

# Formation and characterization of amorphous erbium-based alloys prepared by near-isothermal cold-rolling of elemental composites

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We report the formation of bulk single-phase amorphous Cu-Er and Ni-Er alloys by extensive cold-rolling of elemental foils. The reaction is driven by the negative enthalpies of mixing of the constituent elements and occurs near ambient temperature. The crystallization behavior of the alloys obtained was studied by means of differential scanning calorimetry and found to agree closely with that of the corresponding sputtered and liquid-quenched alloys. Radial distribution functions were measured for sputtered and rolled  $\text{Cu}_{72}\text{Er}_{28}$  and were found to be in good agreement.

## I. INTRODUCTION

In recent years, solid-state reactions have been shown to be an alternative to rapid cooling for the synthesis of amorphous metallic alloys. This was first established by Yeh *et al.*,<sup>1</sup> who formed amorphous  $(\text{Zr}_3\text{Rh})_x\text{H}_{1-x}$  by hydriding the metastable crystalline compound  $\text{Zr}_3\text{Rh}$  ( $\text{Cu}_3\text{Au}$  structure). Later, Schwarz and Johnson<sup>2</sup> reported the formation of an amorphous Au-La alloy by solid-state reaction of alternating thin layers of crystalline Au and La. The driving force for such a metal-metal reaction is the negative enthalpy of mixing of the constituent elements. The reaction occurs by solid-state diffusion at a temperature sufficiently high to allow atomic mobility, but sufficiently low so that the formation of crystalline intermetallic compounds is kinetically suppressed.

We have recently reported the extension of the diffusion couple experiment to three dimensions. Amorphous Cu-Zr and Ni-Zr alloys were produced by solid-state reactions in elemental composites formed by mechanical deformation. The composites were prepared by physically mixing elemental powders or foils and subsequently cold-rolling them. Similar experiments were reported by Schultz.<sup>4</sup> This method provides the possibility of synthesizing amorphous alloys in bulk, since, unlike for rapid quenching techniques, there are no fundamental limits on the external dimensions of a specimen.

Ni-Er and Cu-Er were chosen for this study for several reasons. There exists substantial interest in amorphous rare-earth alloys because of their magnetic applications. In addition, the crystallization behavior and structure of various amorphous rare-earth-transition-metal alloys has been studied by several authors. Erbium was selected as the rare-earth element in this study because of its high ductility and its relatively low oxidation rate in air.

Nikolaenko *et al.*<sup>5</sup> reported measurements of the enthalpy of dissolution of erbium in liquid copper for low erbium concentrations. Using their results and the regular solution approximation,<sup>6</sup> we estimate the enthalpy of formation of liquid CuEr from the crystalline elements to be about 19 kJ/mol. The enthalpy of formation of the glass is

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assumed to be close to that of the liquid. We are not aware of any data concerning the enthalpy of mixing in the Ni-Er system. However, Miedema<sup>7</sup> has reported a general proportionality between negative enthalpies of mixing and the number of intermetallic compounds in a binary system. Therefore, based on the existence of a number of intermetallic compounds in the Ni-Er system,<sup>8</sup> we assume the enthalpy of mixing to be negative and large.

We report here the complete amorphization of Cu-Er and Ni-Er composites by near-isothermal cold-rolling. The high-temperature thermal behavior and the radial distribution functions (RDF) have been measured and compared to those of corresponding alloys produced by sputter deposition. As a result we have explicitly demonstrated that the amorphous alloy phase produced by this technique is essentially the same as that produced by more conventional methods (e.g., sputtering and liquid quenching).

## II. EXPERIMENTAL DETAILS

The samples used in this study were prepared from elemental crystalline foils. Erbium foils were formed by cold-rolling bulk ingots, reducing their thickness to  $\approx 20 \mu\text{m}$ . Nickel and copper foils with a total impurity concentration of 0.02 at. % and thickness of  $25 \mu\text{m}$  were purchased commercially. These foils were later rolled to a thickness appropriate for the desired composition of the composite. The average composition was determined for each sample by weighing the constituent foils. To minimize contamination, the samples were prepared immediately following preparation of the foils.

