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Defects evolution of nanoporous AuAg(Pt) during thermal coarsening

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ABSTRACT

Vacancies and voids evolution within the nanoporous (np) AuAg(Pt) ligaments during thermal coarsening was investigated by positron annihilation spectroscopy and scanning electron microscopy (SEM). Partially dealloyed ternary np AuAg(Pt) samples with 5–8 nm ligaments were prepared by electrochemical dealloying of $(Au_{0.95}Pt_{0.05})_{25}Ag_{75}$ ingots. Positron lifetime experiments demonstrated that nano-ligaments are stable against coarsening below 320 °C. Vacancies play an essential role during the coarsening process. Lifetime parameters changed above 320 °C, associated with a large number of vacancies and divacancies formed via coarsening with large enclosed voids formed at the same time. SEM images demonstrate ligaments growing non-uniformly during thermal coarsening.

Dealloying, a chemical or electrochemical corrosion process, which selectively dissolves elemental components from a homogenous alloy [1,2], is commonly used to fabricate nanoporous (np) metals with a variety of applications including catalysts [3,4], sensors [5–9], actuator [10–13], battery electrodes [14], heat exchanges [15] and supercapacitors [16]. Np metals exhibit a typical sponge-like open cell foam structure with tunable pores and ligaments sizes of 3–50 nm [2,4], which is predominantly determined by the initial composition of the parent alloy [17,18] and the dealloying parameters [19,20]. Also, ligament and pore size can be controlled by post-dealloying treatments, such as thermal annealing process. The metal nanoligament can be coarsened by thermal annealing to the micrometer scale [21,22]. Understanding this thermal annealing process has been of practical interest to tune the pore and ligament sizes in order to optimize mechanical, chemical and optical properties of np metals [23,24]. Furthermore, detailed characterization of the defects structure in np metals during the thermal annealing is an emerging fundamental research field.

Since the formation and coarsening mechanisms of np gold are difficult to determine by experiments, researchers proposed some theoretical models and simulated this process. The primary model of the formation and coarsening of np gold was the classical surface-diffusion-controlled smoothening model, which relies on temperature and time [25–27]. However, such a model is not sufficient to explain all experimental observations in np gold formation, such as small voids within ligaments. A coarsening model based only on surface diffusion would predict that enclosed voids would not form, whereas ligaments in some np gold samples were found to contain voids using Transmission Electron Microscope tomography [28]. Theoretically, Erlebacher [29] showed that the shape evolution is controlled not only by smoothing of the high curvature surface regions, but rather by topological genus-decreasing events manifested as solid state Rayleigh instability. Kinetic Monte Carlo simulations also show void bubble formation during coarsening accompanied by the ligament pinch-off. Viswanath et al. [30] showed the presence of vacancies and the migration of vacancies by the positron annihilation study. These studies point to the importance of defects in nanoligament coarsening process.

Positron annihilation spectroscopy has been widely used as a probe for the determination of defects at the atomic level in solids, including vacancies, vacancy clusters, dislocations and nanometer-scale voids [31,32]. Positrons have high propensity for defects in the materials that lead to a longer lifetime due to lower electron density. Thus positron lifetimes can be directly correlated with the size and concentration of defects. As an example, Shirai et al. have investigated the variation of positron lifetime in quenched gold and have been able to identify the evolution of vacancies to form stacking fault tetrahedra [33]. In this study, the changes of defects in Pt-doped np AuAg (np AuAg(Pt)) were investigated by positron annihilation spectroscopy to understanding the thermal coarsening process. Measurements of lifetime spectra, 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 the coarsening process. A small amount of the Pt element was alloyed into the initial $Au_{25}Ag_{75}$ ingots, hoping that the stability of np structure would be improved [34,35]. It should be noted that Pt, having significantly smaller surface diffusivity than Au, can affect the dealloying

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process and the np structure evolution, and thus suppress the np structure coarsening. The Pt-doped np AuAg samples exhibit small ligament size of about 5 nm, and are stable against coarsening at low temperature.

