

## Calorimetric Study of Amorphization in Planar, Binary, Multilayer, Thin-Film Diffusion Couples of Ni and Zr

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We have utilized differential scanning calorimetry to monitor the solid-state reaction of crystalline metals to form an amorphous alloy in multilayered thin-film diffusion couples of elemental Ni and Zr. The heat of formation of amorphous  $\text{Ni}_{68}\text{Zr}_{32}$  alloy from the elemental metals is measured directly and found to be  $35 \pm 5$  kJ/mole. The kinetics of these reactions has been examined. The activation energy for interdiffusion in the amorphous phase is determined to be  $E = 1.05 \pm 0.05$  eV.

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The discovery of the formation of amorphous alloys<sup>1</sup> under certain conditions in planar, binary, thin-film diffusion couples consisting of elemental crystalline metals has sparked considerable interest. These solid-state reactions are hypothesized<sup>1</sup> to be driven by a large negative heat of mixing. The formation of crystalline equilibrium compounds is frustrated by the kinetic constraints imposed by the low reaction temperatures selected. The present work directly examines these reactions in thin-film multilayers of Ni and Zr via differential scanning calorimetry (DSC).<sup>2,3</sup> Monitoring of a complete solid-state amorphization reaction results in qualitative and quantitative thermodynamic and kinetic data, including a direct measurement of the heat of formation of an amorphous NiZr alloy from the elemental metals.

Samples consisting of Ni/Zr multilayers were prepared by dc planar magnetron sputtering in an UHV chamber with a sputtering gas of Ar. Base pressures prior to sputtering were less than  $4 \times 10^{-8}$  Torr. Pure Ni and Zr targets were sputtered individually and the sample substrate was rotated over each sputtering gun. Deposition rates and resulting film thicknesses were monitored in real time by one quartz-crystal oscillator (Inficon XTC) mounted over each gun. Typical sputtering rates were between 1 and 3 Å/sec. Multilayered thin films with alternating layers of equal thicknesses of Ni and Zr (corresponding to the average stoichiometry  $\text{Ni}_{68}\text{Zr}_{32}$ ) were deposited upon cleaved NaCl substrates. The resultant samples included extra half-thickness layers of Zr on both the top and the bottom of the samples which served as protective caps.<sup>4</sup> After deposition, samples were immersed in distilled water and the Ni/Zr films floated free, were captured, and then were rinsed in ethanol. These free-standing films were dried and immediately hermetically sealed in aluminum pans by cold welding in an inert-gas atmosphere (Ar or He) with a minimal volume of gas sealed in each sample pan. The sample configuration, a flat metal sample in intimate contact with a flat metal pan, is optimal for DSC measurements. Differential scanning calorimetry (a Perkin-Elmer DSC-4 interfaced to an Apple IIE computer for data collection) was employed to monitor the progress of amorphi-

zation via solid-state reaction. Sample scans were followed immediately by a second scan of identical thermal history. This second scan was subtracted from the first, better to elucidate phase transformations undergone by the sample. No attempt was made to compensate for changes in the specific heat of the sample upon transformation. After a DSC run, the cold-welded flanges of the sample pan were cut off and the samples were removed for x-ray diffraction study. A Norelco x-ray diffractometer with Ni-filtered Cu  $K\alpha$  radiation was used for obtaining x-ray diffraction patterns of the materials.

The rate of heat release upon amorphization of a Ni/Zr multilayer, as well as upon subsequent crystallization, is displayed in Fig. 1. This DSC scan was conducted at 10 K/min with a 5.06-mg sample consisting of 45 Ni and 45 Zr layers each; all layers were 300 Å in thickness. The scan reveals two separate reactions: the first reaction (centered at temperature  $T = 580$  K) which we identify with the amorphization of the original multilayers and the second reaction (centered at  $T = 830$  K) which we identify with the subsequent crystallization of the amorphous phase. X-ray scans of the as-deposited sample (a control sample from the same deposition), are shown in Fig. 2(a). Figure 2(b) shows the results for a sample heated up to 670 K and then cooled quickly to

