Enhanced solid-state amorphization by sharp concentration gradients

Yu Zheng*

*Department of Physics and Astronomy, Hunter College of the City University of New York, 695 Park Avenue,
New York, New York 10021*
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The thermodynamic aspects of solid-state amorphization of the Ni-Zr system is reanalyzed considering the effects of concentration gradients. It is shown that during the early stage of the solid-state amorphization the driving force for amorphous-alloy formation will be larger than that for intermetallic-compound formation due to the effects of sharp concentration gradients. This reveals that, in addition to the kinetic constraints, the driving force from sharp concentration gradients also contributes to the solid-state amorphization. The thermodynamic arguments also lead to a three-stage description of the solid-state amorphization, which is in agreement with experimental results.

Solid-state amorphization, which provides an alternative to the conventional routes for amorphous-alloy formation, has been observed in many binary multilayer systems.[1,2] An unsolved problem concerning the thermodynamic and kinetic aspects of solid-state amorphization is why in its early stage amorphous alloys can form and grow without evidence of intermetallic-compound formation. The usual thermodynamic analysis has shown that in solid-state amorphization the driving force for amorphous-alloy formation is smaller, at least, than that for the formation of some intermetallic compounds and then has suggested that the answer for this problem must lie in the kinetic constraints which restrict the nucleation of intermetallic compounds.[1,2] However, the usual thermodynamic analysis has not considered the effects of concentration gradients occurring during the early stage of solid-state amorphization.[3,4] Very recently, it has been shown[5] that the thermal metastability of formed amorphous-alloy layers will be enhanced by sharp concentration gradients. This result leads us to reanalyze the thermodynamic aspects of solid-state amorphization.

The Ni-Zr system, which has been extensively studied previously,[6-8] provides a typical example of solid-state amorphization. In this work the thermodynamic aspects of solid-state amorphization of the Ni-Zr system are reanalyzed by considering the effects of the concentration gradients. It is shown that in the early stage the driving force for amorphous-alloy formation will be larger than that for intermetallic-compound formation because of the effects of the sharp concentration gradients. This result reveals that in addition to the kinetic constraints the driving force from the sharp concentration gradients also contributes to solid-state amorphization. Thermodynamic arguments also lead to a three-stage description of solid-state amorphization, which is in agreement with experimental results. Furthermore, this result provides an example for which the characteristics of first-order phase transformations of nonuniform systems may be different from those of uniform systems because of the effects of nonuniformity. This is very important for the understanding of first-order phase transitions of nonuniform systems such as interfaces.

Solid-state amorphization of the Ni-Zr system has been suggested[9] to proceed by the substantial mutual dissolution of parent metals, which leads to solid-solution layers from which amorphous-alloy layers are formed. In this work a layer of solid Ni_cZr_{1-c} solution is considered, in which a concentration gradient ∇c_s is set up. Figure 1 shows a schematic Gibbs-free-energy diagram for the solid-solution, amorphous-alloy, and intermetallic-compound phases of the Ni-Zr system.

According to the thermodynamic approach,[10] the Gibbs free energy of a volume v of a binary system of concentration gradient ∇c can be expressed as

$$G(v) = \int_v [G_0(c) + N_A \chi (\nabla c)^2] \rho \, dv , \qquad (1)$$

where $G_0(c)$ is the molar Gibbs free energy, N_A is the Avogadro number, χ is the characteristic constant, and ρ is the number of moles of atoms per unit volume of the binary system of uniform concentration c.

The driving force for the transformation at constant ρ of the solid Ni_cZr_{1-c} solution layer of average concentra-
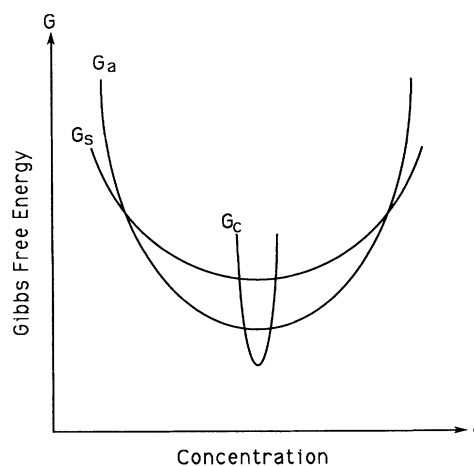

