Microstructure and electrochemical properties of nanoporous gold produced by dealloying Au-based thin film nanoglass

Nanoglass: a new route to nanoporous gold

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Abstract

In this study, Au-based nanoglasses in the form of thin films deposited by magnetron sputtering are comparatively dealloyed. The films have either nanograined or nanocolumnar microstructure, depending on the working pressure of Ar in the sputtering chamber. Nanocolumnar thin films exhibit much higher dealloying rate reducing effectively the dealloying time with respect to nanograined and homogenous thin films. Electrocatalysis experiments indicate that the resulting nanoporous films are active for the methanol electro-oxidation, with promising results in term of stability especially for the dealloyed nanocolumnar film.

Keywords: amorphous, thin film, catalytic

1. Introduction

Conventional dealloying is applied to crystalline foils of Au-Ag [1] or Au-Cu [2] alloys to form porous, coarse-grained gold. A network of interconnected ligaments and pores results from percolation of an electrolyte which removes less noble elements while the Au atoms rearrange by surface diffusion [3,4]. In contrast, dealloying of Au-based metallic glasses, produced in the form of ribbons by rapid solidification, generates ligaments made of numerous nanocrystals germinated from the amorphous phase [5,6]. Ligaments are more defective and their surface is rougher than that of dealloyed crystalline alloys, which is attractive for electrocatalytic and spectroscopic applications [7,8]. However, a long dealloying time, required especially to dealloy tens of microns thick ribbons, may cause coarsening of ligaments and grains due to surface diffusion [9], reducing the specific surface area of the nanoporous gold (NPG). Optimizing the the morphology of dealloyed products requires either the tuning of the dealloying conditions such as acid concentration, temperature and dealloying time or the modification of the precursor composition [2,7,10–12]. In metallic glasses however, the choice of the composition is restricted to the range where the alloy presents a good glass forming ability [13], requiring the use of a different strategy to optimize the dealloying product. Nanoglass is a new class of material formed of amorphous regions separated by amorphous interfaces of lower density [14,15]. In nanoglasses, the size of the amorphous clusters and the density of the interfaces can be tailored to modify the material properties. To date, nanoglasses have been produced by different techniques such as inert gas condensation [16] and magnetron sputtering [17] achieving attractive magnetic [18], mechanical [19] and catalytic properties [20]. We investigated whether we can tailor the nanoglass microstructure to decrease the dealloying time and limit the coarsening of the grains and ligaments in our material.

Here we present the synthesis of Au-based nanoglasses as thin films deposited by magnetron sputtering with controlled nanograined or nanocolumnar microstructure and investigate their dealloying and coarsening behaviour. The dealloying of the films is compared to that of homogeneous glassy thin films and ribbons. It is highlighted that the nanoglass thin films can be properly dealloyed and have a high dealloying rate with respect to homogeneous metallic glasses of the same composition. Additionally, the ligaments are shown to be constituted of crystalline domains of only a few nanometers in size. The dealloyed thin films are shown to be active to the methanol electro-oxidation and can be used as a catalyser for this reaction.

2. Materials and method

Metallic glass thin films were deposited from a 5 cm diameter crystalline target with nominal composition $Au_{40}Cu_{28}Pd_5Ag_7Si_{20}$ (at. %). This composition was selected for its high glass forming ability, among the highest for the Au-based alloys [21]. The master alloy was induction melted and the target was cast in a graphite mold at PX Services, La Chaux-de-Fonds (CH). Thin films were deposited by DC magnetron sputtering with a working distance of 4.5 cm and a discharge power of 30 W. Before deposition, a background pressure below 10^{-4} Pa was reached in the sputtering chamber. The substrates were cover glasses of dimension 24 × 24 mm. An intermediate adhesive layer of Cr, around 5 nm thick, was deposited on the substrate. A Au layer, around 50 nm thick, was then deposited on top of the Cr layer to prevent the corrosion of Cr during dealloying. Finally, the metallic glass was deposited on top of the Au layer. The films were deposited for 5 min at 0.4 Pa, 4 Pa and 10 Pa of Ar working pressure, respectively, to reach a thickness of around 350 nm. The metallic glass thin films have the same composition as the target, as confirmed by energy dispersive X-ray spectroscopy (EDX) measurements performed on the as-deposited thin films. The thin films were dealloyed by free corrosion in a HNO_3 electrolyte solution, with a concentration of 2 M at 70 °C, during different times. The Au intermediate layer, once partially exposed after dealloying, will have a low specific surface area, since there will not be formation of nanopores in it. Therefore, it will not contribute to the signal in CV measurements in a significant way.

