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Interface dominated mechanical properties of ultra-fine grained and nanoporous Au at elevated temperatures

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ABSTRACT

Modern design and engineering of highly efficient devices and machines demand innovative materials to satisfy requirements such as high strength at low density. The purpose of this study was to oppose the mechanical properties and deformation behavior of ultra-fine grained Au to those of nanoporous Au, to study the influence of different types of interfaces. Microstructural investigations of the foam surrendered a ligament size of ~100 nm which themselves consist of 70 nm grains in average, while the ultra-fine grained gold features a mean grain size of 325 nm. Nanoindentation lends itself as a convenient technique to obtain material properties at ambient as well as high temperature conditions. In this work, a substantial indentation test series was performed in order to determine hardness, Young's modulus, strain-rate sensitivity and activation volume at room and elevated temperatures up to 300 °C. On account of the small characteristic dimensions, high hardness values were noted for both materials, which rapidly drop at elevated temperature. Additionally, an enhanced strain-rate sensitivity accompanied by low activation volumes was determined at room temperature, which further increased at elevated temperatures. This behavior is associated with thermally activated interactions between dislocations and interfaces. For nanoporous Au, due to the presence of free surfaces, a considerable increase of hardness was observed upon annealing. This can be attributed to a reduced number of mobile dislocations in the material after annealing, as supported by implemented porosity maps on indent cross-sections, showing distinct differences for tests at varying temperature.

1. Introduction

Metals with characteristic structure dimensions approaching the sub-micron scale are known to differ in their mechanical properties compared to their coarse grained counterparts, especially due to the restrained state of dislocations. This issue, first described by Hall and Petch [1,2], in addition with recently observed hardening effects caused by annealing [3,4], put material classes such as ultra-fine grained (UFG) and nanocrystalline (NC) materials in the spotlight of various fields of applications. Grain boundary strengthening provides the opportunity to increase the strength without undesired effects on the endurable strain of the metal, and thus is widely used for high-performance components. Light-weight constructions on the other hand, are considered to be the key to high efficiency and energy-saving technologies, which are indispensable in the 21st century. Hence, it seems natural to investigate not only UFG bulk materials, but in particular nanoporous (NP) structures which combine the assets of small structure dimensions and light-weight materials. It is not surprising that studies on NP Au revealed exceptional high ligament strengths at room temperature [5–10], since it is well known that strength increases with decreasing structure size, often demonstrated for nano-pillars or nanowires [11–15]. Recently, there was also evidence that NP materials possess a high radiation resistance resulting from self-healing mechanisms

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[16], making them suitable for nuclear applications. The governing deformation mechanisms in such NP structures, in particular at elevated temperatures, are thus of great interest in order to understand their mechanical behavior.

Face-centered cubic (fcc) UFG metals are reported to exhibit multiple deformation mechanisms, such as dislocation emission from grain boundaries [17].Likewise grain boundary diffusion or micro shear banding can play a crucial role [18,19], and grain boundary sliding is known to occur at high temperature (HT) [18,20,21]. The dominating mechanism can be indicated by a noticeable strain-rate sensitivity corresponding to low activation volumes [22–29]. Certainly, this raises the question whether the type of interface exerts a significant influence on the mechanical behavior, since the models of the mentioned deformation mechanisms are based on bulk materials with a high number of grain boundaries. Therefore, the present study will investigate the different behavior of the NP and UFG state of Au to contrast grain boundaries with free surfaces, at RT as well as elevated temperatures up to 300 °C. Nanoindentation proves to be an optimal technique to extract mechanical properties [30], but also rate-dependent parameters, such as the strain-rate sensitivity m and the activation volume V^*[22,31–34], accompanied by minimal material consumption for testing.

Through a unique fabrication route by powder compaction and severe plastic deformation using High Pressure Torsion (HPT) temperature-stable UFG Au bulk samples as well as a NP Au foam with well-defined microstructure will be produced. Additionally, the deformation morphology will be unfolded by Focused Ion Beam (FIB) cross sections of indents, for the first time allowing verification of the dominating deformation mechanisms by the appearance of the plastic deformation underneath an indent. This will enable us to demonstrate that the interface type as well as the temperature have a major impact on the mechanical behavior and rate-dependent properties of nanostructured gold.

