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An overview on the characterization and mechanical behavior of nanoporous Gold

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In this paper we present what we believe are the most pressing issues in understanding the mechanical behavior of nanoporous foams. We have postulated that a gold foam presents the best candidate for a systematic study of nanoporous foams since it can be synthesized with a wide range of ligaments sizes and densities. We have also conducted preliminary tests that demonstrate a) Au foams have a fracture behavior dictated by the ligament size, and b) nanoporous Au is a high yield strength material. Thus, we have demonstrated the potential in developing nanoporous foams as a new class of high yield strength / low density materials.

Keywords: *metallic foam, nanoporous metals, dealloying*

1. Introduction

Metallic foams with pore sizes from 250μm to 2mm have been a subject of research for over two decades due to their high surface area, which allows for a variety of applications, such as thermal and sound insulation [1-3]. Recently, processing of metallic foams at the nanoscale (pores sizes less than 100 nm) has opened the door to new and interesting applications, such as sensors and actuators [4,5]. In general, processing of nanoporous metal foams has been focused on selective dealloying techniques which produce materials with an open sponge-like structure of interconnecting ligaments and a typical pore size distribution on the nanometer length scale.

Selective dealloying is defined as the selective dissolution of one or more components from a metallic alloy [6,7]. Typically, the less noble components are removed, and the more noble components remain behind. In such cases, there must be a significant difference in the reversible metal/metal ion potential of the metals in the alloy. Dealloying occurs when an alloy A_pB_{1-p} is immersed in an electrolyte and held at a potential such that A oxidizes and dissolves into solution, and B remains in its stable metallic form.

The morphology of dealloyed structures is of key importance in many engineering applications. While any alloy which meets the electrochemical criteria may be dealloyed, ideal bicontinuous porous structures are obtained from binary alloys with complete single phase solid solubility across all compositions. An ideal structure can be described as a uniform interpenetrating solid-void composite, with a narrow void/ligament size distribution [7]. The most well known system which meets these criteria is Ag/Au. Au is relatively inert in electrolytes which can dissolve Ag, therefore the dissolution current is solely due to Ag dissolution. Additionally, Au does not oxidize at room temperature and it does not readily form complexes which would prevent surface diffusion and inhibit the formation of a porous structure. Finally, Au does not oxidize in air, allowing the pore size distribution to be varied by a simple furnace anneal.

Currently, research of nanoporous metals has been focused on synthesis. However, in order to further study possible nanoporous foam applications, their mechanical behavior needs to be addressed. Few studies have been focused on macro-foam behavior, such as Li et al.[7] who reported a ductile-brittle transition in porous Au, which seemed to be controlled by the microstructural length scale of the material. Biener et al. reported on the fracture behavior of nanoporous Au as a function of the length scale [8]. Recently, we studied the mechanical properties of nanoporous-Au under compressive stress by depth-sensing nanoindentation, and determined a yield strength of 145 (±11) MPa and a Young's modulus of 11.1 (± 0.9) GPa [9]. A striking result of this study is that the experimentally determined value of the yield strength is almost one order of magnitude higher than the value predicted by scaling equations developed for open-cell foams,[2] thus potentially opening the door to the development of a new class of high yield strength / low density materials. This example illustrates that the mechanical properties of nanoporous metals are not well understood yet.

In this paper we will present an overview of issues which can affect the mechanical behavior of nanoporous metallic foams. Conditions such as ligament size vs processing, grain size, fracture mechanism, testing parameters and yield strength of nanoporous gold will be addressed.

2. Experimental Procedure

The nanoporous Au samples used in the present study were made by electrochemically-driven dealloying and by free corrosion. Polycrystalline $Ag_{75}Au_{25}$ and $Ag_{70}Au_{30}$ alloy ingots were prepared by an Au (99.999%) and Ag (99.999%) melt at 1100°C and homogenized for 70 hours at 875 ºC under argon. Approximately 5.0 mm diameter, 500μm thick disks were cut from the alloy ingot, polished on one side and then

heat-treated for 8 hours at 800 ºC to relieve stress. The alloy composition was confirmed by a fire assay technique.

