Amorphouslike Diffraction Pattern in Solid Metallic Titanium

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Amorphouslike diffraction patterns of solid elemental titanium have been detected under high pressure and high temperature using *in situ* energy-dispersive x-ray diffraction and a multianvil press. The onset pressure and the temperature of formation of amorphous titanium is found to be close to the α-β-ω triple point in the *P-T* phase diagram. Amorphous Ti has been found to be thermally stable up to 1250 °C for at least 3 min at some pressures. By analyzing the conditions for producing amorphous elemental Zr and Ti, we observed a multi-phase-point amorphization phenomenon for preparing single-element bulk amorphous metals. The results reported may open a new way to preparing single-element bulk amorphous metals with a high thermal stability.

Since the discovery of new glassy systems, based on multicomponent alloys, in the early 1990s, bulk metallic glasses have been extensively studied because of their extraordinary mechanical and magnetic properties [1]. Promising technological applications seem to be within reach for this novel class of materials. Thus, the study of bulk metallic glasses has become a most active research field in the past decade [2–11]. Bulk metallic glasses produced so far usually contain three or more elements [1]. They are usually produced by the copper-mold method, typecasting the multicomponent liquid alloy to the mold, and rapidly cooling the liquid alloy to ambient temperature. Complex compositions seem to be necessary in order to inhibit crystallization of the liquid phase during the cooling of the melt. The preparation of single-element and binary bulk metallic glasses is of great interest, fundamentally as well as technologically. However, the equilibrium melt viscosity of a pure metal is usually 3 orders of magnitude smaller than that of an amorphous alloy, and current technology has yet to reach cooling rates in excess of 10^{10}–10^{12} °C/s to make pure metals amorphous [12]. This means insurmountable difficulties to produce bulk glassy materials of pure metals [13]. Zhang and Zhao [14] recently reported the production of bulk metallic glass from pure zirconium metal under high pressure and high temperature. But, the origin of the formation of the pressure-induced elemental metal glass is still unexplained. In this Letter, amorphouslike diffraction patterns of solid elemental titanium have been detected under high pressure and high temperature using *in situ* energy-dispersive x-ray diffraction (XRD) and a multianvil press.

The onset pressure and the temperature of formation of amorphous titanium is found to be close to the α-β-ω triple point in the *P-T* phase diagram. Amorphous Ti, though crystallized when quenched to ambient temperature, has been found to be thermally stable up to 1250 °C for at least 3 min at some pressures. By analyzing the conditions for producing amorphous elemental Zr and Ti, we observe a multi-phase-point amorphization phenomenon for preparing single-element bulk amorphous metals. The results reported may open a new way to preparing single-element bulk amorphous metals with a high thermal stability.

At normal conditions, the group 4 (IVB) transition metals Ti, Zr, and Hf all crystallize in the close-packed hexagonal structure, called the α phase. At high temperature and ambient pressure, they transform to the body-centered cubic structure or the β phase at temperatures of 882 °C, and 863 °C for Ti and Zr, respectively, before reaching the melting temperature [15]. At ambient temperature and high pressure, they undergo a structural transformation to the so-called ω phase (a hexagonal structure with space group $P6/mmm$) at transition pressures of 2.0 and 2.2 GPa for Ti and Zr, respectively [15]. At even higher pressures, both Zr and Hf transform to the β phase. In Ti, no β phase has been observed up to 216 GPa [16]. Zhang and Zhao [14] discovered that an amorphous phase appeared from high purity ω-Zr at 650 °C and 5.3 GPa by performing *in situ* high-temperature and high-pressure x-ray diffraction using synchrotron radiation. However, the amorphous phase crystallized when quenched to room temperature. At higher pressures (6.4 and 8.6 GPa), the amorphous phase

