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Transmission electron microscopy observations of structural modulation in the phase transition from α-Zr to ω-Zr induced by shear strain

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Pure α-Zr samples were processed using unconstrained die sets at 5 and 6 GPa with different numbers of revolutions. The microstructural characteristics of Zr deformed by high pressure torsion was studied using transmission electron microscopy. It was found that shear strain can induce distortion of the hcp structure, which can, in addition, give rise to a variety of modulated structures. Most importantly, one possible phase transition route from α-Zr to ω-Zr is proposed involving intermediate steps with structural modulations.

Keywords: Transmission electron microscopy; Phase transformation; High pressure torsion; Modulation structure

The group IV transition metal zirconium is among the most desirable candidate materials due to its widespread and successful application in recent years, in such roles as fuel rods [1] in the nuclear power industry and as biomaterials [2] for bone implants, etc. As tunable thermodynamic parameters and external pressure and temperature play important roles in the allotropic phase transitions of pure Zr. Numerous experimental studies over the past five decades have revealed that Zr undergoes a phase transition from α phase with a hexagonal close-packed (hcp) structure to β phase with a body-centered cubic (bcc) structure at ambient pressure above 1135 K [3,4]. A further reversible phase transition from β-Zr to ω-Zr, with a simple hexagonal (h) structure, occurs with increasing pressure [5–7]. However, direct evidence for the presence and superior properties of the β and/or ω phases has yet not been obtained after releasie of the high pressure and/or temperature due to the reversibility of the phase transitions. Consequently, synthesizing high quality β-Zr or ω-Zr samples and using them at ambient pressure and temperature are major challenges. In 2009 Pérez-Prado et al. [4] obtained stable β-Zr at room temperature and atmospheric pressure through allotropic phase transitions from α-Zr to β-Zr and ω-Zr induced by high pressure torsion (HPT). HPT, a distinct type of severe plastic deformation (SPD), can produce huge shear stresses during the rotation of compressed plungers and the associated metastable phases.

In previous transmission electron microscopy (TEM) studies of deformed Zr [3,8] Pérez-Prado et al. reported that many nanocrystalline grains with planar faults occurred in HPT samples, which were possibly induced by SPD or phase transition in the ω phase. In addition, Wang et al. [9] observed that HPT α-Zr was retained up to 3.8 GPa with $\{\bar{1}011\}$ twins in coarse grains of a sample subjected to low strain. Despite most researchers confirming the existence of HPT-induced allotropic phase transitions in pure Zr, the mechanism is not yet completely understood. Here we focus on a microstructural investigation of pure Zr processed by HPT in order to clarify the process of shear strain-induced phase

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transition. In particular, we report the observation of modulated structures during the shear strain-induced transition from α-Zr to ω-Zr.

Commercial grade (99.9% pure) α-Zr was used as the original material. It was annealed at 500 °C for 2 h to produce an average grain size of ~10 μm. Sliced disks 10 mm in diameter and 1 mm thick were processed by HPT in unconstrained die sets [10]. Consequently, the samples were subjected to pressure only along the normal direction in a non-hydrostatic environment [4]. In our experiments all three samples were compressed at 5 GPa with $N = 3$ revolutions (sample A) (note that the rotation speed of the plunger was 1 r.p.m., with N indicating the number revolutions), 6 GPa with $N = 0.5$ and 6 GPa with $N = 3$ (samples B and C). Due to sample flow out of the anvil the final thickness of the sample disks decreased to approximately 0.2 mm. Using the above measured parameters the equivalent von Mises strain (ε) is obtained from the equation [10]:

$$\varepsilon = \frac{2}{\sqrt{3}} \ln\left[\left(1 + \frac{\gamma^2}{4}\right)^{\frac{1}{2}} + \frac{\gamma}{2}\right] \quad (1)$$

and the total shear deformation imposed (γ) as a function of distance from the center of the disk (r) is given by [10]:

$$\gamma = \frac{2\pi N r}{h} \quad (2)$$

where N indicates the number revolutions, h represents the thickness of the disk. Three thin TEM specimens of HPT Zr were selected from the edge of the sample disks ($r = 3$ mm, $\varepsilon_A \approx 6.5$, $\varepsilon_B \approx 4.4$, $\varepsilon_C \approx 6.5$) and prepared by argon ion milling after mechanical polishing. A liquid nitrogen cold stage was used during ion milling to reduce damage by the ion beams. An FEI Tecnai F20 transmission electron microscope with a field emission gun operated at 200 keV was used for selected area electron diffraction (SAED), bright (BF) and dark field (DF) TEM, and high resolution TEM (HRTEM) investigations. The nature of the phase transitions was examined by X-ray diffraction (XRD) using CuK_α radiation.

