

Formation of Zirconium Metallic Glass at High Pressure and Temperature

J. Zhang, Y. Zhao

Los Alamos National Laboratory, Los Alamos, NM 87545 USA

Introduction

Bulk metallic materials have commonly been produced by melting and solidification process for the past several thousand years. Below their melting temperatures, however, metallic liquids solidify into the corresponding crystalline phases. This common concept has been changed in the past decade, as a new class of bulk metallic glasses with extraordinary glass-forming abilities (GFA) has been discovered in alloys, such as $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (Vit1) and $Zr_{52.5}Ti_5Cu_{17.9}Ni_{14.6}Al_{10}$ (Vit105). The high elastic strain limit combined with a high yield strength and fracture toughness make metallic glasses ideal for engineering application [1, 2]. It is likely that bulk metallic glasses will replace some conventional materials in our everyday life in the near future.

In multi-component systems, GFA is viewed as the resistance to precipitation of crystalline phases from supercooled liquid metals, and alloys with high GPA all have three common features [3]: (1) the systems consisting of at least three components; (2) significant mismatch in atomic size of the constituent elements; and (3) negative heats of mixing among the major alloying elements. Addition of elements that are chemically and topologically different from the other species not only creates an energy barrier for nuclei to form but also effectively increases melt viscosity or fragility, which results in a reduced rate of both nucleation and growth and an increase in GFA. The production of bulk glassy materials in pure metals, however, remains a long-standing scientific curiosity and technological interest. The difficulties arise from the facts that the equilibrium melt viscosity of pure metals is three orders of magnitude smaller than that of amorphous alloys [4] and that the current technology has yet to reach a cooling rate in excess of $10^{10} \text{ }^\circ\text{C s}^{-1}$ that is needed to make pure metals amorphous [5].

Methods and Materials

We studied zirconium metal at pressure and temperature up to 17 GPa and 1000 °C, using energy-dispersive synchrotron x-ray diffraction and time-of-flight neutron scattering. In x-ray diffraction experiments, we used both DIA-type and T-Cup large-volume high-pressure apparatus installed at APS of Argonne National Laboratory and NSLS of Brookhaven National Laboratory and. The starting sample has a close-packed hexagonal structure (α -phase) and is of extremely high purity, with 35 ppm Hf, less than 25 ppm of C, N, Ti, and less than 50 ppm of O, V, and Fe. The zirconium samples were placed in boron nitride and/or NaCl capsules, with NaCl used as internal pressure standard.

Results

Our results reveal that zirconium metals are in crystalline forms at pressures and temperatures up to 4.3 GPa and 900 °C. The formation of amorphous zirconium was first observed when ω phase (a hexagonal structure but not closed-packed) was heated to 650 °C at 5.3 GPa (Figs. 1 and 2). The lower bound for the glass formation is therefore bracketed between pressures of 4.3

and 5.3 GPa. Upon cooling, we observed crystallization of ω phase from amorphous zirconium at 4.8 GPa and 450 °C, indicating that the crystalline-glass transformation is reversible at this P - T condition (Fig. 2). When zirconium metal was heated at higher pressures of 6.4 GPa and 8.6 GPa in two different experiments, the glass formation was observed at 700 °C and 625 °C, respectively, and was stable on further heating to 1000 °C (Figs. 1 and 4). In both experiments, the transformation sequence is from ω phase to β phase (a body-centered cubic, high-temperature phase) and from β phase to amorphous phase. The temperature interval between first appearance of β and amorphous phases is less than 25 °C. Upon slow cooling, we did not observe crystallization of either ω or β phase even at room temperature, indicating an irreversible process for the glass formation in zirconium metal. These findings demonstrate that pressure plays a critical role in both formation and reversibility of amorphous zirconium. From another perspective, one can conclude that the irreversible formation of amorphous zirconium seems to occur only when glass is formed from the β phase.