was formed from β-Zr at 700 and 625 °C, respectively. This amorphous phase was found to have superior thermal stability, no precipitation of any crystalline phase occurred even at temperatures up to 1000 °C. In contrast, crystallization happens when conventional amorphous alloys are heated to about 500 °C for a few minutes, even for extremely good glass formers, such as the $Pd_{40}Ni_{10}Cu_{30}P_{20}$ alloy [17] and Vit1 ($Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$) [18]. This problem seems to be absent in the elemental metallic glass with its extraordinary thermal stability. We note that the thermally stable amorphous Zr appeared only in a limited pressure range in the work of Zhang and Zhao [14]. No amorphous phase was produced at 4.3 GPa even when the sample was heated to 900 °C. At pressures higher than 9 GPa, Zr was only partially transformed to the amorphous phase, the diffraction pattern being dominated by the β phase. All of these facts indicate that pressure is a key issue for the formation of an amorphous phase from a pure metal. Moreover, we notice that the amorphous phase of Zr is produced in a pressure-temperature range close to the triple point at about 5.5 GPa and 700 °C in the phase diagram of Zr [19–21]. The amorphization of elemental Zr could be explained in the following way. Close to the triple point, Gibbs free energies of the α, β, and ω phases are nearly equal. Therefore, the Zr atoms can choose randomly between any of the three crystal structures, and as an average result they tend to arrange themselves in a disordered way. This may be called a phase-confusion model. A similar element-confusion model was suggested for multicomponent systems [5]. Gibbs free energy of the amorphous phase might be lower than that of any of the crystal phases when its entropy is maximal. If this argument is true, we should be able to turn any multiphase

metal element into an amorphous phase near a multiphase point in the pressure-temperature phase diagram. In particular, it should be possible to produce amorphous Ti and Hf, which belong to the same group 4 (IVB) as Zr. To test our hypothesis, we have investigated highly pure Ti metal (99.99%) at pressures and temperatures up to 7.2 GPa and 1300 °C. A similar method, at triple point to synthesize bulk amorphous Si was also suggested by Angell [22].

In situ high-temperature and high-pressure energy-dispersive XRD spectra were recorded using a multianvil press (MAX 80) and synchrotron radiation at HASYLAB in Hamburg, Germany [23]. The sample chamber is shown in Fig. 1. The central part consists of a cylindrical boron nitride container with an internal diameter of 1 mm. The upper half is filled with the sample (1 mm in diameter and 1 mm in length), the lower half with NaCl powder for pressure calibration. The cubic chamber is compressed by six tungsten carbide anvils in a large hydraulic press. Electric current is sent through a graphite heater via two appropriate anvils. The temperature, which is stable within ± 1 °C, is measured by means of a thermocouple. Samples were held for about 10 min at a given temperature and then heat up to a next temperature with a step about 50 °C in the temperature range of 50–600 °C and about 20–10 °C in the temperature range of 600–1300 °C with about 1 min. Immediately thereafter, the measurements were started again. Above 1100 °C samples were held for about 3 min to avoid gasket explosion. The rod shape of the sample in all experiments remains after high-pressure (up to 7.2 GPa) and high-temperature (up to 1300 °C) treatments. This indicates that melting behavior of Ti metal can be ruled out in the conditions used here.
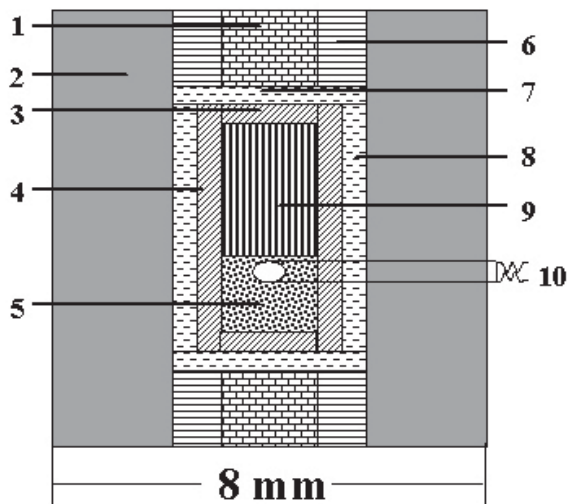

