

Formation of an amorphous metallic hydride by reaction of hydrogen with crystalline intermetallic compounds—A new method of synthesizing metallic glasses

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(Received 5 October 1982; accepted for publication 8 November 1982)

Noncrystalline metallic hydrides can be formed from certain crystalline Zr_3Rh intermetallic phases by hydrogenation. X-ray diffraction patterns, density measurements, and superconducting properties confirmed the transition from the crystalline to the amorphous phase by this solid state reaction. The transition can be explained in terms of a “chemical frustration” effect.

PACS numbers: 61.10. — i, 61.40.Df, 64.70. — p, 64.60.My

Metallic glasses and amorphous metallic alloys can be formed by rapid cooling of liquid metals,¹ or deposition of metallic vapors² at rates sufficient to bypass crystallization. For the formation of a metallic glass, cooling rates in the range 10^4 – 10^{12} K/s are required to suppress nucleation and growth of more stable crystalline phases in undercooled alloy melts.³ These facts lead to severe restrictions in the synthesis of glassy metals. For example, simple heat transfer considerations require at least one of the specimen dimensions to be rather small, typically 10–100 μ . For this reason, it is of considerable interest to explore alternate means of forming metallic glasses.

In this letter we present results of a study of the formation and properties of an amorphous metal hydride $Zr_3RhH_{5.5}$ by reaction of hydrogen gas with the crystalline intermetallic compound Zr_3Rh . By hydriding at sufficiently low temperatures ($\lesssim 200$ °C), an amorphous metallic hydride of composition $Zr_3RhH_{5.5}$ is formed. By rapid quenching, the Zr_3Rh alloy can also be obtained as a metallic glass. The glassy Zr_3Rh alloy can also be hydrided to form an amorphous $Zr_3RhH_{5.5}$. The atomic scale structure and physical properties of the amorphous hydride samples prepared respectively from crystalline and glassy starting materials are compared in detail and found to be identical to within experimental accuracy. In the latter part of the letter, we discuss the thermodynamic and kinetic aspects of the observed glass formation by solid state reaction with hydrogen. We attribute the glass formation to a “chemical frustration” effect. The present observations suggest a more general approach to forming amorphous metals by a solid state reaction. These ideas are discussed with respect to free-energy considerations.

The samples used in this study were prepared by levitation melting of Zr and Rh on a silver boat in an argon atmosphere. The ingots are remelted several times, checked for homogeneity, then quenched by both the melt spinning⁴ and piston and anvil⁵ techniques in the form of foils and ribbons as described elsewhere. By varying the quenching parameters, a variety of quench rates can be obtained. Samples cooled at a rate insufficient to form a glass were found to

crystallize with a metastable “ $L1_2$ ” structure. Such samples are found to contain varying amounts of remaining amorphous material in addition to the $L1_2$ phase. An x-ray pattern of a sample having a nearly single phase $L1_2$ structure is shown in Fig. 1. Notice that this sample also contains several small diffraction peaks not belonging to the $L1_2$ structure. These peaks can be indexed with the $E9_3$ structure. As reported earlier,⁶ amorphous samples of Zr_3Rh can be entirely crystallized by heat treatment at 360–400 °C to form a single phase $E9_3$ structure. Superconductivity measurements for such samples show only a sharp T_c at 2.4 K and thus contain no detectable amorphous material ($T_c = 3.9$ – 4.4 K). The $E9_3$ structure has previously been reported in equilibrium Zr-Rh alloys of similar composition but later was determined to be stabilized by small concentrations of oxygen impurities. The x-ray patterns of several single phase $E9_3$ samples prepared by crystallizing an initially amorphous sample have been indexed with all lines identified with the $E9_3$ structure. The x-ray patterns show no evidence of any remaining amorphous material. To be certain that the entire material was crystallized uniformly, the sample was powdered and again x rayed. Only diffraction lines of the $E9_3$ structure were observed. The three types of samples de-

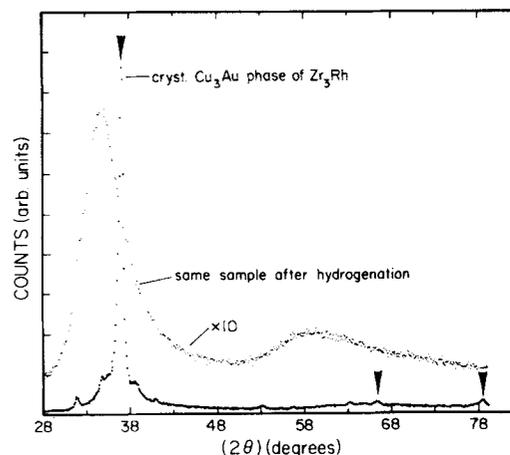


FIG. 1. X-ray diffraction patterns for the same sample of Zr_3Rh before and after hydrogen absorption. Arrows indicate the Cu_3Au phase. The other lines belong to traces of additional phases with $E9_3$ structure.