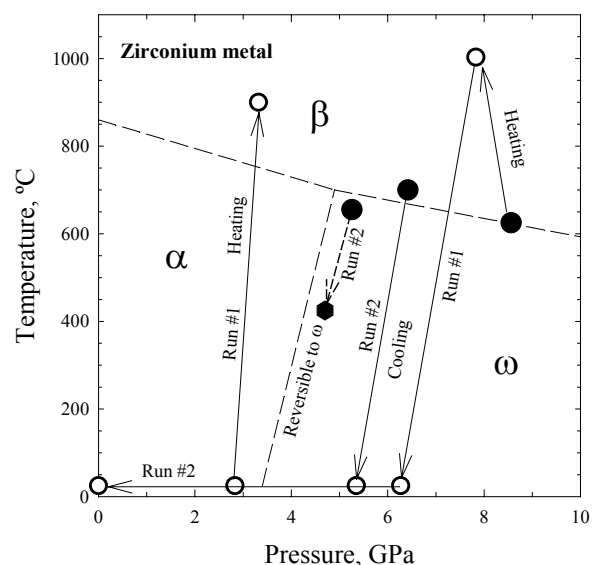


Fig. 1 Glass-forming conditions and stability of amorphous zirconium. Formation of glass was observed in two independent experiments (Run #1 and Run #2). Solid circles refer to pressures and temperatures at which crystalline zirconium metal fully transformed into an amorphous phase on heating. The solid hexagon symbol corresponds to the conditions where the reversed transformation from glass to ω phase was observed upon cooling. Arrows indicate the selected experimental P - T paths along which no precipitation of any crystalline phase was observed after the formation of amorphous zirconium, with open circles denoting a portion of data collected along the paths.

To further explore effect of pressure on the GFA, we performed an additional experiment at 14-17 GPa. We observed the

transformation from ω phase to β phase between 500 and 600 °C; upon further heating, however, zirconium metal is only partially transformed to an amorphous phase at 750 °C and 14.5 GPa, and the diffraction pattern is dominated by the β phase. Compared with our experimental results at lower pressures (Fig. 1), these observations tend to suggest that zirconium metal has a diminishing GFA with increasing pressure between 9–15 GPa. The fully amorphous zirconium can therefore be formed in a limited pressure-temperature space. The glass-forming region needs to be more accurately determined to constrain the phase diagram for zirconium metal as well as to provide a better understanding of glass-forming kinetics.

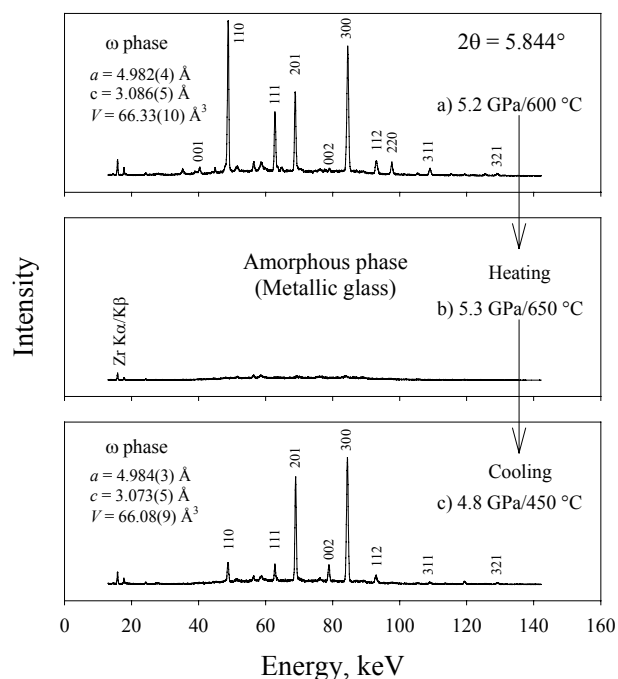


Fig. 2 Selected synchrotron x-ray diffraction patterns showing a reversible transformation between ω and amorphous phases of zirconium metal. Formation of a glass is identified by the disappearance of all diffraction peaks of ω phase and by a significant reduction in the diffraction intensity (pattern b). Intensities have been normalized to the data acquisition time, and all three figures are plotted within an identical intensity range. The weak diffraction peaks observed in the amorphous phase are also present in all patterns collected in this experiment and are from diffraction of materials surrounding the zirconium metal (see patterns a and c).

