

## Interdiffusion during the Formation of Amorphous Alloys by Mechanical Alloying

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By probing the Ni content of Zr crystallites as a function of milling time using Auger spectroscopy, we report the first direct measurements of the interdiffusion which takes place during the amorphization of Ni-Zr by the mechanical alloying of pure-metal powders. Based on the concentration variation of Ni in Zr as a function of the milling time and using a simple interdiffusion model, we can estimate an effective local temperature at the collision site.

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Recently,<sup>1</sup> it was shown that an amorphous alloy can be formed by the isothermal annealing (below the crystallization temperature) of a multilayer metallic system composed of pure elements with large negative heat of mixing, the amorphous phase growing in a planar way from the interfaces.<sup>2</sup> The negative heat of mixing provides the thermodynamic driving force for the amorphization reaction and contributes to the kinetics by increasing the interdiffusion coefficient.<sup>3</sup> Another new technique for producing amorphous powders is mechanical alloying (MA) of pure crystalline powders or intermetallics. At first, the amorphization by MA of intermetallics was attributed to the formation of local melts, produced by the colliding balls, which solidify rapidly to form microscopic amorphous regions.<sup>4</sup> Schwarz, Petrich, and Saw, however, concluded that this process does not involve melting.<sup>5</sup> They estimated that the peak temperature during the collision is not more than 30 to 40 deg above the average processing temperature.<sup>6</sup> For their part, the amorphization was due to the accumulation of structural defects which raise the free energy of the intermetallic above that of the amorphous alloys. More recently, Eckert *et al.*,<sup>7</sup> using a similar approach, argue that the actual local temperature can reach values as high as 400°C, causing partial crystallization in some cases. For the pure-elemental powders, the amorphization could be attributed to a solid-state interdiffusion reaction as in the case of the thin-film coupled system, the kinetics being controlled by the structural defects generated during the milling process. Schwarz and Koch<sup>6</sup> found that for the Ni-Ti system the amorphous-phase production rate (APPR) is approximately the same whether we start the MA using a mixture of the pure components or the corresponding crystalline intermetallics, suggesting that the interdiffusion is not a limiting factor and the heat of mixing plays only a minor role in controlling the kinetics of amorphization. For Ni-Zr, we will show that the APPR is maximum when the concentration reaches approximately the thermodynamic criti-

cal value for single amorphous-phase formation.

The samples were prepared from 99.9% pure-elemental powders. The particles size range from 44 to 74  $\mu\text{m}$  for Ni and from 44 to 250  $\mu\text{m}$  for Zr. The powders were mixed in the ratio NiZr<sub>2</sub> and sealed under argon atmosphere in a steel container (70 ml maximum load) with three 0.5-in.-diam steel balls. The total mass of the powders was about 7 g. The MA was performed in a SPEX 8000 Mixer Mill. A small quantity of powder was picked at regular intervals for analysis. The x ray was performed on a Philips diffractometer with Mo K $\alpha$  radiation. A PHI 660 scanning Auger microscope was used for chemical analysis. The thermal properties of the powders were investigated using a Perkin Elmer DSC-4 calorimeter.

Figures 1(a) and 1(b) show the x-ray patterns of the powder mixture as a function of the milling time. During the first hour, the intensity of the x-ray peaks decreases rapidly and the width increases indicating that the size of the crystallites decreases sharply. There is no significant shift in the position of the major x-ray lines as a function of time. After 2 h, a broad peak located around 17 deg and shown in Fig. 1(a) appears. This broad peak, which is characteristic of an amorphous phase, is clearly visible after 3 h of milling time [Fig. 1(b)]. At 8 h, the powder is almost completely amorphous. Figure 2 (solid line) shows the normalized fraction of amorphous phase as a function of milling time calculated from the size of the crystallization peak using a differential scanning calorimeter. The dashed line is the derivative of the solid line and indicates that the maximum APPR occurs at 3 h of milling time in agreement with the x-ray results.

In order to study the interdiffusion reaction during the milling process and correlate the chemical concentration with the APPR, we used a scanning Auger microscope. Since the amorphization of Ni-Zr bilayer by a solid-state reaction has shown that the Ni is the only moving species,<sup>8</sup> we have measured the Ni content of the Zr