FIG. 1. Schematic map of the sample assembly for high-pressure and high-temperature x-ray powder diffraction studies. (1) Pyrophyllite disk. (2) Boron-epoxy cube. (3) BN disk. (4) BN container. (5) NaCl. (6) Copper ring. (7) Graphite disk. (8) Graphite heater. (9) Ti rod. (10) Thermocouple.
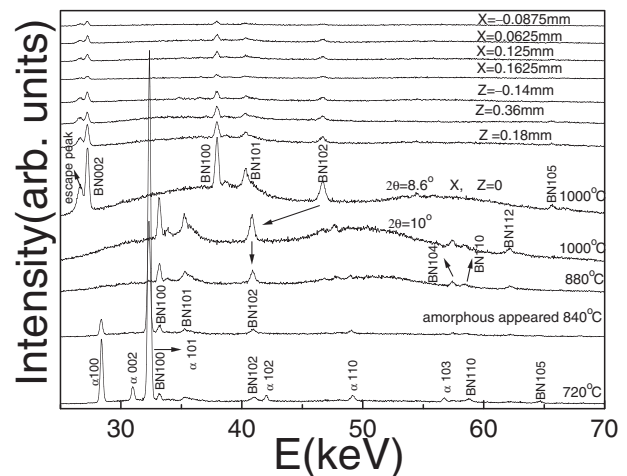

FIG. 2. *In situ* energy-dispersive x-ray powder diffraction patterns recorded at various temperatures for Ti rod at 6.3 GPa ($2\theta = 10°$) together with patterns using $2\theta = 8.6°$ at 1000 °C and various sample positions (along rod longitudinal Z axis and transversal X axis). The escaped peaks and a few Bragg peaks from BN were marked. The patterns for the sample at various positions were recorded for short times.

The original α-phase sample was compressed at room temperature and then heated to high temperatures at constant pressure. Figure 2 shows XRD spectra recorded at various temperatures during an isobaric run at 6.3 GPa. The sample remains in the α phase at 100 °C, but the ω phase appears at 150 °C. Upon further heating, the sample becomes a mixture of α and ω phases in varying proportions. The amount of the α phase first decreases and then increases, so that the sample is back to pure α phase at 720 °C. Linewidths of Bragg peaks for α and ω phases at different temperatures are similar, indicating average crystallite sizes are similar during the heating treatments. The amorphouslike diffraction pattern (hereafter called amorphous phase) appears at 840 °C, and the Ti sample is completely amorphous at 880 °C. The amorphous phase is found to be stable upon further heating to 1000 °C. To confirm that the sample is amorphous throughout, we have (1) changed angle from $2\theta = 10°$ to $2\theta = 8.6°$ and

(2) made a lateral scanning at 1000 °C with the incident x-ray beam of 0.5×0.25 mm^2 cross section in Fig. 2. To further explore the thermal stability, the Ti sample was heated to 1250 °C for about 3 min and as shown in Fig. 3. It is still amorphous.

In a run at the higher pressure 7.2 GPa, the ω phase appeared already at ambient temperature. The amount of α phase was reduced during the heating process and was zero at 150 °C. The precise position of the α-ω transition needs further study. At 780 °C there is a mixture of ω and β phases, and at 920 °C the formation of the amorphous phase is observed (Fig. 3). The amorphous phase is stable at 1250 °C for at least 3 min. Upon cooling, the samples in the 6.3 and 7.2 GPa runs transform to the crystalline α phase at 120 and 90 °C, respectively, as shown in Fig. 3. In order to further confirm the usability of our multi-phase-point method, we have made several additional runs at 4.4, 5.3, 5.7, 6.1, 6.5, and 6.6 GPa. The formation of amorphouslike diffraction patterns of solid Ti rod with a diameter of 1 mm was observed in all of these experiments. Figure 4 shows the phase diagram of Ti in P-T space. There is a large scattering of reported positions of the α-β-ω triple point as determined by various experimenters using static or shock-wave compression: (640 ± 50 °C, 8 ± 0.7 GPa) [15], (827 °C, 9 GPa) [21], (690 ± 20 °C, 5.5 ± 0.5 GPa) [24]. Many problems have to be solved in the phase diagram of Ti: the slope of the β-ω transition line, the α-ω and α-β boundaries, etc. Anyway, we have made it plausible that the glass formation occurs close to the triple point. In all of our experiments, we were unable to retain the amorphous phase when quenching to room temperature and zero pressure. There may be two reasons.
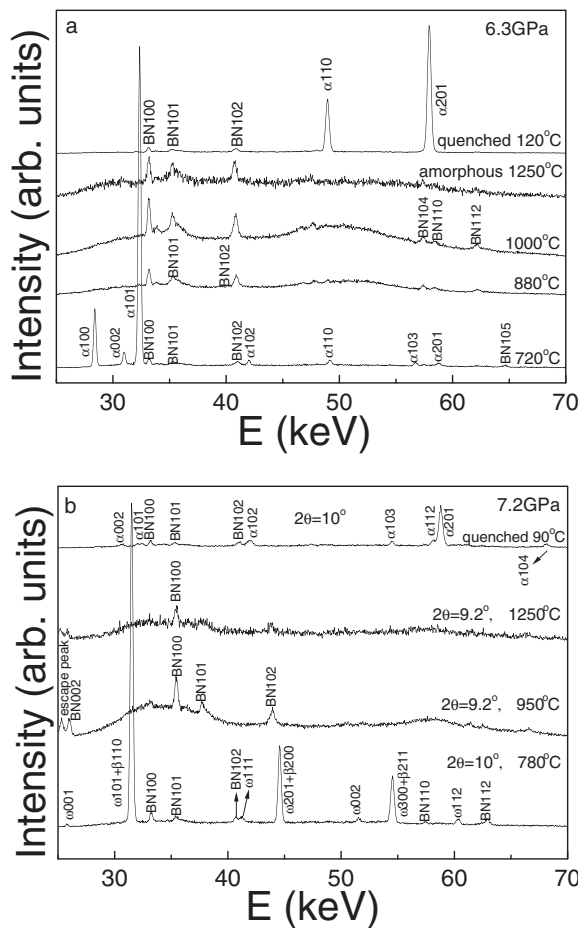

