In-Situ TEM Mechanical Testing of Nanocrystalline Zirconium Thin Films

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Abstract

Mechanical behavior of nanocrystalline zirconium thin films was investigated in-situ inside a transmission electron microscope (TEM). The yield stress measured for specimens with <10 nm grain size was around 450-500 MPa compared to the bulk value of 250-300 MPa. Similar grain size effects are seen on fracture stress and strain of about 0.9 GPa and 1.5-2% respectively. Using in-situ TEM, we demonstrate control of grain size in the specimens using the electro-migration stress and temperature. The experimental results suggest that the critical grain size for inverse Hall-Petch type relationship in nanocrystalline hexagonal close packed metals could be around 15 nm.

Keywords: in-situ TEM, nanocrystalline metals, zirconium; grain size effect

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1. Introduction

Zirconium is a strong and ductile metal with hexagonal close packed (HCP) crystal structure at room temperature. Its strength, resistance to corrosion and irradiation, high melting point and biocompatibility are attractive features for important applications in nuclear, aviation and surgical implant industries. Even though nanocrystalline materials exhibit higher yield strength and resistance to fatigue [1, 2], [more comprehensive studies in the relevant literature considered ultra-fine \(around 100 nm\) grain sizes \[3, 4\]. These studies addressed the challenges in the nanocrystalline materials preparation through severe plastic deformation](#), surface mechanical attrition treatment or cryo-rolling [5, 6]. Such multi-modal grain distribution results in a unique combination of high strength and large ductility, e.g. a high ultimate tensile strength of ~658 MPa and large uniform elongation of ~8.5% [7]. Micro-scale pillars have also been fabricated using focused ion beam machining [8, 9], which are then tested under compression to study role of grain size and pillar diameter.

In this study we take a different approach, where sputtered thin films are patterned and integrated with micro-electro-mechanical system (MEMS) sensors and actuators, thereby limiting the test chip size to 3mm x 5mm. The electron transparent specimens are released from the silicon substrate, which allows us to perform mechanical tests inside a transmission electron microscope (TEM). In-situ TEM tests can reveal microstructural features, (defects, phases, precipitates and interfaces), diffraction patterns and chemical microanalysis in real time [10]. Integration of MEMS sensors allow mechanical stress and strain to be measured [11, 12]. The unique simultaneously quantitative mechanical properties and qualitative defect and microstructural visualization will lead to accurate and quick (direct observation based) modeling of nanocrystalline zirconium deformation.

2. Materials and Methods

Figure 1 shows our experimental setup, where the chip is mounted on a TEM specimen holder (Figure 1a). The holder itself is shown in Figure 1b, with electrical biasing (Figure 1c) for electro-thermal actuation of the test chip inside the TEM. A SEM image of the test chip is shown in Figure 1d, where details of the specimen, force and displacement sensors and actuators are provided. It also shows the electrical contact pads A-A' and B-B' for specimen heating and C-C' for mechanical actuation. Figure 1e shows a schematic diagram of the device design, where the specimen is integrated with a flexure beam force sensor and a set thermal actuator beams. The 20 micron deep and 10 microns wide thermal actuator beams expand due to Joule heating [13], which loads both the specimen and the force sensing beam. The force on the specimen can be obtained from the force equilibrium diagram shown in Figure 1f. If the stiffness values of the force sensor and the specimen are k_{fs} and k_{sp} respectively, then the elongation and force in the specimen are given by,

$$\delta_{specimen} = \delta_1 - \delta_2; F_{specimen} = k_{fs} \delta_2 = \left(\frac{24\kappa}{L_{fs}^3} \right) \delta_2 \quad (1)$$

where δ_1 and δ_2 , are displacements in the thermal actuator and force sensing beams respectively and κ is the in-plane flexural rigidity of the force sensing beam. These displacement values can be read directly from the TEM images. The actuators operate below 100 °C for which infrared microscopy (Figure 1g) suggests no temperature influence on the specimen.

Figure 1. Experimental setup, (a, b, c) front, side and rear ends of the in-situ electrical biasing TEM specimen holder respectively (d) zoomed view of the MEMS thin film tensile testing chip showing specimen, actuators and sensors (e, f) schematic representation and force equilibrium diagram of the test chip respectively [14] (g) infrared image of the test chip after actuation.