Nanoporous Au samples prepared by selective electrolytic dissolution in 1 mole HNO_3 and 0.01 mole of $AgNO_3$ solution. A three-electrode electrochemical cell controlled by a potentiostat (Gamry PCI4/300) was used for these experiments. Dealloying was performed at room temperature, using a platinum wire as a counter electrode and a silver pseudo reference. The alloy samples were held at an applied electrochemical potential of ~ 600mV for a period of 2-3 days until the dissolution current measurement was negligible. The nanoporous samples prepared by free corrosion were submerged in a 67-70% HNO_3 solution for 2-3 days until no further weight loss was detected. Energy dispersive X-ray (EDX) spectra collected from the nanoporous Au samples prepared by both methods confirm that Ag was completely removed during dealloying.

The dealloyed 30% Au foam was divided into several smaller samples; one sample was tested as dealloyed while samples D and E were furnace annealed in air for 2 hours at 400 and 600°C respectively.

Scanning electron microscopy (SEM) was employed for microstructural characterization. The mechanical properties of nanoporous Au were tested by depth-sensing nanoindentation using a Triboindenter (Hysitron). A Berkovich tip (radius of ~ 200 nm) was used for the experiments. Indentations were performed on the planar, "polished" surface (polished before dealloying) of the sample disks as well as on cross-sections produced by fracturing the sample. All nanoindentation experiments were performed using a constant loading rate of 500 μN/s with loads ranging from 200 to 2500 μN. Each sample was tested at four different spots for a total of 100 indents per sample.

3. Results and Discussion

Due to the nanoscale nature of the foams, many questions arise regarding how foam mechanical behavior is affected at the nanoscale. Issues such as the effects of the ligament size at the nanoscale, changes in deformation mechanisms, and the role of relative density need to be addressed.

It is known that in bulk materials at the nanoscale many new factors affect the mechanical properties, such as length scale [10], Hall-Petch relationship [11], and grain growth [12]. Therefore, it is expected that nanoporous materials would behave differently from macro-cellular foams, thus presenting a new field of study. In this section, we will address some pressing issues in understanding nanoporous foam behavior as well as current research status and suggestions of additional research needed in order to begin to understand the mechanics of nanoporous materials.

3.1 Dimensional changes due to processing

Table 1 presents a summary of the results from the different processing conditions. The relative density is defined by conventional terms as stated by Gibson and Ashby: ρ_f/ρ_s where ρ_f is density of foam and ρ_s is density of solid [2]. Note the changes in strut size presented in Table 1 and in Figures 1 and 2. Figure 1 presents an SEM micrograph of 25% relative density Au foam showing the changes in pore and ligament size by comparing two different dealloying methods. Sample A was dealloyed by free corrosion and sample B was dealloyed potentiostatically as described experimental procedures. Figure 2 shows the 30% relative density Au sample which was divided into three samples C, D, E. Sample C was not annealed, sample D was annealed for two hours at 400°C and sample E was annealed for two hours at 600°C. Samples D and E exhibit large pore and ligament size growth up to 15 times larger than the original dealloyed structure. It should be noted that for all samples (A thru E) the pore to ligament size ratio is ~ 1.

Table 1 Mechanical properties of 25% and 30% relative density nanoporous gold

	Relative density (%)	Processing method	Strut size (nm)
Sample A	25	Free corrosion	30
Sample B	25	EC	5
Sample C	30	Free corrosion	60
Sample D	30	Free corrosion HT 400°C for 2 hrs	480
Sample E	30	Free corrosion HT 600°C for 2hrs	940

In order to prepare a comprehensive assessment of the critical issues affecting nanoporous materials, it is necessary to study many length scales. Therefore, it is important to study a foam system that is available with a wide range of densities as well as a wide range of pore sizes (microns to nanometers). Currently, metallic foams made from materials such as Ni or Al are available in large pore sizes; pores diameter sizes less than 250μm are not available [2,13]. Gold foams produced by dealloying can be synthesized for a wide range of pores sizes. There are at least three methods to change the ligament size in gold foams: a) dealloying potentiostatically as can be seen in Figure 1[ref], b) the variation of total dealloying time [14], and c) a simple furnace anneal [7]. Since Au does not oxidize in air, at elevated temperatures the pore/ligament dimensions increase due to Ostwald ripening, allowing the pore size to be varied continuously from ~10 nm to 1 μm.