The structure of the material before and after dealloying was characterized by glancing angle X-ray diffraction (GAXRD, Philips PW3830), measured with a glancing angle of 0.8° under Cu Kα radiation at 40 kV. The microstructure of the thin films, before and after dealloying, was observed on the top and cross section (after cleaving) views by scanning electron microscopy (SEM). Moreover, for the purpose of Transmission Electron Microscope (TEM) only, nanocolumnar thin films were deposited on a glass substrate without Au and Cr intermediate layers at a working pressure of 10 Pa, and then were dealloyed for 10 min and 1 h in a 2 M HNO_3 solution at 70 °C. These samples were easily removed from the glass substrate during dealloying and used for TEM observation. The samples were placed on a Cu grid without any thinning and examined using a JEOL JEM3010 High-Resolution TEM at 300 kV accelerating voltage employing a LaB_6 electron gun source. An Oxford EDX equipment was used for chemical analyses. The electrochemical behaviour of the thin films was studied with electrochemical polarization curves using a typical three-electrode electrochemical cell. The sputtered thin films were used as the working electrode, with Ag/AgCl as reference and a platinum sheet as counter electrodes. The measurements were performed in 2 M HNO_3 solution at 70 °C, immediately after immersion of the films in the electrolyte, to compare the corrosion kinetics at the initial stage of dealloying. The potentiodynamic polarization curves were recorded at a linear scan rate of 5 mV/s from -150 to 500 mV vs. Ag/AgCl versus the open circuit potential. The electrocatalytic activity of the dealloyed samples for the methanol (MeOH) electro-oxidation reaction was tested at room temperature. Before testing, the working electrodes were scanned at a sweeping rate of 20 mV/s in a 0.5 M KOH solution from -0.1 V to 0.5 V vs Ag/AgCl and the active electrochemical surface area was calculated for every working electrode from the area of the reduction peak of the Au oxide species [22]. Cyclic voltammetry was performed for 300 cycles in the same potential range for all the samples in a solution of 0.5 M KOH and 5 M CH_3OH at room temperature with the same scan rate of 20 mV/s. All current densities were normalized with respect to the electrochemical active surface area of the electrodes.

3. Results and discussion

3.1 As-sputtered thin films characterization

The metallic glass thin films, deposited under different working pressures of Ar in the sputtering chamber, have a composition close to the one of the target, as confirmed by energy dispersive X-ray spectroscopy (EDX) measurements (Table S1). The microstructure of the thin films was investigated by SEM measurements (Fig.1). Top views show that sample A, deposited at 0.4 Pa, has homogeneous microstructure (Fig.1a) and sample B, deposited at 4 Pa, is nanograined with clusters having an average diameter of 18 nm, separated by less dense interfaces (Fig.1b). Both corresponding cross section view (Fig.1d and 1e) display vein patterns characteristic of metallic glass fracture surface [23]. The fracture was induced by cleaving the glass substrate of the film. The evidence of plastic deformation mechanism inherent to metallic glasses is taken as an additional proof of the amorphous structure of the film. Sample C, deposited at 100 Pa, contains grouped clusters with an average diameter of 14 nm, separated by less dense interfaces and voids (Fig.1c). Its cross section (Fig.1f) reveals that the voids observed on the top view form the boundaries between nanocolumns along which fracture progresses. The nanograined and nanocolumnar thin films present different variations of the new materials termed nanoglasses [20,24]. The transition from dense to nanocolumnar thin films with an increase in Ar working pressure is well known for crystalline thin films [25,26]. The present results suggest that a similar transition occurs in amorphous thin films. The smaller nanocluster size in sample C with respect to sample B originates certainly from a reduction of the surface diffusivity of the deposited atoms with an increase of Ar working pressures [26,27]. It was indeed reported that the size of the nanoclusters is controlled by a diffusion process [20].

