Suppression of Crystal Nucleation in Amorphous Layers with Sharp Concentration Gradients

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Using simple thermodynamic arguments, it is shown that sharp concentration gradients occurring during diffusive mixing of multilayer composites facilitate amorphization by solid-state reaction by reducing or suppressing the driving force for crystallization ΔG_{ac}. As the concentration gradients diminish during diffusive layer growth, the driving force for crystalline phase formation is restored and the energetic barrier to their nucleation reduced to the classical expression. This evolution yields a critical maximum amorphous-layer thickness as observed experimentally.

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Since the early results of Schwarz and Johnson,[1] amorphization by solid-state reaction has been observed in many binary multilayer systems.[2] Amorphous phases form at the interlayer interfaces as alloying occurs by atomic diffusion. The enthalpy of mixing ΔH_{mix} of the atoms of the different component layers should be strongly negative and the diffusion coefficient D of one element in the matrix of the other, say, B in A, should be much higher than the self-diffusion coefficient of A.

A typical example of easy amorphization by solid-state reaction is NiZr where the heat of mixing is $\Delta H_{\text{mix}} \cong -50$ kJ/gat and Ni diffusion is indeed very rapid. ΔH_{mix} also accelerates atomic interdiffusion[3] and is thus related to the kinetic criterion of fast diffusion of B in A which is not necessarily interstitial.[4] In thin-film configurations, certain crystalline or amorphous phases may grow at the expense of other thermodynamically more stable phases[5] and growth kinetics can be used to derive critical maximum thicknesses d^* for amorphous-phase formation by diffusion in multilayers.[6] Other approaches based on the kinetics of nucleation in the steady state[7] and the incubation (transient) regime[8] have shown that amorphous layers can grow to a critical thickness d^* during the crystal-phase minimum nucleation time.

In this Letter we show for the first time, using simple thermodynamic arguments, that sharp concentration gradients improve the metastability of an amorphous layer by eliminating or reducing the driving force ΔG_{ac} for nucleation of intermetallic phases. The effect increases with increasingly negative ΔH_{mix} and free energy of alloying ΔG. As diffusive mixing proceeds further during amorphous-layer growth, the concentration gradients flatten out and the thermodynamic driving force for crystalline-phase formation is gradually restored. The energy barrier for their nucleation also diminishes towards the value of the classical theory. This evolution yields a critical thickness for the amorphous layer of the order of what is observed experimentally.[2]

Let us consider an amorphous layer of a binary AB alloy in which a sharp concentration gradient is set up. For a $A_{C^*}B_{1-C^*}$ stoichiometric intermetallic compound to nucleate, embryos of the crystalline compound must attain a critical radius r^* as determined by the classical theory of homogeneous nucleation. Figure 1 shows a schematic drawing of such a critical nucleus together with the concentration gradient ∇C along x and the free-energy $G(C)$ curves for the amorphous and the intermetallic phase. $C(-r^*)$ and $C(+r^*)$ indicate the concentrations in the amorphous phase at the two ends of the critical nucleus of dimension $2r^*$ along ∇C. For the nucleus to attain this critical size, the tangents $G_a(C(-r^*))$ and $G_a(C(+r^*))$ of the amorphous-phase free-energy curve must touch the $G_c(C)$ curve of the intermetallic compound. It can be seen that for a sufficiently sharp gradient $\nabla C'$, the tangents from

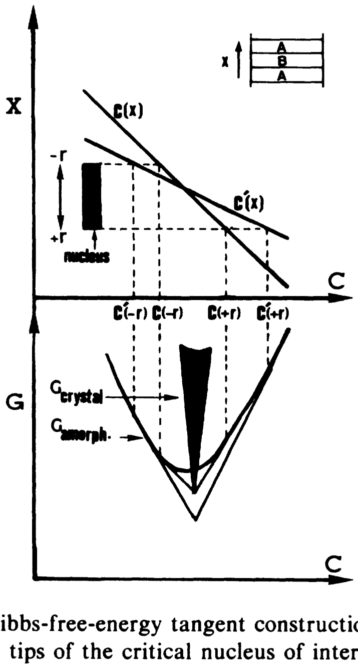

FIG. 1. Gibbs-free-energy tangent constructions for compositions at the tips of the critical nucleus of intermetallic phase in an amorphous layer subject to the concentration gradient ∇C.