The initial layered composites were formed by stacking together two individual elemental foils and winding them into a cylinder. The cylindrical composite was then cold rolled inside a stainless-steel tube. After removal from the tube the sample was further processed in 10 to 55 deformation passes consisting of (1) folding the foil, (2) rolling it between two 0.75-mm-thick stainless-steel plates in many successive small steps to the minimum spacing of the rollers, and (3) removing the resulting foil from the stainless steel. The final composite foils obtained were 20–200  $\mu\text{m}$  thick.

To obtain an estimate of transient heating effects which occur during the mechanical deformation, a chromel-alumel

the thermocouple was observed on a storage oscilloscope with a time resolution of 0.5 ms.

Samples which were to be thermally reacted were vacuum sealed with zirconium getters in long Pyrex ampules. Prior to sample annealing, the getters were separately heated to 550 °C for 8 h while the samples remained at ambient temperature.

The DSC measurements were performed on a DuPont 1090 calorimeter. The baseline was measured separately and subtracted from the signal.

Amorphous  $\text{Cu}_{72}\text{Er}_{28}$  films were also prepared by magnetron sputtering, using Ar as the sputter gas. Base pressures prior to sample deposition were in the  $10^{-7}$  Torr range while the samples themselves were deposited at a pressure of 15 mTorr. Total sample thicknesses ranged from 5 to 10  $\mu\text{m}$ . In addition, liquid quenched foils were prepared by the "piston and anvil" method.<sup>9</sup>

The interference functions for the RDF's were measured using a vertical Norelco diffractometer in step-scanning mode with  $\text{Mo } K_{\alpha}$  radiation and a LiF divergent beam monochromator. For the RDF measurement, the cold-rolled sample used was 0.2 mm thick while several sputtered foils were stacked and glued with diluted Duco cement to obtain a total thickness of about 60  $\mu\text{m}$ . Since the absorption depth for  $\text{Mo } K_{\alpha}$  radiation in the alloy is 20  $\mu\text{m}$ , the infinite thickness approximation applied for both samples. The data were analyzed following Williams and Johnson.<sup>10</sup> The RDF was obtained from

$$G(r) = 4\pi r [\rho(r) - \rho_0] \approx 2 \int_0^{K_{\max}} i(K) U(K) \sin Kr dr, \quad (1)$$

where  $i(K) = K [I(K) - 1]$  is the reduced interference function and

$$U(K) = \frac{\sin(\pi K / K_{\max})}{\pi K / K_{\max}} \quad (2)$$

is the Lorch filter,<sup>11</sup> used as a convergence factor to eliminate termination ripples arising from the finite integration range. Exponential convergence factors gave similar results. The qualitative x-ray diffraction patterns were taken on a Norelco diffractometer in step-scanning mode, using copper  $K_{\alpha}$  radiation filtered with a nickel foil.

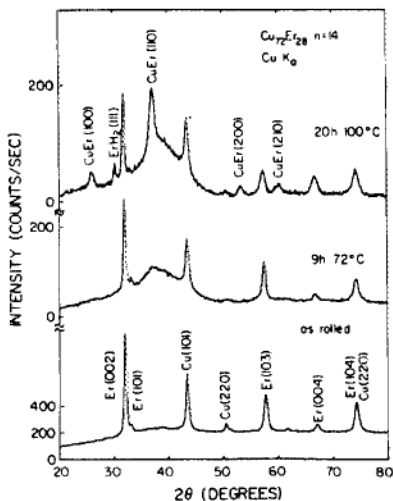


FIG. 1. X-ray scattering intensity as a function of scattering angle for as rolled (bottom) and isothermally reacted (middle and top)  $\text{Cu}_{72}\text{Er}_{28}$  for 14 deformation passes.

