

## Formation of an Amorphous Alloy by Solid-State Reaction of the Pure Polycrystalline Metals

R. B. Schwarz<sup>(a)</sup> and W. L. Johnson

*W. M. Keck Laboratory of Engineering Materials, California Institute of Technology, Pasadena, California 91125*

(Received 13 May 1983)

Single-phase  $Au_{1-x}La_x$  alloys, with  $0.3 \leq x \leq 0.5$ , have been formed through solid-state interdiffusion of pure polycrystalline Au and La thin films (100–600 Å) at temperatures of 50–80 °C. The reaction is driven by the large negative heat of mixing in the amorphous alloy and occurs at low temperatures by the anomalously fast diffusion of Au in La. The composition regime giving a single-phase amorphous product is explained with use of a free-energy diagram.

PACS numbers: 61.40.Df, 44.60.+k, 66.30.Ny

Irreversible processes in which the attainment of equilibrium involves two or more distinct relaxation processes with vastly differing time scales often result in the formation of metastable intermediate states.<sup>1</sup> In particular, solidification of liquid metallic alloys at high cooling rates can result in bypassing the nucleation and/or growth of crystalline phases. This leads to formation of a metallic glass as first shown by Duwez, Wilens, and Klement.<sup>2</sup> Glass formation by rapid quenching requires a critical minimum cooling rate which in practice is normally achieved in the vicinity of deep eutectics.<sup>3</sup> It will be shown in this Letter that the deep-eutectic criterion is specific to the kinetics of amorphous-phase formation by rapid quenching of liquids but is of no fundamental thermodynamic significance.

Recently, it was observed that an amorphous phase is formed during reaction of a crystalline intermetallic compound with hydrogen gas.<sup>4</sup> This unusual reaction to form an amorphous phase was explained in terms of the rapid diffusion behavior of hydrogen in the compound. Studies of solid-state diffusion<sup>5</sup> reveal a number of binary solute-solvent (*A-B*) systems in which a similar "anomalous fast diffusion" behavior occurs. Included among these fast-diffusion systems are numerous pairs of metals known to readily form metallic glasses by rapid quenching from the liquid state. In a survey of diffusion data, we have noted that it is frequently possible to transport *A* in *B* over significant distances ( $\sim 1 \mu\text{m}$ ) in practical times and at temperatures below the known crystallization temperature  $T_x$  of the corresponding rapidly quenched *A-B* glass. This is illustrated for the case of Au-La alloy in Fig. 1, which shows diffusion data together with the characteristic temperature. These observations have led us to investigate the possibility of forming the amorphous phase by solid-state reaction of the pure crystalline metals under low-temperature isothermal conditions (i.e., below  $T_x$ ). Such a reaction re-

quires a chemical driving force. We have investigated the conditions under which this driving force exists. In addition, the reaction must be carried out at temperatures where the nucleation (or growth) of the more favored equilibrium crystalline phases cannot occur. We show that in the case of Au-La alloys, both of these criteria are satisfied. Indeed we observed that amorphous alloys can be formed over a broad range of compositions by a low-temperature reaction of the pure crystalline metals.

The Au-La system was chosen for this study because of the following considerations: (a) Au is a known fast diffuser in crystalline La; (b) Au-