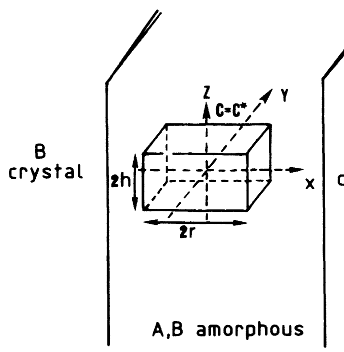

FIG. 2. Parallelepiped- or cube- ($h=r$) shaped intermetallic-phase nucleus in amorphous layer. r is parallel to concentration gradient ∇C along x.

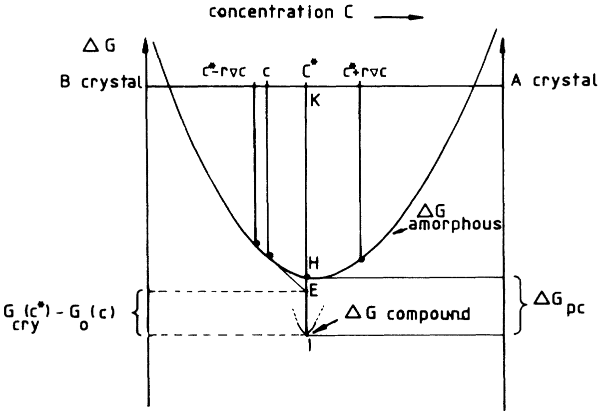

FIG. 3. Gibbs formation free energies of amorphous phase and intermetallic compound of composition C^*.

$C(-r^*)$ and $C(+r^*)$ will miss the tip of the $G_c(C)$ 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 form.

Following the thermodynamic approach of Cahn and Hilliard for nonuniform systems,[9] the Gibbs free energy of a volume v of the amorphous layer can be written as

$$G_a(v)=\rho\int_v [G_0(C)+N_A\chi(\nabla C)^2]dv\,,$$

where ρ is the number of moles of atoms per unit volume, N_A is Avogadro's number, and χ is a constant. $G_0(C)$ is the Gibbs energy per atom of an amorphous phase of uniform composition C.

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

$$\Delta G_{ac}(v)=\rho\left[G_{\text{cryst}}(C^*)v-\int_v [G_0(C)+N_A\chi(\nabla C)^2]dv\right]. \tag{1}$$

At first we treat the case of a cubic nucleus with cube edge equal to $2r$ ($h=r$ in Fig. 2). ∇C is supposed to be constant and unidirectional along x, normal to the A and B layers. The plane parallel to the layers and passing through the center of the nucleus is at concentration C^*. These conditions lead to the more condensed form of (1),

$$\Delta G_{ac}(V)=4\rho r^2\int_{-r}^{+r}[G(C^*)-G_0(C(x))]dx \\ -8\rho r^3 N_A\chi(\nabla C)^2. \tag{2}$$

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

$$\Delta G_{ac}(v)=\frac{4\rho r^2}{\nabla C}\int_{C^*+\mathbf{r}\cdot\nabla C}^{C^*-\mathbf{r}\cdot\nabla C}[G_{\text{cryst}}(C^*)-G_0(C(x))]dC \\ -8\rho r^3 N_A\chi(\nabla C)^2. \tag{3}$$

Figure 3 represents the molar Gibbs free energies of formation of both amorphous phase and compound versus concentration: From the classical tangent rule, the segment $EI=G_{\text{cryst}}(C^*)-G_0(C)$ is the molar driving force for crystallization of an amorphous phase of composition C into the compound of composition C^*. EI can be subdivided as $EI=KI-KE=KI-(KH+HE)=KI-KH+EH$, where $KI-KH=\Delta G_{\text{pc}}$ is the Gibbs free energy for polymorphous crystallization at $C=C^*$ and $EH=\Delta G_{\text{fl}}$ is the molar Gibbs free energy associated with a concentration fluctuation (C^*-C). A series development of ΔG_{fl} to second order in $C-C^*$ leads to

$$\Delta G_{\text{fl}}(C)=\tfrac{1}{2}(C-C^*)^2\partial^2\Delta G/\partial C^2\,, \tag{4}$$

