Available online at www.sciencedirect.com
ScienceDirect
Acta Materialia 57 (2009) 2665–2672
Acta MATERIALIA
www.elsevier.com/locate/actamat

Deforming nanoporous metal: Role of lattice coherency

Hai-Jun Jin [a,*], Lilia Kurmanaeva [a], Jörg Schmauch [b], Harald Rösner [c], Yulia Ivanisenko [a], Jörg Weissmüller [a,b]

[a] Forschungszentrum Karlsruhe, Institut für Nanotechnologie, 76021 Karlsruhe, Germany
[b] Universität des Saarlandes, Technische Physik, Saarbrücken, Germany
[c] Westfälische Wilhelms-Universität Münster, Institut für Materialphysik, Münster, Germany

Received 24 November 2008; received in revised form 10 February 2009; accepted 10 February 2009
Available online 25 March 2009

Abstract

Nanoporous metals prepared by alloy corrosion may assume the form of monolithic, millimeter-sized bodies containing around 10^{15} nanoscale ligaments per cubic millimeter. Here, we report on the fabrication and mechanical behavior of macroscopic, crack-free nanoporous gold samples which exhibit excellent ductility in compression tests. Their yield stress is significantly lower than that expected based on scaling laws or on previous nanoindentation experiments. Electron backscatter diffraction imaging reveals a polycrystalline microstructure with grains larger than 10 μm which acquire a subdomain structure during plastic flow, but remain otherwise intact. We highlight the action of lattice dislocations which can travel over distances much larger than the ligament size. This results in a collective deformation of the many ligaments in each grain. Remarkably, the dislocation cores are partly located in the pore channels. The results suggest a critical view of the conversion between indentation hardness and yield stress in previous work.

Keywords: Nanoporous; Dealloying; Plastic deformation; Compression test; Hardness test

1. Introduction

The strength of crystals is known to increase when the crystal dimensions are reduced [1–5]. For instance, gold—normally a soft metal that supports stresses of the order of 30 MPa—yields to stresses in the GPa range when in the form of nanowires [6]. This finding raises the expectation that one may profit from the favorable mechanical behavior of nano-objects by assembling them into strong macroscopic materials. In this connection, the following questions arise: what microscopic processes act when many nano-objects deform in parallel and what is the macroscopic deformation behavior of the assembly? Nanoporous gold (npg), an interconnected network of about 10^{15} nanoscale ligaments per cubic millimeter, provides an ideal object of study in this context. Yet, conventional wisdom says that npg samples are brittle when of macroscopic size [7,8]. Here, we report on a study of the deformation behavior of millimeter-sized npg samples prepared free of macroscopic crack nuclei. These samples exhibit excellent ductility during compression and, in striking contrast to previous studies, their strength is considerably less than what would be expected based on the accepted scaling laws for the dependency of strength on the ligament size and porosity [9–11]. We argue that the mechanical properties are related to the coordinated deformation of neighboring ligaments over a combination of nano- and macroscopic size scales.

Nanoporous (np) metals prepared by dealloying [12] typically are very fragile in macroscopic form, but strong and plastic under local deformation, as in nanoindentation or micropillar compression. Preformed cracks, a consequence of the volume contraction during dealloying [13], have so far prevented the study of the intrinsic plastic deformation behavior of macroscopic np metal samples. Incorporating a second phase was found to efficiently

* Corresponding author. Tel.: +49 7247 82 6382; fax: +49 7247 82 6368.
E-mail address: haijun.jin@int.fzk.de (H.-J. Jin).

1359-6454/$36.00 © 2009 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.actamat.2009.02.017

reduce the cracking and enhance the strength of bulk np Pt [14], but the complex microstructure of these samples impedes fundamental studies of the intrinsic plastic behavior of np metals. Such experiments require single-phase and crack-free bulk np samples rather than composites. The present approach in this direction was inspired by recent work of Senior and Newman [15], who used slow dealloying at elevated temperatures to obtain npg sheets that exhibited appreciable elastic bending stretch, albeit only in a "wet" state with the pores filled with electrolyte. In the following sections, the preparation and the mechanical response of crack-free bulk npg with appreciable compressive ductility even in the dry state will be highlighted. The findings are of significance for the plasticity of nanostructured materials in general and for applications of np metals in which the mechanical stability is a prerequisite [16–21].

