Amorphous alloys formed by microsecond current pulses

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We report the use of microsecond current pulses to transform layered crystalline nickel-zirconium films to amorphous alloy. Starting material was electron beam deposited multilayers with a composition modulation wavelength of 34 nm, an average composition of $Ni_{63}Zr_{37}$, and a total thickness of 680 nm. Electrical pulses were approximately rectangular and about 3 μs in duration, with an intensity of several hundred amperes, directly coupling 1.6 to 3 J of energy uniformly into the film. By monitoring current and voltage, the reaction and melting of the sample were observed, and the total energy of the pulse was easily computed. A sharp threshold in pulse energy for sample transformation was observed. A simple heat flow calculation demonstrated that the chemical energy released by the reaction, and the change in diffusion kinetics as the sample temperature exceeded the glass transition temperature of the amorphous alloy, are responsible for this sudden onset. The maximum temperature estimated from this calculation is below the melting point of the constituents, and the cooling rate is 10^7–10^8 K/s which is in agreement with the formation of amorphous alloy.

Since the early work of Klement *et al.*,[1] interest has focused on production of metastable alloys by rapid quenching from the melt.[2] We recently reported the use of electrical current pulses to thermally treat metal films, including the first use of this technique to produce amorphous alloys by rapid quenching.[3] Electrical pulses of several microseconds duration produce melting of zirconium-nickel multilayers on sapphire substrates. The subsequent cooling rate is sufficient (10^7–10^8 K/s) to bypass crystallization. Furthermore, the large negative heat of mixing between the constituents results in a sharp threshold in pulse power required to produce melting.

Electrical pulses have several attractive features for rapid thermal treatment of metal films. The energy is deposited uniformly and coupled directly to the film. The pulse shape can be manipulated to give the desired temporal behavior over several orders of magnitude. By monitoring the voltage and current, the sample resistance can easily be monitored, so phase changes can be directly observed, and energy deposited can be easily computed. This provides this method with a built-in diagnostic unavailable with other techniques.

The nickel-zirconium system was chosen for this study for a variety of reasons. The amorphous phase readily forms by conventional liquid quenching over a wide composition range, and its properties have been extensively studied.[4] Solid state reaction during long time anneals of multilayered nickel-zirconium structures also results in amorphous phase formation,[5] and investigations of this process on a fast time scale are of fundamental interest in understanding the role of nucleation of the competing phases. There is a large negative heat of mixing between the constituents in this system, with the result that a multilayered structure contains substantial chemical energy. This results in a self-sustained reaction during thermal treatment on the microsecond time scale.

Nickel-zirconium multilayer samples were prepared by rotating the sapphire substrates above shielded electron beam evaporation sources in a vacuum system with a base pressure below 10^{-8} Torr. The rates were set to produce an average composition of $Ni_{63}Zr_{37}$ and the rotary motion was set to produce a composition modulation wavelength of 34 nm. Twenty bilayers were deposited resulting in a total thickness of 680 nm. X-ray diffraction was performed with Cu K_α in thin-film Seeman–Bohlin geometry. Auger depth profiling was performed on selected samples before and after pulsing to determine the degree of mixing and the level of impurities.

Samples were heated by a pulsed discharge circuit consisting of a multistage artificial transmission line. Currents in the sample and a parallel resistor were inductively measured by current transformers. The ends of the sample were pressed onto copper tape electrodes on a glass plate. Samples were pulsed in air or in argon at atmospheric pressure.

