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# An extraordinary enhancement of strain hardening in fine-grained zirconium

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ABSTRACT

Grain refinement always leads to a high strength but a low ductility that results from a reduced strain hardening. Here, we report an extraordinary enhancement of strain hardening in fine-grained (FG) Zr with an average grain size of 2–3 μm compared with its coarse-grained (CG) counterpart, which yields a uniform elongation of ~15.5% in the same order as that (~13.2%) of the CG Zr. The unusually enhanced strain hardening in the FG Zr is attributed to the formation of nano-scale defect structures within the fine grains. The present work provides a promising way to enhance the ductility of fine- and ultrafine-grained materials without losing their high strength, and thus is of wide interest.



## 1. Introduction

Grain refinement is a common strategy to strengthen materials, which leads to an enhanced strength at the expense of ductility due to a loss of strain hardening [1,2]. The low ductility of fine (FG), ultrafine (UFG) and nano-grained (NG) materials severely limits their applications as advanced engineering materials. To enhance the strain hardening of UFG and NG materials, an appropriate fraction of coarse grain or ductile phase with a size above 1 μm has been introduced into the fine matrixes, e.g. forming multi-modal structures [1,2] and nanostructure-dendrite composites [3]. This strategy has been further extended to the enhancement of ductility in amorphous materials [4]. In general, the enhancement of strain hardening via these approaches is accompanied by a decrease in strength because these coarse grains and ductile phases are very soft [1]. Therefore, despite a substantial progress has been made in the enhancement of ductility in UFG and NG materials through the multi-modal approach, a simultaneous increase of both the ductility and strength remains a challenging task. Recently, studies show that pre-existing dislocations in some UFG and NG materials are movable under high stress, contributing significantly to plastic deformation [5–7]. Therefore, if a lot of preexisting dislocations can be introduced and form special dislocation structures within the grains of FG, UFG or NG materials, an enhancement of ductility without the loss of strength may be expected since these defect structures can also make a significant contribution to the strength [8,9]. Previous studies show that a lot of non-equilibrium dislocations exist in the metals obtained by severe plastic deformation (SPD) after low-temperature recrystallization annealing [10–12]. This may provide a possibility to introduce special defect structures into the fine and ultrafine grains developed from SPD metals through an appropriate recrystallization annealing.

Cryogenic deformation is an effective route to suppress dynamic recovery and thus yields high-density defects in deformed materials, which provides a great room for tailoring defect structures in FG and UFG materials. In the present study, we report an unusually enhanced strain hardening, larger than that of the CG counterpart, in an *hcp* FG Zr via the formation of nano-scale defect structures within the grains, which yields a uniform elongation of $\varepsilon_u \sim 15.5\%$ in the same order as that (~13.2%) of the CG Zr.

## 2. Experimental details

Fully recrystallized pure Zr (99.95%) sheets were cryorolled at a strain rate of $\dot{\varepsilon}=2.24\ s^{-1}$ from 3.0 to 0.25 mm in thickness, i.e., an accumulated strain of $\varepsilon=2.87$, with a reduction of ~2% per pass. The temperature of the samples was lowered to $T=-160$–$90\ ^{\circ}C$ before and after each rolling pass via the liquid nitrogen cooling [9,12,13]. The FG Zr with an average grain size of $d=2$–$3\ \mu m$ was produced by annealing the cryorolled Zr at $T=500\ ^{\circ}C$ for 1 h in a

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vacuum furnace ($p < 10^{-4}$ Pa). For a comparative study, the CG Zr ($d \sim 30$ μm) was produced by annealing the as-received Zr at 830 °C for 10 h.

The microstructure of the samples in the rolling plane was characterized by transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and scanning electron microscopy (SEM) observations using a JEOL-2100F field emission microscopy and a Hitachi S-4800 field emission microscopy. TEM specimens were prepared via the twin-jet electrochemical polishing in a solution (10 vol% perchloric acid + 90 vol% acetic acid) at a voltage of $V = 25$ V and a temperature of $T = 18$ °C. To obtain a statistical size distribution of nano-scale defect structures, the sample regions of $\sim 100$ μm$^2$ were been analyzed by TEM technique, and then the size distribution was statistically determined from the TEM images using a Digitalmicrograph analysis software. To obtain a statistical grain size distribution, SEM images with a sample region larger than 1 mm$^2$ were analyzed. X-ray diffraction (XRD) patterns were recorded from the rolled surface using a Rigaku D/max-2500/PC X-ray diffractometer with Cu Kα radiation operating at 40 kV.

Uniaxial tensile tests of the samples with a gauge length of 10.0 mm and a cross-section of $2.50 \times 0.25$ mm$^2$ (see the inset in Fig. 1) were performed on an Instron-5948 Micro-Tester (2 kN) at a strain rate of $\dot{\varepsilon} = 1 \times 10^{-3}$ s$^{-1}$ at room temperature. The tensile direction was parallel to the rolling direction of the samples. Five samples for each condition were measured, yielding error bars for mechanical properties in Figs. 2 and 7.