$(Au_{0.95}Pt_{0.05})_{25}Ag_{75}$ 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 >100 h, cut into $10 \times 10 \times 1$ mm^3 samples and then annealed at 600 °C for 4 h. The np AuAg(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. A silver wire and a saturated calomel electrode (SCE, Shanghai Leici Instrument Factory) were used as the counter and reference electrodes, respectively. 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.

It is noted that the residual composition of the np AuAg(Pt) samples was measured by EDS and found to be $(Au_{0.95}Pt_{0.05})_{55}Ag_{45}$. There is a significant quantity of residual silver left behind in the core of the ligaments. The silver element is prevented to dissolve further by Au and Pt present on the ligament surface. The SEM images show uniform np structure with a small ligament size of 5–8 nm. In order to investigate the role and the morphology of defects in the coarsening process, positron lifetime measurements of the np AuAg(Pt) samples, which contains 45% residual silver, have been carried out as a function of annealing temperature.

Fig. 1 shows the high resolution SEM images of as-prepared np samples microstructure and its evolution with annealing temperature. The duration of each annealing experiment was 30 min. SEM images were analyzed using the ImageJ software to obtain the ligament size variation with the annealing temperature. The nano-ligaments are stable against coarsening at the annealing temperature below 350 °C, and the ligament size does not change appreciably. Above 350 °C, the increase of the ligament sizes is non-uniform. It is obvious from the 400 °C and 450 °C images that some ligaments grow unusually larger, while others still remain small. There is obvious improvement in the stability of the samples with added Pt compared with basic np gold, whose ligament size coarsens to dozens of nanometers for the same conditions. The ligaments grow non-uniformly due to the non-uniform segregation and accumulation of Pt on the surface, and Pt atoms pinning mobile step edges.

Our earlier positron studies [36] of the np AuAg(Pt) regarding the dealloying process have indicated lots of vacancies forming within the ligaments in the dealloying process, and these defects play a crucial role in the dealloying process. 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. It is noted that the positron lifetime in the as-prepared np AuAg(Pt) is fitted with a sum of two lifetime components with τ_1 ~ 167 ps and τ_2 ~ 348 ps, with the former associated with the positron annihilation in ligaments containing vacancy defects and the latter corresponding to positron annihilation from the encased voids within the ligaments formed in the dealloying process. More experimental [29] and simulation [28,37] results reveal a large amount of 0.5–2.5 nm enclosed voids within the ligaments which are in good agreement with our experimental results.

Fig. 2 shows variations of the positron lifetime components τ_1 and τ_2, and their corresponding intensities I_1 and I_2, as well as the average lifetime $\tau_m = (\tau_1 I_1 + \tau_2 I_2) / (I_1 + I_2)$, with the annealing temperature. In Fig. 2(a) τ_1 increases up to 280 °C with a small peak in the low temperature range, after which there is a second τ_1 peak, followed by a decrease with the annealing temperature, finally reaching a steady value. The variation of τ_2 with the annealing temperature in Fig. 2(b) shows little change below 280 °C, followed by a significant increase around 300 °C, after which the τ_2 variation is found to be very small. The accompanied changes in I_1 and I_2 in Fig. 2(c) exhibit an opposite trend. The average lifetime τ_m in Fig. 2(d) increases at first below 350 °C and then decreases monotonously with the annealing temperature.

The first component of the lifetime τ_1 represents the intensity-weighted average of the positron lifetime in the bulk and at vacancy defects. In the beginning of the annealing process, both atomic and vacancy diffusion increased due to the temperature rise. At the early stage, a small decrease in τ_1 can be assigned to annealing out vacancies in the as-prepared np AuAg(Pt). Ag atoms diffuse from the interior to the surface of the Au ligaments, which leaves non-equilibrium vacancies in the ligaments. When Ag atoms diffuse out completely, further gradual decrease in τ_1 is due to annealing out vacancies, until 280 °C. It is seen

