First Experimental Observation of Shear Induced hcp to bcc Transformation in Pure Zr

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Shear stresses are shown to induce the α (hcp) to ω (simple hexagonal) plus β (bcc) transformation in pure Zr at room temperature. The beta Zr thus fabricated is stable at 1 atm and room temperature. This phase has so far only been found to occur at high pressures ($P > 30$ GPa) and/or at high temperatures ($T > 1135$ K). This experimental observation provides new insights about the physical processes underlying allotropic transformations and opens the door to future investigations aiming to stabilize high temperature or pressure phases at ambient conditions.

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Many metals of key technological importance undergo allotropic phase transformations when subjected to high pressures or high temperatures. In particular, group IV transition metals such as titanium, zirconium, and hafnium, which have applications in the aerospace, nuclear, and biomedical industry, undergo the transformation sequence hcp(α) > simple hexagonal(ω) > bcc(β) with increasing pressure and transform from hcp to bcc with increasing temperature [1]. The transformation pressures and temperatures vary for each metal of the series. The high pressure phases have sometimes excellent properties that, however, cannot be exploited because the reverse phase transformations take place upon unloading. For example, it is known that the critical temperature for superconductivity increases with pressure in Zr, Ti, and Hf [2]. Additionally, bcc Ti has a lower elastic modulus than hcp Ti, and therefore it is much more promising as a material for bone implants.

In particular, the α to β transition temperature for pure Zr upon heating is 1135 K. Experimental observations of the different high pressure phases have been reported gradually over the past 45 years as more advanced pressure devices became available. The alpha to omega transition was observed for the first time using x-ray diffraction by Jamieson in 1963 [3]. The transition pressure ($P_{0\alpha>\omega}$) has since then been an object of debate, as it has been found to depend on composition [4], pressure medium (or degree of hydrostaticity) [5,6], and temperature [7]. Values between 2 and 6.5 GPa have been reported [1]. The omega phase is metastable and retained at ambient conditions after removing pressure. The first experimental evidence of the ω to β transformation in Zr was reported by Xia *et al.* [8] in 1990. It was detected that the transformation occurred at a transition pressure ($P_{0\omega>\beta}$) around 30 GPa. A full bcc to omega back transformation was observed when the pressure decreased below $P_{0\omega>\beta}$. The simultaneous application of temperature during loading leads to lower transition pressures [9].

Pressure-induced phase transformations in group IV transition metals have been predicted theoretically as a consequence of electron transfer from sp to d bands with increasing pressure [10–12]. As the d bands become more filled, the structure of group IV metals resembles that of the neighboring group V transition elements (V, Nb, Ta). This has important consequences. For example, group V metals have significantly higher superconducting transition temperatures (T_c) (5.4 K, 9.5 K, 4.5 K in V, Nb, and Ta vs 0.4 K, 0.6 K, and 0.1 K in Ti, Zr, and Hf, respectively) [13]. Moreover, the T_c has been reported to increase in ω-Ti, ω-Zr, ω-Hf, and ZrNb alloys with increasing pressure, and this phenomenon has been attributed to the increasing occupancy of the d band [14,15]. A maximum T_c of 11 K has been measured in β-Zr at 30 GPa [2].

This Letter reports the first observation of a shear induced hcp to simple hexagonal plus bcc transformation in pure Zr. The pure bcc Zr thus formed is stable at room temperature and atmospheric pressure.

The material under study is rolled commercially pure (99.98%) alpha Zr with a grain size of 240 nm. Disks of 10 mm in diameter and 1 mm in thickness were cut out of the annealed slabs. These samples were processed by high pressure torsion (HPT), a technique consisting of applying, simultaneously, compression and shear [16] using a press with a fixed upper anvil and a lower rotating plunger. The compression stresses utilized ranged from 0.25 GPa to 6 GPa. In all cases, the plunger was rotated 360° 5 times, at an approximate speed of 1 revolution per minute. The total shear deformation imposed, γ, is a function of the radius, r, and thus it varies at different locations in the disk. It may be estimated by [16]

$$\gamma = 2\pi N r/h, \tag{1}$$

where N is the number of turns and h is the disk thickness. At the edge of the disk, where $r = 5$ mm, $\gamma = 78.5$. The equivalent von Mises strain, ε, is then given by [16]

$$\varepsilon = 2/\sqrt{3}\ln[(1+\gamma^2/4)+\gamma/2]. \tag{2}$$

At the edge of the disk, in our case, $\varepsilon \approx 5$.

