Monolithic nanocrystalline Au fabricated by the compaction of nanoscale foam

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We describe a two-step dealloying/compaction process to produce nanocrystalline Au. First, nanocrystalline/nanoporous Au foam was synthesized by electrochemically driven dealloying. The resulting Au foams exhibited porosities of ~60% with pore sizes of 40 and 100 nm and a typical grain size of <50 nm. Second, the nanoporous foams were fully compacted to produce nanocrystalline monolithic Au. The compacted Au was characterized by transmission electron microscopy and x-ray diffraction and tested by depth-sensing nanoindentation. The compacted nanocrystalline Au exhibited an average grain size of <50 nm and hardness values ranging from 1.4 to 2.0 GPa, which were up to 4.5 times higher than the hardness values obtained from polycrystalline Au.

The superior mechanical properties of nanocrystalline materials, such as high yield strength and high wear resistance, have made their study an interesting subject.^{1,2} With some exceptions, processing of nanocrystalline materials with grain sizes <100 nm has been focused mostly on elements such as Ni and Cu.^{2–5} Finding new routes to produce nanocrystalline materials can offer many advantages, such as producing materials that are not readily available, e.g., Au, and producing multiple grain sizes and larger specimens, which allow comprehensive structural and mechanical tests. Synthesis of nanocrystalline gold has undergone limited research, mostly consisting of gas deposition methods^{6,7} and some magnetron sputtering⁸ with few studies on the mechanical behavior.⁹

In this work, we demonstrate that by using a two-step dealloying/compaction process, one can obtain fully compacted, nanocrystalline, monolithic gold with various grain sizes and superior mechanical behavior. The nanocrystalline nanoporous Au is prepared by electrochemically driven dealloying of Au/Ag alloys and subsequently compressed to produce monolithic nanocrystalline Au samples. Selective dealloying is a method by which the more electrochemically active element (Ag) is dissolved, leaving behind a spongelike morphology of interconnecting ligaments made from the less electrochemically active element (Au).^{10,11} Here we report for the first time the preparation of nanocrystalline Au by a

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dealloying/densification method. In general, this procedure could be extended to prepare other nanocrystalline materials.

Polycrystalline Au_{0.4}Ag_{0.6} alloy ingots were prepared by arc-melting Au (99.999%) and Ag (99.999%). The alloy composition was confirmed by a fire assay technique. Nanoporous Au samples were prepared by selective electrolytic dissolution of Ag from the Au_{0.42}Ag_{0.58} alloy.¹¹ A three-electrode electrochemical cell controlled by a potentiostat (Princeton Applied Research, Oak Ridge, TN; Model 363) was used for these experiments. Dealloying was performed at room temperature using a platinum wire as a counter electrode and 75% nitric acid as an electrolyte. The alloy samples were held at an applied electrochemical potential of approximately 1 V (versus a saturated calomel electrode) for a period of 2-3 days until no further weight loss was detected. Energy dispersive x-ray (EDX) spectra collected from the nanoporous Au samples confirm that Ag was almost completely removed during dealloying. Further foam processing details are discussed elsewhere.^{11,12}

Two samples (~500 μ m thick) with two different pore size were produced. Sample A has an average pore size of 100 nm, while sample B exhibits smaller pores on the order of 40 nm. The difference in pore size can be attributed to coarsening of the nanoporous structure during dealloying since the total time to complete the dealloying process was different for both samples.¹³ Both porous samples were characterized for grain size by using transmission electron microscopy (TEM) and x-ray diffraction (XRD) by applying the Scherrer formula for peak broadening to the (111) reflections; both methods demonstrated a grain size below 50 nm.

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The porous samples were then placed in an Instron 4400R universal testing machine (Instron Corporation, Canton, MA) and compressed in air at room temperature. The compaction process was as follows: the nanoporous sample is placed on the bottom plate of the Instron machine without any constraints. Since it is known that foams, in general, have a very high energy absorption and can undergo large compressive strains, we proceeded with a series of steps to ensure complete compaction.¹⁴ First, a small load of approximately 600 N was applied; this load was calculated based on the strength of the material and using Ashby/Gibson scaling laws;¹⁴ the test was then stopped and the sample thickness was measured. This process was repeated with increasing loads until the sample approached the calculated thickness of a fully compressed sample. Currently, more studies are underway to further improve the compression and to control the compaction by using the applied pressure rather than changes in sample dimension. Compressed samples were then tested by XRD to identify the grain size and finally indented using both a Triboindenter (Hysitron, Inc., Minneapolis, MN) with a Berkovich tip and a standard Vickers microindenter to check hardness values.

The development of a nanocrystalline grain structure was observed during dealloying and maintained during the compaction process described above. Two effects contribute to the development of a nanocrystalline grain structure in the compacted sample. First, compression of a nanostructured (i.e., nano-ligaments) material is analogous to methods which produce nanocrystalline monolithic structures by compacting nanocrystalline powders.^{15,16} Since our ligaments are on the nanometer scale, as the material is compacted at room temperature, it is expected that the nano-ligaments would be compacted to become nanocrystalline grains. Second, the foam ligaments themselves are nanocrystalline. This is illustrated by Fig. 1, which shows the typical ligament structure by (a) scanning electron microscope (SEM) images of the original nanoporous structure and (b) a TEM micrograph from a typical ligament from sample A. Indeed, multiple grain boundaries are observed per ligament. Furthermore, the acquired selective area diffraction (SAD) pattern shown in the inset of Fig. 1(b) is typical for a polycrystalline material, thus further proving that the individual ligaments are nanocrystalline. XRD data obtained from the porous samples showed grain size values of approximately 30 nm.





