Ag effects on the elastic modulus values of nanoporous Au foams

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To study both the effect of Ag and the relative density on the elastic properties of nanoporous Au (np-Au) foams, partially as well as fully dealloyed np-Au samples with various ligament sizes were prepared. Additionally, Ag-coated np-Au samples were synthesized by immersing np-Au in a 1 M Ag nitrate solution, followed by drying and thermal decomposition of the deposited Ag nitrate salt to Ag, NO_2, and O_2. Cross-sectional analysis revealed that this method yields a homogeneous Ag distribution and that the Ag concentration can be adjusted within the range of 0 to 20 at.%. Mechanical testing was performed by depth-sensing nanoindentation. It was observed that the effect of the relative density on the elastic properties of np-Au seems to be much stronger than predicted by the Gibson and Ashby relationship: Even Ag contents as low as 1 at.% can significantly change the modulus values. On the other hand, the elastic modulus of np-Au seems to be independent of the ligament size.

I. INTRODUCTION

Nanoporous metals, in particular nanoporous Au (np-Au) foams have gained much interest due to the wide range of rapidly emerging applications.[1–3] One of the unexpected properties of np-Au is its high yield strength,[4] which can be higher than the strength of the fully dense bulk material and that despite their high porosity of 60 to 80%.[5,6] Current testing on nanoporous foam has been focused on strength measurements by techniques ranging from nanoindentation to beam bending tests.[5–11]

The elastic properties of nanoporous Au, on the other hand, have attracted less interest, and consequently there are fewer data available. Most studies report Young's modulus values in the 5 to 13 GPa range with relative densities ranging from 25 to 40%.[4,6,8,10] The data seem to be consistent with the scaling predictions made by Gibson and Ashby[12] if one uses the bulk modulus of Au (~80 GPa), but the scatter of the data points is too large to make definitive conclusions. The narrow range of most of the available data seems to indicate that there are little or no size effects in the elastic properties. An exception to this is the recent study by Mathur and Erlebacher[9] who reported a fourfold increase in the Young's modulus, from ~10 to ~40 GPa, as the ligament diameter decreases from >12 to 3 nm. This result was attributed to a combination of surface stress, density increase caused by shrinkage, and a higher bending stiffness of smaller ligaments. However, in general elastic length scale effects are not observed in nanoscale materials.[13–15] For example, the modulus of Au nanowires (70 GPa) is independent of their diameter (at least in the range 40–240 nm) and similar to that of bulk Au.[16]

Because nanoporous foams can be synthesized by various methods such as free corrosion and electrochemically driven dealloying, the residual silver content in np-Au can vary significantly. Specifically, dealloying conditions that result in the formation of ultrafine np-Au material (ligaments smaller than 30 nm) tend to yield higher concentrations of residual Ag, as they rely on suppressing surface diffusion. For example, Volkert et al.[6] presented the mechanical properties of Au foam pillars fabricated by electrochemically dealloying and reported as much as 10 at.% residual silver. The effect of residual Ag on the elastic properties of np-Au can be twofold: first, it affects the relative density of the material, and second, it could also modify the elastic properties of the ligament material.

The objective of this work is to illuminate the effects of residual Ag on the elastic properties of np-Au. Specifically, we studied the elastic properties of partially as well as fully dealloyed np-Au samples with various ligament sizes. In addition, samples were prepared by Ag coating the np-Au foam by immersing it in a 1 M Ag

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nitrate solution, followed by drying and thermal decomposition of the deposited Ag nitrate salt to Ag. This method yields a homogeneous Ag coating distribution, where the Ag concentration can be adjusted within the range of 0 to 20 at.%. The processing method can be used to modify the density of np-Au foams in a controlled fashion, and it is also interesting in terms of catalysis applications since it has recently been suggested that Ag may play an important role in the catalytical activity of np-Au.[17]