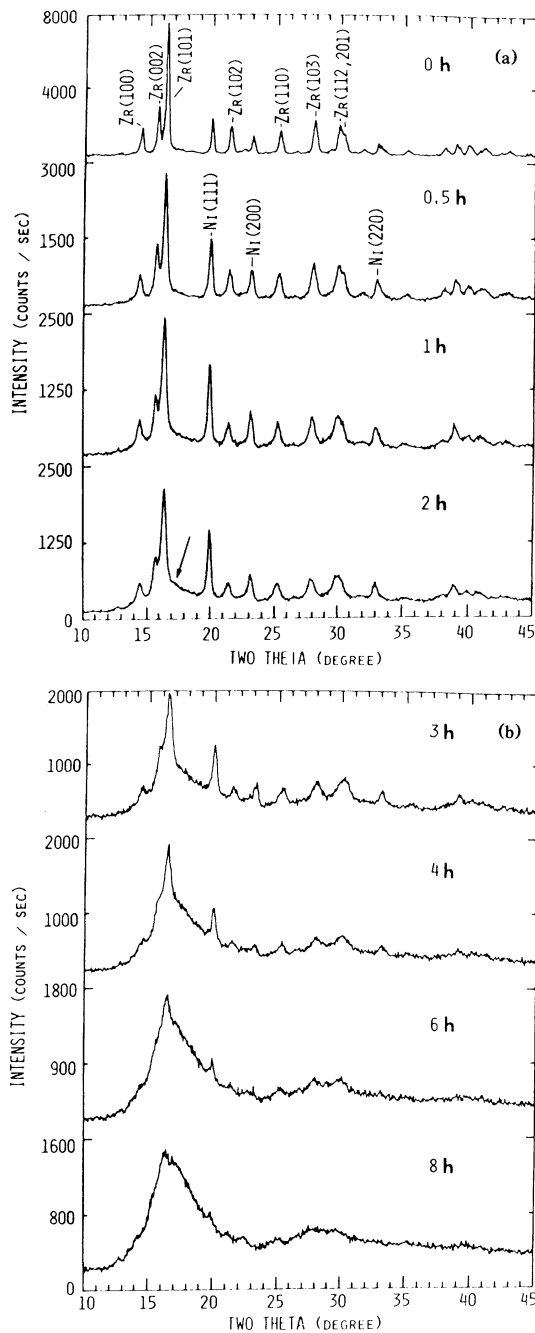


FIG. 1. (a),(b) X-ray diffraction patterns (Mo  $K\alpha$  radiation) of a mixture of Ni and Zr powders (average composition  $NiZr_2$ ) for milling times of 0, 0.5, 1, 2, 3, 4, 6, and 8 h.

crystallites as a function of the milling time. The size of the electron beam of the microscope was chosen to be smaller or on the order of the crystallites dimension whenever possible (the minimum beam size achievable on a PHI 660 is 250 Å). The chemical composition of Zr crystallites was measured as a function of depth using a sputter gun operating at 3 kV and 25 mA with argon

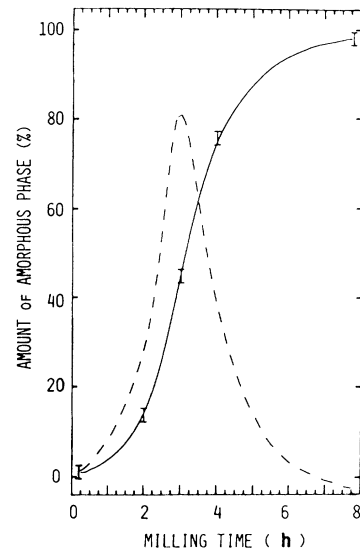


FIG. 2. Normalized fraction of amorphous phase (solid line) as a function of the milling time calculated from the differential scanning calorimeter crystallization peak. The dashed line shows the derivative of the full line and represents the amorphous-phase production rate.

gas. The sputter etch rate is 400 Å/min on  $Ta_2O_5$ .

Figure 3 shows the concentration of Ni and Zr in selected Zr particles as a function of depth for various milling time. The 0.25- and 0.5-h traces show some Ni-Zr interfaces. During the first 3 h we observe large fluctuations in the local concentration. After 8 h, when the

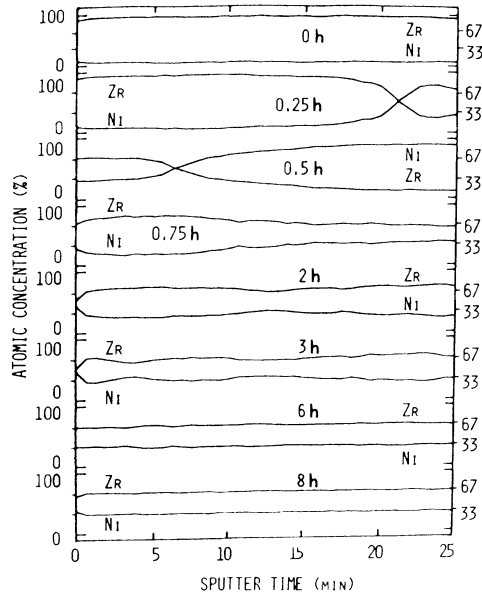


FIG. 3. Auger depth profiles on Zr-rich crystallites showing the concentration of Zr and Ni as a function of the sputter time after various milling time (sputter etch rate, 400 Å/min on  $Ta_2O_5$ ).