FIG. 3. *In situ* energy-dispersive x-ray powder diffraction patterns recorded for Ti rod under (a) 6.3 GPa ($2\theta = 10°$) and (b) 7.2 GPa ($2\theta = 10°$ and $2\theta = 9.2°$) and at various temperatures together with patterns recorded for quenched samples. The escaped peaks and a few Bragg peaks from BN were marked. The patterns at 1250 °C were recorded for about 3 min to avoid gasket explosion.
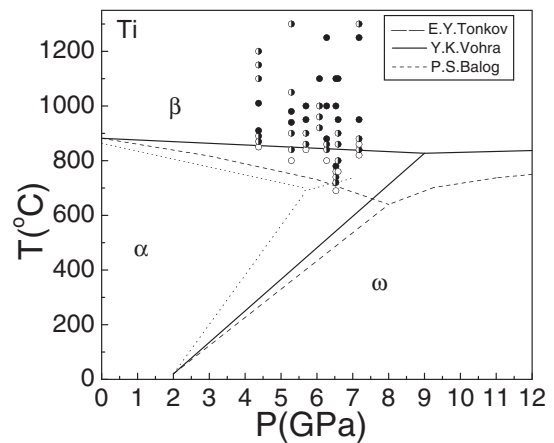

FIG. 4. Phase diagram of Ti, obtained in compression and heating mode. Circle symbols are obtained from present work. Filled circles denote amorphous phase, and partially filled circles are a mixture of amorphous and crystalline phases. Solid lines, broken lines, and dotted lines are from data in Refs. [15,21,24], respectively. $\alpha = $ close-packed hexagonal structure, $\beta = $ body-centered cubic structure, and $\omega = $ hexagonal structure with space group $P6/mmm$.

First, the onset pressures for amorphization are lower than those of Zhang and Zhao [14]. Second, we have cooled the sample isobaric and then decompressed it. During the isobaric cooling, the sample is far from the triple point, and it will crystallize.

It should be mentioned that phonon dispersion measurements of the high-temperature β phase of Ti [25,26], Zr [27], and Hf [28] reveal phonon anomalies at the longitudinal $L\frac{2}{3}(1, 1, 1)$ mode and the transverse $T_1\frac{1}{2}(1, 1, 0)$ mode. The former mode displaces the β lattice toward the high-pressure ω phase, and the latter one shifts the β planes into the stacking sequence of the low-temperature α phase. The β phase, stabilized mainly by the excess vibrational entropy, has a fast self-diffusion dominated by atomic jumps into nearest-neighbor vacancies. Although the phonon dispersion measurements [25–28] were carried out at ambient pressure, it might indicate that at around the α-β-ω triple point of group 4 (IVB) transition metals Ti, Zr, and Hf, large atomic displacements might cause topological disorder of atomic arrangements with a high value of entropy. Consequently, it results in the multi-phase-point amorphization phenomenon, as observed in the present work and Ref. [14].