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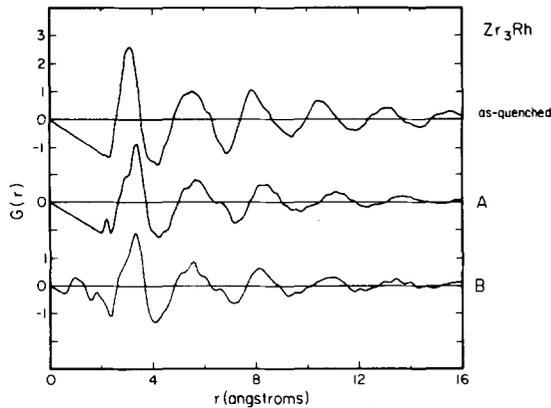


FIG. 2. Reduced radial distribution functions $G(r) = 4\pi r[\rho(r) - \rho_0]$ for as-quenched amorphous Zr_3Rh , hydrided original amorphous $Zr_3RhH_{5.5}$, and hydrided original crystalline $Zr_3RhH_{5.5}$.

scribed were then hydrided. The hydride samples prepared from initially amorphous material, from $L1_2$ and from $E9_3$, are hereafter referred to as A, B, and C, respectively.

All of the samples were hydrided in one of two separate stations which permitted exposure to gaseous hydrogen at pressures below one atmosphere, and up to 50 atmospheres, respectively. Absorption of hydrogen was measured by noting pressure change within the system of known volume at constant temperature. The relative error of the measured hydrogen contents of the samples is 2%. All data given are for samples hydrided at 180 °C. All hydrided samples were found to have nearly the same final hydrogen/metal ratio of $H/M \cong 1.4$. The x-ray diffraction pattern of the same sample after hydriding is also shown in Fig. 1. No evidence for crystalline lines has been found. Only samples, which originally had the $E9_3$ structure, showed some indication for remaining crystals. This is probably due to oxygen contamination of the sample surface which occurs during crystallizing the sample to form the $E9_3$ phase. Using standard procedures⁷ described elsewhere, one can use x-ray diffraction intensity curves to compute the reduced radial distribution function $G(r) = 4\pi r[\rho(r) - \rho_0]$, where $\rho(r)$ is the atomic pair density function and ρ_0 is the average atomic density of the sample. The $G(r)$ functions for samples as-quenched, A, and B are compared in Fig. 2, where the $G(r)$ of the hydrided samples are found to be nearly identical. A detailed comparison of the positions of the various peaks in the $G(r)$ functions (these represent the atomic coordination shell dimensions) is given in Table I. The atomic coordination numbers η for the first neighbor shells are also given. These data agree to well with-

in experimental uncertainty. The mass densities of samples are also given in Table I. These are also found to be identical within experimental error ($\sim 0.5\%$) and are lower than the mass density of glassy Zr_3Rh by about 13%. This implies that the matrix of transition metal atoms is expanded by $\sim 13\%$ on going from glassy Zr_3Rh to glassy $Zr_3RhH_{5.5}$. This can be attributed to the effect of hydriding. We also note that the first peak in $G(r)$ for all the $Zr_3RhH_{5.5}$ samples shows a resolved splitting. These two corresponding distances are referred to as r'_1 and r_1 in Table I. The distance r_1 is equal to 3.35 and 3.33 Å for samples A and B, respectively. This distance is nearly the same as the nearest neighbor Zr distance (3.37 Å) in fcc ZrH and (or) tetragonally distorted δ -ZrH₂ (3.3–3.49 Å).⁸ In crystalline ZrH and ZrH₂, hydrogen occupies tetrahedral interstitial sites. The present evidence and results of other studies of Zr-based glassy metal hydrides^{9,10} suggest that hydrogen preferentially occupies tetrahedral sites defined by four neighboring Zr atoms. This will be further discussed in a more complete article.

We have measured the superconducting transition temperature of the amorphous hydride of samples A and B and found rather sharp transitions with $T_c = 1.16$ – 1.26 K for sample A and $T_c = 1.03$ K for sample B. Glassy Zr_3Rh has $T_c = 4.4$ K. The two amorphous hydride samples have nearly the same T_c 's. We see that hydrogen substantially lowers T_c in these metallic glasses. We have also observed changes in electrical resistivity on hydriding from 150 to 250 $\mu\Omega$ cm for the amorphous hydride samples.