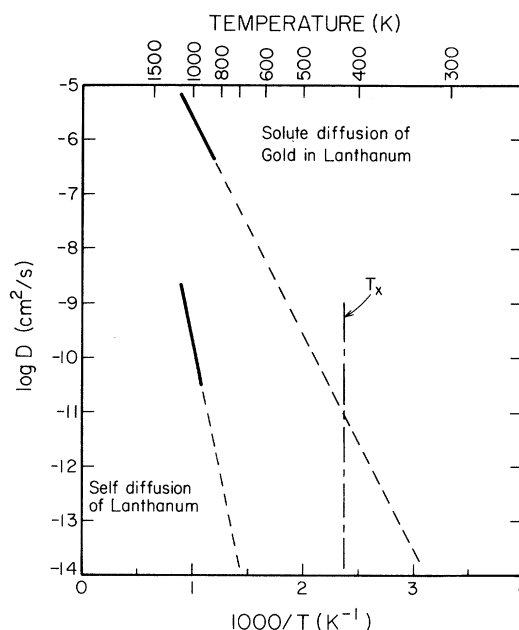


FIG. 1. Lanthanum self-diffusion and solute diffusion of gold in lanthanum as a function of reciprocal temperature. The dashed lines are extrapolations outside the measurement regime of Ref. 6, indicated by the heavy line.  $T_x$  is the crystallization temperature for rapidly quenched  $La_{78}Au_{22}$  (Ref. 7)

La alloys are known to readily form glasses by rapid quenching from the liquid state; (c) Au-La alloys exhibit a large negative heat of mixing which provides the previously mentioned chemical driving force. Thin-film multilayer configurations containing from 6 to 16 alternating layers of the polycrystalline metals were prepared by thermal evaporation of the metals onto Pyrex substrates held at 0°C. The vacuum in the system remained in the  $10^{-7}$ -Torr range during sample preparation and *in situ* annealing. The top layer in all samples was Au. The individual layer thicknesses ranged from 100 to 600 Å. The multilayer configuration permits a total sample thickness adequate for x-ray diffraction studies while maintaining an individual layer thickness which permits completion of the reactions in reasonable times. Several samples were prepared in each of over 25 runs. Half of the samples in each run were subjected to an *in situ* anneal for 2-5 h at a temperature of either 50 or 80°C. The remaining half of the samples were maintained at 0°C and used as control samples. All samples were subsequently removed from the vacuum chamber and characterized by x-ray diffraction scanning using a vertical Norelco diffractometer and Cu- $K\alpha$  radiation. The absorption length of Cu- $K\alpha$  radiation in both Au and La is sufficiently large to permit penetration and characterization of the entire multilayer. Correction of the x-ray data for substrate scattering was thus required. The total thickness of the La and of the Au films was measured with a Dektak thickness monitor.

Curves a-c of Fig. 2 show the x-ray scattering intensity as a function of scattering angle for three samples of differing average composition which were annealed at 80°C for 4 h. These samples are representative of the three composition regimes defined by the reaction products observed. With increasing La content, the three regimes are (a) a two-phase product containing crystalline Au and amorphous alloy, (b) a single-phase amorphous alloy product, and (c) a two-phase product material containing crystalline La and amorphous alloy. In addition, curve d of Fig. 2 shows the scattering intensity for a typical as-evaporated (unannealed) control sample with average composition lying in regime (b) described above. In the figure, the amorphous phase gives typically broad primary and secondary diffraction maxima, while the crystalline phases give a series of sharp Bragg peaks which are identified in the figure. The positions of the amorphous primary maxima were observed to be slightly

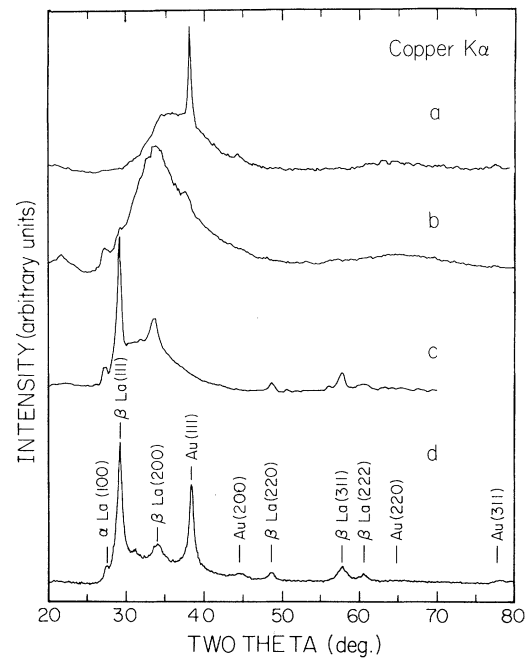


FIG. 2. X-ray scattering intensity as a function of scattering angle for annealed samples of increasing La content (curves a, b, and c) and for an unreacted sample (curve d) with La content similar to that of curve b.

composition dependent, shifting toward lower angles with increasing average La content of the films. This can be seen in curves a-c in the figure. Also note that the as-evaporated crystalline La layers consist primarily of  $\beta$ -La (fcc) which is a high-temperature form of La although traces of  $\alpha$ -La (hcp) are also seen as evidenced by the small but detectable (100) Bragg peak of  $\alpha$ -La in curve d of Fig. 2.