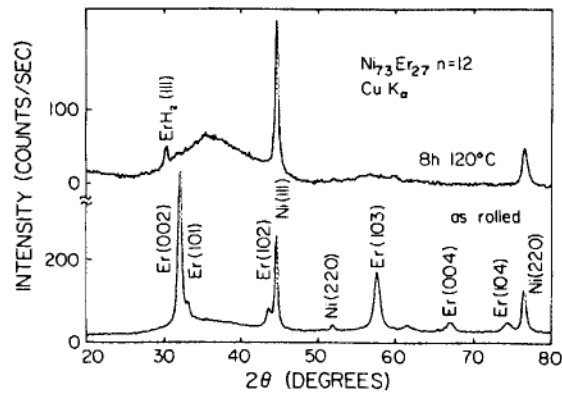


FIG. 2. X-ray scattering intensity as a function of scattering angle for rolled (bottom) and isothermally reacted (top)  $\text{Ni}_{73}\text{Er}_{27}$  for 12 deformation passes.

### III. RESULTS

All samples studied were deformed in 10–55 passes as described in the experimental section. In x-ray diffraction patterns of samples processed in 12–14 passes (Figs. 1 and 2), the hexagonal structure of erbium shows with a texture similar to the one we reported for zirconium in Cu-Zr and Ni-Zr composites.<sup>3</sup> The nickel lines, however, do not show the strong (220) orientation in the rolling plane, which we observed in the above reference.

We plotted the full widths at half maximum of the Bragg peaks  $\Delta K$  as a function of their  $K$  values for samples deformed in 12 passes in Fig. 3. The peak widths were determined by fitting a Lorentzian line shape and correcting for  $K_{\alpha}$  and instrumental broadening, following Ref. 12. The line broadening due to small crystal size (Scherrer broadening) is constant in  $K$  space and is given by<sup>13</sup>

$$\Delta K = 0.9 \times 2\pi / L, \quad (3)$$

where  $L$  is the crystal size. The broadening due to strains is given by

$$\Delta K = A \langle e^2 \rangle^{1/2} K, \quad (4)$$

where  $\langle e^2 \rangle^{1/2}$  is the rms strain.<sup>14</sup>  $A$  is a coefficient which depends on the strain distribution. It is approximately one for a random distribution of dislocations. Since the deformed composites have high dislocation densities,<sup>15</sup> we do not have a good estimate of this coefficient and we use  $A = 1$

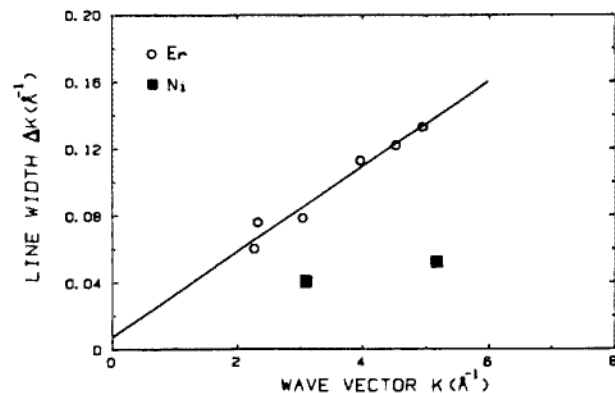


FIG. 3. Bragg peak broadening  $\Delta K$  as a function of magnitude of  $K$  vector for Ni-Er composite deformed in 12 passes.

thermocouple was sandwiched in a sample foil and then rolled between stainless-steel plates. The voltage signal on as a first approximation. The slope of the lines then indicates that the rms strains are on the order of 2%.

Samples processed in 12–14 passes were reacted at 70 to 170 °C for 1–10 h. Typical reaction products are shown in Figs. 1 and 2. One can see that the intensities of the Bragg peaks decrease upon reaction, and that a broad maximum appears, indicating the growth of an amorphous phase. As in the earlier cases of Ni-Zr and Cu-Zr,<sup>3</sup> the reaction is not complete, and an increase in the reaction time or temperature does not lead to a more complete reaction, but rather to the formation of crystalline intermetallic compounds. In Cu-Er composites deformed in 14 passes and annealed for 6 h at 95 °C, the equilibrium compound CuEr with the CsCl structure was observed. A lattice parameter of  $3.438 \pm 0.005$  Å was found in agreement with the reported value of 3.43 Å.<sup>16</sup> The Ni-Er system formed unidentified intermetallic compounds above 130 °C.