Glancing angle XRD patterns of all films show broad diffraction halos due to the respective amorphous phase (Fig.2a). However, reflections of low intensity associated with Au in a face-centered cubic lattice can be found overlapped by the amorphous halos. The formation of small crystals is probably favoured by the underneath Au layer. In fact, in both the intermediate Au layer and the Au-based thin films, the (220) diffraction peak has the highest intensity (Fig.2a) while it should be (111) in polycrystalline Au without preferential orientations.

3.2 Mechanism of dealloying

Previous studies with amorphous ribbons indicated that dealloying involves various steps: germination of crystalline islands of nanometer size, formation of mounds and their undercutting, development of a mixed crystal-amorphous region tens of nanometer thick, and formation of ligaments by crystal impingement [6]. With this guideline, experiments were performed to reveal the mechanism operative in amorphous thin films. Fig.3 shows the top view of films A, B, and C after immersion in 2 M HNO_3 solution for 10 min and 1 h at 70 °C. Relatively large pores and islands of around 50 nm in diameter are seen in sample A after 10 min (Fig.3a) while after 1 h finer continuous ligaments with an average width of 35 nm at their necks are formed (Fig.3d). The microstructure of sample B is definitely finer after 10 min, with ligaments of around 30 nm in width and pores around 20 nm in diameter (Fig.3b). After 1 h, the size of both ligaments and pores increased, with ligaments necks around 70 nm in width and pore diameter ranging from tens to hundreds of nanometers (Fig.3e). In sample C fine crystalline islands of around 20 nm in width started evolving into ligaments after 10 min while the pores formed a continuous network surrounding the crystals (Fig.3c). After 1 h, the ligaments became continuous by coarsening and reached a width of 30 nm (Fig.3f). The interconnected pores in between the ligaments had a width of around 25 nm in average.

Images of the cross sections show large pores in the top part of sample A while the internal part fractured as bulk metallic glass with vein patterns [23] proving it was still not dealloyed (Fig.3g). Broad diffraction halos were found in the XRD pattern confirming this statement (Fig.2b). Sample B was dealloyed in its whole thickness (Fig.3h). Sample C was fully dealloyed with ligaments of constant size elongated in the vertical direction, vestiges of the original columnar microstructure (Fig.3i). The XRD patterns of dealloyed samples B and C (Fig.2b), containing only reflections associated with Au in a face-centered cubic lattice, confirms the complete dealloying of the films.

The corrosion potential and current density obtained in polarization curves (Fig.4) explain the different dealloying behaviours of the films. For sample A they are 0.73 V and 1.7×10^{-5} A/cm^2, respectively, reproducing values obtained for amorphous ribbons with the same composition [6]. The potential decreases to 0.65 V for sample B and 0.55 V for sample C while the current density increases to 9.9×10^{-5} A/cm^2 and 2.6×10^{-4} A/cm^2, respectively. The approximately 15 times increase in current density with respect to sample A, accompanied by the decrease in corrosion potential, suggests faster corrosion kinetics in nanoglass films with respect to homogeneous samples.

EDX measurements were performed on the samples after 1 h dealloying in 2 M HNO_3 (Table 1). The concentration of Cu is the largest in sample A (17.6 at. %). This concentration is reduced in sample B but still reaches 11.6 at. %. In sample C, however, only a small amount of Cu could be detected. Sample A and B contain a small amount of Pd and Ag after dealloying. The Pd concentration is further reduced in sample C and Ag was not in sufficient quantity to be detected in this sample. The presence of residual Pd is considered beneficial to the ligament stability against coarsening in NPG [29]. On the other hand, the concentration of Au was the highest in sample C. It suggests a better dissolution of the less noble elements in the nanoglass thin films in respect to the homogeneous thin film. Si was also detected in all the samples, in relatively large quantities. This reproduces the finding of SiO_2 patches in the case of chemically dealloyed Au-Si metallic glass ribbons [30] which were shown to originate from Si oxidation. The silica particles are placed at random in between the ligaments when they are not released into the electrolyte. They do not appear to hinder the electrolyte from penetrating into the pores of the material.

