Formation and growth of amorphous phases by solid-state reaction in elemental composites prepared by cold working

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Amorphous alloys of Ni-Zr and Cu-Zr have been synthesized by solid-state reaction of composite metal mixtures produced by mechanical deformation of metal powder mixtures and intercalated foil layers. The materials obtained were investigated by means of x-ray diffraction and differential scanning calorimetry. The results are compared with known data for thin films and rapidly quenched alloys.

Recently, Schwarz and Johnson[1] showed that an amorphous alloy can form and grow during a relatively low-temperature solid-state reaction of evaporated thin-film layers of two polycrystalline metals. In a related experiment, Koch[2] demonstrated that mechanical alloying of elemental Ni and Nb powders by high-energy ball milling for extended times leads to the formation of an amorphous alloy powder. A three-dimensional analogue of the thin-film diffusion couple experiment could offer a means of synthesizing bulk amorphous alloy structures. In an effort toward this goal, we have studied the reaction of mechanically deformed powder and foil mixtures of two crystalline metals. Mechanical deformation serves to (1) consolidate the binary mixture, (2) increase the interfacial area between the two metals, and (3) reduce at least one of the characteristic dimensions of the mixture. Point (2) is essential for achieving clean metal-metal interfaces free of oxides or surface contaminants present on the starting materials. Point (3) is required if completion of a reaction is to occur in practical times. A recent review article by Bevk[3] describes the preparation, morphology, and properties of ultrafine filamentary composites. Such composites with filaments as thin as 50 Å have been reported and are described and referenced in this article.

Two binary systems were chosen for this study: Ni-Zr and Cu-Zr. Solid-state reactions in Ni-Zr were reported previously by Clemens *et al.*[4] The Cu-Zr system was selected because of its similarity to Ni-Zr. The present study is the first report on the formation of amorphous Cu-Zr by solid-state reaction.

Two different methods were used for sample preparation. Ni-Zr was prepared by consolidating a thoroughly tumbled mixture of 40-μm size Ni and Zr powders in an argon atmosphere, sealing it in vacuum in a stainless steel can, and subsequently cold rolling the sample plus can, reducing its thickness by a factor of 8. Ni-Zr and Cu-Zr samples were made by winding two annealed elemental foils of $\sim 10\,\mu$m thickness in spiral form and then cold rolling them in a stainless steel jacket. For both methods, the foils obtained were removed from their containers and subsequently processed in 10–12 passes, each consisting of (1) folding the foil to double its thickness and (2) rolling it in between two 0.75-mm-thick stainless steel plates to the limit of the rolling mill.

The scanning electron micrograph in Fig. 1 shows a cross section of a Ni-Zr sample prepared by the powder metallurgical technique. Individual lamellae consisting of about 1000-Å-thick Ni and Zr layers can be seen. Figure 2(a) shows an x-ray diffraction pattern of an as-rolled $Ni_{62}Zr_{38}$ composite, taken with a vertical diffractometer in reflection geometry. In this configuration, the x-ray scattering vector K is perpendicular to the foil surface. The Scherrer formula[5] allows one to estimate the typical size t (parallel to K) of an individual microcrystal as

$$t = 0.9\lambda /B \cos \theta,$$

where λ is the wavelength of the radiation, B is the linewidth, and 2θ is the scattering angle. This microcrystal size is a lower bound on the lamella thickness since the thickness of the lamella must contain at least one microcrystal. The instrumental line broadening was measured with a single crystal and found to be 0.15°. After appropriate account of the instrumental broadening was taken, t values of 500 and 600 Å were obtained for Zr and Ni, respectively. For the copper in Cu-Zr, t is equal to 250 Å. In both Ni-Zr and Cu-Zr composites, strong texture is observed. For Ni and Cu, the relative intensity of the (220) lines is higher than expected for the diffraction pattern of a randomly distributed powder. This is consistent with the description of the texture in cold-rolled face centered cubic metals given in the literature.[6] Among the Bragg peaks corresponding to zirconium, the (100) is barely present before the reaction while the (002) is relatively intense.

FIG. 1. Scanning electron micrograph of a cross section of a Ni-Zr composite foil as rolled.