The glass formed at 8.6 GPa and temperatures above 625 °C (Fig. 4) was annealed several times up to 900 °C at pressures as low as 2.8 GPa to investigate thermal stability of amorphous zirconium outside its formation P-T conditions. At these experimental conditions, we did not observe the precipitation of any crystalline phase from amorphous zirconium. The glass formed at high pressure and temperature appears to have a superior thermal stability when compared to amorphous alloys formed from the conventional melting-cooling process, which typically start crystallization when annealed at temperatures between 450–500 °C [3, 6]. Whether amorphous zirconium

shows a similar thermal behavior at atmospheric pressure remains to be an interesting problem to be explored. As a final note on the stability, both energy and angle dispersive diffraction on the recovered zirconium sample shows patterns that are characteristic of an amorphous phase, but they do not reveal any diffraction lines of crystalline zirconium (see Figs. 2 and 3). Both recovered and starting samples do not show any Raman shifts except for surface oxidation, indicating that the bulk zirconium sample remains in an elemental form at our experimental conditions. The microstructure and/or atomic scale structure of the recovered sample, however, need to be characterized by other experimental techniques, such as high-resolution transmission electron microscopy and neutron pair distribution function.

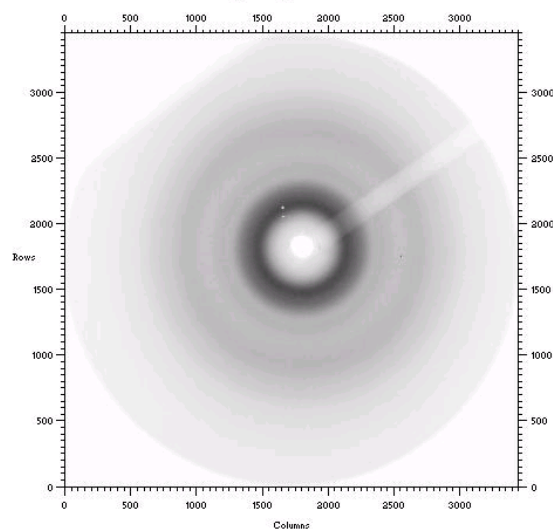


Fig. 3 An x-ray scattering image recorded in a CCD detector for the sample recovered from the experiment for Fig. 2. The pattern is characteristic of zirconium-based bulk metallic glass.

Formation of an amorphous phase within a solid state by application of pressure has been found to be a phenomenon of widespread occurrence among condensed matters, such as silicates, ice, and alloys [7]. There are, however, major differences between these observations and the present findings. Pressure-induced amorphization is a process in which amorphous phase is formed because transformation from a crystalline solid to its high-pressure phase is kinetically hindered at ambient or low temperature. In zirconium metal, formation of a glass occurs after α phase transforms to its high-pressure and/or high-temperature phases. For pressure-induced amorphization, the glass would crystallize into its equilibrium, high-pressure phase when subjected to elevated temperatures. In zirconium glass, no precipitation of any crystalline phases was found at temperatures up to 1000 °C. In fact, it is not known that there exists another high-temperature polymorph of zirconium metal except the β phase. This leads to an unusual situation where amorphous zirconium would eventually “melt” at somewhat higher temperatures, which could infer an extremely high thermal stability. Finally, no previous works have demonstrated that pure metals would undergo a pressure-induced amorphization.