An attempt was made to reversibly desorb hydrogen from the amorphous hydride samples by placing the hydride samples in high vacuum ($\sim 10^{-6}$ Torr) and reheating to $T = 180$ °C. A fraction of the hydrogen is desorbed by this treatment. More interestingly, a partial crystallization of the sample is observed resulting in the formation of an fcc ZrH_{-2} phase with lattice parameter $a = 4.77$ Å. The x-ray pattern of the sample shows both an amorphous band and a series of broad Bragg peaks arising from the crystalline ZrH_{-2} fcc phase. Using the observed widths of the Bragg peaks and the Scherrer formula¹¹ we estimate the grain size of the ZrH_{-2} crystallites to be 45 Å. Finally, we point out that samples hydrided at temperatures above 220 °C also show nucleation of the crystalline ZrH_{-2} phase.

We now discuss the mechanism by which the crystalline $L1_2$ and $E9_3$ phases are transformed to the glassy state during hydriding. In the equilibrium binary Zr-Rh system, the free energy of a two-phase material with 25 at. % Rh [determined by the common tangent rule and consisting of the known equilibrium phases¹² $\alpha(\beta)$ -Zr and Zr_2Rh] is lower

TABLE I. Experimental data for the as-quenched, hydrided originally amorphous and hydrided originally crystalline Zr_3Rh samples.

	r'_1	r_1	$\frac{r'_2}{r'_1}$	$\frac{r_2}{r_1}$	$\frac{r_3}{r_1}$	$\frac{r_4}{r_1}$	η	ρ	T_c	ΔT_c	c^a
		(Å)						(g/cm ³)	(K)	($\times 10^{-3}$ K)	(H/M)
as-quenched	...	3.14	...	1.75	1.98	2.51	13.57	7.58	4.40	23	...
A	2.93	3.35	1.78	1.68	1.96	2.47	12.72	6.54	1.16–1.26	~ 100	1.38
B	2.90	3.30	1.79	1.66	1.98	2.44	12.89	6.53	1.03	75	~ 1.5

^a Equilibrium H content at pressure of 1 atmosphere (H_2) and $T = 180$ °C.

than either that of a single phase $L1_2$ (or $E9_3$) structure or that of a homogeneous amorphous phase. In the ternary Zr-Rh-H system with $H/M \cong 1.4$, there have been no coherent hydrides of $L1_2$ or $E9_3$ phases observed in any of our experiments. We assume therefore that the free energy of such single phase crystalline hydrides is relatively higher than that of a single phase noncrystalline hydride. On the other hand, ZrH and ZrH_2 are comparatively stable crystalline hydrides with low free energy. By hydriding crystalline Zr_3Rh , one would thus expect to find a two-phase reaction product containing ZrH (or ZrH_2) in equilibrium with some Rh-rich crystalline phases. However, the formation of ZrH or ZrH_2 nuclei requires interdiffusion of Zr and Rh over a distance at least as large as the critical nucleus size¹³ of ZrH or ZrH_2 . Although hydrogen is highly mobile at low temperatures,¹⁴ the metal species are not. The necessary gradient in Zr (Rh) concentration required to form ZrH_2 nuclei does not develop due to the restricted interdiffusion of Zr and Rh. On the other hand, the glassy hydride is a metastable alternative which does not require such interdiffusion of Zr and Rh. The transformation to the amorphous hydride is polymorphic whereas the crystalline alternative requires chemical segregation. This "chemical frustration" effect provides the underlying mechanism for the transition to the glassy state.

Based on the above picture, the general requirements for glass formation in a solid state reaction would thus be (1) at least a three-component system, (2) a large disparity in the

atomic diffusion rates of two of the species, (3) an absence of a polymorphic crystalline alternative as a final state. It is of interest to search for other systems in which such conditions are satisfied.

The authors gratefully acknowledge the support of the U.S. Department of Energy, under Contract No. DE-AM03-76SF00767. We thank Lowell Hazelton for his contributions to the experiment and for useful discussions.

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Initial stage of sputtering in silicon oxide

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(Received 20 July 1982; accepted for publication 7 November 1982)

The effect of argon ion bombardment on a silicon oxide film prepared on a Si(111) surface by dry oxidation was investigated by measuring partial yield spectra in addition to the oxygen induced Si 2p core level shift. The experimental observations can be understood such that the SiO_2 network is decomposed at the initial stage of argon ion bombardment. In the following stage of bombardment, the silicon oxide films are sputter etched resulting in a decrease in the oxide film thickness.

PACS numbers: 61.80.Jh, 68.48. + f, 71.20. + c

As a result of the decrease in the dimensions of a Si metal-oxide-semiconductor field-effect transistor (MOSFET) device, the electronic states at the Si-SiO₂ interface and those in SiO₂ play a vital role in device operation.¹ Because of this, the chemical bonding configuration and

composition of the Si-SiO₂ interface and SiO₂ have been studied extensively by using various surface sensitive techniques.² The change in the chemical bonding configuration and composition of silicon oxide films as a function of distance from the Si-SiO₂ interface has been studied by using