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Size-dependent ion-induced densification of nanoporous gold

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ABSTRACT

Relative density is a major factor governing the mechanical properties of (nano-)porous materials. In nanoporous gold, a correlation between relative density and the ligaments aspect ratio was recently reported as the result of a meta-study that measured hundreds of published images. The effects of ion-irradiation on nanoporous structures however are not yet well explored. We irradiated samples of nanoporous gold of two different initial characteristic lengths with 30 keV Ga⁺ ions. The degree of densification was found to be higher for the samples with finer ligaments and to proceed by thickening of ligaments besides the reduction in length also observed in the coarser samples. The proportionality between relative density and aspect ratio in the ion irradiated samples was found to agree well with the previously reported results from specimens of various processing and coarsening routes. The present study points at ion irradiation as a tool to tune these parameters in nanoporous structures and suggests that the correlation between relative density and aspect ratio may be involved in the volume contraction observed during the formation of nanoporous samples by dealloying.

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1. Introduction

Nanoporous gold (np-Au) has been extensively studied in recent years due to the unusual properties arising from its high surface-to-volume ratio, making it an appealing material for applications as catalyst, sensor, actuator, et cetera. Recently, attention has been focused on the precise characterization of its structure that generally consists of a bicontinuous network of ligaments and pores with a relative density that spans from 0.3 to 0.9 [1–3]. One motivation of these studies is the observation that the networks effective Young's modulus shows an anomalous dependence on the relative density and deviates from the Gibson-Ashby power-law descriptor for macroporous cellular materials [4,5]. Despite nanoporous materials being usually described by their relative density (or solid fraction) and average ligament size, it has been shown that network topology is one of the main parameters governing the mechanical behavior [6]. In this description, it is rather the connectivity density, or the density of load-bearing 'ring' structures that defines a given nanoporous response [1,7]. Nanoporous structures with varying relative densities but constant connectivity were shown to agree well with the classical Gibson-Ashby equation describing modulus as a function of relative density with respect to the dense counterpart in a power law fashion (power of 2) [8].

Ion-induced effects on nanoporous gold so far have either been reported as secondary observations [9–11] or with a focus on the effects on single ligaments or pores [12]. In the present communication, the evolution of the nanoporous network in samples with two distinct initial ligament average sizes is shown to differ under irradiation with Ga⁺ ions. Both samples showed an increase in the irradiated surface relative density associated with an increase in the ligaments width-to-length (d/l) ratio. Interestingly, the densification rate was higher for the sample with smaller characteristic sizes ($d_0 \sim 15$ nm), where the increase in d/l proceeded by simultaneous increase in diameter and decrease in length. For the sample with $d_0 \sim 35$ nm, the change in aspect ratio occurred only by decrease of ligament length with no observed thickening. A detailed understanding of the effects of ion irradiation on nanoporous structures may provide a practical tool to tune their parameters over the ion-implantation range with a FIB.

2. Methods

Nanoporous Au samples were synthesized by free corrosion of commercial AuAg foils on nitric acid solution. Different alloy compositions Au₂₅Ag₇₅ and Au₃₅Ag₆₅ and different etching times (5, 30 and 180 min) were used to achieve diverse structure size distributions. The samples were collected with gold TEM grids, rinsed with distilled water and dried in air. Finally they were mounted on a home-made holder to allow positioning of the films normal parallel to the ion beam in a Tescan Lyra SEM-FIB dual-beam system. The samples were irradiated with 30 keV Ga⁺ ions in steps up to a fluence $\sim 1.3 \times 10^{15}$ cm⁻².

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It is interesting to note that the methods for measuring nanoporous structures vary in literature and often depend on presumptions. For instance when measuring the characteristic peak of a micrographs FFT power spectrum [13], the determination of ligament and pore sizes relies on an assumption of their size ratios. Similarly, when measurements are made on a binarized image, the choice of the threshold value obviously determines the ligament/pore size ratios as well as the relative

density ϕ . The assumption of a 1:1 ratio (implying $\phi = 0.5$) has been used to justify the choice of threshold value in one early transmission electron tomography study [14]. The Au content in the alloy prior to dealloying and the ensuing macroscopic volume reduction were also used to justify calculated relative densities in the range of 0.25–0.35 [15,16]. To avoid the need for such assumptions the measurements presented here were made automatically by the AQUAMI software [17]

Fig. 1. Comparison of probability density functions of nanostructure network parameters of samples with $d_0 = 15$ nm (a–c) and $d_0 = 35$ nm (d–f) before and after irradiation to the indicated fluence. The ligament and pore diameters were fitted to Gaussian distributions while the ligament lengths were fitted to log-normal distributions. The micrographs from which the measurements originate had all the same field of view.

using scanning electron microscopy images made under identical imaging parameters with a Nova NanoSEM 650.

3. Results and discussion

The measurements of ligament diameter, ligament length and pore diameter were fitted to Gaussian (diameters) and log-normal (lengths) distributions to produce probability density functions (PDF). The PDF distributions before and after irradiation to the maximum fluence are shown in Fig. 1 for the samples with $d_0 = 15$ nm and $d_0 = 35$ nm. All ligament diameter distributions showed standard deviations in the range of 0.33–0.35, in accordance with [11].