II. EXPERIMENTAL PROCEDURES

For this study, we used approximately 300 μm thick, disk-shaped Ag–Au samples with at.% compositions of Au25/Ag75, Au30/Ag70, and Au35/Ag65. All np-Au samples were prepared by free corrosion as described in an earlier publication.[5] To fully access the changes in elastic modulus for a wide range of Ag compositions, several types of samples were prepared. Samples 1 to 5 were partially dealloyed as indicated in Table I. Samples in Table II were completely dealloyed then additionally heat treated in air at 300 °C to allow for pore growth. Here, we use the term "completely dealloyed" to describe samples that have a residual Ag concentration of less than 1 at.%. Homogeneously Ag coated np-Au foams (samples 30 B, C, D and 35 C, D, E) were then prepared by immersing "completely dealloyed" np-Au samples in a 1 molar (1 M) solution of $AgNO_3$ for 30 min and then drying the samples at 60 °C for 1 h in air, similar to the procedure described by Chan et al.[18] Finally, the deposited $AgNO_3$ salt was reduced to Ag by baking the samples at 300 °C for 30 min in an argon/4% hydrogen atmosphere (the samples were allowed to cool in the Ar/H_2 atmosphere). Using a reducing atmosphere instead of ambient air allowed us to perform the $AgNO_3$ decomposition at lower temperatures and thus to keep the pore size in the 100 to 200 nm range. The heat treatment is not only necessary to decompose the $AgNO_3$ salt, but also to ensure the formation of a homogenous alloy (see Sec. III). To increase the Ag concentration, the Ag coating process was repeated up to three times (see Table II). We are assuming little or no shrinkage in our samples given the processing method and sample thickness (~300 μm).[19]

TABLE I. 70/30 alloy dealloyed at various times—ligament size 50 nm.

Sample ID	Dealloying time (h)	Ag at various surfaces (by EDAX), at.% Edge	Center	Average	Reduced modulus (GPa), top surface
1	0.5			65.48	
2	4			60.20	
3	8	3.20	51.98	50.31	2.59 ± 0.09
4	24			0.0	
5	48	0.0	0.0	0.0	2.29 ± 0.13

TABLE II. Silver additions on completely dealloyed samples.

Sample ID (original density)	Treatments	Final ligament size (nm)	Average residual Ag (at.%)	Corrected relative density (%)
30A	HT 300C	160	0.0	30
30B	1 Ag	200	6.9	32
30C	2 Ag	212	8.7	33
30D	3 Ag	246	24.2	37
35A	HT 300C		0.0	35
35B	HT 300C	162	3.1	36
35C	1 Ag	172	10.3	39
35D	2 Ag	184	11.1	39
35E	3 Ag	227	17.6	41

Morphology (ligament size) and composition (amount of residual/deposited Ag) was assessed by cross-sectional scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). To verify the EDS results, weight measurements were performed before and after dealloying, as well as before and after silver treatments using a Mettler Toledo XP series balance (Columbus, OH) with a readability of 0.01 mg. The mechanical properties of both bulk and nanoporous samples were tested by depth-sensing nanoindentation using a Triboindenter (Hysitron, Minneapolis, MN) with a Berkovich tip (radius of ~200 nm). Indentations were performed on a planar polished surface of the sample disks (polished before dealloying to a mirror finish). All nanoindentation experiments were performed using a constant loading rate of 500 μN/s with loads ranging from 2000 to 4000 μN. A minimum of 125 indents (arranged in groups of 25) were collected from each sample.

The elastic modulus values reported in this manuscript are actually E_r (reduced modulus) values, which are defined as:

$$\frac{1}{E_r} = \frac{(1-\nu_i^2)}{E_i} + \frac{(1+\nu_s^2)}{E_s} \quad , \qquad (1)$$

where E is the elastic modulus and ν is the Poisson's ratio of the indenter (i) and the sample (s), respectively. However, for an elastic Poisson's ratio of 0.2 to 0.3 (typical for foams) and using a diamond indenter, the value from E_s and E_r are almost identical.[20] Further discussion about both elastic and plastic Poisson's ratio of foams can be found elsewhere.[5,21,22]