The initial composition of the composite and the relative consumption of the constituent elements, as seen from the decrease of the Bragg peak intensities, served as a rough estimate for the composition of the amorphous phase formed. The Cu-Er phase contained approximately 72 at. % copper whereas the Ni-Er amorphous phase had approximately 55 at. % nickel. In the experiments described in the following paragraphs, the samples were prepared at these compositions.

The only sample in which thermal treatment led to a complete consumption of one phase was a Ni-Er composite with 70 at. % nickel. After reaction at 120 °C for 8 h the erbium peaks disappeared, and an amorphous phase was observed in addition to unreacted nickel (Fig. 1). The (111) peak of ErH<sub>2</sub> is also seen (see below).

Complete amorphization was achieved for Cu<sub>72</sub>Er<sub>28</sub> and Ni<sub>55</sub>Er<sub>45</sub> by continuous deformation through 40 to 55 passes (Figs. 4 and 5). The sample temperature as measured during the deformation process initially reached 40 °C and subsequently dropped to 30 °C over a time period of 50 ms. Following the rolling, only very weak Bragg peaks corresponding to face centered cubic ErH<sub>2</sub> with a lattice constant of  $5.125 \pm 0.005$  Å appeared for both alloys. The use of distilled erbium having less than 0.1 at. % hydrogen in a later

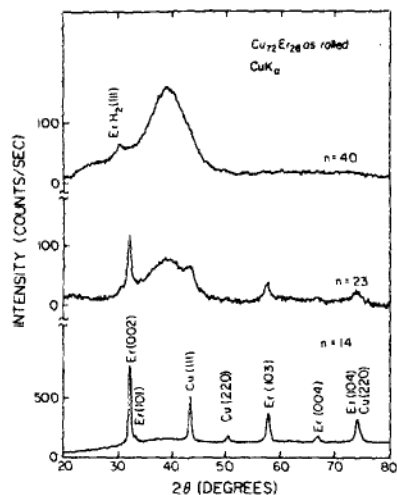


FIG. 4. X-ray scattering intensity as a function of scattering angle for rolled Cu<sub>72</sub>Er<sub>28</sub> at different numbers of deformation passes *n*.

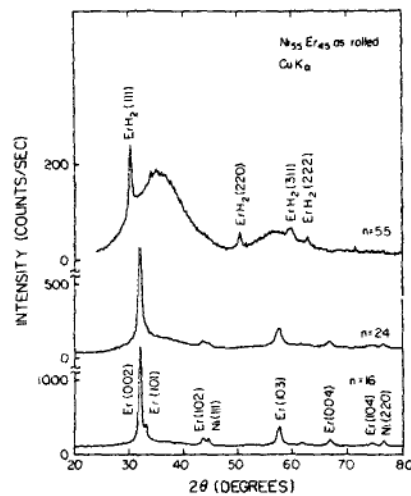


FIG. 5. X-ray scattering intensity as a function of scattering angle for rolled Ni<sub>55</sub>Er<sub>45</sub> at different numbers of deformation passes *n*.

experiment resulted in a product with substantially less intense hydride peaks. This indicates that the ErH<sub>2</sub> phase originates from hydrogen present in the erbium as a dilute impurity.

In Fig. 6, DSC scans are shown for amorphous Cu<sub>72</sub>Er<sub>28</sub> produced by rolling, sputtering, and liquid quenching. The heating rate was 40 °C/min for each case. The latter sample contained a small percentage of crystalline material, as seen by x-ray diffraction. The alloy produced by rolling shows a sharp exothermic peak at 367 °C. By heating different samples to temperatures above and below the peak and comparing the resulting phases by x-ray diffraction, the exothermic peak was verified to be a result of crystallization of the amorphous phase. The sputtered and liquid-quenched alloys both show similar exothermic peaks, at 352 and 371 °C, respectively. The liquid-quenched alloy shows a tail on the low-temperature side of the peak. This is believed to result from the presence of crystalline material in the original samples which serves as a site from which growth of crystalline material occurs. The DSC scans also indicate secondary exothermic events above 400 °C. These are seen to vary among the types of samples. In addition, for Ni<sub>55</sub>Er<sub>45</sub>, the crystallization temperature at 29 °C/min was found to be 276 °C, as evidenced by a well-defined exothermic peak.

