) has been obtained for $T = 600 \text{ K}$ with the following thermodynamic data (Dupin 1995): $\alpha = 1.36 \times 10^5 \text{ J mol}^{-1}$, $\alpha' = \infty$, $\Delta G_{pc} = -1.53 \times 10^4 \text{ J mol}^{-1}$, $\rho = 1.1 \times 10^5 \text{ mol m}^{-3}$ and $\sigma = 0.3 \text{ J m}^{-2}$. As we are mostly interested in the deviation of the aspect ratio φ_m from s we have taken for simplicity $s = 1$. ΔG_n is shown in figure 2 against the volume v of the embryo for different values of ∇c . On each curve some values of the corresponding aspect ratios are reported. It is seen that the maximum of ΔG_n which is the critical Gibbs energy barrier of nucleation increases with increasing concentration gradient.

The critical nucleation barrier ΔG_n (10^{19} J), the corresponding critical volume v_c (nm^3) and the aspect ratio $\varphi_{m,c}$ at $v = v_c$ are shown in figure 3 against the concentration gradient ∇c . Application of equations (6) and (11) yields $\nabla c_c = 1.77 \times 10^9 \text{ m}^{-1}$ and $\nabla c^* = 5 \times 10^8 \text{ m}^{-1}$ respectively.

The second application concerns the potency of intermetallic nucleation of the compound $\text{Ni}_{10}\text{Zr}_7$ in an amorphous binary metallic layer Ni-Zr formed by solid-state reaction between polycrystalline Ni and Zr layers. By application of equation (2) and using equation (3), the Gibbs energy of nucleation is of the form

$$10^{19} \Delta G_n = -4.7v + 3(\varphi_m^{2/3} + 2\varphi_m^{-1/3})v^{2/3} + 2.1 \times 10^{-17} \varphi_m^{-4/3} v^{5/3} (\nabla c)^2, \quad (13)$$

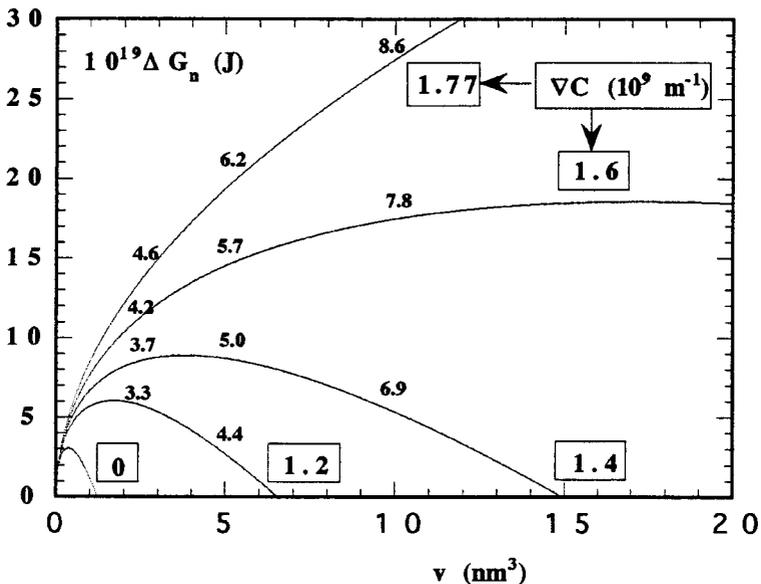


Figure 2. Gibbs energy ΔG_n of nucleation of Al_3Ni against the volume v of the embryo for different concentration gradients. Corresponding values of the aspect ratio φ_m are reported on each curve $\Delta G_n(v)$.

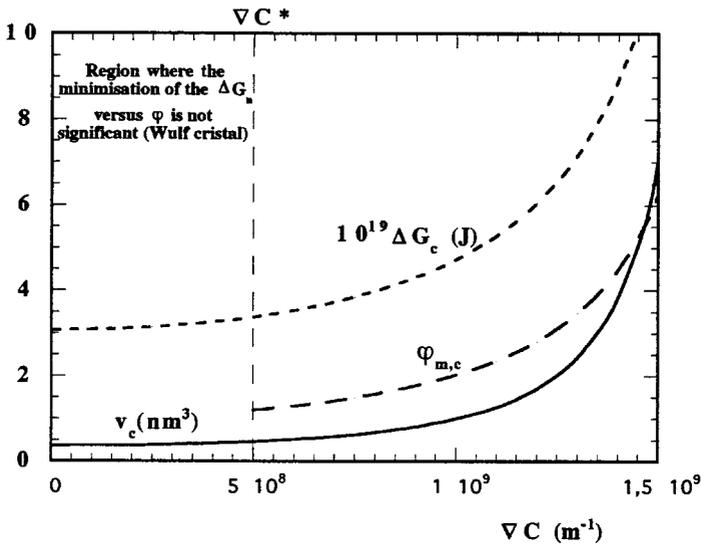


Figure 3. Curves representing the critical nucleation barrier ΔG_c , the corresponding critical embryo volume and the aspect ratio $\phi_{m,c}$ at $v = v_c$ against concentration gradient ∇c for the Al_3Ni embryo.

