

Formation of amorphous alloys by the mechanical alloying of crystalline powders of pure metals and powders of intermetallics

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Amorphous powders of $\text{Ni}_{32}\text{Ti}_{68}$ and of $\text{Ni}_{45}\text{Nb}_{55}$ were synthesized by mechanical alloying (MA) starting from either a mixture of pure metal powders (in the appropriate molar ratio) or from powders of the crystalline intermetallics NiTi_2 and $\text{Ni}_{45}\text{Nb}_{55}$, respectively. For both alloys, the peak temperature increase (above the average processing temperature) in the powder particles trapped between colliding balls is estimated at 38 K. Thus, the amorphization is attributed to a process other than the formation of local melts followed by the rapid solidification of these melts into the amorphous phase. The amorphization by MA starting from a mixture of pure crystalline powders is attributed to a solid state interdiffusion reaction, the kinetics of which is controlled by the excess point and lattice defects generated by plastic deformation. The amorphization by MA starting from powders of crystalline intermetallics is attributed to the accumulation of point and lattice defects which raise the free energy of the faulted intermetallic above that of the amorphous alloy.

At temperatures well below the liquidus, binary metallic systems with negative heats of mixing are most stable in the form of crystalline intermetallics at a discrete number of stoichiometric compositions. In general, such systems can also exist as metastable amorphous alloys with free energies higher than those of a crystalline intermetallic of the same composition or a heterogeneous mixture of intermetallics. Amorphous alloys have been traditionally synthesized by the rapid solidification technique,¹ whereby an amorphous structure is first achieved in the molten state; this structure is then preserved while the melt is rapidly cooled below its crystallization temperature at rates between 10^4 and 10^8 K/s. Amorphous alloys can be formed by isothermal solid state reactions as well. For example, it was recently found in thin-film couples of metallic systems with negative heats of mixing that an isothermal anneal at a temperature which kinetically favors the interdiffusion of the two metals but precludes the nucleation of crystalline intermetallics leads to the formation of a homogeneous amorphous alloy.² While in this solid state reaction the mixing of the two pure metals occurs by thermal interdiffusion, the reaction can be further assisted by mechanical deformation^{3,4} or by irradiation with energetic particles.⁵

A method particularly promising for the manufacture of homogeneous amorphous alloy powders, and in large quantities, is that of MA crystalline powders of the pure constitutive elements.⁶⁻⁸ The binary systems that have been amorphized by solid state reactions in thin films and by the MA of pure crystalline powders, have all in common that the starting elements have negative heats of mixing. Indeed, the MA of Ni and Cu powders, which have a positive heat of mixing of 10 kJ/g atom,⁹ leads to the formation of a crystalline fcc alloy.¹⁰ The negative heat of mixing not only provides a thermodynamic driving force for the reaction but also favors the reaction kinetics by increasing the interdiffusion coefficient.¹¹

Yermakov *et al.*¹² reported the formation of amorphous $\text{Co}_x\text{Y}_{1-x}$ alloys through the mechanical grinding of crystal-

line intermetallics of Co and Y (Co_{17}Y_2 , Co_5Y , Co_7Y_2 , Co_3Y). In this method the Co and Y are already atomically mixed so that the negative heat of mixing of Co and Y ($H = -30$ kJ/g atom) (Ref. 9) does not provide an added incentive for the crystalline to amorphous reaction. Yermakov *et al.* attributed the amorphization reaction to a combination of fragmentation and plastic deformation which heats local regions of the powders above their melting temperature; these melts presumably solidify sufficiently fast so as to preserve the amorphous structure. Thus the amorphous alloy would develop through a repetitive and cumulative microscopic rapid solidification process. On the other hand, Schwarz *et al.*⁷ conclude, based on their study of the synthesis of amorphous $\text{Ni}_x\text{Ti}_{1-x}$ powders by MA crystalline Ni and Ti powders, that this process does not involve the formation of melt. This conclusion follows from a comparison of the peak pressures that develop between the colliding steel balls in the mill and the measured pressure for the onset of melting in powders being shock loaded. The present study was designed to study the influence of the negative heat of mixing in the process of amorphization by MA and to further investigate the possible formation of melt pools. For this, amorphous $\text{Ni}_{32}\text{Ti}_{68}$ powders were synthesized by MA starting both from a mixture of pure crystalline Ni and Ti powders and from crystalline NiTi_2 alloy powders. A similar study was performed in the NiNb system, where amorphous $\text{Ni}_{45}\text{Nb}_{55}$ powders were synthesized from both pure crystalline Ni and Nb powders and from crystalline $\text{Ni}_{45}\text{Nb}_{55}$ alloy powders.

