International Journal of Plasticity xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

International Journal of Plasticity

journal homepage: www.elsevier.com/locate/ijplas

Microstructural effect on time-dependent plasticity of nanoporous gold

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ARTICLE INFO

Keywords:
Creep
Dislocation
Grain boundaries
Porous material
Microstructures

ABSTRACT

Annealed, prestrained, and ball-milled nanoporous gold (np-Au) samples were prepared. Since the microstructures of the precursor alloys, such as the crystallographic orientation and grain size, were mostly preserved during the dealloying process, prestrained np-Au is believed to have higher initial dislocation density, and ball-milled np-Au is believed to have higher densities of initial dislocation and grain boundary comparing to annealed np-Au. The time-dependent deformation behavior of np-Au samples with various microstructures was characterized with two parameters; creep strain exponent n and activation volume V^* using spherical nanoindentation creep tests. We found that primary mechanism of time-dependent plasticity for annealed and prestrained np-Au samples is dislocation slip and that for ball-milled np-Au sample is grain boundary sliding. In dislocation slip-dominant time-dependent deformation in np-Au, a higher initial dislocation density lowers n and V^*. In grain boundary sliding-dominant time-dependent deformation in np-Au, the values of n and V^* are similar to those for dislocation slip-dominant time-dependent deformation; however, the creep strain rate in quasi-steady-state is higher than that for dislocation slip-dominant time-dependent deformation.

1. Introduction

Nanoporous gold (np-Au) has attracted increasing attention due to its high specific surface area and electric conductivity, and its potential for use as a catalyst (Biener et al., 2011; Fujita et al., 2012), sensor (Chen-Wiegart et al., 2012; Zhang et al., 2013), or actuator (Biener et al., 2009; Detsi et al., 2011). The mechanical properties of np-Au have been intensively studied (Biener et al., 2006; Gwak and Kim, 2016; Jeon et al., 2017; Kang et al., 2017; Kim et al., 2017, 2018; Lee et al., 2007; Li and Sieradzki, 1992) because it exhibits brittle behavior even though the constituent material Au is ductile, which makes it difficult to use for many applications. Li and Sieradzki (1992) reported that mechanical failures in np-Au undergo a microstructurally-controlled ductile-brittle transition depending on the ligament size in three-point bending. Biener et al. (2006) found that the nanoindentation hardness and compressive strength depend on the ligament size of np-Au, and the hardness increases as the ligament size decreases. Lee et al. (2007) synthesized free-standing dog-bone-shaped np-Au sample and measured tensile properties by deflective tensile testing using nanoindentation. Gwak and Kim (2016) fabricated nanocrystalline np-Au using high-energy ball-milling and found that a high density of grain boundaries weakens the flexural strength while the nanoindentation hardness is independent of the internal microstructure in the ligaments. Meanwhile, few studies on time-dependent mechanical behavior of np-Au have been carried out even though time-dependent mechanical behavior is critical in understanding long-term durability. Besides, individual ligaments experience typical ductile deformation and failure even though macroscopic fracture of np-Au is brittle in general especially in tension.

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https://doi.org/10.1016/j.ijplas.2018.05.011
Received 22 February 2018; Received in revised form 16 May 2018; Accepted 23 May 2018

The ductile deformation of individual ligaments also suggests possibility for creep deformation at macroscopic stress lower than yield strength of np-Au. Np-Au possesses conditions that time-dependent deformation occur actively in terms of primary mechanisms in solid metals such as atomic surface diffusion and grain-boundary sliding. Np-Au has very high surface-to-volume ratio and rare native oxide, which could yield pronounced atomic surface diffusion. Grain-boundary sliding in np-Au can easily occur without distortions of neighboring grains as in the nanocrystalline materials. Because ligaments of np-Au are surrounded by free volume, grain boundary sliding can occur easily comparing with solid nanocrystalline metals where severe rotations and distortions of neighboring grains should be accompanied for grain boundary sliding.

We applied spherical nanoindentation testing to investigate the effects of the microstructure of np-Au, such as the initial dislocation density and grain size, on the time-dependent deformation behavior stress. Owing to the characteristic brittleness of np-Au, a spherical nanoindentation test was conducted to measure the time-dependent deformation behavior. The use of nanoindentations when evaluating the time-dependent deformation behavior is advantageous because the testing procedure and method of sample preparation are straightforward, only small volume of sample is required, and nanoindentation can provide sub-nanometer scale spatial resolution suitable for measuring very small plasticity. By applying Garofalo's equation (Dieter, 1986), creep stress exponents of np-Au samples with different initial dislocation density and different grain size were evaluated. Effects of these microstructural defects on time-dependent deformation of np-Au are discussed and primary mechanisms for time-dependent deformation are suggested.

