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Defects evolution in nanoporous Au(Pt) during dealloying

Panpan Gao [a], Zhejie Zhu [b], Xinglong Ye [c], Yichu Wu [b], Haijun Jin [c], Alex A. Volinsky [d], Lijie Qiao [a], Yanjing Su [a,*]

[a] Corrosion and Protection Center, Key Laboratory for Environmental Fracture (MOE), University of Science and Technology Beijing, Beijing 100083, People's Republic of China
[b] School of Physics and Technology, Hubei Nuclear Solid Physics Key Laboratory, Wuhan University, Wuhan 430072, People's Republic of China
[c] Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, People's Republic of China
[d] Department of Mechanical Engineering, University of South Florida, Tampa, FL 33620, USA

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ABSTRACT

The vacancies and small voids evolution within the ligaments of nanoporous (np) Au(Pt) in dealloying processes were investigated by positron annihilation spectroscopy. The np Au(Pt) samples with 5–8 nm ligaments were prepared by electrochemical dealloying of $(Au_{0.95}Pt_{0.05})_{25}Ag_{75}$ ingots. The positron lifetime of as-prepared np Au(Pt) consists of the two main components. One is assigned to the positron annihilation at vacancies within the nano-ligaments and the other to the positron annihilation in the enclosed voids in the ligaments. Vacancy concentration increased significantly when silver atoms leached out further from the np structure, which supports the vacancy-mediated lattice diffusion mechanism of porosity evolution.

Nanoporous (np) metals with bicontinuous open porosity have attracted researchers in recent years. They are of critical importance in many technological applications, such as catalysts [1,2], sensors [3–7], battery electrodes [8], super-capacitors [9] and actuators [10–13], due to the small pore size and high porosity. The np metals are commonly synthesized by dealloying in which one or more elements are chemically or electrochemically dissolved from a homogenous alloy. Nanoporous gold (npg) is a typical np structure formed by dealloying silver from the Au–Ag alloy and exhibits sponge-like open cell foam structure characteristics. The mechanism of the dealloying process and detailed characterization of the structure formed in the dealloying process have been extensively studied in previous publications [14–20].

The morphological evolution in dealloying process is multi-scale, involving dissolution kinetics, surface diffusion and mass transport through the bulk of both the alloy and the electrolyte. Understanding the process of porosity formation during dealloying has been the subject of considerable discussion both theoretically and experimentally. Theoretically, Erlebacher et al. employed a kinetic Monte Carlo method to study the evolution of nanoporosity during dealloying, where porosity evolution is controlled by the rate at which gold atoms diffuse with receding step edges rather than being left behind as a nonequilibrium supersaturated adatom lattice gas when silver in terraces is attacked by an electrolyte [14]. Further work by Zinchenko et al. presented the Metropolis Monte Carlo study of the dealloying mechanism leading to the formation of the np structure [17]. They simulated both the chemical reaction processes and the movement of the various particles (gold, silver, acid, reaction products and vacancies), and showed that only a narrow range of interaction parameters yields acceptable physically realistic structures. Recently, Ye et al. [20] demonstrated experimentally that dealloying occurred by two steps: a primary dealloying process that selectively dissolved Ag from the parent alloy and created a np structure, and a secondary dealloying process that occurred behind the corrosion front and further dissolved residual Ag from the nanoligaments. They also pointed out that the mechanism of the primary dealloying was the percolation dissolution. However, the secondary dealloying mechanism remained unclear. The existing mechanisms, i.e., the vacancy-mediated lattice diffusion, suggests that the Ag atoms diffuse to the surface and then get dissolved, leading to the Au-rich surface layer and Ag-rich core structure [21]. The other mechanism is the surface dealloying, which occurs only in a few monolayers thick surface layer during dealloying of the Au–Ag particles [22]. They gave an implication that the change of vacancy concentration during the secondary dealloying was a challenging issue. Also, Rösner et al. [23] discovered abundant enclosed voids within the ligaments, which are much smaller than the ligament size, using TEM tomography. Viswanath et al. [24] recently showed the presence of vacancies and the migration of vacancies by the positron annihilation study. These studies point to the importance of defects in the formation of np structure and the coarsening process.