The etching of sample A is slow in comparison with the other films because it is constituted of a fully dense amorphous phase in contact with the electrolyte only through its external surface. The resulting microstructure both in the early stage and after prolonged dealloying is akin to that found with bulk amorphous ribbons of the same composition whose dealloying mechanism was elucidated earlier [6]. In short, crystalline mounds are formed first by spontaneous germination and surface diffusion of Au atoms freed from less noble nearest neighbours. Ligaments form later when the mounds are undercut by electrolyte penetration. The crystal growth in this film is influenced by the presence of fine crystals, as it has been demonstrated with bulk metallic glasses [31–33]. Here, the enhanced intensity of the (220) diffraction peak after dealloying suggests that crystals with (220) orientation originally embedded in the amorphous phase constitute heterogeneous seeds for growth of Au crystals with preferential orientation (Fig.2).

Sample C has less dense interfaces and voids at boundaries in between nanocolumns where the electrolyte can percolate initiating corrosion at multiple sites, not only from the top but also laterally, resulting in increased dealloying rate. The identical ligaments morphology across the thickness suggests indeed that the whole film was dealloyed simultaneously (Fig.3i). The inter-columnar voids present in the as-sputtered state may also hamper the diffusion of Au across nanocolumns, limiting coarsening of the ligaments in the early stages of dealloying. The ligaments become finally interconnected after 1 h, but their thickness is still limited (Fig.3f). As a comparison, the size of the ligaments is around 8 times lower than that of Au-based glassy ribbons of the same composition as the film which were dealloyed at 70°C for the same amount of time [34]. The presence of residual Cu, Ag and Pd is also less in this sample than it is in samples A and B (Table 1).

Sample B is an intermediate case in that it has no voids but interfaces of lower density in between nanoclusters which apparently provide preferential sites for corrosion, as shown by the formation of thin ligaments and pores after 10 min of dealloying (Fig.3b). However, the electrolyte did not penetrate immediately in the film, at variance with sample C which has inter-columnar voids. It is observed that the pores near the top of film B are larger than those at the bottom (Fig.3h), suggesting that dealloying and coarsening occurred progressively across the film section. At variance with sample A, in sample B and C the crystals germinated without preferential orientation directly from the amorphous phase as testified by the normal ratio of the intensity of the diffraction peaks (Fig.2b). They grew to a limited extent and then impinged on each other forming ligaments.

Images of sample C deposited for TEM observation are reported in Fig.5 after dealloying for 10 min (a, b) and 1 h (c, d). The presence of less noble elements was confirmed by EDX analyses. Their atomic percentages after 10 min were measured to be 4.5 ± 1.8 for Pd, 0.9 ±

0.6 for Ag, 21.4 ± 2.0 for Si; and after 1 h, 2.1 ± 0.5 for Pd, 0.7 ± 0.4 for Ag and 21.5 ± 0.7 for Si. Cu was not considered since the sample holder was a Cu grid. Fig.5 shows the 10 min dealloyed columns evolving into ligaments and the final ligament network. Ligaments are constituted by crystals with an average size below 10 nm. Their surface is rough with kinks and necks, especially at grain boundaries. Necks result from impingement of ligaments during growth. High-resolution images of portions of ligaments reveal the Au-based crystals, clearly identified from the lattice fringes of {111} and {200} planes (Fig.5b, d). Amorphous portions of the material can be distinguished locally, attached to the ligaments. They are identified with EDX analysis as silica patches which are usually obtained in dealloying Au-Si based metallic glasses. Atomic steps are clearly visible on the surface of ligaments with favorable orientation. Atomic steps and surface defects were evidenced on dealloyed rapidly solidified ribbons and were shown to constitute active sites for catalytic reactions [35]. TEM studies of Au-based amorphous ribbons showed the occurrence of fine ligaments as those reported in Fig.5 only in the interlayer between the still glassy region and the region with grown ligaments [6]. It is apparent that dealloying thin films from both the surface and internal channels provides a mean to obtain a fine microstructure which is seen in ribbons only in a transition zone.