FIG. 1. Schematic Gibbs-free-energy diagram for the solid-solution, amorphous-alloy, and intermetallic-compound phases of the Ni-Zr system.

tion c^* and concentration gradient ∇c_s into the amorphous $Ni_c Zr_{1-c}$ alloy layer of average concentration c^* and concentration gradient ∇c_a is then defined as

$$\Delta G_{as}(v) = \int_v [G_{ao}(c) + N_A \chi_a (\nabla c_a)^2] \rho \, dv$$
$$- \int_v [G_{so}(c) + N_A \chi_s (\nabla c_s)^2] \rho \, dv \ . \qquad (2)$$

According to the above definition, the driving force for solid-state amorphization will be larger when it becomes more negative.

The cubic layer in Fig. 2 is treated in the following calculation of the driving force for simplicity, in which the concentration gradient ∇c is supposed to be constant and unidirectional along x and the average concentration c^* is supposed to be at the central plane between the Ni and Zr layers. Then the driving force is obtained as

$$\Delta G_{as}(v) = 4\rho r^2 \int_{-r}^{+r} [G_{ao}(c^* + x\nabla c_a)$$
$$- G_{so}(c^* + x\nabla c_s)] dx$$
$$+ 8\rho r^3 N_A [\chi_a (\nabla c_a)^2 - \chi_s (\nabla c_s)^2] \ . \qquad (3)$$

Figure 3 shows the schematic molar Gibbs free energies of the solid solution and amorphous-alloy phases of the Ni-Zr system. According to the classical tangent rule, the segment

$$AS = G_{ao}(c^* + x\nabla c_a) - G_{so}(c^* + x\nabla c_s) \ ,$$

in Fig. 3, is the molar driving force for the transformations of the solid-solution phase of uniform concentration $c_s = (c^* + x\nabla c_s)$ into the amorphous-alloy phase of uniform concentration $c_a = (c^* + x\nabla c_a)$. Through the calculation the segment AS is obtained as

$$AS = G_{ao}(c^*) - G_{so}(c^*) + \tfrac{1}{2}\beta_a x^2 (\nabla c_a)^2$$
$$+ \tfrac{1}{2}\beta_s x^2 (\nabla c_s)^2 - \beta_s x^2 \nabla c_a \nabla c_s \ , \qquad (4)$$

where β_a and β_s denote, respectively, the curvatures of the Gibbs free energies $G_{ao}(c)$ and $G_{so}(c)$. In this work β_a and β_s are assumed to be constants.

Finally, the driving force $\Delta G_{as}(v)$ for solid-state amorphization, which includes the interfacial energy term, is obtained as
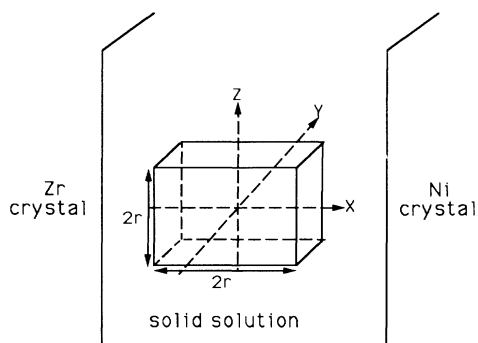

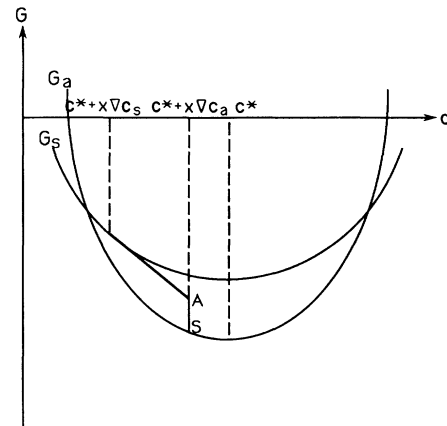FIG. 2. Cubic layer in the calculation of the driving force.