The crystallization behavior of rapidly quenched amorphous alloys has been interpreted in terms of hypothetical free-energy diagrams.<sup>8</sup> We introduce a similar concept to explain the thermodynamics which govern the present reaction. The Gibbs free energy of the pure crystalline metals is obtained from available thermodynamic data.<sup>9,10</sup> The difference in free energy  $\Delta G_{X,L}$  between the amorphous and crystalline phases of the pure metals at a temperature  $T$  below the glass transition temperature  $T_g$  could, in principle, be determined by measurements of the specific heats of both phases in the regime  $0-T$  (yielding the entropy difference at  $T$ ) and the heat of crystallization at  $T$ . In the absence of such data, we simply treat the amorphous alloy as an extension of the liquid phase to temperatures in the undercooled regime, neglecting the configurational freezing

of the undercooled liquid as  $T_g$  is approached. Using a linear extrapolation from the melting temperature and the observed enthalpy of fusion  $\Delta H_{X,L}(T_m)$ , we estimate

$$\Delta G_{X,L} = [(T_m - T)/T_m] \Delta H_{X,L}(T_m). \quad (1)$$

The free energy of mixing of the liquid (amorphous) phase was estimated with the method of Miedema,<sup>11</sup> taking into account both atomic size effects and corrections for deviation from regular solution behavior. The complete free energy versus composition curve for amorphous Au-La alloys, evaluated at the reaction temperature of 100 °C, is shown in Fig. 3. Of primary importance is the large negative free energy of mixing observed for amorphous Au-La alloys. This is a direct result of the large negative heat of mixing predicted by Miedema for liquid alloys of Au and La. In contrast, we know that the pure crystalline metals exhibit very restricted mutual solubility<sup>12</sup> as would be expected on the basis of the Hume-Rothery rules for terminal solid solutions. This implies that the terminal crystalline solid solutions are characterized by a large positive heat of mixing in contrast to the amorphous solution. In the absence of a reliable heat of mix-

ing for the crystalline solid solutions, we simply take the terminal solubilities to be zero. The metastable free-energy diagram which we show in Fig. 3, though approximate, contains all of the essential features required to interpret the present results.

When pure polycrystalline Au and La are brought into contact, the free energy for the system as a whole lies along the dotted line in Fig. 3. The free energy can be substantially lowered when the pure metals react to form the amorphous phase (solid curve). The fast diffusion of Au in La permits this reaction to be carried out at temperatures below the crystallization temperature of the amorphous phase. Furthermore, reaction at this low temperature suppresses the nucleation and growth of intermetallic compounds which may have an even lower Gibbs free energy. On the other hand, the well-known common tangent rule which is also illustrated in the figure (dashed lines) shows that a single amorphous phase will form only when the average composition of the film lies in the central region indicated in the figure. Outside of this region, thermodynamics suggests that the amorphous phase should coexist with unreacted pure metal. The circles in Fig. 3 show the reaction results of several films of differing composition. The observed products are found to be in good agreement with those predicted by the common tangent rule and the metastable free-energy diagram. In particular, a single-phase amorphous product is obtained in the central composition region indicated in the figure.