Smaller ligament size leads to better performance. Higher potential in electrochemical dealloying process yields a smaller ligament diameter and pore size for npg. To get ultrafine structure np samples and stabilize the nanoscale structure, some strategies have been devised, such as tuning the ratio of the alloy precursor elements [25,26], controlling the dealloying conditions [27,28], and through addition of noble alloying elements [10,29,30]. Some studies showed that adding small amounts of Pt to the precursor Ag–Au master alloy stabilized its

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* Corresponding author.
E-mail addresses: volinsky@usf.edu (A.A. Volinsky), yjsu@ustb.edu.cn (Y. Su).

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morphology and prevented coarsening. In this study, very small amount of Pt was added into the initial $Au_{25}Ag_{75}$ ingots, hoping to stabilize npg. Pt-doped npg samples exhibit small ligament size (~5 nm), and are stable against coarsening at low temperature. It should be noted that Pt, having significantly smaller surface diffusivity than Au, can affect the dealloying process and the np structure evolution, and thus suppress the np structure coarsening.

Positron annihilation is a well-established technique to study electronic and defect properties of materials. Measurements of lifetime spectra and analysis in terms of various annihilation components, coupled with theoretical estimates of positron lifetime in various defect clusters, have been successfully used to investigate the evolution of defects in dealloying. In this study, the changes of defects in Pt-doped npg (np Au(Pt)) were investigated by positron annihilation spectroscopy to reveal the dealloying mechanism during the two dealloying processes.

$(Au_{0.95}Pt_{0.05})_{25}Ag_{75}$ ingots were prepared by the arc-melting of the high purity (>99.99%) silver, gold and platinum wires in argon atmosphere. The ingots were homogenized at 850 °C for more than 100 h, cut into $10 \times 10 \times 1$ mm^3 samples and then annealed at 600 °C for 4 h. The np Au(Pt) samples were prepared by dealloying $(Au_{0.95}Pt_{0.05})_{25}Ag_{75}$ ingots at 1.04 V under potentiostatic control (AUTOLAB PGSTAT302N) in 1 M $HClO_4$ at ambient temperature, and then higher 1.35 V potential was applied to dissolve the residual Ag atoms. A silver wire and a saturated calomel electrode (SCE, Shanghai Leici Instrument Factory) were used as the counter and reference electrodes, respectively. For the post-dealloying treatment, a large piece of npg as the counter electrode was used. Aqueous solution was prepared from guaranteed reagent grade $HClO_4$ (Sinopharm Chemical Reagent Co., Ltd.) and ultrapure water (18.2 MΩ). The morphology and the ligament size were characterized using scanning electron microscopy (SEM, FEI NOVA SEM430) of the cross-sectioned np sample surfaces. The residual Ag content was measured using energy dispersive spectroscopy (EDS, FEI NOVA SEM430) on the np samples cross-section surface. Positron lifetime spectrum was measured using a fast–fast coincidence system with the 220 ps time resolution of full width at half maximum. Two lifetime spectra were measured for the samples to check the measurement reliability. The ^{22}Na positron source with intensity of about 5 μCi was sandwiched between two identical sample pellets for the measurements. All measurements were carried out at room temperature.

The np Au(Pt)-1 samples were prepared by dealloying the $(Au_{0.95}Pt_{0.05})_{25}Ag_{75}$ ingots at 1.04 V, and the residual composition of the dealloyed material was measured by EDS and found to be 45 at.%. It is noted that there is a significant quantity of residual silver left behind in the core of the ligaments. The silver is prevented to dissolve further by Au and Pt present on the ligament surface. The latter np Au(Pt)-2 samples were prepared by applying a higher potential of 1.35 V to dissolve the residual Ag atoms further in the np Au(Pt)-1 sample, and the EDS results show around 5 at.% of the residual silver. The SEM images show uniform np structure of np Au(Pt)-1 and Au(Pt)-2 samples with a small ligament size of 5–8 nm, as shown in Fig. 1. The Pt-doped np gold samples exhibit small ligament size compared with the Pt-free np Au samples. In order to investigate the role and the morphology of defects in the two dealloying processes, positron lifetime measurements of the two different states of the samples have been carried out.