It is important to note that the specimens are co-fabricated with the MEMS devices, so that specimen alignment and gripping issues are automatically achieved during nanofabrication. In this study, we fabricated 100 nm thick, 99.97% pure zirconium films as 100 microns long and 5 microns wide specimens. Figure 2 shows the TEM bright field image and selected area diffraction pattern. The average grain size of the 100 nm thick films is <10 nm.

Figure 2. (a) Bright-field TEM image of the as-deposited specimen and (b) selected area electron diffraction pattern.

3. Experimental Results and Discussion

In-situ TEM tests were performed on a set of ten as-deposited zirconium specimens, which was followed by calibration of the force sensor beam to ensure experimental accuracy. Figure 3a shows a typical stress-strain diagram, where yield stress is around 500 MPa and fracture stress and strain are about 900 MPa and 1.5% respectively. In comparison, the yield stress and fracture strain of bulk poly-crystalline zirconium is about 250 MPa and 40% respectively. The inset in Figure 3a is a zoomed view of the linear elastic part of the overall stress-strain diagram. The Young's modulus value was measured to be about 87.6 GPa, which validates the satisfactory calibration of the procedure since the accepted value in the literature is about 90 GPa. The experimental results for the <10 nm grain size specimens show remarkable size effect when compared to the literature [3], especially in terms of plastic strain. For about 300 nm grain size [3], the observed plastic strain of 15% overshadows our observation of only 1.5% strain for >10 nm grain size. Such size effect

could also emanate from the specimen (bulk nanocrystal vs thin film nanocrystal), since thin films have orders of magnitude higher surface area compared to the bulk. As a result, thin film nanocrystals may show strain hardening (as suggested by our in-situ TEM experiments) but the dislocations may escape through the surface, leaving atomic scale defects in the surface to trigger fracture at very low strain. The very small value of the plastic strain in this study can also be explained by the appearance of relative large voids as shown in Figure 3b. It is well known that mechanical deformation is localized at the grain boundaries in nanocrystalline metals. In addition the strain incompatibility among neighboring grains of different crystallographic orientations may pronounce the grain boundary stress, creating voids at the grain boundaries.

Figure 3. (a) Representative stress-strain diagram for nanocrystalline zirconium specimens measured in situ inside a TEM (b) nanoscale voids appear at the grain boundaries at the onset of fracture.

To study the effects of external stimuli (thermal, electrical, mechanical) on grain growth kinetics, we passed electrical current through the specimen using contact pads A-B in Figure 1d. The dc current creates mechanical stress (compressive stresses near anode and tensile stresses near cathode) and temperature fields in the specimen, which trigger the grain boundary diffusion processes. This is similar to electro-migration, except we applied one order of magnitude lower current density to avoid any damage. The results are shown in Figure 4 for various current levels and polarity. The highest temperature in the specimen is about 350°C, which is only 20% of the melting temperature, which suggests that synergy of multiple stimuli has stronger effects than a single stimuli.

Figure 4. Grain growth as function of polarity and magnitude of dc electrical current passed through the freestanding specimen.

The literature suggests decrease of strength below a critical average grain size, known as the inverse Hall-Petch relationship. This size is around 15 nm for most FCC metals [15]. Since no study exists for nanocrystalline zirconium, we attempted to grow the grain size to about 25 nm by passing a current at density of $0.5 \times 10^6 \text{ A/cm}^2$ through the specimen for about 5 min. The microstructure and selected area diffraction pattern after grain growth are shown in Figure 5(a) and 5(b). Figure 5(c) shows a typical stress-strain diagram for average grain size of 25 nm. The yield stress is around 800 MPa, which is higher than the bulk (250 MPa) or 5-10 nm grain size (500 MPa). This suggests inverse Hall-Petch relationship, however extensive experimentation is needed to substantiate this phenomenon. Unfortunately, the proposed electro-migration stress technique is difficult for more than 500% growth and largest grain size studies was about 50 nm. Interestingly, the measured yield stress was in the same range as the 25 nm grain sized specimens considering experimental error of about 7%. Therefore the suggested observation of inverse Hall-Petch behavior needs to be confirmed after s that other factors, such as strain rate, temperature and grain size distribution may play role in the mechanical properties for this grain size range [15].