III. RESULTS AND DISCUSSION

A. Partially dealloyed np-Au

When testing partially dealloyed samples by nanoindentation, it is important to realize that partial dealloyed samples have an inhomogeneous Ag distribution, with almost “completely” dealloyed surfaces and a Ag-rich core. An extreme example is presented in Fig. 1, which shows cross-sectional scanning electron microscopy (SEM) and elemental detection by analytical x-ray (EDAX) data obtained from a Au30/Ag70 sample after dealloying for 8 h. The data revealed that the edge surfaces are almost completely dealloyed, while the center of the sample showed a porous structure containing a large amount of residual silver. We studied the effect of dealloying time on the residual Ag concentration in more detail, and the results are summarized in Table I. In general, we observed that short dealloying times resulted in higher Ag concentrations, but the Ag is inhomogeneously distributed throughout the foam. This limits the usefulness of this approach to study the effect of residual Ag (and density) on the elastic properties of np-Au by nanoindentation: because of the shallow indentation depth (less than 3 μm in the current study), nanoindentation tests typically probe only the “completely” dealloyed surface layer and not the Ag-modified bulk properties. This conclusion is confirmed by the nanoindentation results presented in Table I. However, the testing method could allow for some of the wide range of values found in literature. For example, bending tests probe the bulk of the material and thus are more sensitive toward the effects of partial dealloying. Gall et al.[23] showed that the agreement between microbending test and indentation test depends on the degree of heterogeneity of the samples and values can differ by as much as 50%. Microbending-type tests provide an average transverse modulus highly biased toward the modulus of the outlying surfaces. The modulus and the thickness of the outlying (Ag-poor) surfaces are strongly affected by the degree of dealloying that will further influence the result of microbending tests. As demonstrated previously, partially dealloying can lead to foams with inhomogeneous silver (density) distributions. Therefore, to assess the effect of Ag (and relative density) on the elastic properties of np-Au, samples with homogeneous Ag distributions were prepared by coating completely dealloyed np-Au samples with various amounts of Ag.

B. Ag coated np-Au foams

To obtain homogeneously Ag-coated nanoporous Au foams, samples were fabricated by coating completely dealloyed np-Au samples with metallic Ag using the method described by Chan et al.[18] Specifically, we used np-Au samples (prepared from Au30/Ag70 and Au35/Ag65 alloys) then coated up to three times with 1 M Ag nitrate solution followed by drying and thermal decomposition of the deposited Ag nitrate salt to Ag, NO_2, and O_2. The results obtained from Ag-coated np-Au samples are summarized in Table II. Scanning electron micrographs collected from a fracture cross section of the 35% relative density Au foam are shown in Fig. 2(a) as prepared, as well as Fig. 2(b) after one, Fig. 2(c) after two, and Fig. 2(d) after three Ag coatings and heat treatment at 300 °C. In addition, EDS performed at the edge and center surfaces of these samples show a homogeneous silver distribution. During the process, the ligament size slightly increases from 160 to 246 nm, but the overall morphology (open porosity) of the material remains the same. Given the ligament thickness, the heat treatment times, and the overall Ag in the system, one can estimate the ligament composition to be between 100 and 80 at.% Au. We expect that the Ag addition procedure described here results in an almost homogeneous Ag distribution (on the ligament level as well as on macroscale) rather than producing core-shell structures or density-graded samples (i.e., the Ag coated on the surface diffuses into the Au ligament).[24] Further diffusion results can be obtained by following similar calculations performed by Ding and Erlebacher using a multistep dealloying technique for two-dimensional nanoporous foams at 400 °C.[25] The main point is that the ligament composition at any region of the foam was found to have a homogenous Ag content; any compositional changes in the samples are accounted by using

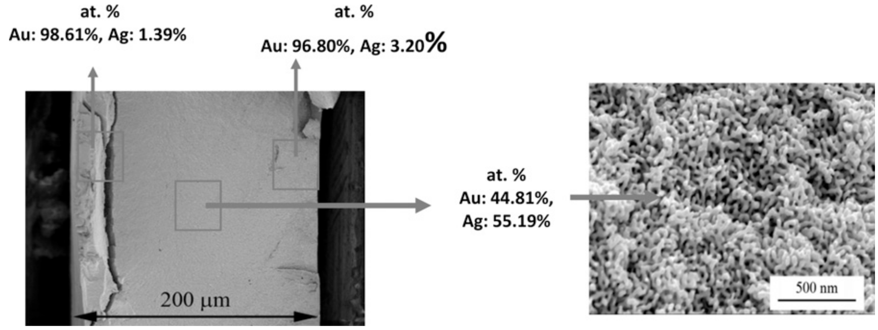

FIG. 1. Scanning electron micrograph of a Au30/Ag70 sample dealloyed for 8 h. Spot EDS measurements demonstrate that the edge surfaces are almost entirely dealloyed while the center surface shows a porous structure maintaining a large amount of silver.

