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Scripta Materialia 69 (2013) 195–198

Scripta MATERIALIA

www.elsevier.com/locate/scriptamat

Nanoporous silver as electrochemical actuator

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Received 28 February 2013; revised 30 March 2013; accepted 1 April 2013
Available online 6 April 2013

We report on reversible dimensional changes in nanoporous silver made by selective dissolution of Al from Ag–Al alloys. Strain amplitudes of between ~0.2 and 0.5% were recorded during cyclic voltammetry experiments in 0.5 M NaOH. These reversible displacements are comparable to, if not higher than, those reported in the noblest nanoporous metals such as Pt and Au under similar experimental conditions. Our new findings indicate that Ag could be a good candidate material for low-cost electrochemical actuation applications.

Keywords: Nanoporous silver; Electrochemical actuation; Dealloying; Strain

Electrochemical actuators based on nanoporous metals with high surface-area-to-volume ratios, so-called metallic muscles [1], represent a novel class of smart materials that undergo reversible dimensional changes upon injection of electronic charge in the space charge region at the nanoporous metal/electrolyte interface [2–6]. These nanoporous metals commonly involve expensive materials such as Au and Pt [2–6], which in turn are made of expensive precursor alloys such as the Au–Ag binary system [4], or the Au–Pt–Ag and Au–Pd–Ag ternary systems [3,6]. Metallic muscles made from low-cost precursor materials are desirable. In this context, nanoporous silver (NPS) synthesized from the Ag–Al binary system is a candidate for a relatively low-cost material. However, so far NPS has not been attractive for electrochemical actuation. One reason is the relatively large characteristic ligament size in dealloyed NPS structures [7–12], which is in the range of 100–500 nm, compared to small feature sizes of the order of 5–50 nm achieved in nanoporous gold (NPG) during dealloying [7–10]. In a recent paper [13], we have shown that by controlling the phases present in the Ag–Al starting alloy, the characteristic feature size in NPS achieved by chemical dissolution of Al from Ag–Al can be reduced from the submicrometer regime down to 30–60 nm. The objective of this paper is to further show that NPS with these relatively small feature sizes is a suitable material for electrochemical actuation. Reversible dimensional changes between ~0.2 and 0.5% (depending on the scan rate) were recorded during cyclic voltammetry experiments in 0.5 M NaOH. Although large strain amplitudes up to 1.3% have been reported in binary nanoporous Au–Pt alloys [3], the 0.5% strain amplitude reported here in NPS is comparable to, if not higher than, those reported in nanoporous Pt (NPP) [2,5] and NPG [14] under similar experimental conditions. Note that we consider here charged-induced strain, i.e. not only the value of the strain amplitude that is relevant, but also: (i) the amount of electronic charge per unit area injected at the nanoporous metal/electrolyte interface, and (ii) the electrical potential applied to the system. A full comparison can be made with Ref. [5] because all experimental data including the electronic charge per unit area injected at the NPP/electrolyte interface are given, whereas in Ref. [3].

Properly synthesized samples with a continuous porous microstructure and minimum residual less noble element (i.e. Al) are a prerequisite for the investigation of the charge-induced strain in NPS. Therefore, in this section we pay attention to the processing steps. A starting alloy precursor with composition $Ag_{20}Al_{80}$ (at.%) and thickness ~5 mm was made by arc melting of pure Ag and Al, under an argon atmosphere [13]. Figure 1a displays a typical Ag–Al button obtained from arc melting and the corresponding energy spectrum obtained by energy dispersive X-ray spectroscopy (EDX). Next, this alloy precursor was cold-rolled from its initial thickness of

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http://dx.doi.org/10.1016/j.scriptamat.2013.04.003

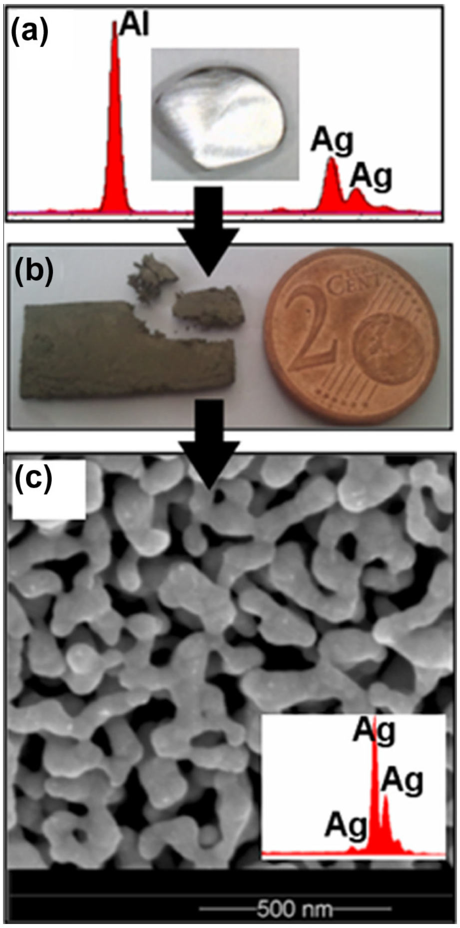

Figure 1. (a) Starting alloy precursor before cold-rolling and corresponding EDX spectrum. (b) Robust NPS sample obtained after dealloying. The sample is broken into smaller specimens to demonstrate its brittle nature. (c) SEM image of NPS and the corresponding EDX spectrum.