The radial distribution function was measured in reflection geometry for a 0.2-mm-thick amorphous Cu<sub>72</sub>Er<sub>28</sub> sample produced in 55 deformation passes. In the diffraction pattern, a weak ErH<sub>2</sub> (111) peak was still visible. Its intensity was considerably below 1% of the total diffracted intensity, and it was subtracted from the interference function. Figure 7 shows the reduced interference functions obtained and Fig. 8 shows the corresponding radial distribution functions for amorphous Cu<sub>72</sub>Er<sub>28</sub> obtained by rolling and by sputtering.

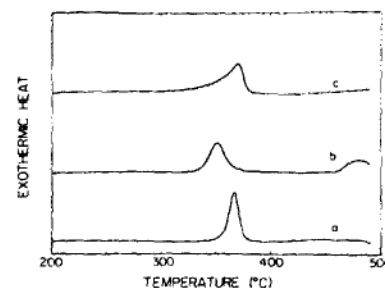


FIG. 6. DSC scans at 40 °C/min for amorphous Cu<sub>72</sub>Er<sub>28</sub> prepared by (a) rolling, (b) sputtering, and (c) rapid quenching. Sample (c) contains a small percentage of crystals.

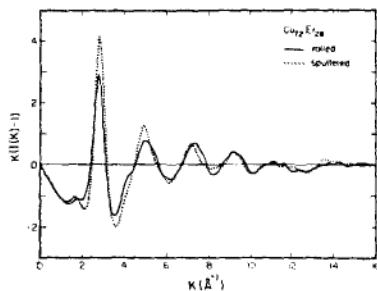


FIG. 7. Reduced interference functions for amorphous  $\text{Cu}_{72}\text{Er}_{28}$  prepared by rolling (solid line) and sputtering (dotted line), respectively.

#### IV. DISCUSSION

As in Ref. 3, we observe that an amorphization reaction cannot be completed by thermal annealing for intermediate reduction ratios ( $\approx 12$  passes). For uniform deformation, the reduction is expected to be  $2^{12}$  ( $\approx 4000$ ), producing a layer thickness of about  $50 \text{ \AA}$ . We suggest a nonuniform distribution of layer thicknesses as an explanation for the significant slowdown after the initial reaction. Every time the sample foil is folded, there are areas which do not overlap other parts of the sample and are therefore reduced to a lesser extent during the subsequent deformation. In a simple model, we assume that a randomly located area, which constitutes 10% of the sample, does not overlap any other part of the sample. This area is assumed not to be deformed in the subsequent pass. The resulting thickness distribution is binomial:

$$p_m^n = \binom{n}{m} (0.9)^m (0.1)^{n-m}, \quad (5)$$

where  $p_m^n$  is the fraction of the sample reduced by  $2^m$  after  $n$  passes. For  $n = 12$ , 0.5% of the sample is deformed by only  $2^7 = 128$  to a thickness of  $1600 \text{ \AA}$ . In addition to this effect, the development of cracks can cause nonhomogeneous deformation. The absence of the nickel texture observed in Ni-Zr composites for similar deformation ratios implies that the deformation behavior of nickel in a composite depends on the second component. This observation also implies a nonhomogeneous deformation. In addition, as we mention in Ref. 3, contaminants present on the interfaces could act as diffusion barriers in some parts of the sample.

