

## Nanoindentation hardness and atomic force microscope imaging studies of pressure-quenched zirconium metal

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We have carried out mechanical property measurements on zirconium metal compressed in a diamond anvil cell to 19 GPa at room temperature with subsequent quenching to room pressure. The irreversible transformation from the ambient hexagonal-close-packed phase to the simple hexagonal  $\omega$  phase (AlB<sub>2</sub> structure) is confirmed by synchrotron energy dispersive x-ray diffraction followed by nanoindentation of the pressure-quenched sample. We document an 80% increase in hardness as a consequence of the pressure-induced transformation to the  $\omega$  phase at room temperature. This is a large increase for a metallic phase transformation and can be attributed to the presence of  $sp^2$ -hybrid bonds forming graphite-like nets in the (0001) plane of the AlB<sub>2</sub> structure. Atomic force microscopy of the indents shows that a plastic deformation of 2  $\mu\text{m}$  in depth was achieved with a force of 200 mN. © 2000 American Institute of Physics. [S0003-6951(00)00549-0]

The diamond anvil cell (DAC) can effectively generate static pressures in materials of up to 400 GPa at temperatures as high as 4000 K. The opportunity for investigating materials over such a large pressure and temperature range has resulted in the identification of new structures and has provided a fundamental understanding of the behavior of materials under extreme conditions.<sup>1</sup> Characterization of materials using DACs is typically performed *in situ* (under high pressure/temperature) via the use of x-ray diffraction, Raman scattering, or electrical transport measurements. In some cases, the high pressure and/or high temperature phase of interest can be quenched to ambient conditions, allowing further *ex situ* characterization. Of particular interest is investigation of mechanical properties, such as hardness, of the quenched phase.<sup>2</sup> Until recently, this has been impractical due to the very small sample volumes required in DAC devices in which the sample chamber is typically 25–150  $\mu\text{m}$  in diameter, depending on the maximum pressure requirement. We have overcome this difficulty by taking advantage of the small probe volume available from a depth-sensing nanoindenter. The group IV transition metals Ti and Zr are unique amongst metals because of a pressure-induced  $\omega$  phase, which can be retained at ambient conditions.

The  $\omega$  phase has been the focus of intense theoretical and experimental work due to its complex morphology, its interesting kinetics of formation, and its effects on physical properties such as ductility and superconductivity.<sup>3</sup> The increase in microhardness with the formation of the  $\omega$  phase during temperature quenching in group IV transition metal alloys has been well documented.<sup>3</sup> The pressure-induced transformation in zirconium from the hexagonal-close-packed structure (hcp)  $\alpha$  phase to simple hexagonal  $\omega$  phase usually starts at approximately 4 GPa at room temperature. The equilibrium  $\alpha$ - $\omega$  transformation in Zr is around 2 GPa in the presence of shear stresses. The  $\omega$  phase has the AlB<sub>2</sub> structure with a  $c/a$  ratio of 0.612. The (0001) planes form a

sequence of the type (ABAB...) and trigonal bonds are formed in the B plane, resulting in a graphite-like net structure. Formation of the  $\omega$  phase leads to an increase in hardness and a consequent loss of ductility. This has previously been experimentally verified for bulk samples of  $\omega$  titanium in which the hardness was greater than the  $\alpha$  phase by a factor of 1.8 at room temperature.<sup>4</sup> We report a similar increase in hardness exhibited by pressure-quenched zirconium metal that has undergone a phase transformation to the simple hexagonal  $\omega$  phase in a diamond anvil cell.

Zirconium metal foil (annealed) of 0.25 mm thickness and 99.8% purity was purchased from Alfa AESAR. The high pressure DAC experiments employed diamonds with culet size of 600  $\mu\text{m}$ . After light abrasion with 600 grit SiC sandpaper and subsequent cleaning in methanol, small pieces (less than 150  $\mu\text{m}$ ) of the zirconium metal completely filled the pressure chamber of 150  $\mu\text{m}$  diameter drilled in a spring steel gasket. A small piece of ruby was placed near the center of the sample for use as a pressure marker. No pressure medium was employed since nanoindentation requires a flat sample surface after decompression. Energy dispersive x-ray diffraction spectra were recorded at the superconducting wiggler beam line X-17C at National Synchrotron Light Source, Brookhaven National Laboratory. The x-ray diffraction experiments were performed with a microcollimated beam using a focusing mirror to produce a spot size of 10  $\mu\text{m}$  × 11  $\mu\text{m}$ . Nanoindentation studies were carried out using a Materials Testing System-NanoInstruments XP system with a Danish Micro Engineering atomic force microscope (AFM) attachment. The diamond tip used for indentation was an Accutip brand with a nominal radius of 50 nm.