Figure 5. (a) Bright-field TEM image of specimen after 5 mins of current flow at $0.5 \times 10^6 \text{ A/cm}^2$ density (b) TEM selected area electron diffraction.

4. Conclusions

We present in-situ TEM mechanical test results for nanocrystalline zirconium thin films. The measured Young's modulus of as-deposited specimen with an average grain size 5-10nm is 85-90 GPa which falls very close to the bulk value. In-situ TEM tests showed yielding around 400-500 MPa and fracture strain around 1.5-2% strain. In comparison, ultra-fine grained zirconium in the literature shows yield strength of 500 MPa and 15% fracture strain. The measured yield stress of zirconium thin films with an average grain size 25 nm is about 60% higher than that of as deposited specimen with an average gain size of 5-10 nm, which suggests inverse Hall-Petch behavior in nanocrystalline zirconium.

Acknowledgement

We acknowledge the support of the US Department of Energy through a NEUP funding (DE-NE0000696).

References

1. Shi, Y., et al., *Tailoring grain size distribution for optimizing strength and ductility of multi-modal Zr*. Materials Letters, 2013. **108**(0): p. 228-230.
2. Kumar, S., M.T. Alam, and M.A. Haque, *Fatigue Insensitivity of Nanoscale Freestanding Aluminum Films*. Journal of Microelectromechanical Systems, 2011. **20**(1): p. 53-58.
3. Tabachnikova, E.D., et al., *Mechanical properties of ultrafine-grain zirconium in the temperature range 4.2-300 K*. Low Temperature Physics, 2008. **34**: p. 969-975.
4. Kad, B.K., et al., *Ultrafine-grain-sized zirconium by dynamic deformation*. Acta Materialia, 2006. **54**(16): p. 4111-4127.
5. Yuan, C., et al., *The tensile properties and fracture behavior of gradient nano-grained/coarse-grained zirconium*. Materials Letters, 2013. **107**(0): p. 134-137.
6. Guo, D., et al., *Simultaneously enhancing the ductility and strength of cryorolled Zr via tailoring dislocation configurations*. Materials Science and Engineering: A, 2012. **558**(0): p. 611-615.

7. Guo, D., et al., *High strength and ductility in multimodal-structured Zr*. Materials & Design, 2012. **34**(0): p. 275-278.
8. Zhang, J.Y., et al., *Deformation crossover in nanocrystalline Zr micropillars: The strongest external size*. Scripta Materialia, 2013. **68**(8): p. 639-642.
9. Liu, M.C., et al., *A nanoscaled underlayer confinement approach for achieving extraordinarily plastic amorphous thin film*. Scripta Materialia, 2009. **61**(8): p. 840-843.
10. Shu, B.P., et al., *Deformation twinning and detwinning in the lamella copper observed by in-situ TEM*. Materials Letters, 2013. **106**(0): p. 225-228.
11. Kumar, S., T. Alam, and A. Haque, *Quantitative in-situ TEM study of stress-assisted grain growth*. MRS Communications, 2013. **3**(02): p. 101-105.
12. Mohan Prasad, M., et al., *Room temperature amorphous to nanocrystalline transformation in ultra-thin films under tensile stress: an in situ TEM study*. Nanotechnology, 2010. **21**(50): p. 505707(1-6).
13. Yong, Z., C. Alberto, and D.E. Horacio, *A thermal actuator for nanoscale in situ microscopy testing: design and characterization*. Journal of Micromechanics and Microengineering, 2006. **16**(2): p. 242.
14. Manoharan, M.P., et al., *Elastic Properties of 4-6 nm-thick Glassy Carbon Thin Films*. Nanoscale Research Letters, 2010. **5**(1): p. 14-19.
15. Carlton, C.E. and P.J. Ferreira, *What is behind the inverse Hall–Petch effect in nanocrystalline materials?* Acta Materialia, 2007. **55**(11): p. 3749-3756.