Thermodynamic and Kinetic Justification for Amorphization by Mechanical Alloying of *A*-*B* Metal Couples with Zero Heat of Mixing ΔH_{mix}

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While amorphization by solid-state reaction is limited to multilayers of *A*-*B* metal couples with large negative heat of mixing $\Delta H_{\text{mix}} \ll 0$, mechanical alloying allows amorphization of mixtures of some pure metals with $\Delta H_{\text{mix}} \approx 0$. We have recently shown that for an amorphous phase with a sharp concentration gradient there is a critical thickness x_c below which crystallization is thermodynamically disallowed. We show here that x_c is very small when $\Delta H_{\text{mix}} \approx 0$ but that in mechanical alloying the simultaneous growth and deformation of the amorphous interlayers allows them to grow substantially in volume while remaining under the critical thickness x_c.

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The first reports of amorphization during isothermal annealing of *A*-*B* multilayers by solid-state reaction[1] and amorphization during mechanical alloying of mixtures of metal powders[2] both appeared in 1983. While amorphization by solid-state reaction refers to amorphous alloy formation during thermal annealing of as-prepared elemental multilayers, amorphization by mechanical alloying occurs during heavy codeformation (such as in ball milling) of the constituent elements. Since those early reports, many metal-metal binary systems have been amorphized by one and/or the other technique. All multilayer diffusion couples in which significant fractions of amorphous phases form upon annealing have the common properties of a large negative heat of mixing ΔH_{mix} and a large asymmetry of atomic diffusivities of the two constituent species,[3] or $D_B \gg D_A$. These common properties were found to favor nucleation and growth of the amorphous phases over those of *AB* intermetallic compounds.[4,5] However, amorphization by mechanical alloying was reported in systems such as NbSn (Ref. 6) which exhibit neither abnormally fast diffusion of one constituent nor a strongly negative ΔH_{mix}.

In the case of mechanical alloying, the intense deformation accelerates interdiffusion and the large defect densities increase the free energies of both pure components and intermetallic compounds with respect to an amorphous product, but these energy gains are small[3] compared to heats of mixing ΔH_{mix} involved in the amorphization of multilayers such as NiZr.

It has been shown that before significant mixing occurs by mechanical alloying, *A*-*B* powders are deformed into agglomerates of *AB* multilayers[7,8] much like those prepared for solid-state reaction. Thus, although the kinetics of amorphization by mechanical alloying have lower activation energies than those measured for solid-state reaction during isothermal annealing,[9] both processes consist of atomic mixing in multilayers.

We have recently shown[10] that sharp concentration gradients in an amorphous layer suppress the thermodynamic driving force for nucleation of intermetallic compounds. These gradients flatten out with subsequent growth of the amorphous layer and the driving force for crystallization is reestablished beyond a certain critical thickness x_c, which is larger the more negative the enthalpy of mixing ΔH_{mix}. For thickness $x > x_c$, compounds can nucleate if kinetically allowed.[4,5] x_c was estimated to be approximately 60 nm for NiZr and 20 nm for AlPt.[10]

In the present Letter we apply these concepts to amorphization by mechanical alloying. We show that under certain deformation conditions, the fact that critical concentration gradients disallow compound nucleation provides a thermodynamic justification for amorphization by mechanical alloying of metal couples with $\Delta H_{\text{mix}} \approx 0$.

Consider an amorphous layer of a binary *AB* alloy in which a sharp concentration gradient is set up. For a $A_{C^*}B_{1-C^*}$ 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 (see inset) and curves for the free energy of formation $G_a(C)$ and $G_c(C)$ of the amorphous and the intermetallic phases, respectively. $C(-r^*)$ 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 to the amorphous-phase energy curve at $G_a(C(-r^*))$ and $G_a(C(+r^*))$ 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 $C(-r^*)$ 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