Figure 1 shows the angle dispersive x-ray diffraction of the hcp phase at ambient conditions. The measured lattice parameters were  $a=3.231\pm 0.005 \text{ \AA}$  and  $c=5.139\pm 0.002 \text{ \AA}$  giving a  $c/a$  ratio of 1.59. Figure 2 shows the energy dispersive x-ray diffraction pattern of the pressure-quenched sample from 19 GPa in a diamond anvil cell. The diffraction angle for this experiment was set to  $2\theta=15^\circ$ . The pressure-quenched sample is fully indexed to simple

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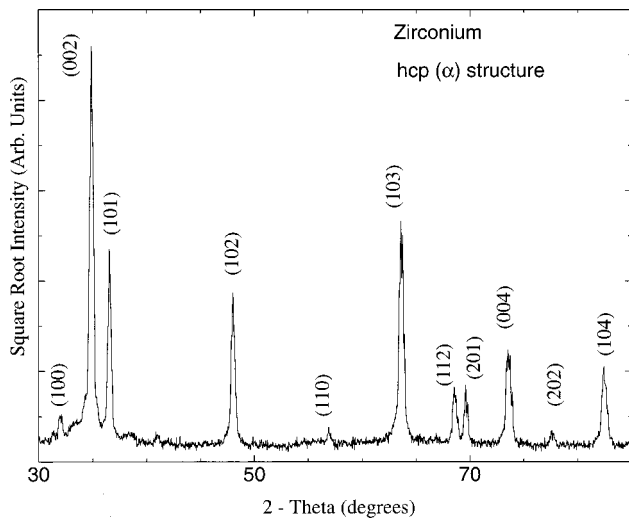


FIG. 1. Angle dispersive x-ray diffraction of the ambient hcp phase of zirconium metal ( $\text{CuK}\alpha$  radiation,  $\lambda = 1.54184 \text{ \AA}$ ). The ambient phase of this metal is indexed to the hcp  $\alpha$  phase of zirconium ( $a = 3.231$ ,  $c = 5.139 \text{ \AA}$ ).

hexagonal zirconium ( $a = 5.017 \pm 0.007 \text{ \AA}$ ,  $c = 3.122 \pm 0.001 \text{ \AA}$ ), indicative of complete transformation to the  $\omega$  phase. The transformation was previously shown<sup>5</sup> to occur according to the progression  $\alpha \rightarrow \beta \rightarrow \omega$ , where  $\beta$  is an intermediate body-centered-cubic (bcc) phase that is thermodynamically unstable at the temperatures and pressures under consideration. The  $\omega$  phase can appropriately be described as a distorted bcc structure and the  $\alpha \rightarrow \beta \rightarrow \omega$  transformation mechanism is consistent with the martensitic nature of its kinetics.

To investigate the change in hardness between the uncompressed and pressure-quenched zirconium samples, nanoindentation was performed. Figure 3 shows a low magnification optical micrograph of the nine indentations made on the pressure-quenched sample along with an AFM image of one indent made in the unquenched sample. Also shown is the profile trace corresponding to the arrow on the AFM image, which reveals the plastic depth of the indent to be approximately  $1.8 \mu\text{m}$ . The maximum applied force during