The hydride formation during the metal-metal reaction can be understood on the basis of different time scales for atomic transport. Since the diffusion coefficient for hydrogen in metals is orders of magnitude greater than for transition metals in metals, the hydrogen concentration profile remains in equilibrium with the sample during the Er-Cu or Er-Ni reaction. It has been observed<sup>17</sup> that in amorphous  $\text{Zr}_3\text{Rh}$  and  $\text{Zr}_2\text{Pd}$ , hydrogen preferentially occupies  $\text{Zr}_4$  tetrahedral sites. If one assumes that hydrogen preferentially occupies erbium-coordinate sites in the erbium composites,

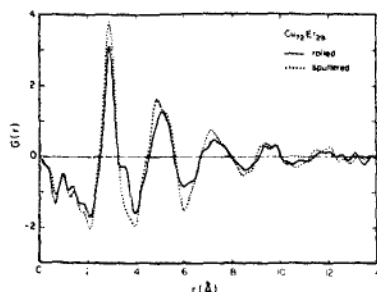


FIG. 8. Reduced radial distribution functions for amorphous  $\text{Cu}_{72}\text{Er}_{28}$  prepared by rolling (solid line) and sputtering (dotted line), respectively.

one concludes that most of the hydrogen will remain in the unreacted crystalline erbium phase as the deformation proceeds. When its concentration reaches a certain critical level,  $\text{ErH}_2$  will be formed. The fcc structure and the lattice constant of  $5.125 \text{ \AA}$  we mentioned earlier are in agreement with previous work.<sup>18</sup>

The following considerations lead us to conclude that there is no substantial heating effect within the sample during the mechanical deformation and that the amorphization by rolling occurs at near-isothermal conditions at roughly ambient temperatures. The thermal relaxation time within the sample is estimated to be  $10^{-6} \text{ s}$  for layers  $10 \mu\text{m}$  thick, and it decreases with decreasing thickness of the individual layers. The geometry and speed of the rolling mill together with the deformation step size for a single pass are such that it takes roughly  $10^{-3} \text{ s}$  to deform a local volume element. Therefore the heat should be deposited rather uniformly within the sample (i.e., the sample is under locally isothermal conditions during deformation). The direct temperature measurement shows a rise of less than  $25 \text{ }^\circ\text{C}$  during the deformation, and a relaxation with the stainless-steel container on a time scale of 50 ms. In addition, a rough calculation was made based on the theoretical limit for the yield stress of a metal<sup>19</sup> which gave an upper limit on the temperature increase of  $80 \text{ }^\circ\text{C}$ . The temperature rise of the stainless steel surrounding the sample, which provides a heat sink, is only  $20 \text{ }^\circ\text{C}$ , as obtained by both calculations and measurement. In summary, we conclude that slight heating of  $20\text{--}40 \text{ }^\circ\text{C}$  occurs within the sample and persists for a total of a fraction of a second as the sample and stainless steel come to thermal equilibrium. These temperatures are lower than those used to induce reaction by thermal treatment and the time spans involved are substantially shorter.

Koch *et al.*<sup>20</sup> showed that nickel and niobium powders could be alloyed to form amorphous powders by high-energy ball milling for extended times. Such mechanical alloying occurs under a very high strain rate and therefore under highly nonequilibrium conditions. Local heating and even melting are then possibly involved. In contrast, the mechanical alloying reported here for Cu-Er and Ni-Er is near isothermal. The small temperature rise does not exceed  $60 \text{ }^\circ\text{C}$ , and persists for time scales at most on the order of one minute. We believe that the amorphization reaction occurs by diffusion over several atomic layers and/or atomic rearrangement at or near ambient temperatures, and in the vicinity of the interfaces between the two metals comprising the composite. Small layer sizes make the reaction rates sufficiently high at ambient temperature so that amorphization is completed before crystalline intermetallic compounds can nucleate. As described earlier, this was not the case for the Cu-Er thermally reacted at intermediate reduction ratios. In this case, any practical amorphization rate was observed to be accompanied by the formation of crystalline CuEr. One should also note that during rolling, a substantial rms strain was observed which increases with reduction ratio. These strains may possibly play a role in enhancing the diffusion rates and allowing reaction at near ambient temperature.