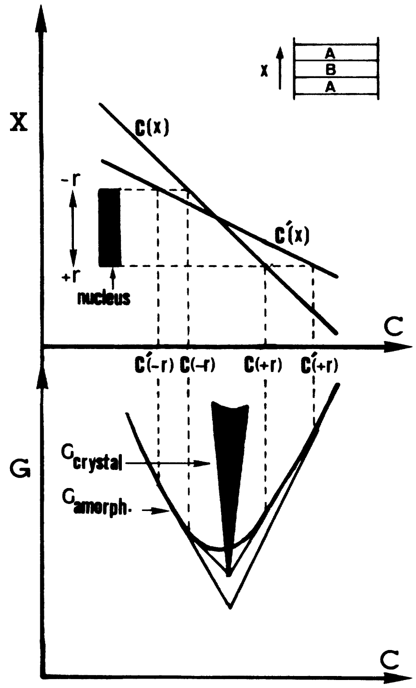

FIG. 1. Gibbs-free-energy tangent construction for compositions at the tips of the critical nucleus of intermetallic phase in an amorphous layer subject to the concentration gradient ∇C.

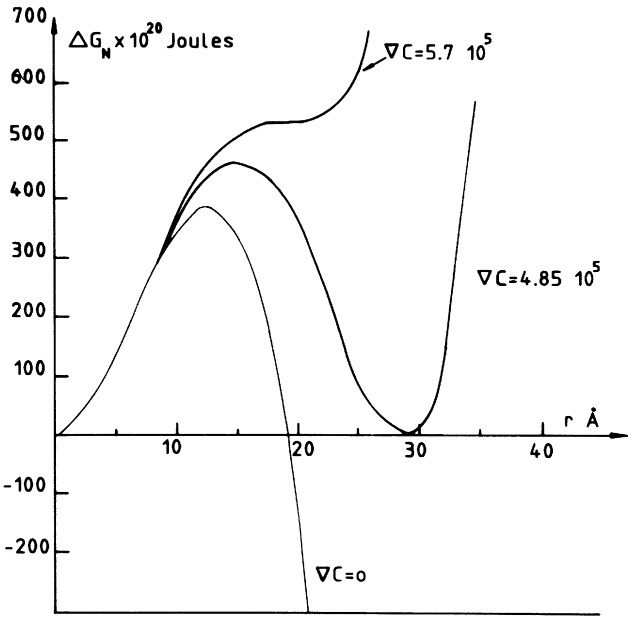

FIG. 2. Gibbs free energy $\Delta G_N(r)$ of formation of crystalline embryo of radius r in amorphous phase with different concentration gradients ∇C. For ∇C above a critical value, $\Delta G_N > 0$ and nucleation is disallowed.

the intermetallic phase will not form.

Using the classical homogeneous nucleation theory, the free-energy change upon formation of a cubic nucleus, of dimension $2r$ along x, of the AB compound with $C_A = C^*$ from an amorphous phase of the same concentration would be $\Delta G_N = 24\sigma r^2 + 8\rho \Delta G_{\rm pc} r^3$, where the first term is the nucleus surface area times the interfacial energy σ and the second term is the usual molar free energy of polymorphous crystallization $\Delta G_{\rm pc}$ times the nucleus volume $8r^3$ and the atom density ρ (mol/cm^3). We have recently shown that for the present case of a compound embryo of dimensions $2r$ and composition C^*, forming from an amorphous phase of concentration ranging from $C(-r)$ to $C(+r)$, the expression for the Gibbs free energy of nucleation taking into account the effect of the concentration gradient ∇C in the amorphous phase will be

$$\Delta G_N = 24\sigma r^2 + 8\rho \Delta G_{\rm pc}(C^*) r^3 + \tfrac{4}{3}\rho a (\nabla C)^2 r^5 , \quad (1)$$

where $a = \partial^2 G_a / \partial C^2 > 0$. The additional third term scaling with r^5 is positive and suppresses the driving force for nucleation by compensating for the second term with $\Delta G_{\rm pc} < 0$ for sufficiently sharp gradients ∇C. The reader is referred to the original papers for full details.[10,11]