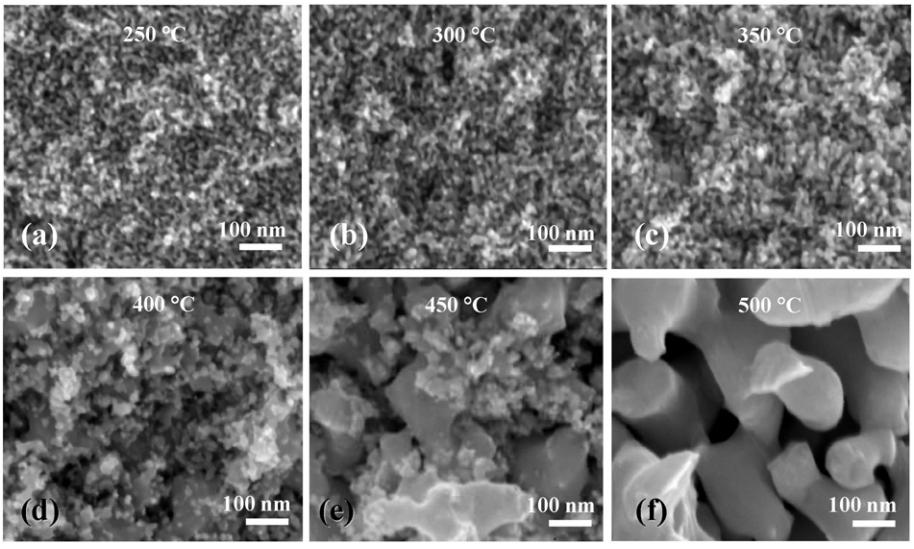

Fig. 1. Microstructure evolution of the np AuAg(Pt) with the annealing temperature. SEM micrographs of the np AuAg(Pt) obtained after annealing at various temperatures: (a) 250 °C; (b) 300 °C; (c) 350 °C; (d) 400 °C; (e) 450 °C and (f) 500 °C for 30 min.

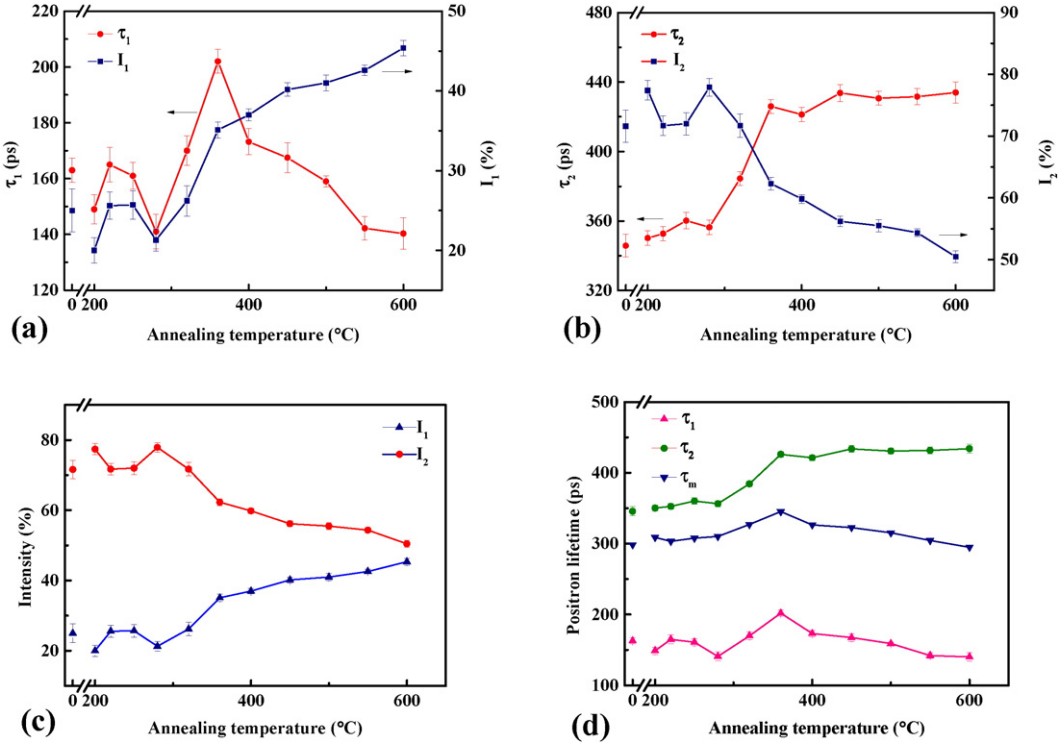

Fig. 2. Variation of the positron lifetime parameters: (a) τ_1 and I_1; (b) τ_2 and I_2; (c) I_1 and I_2; (d) τ_1, τ_2 and τ_m with the annealing temperature of the np AuAg(Pt).

that τ_1 has a sharp increase at 320 °C when the ligament starts growing, and the ligament growth is non-homogeneous. A number of vacancies are generated in the ligaments with the growth of the ligaments. Also, the accompanied change in I_1, which has similar variation with τ_1, means the generation of vacancies. It should also be noted that the variation of τ_1 starts decreasing above 360 °C.