One can use the values obtained for the strains in the elemental phases to estimate the strain energies  $u$  involved:

$$u = E/2(\epsilon^2), \quad (6)$$

where  $E$  is Young's modulus. The number obtained is about 1 kJ/mol. Chemical enthalpies of mixing for the constituent metals are typically 20 kJ/mol (see Introduction) while the heats of crystallization of metallic glasses are known to be of order of 4 kJ/mol.<sup>21</sup> One concludes that the strain energies introduced by mechanical deformation do not change the thermodynamic driving force for the crystalline-amorphous reaction significantly. On the other hand, stresses can introduce substantial changes in the reaction kinetics, as has been shown by Unruh *et al.*<sup>22</sup> for Ni-Zr multilayered thin films. In addition to the strain energies due to the presence of defects in the bulk, one should also consider the energy associated with the increase of interfacial area. For layers below a thickness of 50 Å, for example, a positive interfacial energy could make a contribution on the order of 1 kJ/mol to the balance of Gibbs free energy. This could increase the driving force for a transformation into a homogeneous amorphous phase. Nevertheless, one sees that interfacial energies are not the dominant driving force. To support this claim, a separate study of Cu-Nb composites were made. No evidence of an amorphous phase was found in the Cu-Nb composite prepared as described above for the Er-based composite and rolled in 35 passes. In contrast to the Cu-Er system, the enthalpy of mixing for Cu and Nb is small (+ 3 kJ/mol for liquid CuNb according to Ref. 23). Thus there should be little chemical driving force for reaction of Cu-Nb composites to form an amorphous phase. The absence of any reaction in Cu-Nb after severe deformation thus, at least indirectly, supports the view that chemical driving forces are primarily responsible for amorphous phase formation in Cu-Er and Ni-Er.

The DSC results show a similarity in the crystallization behavior of the amorphous alloys produced by three different methods. For identical heating rates, the samples produced by rolling and by liquid quenching crystallize within 4 °C of each other. The sputtered sample crystallizes at a temperature 15 °C lower than the rolled one, possibly due to a difference in the composition or entrapped argon. Since the crystallization temperature ( $T_x$ ) of amorphous alloys with a large negative heat of mixing depends strongly on the composition,<sup>24</sup> the sharpness of the crystallization peak indicates a considerable degree of homogeneity in the rolled sample near  $T_x$ . The different structure observed in the DSC scans above  $T_x$  is possibly the result of differences in the impurity content and the morphology of the crystallized samples.

The RDF's obtained for sputtered and rolled Cu<sub>72</sub>Er<sub>28</sub> (Fig. 8) show good agreement, indicating that the two preparation methods produce alloys with similar atomic-scale structure. The shoulder on the first coordination peak for the rolled sample is believed to be a result of the presence of the erbium hydride. The shoulder is positioned at 3.63 Å, and the Er-Er distance in ErH<sub>2</sub> is 3.624 Å. A confirmation of this assumption is given by the fact that before subtracting the ErH<sub>2</sub> (111) peak from the interference function, the shoulder in the RDF was more intense. A complete subtraction of the crystalline contribution is apparently not possible. One cannot exclude the possibility that Er-Er coordination causes the above shoulder in the RDF, since it is positioned at ap-

proximately twice the Goldschmidt radius of erbium (1.78 Å). As can be seen from Fig. 7 the low  $K$  (i.e., small angle) x-ray peaks are relatively less intense for the cold-rolled sample as compared to the sputtered sample. This may be the result of shadow effects caused by the rough surface on the rolled sample.

The RDF for the sputtered sample gave a coordination number of 12.4. For the rolled alloy the coordination number was 13.5. This difference is attributed to the shoulder present on the first peak, as discussed above.

## V. SUMMARY

We have shown that single-phase amorphous Cu-Er and Ni-Er alloys can be synthesized by mechanical deformation of elemental composites under near-isothermal conditions at a temperature near ambient. The reaction is driven primarily by the negative enthalpy of mixing of the constituent elements. In addition, the diffusion lengths are believed to be of the order of several atomic diameters.

The crystallization behavior of the alloy obtained is close to that of the corresponding alloys produced by rapid quenching and sputtering. For cold-rolled Cu<sub>72</sub>Er<sub>28</sub> the RDF has been measured and found to be in good general agreement with that of a sputtered amorphous alloy.

Further information about the amorphization process and the morphology of the composites could be gained by means of transmission electron microscopy. In addition, it would be instructive to study the effect of applied pressure on the reaction rates.

## ACKNOWLEDGMENTS

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