Figure 2 shows the influence of increasingly sharp concentration gradients on ΔG_N for the case of NiZr.[10] The concentration gradient $\nabla C_c = 4.85 \times 10^5$ cm^{-1}, which is the lowest ∇C for which ΔG_N no longer becomes negative, is the critical concentration gradient. If the concentration variation from the A side to the B side of the amorphous interlayer is ΔC, this gradient defines the critical thickness $x_c = \Delta C / \nabla C_c$. Following Fig. 2, we obtain the critical concentration gradient by setting both ΔG_N and $d\Delta G_N / dr = 0$. After manipulation we obtain

$$\nabla C_c = \rho(-2\Delta G_{\rm pc})^{3/2} / 9\sigma (a)^{1/2} . \quad (2)$$

Using $\Delta C \approx 0.6$ we obtain for the critical thermodynamic thickness x_c beyond which the driving force for crystallization is restored

$$x_c = \Delta C / \nabla C \approx 2\sigma (a)^{1/2} / \rho (\Delta G_{\rm pc})^{3/2} . \quad (3)$$

Since we are interested in AB amorphous alloys with $\Delta H_{\rm mix} \approx 0$, we set

$$\Delta G_a = \Delta H_{\rm mix} - T\Delta S_{\rm mix}$$
$$= -RT[C \ln C + (1-C)\ln(1-C)]$$

such that

$$(a)^{1/2} = [\partial G_a^2 / \partial C^2]^{1/2} = [RT/C(1-C)]^{1/2}$$

and

$$x_c \approx 2\sigma [RT/C(1-C)]^{1/2} / \rho |\Delta G_{\rm pc}|^{3/2} . \quad (4)$$

For 0.5 and $T = 600$ K, we obtain $x_c = 2.4$ nm compared to, for example, $x_c \approx 60$ nm for NiZr with a large negative $\Delta H_{\rm mix}$. x_c will be slightly larger if we take into account the cold-work energy stored in the crystalline phases[3] and assume that it is released upon amorphization.

Nevertheless, for a multilayer with thickness per metal layer of $x_m \approx 100$ nm, an amorphous film of only about 2 nm constitutes a volume fraction that is nearly impossible to detect by bulk measurements and growth much beyond this thickness will be likely to lead to its crystallization, especially since the condition $D_B \gg D_A$ is not fulfilled and the kinetics of amorphization and crystallization are likely to be of the same order. This multilayer is therefore not amorphizable by solid-state reaction. However, it can be amorphized by mechanical alloying in the following manner: Each multilayer powder particle, when deformed during ball milling between two colliding balls or a ball and the jar, will be rapidly heated up to temperatures

$$T^* = T_{\rm jar} + \Delta T = T_{\rm jar} + \int \frac{\tau_y \, d\gamma}{C_p/V_m}, \tag{5}$$

where C_p and V_m are molar specific heat and volume equal to about 25 J/K at. g and 10 cm^3/at. g, respectively, τ_y is the yield stress and γ the strain,[12] and the integral is the deformation work presumed to remain in the sample during collision time and to raise the particle temperature by ΔT adiabatically. The growth of the amorphous layer during this heating cycle can be estimated as $\Delta x \approx [2D(T^*)\Delta t]^{1/2}$, with $D(T^*)$ being an interdiffusion coefficient corresponding to the conditions prevailing during this thermomechanical cycle [$D(T^*)$ is likely to be well above diffusivities measured in undeformed materials as the defects generated during the deformation cycle are expected to strongly enhance atomic mobility]. Now as the amorphous layer thickens by this interdiffusion, upon each collision it will also be subjected to a deformation $\gamma = \ln x_0/x$ which will reduce its thickness much like in cold rolling.[13] If we now suppose for simplicity that collisions are all identical such that the strain rate $\dot\gamma = d\gamma/dt$ and ΔT are well defined (as in mechanical alloying by cold rolling), we obtain

$$\Delta x = [D(T^*)/x - x\,\partial\gamma/\partial t]\Delta t\,, \tag{6}$$

where $\partial x/\partial t = D/x$ is the diffusion-controlled layer growth rate derived from $x^2 = 2Dt$ and $\partial x/\partial t = -x\dot\gamma$ is the thickness reduction rate with time.

It can be seen that as the layer thickness x increases by diffusion, its diffusion-controlled growth rate D/x decreases while the simultaneous thickness reduction $-x\dot\gamma$ due to deformation increases. This situation leads to a steady-state amorphization rate at constant layer thickness with $\Delta x = 0$.