The structure of the starting material was polycrystalline elements as shown by the x-ray diffraction in Fig. 1(a). Pulses with an energy of 2.3 J or greater resulted in amorphous phase formation. Figure 1(b) shows x-ray diffraction for a sample pulsed with 2.3 J electrical energy input. The nickel and zirconium crystalline peaks are no longer evident, and a broad band characteristic of amorphous material has appeared. There is also a weak peak which can be identified as zirconium oxide, which Auger depth profiling shows to be confined to the top 15 nm of the surface region. This oxide peak is more pronounced in samples pulsed in air than in those pulsed in Ar, indicating that the oxidation is occurring during pulsing. Auger depth profiling also showed that the initial strong composition modulation was completely destroyed by the pulse. The surface of the sample both before and after pulsing is mostly smooth and featureless as seen by scanning electron microscopy. However, after pulsing there are some pinholes with smooth, rounded edges which presumably are the result of defects or dust introduced during sample handling prior to deposition which are blown away

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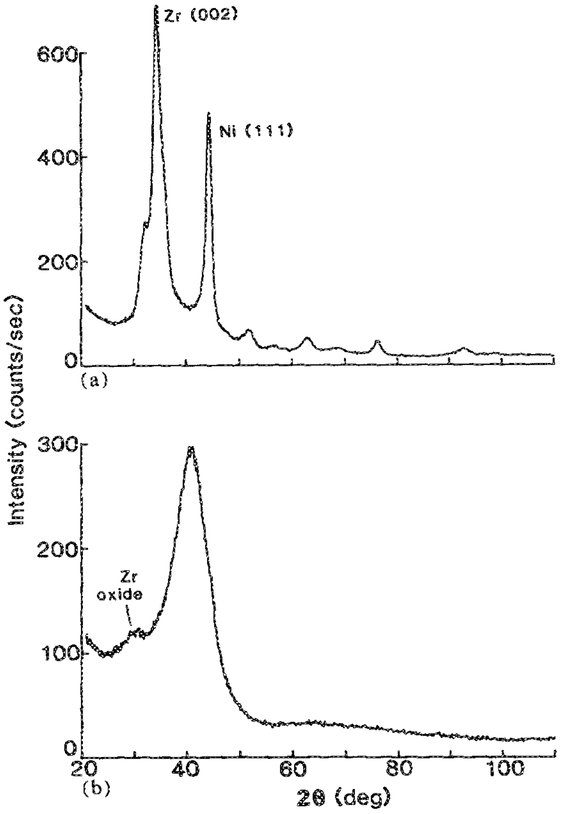

FIG. 1. Seeman–Bohlin x-ray diffraction for nickel-zirconium samples (a) before and (b) after 2.3 J current pulse.

by the pulse. These rounded edges and some wrinkling near the contact area are evidence that the sample was melted by the pulse.

The melting transition can be clearly observed in the current and voltage traces during the pulse. Shown in Figs. 2(a) and 2(b) are the voltage and current traces for a sample pulsed with 2.9 J. The rapid rise in resistance which accompanies mixing and melting of the layers results in a sharp rise in sample voltage and a drop in current which occurs between about 1.8 and 2.3 μs. This corresponds to about a 40–60% increase in sample resistivity. The position of this transition is determined by the pulse power with lower pulse powers resulting in a later transition. Pulses with an energy of 2 J or less produced no transition as shown in Figs. 2(c) and 2(d) which show voltage and current traces for a 2-J pulse. A pulse energy of 2.16 J produced a small (12%), rapid rise in resistance.

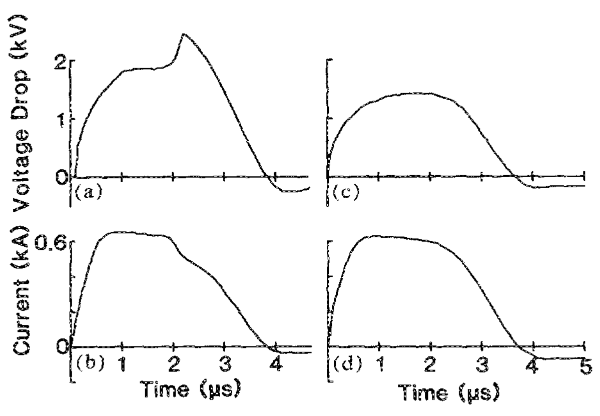

FIG. 2. Voltage and current traces for current pulses: (a) voltage for 2.9 J pulse, (b) current for 2.9 J pulse, (c) voltage for 2.0 J pulse, and (d) current for 2.0 J pulse.