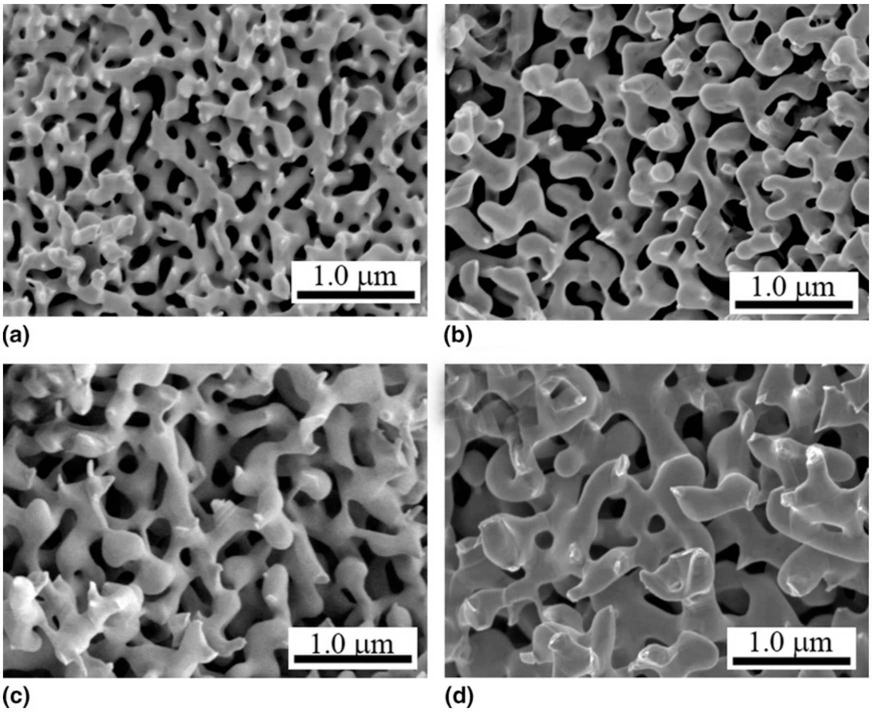

FIG. 2. Scanning electron micrographs of fracture cross sections of 35% relative density Au foam from Table II. (a) As prepared. (b) After 1 Ag treatment and subsequent diffusion at 300 °C. (c) After 2 Ag treatments and an additional diffusion at 300 °C. (d) After three Ag treatments and an additional diffusion at 300 °C.

the relative density. It should be noted that because of Ag surface segregation, the Ag concentration on the ligament surfaces tends to be higher than in the bulk of the ligament (e.g., 4.4 versus 0.7 at.% in Ref. 3). Thus even "completely" dealloyed samples will have appreciable amounts of Ag on the ligament surfaces. However, this should not affect the nanoindentation tests presented here.

C. Nanoindentation testing

Nanoindentation was used to study the effect of residual silver on the elastic properties of homogeneously Ag-coated np-Au foams. For comparison, we also performed nanoindentation tests on bulk (nonporous) samples of Au, Au25/Ag75, Au30/Ag70, and Au35/Ag65. As expected, changing the alloy composition from 0 to 65% Ag only marginally affected the measured Young's modulus (average value of ~89 GPa). This observation is consistent with the fact that Ag–Au is a solid-solution system where the components have very similar elastic properties (Ag, 83 GPa; Au, 78 GPa).[26]

