



Advances in nanoscale characterization of refined nanoporous gold

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ABSTRACT

The effect of Pt on the structural evolution of nanoporous gold (NPG) is complex and is controlled by processes including secondary dealloying of Ag, surface diffusion of Au, and Pt segregation. High-resolution studies are carried out to investigate the interplay of the inherent processes. Observations such as Pt segregation at nanoligament surfaces, core-shell structures of nanoligaments, and Ag retention inside individual nanoligaments are seen at unprecedented detail using high resolution characterization techniques, including Atom Probe Tomography (APT) and Electron Energy Loss Spectroscopy (EELS). Quantitative estimates of the surface area-to-volume ratios of nanoporous layers with different Pt content indicate their relative functionalities for surface area driven applications.

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1. Introduction

Nanoporous gold is usually formed by the selective dissolution of Ag from a binary matrix of Ag and Au (NPG-AgAu) [1–3]. This process, also known as dealloying, could be accomplished chemically in nitric acid [4], or electrochemically in perchloric or sulfuric acid at oxidative potentials [5]. As a result, a 3D, open-pore network with a high surface area-to-volume ratio is formed, making it a promising material for surface area intensive applications such as catalysis [6–8], and actuation [9,10].

The addition of trace concentrations of Pt to the precursor of NPG was shown to have a refining effect on the as-dealloyed structure [11,12]. Newman and Vega showed the systematic effect on the resulting NPG nanostructure (NPG-AgAuPt) due to the addition of Pt concentrations as low as 1–3 at.% [12]. Furthermore, the interaction of Pt atoms with oxygen at temperatures 200–500 °C causes the inhibition of thermal coarsening [13].

The optimization of NPG is important and relies mainly upon a deeper understanding of the inherent dealloying process and the effect of Pt on it. The enhanced characterization of NPG made by dealloying different precursors could reveal structural aspects of the nanoporous layer that remain unclear. In that context, several advances in the atomic scale characterization of nanoporous gold using TEM (Transmission Electron Microscopy) [7,14] and APT

(Atom Probe Tomography) [15], were recently reported. More specifically, the pioneering study by Krekeler et al. [14] presented the first 3D tomographic reconstruction of the chemical microstructure in nanoporous gold, showing ligaments to be consisting of Ag-rich cores with Au-rich shells. The underlying mechanisms that are responsible for the formation of ligaments were also discussed using atomistic simulations.

Limitations imposed by TEM could be overcome using APT, a technique that offers a 3D probe into the atomic-scale features of interest, at a superior resolution [16–18]. A previous publication by the authors reported a novel technique to enable enhanced APT of NPG-AgAu. In that article, the crucial pore infiltration of NPG-AgAu, vital for success of APT, was made possible through a repeatable, straightforward method of inner pore electrodeposition of Cu from acidic solution of copper sulfate [19]. The Cu deposition phenomenon is interesting in its own right as it is crucial for the possible use of NPG as a template for growing functional metallic and metal oxide nanostructures.

The analysis presented in this article provides a systematic comparison of APT results on NPG-AgAu and NPG-AgAuPt with different Pt contents. The effect of Pt on vital properties such as surface area and porosity will be shown to have clear links with the chemical composition of nanoligaments. This in turn leads to a discussion on the effect of Pt on Ag dissolution from ligaments, known as secondary dealloying [20]. Segregation of Pt and Au at the surfaces of nanoligaments will be revealed using APT and EELS analysis of single ligaments from as-dealloyed NPG-AgAuPt.

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2. Experimental

2.1. Dealloying and pore infiltration

Rectangular samples with nominal surface areas of ~ 0.15 – 0.25 cm² were cut out of 200 μ m sheets of cold-rolled Ag₇₇Au₂₃, Ag₇₇Au₂₂Pt₁ and Ag₇₇Au₂₀Pt₃ (at.%) from Goodfellow Metals, Cambridge, UK. The samples were annealed at 925 °C for 15 h in 2.5% H₂–Ar atmosphere. Samples were soldered to Cu electrical wires from one end (taking care not to alter the active surface area to be dealloyed). A fine coating of Microshield TM lacquer supplied by SPI was applied to the solder-Cu-sample junction to insulate it from the solution used.

All solutions were prepared with 18 M Ω cm de-ionized water and de-aerated by high-purity nitrogen purging (min purity: 99.998%). The samples were dealloyed (separately) potentiostatically in a solution of 0.5 M HClO₄ from Analar grade HClO₄ (Alfa-Aesar, 62%), at a potential of 550 mV vs. MSE (Mercury/Mercurous Sulfate Electrode/sat. K₂SO₄), until the removal of 5 C/cm² for the AgAu sample and 0.25 C/cm² for the two AgAuPt samples. The dealloyed samples were then immersed in de-ionized water for approximately 1 h to remove residual acid.