FIG. 3. Schematic molar Gibbs-free-energy curves for the solid-solution and amorphous-alloy phases of the Ni-Zr system.

$$\Delta G_{as}(v) = 24 r^2 \sigma_{as} + 8\rho r^3 [G_{ao}(c^*) - G_{so}(c^*)]$$
$$+ \tfrac{4}{3}\beta_a r^5 (\nabla c_a)^2 + \tfrac{4}{3}\beta_s r^5 (\nabla c_s)^2 - \tfrac{8}{3}\beta_s r^5 \nabla c_a \nabla c_s$$
$$+ 8\rho r^3 N_A [\chi_a (\nabla c_a)^2 - \chi_s (\nabla c_s)^2] \ , \qquad (5)$$

where the interfacial energy σ_{as} is assumed to be isotropic. In the above expression, the last term is usually much smaller than the other terms and can be neglected.[5] The driving force is then approximated as

$$\Delta G_{as}(v) = \Delta G_{aso}(v) + \tfrac{4}{3}\beta_a r^5 (\nabla c_a)^2$$
$$+ \tfrac{4}{3}\beta_s r^5 (\nabla c_s)^2 - \tfrac{8}{3}\beta_s r^5 \nabla c_a \nabla c_s \ , \qquad (6)$$

where

$$\Delta G_{aso}(v) = 24 r^2 \sigma_{as} + 8\rho r^3 [G_{ao}(c^*) - G_{so}(c^*)]$$

is the driving force for the polymorphous transformation of the solid-solution layer of uniform concentration c^* into the amorphous-alloy layer of uniform concentration c^*.

Assuming that the concentration gradient ∇c_s is fixed, the driving force $\Delta G_{as}(v)$ will be largest at $\nabla c_a = (\beta_s/\beta_a) \nabla c_s$, when the concentration gradient ∇c_a is changing. At this time Eq. (6) becomes

$$\Delta G_{as}^{mx}(v) = \Delta G_{aso}(v) + \tfrac{4}{3}\beta_s (1 - \beta_s/\beta_a) r^5 (\nabla c_s)^2 \ . \qquad (7)$$

It can be seen from Eq. (7) that since the curvature constant β_s is usually smaller than the curvature constant β_a,[9] the driving force $\Delta G_{as}^{mx}(v)$ will be more positive than the driving force $\Delta G_{aso}(v)$. This means that the driving force for solid-state amorphization of nonuniform solid-solution layers will be usually smaller than the driving force for solid-state amorphization of uniform solid-solution layers, as a result of the effects of the concentration gradients. Furthermore, the driving force $\Delta G_{as}(v)$ will not be available at very sharp concentration gradients, and the solid-state amorphization of nonuniform solid-solution layers will not happen. The critical concentration gradient ∇c_{as} can be determined from Eq. (7).

Similarly, the driving force for the transformation at constant ρ of the solid $Ni_c Zr_{1-c}$ solution layer of average

concentration c^* and concentration gradient ∇c_s into the intermetallic Ni_cZr_{1-c} compound layer of concentration c^* is obtained as

$$\Delta G_{cs}^{mx}(v)=\Delta G_{cso}(v)+\tfrac{4}{3}\beta_s r^5(\nabla c_s)^2 , \tag{8}$$

where $\Delta G_{cs0}(v)$ is the driving force for the polymorphous transformation of the solid-solution layer of uniform concentration c^* into the intermetallic-compound layer of concentration c^*. In this case the effects of the concentration gradients are the same as those in the previous case. The critical concentration gradient ∇c_{cs} can be determined from Eq. (8).

The difference between the driving forces for intermetallic-compound formation and amorphous-alloy formation is then

$$[\Delta G_{cs}^{mx}(v)-\Delta G_{as}^{mx}(v)]$$
$$=\Delta G_{cao}(v)+\tfrac{4}{3}(\beta_s^2/\beta_a)r^5(\nabla c_s)^2 , \tag{9}$$

where
$$\Delta G_{cao}(v)=\Delta G_{cso}(v)-\Delta G_{aso}(v)$$

is the driving force for the polymorphous transformation of the amorphous-alloy layer of uniform concentration c^* into the intermetallic-compound layer of concentration c^* and is usually negative.