Figure 1 shows XRD patterns illustrating the occurrence of an allotropic phase transition from α-Zr to ω-Zr for sample A (5 GPa with $N = 3$), sample B (6 GPa with $N = 0.5$), and sample C (6 GPa with $N = 3$). The

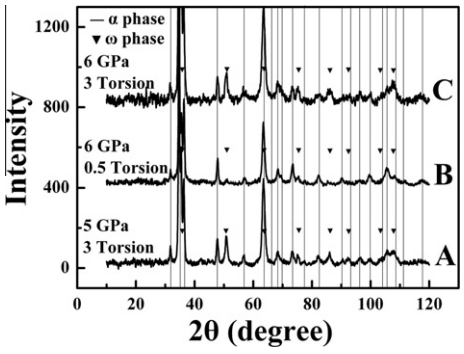

Figure 1. The XRD patterns for samples A, B, and C after the HPT process. The solid lines (|) and triangles (▼) indicate diffraction peaks corresponding to the α and ω phases, respectively.

diffraction peaks belonging exclusively to the α and ω phases are indicated by solid lines (|) and triangles (▼), respectively. The α phase has a hcp structure with space group $P6_3/mmc$ ($a = 3.23$ Å, $c = 5.14$ Å [11]), while the ω phase retains a h lattice ($P6/mmm$, $a = 5.039$ Å, $c = 3.136$ Å [12]). Although most of the α peaks overlap ω peaks, those peaks corresponding to 2θ at about 51°, 75° and 86° can still be clearly distinguished for individual structural identification. Consistent with previous results [4,8], it was found that part of the α phase was retained in all the samples after unconstrained HPT processing. On comparing the peaks for samples A and C with that of the sample B around 50° in Figure 1 it can be seen that the intensity ratio between the ω and α peaks is higher in the former because the phase transition is further promoted by the higher shear strain (both ε_A and ε_C are above ε_B). Moreover, using the Debye–Scherrer formula

$$D = \frac{k\lambda}{\beta \cos\Theta} \quad (3)$$

in which k is the shape factor, λ is the X-ray wavelength, β is the full width at half maximum of the peak, and Θ is the diffraction angle, the average grain size D of the ω phase was determined to be ~10 nm.

To study the microstructural evolution of the samples we carried out careful TEM analyses. The SAED pattern for sample A is presented in Figure 2a, in which the typical crystalline planes of the α and ω phases can be well indexed. It can be seen that the ω phase shows only diffraction arcs because of the random orientation of nanocrystalline ω-Zr [3], whereas the α phase gives diffraction spots, indicating coarse crystalline grains in the same area. In addition, the coarse grain electron diffraction patterns present textured characteristics. For example, Figure 2b can be indexed to the $[1\bar{2}1\bar{3}]$ zone axis of α-Zr. The diffraction arcs in Figure 2b indicate that a large continuous bending misorientation [9] of up to ~16° exists in the sample. Figure 2d is the SAED pattern along the $[01\bar{1}0]$ zone axis of α-Zr corresponding to the marked white circular region in Figure 2c. Interestingly, a pair of weak satellite spots marked by black arrows appears on both sides of the main diffraction points, implying an incommensurate modulation along $g_{(\bar{2}110)}$. To further confirm the existence of weak modulation structure we utilized an objective aperture to select the (0002) diffracted spot and its twin satellites, which are magnified in the inset in Figure 2d, and acquire the DF micrograph in Figure 2e from the same region as Figure 2c. A comparison of the BF and DF images reveals the incommensurate modulation structure apparent as zebra stripes spread across the whole region, which is magnified in the inset in Figure 2e. In Figure 2f a HRTEM image along $[01\bar{1}0]$ zone axis reveals a modulation wavelength close to 2.84 nm, consistent with that obtained from the distance between the satellites in Figure 2d, whose direction is normal to the c-axis. Based on the above observations we propose that the shear strain originating from HPT causes distortion of the hcp structure and further gives rise to long-range ordering. Strain-induced modulated structures have been reported in some alloys. For example,