3.3 Electrochemical properties

After dealloying for 1 h in 2 M HNO_3 at 70 °C, cyclic voltammetry (CV) scans were performed in 0.5 M KOH aqueous solution for 15 cycles in order to explore the electrochemical surface status of the A, B and C dealloyed samples (Fig.6). The results suggest the occurrence of various processes due to their different microstructure and amount of less noble elements. The formation of Au oxides at around 0.25 V [29,34,36,37] is apparent from a current peak only in the case of sample C. For samples A and B, the total current density comes not only from the Au redox couple, but also from the redox states of the remaining less noble elements overlapping the peak of Au oxidation. In fact, literature reports that Cu [38,39] Ag [40,41] and Pd [42,43] form oxide species from -0.1 V to 0.5 V vs Ag/AgCl (details in supplementary). We confirmed these results by performing CV experiments in 0.5 M KOH solution with Ag, Cu and Pd electrodes. The highest current density from 0.3 to 0.5 V is observed on sample A, suggesting a larger presence of Cu, Ag, and Pd, oxidizing in this range. The substantial presence of Cu on this sample was indeed confirmed by EDX measurements (Table 1). For sample B, the current density also increased in this range, but less than in sample A. This is consistent with the lower Cu concentration measured in this sample (Table 1). A negative current peak was observed for all the samples at around 0.05 V. This peak can be associated with the reduction of Au oxide [29,36,37]. However, the lower current density of sample A in this range suggests that the reduction of residual Ag and Pd contributes as well to the signal with this sample [36–39] whereas sample C is closer to the pure NPG state.

Fig.7 shows CV scans performed in 0.5 M KOH + 5 M CH_3OH (MeOH) solution in the presence of samples A, B, and C, after 1 h dealloying. The first cycle with sample C has a current density peak of 0.9 mA/cm^2 at 0.27 V (Fig.7c), consistent with the assignment of MeOH electro-oxidation catalyzed by NPG to formate ions expected in the potential range from -0.1 V to 0.4 V [36,37,44]. A small increase in current density is detected above 0.45 V, consistent with the MeOH electro-oxidation to carbonates expected above this potential [36,37]. Scanning the potential back to -0.1 V, a current density peak appears in the range from 0.25 V to -0.1 V due to oxidation of MeOH on Au after Au oxide reduction occuring during the reverse scan at around 0.25 V. The first cycles for samples A and B give broader current peaks associated to MeOH electrooxidation below 0.4 V (Fig.7a, b). It is believed that the less noble elements both residual and re-deposited in these films, present in their oxidized or metallic state on the exposed surface, lead to a broader potential range for MeOH electrooxidation [34]. The rise in current density at 0.35 V in Fig. 7 is described as a result of the methanol electro-oxidation, not only on Au oxides [36,37] but also on Cu oxides [38,39]. Residual Cu is both trapped in ligaments and contained in the remaining amorphous phase, particularly in sample A.

The electrochemical stability of the samples dealloyed 1 h in 2 M HNO_3 at 70 °C was investigated by performing multiple CV cycles. For both samples A and B, the normalized current density decreased rapidly and reached values below 0.1 after 300 cycles (Fig.7d) because of the progressive coverage of Au active sites by oxidized species of less noble elements, especially Cu, formed during the upward scan [34]. For sample C, the concentration in less noble elements is reduced and the normalized current density is still 0.48 after 300 CV cycles. A sample C dealloyed for only 10 min in 2 M HNO_3 at 70 °C showed a normalized current density of 0.42 after 300 cycles (Fig.S1), demonstrating the good stability of this thin film, even after short dealloying time. Finally, it is remarked that the ligament morphology and size is retained after the electrocatalysis experiments for the two C samples (Fig.S2).