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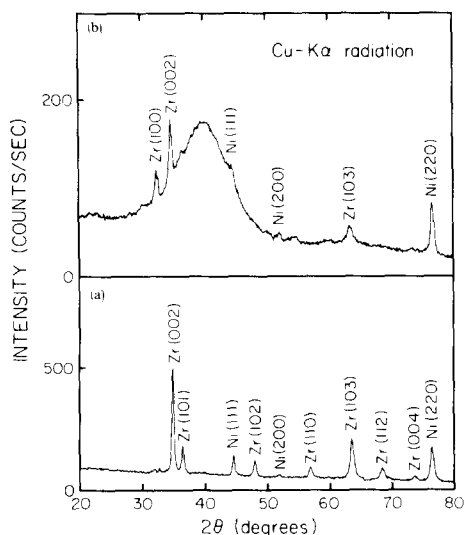
FIG. 2. X-ray diffraction pattern for a $Ni_{62}Zr_{38}$ composite (a) as rolled and (b) reacted at 260 °C for 14 h.

Prior to annealing the sample foils were sealed under vacuum in pyrex tubes containing Zr getters, which were separately heated above 500 °C for 10 h while the samples remained at ambient temperature. Then the samples were annealed at temperatures ranging from 250 to 370 °C for times of 1–32 h. For both Ni-Zr and Cu-Zr, crystalline intermetallic compounds were obtained at annealing temperatures above 280 °C, as observed with x-ray diffraction. Figure 2(b) shows the x-ray diffraction pattern in the same geometry as in Fig. 2(a) for a $Ni_{62}Zr_{38}$ sample, reacted at 260 °C for 14 h. A broad diffuse diffraction maximum (width $\sim 10°$) is observed in a range of K values, in which no Bragg peaks were present before the reaction. The original Ni and Zr phases are not completely reacted, as can be seen from the remaining peaks. The fraction of unreacted material can be estimated from the ratio of the area under the Bragg peaks to the area under the diffuse maximum. It is approximately 20%. For a reaction time of 32 h at the same temperature, little further growth of the amorphous phase is observed, but one or more crystalline intermetallic compounds are formed. There still remains some elemental material. The incompleteness of the reaction can have several causes: surface oxides or other contaminants may be present on some interfaces and act as diffusion barriers; the occurrence of several adjacent layers of the same metal could lead to rather thick regions of one metal. Thus much longer times would be required to react these regions. In such long times, crystalline compounds are observed to form and thus a completely amorphous by-product is precluded.

It should be noted that the original Bragg peak intensities do not all decrease at the same rate during the reaction. In particular, the Zr(110) and the Ni(111) show the fastest rate of decrease while the Ni(220) increases slightly. The latter observation was shown to be related to preferred (220) coarsening of Ni grains by separate annealing of cold rolled

Ni foils at 260 °C.

Differential scanning calorimetry was performed on several samples of Ni_xZr_{1-x} ($x = 62, 68$; reacted at 270 °C for 8–16 h) and $Cu_{60}Zr_{40}$ reacted at 275 °C for 16 h. For all Ni-Zr samples, an exothermic peak at 550–565 °C was obtained for a heating rate of 20 °C/min. X-ray diffraction patterns of a sample heated to 500° and cooled rapidly show the presence of a new crystalline intermetallic compound and a remaining amorphous phase. This compound is likely to be a result of the completion of the reaction of the pure zirconium and nickel. After heating the sample to 570 °C and cooling it down, the x-ray diffraction pattern shows no remaining amorphous material and a new set of Bragg peaks. We therefore attribute the exothermic peak to the crystallization of the amorphous phase. Our result for the crystallization temperature T_x is in close agreement with Dong et al.[7] who report that for Ni-Zr metallic glasses produced by rapid quenching, T_x has a maximum as a function of composition equal to 575 °C at 64 at. % nickel. Preliminary results for $Cu_{60}Zr_{40}$ yield an endothermic peak at 440 °C and two sharp exothermic peaks at 475 and 500 °C, respectively. The endothermic peak is characteristic of a glass transition. Kerns et al.[8] report for the rapidly quenched metallic glass $Cu_{60}Zr_{40}$ a glass transition temperature T_g of 450 °C and a crystallization temperature of 490 °C. Our values of T_g and T_x are again in close agreement with those obtained for rapidly quenched glasses.

In summary, we have demonstrated the feasibility of solid-state reactions for synthesizing amorphous alloys in three dimensions. For the first time, thermal analysis of the product of such reaction has become possible, and the results indicate that the crystallization and glass transition temperatures of the amorphous phases formed by respectively solid-state reaction and rapid quenching of an alloy of similar composition are nearly identical.

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