It can be seen from Eq. (9) that at small concentration gradients, the driving-force difference will be negative, and then the driving force for intermetallic-compound formation will be larger than that for amorphous-alloy formation; on the other hand, at sufficiently sharp concentration gradients, the driving-force difference will be positive, and then the driving force for amorphous-alloy formation will be larger than that for intermetallic-compound formation. The critical concentration gradient ∇c_{ca} can be determined from Eq. (9).

It has been shown in the previous discussion that the driving force for amorphous-alloy formation will not be available at sufficiently sharp concentration gradients. So it is necessary to examine whether the driving force is still available at least for amorphous-alloy formation when the driving force for amorphous-alloy formation becomes larger than that for intermetallic-compound formation at sufficiently sharp concentration gradients. In order to do this, the critical concentration gradients ∇c_{as} and ∇c_{ca} are compared, in which the nonuniform solid Ni_cZr_{1-c} solution layer of average concentration $c^*=0.6$, the nonuniform amorphous Ni_cAr_{1-c} alloy layer of average concentration $c^*=0.6$, and the intermetallic $Ni_{10}Zr_7$ compound layer are concerned. According to the calculated Gibbs-free-energy diagram of the Ni-Zr system,[9] if the solid Ni_cZr_{1-c} solution is of the hcp structure, the ratio of the terms

$$[G_{ao}(c^*)-G_{so}(c^*)]/\beta_s(1-\beta_s/\beta_a)$$

and

$$[G_{co}(c^*)-G_{ao}(c^*)]/(\beta_s^2/\beta_a)$$

is about 1.7, and then the critical concentration gradient ∇c_{as} is larger than the critical concentration gradient ∇c_{ca}; if the solid Ni_cZr_{1-c} solution is of the bcc structure, the ratio is about 2.7, and then the critical concentration gradient ∇c_{as} is also larger than the critical concentration gradient ∇c_{ca}. This indicates that the driving force will be indeed available at least for amorphous-alloy formation when the driving force for amorphous-alloy formation becomes larger than that for intermetallic-compound formation at sufficiently sharp concentration gradients. It is noted that the interfacial energy term in the driving force is not considered in the above analysis because of the absence of related data.

Sharp concentration gradients will occur in both initially formed solid-solution and amorphous-alloy layers during the early state of real solid-state amorphization. So, according to the above result, the driving force for amorphous-alloy formation will be really larger than that for intermetallic-compound formation during the early stage of solid-state amorphization. This reveals that in addition to the kinetic constraints the driving force also contributes to solid-state amorphization of the Ni-Zr system. This result may be also applicable to other binary systems.[6,11,12]

According to the above discussion, solid-state amorphization of the Ni-Zr system, in which very sharp concentration gradients occur at the beginning and then gradually flatten out, can be divided into three stages.

(1) In the first stage, the concentration gradients are very sharp so that no driving forces are available for both amorphous-alloy and intermetallic-compound formation. As a result, both amorphous-alloy and intermetallic-compound formation will be not observed during this stage.

(2) In the second stage, the concentration gradients are not very sharp, but sufficiently sharp so that driving forces are available at least for amorphous-alloy formation, which is larger than that for intermetallic-compound formation. As a result, amorphous-alloy formation will be observed and intermetallic-compound formation will not be apparently observed during this stage.

(3) In the third stage, the concentration gradients are small so that driving forces are available for both amorphous-alloy and intermetallic-compound formation, and the driving force for intermetallic-compound formation is larger than that for amorphous-alloy formation. As a result, intermetallic-compound formation will be observed and continuing amorphous-alloy formation will not be apparently observed during this stage.

The above three-stage description of solid-state amorphization of the Ni-Zr system is basically in agreement with experimental results.[8]

*Present address: Mail stop 2-300, Chemical Sciences Division, Lawrence Berkeley Laboratory, 1 Cyclotron Road, Berkeley, CA 94720.
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