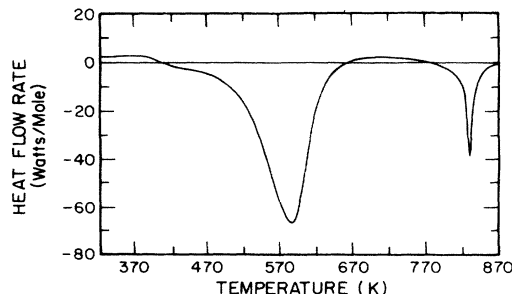


FIG. 1. The heat-flow rate as a function of temperature for a sputtered, multilayered thin film of the average stoichiometry  $\text{Ni}_{68}\text{Zr}_{32}$ . The heat-flow rate is measured via differential scanning calorimetry at constant temperature scanning rate of 10 K/min. The thin film is comprised of equal-thickness (300 Å) layers of Ni and Zr with half-layer Zr caps (see text).

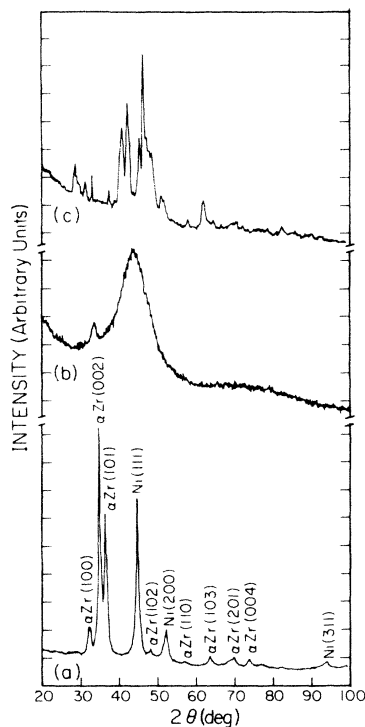


FIG. 2. X-ray diffraction profiles (Copper K $\alpha$  radiation) for the thin film sample of Fig. 1: (a) as deposited, (b) after a DSC scan at 10 K/min to 670 K and quench to room temperature, (c) after a DSC scan at 10 K/min to 870 K and quench to room temperature.

room temperature. Finally, Fig. 2(c) shows results for a sample heated up to 870 K and then cooled quickly to room temperature. Diffraction of the as-deposited sample reveals elemental Bragg peaks corresponding to Ni and Zr. After the sample has been heated to 670 K at 10 K/min, the elemental peaks have vanished from the x-ray pattern and a broad diffuse maximum characteristic of an amorphous phase and centered at  $2\theta = 41.4^\circ$  has appeared, with a secondary maximum visible at higher angle. The residual (002) reflection of Zr corresponds to the thicker external Zr layers on the sample, which we do not expect to react fully.<sup>4</sup> By examining the correlation between the position of the first diffraction maxima of various liquid-quenched amorphous NiZr alloys and their compositions,<sup>5</sup> we interpolate the average composition of the amorphous NiZr alloy formed during this *in situ* reaction to be  $68 \pm 2$  at. % Ni. This agrees with the nominal overall composition of the as-deposited multilayer.

The nearly constant heat-flow rates observed at temperatures in the range up to 350 K and the range near 720 K are interpreted as corresponding to solid-state reaction rates equal to zero. The growth rate of the amorphous interlayers first becomes observable at  $T \cong 370$  K and finally falls to zero at  $T \cong 720$  K. At the latter temperature, the amorphization process is apparently completed. The heat release of the crystalline-to-amorphous

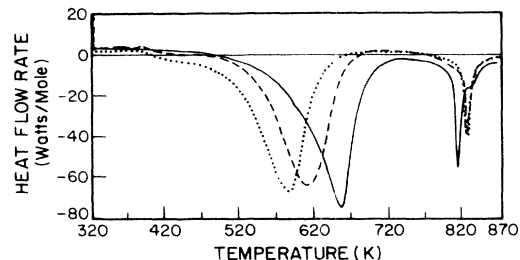


FIG. 3. The heat-flow rate as a function of temperature for sputtered, multilayered thin films of equal-thickness layers of Ni and Zr (average stoichiometry Ni<sub>68</sub>Zr<sub>32</sub>) with varying layer thicknesses. Dotted line, 300-Å layers; dashed line, 450-Å layers; solid lines, 1000-Å layers. The heat-flow rate is measured as a function of temperature via differential scanning calorimetry at a constant temperature scanning rate of 10 K/min.