## 3. Results and discussions

### 3.1. An extraordinary enhancement of strain hardening

High-density dislocations have been introduced into the cryorolled Zr, which has been reported in our earlier works [9,12]. The FG Zr with an average grain size of 2–3 μm was produced through a complete recrystallization annealing of the cryorolled Zr at $T = 500$ °C (1 h). The engineering and true stress–strain curves of the FG and CG Zr samples are presented in Fig. 1a and b, respectively, and the multiple tensile tests give a similar strength and elongation for each sample. The CG Zr shows a uniform elongation of $\varepsilon_u \sim 13.2\%$, a yield strength of $\sigma_s \sim 317$ MPa and an ultimate tensile strength of $\sigma_b \sim 370$ MPa (Fig. 1a). It is a striking result that the FG Zr presents an elongation ($\varepsilon_u \sim 15.5\%$) in the same order as the one for CG Zr while keeping a higher strength ($\sigma_s \sim 415$ MPa and $\sigma_b \sim 510$ MPa). This result is in contrast with the belief that grain refinement always leads to an increase in strength but a decrease in ductility.

A comparison of tensile properties between the FG Zr and the *hcp* pure Zr from previous studies [12,14–17] is shown in Fig. 2. An inverted relationship between the strength and ductility is clearly observed (see the shade area in Fig. 2). The most striking result is that the FG Zr achieved in the present study is far away from the shaded, showing a simultaneous enhancement of both the $\varepsilon_u$ and $\sigma_b$ as compared with those of CG Zr. As a consequence, the mechanical behavior of FG Zr is improved compared to the multi-modal structured Zr (indicated with MG in Fig. 2) yielded in our earlier works [12].

For a better understanding of the large ductility achieved in the FG Zr, the strain hardening capability of the sample was investigated. The ratio of yield strength ($\sigma_s$)/ultimate tensile strength ($\sigma_b$) is an indicator of strain hardening capability, where a small value of $\sigma_s/\sigma_b$ indicates a high capacity of strain hardening [18]. The FG Zr has a value of $\sigma_s/\sigma_b \sim 0.81$, smaller than that ($\sim 0.86$) of the CG Zr, indicating a high strain hardening capability. The strain hardening exponent $n$ defined by the Hollomon equation,

$$\sigma_t = K\varepsilon_t^n \quad (1)$$

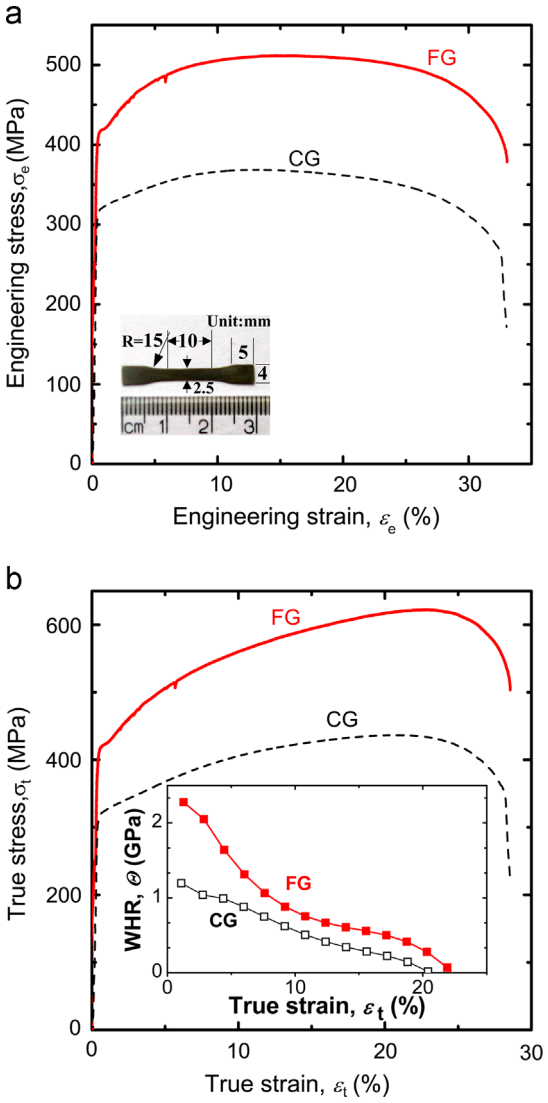


**Fig. 1.** Engineering stress–strain tensile curves (a) of the coarse-grained (CG) Zr and the fine-grained (FG) Zr that were produced by annealing the cryorolled Zr at $T = 500$ °C for 1 h, and corresponding true stress–strain tensile curves (b). The insets in (a) and (b) show the tensile specimen geometry and the work hardening rate (WHR)–true strain curves, respectively.

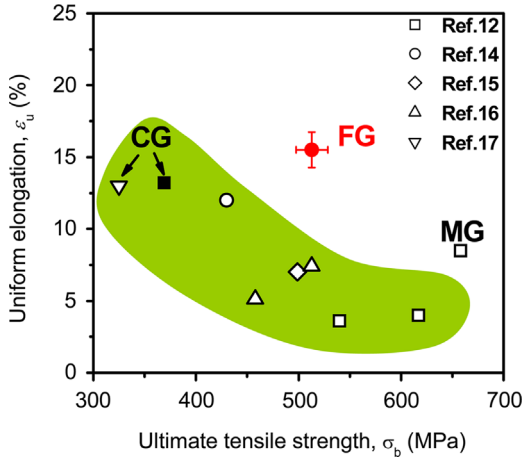


**Fig. 2.** Representative tensile properties of pure Zr. The solid symbols (■, ●) represent the mechanical properties of the CG and FG Zr from the present study and the hollow symbols are reported data [12,14–17].