where ΔG is the molar Gibbs free energy of formation of the amorphous alloy from pure crystalline A and B and the first-order term is zero for all nonzero concentrations. 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 $G_{\text{cryst}}-G_0=\Delta G_{\text{pc}}+\Delta G_{\text{fl}}$ to integrate (3), we obtain

$$\Delta G_{ac}(v)=8\rho[\Delta G_{\text{pc}}(C^*)-N_A\chi(\nabla C)^2]r^3 \\ +\tfrac{4}{3}\rho a(\nabla C)^2 r^5\,, \tag{5}$$

where $a=\partial^2\Delta G/\partial C^2$ has been assumed to be constant in the range $C^*-\mathbf{r}\cdot\nabla C<C<C^*+\mathbf{r}\cdot\nabla C$.

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 curvature a of the ΔG of alloying which itself increases with $|\Delta H_{\text{mix}}|$. Finally, the expression for 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

$$\Delta G_N=24\sigma_{\text{pc}}r^2+8\rho[\Delta G_{\text{pc}}(C^*)-N_A\chi(\nabla C)^2]r^3 \\ +\tfrac{4}{3}\rho a(\nabla C)^2 r^5\,, \tag{6}$$

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

We take as an example the homogeneous nucleation of $Ni_{10}Zr_7$, which is the stable crystallization product in glassy $Ni_{64}Zr_{36}$,[10] in an amorphous layer under a concentration gradient ∇C. The enthalpy of crystallization of amorphous $Ni_{10}Zr_7$ obtained by calorimetric measurements[11] is $\Delta H_{pc} = -4.5$ kJ/mol. Neglecting the entropic contribution by virtue of the Kauzmann argument,[12,13] the Gibbs free energy for crystallization is $\Delta G_{pc} \cong -4.5$ kJ/mol. A crude evaluation of Cahn's term,[9] $N_A \chi(\nabla C^2)$ 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.[9] With $\lambda \cong -200$ kJ/mol for NiZr,[14] $a = 3$ Å (0.3 nm), and $\nabla C = 6\times10^5$/cm (of the order of the gradients which will be considered later), we obtain $N_A \chi(\nabla C^2) \cong -33$ J/mol which is less than 1% of ΔG_{pc}. The interfacial energy σ_{pc} is not known experimentally. Skapski's model[15] for a liquid-solid alloy interfacial energy σ_{sl}, using a linear approximation from the pure component σ values, yields $\sigma_{pc} = 270$ mJ/m^2. Another possibility is to approximate σ_{pc} by σ_{sl} for a crystal in perfect wetting conditions with the disordered phase and $\sigma_{sl} \cong \sigma_{lv}/5.25$ (following Warren[16]), where σ_{lv} is the pure liquid surface energy at its melting temperature. To obtain σ_{sl} at the amorphization temperature $T \cong 560$ K, we use a temperature extrapolation with $d\sigma/dT = -0.1$ mJ/m^{2}K for Zr (as the experimental value is not known[17]) and $d\sigma/dT = -0.3$ mJ/m^{2}K for Ni.[17] This together with a linear extrapolation from the pure component values gives $\sigma_{pc} \cong 370$ mJ/m^2. We have used, for the present application of Eq. (6), the value $\sigma_{pc} = 300$ mJ/m^2. The value of $\alpha(T = 560$ K$) = \partial^2 \Delta G/\partial C^2 = 468$ kJ/mol has been calculated from available thermodynamic data for liquid NiZr.[14] With $\rho = 0.105$ g-at./cm^3 of $Ni_{10}Zr_7$, ΔG_N in (6) becomes

$$10^{20}\Delta G_N(r) = 7.20r^2 - 0.38r^3 + 6.55\times10^{-16}(\nabla C)^2 r^5 , \tag{7}$$

where r in angstroms (0.1 nm) yields $\Delta G_N(r)$ in joule units as given for three different ∇C values plotted versus r in Fig. 4. For a critical gradient $\nabla C_c = 4.85\times10^5$/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 $\Delta G_N(r)$ vs r no longer occurs in the ∇C range greater than 5.7×10^5/cm.