Formation of amorphous phase material occurred at the same pulse energies as the resistance transition. Shown in Fig. 3 is the fraction of crystalline material remaining, extracted from the x-ray diffraction data, plotted versus pulse energy. A sharp drop occurs between 2 and 2.3 J, which is where the resistive transition begins to appear. An increase of 15% in pulse power in going from 2 to 2.3 J results in a decrease in crystalline peak intensity from 97% to 4%.

Several physical phenomena are occurring as the sample heats during the pulse. Extrapolation of low-temperature data[5] reveals that solid state formation of an amorphous alloy will begin to occur on the microsecond time scale at a temperature of about 1000 K, well below the melting point of the constituents. This reaction will release the substantial heat of mixing which will cause a further temperature increase, resulting in a self-sustained reaction. Furthermore, the diffusion kinetics in the reacted amorphous product will change in nature as the glass transition temperature (T_g) of the amorphous phase is exceeded. Diffusion in the solid state follows an Arrhenius form while diffusivity in liquid metals follows the Fulcher–Vogel form,

$$D = D_0 \exp[-B/(T - T_0)]. \qquad (1)$$

In equilibrium, the crossover between these two regimes will occur at T_g, which for amorphous nickel-zirconium depends on composition and is between 600 and 850 K.[4] In conditions of rapid heating, the crossover temperature will occur when the atomic jump frequency becomes comparable to the time scale of the experiment.[6] Using the diffusivity from low-temperature solid state reaction studies,[5] we find a crossover temperature of 900 K.

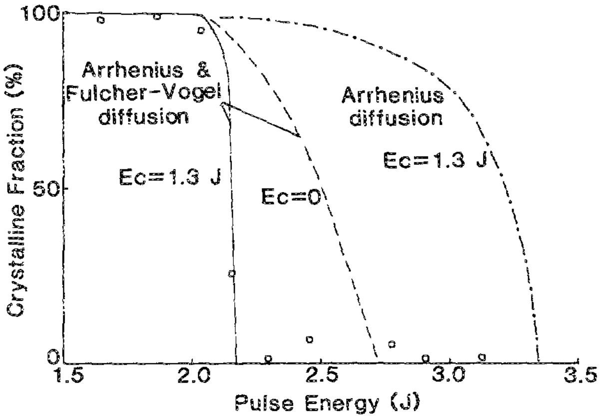

FIG. 3. Volume fraction of sample remaining crystalline after pulse vs pulse energy. Circles are derived from experimental x-ray data; solid line is the results of a model calculation which includes a chemical driving term and both Arrhenius and Fulcher–Vogel behavior for the diffusivity. Dashed line shows the results of the model with no chemical driving term, and dot-dashed line shows the results of the model with a chemical driving but only Arrhenius behavior for the diffusivity.

In order to gain insight into the temporal behavior of the sample temperature during these pulses, and to understand the effects of the exothermic reaction between the constituents and the change in diffusion kinetics above T_g, a simple heat flow calculation was performed. We used the Green's function solution to the heat diffusion equation,[7] assuming the only impediment to heat flow was the finite thermal diffusivity of the substrate. The thermal driving function was taken to be the sum of the measured electrical power and a chemical power term, divided by the heat capacity of the film (taken from data for the elements in the literature).[8] The magnitude of the chemical energy term was calculated by the method of Miedema[9] to be 1.3 J, which is a substantial fraction of the electrical pulse energy of about 2 J. The rate of chemical energy release is proportional to the growth rate of the interfacial alloy, calculated from the square root of time growth law. For temperatures below the diffusion crossover temperature, the diffusivity D followed an Arrhenius form with prefactor and activation energy taken from solid state reaction data.[5] Above the crossover temperature the Fulcher–Vogel form [Eq. (1)] was used for the diffusivity, with rough estimates for the parameters selected in a manner similar to that used by Spaepen and Lin.[10] B was taken to be 1300 K, T_0 and D_0 were calculated using the Stokes–Einstein relation between the viscosity and diffusivity, and assuming that the viscosity is 10^{12} Poise at T_g (700 K),[4] and 10^{-2} at the melting point of the alloy (1550 K).[4] The thermal diffusivity of the substrate was used as an adjustable parameter so the model calculation produced reaction at the observed pulse input energy. The value found in this manner (0.036 cm^2/s) is in good agreement with published data for this temperature range,[11] indicating that the assumption of infinite thermal conductivity of the sample-substrate interface is reasonable.