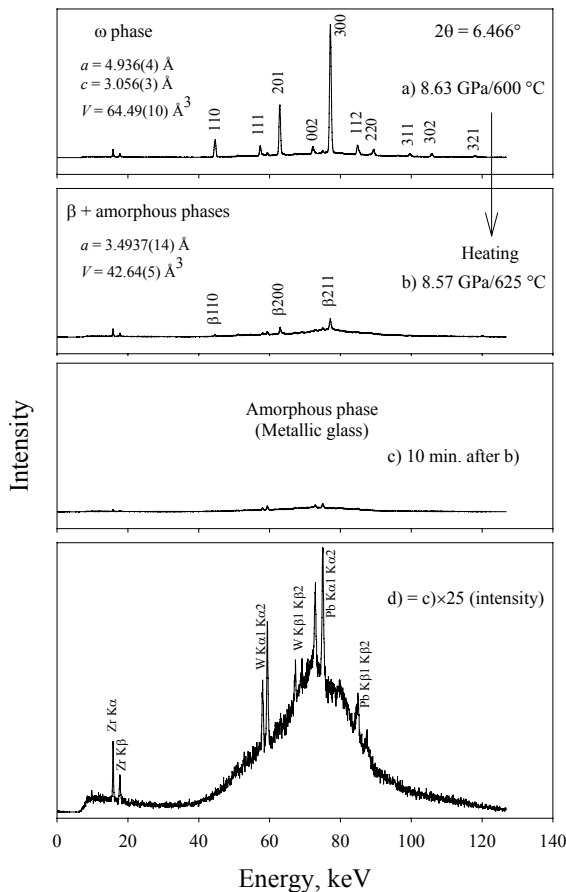


Fig. 4 Selected diffraction patterns showing the ω - β phase transition and formation of glass from the β phase of zirconium metal at 8.6 GPa. Pattern (d) is a blow-up of the pattern (c). Weak diffraction lines in all patterns are fluorescence peaks of W, which was used to define collimation of multi-element detector, and Pb, which was used as a shielding material to avoid air scattering.

Discussion

Phase transformations in zirconium metal have previously been studied at pressures and temperatures up to 6 GPa and 840 °C [8], and at 31-36 GPa up to 175 °C [9]. Our experimental conditions have therefore not been explored by any previous work. In addition, no theoretical calculations have predicted the instability of ω and β phases of zirconium metal relative to a solid amorphous phase. At atmospheric pressure, zirconium metal melts at 1855 °C; the melting curve at high pressures, however, is not known. It is inconceivable though that the observed glass formation can be attributed to the melting of zirconium at the experimental pressures, which would require an unusually large negative dT/dP slope of ~ 240 °C GPa⁻¹. The melting explanation is further unlikely because the observed glass-forming temperature between 5 and 9 GPa only has a slightly negative dependence on pressure (Fig. 1). We therefore conclude that the formation in zirconium metal bypasses the conventional required liquid state, which represents a novel approach of making metallic glass. This experimental study

presents the first finding that bulk metallic glass can be produced from a pure elemental metal.

Currently, the liquid/liquid phase decomposition of deeply undercooled metallic liquids is a major problem faced in the fundamental study and technological processing of bulk metallic glasses, even for extremely good glass formers [10]. Similarly, decomposition happens when amorphous alloys are annealed at the temperatures above those of glass transition [10]. Experiments revealed that such decomposition is responsible for the embrittlement of some bulk metallic glasses [1,10]. For mechanical applications, it is important to find metallic glasses that have higher thermal stability (*i.e.*, a smaller difference between the critical temperature¹ and glass transition, $T_c - T_g$) and thus a lower probability for decomposition. As the $T_c - T_g$ reduces, however, the amorphous alloys, such as derivatives of Vit1 and Vit105, tend to have a somewhat diminished GFA. The extraordinary glass-forming ability in pure zirconium metal combined with its superior thermal stability discovered in this work will overcome the problems existed in amorphous alloys. In addition, the glass formed within a solid state may represent a distinct state of matter that should have other distinct properties yet to be explored, which may open new opportunities for research and development in the area of metallic glasses.

Acknowledgments

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