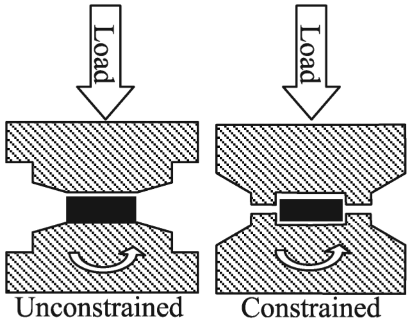

FIG. 1. Schematic illustration of the principle of high pressure torsion.

HPT processing was carried out using both constrained and unconstrained die sets [16], illustrated in Fig. 1. In the former, the disk is fitted into a cavity in the lower anvil which does not allow any outward flow of material during torsional pressing; in the latter, the disk simply lies on the flat surface of the lower anvil, and thus the material is free to flow outwards. As a result, disks processed by unconstrained HPT are thinned down to a thickness of 200 μm (or 0.2 mm).

The crystalline phases present in the processed samples were examined by conventional x-ray diffraction using Cu $K\alpha$ radiation, and 2θ angles ranging from 25° to 140° were scanned at steps of 0.017°. The total measurement time was approximately 45 minutes per diffractogram. Additionally, x-ray microdiffraction measurements were performed in areas close to the edge and to the center of the disks, with the aim of investigating the possible variations of the crystalline structure with increasing shear strain.

Figure 2 contains three x-ray diffractograms illustrating the crystalline phases present in commercially pure alpha Zr processed by high pressure torsion in a constrained die and using compression stresses of 1 GPa [Fig. 2(a)], 3 GPa [Fig. 2(b)], and 6 GPa [Fig. 2(c)]. In all cases, the number of turns of the plunger was equal to 5. A pressure of 1 GPa was not found sufficient to trigger any phase transformation, and thus alpha Zr is still retained after processing [Fig. 2(a)]. The peaks corresponding to the alpha phase are indicated using dotted lines. After HPT using a pressure of 3 GPa the α phase transforms partially into the ω and β phases [Fig. 2(b)]. This can be clearly inferred from the gradual disappearance of the α peaks (dotted lines) in Figs. 2(b) and 2(c) and the appearance of peaks corresponding to the two newly formed phases (solid lines—β; triangles—ω). Identifying the β phase can be complicated, as most β peaks overlap with ω peaks. Only those corresponding to 2θ angles of approximately 97° and 120° are isolated enough to be clearly resolved by current conventional x-ray diffraction methods. These peaks are in general weak, and thus noise in the measurement can make their detection difficult. Moreover, texture effects might result in their complete suppression, thereby masking the presence of the β phase. In this study, even though the peak at 120° is absent, the one at 97° is clearly visible in Figs. 2(b) and 2(c). We will thus use the latter as evidence of the presence of the β phase. The transformation is further enhanced with increasing pressure [Fig. 2(c)]. The α to ω transformation by HPT has been previously reported by the present authors in pure Zr [17], and it has also been observed by others in Ti [18]. However, this is the first direct observation of the beta phase stable at room temperature and atmospheric pressure in pure Zr. This phase was, additionally, found to be still present after 1 yr at room temperature and 1 atm.

The effect of the applied shear strain as a stimulus for the α to $\omega + \beta$ transformation is demonstrated in Fig. 3. There, the x-ray microdiffraction patterns corresponding to areas at the edge and at the center of the disk processed