For pulses with energy greater than 2.3 J this model predicts a sharp rise in sample temperature due to the influence of chemical energy. This is reminiscent of the sharp rise in sample resistance observed in these pulses. The self-sustained reaction produces a sharp threshold in pulse energy for transformation as shown in Fig. 3, where the fraction remaining crystalline is plotted versus pulse energy for the model calculation both with and without the chemical driving term. Also shown are the results of the model for the case where the diffusivity follows an Arrhenius form throughout the temperature range. The reaction temperatures predicted by this model are around 1000 K, which is above T_g for the amorphous phase, so this is not a solid state reaction, but a reaction taking place with the product in an undercooled liquid state.

An estimate of the cooling rate can be calculated from this model by dividing the difference between the maximum temperature and T_g by the time it took the sample to cool over this range. This is about 10^7–10^8 K/s, which is in good agreement with the observation of amorphous phase formation. The heating rate found from this calculation is about 4×10^8 K/s.

Electric current pulses offer the ability to thermally treat films on a microsecond time scale. This technique has several advantages over conventional techniques including a built-in diagnostic which allows calculation of deposited energy and sample resistance. We have used this technique to produce amorphous nickel-zirconium from layered crystalline film. A simple model calculation demonstrates the role of chemical energy which in this system induces a self-sustained reaction. The transformation from layered crystalline elements to amorphous alloy does not involve melting of the constituents, but occurs above the glass transition temperature of the amorphous alloy and below the melting point of the crystalline phases.

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[1] W. Klement, R. H. Willens, and P. Duwez, Nature **187**, 869 (1960).

[2] *Rapidly Quenched Metals, Proceedings of the Fifth International Conference on Rapidly Quenched Metals, Wurzburg, Germany, September 1984*, edited by S. Steeb and H. Warlimont (North-Holland, Amsterdam, 1985).

[3] B. M. Clemens, J. C. Buchholz, R. M. Gilgenbach, and S. Bidwell, Proceedings of The Materials Research Society, Turnbull Symposium, 1985 (in press).

[4] Z. Altounian, Tu Guo-hua, and J. O. Strom-Olsen, J. Appl. Phys. **54**, 3111 (1983).

[5] B. M. Clemens, W. L. Johnson, and R. B. Schwarz, J. Non-Cryst. Solids **61 & 62**, 817 (1984); B. M. Clemens, Phys Rev. B **33**, 7615 (1986).

[6] F. Spaepen (private communication).

[7] E. Butkov, *Mathematical Physics* (Addison–Wesley, Reading, Massachusetts, 1968), p. 526.

[8] *CRC Handbook of Chemistry and Physics*, 55th ed., R. C. Weast, ed. (CRC, Cleveland, Ohio, 1975).

[9] A. R. Miedema, Philips Tech. Rev. **36**, 217 (1976).

[10] F. Spaepen and C. J. Lin, in *Amorphous Metals and Non-Equilibrium Processing, Materials Research Society Proceedings*, edited by M. von Allmen (Les Editions de Physique, Les Ulis, France, 1984), p. 65.

[11] Y. S. Touloukian and C. Y. Ho, eds., *Thermophysical Properties of Matter* (IFI/Plenum, New York, 1970), Vol. 2, p. 93 and Vol. 5, pp. 24,25.