Since the total concentration variation across the amorphous layer is of the order of $\Delta C \approx 1$, the critical concentration gradient corresponds to a critical thickness $\epsilon_c \cong 1/\nabla C_c$ of the amorphous phase forming by solid-state reaction across which crystallization is thermodynamically disallowed. For $\nabla C_c \cong 5\times10^5$/cm, we obtain a critical thickness $\epsilon_c \cong 200$ Å. However, the crystal structures of NiZr intermetallic compounds are complex, often orthorhombic with highly asymmetric unit cells (ASTM powder-diffraction files). For such structures one expects a low number of distinct rapid growth directions. In fact, the growth morphology of $Ni_{10}Zr_7$ from the amorphous phase is known to be extremely anisotropic resulting in needlelike crystals[10] with aspect ratios greater than 100. For these reasons and the influence of the much more rapid diffusion of Ni atoms compared to Zr atoms, it can be shown that if such crystals appear, their rapid growth direction and their length direction will be oriented along the concentration gradient ∇C. As such we must consider the effect of the nucleus shape anisotropy on ΔG_N in Eq. (6). We consider a parallelepiped-shaped nucleus as shown in Fig. 2 with an aspect ratio $\phi = h/r < 1$ and the length $2r$ along ∇C. For simplicity, we use a ratio of interfacial energies $\sigma_{pc}^{y,z}$ along and σ_{pc}^{x} perpendicular to the rapid growth axis given by $\sigma_{pc}^{y,z}/\sigma_{pc}^{x} = h/r = \phi$. The procedure leading to (6) then yields

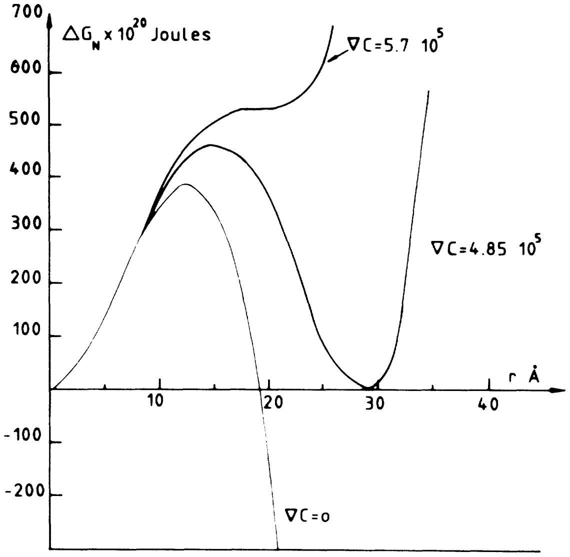

FIG. 4. Gibbs free energy $\Delta G_N(r)$ of formation of crystalline embryo of radius r in amorphous phase with different concentration gradients ∇C. For ∇C above a critical value, $\Delta G_N > 0$ and nucleation is disallowed.

$$\Delta G_N(\phi) = 8\phi(\phi+2)\sigma_{pc}^{x} r^2 + 8\rho\phi^2 \Delta G_{pc}(C^*) r^3 + \tfrac{4}{3}\rho\alpha\phi^2 \nabla C^2 r^5 .$$

When applied to the nucleation of $Ni_{10}Zr_7$ with $\sigma_{pc}^{x} = 300$ mJ/m^2 and $\phi = 0.2$, the critical concentration gradient here is found to be $\nabla C_c = 1.6\times10^5$/cm which leads to a critical thickness $\epsilon_c \cong 600$ Å (60 nm) as compared to $\epsilon_c \cong 1000$ Å observed experimentally.[18] We note that for $\phi = 1$ (cubic nucleus) the critical layer thickness is only 200 Å (20 nm). This is consistent with TEM observations[19] of a thickness of $\cong 200$ Å for amorphous layers in AlPt composites[4] which crystallize into cubic Al_2Pt and for which no shape anisotropy of nucleus is expected ($\phi = 1$). The use of $\Delta C = 1$ overestimates this thickness but our interfacial-energy value is likely to underestimate it. It has been suggested[20] that the presence of a large density of defects in the initial crystalline layers and the usual presence of a few atom percent of oxygen in Zr-type metal layers increases the composition range ΔC up to nearly 0.9. Furthermore, the results in Fig. 4 indicate that the effect of the sharp concentration gradients persists at higher thicknesses 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 homogeneous nucleation of such compound crystals inside the NiZr (and similar) amorphous layers formed by solid-state reaction has never been experimentally detected. TEM observations[18] indicate, on the contrary, that crystallization occurs by planar growth of a crystalline compound layer formed heterogeneously at the amorphous-pure-Zr interface.

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