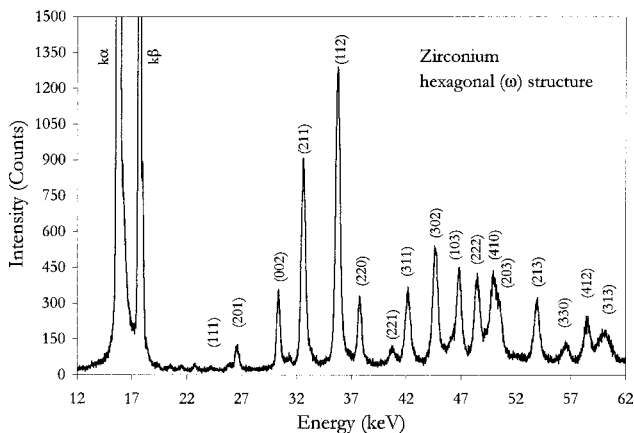


FIG. 2. Energy dispersive x-ray diffraction spectra of the pressure quenched zirconium metal (from 19 GPa). The pressure-quenched metal is fully indexed to the simple hexagonal  $\omega$  phase ( $a = 5.017$ ,  $c = 3.122 \text{ \AA}$ ) of zirconium. The product of energy and interplanar spacing is  $E_d = 47.40 \pm 0.06 \text{ keV \AA}$ . The peaks marked  $K\alpha$  and  $K\beta$  are the fluorescence lines from the zirconium sample.

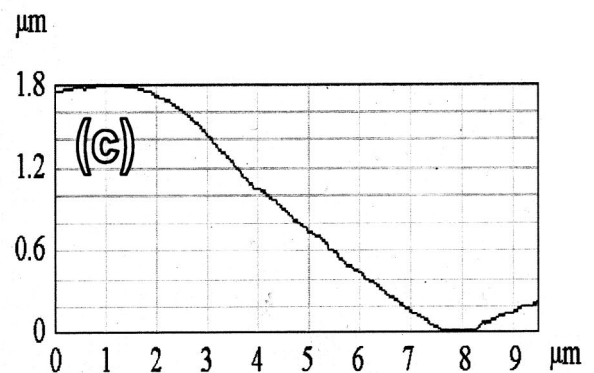
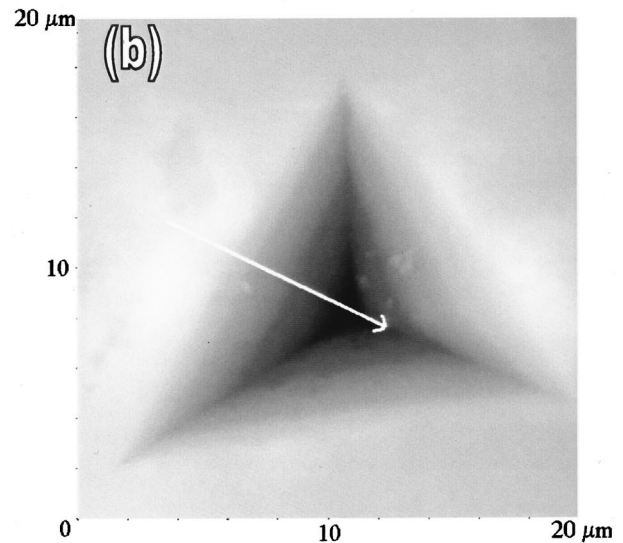
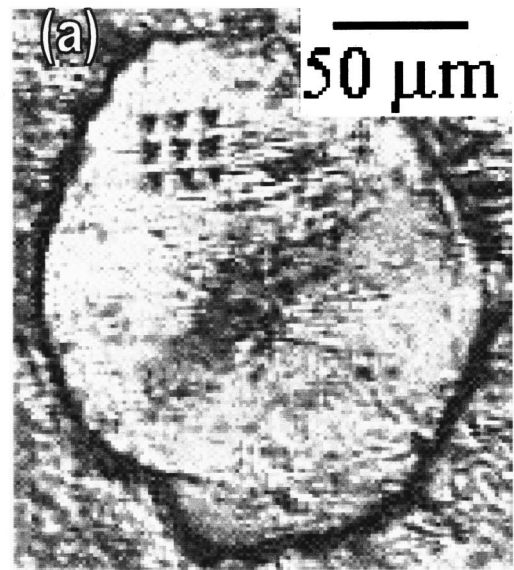


FIG. 3. (a) Optical micrograph in reflection of the pressure-quenched  $\omega$ -phase sample in a diamond anvil cell. The upper left hand corner of the sample shows nine indentations made by our nanoindenter. This sample is  $150 \mu\text{m}$  in diameter. (b) An AFM image of an indentation made in the ambient phase of zirconium metal. (c) A profile trace corresponding to the arrow in the AFM image.