On the other hand, we observed pronounced changes in the elastic properties of Ag-doped np-Au samples as we increase the Ag content from 0 to 25 at.% (Fig. 3). For example, the modulus of a np-Au foam with the nominal density of 0.35 increases from ~2 to ~25 GPa as the Ag content increases from 0 to ~18 at.%. To exclude artifacts from size effects, we included only data taken from samples with similar ligament sizes (160–246 nm). This and the fact that the elastic properties of fully dense Ag–Au alloys (and thus also of the ligaments) are independent of the Ag content allows us

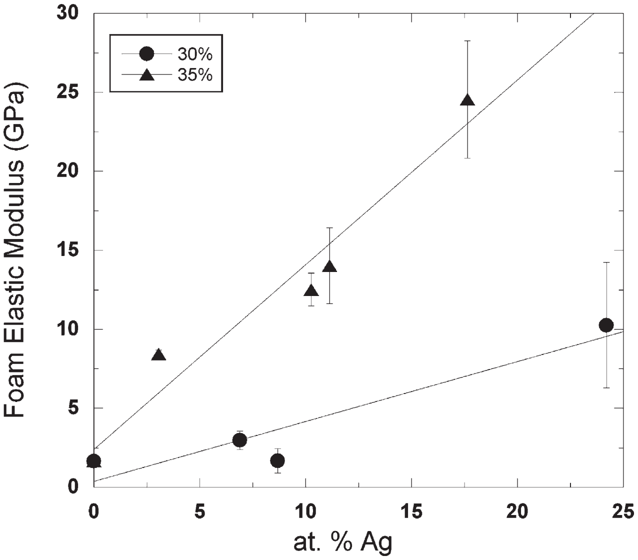

FIG. 3. Average elastic modulus values (including standard deviation from 125 indents per sample) as a function of at.% silver additions for both a 30% and 35% foam with Ag treatments as detailed in Table II. The 30% and 35% are used to denote the initial fully dealloyed density as a mean for comparison only (density corrections not included). The details of the sample preparations can be found in Table II.

to attribute the observed increase of the modulus with increasing silver content to changes in the relative density.

For a porous material, it is common to express the properties as a function of the relative density. For example, the correlation between relative density and modulus of macroporous foams can be described by:

$$E^* = CE_\mathrm{s}\left(\frac{\rho^*}{\rho_\mathrm{s}}\right)^n \quad , \qquad (2)$$

where * refers to foam properties and s to the bulk properties, and C and n are empirical constants. The proportionality constant C and the density exponent n describe the cell geometry. Experimental data indicate that a wide range of open-cell macroporous foam materials can be adequately described by $C = 1$ and $n = 2$.[12] The validity of Eq. (2) can be checked by comparing its predicted relative density dependence with the experimental modulus data shown in Fig. 3. Note that this comparison requires correction of the nominal relative density of our samples for Ag addition. For example, a Ag-coated np-Au sample with a nominal density of 0.3 and an added Ag content of 10% has a corrected density of 0.33. Figure 4 shows a comparison between the predicted (normalized) elastic modulus (E^*/E_s) data and our experimental (density-corrected) data points for 25 to 40% nanoporous Au foams with and without silver treatments (ligament sizes range from 50 to 246 nm). From Fig. 5, it is observed that (i) the modulus values seem to be independent of the ligament size, which is in contrast to findings on the hardness values where we observed a strong ligament size effect[5] and (ii) that the modulus increases with increasing density as predicted by Eq. (2), but the density exponent n seems to be much larger than 2. For example, for relative density values of 25 to 41%, Eq. (2) predicts modulus values in the range of 5 to 13 GPa, whereas our results range from 0.8 to 24 GPa. Unfortunately, the density range accessible by our synthesis method was too small to determine the density exponent n quantitatively. For relative densities higher than 35% (<40%), the experimental values are in the range predicted by the Gibson and Ashby relationship. Roberts and Garboczi[27] suggested the existence of distinct regions of the relative density with different values of n; where n ranges from 1 to 3.