In conclusion, we observe amorphouslike diffraction patterns for the solid elemental Ti rod with a diameter of 1 mm at high-pressure and high-temperature conditions close to the triple point in the *P-T* phase diagram of the investigated element using *in situ* high-temperature and high-pressure energy-dispersive XRD. The Ti amorphous phase is found to have a superior thermal stability compared with conventional multielement amorphous alloys. A multi-phase-point amorphization phenomenon is proposed for forming single-element bulk amorphous phase, which has been applied to Ti and Zr metals and can probably also be applied to other multiphase metal elements into an amorphous phase near a multiphase point in the pressure-temperature phase diagram. Thus, the method may open new routes for producing and understanding bulk amorphous alloys. It is the aim of this work to stimulate further theoretical and experimental works to shed light on the origin of the formation of amorphouslike diffraction patterns in solid single elements, Ti and Zr.

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[1] A. Inoue, *Bulk Amorphous Alloys 2* (Trans Tech Publications, Switzerland, 1998).
[2] W. L. Johnson, MRS Bull. **24,** 42 (1999).
[3] A. Inoue, Acta Mater. **48,** 279 (2000).
[4] Y. He, S. J. Poon, and G. J. Shiflet, Science **241,** 1640 (1988).
[5] A. L. Greer, Science **267,** 1947 (1995).
[6] X.-P. Tang, U. Geyer, R. Busch, W. L. Johnson, and Y. Wu, Nature (London) **402,** 160 (1999).
[7] G. He, J. Eckert, W. Loser, and L. Schultz, Nat. Mater. **2,** 33 (2003).
[8] A. Inoue, B. L. Shen, H. Koshiba, H. Kato, and A. R. Yavari, Nat. Mater. **2,** 661 (2003).
[9] J. Schroers and W. L. Johnson, Phys. Rev. Lett. **93,** 255506 (2004).
[10] J. Das *et al.*, Phys. Rev. Lett. **94,** 205501 (2005).
[11] B. Zhang *et al.*, Phys. Rev. Lett. **94,** 205502 (2005).
[12] R. Busch, A. Masuhr, E. Bakke, and W. L. Johnson, Mater. Sci. Forum **269,** 547 (1998).
[13] M. F. Ashby and D. R. Jones, *Engineering Materials 2: An Introduction to Microstructures, Processing and Design* (Pergamon, Oxford, 1986).
[14] J. Z. Zhang and Y. S. Zhao, Nature (London) **430,** 332 (2004).
[15] E. Y. Tonkov, *High Pressure Phase Transformations* (Gordon and Breach Science Publishers, Philadelphia, 1992).
[16] A. L. Kutepov and S. G. Kutepova, Phys. Rev. B **67,** 132102 (2003).
[17] N. Nishiyama and A. Inoue, Mater. Trans., JIM **37,** 1531 (1996).
[18] A. Peker and W. L. Johnson, Appl. Phys. Lett. **63,** 2342 (1993).
[19] H. Xia, S. J. Duclos, A. L. Ruoff, and Y. K. Vohra, Phys. Rev. Lett. **64,** 204 (1990).
[20] H. Xia, A. L. Ruoff, and Y. K. Vohra, Phys. Rev. B **44,** 10 374 (1991).
[21] Y. K. Vohra, J. Nucl. Mater. **75,** 288 (1978).
[22] C. A. Angell (private communication).
[23] J. Z. Jiang *et al.*, J. Appl. Phys. **87,** 2664 (2000).
[24] P. S. Balog and R. A. Secco, J. Phys. Condens. Matter **11,** 1273 (1999).
[25] W. Petry *et al.*, Phys. Rev. Lett. **61,** 722 (1988).
[26] W. Petry *et al.*, Phys. Rev. B **43,** 10 933 (1991).
[27] A. Heiming *et al.*, Phys. Rev. B **43,** 10 948 (1991).
[28] J. Trampenau *et al.*, Phys. Rev. B **43,** 10 963 (1991).