(b)

(a)

FIG. 1. SEM micrograph obtained from (a) synthesized Au porous samples and (b) dark-field and bright-field TEM micrographs of sample A showing four distinct grains <50 nm. The corresponding selected area diffraction pattern is shown in the inset.

The grain structure of the compressed Au sample was characterized by x-ray diffraction and high resolution TEM (HRTEM). Both methods reveal a grain size below 50 nm. The compacted samples exhibit some small voids, as can be seem in the SEM micrographs in Fig. 2(a), which shows an unpolished surface of a fully compressed sample. Figure 2(b) depicts the nanocrystalline grains, which are observed in the fully compacted sample by using HRTEM. Table I presents a summary of the results regarding grain size dimensions of the fully compacted sample.

The development of a nanocrystalline grain structure in the compressed monolithic sample was expected due to the analogous nature of our process to nano-powder compaction; however, that the foam ligaments themselves exhibit a nanocrystalline grain is an unexpected



(b)

FIG. 2. Micrograph of compressed sample taken by (a) SEM of unpolished surface and (b) HRTEM. Note that apparent lines in (a) are due to impressions from the compression plates. Arrows in (b) point to typical grains.

result. It has been reported that the dealloying process does not change the grain structure^{10,11,17} and singlecrystal ligaments have been observed in nanoporous gold leaves (100 nm thick).¹³

We can only speculate why other researchers did not observe the evolving nanocrystallinity of the Au ligaments during dealloying, which is one of the factors that allows for the production of a compressed monolithic nanocrystalline Au sample. However, a recent model proposed by Erlebacher et al.¹⁰ suggests that dealloying of a Ag-Au alloy involves a dynamic rearrangement of the Au atoms, which could explain the evolution of the nanocrystalline microstructure of the nanoporous Au observed in the present study: selective dissolution of Ag atoms generates a supersaturation of Au adatoms and vacancies, which in turn could then result in the nucleation of Au adatom clusters and vacancy islands. The actual morphology evolving under these conditions should be influenced strongly by the mobility of vacancies and adatoms and, in particular, of the presence of nucleation sites. Thus, the observed discrepancy could indicate that electrochemically driven dealloying produces a higher supersaturation of Au adatoms, which in turn should increase the nucleation rate.

We have so far shown, by the use of TEM and XRD, that our porous and compressed samples are indeed nanocrystalline. To further verify the nanocrystalline nature of the compressed samples, results of indentation studies are presented in Table I; the nanocrystalline Au exhibits hardness values as high as 2.0 GPa. As a reference, we tested a polycrystalline Au sample by nanoindentation and Vickers microhardness; both tests resulted in nearly identical values around 0.45 GPa, which are accepted values for polycrystalline Au.¹⁸ It has been demonstrated in other nanocrystalline materials that in the range of grain sizes from 10 to 50 nm, the Hall-Petch relationship dictates that, as the grain size decreases, the hardness values should increase.^{2,4} Previous papers have presented nanoindentation experiments on Au but not on nanocrystalline Au.^{19,20} However, a direct comparison can be made with Sakai et al.,⁹ where nanocrystalline Au specimens with 20-60 nm grain size were prepared by the gas deposition method and showed hardness values in the range of 0.8 to 2.0 GPa by Vickers microhardness; grain sizes <25 nm show hardness values above 1.0 GPa, which are in good agreement with our findings. It should be noted that nanoindentation could produce slightly higher hardness values than microhardness tests due to artifacts such as work hardening from polishing and "indentation size effects." Our compressed sample was not polished, as can be seen in Fig. 2(a), so there should be no work hardening due to polishing. Using Vickers indentation allowed us to check for indentation size effects. Tests on the compressed samples by Vickers indentation vielded slightly lower values than those acquired by the

	Grain size		Hardness	
	X-ray (nm)	TEM (nm)	Triboindenter (GPa)	Vickers (GPa)
Sample A	21	10-50	1.44 ± 0.63	1.60 ± 0.24
Sample B	36.3	10–50	1.97 ± 0.48	1.26 ± 0.04
Polycrystalline Au (99.99%)	By optical microscopy ~140 µm		0.44 ± 0.04	0.45 ± 0.03

TABLE I. Grain size and hardness values for compressed monolithic samples.

Triboindenter, but the values were still up to 3.5 times higher than the polycrystalline sample, thus proving that there is a true increase in hardness values, consistent with the nanocrystalline character of our compressed Au samples.

In summary, we have presented a method to produce monolithic nanocrystalline Au via a two-step dealloying/ compaction process. The monolithic nanocrystalline Au presented here has a grain size <50 nm and exhibits an increased hardness over polycrystalline Au by a factor of 4.5. Further studies to improve the compaction process are underway.

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