Based on the kinetic Monte Carlo simulations performed using dealloyed nanoparticles, Erlebacher [28] concluded that coarsening is controlled by the ligament pinch-off associated with the Rayleigh instabilities, and the bubbles are formed naturally during surface-diffusion-controlled coarsening, and are topologically complementary to ligament pinch-off. It is said that in porous metals, coarsening proceeds by reduction of the overall surface energy, surface-diffusion currents proportional to gradients in the local surface chemical potential, and also by ligament pinch-off in which surface diffusion pulls material away from the saddle-point curvature ligament, which thins to one atom thick and then breaks. Also, Kolluri et al. [37] showed that restructuring of the network of interconnected ligaments causes coarsening in np gold using atomistic modeling. It is said that the restructuring arises from the collapse of some ligaments onto neighboring ones and is enabled by localized plasticity at ligaments and nodes. Competitively, these two mechanisms may explain the occurrence of enclosed voids and reduction in volume in np metals.

In our study, the positron lifetime τ_2 indicates annihilation in the enclosed voids in the ligaments. It is seen that the variation of τ_2 is found to be very small before 280 °C, meaning that there is almost no coarsening at this stage. It is noted that around 320 °C, some ligaments pinch-off into coarser ligaments, leading to larger voids formation. Also a very small variation above 360 °C means that the void diameter remains unchanged when the ligament size increases further. It gives an implication that the coarsening mechanism may change when the ligament size reaches a certain value. However, more experiments and simulations are needed to provide a clear explanation of the coarsening mechanism.

It was demonstrated that the vacancies in the AuAg ligaments, which are retained during the dealloying process, are the vital part of the np structure formation. The thermal stability is improved by the addition of Pt atoms, and the positron lifetime experiments demonstrated that the nanoligaments are stable against coarsening at the annealing temperature below 320 °C. The increase of the ligament size is non-uniform around 320 °C with the increase, migration and diffusion of vacancies. This implies that the vacancy defects play a critical role in the ligament coarsening.

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References

[1] J. Erlebacher, M.J. Aziz, A. Karma, N. Dimitrov, K. Sieradzki, Nature 410 (2001).
[2] J. Weissmüller, R.C. Newman, H.J. Jin, A.M. Hodge, J.W. Kysar, MRS Bull. 34 (2009) 577.
[3] A. Wittstock, V. Zielasek, J. Biener, C.M. Friend, M. Baeumer, Science 327 (2010) 319.
[4] Y. Ding, M.W. Chen, J. Erlebacher, J. Am. Chem. Soc. 126 (2004) 6876.
[5] S.O. Kucheyev, J.R. Hayes, J. Biener, T. Huser, C.E. Talley, A.V. Hamza, Appl. Phys. Lett. 89 (2006) 053102.
[6] J.F. Huang, I.W. Sun, Adv. Funct. Mater. 15 (2005) 989.
[7] M. Hieda, R. Garcia, M. Dixon, T. Daniel, D. Allara, M.H.W. Chan, Appl. Phys. Lett. 84 (2004) 628.
[8] E. Detsi, Z.G. Chen, W.P. Vellinga, P.R. Onck, J.T.M. De Hosson, J. Nanosci. Nanotechnol. 11 (2012) 4951.
[9] E. Detsi, Z.G. Chen, W.P. Vellinga, P.R. Onck, J.T.M. De Hosson, Appl. Phys. Lett. 99 (2011) 083104.
[10] H.J. Jin, X.L. Wang, S. Parida, K. Wang, M. Seo, J. Weissmüller, Nano Lett. 10 (2010) 187.
[11] J. Weissmüller, R.N. Viswanath, D. Kramer, P. Zimmer, R. Wurschum, H. Gleiter, Science 300 (2003) 312.
[12] E. Detsi, S. Punzhin, J. Rao, P.R. Onck, J.T.M. De Hosson, ACS Nano 6 (2012) 3734.
[13] E. Detsi, S.H. Tolbert, S. Punzhin, J.T.M. De Hosson, J. Mater. Sci. 10 (2015) 1007.
[14] Y. Yu, L. Gu, X.Y. Lang, C.B. Zhu, T. Fujita, M.W. Chen, J. Maier, Adv. Mater. 23 (2011) 2443.
[15] Y. Tang, B. Tang, J. Qing, Q. Li, L. Lu, Appl. Surf. Sci. 258 (2012) 8747.
[16] X. Lang, A. Hirata, T. Fujita, M.W. Chen, Nat. Nanotechnol. 6 (2011) 232.
[17] E. Detsi, E. De Jong, A. Zinchenko, Z. Vuković, I. Vuković, S. Punzhin, K. Loos, G. Ten Brinke, H.A. De Raedt, P.R. Onck, J.T.M. De Hosson, Acta Mater. 59 (2011) 7488.