transformation seen in Fig. 1 can be calculated via integration between these two temperatures. We find for this sample (average stoichiometry Ni<sub>68</sub>Zr<sub>32</sub>) a heat release upon amorphization of 510 J/g, or 35 kJ/mole. The crystallization peak observed at 830 K falls between the previously measured crystallization temperatures (with the same heating rate of 10 K/min) of liquid-quenched amorphous Ni<sub>67</sub>Zr<sub>33</sub> and Ni<sub>68.8</sub>Zr<sub>31.2</sub>.<sup>6</sup> The integrated enthalpy release for this crystallization peak (830 K, Fig. 1) is  $4.2 \pm 0.2$  kJ/mole which compares with an enthalpy release of 3.9 kJ/mole previously observed for liquid-quenched Ni<sub>67</sub>Zr<sub>33</sub>.<sup>6</sup> This is viewed as further evidence that upon heating of the Ni-Zr multilayer to 670 K at 10 K/min, a completed solid-state reaction to a relatively homogenous amorphous state has occurred.

We have further examined these solid-state amorphization reactions in Ni/Zr multilayered samples of varying individual layer thicknesses. In Fig. 3, one observes that the basic shape of the DSC scans is repeated for multilayer samples with individual layer thicknesses of 300 Å, 450 Å, and 100 Å. For the samples with increasing individual layer thickness, the maximum rate of heat release is observed to occur at higher temperatures. Nevertheless, the total amount of heat release per mole, obtained upon integration of a DSC curve, remains constant independent of the individual layer thicknesses in a multilayered sample.

The enthalpy release of the amorphization transformation displayed in Figs. 1 and 3 should closely correspond to that of the formation enthalpy of the amorphous phase. Evaluation of the reaction product by use of x-ray and DSC analysis indicates an amorphous alloy with a high degree of homogeneity, similar to that obtained in liquid-quenched samples. X-ray analysis of the initial multilayered sample indicates that it is composed of polycrystalline layers of elements, although there may be some initial intermixing at the original Ni/Zr interfaces during film deposition.<sup>7</sup> We note that examination of samples with thicker individual layers showed no marked

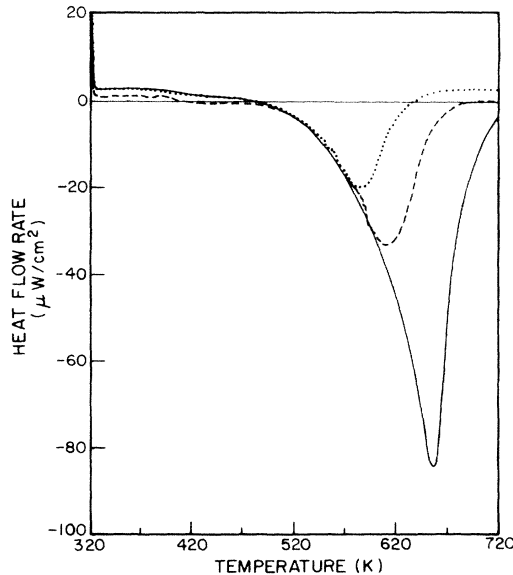


FIG. 4. The heat-flow rate as a function of temperature normalized to the interfacial area of multilayered thin films of equal-thickness layers of Ni and Zr. The thickness of the layers is varied. The average stoichiometry of the samples is  $\text{Ni}_{68}\text{Zr}_{32}$ . The data are those of Fig. 3: dotted line, 300 Å layers; dashed line, 450 Å layers; solid, 1000 Å.

dependence of the measured enthalpy release during amorphization on layer thickness, an indication that any prior intermixing does not significantly influence the measured heat of formation within the precision of the measurement. Internal stresses are also known to accompany the formation of amorphous interlayers in these multilayered diffusion couples,<sup>8</sup> but any resultant strain energy should be 1 to 2 orders of magnitude less than the relevant chemical energy. We therefore conclude that the present measurement yields an accurate determination of the heat of formation of the amorphous phase. Including the experimental precision, we thus arrive at  $35 \pm 5$  kJ/mole for the heat of formation of amorphous  $\text{Ni}_{68}\text{Zr}_{32}$  alloy from the elemental metals. Our measurement is consistent with previous measurements via dissociation calorimetry on amorphous NiZr alloys of similar compositions.<sup>9,10</sup>