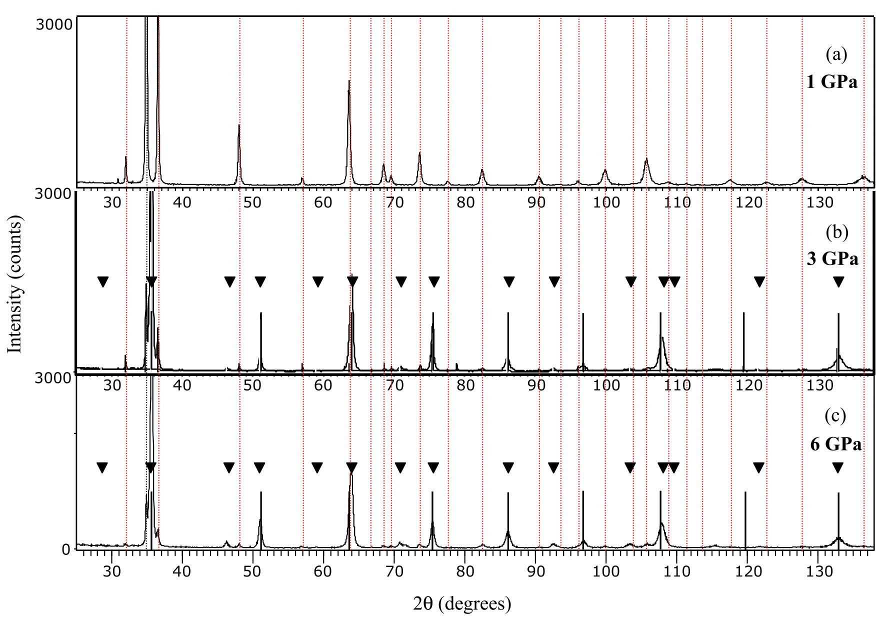

FIG. 2 (color online). X-ray diffractograms corresponding to cp Zr processed by HPT in a constrained die using 5 turns and different compression stresses (P): (a) $P = 1$ GPa; (b) $P = 3$ GPa; (c) $P = 6$ GPa. Red dotted lines indicate α peaks, black solid lines point out β peaks, and solid triangles signal ω peaks.

using 3 GPa and 5 turns have been superimposed. The fragment of the patterns comprising 2θ angles between 30° and 40° has been blown up since it is in that interval where the changes between both x-ray patterns can be appreciated better. The alpha peaks, present at the center regions, practically disappear in the edge areas, where the shear strain, γ, increases to approximately 78.5. Thus, shear stimulates the α to $\omega + \beta$ transformation in pure Zr. Furthermore, when analyzing Fig. 3, it must be taken into account that the irradiated areas are elliptical. The probed regions are depicted schematically in Fig. 3. The measurement carried out in the so called ''center'' area therefore also contains information about somewhat outer regions. It is thus foreseen that the alpha peaks would be even more pronounced in the measurement taken at the center of the disk had a smaller probe been available. The present results thus prove that shear enhances the transformation kinetics. Since the x-ray beam width is about 100 μm, our experiments reveal that the critical shear needed to complete the transformation is higher than 2. Further evidence of the influence of the applied shear can be found by comparing Figs. 2(c) and 4, both of which correspond to HPT performed under the same conditions of pressure and number of turns (6 GPa and 5 turns) but utilizing different types of dies. It must be taken into account that the stress state in the sample disks is different for each die set. During unconstrained HPT, only compression in the normal direction and pure shear are applied. In a constrained die, however, the material is not allowed to flow outward, and thus a compression force in the radial direction is exerted on the sample by the die walls. Thus, even though both unconstrained and constrained HPT are nonhydrostatic environments, the latter could be regarded as closer to hydrostaticity (i.e., the relative amount of shear is smaller). As expected, when using a constrained die [Fig. 2(c)], some alpha phase remains present after torsional straining. However, when an unconstrained die is employed (Fig. 4), the transformation is complete and no alpha phase could be detected after processing. These observations further confirm that shear favors the α to $\omega + \beta$ transformation in pure Zr.

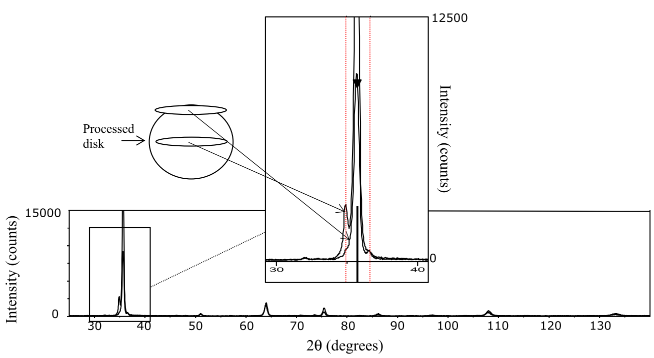

FIG. 3 (color online). Cp Zr processed by HPT using 3 GPa and 5 turns. X-ray microdiffraction patterns corresponding to areas located at the edge and at the center of the disk. A section of the patterns comprising 2θ angles between 30° and 40° has been blown up in order to clarify the disappearance of the alpha peaks in the vicinity of the edge regions. The alpha peaks are indicated in the inset by red dotted lines. A solid black line points out the β peak, and a solid triangle signals the ω peak. The ellipses indicate the irradiated zones.