with

$$\phi_m = 0.5 + [0.25 + 1.4 \times 10^{-17} v(\nabla c)^2]^{1/2},$$

where ΔG_n is in joules, ∇c in reciprocal metres and v in cubic nanometres. Equation (13) has been obtained for $T = 600\text{ K}$ from the following data (Henaff *et al.* 1987): $\alpha = 4.68 \times 10^5\text{ J mol}^{-1}$, $\alpha' = \infty$, $\Delta G_{pc} = -4.5 \times 10^{-3}\text{ J mol}^{-1}$, $\sigma = 0.15\text{ J m}^{-2}$, $\rho = 1.05 \times 10^5\text{ mol m}^{-3}$ and $s = 1$. ΔG_n is shown in figure 4 against the volume of the embryo for different ∇c . The critical nucleation barrier ΔG_c (10^{19} J), the

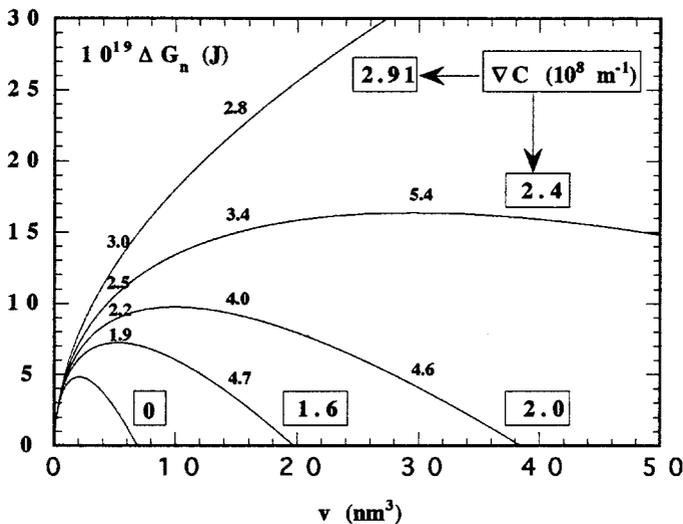


Figure 4. Gibbs energy ΔG_n of nucleation of $Ni_{10}Zr_7$ against the volume v of the embryo for different concentration gradients. Corresponding values of the aspect ratio ϕ_m are reported on each curve of $\Delta G_n(v)$.

corresponding critical volume v_c (nm^3) and the aspect ratio $\varphi_{m,c}$ at $v = v_c$ given in figure 5 against the concentration gradient. In this case, one finds that $\nabla c_c = 2.91 \times 10^8 \text{ m}^{-1}$ and $\nabla c^* = 7.5 \times 10^7 \text{ m}^{-1}$ respectively.

§4. DISCUSSION AND CONCLUSION

It must be noted at first that, in both applications, the effect of ∇c becomes significant in the Gibbs energy nucleation barrier only for sharp concentration gradients. More specifically, it is only when a certain order of magnitude of the concentration gradient is attained (10^9 m^{-1} for the Al_3Ni compound and 10^8 m^{-1} for the $\text{Ni}_{10}\text{Zr}_7$) that a significant effect of the concentration gradient on the nucleation barrier is observed. A further increase in ∇c is expected to suppress intermetallic nucleation first for a kinetic reason and then for a thermodynamic reason when $\nabla c > \nabla c_c$. It must be pointed out that the order of magnitude of the critical gradient is mostly dependent on the value of the polymorphic Gibbs energy ΔG_{pc} of transformation and on the interface energy.

Focusing on the central aspect of the present work, devoted to the embryo shape, it has been shown that the concentration gradient makes the embryo shape deviate significantly from the Wulff condition only when ∇c is greater than a limit value given by equation (11). This result is due to significant embryo shape fluctuations around the Wulff crystal shape when subjected to smaller ∇c which render the minimization of the thermodynamic potential inoperative. This is why the curves which represent φ_m against ∇c in figures 3 and 5 are only given for $\nabla c > \nabla c^*$.

Furthermore in the region where $\nabla c > \nabla c^*$, it is found that the theoretical critical gradient ∇c_c is increased when the aspect ratio is taken into account (in comparison with the case when $\varphi = s$).