The steady-state-rate thickness is then given by

$$x^2 = \frac{D}{d\gamma/dt}\,. \tag{7}$$

The present result indicates that when the deformation rate $\dot\gamma$ and interdiffusion $D(T^*)$ are such that $x < x_c$, crystallization is disallowed and the amorphous volume $V_{\rm am}$ will continue to grow at constant thickness x while its interfacial surface per volume S increases, with $dS(t)/dt = S_0\,\partial\gamma/\partial t$ or $\Delta S/S = \Delta x_m/x_m$ per deformation time interval Δt, where x_m is the thickness per metal layer of the multilayer powder particle.

The amorphous phase volume after n collisions can be written as

$$\begin{aligned} V_{\rm am} &= S_0[(S+\Delta S)/S]^n x \\ &= S_0[x_m/(x_m - \Delta x_m)]^n x\,. \end{aligned} \tag{8}$$

Of course in ball-milling experiments, a spectrum of deformation increments per collision occurs with powder particles attaining a range of temperatures T^* and diffusivities $D(T^*)$ in the various collision configurations.

A simpler situation is that of mechanical alloying by repeated cold rolling.[12,14] We have studied this process in AlPt and NiZr multilayers. The deformation per pass, $\Delta x_m/x_m$, is of the order of 0.1. We have established that multilayers with thickness per layer $x \le 1$ μm are about 50% amorphized in volume after about $n = 30$ rolling passes.[9,12] As such, Eq. (8) indicates that the amorphous layer thickness can remain constant at $x \approx 20$ nm which is consistent with the calculated x_c for NiZr and AlPt.

The present analysis assumes that the amorphous layer deformation follows the global multilayer deformation (with $\Delta x_m/x_m = \Delta x/x$). This implies that certain experimental conditions must be fulfilled for amorphization by mechanical alloying of AB couples with $\Delta H_{\rm mix} \approx 0$. Actually the assumption is not so severe because if the amorphous layer thickness reduction $\Delta x \approx -x\dot\gamma\Delta t$ per deformation cycle decreases, the layer growth rate ($dx/dt = D/x$) will also decrease and vice versa. For alloys with $\Delta H_{\rm mix} \approx 0$ the thickness x is expected to be only of the order of 7 or 8 atomic layers and such thin amorphous layers forming *during* deformation of a metal layer are expected to have a large free volume density and low viscosity η such that their deformation rate $\dot\gamma \approx \tau_y/\eta$ with yield stress τ_y is expected to follow that of the matrix.

The viscosity η, which is about 10^9 Pas at T_g,[15] is given by $\eta = \eta_0(T)\exp\delta v^*/v_f$, where δv^* is a constant activation volume and v_f is the free volume[16] per unit volume v_0. It has been shown[17] that v_f in metallic glasses is of the order of 1% of v_0 and a decrease from $v_f/v_0 = 0.01$ to 0.009 can result in viscosity increases by a factor of 10 when $\eta \approx 10^{13}$ Pas, while cold rolling of amorphous alloys results in a density decrease and a free volume increase $\Delta v_f/v_0$ of the order of 0.01 or more.[18,19] Thus the viscosity *during deformation* (before excess volume precipitates into large immobile voids[20]) is expected to be several orders of magnitude lower than in its undeformed state. We estimate this viscosity to be in the range $10^5 < \eta_{\mathrm{def}} < 10^9$ Pas. Such strain softening of amorphous alloys together with the sharp rise in the multilayer powder temperatures up to T^* (sometimes up to crystallization[21] at T_x) during deformation seem to add to the generality of the present picture of amorphization by mechanical alloying.

In conclusion, we have extended the study of the role of sharp concentration gradients in amorphization by solid-state reaction to the conditions of mechanical alloying. Sharp concentration gradients suppress crystallization in amorphous layers with thickness below a critical value x_c which scales with the alloy heat of mixing. x_c is thus very low for alloys with $\Delta H_{\mathrm{mix}} \approx 0$ and only negligible amorphization can occur during isothermal annealing. On the other hand, for mechanical alloying, we show for the first time that multilayer deformation conditions can be such that simultaneous diffusive layer growth and thickness reduction during deformation cycles can result in amorphization with a near constant steady-state critical thickness that remains below x_c even for alloys with $\Delta H_{\mathrm{mix}} \approx 0$, and significant amorphous layer volume fractions can be formed by mechanical alloying.

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