Based on the theory of positron lifetime, Viswanath et al. [24] inferred that in the npg the first lifetime component τ_1 is associated with positron annihilation in the ligaments containing vacancy type defects. The second component τ_2 corresponds to positron annihilation at the vacancy clusters/voids at the ligament-pore interface. In the early studies [31] of positron behavior in nanocrystalline gold prepared by gas condensation method, two lifetime components with $\tau_1 = 180$ ps and $\tau_2 = 370$ ps were observed. The presence of a second component pointed to the presence of micro-voids in nanocrystalline gold. Recently more experimental [23] and simulation [32,33] results revealed a large amount of 0.5–2.5 nm enclosed voids within the ligaments in npg. Thus, one would be inclined to think that the second component τ_2 corresponds to positron annihilation in the enclosed ligament voids, which formed in the dealloying process. The longest lifetime τ_3 is the ortho-positronium annihilation lifetime, and its intensity I_3 is relatively small at about 3%.

Table 1 shows the positron lifetime parameters in the np Au(Pt), compared with the bulk Au samples and the initial alloy. From Table 1, the first component τ_1 value (~167 ps) of the as-dealloyed np Au(Pt)-1 samples containing 45 at.% residual silver, is significantly increased compared with the bulk Au and the initial alloy, while the τ_1 value (207 ps) of the np Au(Pt)-2 samples, which dissolved residual Ag from np Au(Pt)-1 samples, containing around 5% residual silver, has the largest value than others. The τ_1 value implies that abundant vacancies are present in the ligament of the np Au(Pt) samples, and these defects play a crucial role in dealloying. It can be expected that the vacancies in the np Au(Pt) ligaments were produced by electrochemical leaching of Ag.

From the experimentally measured values of τ_1, the vacancy concentration can be estimated using a positron-trapping model [34], and the specific positron trapping coefficient μ_v value of 1.35×10^{14} s^{-1} for vacancies in Au [35] has been assumed. The vacancy concentration computed in the pre-annealed npg (τ_1 ~ 209 ps) is ~0.4% [36]. In this study, the computed vacancy concentration from the τ_1 value of 167 ps in np Au(Pt)-1 samples prepared by the primary dealloying process and 207 ps in np Au(Pt)-2 after the secondary dealloying process is on the order of 10^{-5} and 10^{-3}, respectively. This is a significantly higher excess vacancy concentration than the equilibrium vacancy concentration of ~10^{-15} at room temperature. The Metropolis Monte Carlo study [17] also showed that vacancies in the sample are represented by voids that are randomly located in the initial configuration. During the dealloying process, a large number of vacancies formed as the

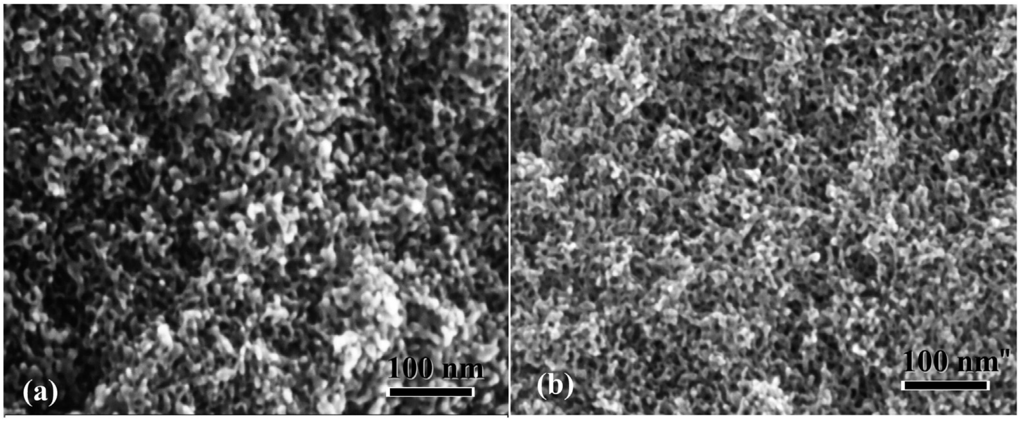

Fig. 1. SEM images of (a) np Au(Pt)-1 sample dealloyed from $(Au_{0.95}Pt_{0.05})_{25}Ag_{75}$ ingots at 1.04 V and (b) np Au(Pt)-2 sample dealloyed from np Au(Pt)-1 sample at 1.35 V.