It is observed that the discrepancy between the scaling prediction and the experimental data is the result of the assumptions included in the Gibson and Ashby derivation. In particular, Eq. (2) is based on the assumption that the foam primarily deforms via ligament bending, which is only valid in the limit of low relative densities (pore diameter much larger the ligament size). However, for the foam densities (25–40%) included in the present study, the pore diameter and ligament size are almost identical; therefore, contributions from ligament compression and extension become more important.

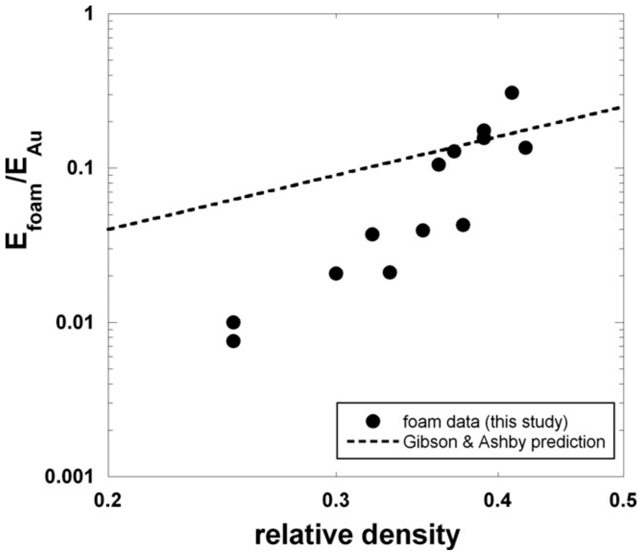

FIG. 4. Plot of foam relative density versus normalized elastic modulus measurement for 25–40% relative density nanoporous Au foams with and without silver treatments. A value of 80 GPa was used for the bulk Au modulus (E_au).

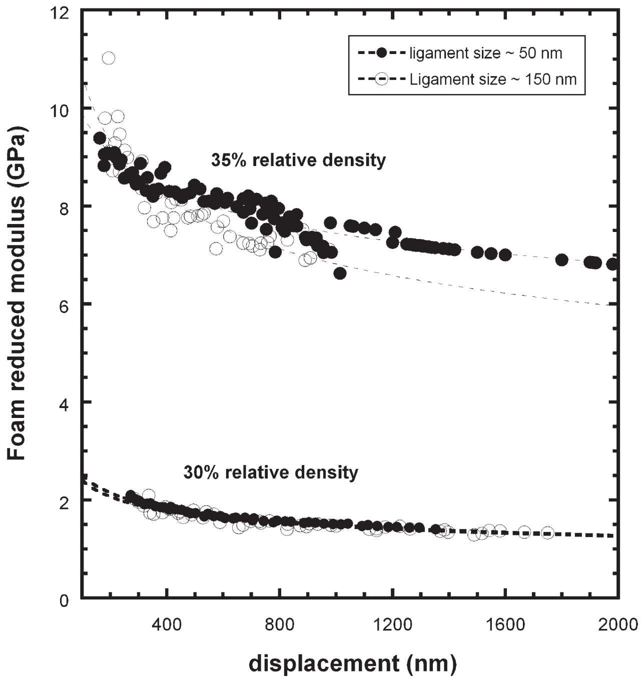

FIG. 5. Effect of nanoindentation depth on measuring the reduced modulus of the nanoporous foam. The 30% and 35% relative density foams were prepared with ligament diameters of 50 and 150 nm and had no additional Ag treatments prior to testing. As the nanoindentation depth was increased, the reduced modulus was found to decay as an inverse power law until reaching a plateau at a depth of ~800 nm for the 30% relative density foams and ~1200 nm for the 35% relative density foams. All of the data presented in this paper were taken from these two plateaus.

To truly assess the bending model limitations and the cell geometry relationship to the relative density, a new model must be developed; this will be the subject of a future study. There are several other factors that potentially could affect the test results shown in Fig. 4 such as: the testing direction compared with cell direction (longitudinal versus transverse), cell curvature, cell size, indentation size effects, and other nanoscale effects. In the following sections we address some of these points.