The significant influence of shear in pressure-induced martensitic transformations has been recently demonstrated theoretically by Caspersen *et al.* [19] using multiscale modeling based on first principles. These authors predict that the transformation pressure decreases with increasing shear, an observation which is fully consistent with the experimental results presented in this Letter. The impossibility to reach perfectly hydrostatic conditions would then explain the wide scatter in measured transition pressures. The importance of shear in phase transformations has also been highlighted very recently by Wu *et al.* [20], who predicted by molecular dynamics simulations that, under shear, bcc Ta transforms into a Bingham plastic before melting. Errandonea *et al.* [5] analyzed the influence of the pressure medium $P_{0\alpha>\omega}$ in Ti by angle dispersive powder x-ray diffraction in a diamond anvil cell using 4 different environments: argon, methanol:ethanol, NaCl and no medium. They demonstrated that, as the degree of hydrostaticity decreases, i.e., as uniaxial stresses become more significant, $P_{0\alpha>\omega}$ decreases. This work confirmed previous observations by Zilbershtein *et al.* [21]. However, the magnitude of the shear components in a diamond anvil cell is unknown, and thus, linking the shear strain to transformation parameters is impossible. Therefore the present experimental results constitute a first step toward establishing a quantitative relationship between the applied shear and, for example, the transition pressure.

Because of the martensitic nature of the phase transformations taking place at high pressures, it is not possible to observe *in situ* the underlying mechanisms, which have been the subject of debate for decades. Several mechanisms have been proposed to explain the α to ω transformation in group IV transition metals. Silcock [22] suggested a direct transformation from the hcp to the simple hexagonal (ω) lattice in which, in each α stacking plane, three out of six atoms shuffle by 0.74 Å along $[1120]_\alpha$, while the other three shuffle in the opposite direction $[1120]_\alpha$. Usikov and Zilbershtein [23] proposed that the transformation proceed via an intermediate bcc

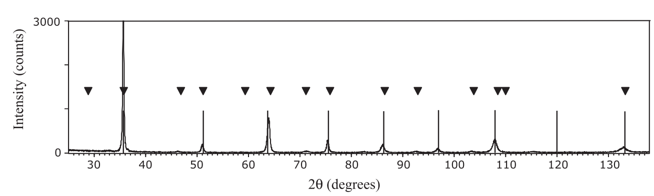

FIG. 4. X-ray diffractogram corresponding to cp Zr processed using 5 turns and 6 GPa in an unconstrained die. The solid triangles indicate the position of the peaks of the ω phase. The solid black lines point out the peaks of the β phase.

phase, i.e., following the $\alpha > \beta > \omega$ sequence. The intermediate β phase is reported to be thermodynamically unstable under ambient conditions in pure Ti and Zr, but it was observed by TEM in dilute Ti-V alloys by Vohra *et al.* [24]. Later studies in pure Zr also inferred indirectly the presence of an intermediate (unstable) beta phase through the analysis of the variants of the stable final omega phase [25,26]. Recently Trinkle *et al.* [27] carried out tight binding and *ab initio* calculations in order to find out the α to ω pathway involving the smallest energy barrier in Ti, thus defining a new direct $\alpha > \omega$ pathway (TAO-1). This pathway also involves shuffling of atoms in the α lattice to create an intermediate supercell plus subsequent shear of the latter. Errandonea *et al.* [5] claimed this mechanism is consistent with their experimental observations. Our results show evidence of the presence of stable beta and omega phases at ambient conditions upon HPT of pure Zr. Both phases seem to appear simultaneously when torsional straining is carried out at pressures higher than 3 GPa and when the plunger is rotated 5 times. The present results do not allow us to infer whether the beta phase observed is an intermediate state between the alpha and the omega phases, an inference that would support Usikov‘s model, or whether the omega phase is itself an intermediate state toward the high pressure beta phase. The presence of a mixed phase structure upon the application of shear and pressure was predicted theoretically by Caspersen *et al.* [19]. These authors relate the pressure hysteresis (the transformation pressure corresponding to the back transformation being lower than that corresponding to the forward transformation), often observed experimentally, to the presence of this complex microstructure. Similar arguments might also be used to explain the retention of both the beta and omega phases after HPT.