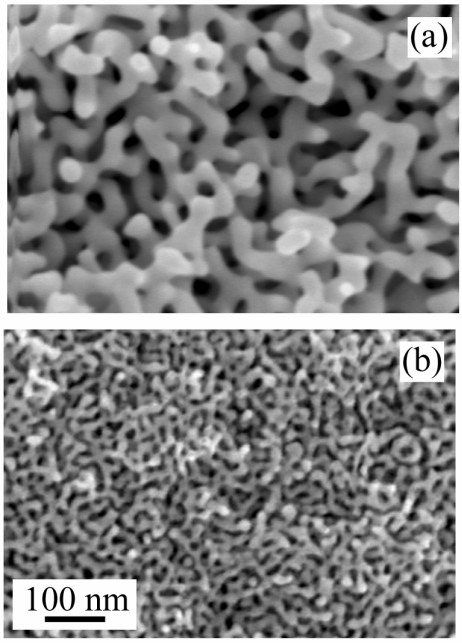

Fig. 1 SEM micrographs of dealloyed 25% Au foam by a) free corrosion and b) electro-chemically driven (EC).

So far we have demonstrated the wide range of ligament size that can be produced from dealloyed Au foams; however, in order to make a complete assessment of the mechanical properties, a wide range of densities is also necessary. Currently, Au foam can be produced in a range between 20 to 40% relative density. In order to produce lower densities, such as 10 and 5%, different approaches to the dealloying must be used such as casting ternary alloys (i.e.$Ag_{100-x-y}Cu_xAu_y$). This endeavor is currently underway and will be discussed in a future publication.

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3.2 Grain size and Processing

Processing techniques also should affect the grain size of the struts (ligaments). However this is a more controversial topic. Some researchers have presented that the dealloying process does *not* change the grain structure [7,15,16] and single crystal ligaments have been observed in nanoporous gold leaves (100 nm thick) dealloyed by free corrosion [14]. More recently Biener et. al has shown by TEM that a 40% electrochemically driven Au foam appears to have multiple grain boundaries in one ligament [17]. Furthermore, HRTEM micrographs of compressed foam samples (with ligaments of ~100 nm) clearly show grains in the order of 5 nm diameter [18].

Hodge et. al attributed the nanocrystalline nature of dealloyed Au foams to be due to the selective dissolution of Ag atoms generating a supersaturation of Au adatoms and vacancies, which in turn could then result in the nucleation of Au adatom clusters and vacancy islands. Thus, the observed discrepancy in whether the ligaments are single crystal or nanocrystalline could be an indicatation that electrochemical driven dealloying produces a higher supersaturation of Au adatoms, which in turn should increase the nucleation rate [18].

It is evident that the subject of crystallinity needs further research and the implementation of multiple techniques to verify any changes in grain size.

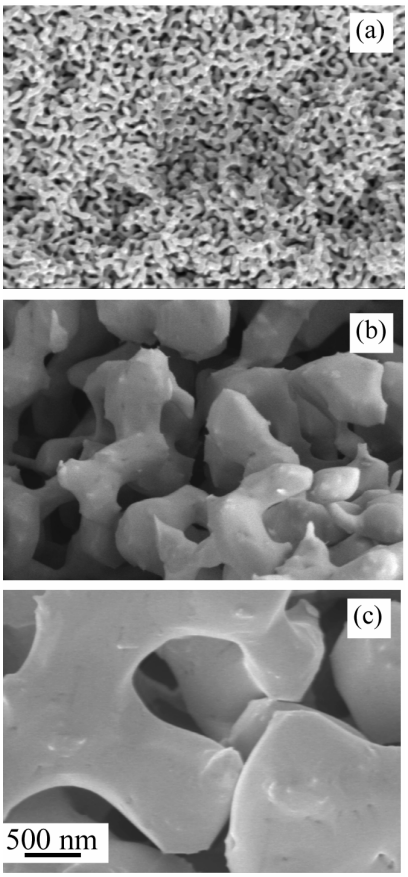

Fig. 2 SEM micrographs of dealloyed 30%Au foam annealed at a) room temperature b) 400°C and c) 600°C.

3.3 Fracture behavior and ligament size

As mentioned in the introduction, there have been studies on the ductile-brittle transition of nanoporus Au. More recently, work performed by Biener et.al has shown that there is a significant difference in the fracture behavior due to the ligament length scale [8]. Figure 3 presents two SEM micrographs which reveal changes in the fracture behavior due to ligament size. Figure 3a shows the original ligament size (60nm), which exhibits failure due to necking, while the sample annealed at 600°C with ligament size of ~900 nm shows the formation of slip bands. From this investigation into fracture behavior and ligament size, new questions arise about whether or not Gibson and Ashby deformation models for open-cell foams still hold for nanoporous materials. The study of the fracture behavior could allow for the development of new models of deformation mechanisms in nanoporous foams.