The mechanical alloying was performed in a laboratory ball mill/mixer using hardened steel vials and balls. The vial was sealed in an Ar-filled glove box. The mixer agitated the vial at about 20 Hz with an amplitude of 5 cm. Hence, the balls inside the vial reached velocities of 1 m/s. During the ball milling the vial was kept below -40°C . Further experimental details were reported in Refs. 6 and 7.

The structure of the mechanically alloyed powders was characterized by x-ray diffraction with $\text{Mo } K_\alpha$ radiation and

a horizontal diffractometer with a solid state Si(Li) detector. Curve (a) in Fig. 1 shows the diffracted intensity of a mixture of crystalline Ni and Ti powders in molar ratio 1:2 after only 2 h of MA. Bragg diffraction peaks of Ni and Ti are clearly visible as well as weak broad maxima of the amorphous alloy. Curve (b) in Fig. 1 shows the diffracted intensity after 17 h of MA. In Ref. 7 we reported ample evidence that this powder is a single phase amorphous alloy. Curve (c) in Fig. 1 shows the x-ray diffracted intensity of the powder in curve (b) following an annealing for 3 h at 750 K (above the crystallization temperature). Twenty-eight sharp Bragg peaks were detected, all of which corresponded to crystalline NiTi₂ (fcc, Cu₂Mg-type structure). The crystalline NiTi₂ powder of curve (c) was mechanically alloyed for 14 h, giving the x-ray diffraction pattern (d) of Fig. 1. Heating the amorphous powder of curve (d) above 750 K caused it to crystallize back into NiTi₂.

Figure 2 shows x-ray diffraction intensities for similar experiments in the NiNb system. Curve (a) corresponds to amorphous Ni₄₅Nb₅₅ powder obtained by MA pure crystalline Ni and Nb powders for 11 h. Curve (b) shows the diffracted intensity of crystalline Ni₄₅Nb₅₅ powder prepared by crushing an ingot of arc-melted Ni₄₅Nb₅₅ in a mortar and pestle. The 15 Bragg peaks detected in this pattern correspond to the equilibrium near-equiatomic intermetallic with a hexagonal phase typified by W₆Fe₇.¹³ Curve (c) in Fig. 2 is the diffracted intensity of the powder (b) after 14 h of MA. This diffraction pattern is almost identical to that of powder (a).

Figure 3 shows schematically the free energies for the different phases that may form in a binary alloy *AB* which has a negative heat of mixing. Quantitative diagrams of this type have been found useful in predicting the products of solid state amorphizing reactions in thin films² as well as in the MA of pure powders.⁷ The straight line in Fig. 3 is the free energy of a heterogeneous mixture of pure crystals of *A* and *B*. The broad parabola is the free energy of the amorphous phase (treated in the framework of the quasichemical approximation) and the narrow parabola is the free energy of a crystalline intermetallic compound *A_nB_m*. This qualitative diagram is appropriate for a discussion of both alloy systems investigated here.

The present results show that the amorphous state² can

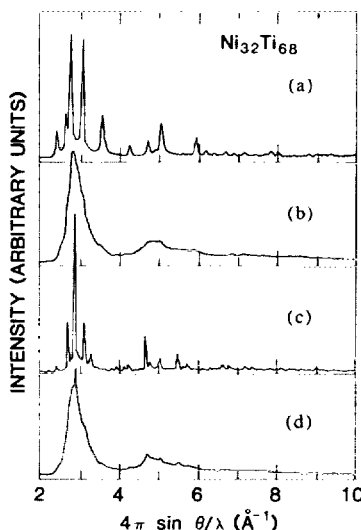


FIG. 1. X-ray diffraction intensities for the NiTi system. Curve (a) is from a mixture of pure Ni and Ti powders at molar ratio 1:2, following 2 h of MA. Curve (b) is from amorphous Ni₃₂Ti₆₈ obtained after 16 h of MA. Curve (c) corresponds to crystalline NiTi₂ (FCC, Cu₂Mg-type structure) obtained by a high-temperature anneal of the amorphous powder of curve (b). Curve (d) corresponds to amorphous Ni₃₂Ti₆₈ obtained by MA the crystalline powder of curve (c) for 14 h.