As growth of the amorphous interlayer becomes diffusion controlled, the interfacial compositions of the amorphous alloy in contact with pure Ni and pure Zr are fixed by thermodynamic equilibrium conditions.<sup>1</sup> The average composition of the growing amorphous interlayer remains constant in time.<sup>11-14</sup> Thus, the measured rate of heat release from the DSC is proportional to the rate of interlayer growth at every instant. Within this approximation, the DSC makes possible a direct measurement of the growth kinetics of the solid-state amorphization reactions.

The kinetics of these solid-state reactions are essentially independent of the individual elemental layer

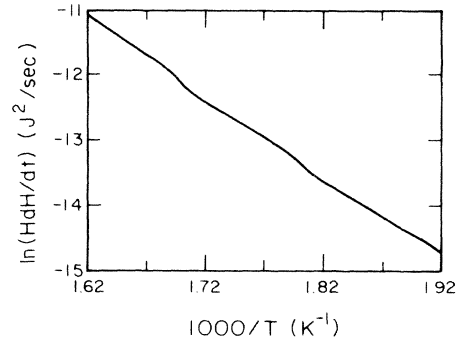


FIG. 5. The integrated enthalpy release multiplied by the rate of enthalpy release as a function of reciprocal temperature for a sputtered, multilayered thin film of Ni and Zr (average stoichiometry  $\text{Ni}_{68}\text{Zr}_{32}$ ). The thin film is comprised of equal thicknesses of 1000-Å layers. The integrated enthalpy release was obtained by integration of the rate of enthalpy release from 370 K.

thicknesses, provided that the starting layers are at least a few hundred angstroms thick. This is illustrated in Fig. 4 where the data between 320 K and 720 K of Fig. 3 are redrawn after normalization of each curve by the total interfacial area of the corresponding Ni/Zr multilayer (as calculated from the number of Ni and Zr layers in the original multilayer, individual layer thicknesses, and the measured sample mass). All the DSC curves show qualitatively the same form up to the point where each individual curve breaks away and falls to zero growth rate, as the supply of the elemental layers is apparently exhausted.

In the limit of diffusion-controlled, one-dimensional growth with a constant interdiffusion coefficient within the growing amorphous layer (an averaged interdiffusion constant in our case), the following relationship holds between the growth rate, the interlayer thickness, and the diffusion constant:

$$dX/dt = \text{const} \times D/X, \quad (1)$$

where  $X$  is the thickness of the grown interlayer.<sup>12</sup> Assuming that the diffusion process is thermally activated with a single activation energy  $E$ , and noting the proportionality between the growth velocity and rate of heat release, we thus obtain a means of estimating the activation energy of diffusion:

$$\ln(H dH/dt) = -E/kT + \text{const}, \quad (2)$$

where both the rate of heat release and the integrated heat release are functions of temperature. Analysis of data in Fig. 3 in accordance with Eq. (2) in the temperature range between 520 and 620 K is shown in Fig. 5. A linear fit to the data yields an activation energy of  $1.05 \pm 0.05$  eV. This result compares favorably with previously estimated values,<sup>8,15</sup> and thus demonstrates that the growth of the amorphous interlayer is consistent with

diffusion-controlled growth.

In summary, we have monitored transformations from the crystalline to the amorphous state, and subsequent crystallization, in planar, binary, multilayer, thin-film diffusion couples of Ni and Zr via differential scanning calorimetry. The heat of formation of an amorphous alloy is measured directly and found to be  $35 \pm 5$  kJ/mole for  $\text{Ni}_{68}\text{Zr}_{32}$ . The kinetics of these reactions has been examined. We observe no significant dependence of the kinetics upon layer thickness. The observed kinetics is consistent with a diffusion-controlled growth model, and within the auspices of such a model, we observe thermally activated diffusion with activation energy  $E = 1.05 \pm 0.05$  eV. Differential-scanning-calorimetry measurements on such thin-film diffusion couples yield detailed information on the amorphization processes. The direct monitoring of interdiffusion in thin-film multilayers via DSC is a relatively straightforward method which should be applicable in the study of other thin-film structures.

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