2. Experiments

2.1. Fabrication of np-Au

We fabricated three np-Au samples with different microstructures based on our previous work (Gwak and Kim, 2016). Au-Ag precursor alloys ($Au_{30}Ag_{70}$ in at.%) were prepared by melting Au (99.99%) and Ag (99.99%) pellets at 1100 °C followed by homogenization at 800 °C for 72 h in a N_2 environment. After homogenization, three different precursor alloys were fabricated, which are referred to as “annealed,” “prestrained,” and “ball-milled” samples. The annealed and prestrained precursor alloys were cut into an approximately 1-mm-thick disc-shape, gently polished using 0.25 μm diamond suspension, and annealed at 800 °C for 24 h to relieve any stress induced during the mechanical cutting and polishing process. This well-annealed sample is referred to as the “annealed” precursor alloy. The “prestrained” precursor alloys were prepared by compressing “annealed” precursor alloys to an engineering strain of 10% using a universal testing machine (Instron 5982) to increase the initial dislocation density. The “ball-milled” precursor alloys were made using a high-energy ball milling machine (SPEX Mixer Mill 8000D). After homogenization, the precursor alloy for the ball-milled sample was sealed in a hardened steel vial together with hardened steel balls, and shaken at 1060 back-and-forth cycles/min for 90 min. The ball-milled precursor alloys were then cut into an approximately 1-mm-thick disc-shape and polished using a 0.25 μm diamond suspension. The np-Au samples were fabricated using a free corrosion dealloying process that selectively etched Ag atoms from Au-Ag precursor alloys. The three different precursor alloys were dipped in a 35% nitric acid solution at 80 °C for 72 h. The np-Au samples fabricated from the “annealed,” “prestrained,” and “ball-milled” precursor alloys are referred to as “annealed,” “prestrained,” and “ball-milled” np-Au, respectively. To investigate the density effects of the grain boundary and initial dislocation, two np-Au samples were prepared by additional heat treatments at 300 °C for 4 h using the ball-milled and annealed np-Au. The microstructures of the np-Au samples were examined using a field-emission scanning electron microscope (FE-SEM, FEI NovaNano 230), and electron backscatter diffraction (EBSD, TSL-OIM) to determine the grain size.

2.2. Spherical indentation creep testing

Nanoindentations were applied to the np-Au samples using a nanoindenter (Keysight G200) and diamond spherical indenter in the XP module. The nominal tip radius of the spherical indenter was 50 μm. The spherical nanoindentation process applied different maximum forces P_{max} at a constant loading rate (dP/dt) of 0.2 mN/s, the force was maintained at P_{max} for 300 s before being fully unloaded. We set low allowable thermal drift limit as 0.05 nm/s to minimize thermal drift issue. We also use low constant loading rate of 0.2 mN/s because if this rate is not low enough, time-dependent displacement measured at early stage of the holding at P_{max} could be affected by acceleration or deceleration of the indenter head mass. At least five reproducible indentation force-displacement curves were obtained for each sample and testing condition.

3. Results and discussion

3.1. Microstructure of Au-Ag precursor alloys and np-Au samples

Fig. 1(a)–(c) show the typical EBSD inverse pole figure (IPF) maps of the annealed, prestrained, and ball-milled Au-Ag precursor alloys. The average grain sizes were determined by the intercept method with more than 10 EBSD IPF images. The grain sizes were found to be 320 (± 42) μm for the annealed precursor alloy, 305 (± 29) μm for the prestrained precursor alloy, and 220 (± 23) nm for the ball-milled precursor alloy. Fig. 1(d) – (f) show SEM images of the annealed, prestrained, and ball-milled np-Au. The ligament sizes were measured based on the diameter of the connecting ligament necks, which were possibly the thinnest parts, for more than 100 measurements in the SEM images. The ligament sizes of the np-Au were 72.5 (± 12) nm for the annealed, 75.7 (± 11) nm for the prestrained, and 71.5 (± 14) nm for the ball-milled samples. Regardless of the prestraining and ball-milling processes used in the