Finally, it must be pointed out that the critical volume of the embryo to be considered in the previous applications must be in agreement with the classical kinetic theory of nucleation. More specifically, the critical embryo volume v_c must be such that the corresponding Gibbs energy barrier of nucleation is of the order of $60kT$ ($5 \times 10^{-19} \text{ J}$ at $T = 600 \text{ K}$). In fact, $60kT$ is an energy barrier allowing a detectable nucleation rate in the absence of faceting (Johnson *et al.* 1975). Thus it appears that $60kT$ is an overestimated value for the present application where the embryo is modelled with a parallelepiped.

APPENDIX A

Following Callen (1960), the probability of fluctuations in the extensive variables denoted X_0, X_1, \dots, X_n of a small system in contact with its surroundings is given by the following relation:

$$w = C \exp \left[\left(\hat{S} - \sum_0^n \hat{\phi}_i - S[\phi_0, \dots, \phi_n] \right) / k \right] \quad (\text{A } 1)$$

where \hat{S} and \hat{X}_i are the instantaneous entropy and any extensive parameters respectively, k is Boltzmann's constant, ϕ_i are the intensive variables of the reservoir (the surroundings in the present case), $S[\phi_0, \dots, \phi_n]$ is the maximum value of $\hat{S} - \sum_0^n \phi_i \hat{X}_i$ identical with the Legendre transform of the equilibrium entropy, and C is a constant.

The application of equation (A 1) to the case of area fluctuations, for fixed temperature and volume of the embryo, yields

$$w = C \exp\left(-\frac{\hat{F} - \langle F \rangle}{kT}\right), \quad (\text{A } 2)$$

where $\hat{F} = \hat{U} - T\hat{S}$ is the instantaneous free energy associated with the area between the embryo and the parent phase. $\langle F \rangle$ is the corresponding minimum of the free energy surface. For an embryo presenting n facets, $\hat{F} - \langle F \rangle = \Delta F$ is of the form $\Delta F = \sum_1^n (\hat{A}_i - \langle A_i \rangle) \sigma_i$ where \hat{A}_i is the instantaneous area of facet i of free energy σ_i . When applied to a parallelepiped embryo, the expression for ΔF becomes merely

$$\Delta F = 2v^{2/3} \sigma_x [2s(s^{-1/3} - \varphi^{-1/3}) + (s^{2/3} - \varphi^{2/3})]. \quad (\text{A } 3)$$

ΔF presents a minimum against φ for $\varphi = s$ provided that $(\varphi - s)/s < 3$. This is not a restrictive condition as the relative aspect ratio $[\langle (\varphi - s)^2 \rangle]^{1/2}/s$ fluctuations are expected to be much smaller than three as verified in the applications presented in the text. A development of ΔF to the second order around s leads to

$$\Delta F = \frac{4}{3} v^{2/3} s^{-4/3} \sigma_x. \quad (\text{A } 4)$$

From equations (A 2) and (A 4) and after normalization of the probability it follows that

$$\omega = \left(\frac{2v^{2/3} s^{-4/3} \sigma_x}{3\pi kT}\right)^{1/2} \exp\left(-\frac{2v^{2/3} s^{-4/3} \sigma_x}{3\pi kT} (\varphi - s)^2\right),$$

which gives finally

$$\frac{[\langle (\varphi - s)^2 \rangle]^{1/2}}{s} = \frac{(3kT/4\sigma_x)^{1/2}}{(sv)^{1/3}}. \quad (\text{A } 5)$$

REFERENCES

- CALLEN, H. B., 1960, *Thermodynamics* (New York: Wiley).
 DESRÉ, P. J., 1991, *Acta metall. mater.*, **39**, 2309.
 DESRÉ, P. J., and YAVARI, R., 1990, *Phys. Rev. Lett.*, **64**, 1533.
 DUPIN, N., 1995, Thèse de Docteur, Institut National Polytechnique de Grenoble.
 EDELSTEIN, A. S., EVERETT, R. K., RICHARDSON, G. Y., QADRI, S. B., ALTMAN, E. I., FOLEY, J. C., RUSSELL, K. C., and PEREPEZKO, J. H., 1994, *J. appl. Phys.*, **76**, 7850.
 GUSAK, A. M., 1990, *Ukr. Phys. J.*, **35**, 725.
 GUSAK, A. M., DUBIY, O. V., and KORNIENKO, S. V., 1991, *Ukr. Phys. J.*, **36**, 286.
 GUSAK, A. M., HODAJ, F., and KOVALCHUK, A. O., 1998, *Transactions of Cherkassy State University* (in the press).
 HENAFF, M. P., COLINET, C., and PASTUREL, A., 1987, *J. appl. Phys.*, **56**, 2.
 HODAJ, F., and DESRÉ, P. J., 1996, *Acta Mater.*, **44**, 4485.
 JOHNSON, W. C., WHITE, C. L., MARTH, P. E., RUF, P. K., TUOMINEN, S. M., WADE, K. D., RUSSELL, K. C., and AARONSON, H. I., 1975, *Metall. Trans. A*, **6**, 911.