4. Conclusion

In summary, Au-based glassy thin films prepared by magnetron sputtering were carefully tailored to obtain homogeneous, nanograined and nanocolumnar microstructures. The films were dealloyed by free corrosion obtaining a range of behaviour according to their defect content (i.e. interfaces and voids). The homogeneous thin film was partially dealloyed; the nanograined film was dealloyed on its whole thickness obtaining a range of pore sizes not completely interconnected; the nanocolumnar thin film was fully dealloyed forming a nanoporous material where thin ligaments are separated from each other by interconnected nanopores. Polarization curves demonstrate that the dealloying rate of the nanocolumnar thin film is around 15 times higher than that of the homogeneous thin film under the same conditions. Voids and lower density regions at the interfaces between nanocolumns provide sites for electrolyte penetration, allowing dealloying not only from the top but also from lateral sides. The resulting NPG contains a higher Au concentration than the other two dealloyed thin films while keeping the ligament width finer. This work shows a novel strategy to produce nanoporous materials in a short time, starting from nanoglass precursors, to limit coarsening of the grains and ligaments, and therefore increase the specific surface area of the NPG. The resulting nanoporous films are catalytically active for methanol electro-oxidation with good stability of the dealloyed nanocolumnar thin film.

Supporting Information

Detailed description of the current contribution of the redox couples from the residual elements in dealloyed thin films during CV scans in 0.5 M KOH solution, CV Cycles of samples C dealloyed in 2 M HNO_3 at 70 °C for 10 min and 1 h (FIG. S1), SEM images of samples C dealloyed for 10 min and 1 h in 2 M HNO_3 at 70 °C, before and after methanol electro-catalysis experiments (FIG. S2) and EDX measurements of the as-sputtered thin films (Table S1).

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FIG. 1 SEM top views and cross section views of Au-based metallic glass thin films deposited under different working pressures of Ar. Sample A was deposited under 0.4 Pa, sample B under 4 Pa and sample C under 10 Pa.

FIG. 2 Glancing angle XRD patterns of sample A, B and C before (a) and after (b) dealloying for 1 h in a 2 M HNO3 solution at 70 °C. On (a) the glancing angle XRD pattern of the Au intermediate layer is also shown. The positions of the Au reflections in a face-centered cubic lattice are also indicated.

FIG. 3 SEM images (top and cross section views) of samples A, B and C after dealloying 10 min and 1 h in a 2 M HNO3 solution at 70 °C

FIG. 4 Potentiodynamic polarization curves for samples A, B and C dealloyed in 2 M HNO_3 at 70 °C for 1 h, obtained with a scan rate of 5 mV/s in a 2 M HNO_3 aqueous solution at 70 °C. The anodic branch refer to oxidation of less noble elements (Si and Cu) and the cathodic one to reduction of nitrate ions to nitrite. The corrosion current density (j_{corr}) were calculated using the Tafel extrapolation of the cathodic branch at zero overvoltage [28].

FIG. 5 TEM images of sample C after dealloying (a, b) 10 min and (c,d) 1 h in a 2 M HNO3 solution at 70 °C. Samples were deposited employing the same sputtering parameters as for other samples of type C but without the Cr and Au adhesion layers in order to detach them easily from the glass substrate after dealloying and observe them in TEM without cutting or thinning. (a,c) In bright field images, ligament size and shape are consistent with SEM observations. On HRTEM images, arrows evidence a (b) twin boundary and a (d) grain boundary.

FIG. 6 Cyclic voltammetry (CV) cycles in 0.5 M KOH solution with a scan rate of 20 mV/s for samples A, B and C dealloyed in 2 M HNO_3 at 70 °C for 1 h

FIG. 7 The electrocatalytic performance of dealloyed samples (a) A, (b) B and (c) C for 1 h in 2 M HNO3 at 70 °C. The samples were tested for 300 cycles with a scan rate of 20 mV/s in 0.5 M KOH+5 M CH3OH. Current densities are reported with respect the effective surface area obtained from I-V plots. The effective surface area is: 0.98, 3.75 and 5.87 cm2 for samples A, B and C, respectively. (d) The maximum current density in the selected CV scans is normalized with respect to the maximum value of the first scan and reported as a function of the number of cycles.

	Sample A	Sample B	Sample C
Au	60.6	63.9	72.9
Cu	17.6	11.6	0.2
Pd	4	3.9	1.7
Ag	3.6	2.5	---
Si	14.2	18.1	25.2

Table 1 Concentration in at. % measured by EDX in samples A, B and C dealloyed in 2 M HNO_3 at 70 °C for 1 h. The concentration of Ag in sample C was too low to be detected.