In summary, this Letter reports the first experimental observation of the shear induced hcp to omega plus bcc transformation in pure Zr. We have fabricated pure beta Zr by high pressure torsion at room temperature, using compression stresses higher than 3 GPa and 5 plunger turns. The crucial role of shear, predicted previously by modeling [19,20], is demonstrated, thus providing new insights into the underlying physical mechanisms of the investigated transformations. The bcc Zr thus fabricated is stable at ambient conditions. We expect that the possibility of stabilizing high pressure phases at ambient conditions by the controlled application of shear might be exploited in a wide range of materials, and thus this work provides a starting point for subsequent studies.

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[1] S. K. Sikka, Y. K. Vohra, and R. Chidambaram, Prog. Mater. Sci. **27**, 245 (1982).
[2] C. Buzea and K. Robbie, Supercond. Sci. Technol. **18**, R1 (2005).
[3] J. C. Jamieson, Science **140**, 72 (1963).
[4] R. G. Hennig, D. R. Trinkle, J. Bouchet, S. G. Srinivasan, R. C. Albers, and J. W. Wilkins, Nature Mater. **4**, 129 (2005).
[5] D. Errandonea, Y. Meng, M. Somayazulu, and D. Häusermann, Physica (Amsterdam) **355B**, 116 (2005).
[6] J. Zhang, Y. Zhao, C. Pantea, J. Qian, L. L. Daemen, P. A. Rigg, R. S. Hixson, C. W. Greeff, G. T. Gray III, Y. Yang, L. Wang, Y. Wang, and T. Uchida, J. Phys. Chem. Solids **66**, 1213 (2005).
[7] Y. K. Vohra, S. K. Sikka, and R. Chidambaram, J. Phys. F **9**, 1771 (1979).
[8] H. Xia, S. J. Duclos, A. L. Ruoff, and Y. K. Vohra, Phys. Rev. Lett. **64**, 204 (1990).
[9] H. Xia, A. L. Ruoff, and Y. K. Vohra, Phys. Rev. B **44**, 10 374 (1991).
[10] R. Ahuja, J. M. Wills, B. Johansson, O. Eriksson, Phys. Rev. B **48**, 16 269 (1993).
[11] Y. K. Vohra, Acta Metall. **27**, 1671 (1979).
[12] I. Schnell and R. C. Albers, J. Phys. Condens. Matter **18**, 1483 (2006).
[13] C. Kittel, *Introduction to Solid State Physics*, (Wiley, New York, 1996).
[14] I. O. Bashkin, V. G. Tissen, M. V. Nefedova, and E. G. Ponyatovsky, Physica (Amsterdam) **453C**, 12 (2007).
[15] I. O. Bashkin, V. G. Tissen, M. V. Nefedova, and E. G. Ponyatovsky, Physica (Amsterdam) **434C**, 191 (2006).
[16] A. P. Zhilyaev and T. G. Langdon, Prog. Mater. Sci. **53**, 893 (2008).
[17] M. T. Pérez-Prado, A. A. Gimazov, O. A. Ruano, M. E. Kassner, and A. P. Zhilyaev, Scr. Mater. **58**, 219 (2008).
[18] Y. Todaza, J. Sasaki, T. Moto, M. Umemoto, Scr. Mater. **59**, 615 (2008).
[19] K. J. Caspersen, A. Lew, M. Ortiz, and E. A. Carter, Phys. Rev. Lett. **93**, 115501 (2004).
[20] C. J. Wu, P. Söderlind, J. N. Glosli, and J. E. Klepeis, Nature Mater. **8**, 223 (2009).
[21] V. A. Zilbershtein, N. P. Chistotina, A. A. Zharov, S. S. Grishina, and E. I. Estrin, Fiz. Met. Metalloved. **39**, 445 (1975).
[22] J. M. Silcock, Acta Metall. **6**, 481 (1958).
[23] M. P. Usikov and V. A. Zilbershtein, Phys. Status Solidi A **19**, 53 (1973).
[24] Y. K. Vohra, E. S. K. Menon, S. K. Sikka, and R. Krishnan, Acta Metall. **29**, 457 (1981).
[25] S. C. Gupta, S. K. Sikka, and R. Chidambaram, Scr. Metall. **19**, 1167 (1985).
[26] E. S. K. Menon, Scr. Metall. **16**, 717 (1982).
[27] D. R. Trinkle, R. G. Hennig, S. G. Srinivasan, D. M. Hatch, M. D. Jones, H. T. Stokes, R. C. Albers, and J. W. Wilkins, Phys. Rev. Lett. **91**, 025701 (2003).