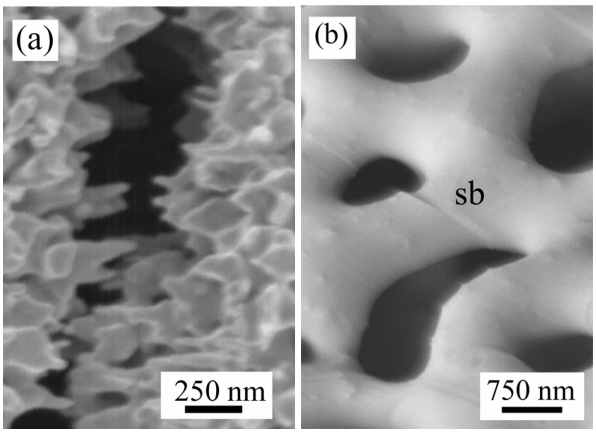

Fig. 3 SEM micrographs of fracture surface for 30% Au foam showing a) failure by necking of 60 nm ligament size sample and b) formation of slip bands on 940 nm ligament size sample

3.4 Testing parameters

Testing of macro-cellular foams has been well researched for many types of foam materials [1-3,19,20]. As the foam ligaments become smaller and smaller, such as in the case of nanoporous foams, new testing techniques are required. In the case of nanomaterials, the use of nanoindentaion is a reliable and widely used method to perform mechanical testing and overcome sample size limitations. By having a loading-unloading curve, one can obtain the foam Elastic modulus as well as the hardness. Of course, some assumptions are necessary. It has been presented by Gibson and Ashby [2] that as the foam is compressed, the cell walls collapse with very little lateral spreading. Therefore, it can be assumed that for a foam, $H \sim \sigma$ where H is the sample hardness and σ is the yield strength. However, using indentation tests as the main mode of testing can give rise to issues due to foam densification. If the sample is compressed too much, at some point, you will have a denser material. In order to minimize densification issues, all of our tests are performed in less than 0.5% of the total sample thickness. We have also tested samples to depths as much as 3% of the total sample thickness and found that the numbers are identical to those at 0.5% thickness; thus, no evidence of densification effects on the hardness and elastic modulus values has been detected.

Currently, other methods of testing dealloyed materials are being carried out by producing columns of nanoporous Au foams by focused ion beam (FIB), and then compressing them directly with a flat punch [21]. These tests will present new data that can then be compared to the nanoindentation data and should give a better understanding of the mechanical behavior.

3.5 Au as a high strength material

As mentioned in the introduction, Biener et. al have shown by nanoindentation that the experimentally determined value of the yield strength of 40% nanoporous Au is almost one order of magnitude higher than the value predicted by scaling equations. Nanoindentation tests on samples A, B and C (25 and 30% relative density) performed for this study produced experimental hardness values as high as 250 MPa, which is also an order of magnitude higher than expected results. The scaling equation for the yield strength of open-cell foams is $\sigma_f = 0.3*\sigma_s*(\rho_f/\rho_s)^{3/2}$, where σ_s is the yield strength of bulk gold, which can have a wide range of values. For example, the yield strength can vary from ~200 MPa for polycrystalline Au [22] to ~ 650 MPa for nanocrystalline Au [18] , thus predicting values in the range of 7 to 32 MPa. However, using the value for the intrinsic yield strength of Au (1500-8000 MPa) [23-26] for the scaling equation, predicts values from 56 to 400 MPa. Typically, when predicting yield strength values from macro-cellular foams, the bulk material value is the one given for a polycrystalline material.

The above results suggest that the yield strength of the ligaments in nanoporous Au approaches the intrinsic yield strength of gold. However, a comprehensive study of the scaling equations at the nanoscale is still needed.

4. Conclusion

Many advances have been made in understanding nanoporous materials, specifically nanoporous gold. New issues arise regarding the mechanical behavior of nanoporous foams compared to macro-cellular foams. These issues are somewhat analogous to comparisons between metals with nanocrystalline grain sizes vs. micron-millimeter size grains and their effect on mechanical behavior.

We have presented in this paper what we believe are the most pressing issues in understanding the mechanical behavior of nanoporous foams. We have demonstrated that a gold foam currently presents the best candidate for such a study, since it can be synthesized with a wide range of ligaments sizes and densities.

We have also shown that preliminary tests have demonstrated that a) Au foams have a fracture behavior dictated by the ligament size and b) nanoporous Au is a high yield strength material. Overall, this overview presents the potential in developing nanoporous foams as a new class of high yield strength / low density materials.

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