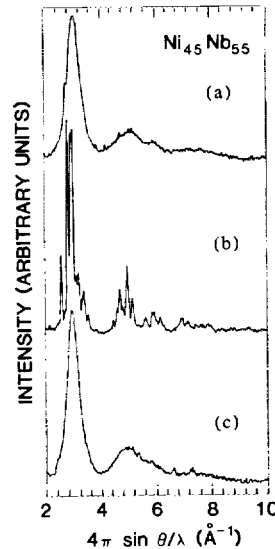


FIG. 2. X-ray diffraction intensities for the NiNb system. Curve (a) is from amorphous Ni₄₅Nb₅₅ obtained after MA pure crystalline Ni and Nb powders for 11 h. Curve (b) is from crystalline Ni₄₅Nb₅₅ powder prepared by crushing an arc melted ingot of the intermetallic. Curve (c) is from amorphous Ni₄₅Nb₅₅ powder obtained by MA powder in curve (b) for 14 h.

be achieved in Ni₃₂Ti₆₈ and Ni₄₅Nb₅₅ by MA either a mixture of the pure elemental powders [state (1)] or powders of the corresponding crystalline intermetallic [state (3)]. A more detailed study in the NiTi system¹⁴ shows, furthermore, that for a same composition and for identical experimental conditions, the rate of production of the amorphous phase for processes 1–2 and 3–2 is approximately the same. Because in process 1–2 the negative heat of mixing provides a thermodynamic driving force which favors interdiffusion, while no such force is present for reaction 3–2, the near equality in processing rates suggests that the heat of mixing plays a minor role in controlling the kinetics of amorphization by MA. This contrasts with what happens in the amorphization of thin films by thermal interdiffusion² and by ion beam mixing,⁵ where the reaction kinetics are thought to be enhanced by the negative heat of mixing between pure *A* and *B*.

The amorphization mechanism suggested in Ref. 12 is based on the formation of melted regions in the powder particles as the result of localized plastic deformation, followed by rapid solidification of these melts by heat conduction into the less deformed regions. This mechanism is attractive in that it can explain both processes 1–2 and 3–2. However, the comparison made in Ref. 7 of the pressures achieved in the powder particles trapped between colliding balls with that necessary for creating melt pools during the shock-wave consolidation of powders¹⁵ strongly suggests that the peak temperature reached by the particles during MA is well below the melting temperature of the starting intermetallics (1015 °C for NiTi₂ and 1230 °C for Ni₄₅Nb₆₅). An upper estimate for the peak temperature reached in the powder particles during MA can be obtained as follows. We assume that a given particle trapped between two colliding balls deforms by localized shear. The normal stress developed by the

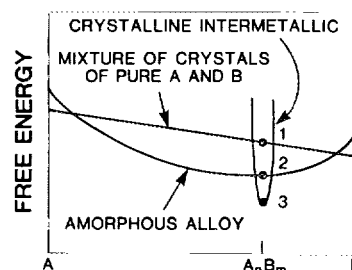


FIG. 3. Schematic free-energy diagram for a binary system *AB* with a negative heat of mixing in the amorphous state.