[18] E. Detsi, S. Punzhin, J. Rao, P.R. Onck, J.T.M. De Hosson, J. Mater. Chem. 22 (2012) 4588.
[19] X.L. Ye, N. Lu, X.J. Li, K. Du, J. Tan, H.J. Jin, J. Electrochem. Soc. 161 (2014) C517.
[20] E. Detsi, M. Van de Schootburgge, S. Punzhin, P.R. Onck, J.T.M. De Hosson, Scr. Mater. 64 (2011) 319.
[21] F. Kertis, J. Snyder, L. Govada, S. Khurshid, N. Chayen, J. Erlebacher, JOM 62 (2010) 50.
[22] E. Seker, J.T. Gaskins, H. Bart-Smith, J. Zhu, M.L. Reed, G. Zangari, R. Kelly, M.R. Begley, Acta Mater. 55 (2007) 4593.
[23] A.M. Hodge, J. Biener, J.R. Hayes, P.M. Bythrow, C.A. Volkert, A.V. Hamza, Acta Mater. 55 (2007) 1343.
[24] S.O. Kucheyev, J.R. Hayes, J. Biener, T. Huser, C.E. Talley, A.V. Hamza, Appl. Phys. Lett. 89 (2006) 3.
[25] L.H. Qian, M.W. Chen, Appl. Phys. Lett. 91 (2007) 083105.
[26] C. Herring, J. Appl. Phys. 21 (1950) 301.
[27] J. Erlebacher, J. Electrochem. Soc. 151 (2004) C614.
[28] J. Erlebacher, Phys. Rev. Lett. 106 (2011) 225504.
[29] H. Rösner, S. Parida, D. Kramer, C.A. Volkert, J. Weissmüller, Adv. Eng. Mater. 9 (2007) 535.
[30] R.N. Viswanath, V.A. Chirayath, R. Rajaraman, G. Amarendra, C.S. Sundar, Appl. Phys. Lett. 102 (2013) 253101.
[31] M. Mukherjee, D. Chakravorty, P.M.G. Nambissan, Phys. Rev. B 57 (1998) 848.
[32] P.M.G. Nambissan, C. Upadhyay, H.C. Verma, J. Appl. Phys. 93 (2003) 6320.
[33] Y. Shirai, K. Furukawa, J. Takamura, W. Yamada, S. Iwata, Appl. Phys. A Mater. Sci. Process. 37 (1985) 65.
[34] J. Snyder, P. Asanithi, A.B. Dalton, J. Erlebacher, Adv. Mater. 20 (2008) 4883.
[35] A.A. Vega, R.C. Newman, J. Electrochem. Soc. 161 (2014) C1.
[36] P.P. Gao, Z.J. Zhu, X.L. Ye, Y.C. Wu, H.J. Jin, A.A. Volinsky, L.J. Qiao, Y.J. Su, Scr. Mater. 113 (2016) 68.
[37] K. Kolluri, M.J. Demkowicz, Acta Mater. 59 (2011) 7645.