In conclusion, we have found that binary amorphous alloys can be formed by a solid-state diffusion reaction of pure polycrystalline metals under isothermal conditions. The essential factors which permit such a reaction are the fast diffusion behavior of one metal in the other, and the existence of a negative heat of mixing in the amorphous alloy. The latter provides the necessary chemical driving force for the reaction. In addition, the reaction must be carried out at sufficiently low temperatures to suppress either the nucleation or growth of thermodynamically preferred crystalline intermetallic compounds. Single-phase amorphous alloys can be obtained over a substantial range of compositions centered near a minimum in the amorphous-alloy free energy versus composition curve. This is in contrast with the deep-eutectic criterion for glass formation by quenching of liquid alloys.

The authors would like to thank David Baxter

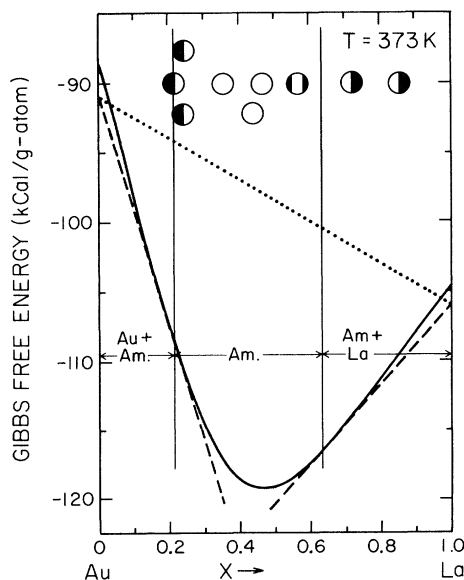


FIG. 3. Gibbs free energy vs composition for a mixture of crystalline Au and La (dotted line) and for amorphous  $Au_{1-x}La_x$  alloy. The left-filled, open, and right-filled circles correspond to byproducts (a), (b), and (c) of the text, respectively, obtained by solid-state reaction of films of average composition indicated by the abscissa.

for assistance with the sample preparation. This work was supported by the U. S. Department of Energy, Project Agreement No. DE-AT03-81ER-10870 under Contract No. DE-AM03-76SF00767, and by the Argonne National Laboratories.

---

<sup>(a)</sup>On leave from the MST Division, Argonne National Laboratory, Argonne, Ill. 60439.

<sup>1</sup>O. Penrose and J. L. Lebowitz, in *Fluctuation Phenomena*, edited by E. W. Montroll and J. L. Lebowitz (North-Holland, New York, 1979), Chap. 5.

<sup>2</sup>P. Duwez, R. H. Willens, and W. Klement, *J. Appl. Phys.* **31**, 1136, 1500 (1960).

<sup>3</sup>M. H. Cohen and D. Turnbull, *Nature (London)* **189**, 131 (1961).

<sup>4</sup>X. L. Yeh, K. Samwer, and W. L. Johnson, *Appl. Phys. Lett.* **42**, 242 (1983).

<sup>5</sup>A. D. Le Claire, in *Properties of Atomic Defects in Metals*, Proceedings of the International Conference, Argonne, Illinois, 1976, edited by N. L. Peterson and R. W. Siegel (North-Holland, New York, 1978), p. 70.

<sup>6</sup>M. P. Dariel and G. Erez, *Philos. Mag.* **19**, 1053 (1969).

<sup>7</sup>W. L. Johnson, S. J. Poon, and P. Duwez, *Phys. Rev. B* **11**, 159 (1975).

<sup>8</sup>U. Köster and U. Herold, in *Glassy Metals I*, edited by H. J. Güntherodt and H. Beck (Springer-Verlag, Heidelberg, 1981), p. 225.

<sup>9</sup>R. C. Weast, *CRC Handbook of Chemistry and Physics*, 55th Ed. (Chemical Rubber, Cleveland, 1974), p. D-55.

<sup>10</sup>K. A. Gschneidner, Jr., in *Solid State Physics: Advances in Research and Applications*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1964), Vol. 16, p. 343.

<sup>11</sup>A. R. Miedema, *Phillips Tech. Rev.* **36**, 217 (1976).

<sup>12</sup>F. A. Shunk, *Constitution of Binary Alloys*, 2nd suppl. (McGraw-Hill, New York, 1969), p. 73.