D. Testing issues

For a bulk material tested by nanoindentation, the elastic modulus values are generally independent of indentation depth.[20] However, in the case of foams it has been shown that the indentation depth can affect the results, and a valid test requires at least five cells in each testing direction.[28] For example, Andrews et al.[28] observed that the indentation strength of macroporous open-cell aluminum foams decreases inversely with the normalized indenter size, that is, the size of the indenter relative to the cell size. Similar effects have been reported for nanoporous foams.[5] The effect of indentation depth on the elastic modulus, on the other hand, has not been analyzed yet. Here, we observe (Fig. 5) that the modulus decreases with increasing indentation depth and appears to plateau after reaching 600 nm in depth. Note that all values reported in this study were taken from the plateau region (600–2000 nm).

Cell shape (foam morphology) is another variable that has been shown to affect the elastic properties of open-cell foams. For example, compression tests performed by Nieh et al.[29] on macroaluminum foams demonstrated that the modulus is higher for the longitudinal direction than the transverse direction by as much as 14%. However, because of the random network structure of the np-Au samples studied here, we do not expect this effect to be important.

E. Cell parameters

According to Simone and Gibson,[30] the cell curvature can decrease the values of elastic modulus by as much as 40% and the effect is more pronounced for lower densities. There are critical values for $l/2R$ that represent the ratio of the edge length (l) to the radius of curvature (R). In our data we observed that the elastic modulus values of the lowest density foams (25%) deviates the most from the Gibson and Ashby prediction, which seems to agree with the overall trend. Basically, this can be an effect of the high density of our material since pore size approaches the ligament size.

Brezny and Green[31] studied the effect of cell size (4.5 mm to 400 μm) on the elastic properties of macroporous foams and demonstrated that modulus values were independent of cell size as long as the modulus of the solid ligament (strut) material did not change. On the other hand, Mathur and Erlebacher[9] reported a fourfold increase in the Young's modulus, from ~10 to ~40 GPa, as the ligament diameter decreases from >12 to 3 nm. In principle, the high surface-to-volume ratio of the nanoscale ligaments in nanoporous Au could affect the elastic properties of the ligaments: one can think of the ligaments as core-shell structures, where the core has bulklike properties, and the shell exhibits elastic properties reflecting the reduced coordination number of surface atoms. Depending on the actual electron redistribution caused by reduced coordination of surface atoms, the surface can become either softer or stiffer. Recent theoretical studies on Cu[32] showed that the effect of free surfaces on elasticity depends also on crystal orientation. Typically, the effect is relatively small, and the Young's modulus does not change by more than 50%. In the case of Au nanowires, the elastic properties seem not to be affected by the diameter (40–240 nm diameter).[16] Thus, the pronounced increase in stiffness of ultrafine np-Au reported by Mathur and Erlebacher[9] could potentially be an artifact of an increased level of residual Ag which, in turn, increases the density (the preparation of ultrafine material requires dealloying conditions that strongly suppress surface diffusion). In conclusion, most of the available data for np-Au (including this work) seems to support the idea that there are little or no ligament size effects in the elastic properties. The relative density of np-Au, on the other hand, seems to affect the elastic properties more strongly than predicted.

IV. CONCLUSIONS

In this manuscript, the effects of residual Ag on the elastic properties of np-Au foams by using two different sets of samples: partial dealloyed and Ag coated np-Au samples prepared by a wet impregnation technique are presented. Partial dealloyed samples exhibit a strong Ag concentration gradient with Ag-poor surfaces and a Ag-rich bulk, whereas the wet impregnation technique leads to a homogeneous Ag coating distribution that can be adjusted within the range of 0–20 at.%.

This work supports the argument that there are important limitations inherent in the Gibson and Ashby derivation for predicting the elastic modulus of foams based solely on deformation via ligament bending. For foams with densities between 25 and 40%, other contributions to deformation, such as from ligament compression and extension must be included. These deformation modes can be affected by the density of the metal comprising the ligaments, hence the dramatic changes observed in the modulus as the silver concentration changed from 1 to 20 at.%. The final results do not support the idea of ligament size effects of the elastic modulus in np-Au. Overall, the addition of small amounts of silver to np-Au allows one to adjust the elastic modulus by increasing the foam's density, thus providing the possibility of tailoring the elastic properties for future applications.

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