2. Experimental details

2.1. Sample fabrication and microstructure analysis

For this study, spherical Au powder (Alpha Aesar GmbH & Co KG) with a purity of 99.96% and an average particle size of 5.5–9.0 μm was used as a base material. The powder was poured into a copper ring, which in turn was glued on an HPT anvil before. Subsequently the powder was consolidated and deformed via HPT [35,36] to produce UFG Au disks with a diameter of 8 mm and a height of 0.8–1 mm. Likewise, a Au/Fe powder mixture (50/50 vol %) was densified to create a nanostructured composite [37–39], where the spherical Fe powder (obtained from Merck KGaA) features a purity of 99.9% with particle sizes < 10 μm. Since the formation of supersaturated phases after extensive severe plastic deformation has been observed [38], all samples were annealed at 300 °C for 1 h in a vacuum furnace (SERIES XRETORT, Xerion Advanced Heating Ofentechnik GmbH, Germany) to allow a reduction of the forced mixing. The pure UFG Au samples were annealed the same way in order to maintain comparable material conditions for both material types.

Subsequently, the HPT disks were ground from one side to 0.4–0.5 mm thickness to eliminate surface artefacts and reach the most homogenous zone of the sample. Next, Au/Fe specimens underwent a selective etching process to remove the Fe and obtain a novel nanoporous Au structure, similar to a procedure recently described to produce NP Cu [37]. For this purpose, a 5 wt% hydrochloric acid served as an etchant, in which the Fe in the composite was entirely dissolved after 24 h at 55 °C, leaving behind a Au foam with ~50% porosity. Finally, UFG and NP samples were annealed at 100 °C, 200 °C and 300 °C to study the microstructure stability.

The resultant microstructures were characterized using a scanning electron microscope (SEM; LEO type 1525, Carl Zeiss GmbH, Germany) combined with Electron Backscatter Diffraction (EBSD, EDAX Inc. Mahwah, USA). For the latter a 15° misorientation angle was set as threshold to differentiate low-angle from high-angle grain boundaries. An ultra-fine grained structure was revealed for compact Au samples with an average grain size of about 325 nm at room temperature (RT) (Fig. 1a). As evident from Fig. 1a–d and Fig. 2a, minor grain coarsening can be observed after high temperature (HT) annealing up to 300 °C. Energy dispersive X-ray (EDX) spectra show that the UFG Au disks contain small amounts of Cu (<1 at.%), which most likely originates from the copper ring used in the production process via powder consolidation.

SEM micrographs illustrate the NP topology of the Au foam after tests at the inscribed temperatures (Fig. 1e–h). The foam features a porosity of approximately 50% and ligaments with an average diameter of about 100 nm at RT. Using EBSD, it is shown that the ligaments themselves consist on average of approximately 70 nm diameter small grains with a narrow size distribution, see Fig. 1i. Information from the black area was not considered, since the image quality of the Kikuchi patterns in this zone falls below a critical value of 35%, and therefore an accurate determination of the grain structure could not be guaranteed. While a slight coarsening of grains takes place upon annealing, the ligament diameter remains rather unaltered (Fig. 1e–l), evaluated quantitatively in Fig. 2. The grain size of the foam may exceed the ligament's diameter, as intersections where ligaments converge are not considered in the analysis of the diameter. Several EDX scans performed at different areas show that despite the preceded annealing up to 5.5 at.% Fe is still remaining within the Au matrix.

2.2. Nanoindentation

2.2.1. Experimental setup

Depth sensing nanoindentation enables the determination of fundamental mechanical properties and parameters for the indication of the predominating deformation mechanism expending minimal material volumes. The experiments were performed using a Micro Materials NanoTest Platform 3 (Micro Materials, UK) nanoindentation device including a hot stage option. Common Berkovich tips were used, made from diamond for room temperature (RT) and from cubic boron nitride (cBN) for elevated temperature testing. Both tip materials are well-suited for HT testing since no tip/sample interaction is expected [40]. Calibrations of the indenter tips were conducted on fused silica according to the method proposed by Oliver and Pharr [30] to maintain an accurate area function and machine compliance. For high temperature measurements the sample was fixed with a ceramic adhesive (Omegabond 600, Omega Engineering Inc., Stamford, USA), likewise a reference sample was mounted. The indenter cabinet was purged with a reductive protective gas (hydrogen/argon mixture) in order to avoid any oxidational effects on the material. In addition to the thermocouples preinstalled on the nanoindenter device, an additional one was externally mounted on the surface of the reference sample to double-check the temperature conditions as close to the sample as possible.

A Nanoindenter G200 (Keysight Technologies, USA) featuring a continuous stiffness measurement (CSM) option was used to double-check the obtained RT indentation values by conducting CSM constant strain-rate (0.05 s^{-1}) measurements and nanoindentation strain-rate jump tests [32].

2.2.2. Testing procedure

Displacement controlled (DC) runs with proportional load ramps (equivalent to a constant strain-rate) with 5 s dwell time at maximum load were performed to obtain the hardness (H) and