the nanoindentation was  $200 \text{ mN}$ . The results of hardness versus depth are shown in Fig. 4. The hardness is plotted only for depths greater than  $600 \text{ nm}$  since surface asperities associated with these samples resulted in significant scatter

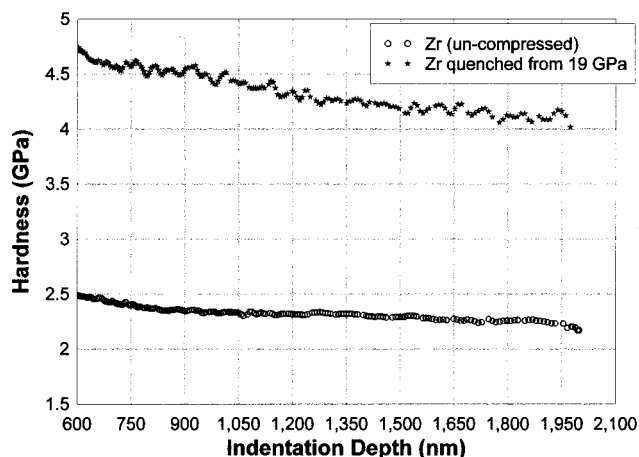


FIG. 4. Comparison of nanoindentation hardness vs depth for uncompressed and pressure-quenched zirconium metal (from 19 GPa). The hardness of the pressure-quenched zirconium (upper curve) is higher than the uncompressed zirconium (lower curve) by a factor of 1.8.

at shallow depths. The average measured hardness values for the uncompressed and pressure-quenched zirconium are  $2.4 \pm 0.4$  and  $4.3 \pm 0.5$  GPa, respectively. A fused quartz standard was tested before and after the measurement to insure that the tip calibration was accurate. Its hardness was consistently measured to be 9.5 GPa, as expected for this material. The increase in hardness of the pressure-quenched zirconium by 80% over the uncompressed sample is quite large for a phase transformation in a pure metal. This large change can be attributed to the unique bonding of the  $\omega$  phase, which is expected to exhibit some covalent nature due to the presence of trigonal bonds forming graphite-like nets in the (0001) plane of the  $\text{AlB}_2$  structure. It should be added that this increase in hardness in pressure-quenched samples is similar to the increase seen in temperature-quenched samples produced in group IV metal alloys as well as in bulk samples produced at high pressures.<sup>3,4</sup>

In conclusion, we have experimentally verified using diamond anvil cell high-pressure studies that zirconium metal undergoes an 80% increase in hardness associated with the phase transformation from hcp  $\alpha$  phase to the simple hexagonal  $\omega$  phase. This hardness measurement was achieved using nanoindentation techniques on the very small sample volume ( $150 \mu\text{m}$  diameter) required by the high-pressure cell. The 80% increase in hardness is quite large for a phase transformation in a pure metal and can be attributed to the presence of  $sp^2$ -hybrid bonds forming graphite-like nets in the (0001) plane of the  $\text{AlB}_2$  structure. The samples for nanoindentation studies could be as small as  $1\text{--}10 \mu\text{m}$  in diameter. Therefore, samples quenched from megabar (100 GPa) pressures in the diamond anvil cell can also be investigated by this technique. The ability to perform nanoindentation and nanoimaging of pressure-quenched materials produced in a diamond anvil cell provides new opportunities for investigating high pressure and/or high temperature synthesized structures.

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<sup>1</sup>H. K. Mao and R. J. Hemley, *Philos. Trans. R. Soc. London, Ser. A* **354**, 1315 (1996).

<sup>2</sup>J. R. Patterson, S. A. Catledge, and Y. K. Vohra, *Appl. Phys. Lett.* **77**, 851 (2000).

<sup>3</sup>S. K. Sikka, Y. K. Vohra, and R. Chidambaram, *Prog. Mater. Sci.* **27**, 245 (1982).

<sup>4</sup>F. Yu Bychkov, N. Yu Likhnan, and V. A. Maltsev, *Fiz. Met. Metall.* **36**, 413 (1973).

<sup>5</sup>Y. K. Vohra, E. S. K. Menon, S. K. Sikka, and R. Krishnan, *Acta Metall.* **29**, 457 (1981).