Table 1
Positron annihilation lifetime parameters τ_1, τ_2, τ_3, I_1, I_2, I_3 for bulk Au, $Au_{25}Ag_{75}$ alloy, np Au(Pt)-1 prepared by primary dealloying (containing 45 at.% residual silver), and np Au(Pt)-2 prepared by the secondary dissolution of Ag (containing 5 at.% residual silver).

Positron annihilation lifetime parameters						
Sample	τ_1, ps	τ_2, ps	τ_3, ps	I_1, %	I_2, %	I_3, %
Bulk Au	122	–	–	100	–	–
$Au_{25}Ag_{75}$	129	–	–	100	–	–
np Au(Pt)-1	167	348	2336	26.1	70.5	3.4
np Au(Pt)-2	207	365	2332	37.7	59	3.3

Values for bulk Au and $Au_{25}Ag_{75}$ alloy are from the reference [24].

results of chemical reactions. Simulations also showed high density of sources for “vacancy-injection” in dealloying. This physical model is in good agreement with the experimental results of this paper.

In the secondary dealloying process, the vacancy concentration vastly increased when silver atoms leached out further from the np structure. This high vacancy concentration in nano-ligaments reflects the non-equilibrium conditions of the np structure evolution and the high driving force for dissolution relative to surface diffusion. A combination of surface and volume diffusion leads to a geometrical instability of the surface during selective dissolution [37]. It also shows that selective dissolution of the less noble atoms in the alloy should lead to the creation of surface vacancies. These vacancies can then migrate across the surface to form pits, steps and other surface roughening features, or they can assist the migration of the residual more noble atoms, leading to island growth. These surface vacancies (or divacancies) can also diffuse into the underlying alloy to assist volume diffusion of the less noble metal at the corroding surface. The results of this study imply that there are large amounts of vacancy defects forming within the ligaments due to the complicated morphology evolution of the np structure, and a large amount of surface vacancies diffuse into the ligaments when the Ag atoms leach out further due to the higher applied voltage. High concentration of excess vacancies in the ligaments revives the vacancy-mediated lattice diffusion mechanism of porosity evolution.

The second component of lifetime, τ_2 has a value of ~348 ps in the np Au(Pt)-1 samples prepared by the primary dealloying process and ~365 ps in the np Au(Pt)-2 prepared further by the secondary dealloying process for the dissolution of residual Ag from the np Au(Pt)-1 samples. This lifetime value indicated positron annihilation in vacancy clusters or small voids within the ligaments. There is a very tiny increase in the second component τ_2, meaning that small voids gather together or new larger voids form within the ligaments through coarsening by leaching Ag. Although void bubbles in metals are often associated with vacancy agglomeration, Erlebacher [32] used large-scale kinetic Monte Carlo simulations to show that the bubbles were formed naturally during surface-diffusion-controlled coarsening, and are topologically complementary to ligament pinch-off. In our study, the np structure coarsening has been suppressed by the addition of Pt atoms, and the τ_2 value changes slightly in the secondary dissolution of residual Ag from the np Au(Pt) samples.

Doppler broadening of annihilation radiation technique was used to study the defects evolution at different depths in dealloyed npg samples by using slow positron beam apparatus. The Doppler broadening was characterized by the conventional S parameter, i.e. the low-momentum annihilation fraction, which is defined as the ratio of the central area (510.24–511.76 keV) to the total area. The S parameter results as a function of positron incident energy (mean depth) varied from 0.18–20.18 keV show that the S parameter in fresh npg increased significantly at the same depth compared with the initial Au–Ag alloy. This result further proved that many vacancies formed in the dealloying process, and also showed that the vacancy concentration increased with the dealloying time.

It was demonstrated that the initial np Au(Pt) samples, where coarsening was suppressed by the addition of Pt, contained 45% residual Ag in the primary dealloying process. In the secondary dealloying of residual Ag dissolution from the np Au(Pt) samples, there was ~5% Ag content left behind. The vacancies in the Au ligaments, which are retained during the dealloying process, are the vital part of the np structure formation. The vacancy concentration increased significantly when silver atoms leached out further from the np structure by the secondary dissolution of residual Ag compared with primary dealloying. This high concentration of excess vacancies in the ligaments formed in the dealloying process supports the vacancy-mediated lattice diffusion mechanism of porosity evolution.

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