~5 mm down to ~0.9 mm. The cold-rolling procedure was performed in three steps in order to avoid the formation of layers in the porous microstructure of NPS during dealloying [6]. During each step, the alloy was heat treated at ~300 °C for ~1 h before further rolling. Next, the cold-rolled alloy was sandwiched between two glass plates and kept at 546 °C for ~8 h, in order to suppress the Ag_2Al intermetallic compound present in the precursor. By rapidly cooling this alloy precursor from 546 °C down to ~3 °C using a water bath, one ends up with a single α-Al(Ag) phase [13]. Finally, the oxide formed onto the alloy precursor during heat treatments was removed by mechanical polishing using Struers silicon carbide papers. NPS was obtained by selective removal of Al from the rapidly cooled alloy precursor, using diluted hydrochloric acid (concentration 3 wt.%) [13]. This chemical dealloying process was carried out at room temperature. In contrast to NPG, which undergoes a volume contraction during dealloying [6,15], a volume expansion takes place in NPS during dealloying. This has to do with the large amount of gas bubbles released during the dissolution of Al from Ag–Al [13], which causes the bulk of the foam to dilate. Under extreme dealloying conditions, these gas bubbles eventually give rise to a bimodal pore size distribution in the foam [13]. Because of the volume dilation, the dealloyed NPS sample is further sandwiched between two glass plates and compressed in order to restore the initial volume. Figure 1b displayed the corresponding robust NPS sample, broken into smaller specimens to demonstrate its brittleness. It can be seen from the scanning electron microscopy (SEM) image of Figure 1(c) that the microstructure of this NPS consists of randomly interconnected solid struts (ligaments) and nanochannels (pores). The average size [16] of ligaments and pores in this sample varied between 50 and 60 nm. It is emphasized that it is not straightforward to achieve a more uniform feature size distribution in such a robust sample. No trace of Al was detected during EDX analysis (see inset Fig. 1c).

In the following we report on the charge-induced strain in NPS. During a first set of experiments, rectangular specimens were cut from the above-mentioned NPS sample for electrochemical actuation. The charge-induced strain was investigated by cyclic voltammetry experiments using a potentiostat (μAutolab IIIFRA2, Eco Chemie) in combination with a three-electrode electrochemical cell setup [6]. The working electrode was made of a solid Au foil, onto which the NPS specimen was placed. The counter-electrode was also made of a solid Au foil, onto which another NPS specimen was placed in order to balance charges between the two electrodes. The third electrode was a Ag/AgCl reference electrode, and 0.5 M NaOH was used as electrolyte. Successive cyclic voltammetry experiments were carried out in a potential range between −0.3 and 0.2 V with respect to the Ag/AgCl reference electrode. During these cyclic voltammetry experiments, dimensional changes in the NPS specimen on the working electrode were probed in situ, using a confocal displacement sensor (IFS2401-0.4 Micro-Epsilon) [6]. The typical reversible dimensional changes recorded during 30 successive cyclic voltammetry experiments from −0.3 V to 0.2 V and back to −0.3 V, at a scan rate of 10 mV s^{-1}, are shown in Figure 2a. At this scan rate, the average strain amplitude is of the order of ~0.2% (Fig. 2b). The freshly dealloyed NPS specimen was observed to shrink during the forward sweep (from −0.3 V to 0.2 V) and to expand back to its initial shapes during the reverse sweep (from 0.2 V to −0.3 V). A detailed discussion on the sign of the strain will be provided in the following section. Actuation was further investigated on other NPS specimens obtained from the main sample in Figure 1b. The dimensional changes were highly reproducible from each specimen and the strain amplitude was consistent.

A second set of experiments was performed with new NPS specimens made from a different precursor, also with composition $Ag_{20}Al_{80}$ (at.%). The dealloying time was reduced in order to achieve smaller feature sizes. The average size [16] of ligaments and pores in these new NPS specimens was found to vary between 40 and 50 nm. Prior to strain measurements, each NPS specimen was subjected to electrochemical cleaning (repeated cathodic sweeps) [6,14] in order to remove the oxide that forms onto the ligaments during the dealloying process [14]. Next, the charge-induced strain was investigated at various scan rates ranging from 1 to 50 mV s^{-1}, and