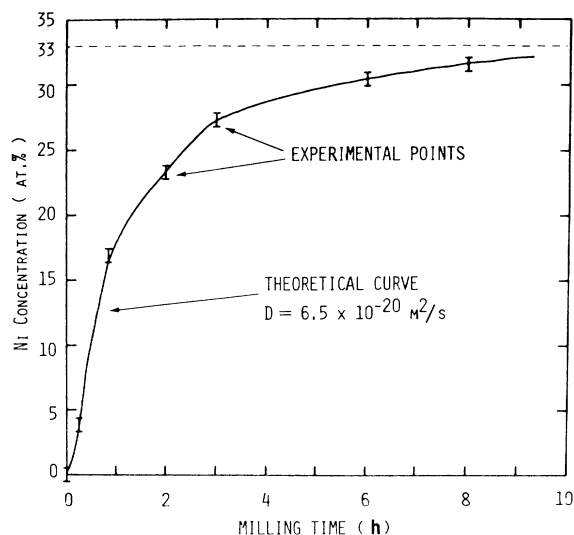


FIG. 4. Concentration of Ni inside the Zr crystallites as a function of the milling time. The solid line is a calculation based on the size of the Zr crystallites measured by x-ray diffraction and for a value of  $D = 6.5 \times 10^{-20} \text{ m}^2/\text{s}$ .

material is almost completely amorphous, the Ni concentration is uniform and equals the average concentration of the powder mixture  $\text{Ni}_{33}\text{Zr}_{67}$ . The minimum Ni concentration measured during several depth profiles on various Zr crystallites is presented in Fig. 4 as a function of the milling time. This value represents approximately the amount of Ni which has been dissolved in the Zr through a diffusion process. The measured concentration is, in fact, an average over the beam size and comes from two contributions. The first one is the lattice diffusion which is described by an atomic level process, while the second comes from the physical mixing of Ni and Zr particles. At the beginning of the milling, the number of Ni particles with dimensions smaller than the beam size are negligible and the measured concentration is characteristic of the diffusion process. After several hours, however, some Ni particles become smaller than the beam size and the above approximation is not valid anymore.<sup>9</sup> This contribution from the Ni particles is, however, minimized by the fact that we keep only the minimum concentration value encountered during several depth profiles.

Figure 4 shows that the Ni concentration increases very rapidly in the first few hours and saturates to the average value of 33% after approximately 10 h. The interdiffusion during ball milling is a difficult problem to solve theoretically because the geometry is not fixed. A reasonable assumption to make is that the Ni is dispersed very rapidly within all the Zr grain boundaries followed by Ni diffusion from the boundary to the center of the Zr crystallites, the latter being the rate limiting process. This is reasonable since it is well known that the activation energy for grain boundary diffusion is a

few times smaller than the one for lattice diffusion. The problem would therefore consist of solving the diffusion equation of a Zr particle of size "a" varying with time inside a semi-infinite medium of Ni.

It is possible to show that the average Ni concentration inside a cubic Zr particle of fixed size  $a$  is given by

$$\bar{c} = \left\{ \frac{2(Dt)^{1/2}}{a} \int_0^{a/2(Dt)^{1/2}} \text{erfc}(x) dx \right\}^3, \quad (1)$$

where  $D$  is the diffusion coefficient and  $a$  is the edge of the cube.

The size of the Zr crystallites has been measured from the width of the x-ray peaks after proper correction for  $K\alpha_2$ , instrumental and strain broadening.<sup>9</sup> After a rapid decay during the first hour, the size of the crystallites decreases at a slow rate compared to the rate of change of the concentration. We can therefore assume, in a first approximation, that the measured average concentration will be given by Eq. (1) where  $a$  is replaced by the time-dependent crystallite size measured by x-ray diffraction.

The solid line shown in Fig. 4 is the result of such a calculation using  $D = 6.5 \times 10^{-20} \text{ m}^2/\text{s}$  and the experimental crystals size. The agreement with the experimental data is very good. From the value of  $D$  and previous Ni tracer diffusion experiments in Zr,<sup>10</sup> we can estimate an effective local temperature of 180°C in the particles during the collisions.

Note that, at the maximum APPR (3 h of milling time), the Ni concentration in the Zr reaches 27%. This value was found to be the lower Ni concentration limit of the amorphous range by ball milling in the Ni-Zr binary system<sup>11</sup> and equals approximately the evaluated thermodynamic critical Ni concentration for single amorphous phase formation.<sup>12</sup>

We studied the amorphization reaction of a Ni-Zr mixture and showed that the maximum APPR occurs when the Ni concentration in the Zr crystallites reaches the minimum level for homogeneous amorphous phase formation in this binary system, suggesting that the large negative heat of mixing is the driving force for the reaction. Based on the variation of the Ni concentration in Zr and using a simple model for the interdiffusion mechanism we estimate the diffusion coefficient to be  $6.5 \times 10^{-20} \text{ m}^2/\text{s}$ . From this value, an effective local temperature of 180°C is estimated in the powder at the collision site.

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