2. Materials and methods

2.1. Sample preparation

The master alloy with a nominal composition of $Au_{25}Ag_{75}$ was prepared by arc melting the constituents (Au 99.995%, Ag 99.999%). The ingots were sealed in quartz and homogenized (>70 h, 1223 K), cut into $\sim 1 \times 1 \times 2\ mm^3$ cuboids, polished to 1 μm diamond finish, and annealed (1 h at 800 °C) for recovery.

The samples referred to as "type I" were prepared by 17 h of dealloying in 1 M $HClO_4$ at 330 K and at a potential of 650 mV vs. Ag/AgCl. The potential was controlled by a potentiostat (VoltaLab) and silver wire was used as counter electrode (CE). Samples with a ligament diameter, L, of 55 nm were dealloyed in situ in a dilatometer (Linseis) to monitor the dimension change. A miniaturized electrochemical cell of volume around 10 ml was used. Npg samples with $L = 15$ nm were prepared in a larger cell with around 60 ml electrolyte volume under otherwise identical conditions. Since the dealloying potential was very close to the critical dealloying potential of $Au_{25}Ag_{75}$, the dealloying rate which determines the resultant structure size was sensitive to the experimental conditions. A slight variation of the above-mentioned parameters led to a completion of dealloying (when current fell to below 10 μA) after 300–450 min (for $L = 55$ nm) or 200 min ($L = 15$ nm). Further increase in the dealloying rate typically leads to cracking. Some samples were annealed in Ar flow for coarsening.

The npg samples referred to as "type II" were prepared under more conventional dealloying conditions [8,10,13]. We used the same solution as above, but a lower temperature (300 K) and a more positive potential, typically 850 mV. All samples were rinsed repeatedly before testing to remove residual electrolyte.

2.2. Structural characterization

A field-emission scanning electron microscope (FESEM; LEO 1530) operated at 20 kV and equipped with an energy-dispersive X-ray fluorescence (EDX) attachment (Oxford INCA EDS system) was used for pore structure characterization and chemical analysis. Electron backscatter diffraction (EBSD) data was collected in a separate FESEM (JEOL JSM-7000F) using a DIGI-VIEW 1612 camera and the OIM data collection software (version 5.2) at an acceleration voltage of 20 kV. Orientation maps were recorded over a 10 μm × 10 μm area with 100 nm step size or over 2 μm × 2 μm with a 20 nm step size. This study focused on the lateral surface parallel to the compression direction. Samples were deformed ex situ and then remounted for the measurements at different strains. A given area on the surface was readily relocated due to carbon contamination from the previous SEM imaging.

2.3. Mechanical tests

Compression tests were carried out on a testing machine [22] for miniature samples under controlled cross-head speed. The displacement of the cross-head was recorded, and empty runs produced a baseline for correcting the machine compliance. Vickers hardness was measured on a microhardness testing machine (Buehler Micromet 5104) with a load of 10 g and indentation time of 15 s.

3. Results

3.1. Samples and initial microstructure

As described above, the plastic deformation behavior of two types of samples was investigated. Our focus was on the type I material, for which we found that shrinkage during dealloying was less than 2 vol.%. This is a prerequisite for avoiding crack formation during synthesis. Type II samples were studied for comparison. Here, the faster dissolution at lower temperature and elevated potential yields smaller ligaments, but also a pronounced volume contraction (up to 30%) [13] upon dealloying. Consequently, type II samples exhibit many cracks in their as-dealloyed state.

All samples were found to be brittle in bending. This enables SEM studies of their in-bulk microstructure on fracture surfaces. In this way we confirmed that type I samples with ligament diameters of $L = 55$ and 15 nm are entirely free of cracks. Fig. 1a displays a representative SEM image of an $L = 55$ nm npg sample. It reveals a uniform structure throughout the bulk. EDX finds a residual Ag content below the detection limit of around 2 at.%. The $L = 15$ nm samples which were prepared by a faster dealloying show a nonuniform structure (ligament diameter decreases gradually from 20 nm on the surface to 10 nm in the center) and higher residual Ag content of 6–8 at.%. Based on the amount of Ag removed and on the volume change during dealloying, the solid volume fraction, v_S, was estimated to be 0.260 and 0.275 for $L = 55$ and 15 nm samples, respectively.

EBSD results (Fig. 1b) reveal a grain size ranging from 10 to 100 μm for an $L = 55$ nm ligament type I sample. We will