head-on collision of two balls is $\sigma_n \approx \rho_b v_s v_r$, where $\rho_b = 7.8 \text{ g cm}^{-3}$ is the density of the steel balls, $v_s = 5800 \text{ ms}^{-1}$ is the speed of a longitudinal wave in steel, and $v_r = 2 \text{ ms}^{-1}$ is the relative velocity of the balls before impact. This state of stress lasts for $\Delta t \approx 2d/v_s$, where $d = 0.6 \text{ cm}$ is the diameter of the balls. We assume that a particle trapped between two colliding balls deforms by shear under the stress σ_n . The shear process lasts Δt , and the two halves of the particle slide at the relative speed v_r . The energy flux dissipated on the glide plane is $F = \sigma_n v_r$. The temperature increase ΔT at the surface of a semi-infinite solid irradiated by the heat flux $F/2$ for time Δt is,¹⁶ $\Delta T = F(\Delta t/\pi K_0 \rho_p c_p)^{1/2}$. For the powder density ρ_p and specific heat c_p , we use weighted averages of the pure components. This gives $\rho_p = 5.9$ and 8.6 g cm^{-3} , and $c_p = 500$ and $340 \text{ J kg}^{-1} \text{ K}^{-1}$ for $\text{Ni}_{32}\text{Ti}_{68}$ and $\text{Ni}_{45}\text{Nb}_{55}$, respectively. We estimate the thermal conductivity K_0 from the Wiedermann–Franz law assuming that the resistivity of the amorphous phase is $1.5 \times 10^{-6} \Omega \text{ m}$ for both alloys. This gives $K_0 = 5.0 \text{ W m}^{-1} \text{ K}^{-1}$. With these values we obtain $\Delta T = 38 \text{ K}$ for both alloys.

In the foregoing calculation we considered localized heating due to plastic shear. In an alternative mechanism, surface heating could occur due to friction between sliding particles. However, for a friction coefficient less than 1, the temperature increase due to friction is less than ΔT . The time between successive ball collisions is approximately 5 ms,⁷ which is sufficiently long for the heated regions to thermally relax to the near-ambient temperature of the container and balls. It is thus concluded that the amorphization process does not result from the rapid quenching of molten pools. Other mechanisms must be, therefore, explored.

A model first proposed by Swanson *et al.*¹⁷ has been used to explain the amorphization by irradiation of crystalline solids. In particular, Brimhall *et al.*¹⁸ have used these ideas to describe amorphous phase formation in irradiated intermetallic compounds. The basic premise is that a critical defect concentration introduced by irradiation will promote spontaneous transformation to the amorphous state. At this defect concentration, $G_c + \Delta G_d > G_a$, where G_c is the free energy of the crystalline phase, ΔG_d is the increase in free energy due to the defects produced by irradiation, and G_a is the free energy of the amorphous phase. Consistent with this concept are the experimental observations^{18,19} that intermetallic compounds with narrow homogeneity ranges tend to become amorphous during irradiation, while compounds with wide solubilities tend to remain crystalline. This difference was attributed¹⁸ to the smaller increase in ΔG_d for a given defect density for the later alloys, reflected by their ability to exist away from perfect stoichiometry. Koch and Kim²⁰ suggested that such a mechanism may be responsible for the amorphization by MA since severe plastic deformation generates point and lattice defects—vacancies, interstitials, dislocations, antiphase domain boundaries, etc.—which raise the free energy of crystalline phases. This mechanism may explain the amorphization by MA when starting from crystalline powders of intermetallics. It does not seem adequate, however, to explain the amorphization by MA when starting from a mixture of pure crystalline powders. Indeed, x-ray diffraction patterns taken at regular time intervals during the MA of pure Ni and Ti powders⁷ showed

that as the Bragg peaks of Ni and Ti decreased in strength, the broad bands of the amorphous alloy increased in strength. Bragg peaks of crystalline intermetallics were not observed. Thus, at least in the NiTi system, reaction (1–2) occurs directly, without an intermediate step (1–3–2). Schwarz *et al.*⁷ suggested that in NiTi, process (1–2) occurs by a solid state interdiffusion reaction near clean boundaries between polycrystalline Ni and Ti. The mixing is driven by the excess point and lattice defects created by plastic deformation.

Even though the amorphization by MA seems to occur by different mechanisms, when the starting powder is a crystalline intermetallic or a mixture of pure metal powders, the required processing time for a fully amorphous product is approximately the same.¹⁴ This suggests that for both processes the rate-limiting step is the production of point and lattice defects by mechanical attrition. When the starting powder is a crystalline intermetallic (reaction 3–2), the defect concentration must reach a critical value at which the free energy of the faulted intermetallic is above that of the amorphous phase. When the starting product is a mixture of pure elemental powders (reaction 1–2), the rate of defect production controls the kinetics of interdiffusion. Additional research is required to explore the validity of the suggested mechanisms for amorphization by mechanical alloying.

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