While the diameters of the ligaments in the sample with $d_0 = 15$ nm show a small but clear increase ($\Delta d \sim 4$ nm) after ion irradiation, they remain virtually unchanged for the sample with $d_0 = 35$ nm. The decrease in (average) ligament length however is more marked in the latter ($\Delta l \sim 12$ nm) than in the sample with finer ligaments ($\Delta l \sim 7$ nm). In both cases the pore diameters are practically unchanged, although their measured connected lengths decreased (not shown) indicating densification. This counterintuitive effect of densification without decrease in pore diameter is possible due to the latter definition as the distance between each pixel along the pore phase Medial Axis Transform and its closest pixel in the ligament phase (for a detailed description refer to [17]). Because of that, it is possible to have an increase in ligament diameter and length at the expense of the pores connectivity only.

The shape of these distributions stresses the inadequacy of describing nanoporous structures in terms of averaged values. It has been pointed out that properties such as plastic yield and fracture are sensitive to the smallest ligament diameters and lengths within the distribution tail [11]. As can be seen in Fig. 2, a small volume of these samples can present variations of ligament diameters in the range of roughly one order of magnitude.

The different responses to ion irradiation between samples is suggested to stem from the smaller ligament diameters in the sample with $d_0 = 15$ nm (Fig. 1a) being subject to direct breakage by the ion cascades. In the case of thermal coarsening of nanoporous gold, topology has been shown to be an important driving factor – in MD simulations, a decrease in the topological genus caused by ligament ‘pinch-off’ events preceded the increase in ligament diameter [18]. Additionally, studies using a conserved dynamics phase-field model showed that bicontinuous structures exhibit an asymptotic behavior of the scaled genus upon coarsening, with samples of different relative densities reaching the same value of scaled genus [19]. Direct breakage of fine ligaments by the ion beam followed by surface-mediated rearrangement provides a probable explanation for the ion-induced coarsening of the sample with finer ligaments. The decrease in ligament length

observed in both samples is likely to result from plastic flow inside the ligaments due to the formation of highly mobile interstitial defects.

Other effects may arise from high local curvature of small ligaments – enhanced sputtering, for instance. Irradiation of gold nanoparticles and thin films with 25 keV Ga⁺ ions have been simulated with Molecular Dynamics and the sputtering yield was found to be size-dependent with a maximum of roughly three times that of a bulk surface [20]. This effect can be expected to result in high amounts of internal redeposition and subsequent reconfiguration or densification of irradiated nanoporous structures.

Contrary to the present observations under ion-irradiation, for thermal coarsening both the length and diameter of ligaments were observed to increase monotonically with time while the ligaments aspect ratio reach a constant value of ~ 0.66 [21]. The change in the ligaments aspect ratio during thermal coarsening is absent or very small, i.e. (roughly) self-similar [2,3,22].

In pioneering work on the volume change induced by dealloying in the formation of nanoporous gold, coarsening was considered unlikely to be the main mechanism of shrinkage due to the short-range nature of the involved mass transport [23]. Plastic deformation was suggested to play an important role and this concept received support from a recent study using dilatometry techniques [24]. Analysis of the observed shrinkage using sintering models revealed an intermediate value for the exponent regarding mass transport mechanism in the equation for time-dependent isothermal shrinkage. This was interpreted to stem from a main contribution of plastic flow and a smaller degree of surface diffusion.

In a recently published study [3], the AQUAMI code was used to analyze a great number of published images of NPG independent of processing method and degree of coarsening. A proportionality was found between relative density and the ligaments aspect ratio, as opposed to ligament length or diameter alone. As shown in Fig. 3, our measurements of ion-irradiated NPG present the same correlation. These observations support the assumption that the correspondence between ligaments aspect ratio and relative density is a geometric requirement coming from the structures topological equivalence, meaning that any process of densification must lead to an increase of the ligaments thickness-to-length ratio and vice-versa.

From these considerations a resemblance can be drawn between 1. the ion-induced densification due to the bulk diffusion of highly mobile interstitial defects and 2. the shrinkage observed during the formation of nanoporous gold by capillarity-driven densification of the initially formed structure. Since the initial ligament diameters lie in the range of 2 to 3 nm according to simulations [25,26], the change in ligaments aspect ratio as the structure coarsens may be responsible for the observed macroscopic contractions.

4. Conclusion

A size-dependent behavior for coarsening and densification of nanoporous gold irradiated with 30 keV Ga⁺ ions is reported. Two average length scales i.e. 15 nm and 35 nm were studied and the higher rate of densification of the finer samples was attributed to an increase in average ligament diameter which was not observed for the sample with larger ligaments. The relation between relative density (as assessed by 2D micrographs) and ligaments aspect ratio follow the trend reported in the literature and is suggested to be associated with the volume change observed during the formation of nanoporous gold by dealloying.

Our observations suggest that nanoporous materials with open-cell porosity are ill-suited for nuclear applications as structural materials. On the one hand, the high specific surface area facilitates the removal of radiation defects from the bulk of ligaments; on the other hand, it stimulates the radiation-induced coarsening and sintering, which results in negative swelling, i.e. dimensional instability.

Fig. 2. Bright field image of sample with $d_0 = 35$ nm. Red arrows highlight the variation in ligament diameter. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. Correlation between relative density (as assessed by 2D area fraction from SEM images) and ligament aspect ratio for samples with $d_0 = 15$ nm (squares) and $d_0 = 35$ nm (circles). The insets show SEM images of the initial and final structures for the sample with $d_0 = 15$ nm (field of view of 500 nm). The crosses are measurements performed with the same code for NPG from various processing methods and degrees of coarsening from the Supplementary Dataset provided in [3].

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