Pore infiltration was then achieved by stepped potentiostatic deposition of Cu in CuSO₄ + H₂SO₄ solution, following the deposition method explained in a previous APT analysis published recently [19]. As shown in Fig. 1, a shallower depth of dealloyed layer was used for the AgAuPt as the range of complete infiltration of porosity before blockage of the surface is limited, possibly due to the refined pore sizes in NPG-AgAuPt. Further studies on the Cu infiltration process and the influence of factors such as pore/ligament diameter, concentration and deposition parameters on the infiltration are ongoing.

2.2. HRTEM-EELS procedure

HR-STEM Analysis on as-dealloyed NPG-AgAuPt₃ was performed using an aberration-corrected FEI Titan 80–300 (FEI Company, The Netherlands) transmission electron microscope equipped with a Gatan Quantum energy filter (Gatan Inc. USA) and a high-brightness electron source. Imaging was carried out using a high-angle annular dark field (HAADF) detector, with compositional mapping obtained using electron energy loss spectroscopy (EELS).

2.3. APT procedure

Samples for APT were prepared via FIB liftout (see Fig. 2). Specimens were extracted and mounted to pre-sharpened Si posts using W deposition, then sharpened into nanoscale needles by annular milling at 30 kV (Fig. 2b). A final sharpening step was performed at 10 kV, in which the tip apex was positioned in the Cu-filled NPG layer (Fig. 2c).

A Cameca local electrode atom probe (LEAP) 4000X HR (Cameca Instruments, USA) was used for APT analysis. Data were acquired in laser-pulsing mode, using a 355 nm UV laser, pulsing at 125 kHz. Laser pulse energy was set to either 35 or 50 pJ/pulse. A DC voltage, ranging from approximately 2–5 kV, was applied to the sample to maintain a target evaporation rate of 0.005 ions/pulse (0.5%). The specimen temperature during analysis was ~ 60 K, and the chamber pressure was $\sim 10^{-8}$ Pa. Reconstruction and analysis of the acquired data were performed using IVAS 3.6.14 software. Reconstructions were spatially-calibrated using SEM images of the tips, taken during FIB preparation.

3. Results and discussion

3.1. Atom maps

Atom maps for all three nanoporous layers were obtained by APT, with results shown in Fig. 3 and Fig. 4. Due to the ability to fill large volumes of the nanoporous layers with Cu, large volumes of the nanoporous layers could be captured (i.e. with lengths > 100 nm along the tip axis). This facilitates the analysis of several different parts of the nanoporous layer, with different proximities to the dealloying front.

3.2. Core shell structure of nanoligaments

Using APT data acquired for NPG-AgAu, chemical mapping across single nanoligaments has been demonstrated. As shown in Fig. 5, a 2nm cross-section along a selected area of NPG-AgAu atom map shows the core-shell structure of NPG-AgAu nanoligaments, in agreement with previous TEM investigations [7] [14]. Ag rich cores are fully surrounded by Au-rich shells, where the composition of the Ag rich cores is approximately equal to the precursor composition (Ag₇₇ at.%). Au atoms rearrange into Au rich areas while Ag atoms dissolve further [20–23].

Fig. 6(a–c) shows chemical composition maps of all elements

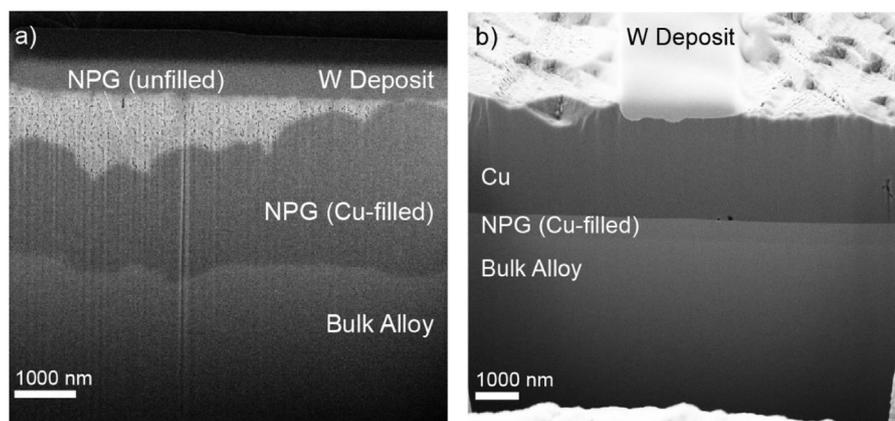


Fig. 1. a) FIB cross-section of NPG-AgAu filled with Cu which was electrodeposited in a solution of 50 mM CuSO₄+0.1 M H₂SO₄, b) FIB cross-section of NPG-AgAuPt filled with Cu which was electrodeposited in a solution of 1M CuSO₄+0.1 M H₂SO₄. Reproduced from Ref. 19 and Ref. 23 with permission from Elsevier and the Royal Society of Chemistry respectively.

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