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Nanoporous gold by dealloying of an amorphous precursor

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ABSTRACT

Nanoporous gold has been produced by the electrochemical dealloying of a Au₄₀Cu₂₈Ag₇Pd₅Si₂₀ metallic glass. Suitable conditions of potential and temperature of dealloying have been established from polarization curves and dealloying has been conducted at the critical potential of 1.05 V in three different electrolytes: 1 M HNO₃, 1 M HClO₄ and 1 M H₂SO₄. The resulting material after 6 h of dealloying was constituted by ligaments made of pure Au and pores. The morphology was determined by SEM: ligaments of about 100 nm was observed and their size appears slightly larger (130 nm) when HNO₃ is used.

In the first stages of dealloying (30–300 s), nanopores and nanocrystals, randomly oriented, were found by HRTEM. From these observations a diffusivity value for crystal growth was estimated. A change in growth mechanism was suggested when impingement occurs for long dealloying times.

It is suggested that the ligament and pore morphology can be tailored in order to obtain materials with different chemical and physical properties.

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1. Introduction

Nanoporous metals have achieved an important place in literature, because of different possible applications such as catalysis [1,2], surface-enhanced Raman scattering [3,4] and actuators [5]. They can be prepared by electrochemical dealloying of a metallic precursor that can be either crystalline or amorphous. During dealloying, the less noble elements of the alloy are removed while the atoms of the noble element reorganise themselves by surface diffusion [6,7] forming ligaments and porosities that can have dimensions of the order of tens of nanometers. When the precursor is a crystalline alloy, the ligaments retain the crystallographic orientation of the grain from which they originate and have angular displacement of a few degrees between each other [8]. On the contrary, when dealloying of amorphous alloys is undertaken, the noncrystalline structure and the absence of grain boundaries suggest that nucleation and growth of crystals must occur to form ligaments. The process parameters that play a role during dealloying are: the difference in electrochemical potential between the alloy components, the critical potential for corrosion [9,10], the amount of noble element i.e. the parting limit [11,12], the composition, pH and temperature of the electrolyte. The influence of the process parameters on the final morphology of ligaments and pores is not vet completely understood and it is of interest to study this correlation for applications requiring the design of specific patterns. In particular the effect of the electrolyte on the dimension of ligaments and pores is not jet completely understood for dealloying of crystal-

* Corresponding author. E-mail address: paola.rizzi@unito.it (P. Rizzi). line precursors and it has not been analysed for dealloying of amorphous alloys. Moreover, little is known in literature on the mechanism of dealloying when an amorphous alloy is used as a precursor.

In this paper, we report on the production of nanoporous gold starting from a $Au_{40}Cu_{28}Ag_7Pd_5Si_{20}$ amorphous alloy by means of electrochemical etching. Different electrolytes are used in order to compare the morphologies obtained. Moreover, the first stages of the dealloying are examined and a mechanism of dealloying is proposed based on of High Resolution Transmission Electron Microscopy observations.

2. Experimental

Ingots of composition Au₄₀Cu₂₈Ag₇Pd₅Si₂₀ were prepared by arc-melting the pure elements (Au: 99.99%, Ag, Cu and Pd: 99.99%, Si: 99.9995%) in Ar atmosphere and using Ti getters. Ribbons about 25 μ m thick and 2 mm wide were obtained completely amorphous by melt spinning using a linear velocity of the copper wheel of 22 m/s. Samples of 15 mm in length were cut from ribbons. Detailed information on production and characterization of the as spun ribbon are reported in a previous work [13].

A Potentiostat/Galvanostat (Model 7050, Amel Instruments) has been used for electrochemical de-alloying. The cell is composed of the sample as working electrode, a Pt counter electrode and a Ag/AgCl reference electrode; a double bridge configuration has been employed to avoid deposition of the de-alloyed ions as insoluble salts.

The critical potential for dealloying has been determined by performing polarization curves as a function of the temperature of the electrolyte [10]. Once the suitable conditions for etching have been found, i.e. 1.05 V (vs Ag/AgCl) at 70 °C, electrochemical dealloying has been performed in three different electrolytes: $1 M HNO_3$, $1 M HClO_4$ and $1 M H_2SO_4$ for 6 h.

Ribbons have been analyzed before and after electrochemical etching using X-ray diffraction (XRD) in Bragg-Brentano geometry with monochromatic Cu K α radiation, Scanning Electron Microscopy (SEM), Energy Dispersive X-ray







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Spectroscopy (EDS) (calibrated with a pure Co sample). Transmission Electron Microscopy (TEM) observations were done with samples thinned by mechanical polishing and, successively, electrochemically etched for 30 s and 300 s with the procedure specified above.

3. Results and discussion

3.1. Electrochemical behaviour

In order to determine the critical potential for de-alloying, the electrochemical behavior was studied by performing polarization curves with a scan rate of 5 mV/s, using as electrolyte 1 M H₂SO₄ solution at different temperatures. Results are shown in Fig. 1. At room temperature the sample shows an excellent corrosion resistance due to the presence of a passivation zone extended from 0.53 V to about 1 V (vs Ag/AgCl) and characterized by low current densities of the order of 10^{-6} – 10^{-5} A/cm². In the anodic branch of the curve an active region appears at about 1 V where the current density reaches higher values. The passivation zone is followed at higher potential values by the trans-passivation zone, where the current density increases rapidly.

When polarization curves are performed at higher temperatures, a similar trend is observed as the one described for the RT experiment, but the current densities raise in the whole range of potential as the temperature is increased. The E_{corr} values generally decrease with increasing temperature although with some scatter probably due to the state of the surface of individual samples. This has, however, no influence on the current densities at higher potential.

Polarization curves in 1 M HNO₃ and 1 M HClO₄ at 70 °C show that the active region for dealloying is maintained and the current density at 70 °C follows the trend HNO₃ > H_2SO_4 > HClO₄ over the whole range of potentials.

The critical potential E_c has been fixed for all electrolytes as 1.05 V, where the current densities are. The temperature of 70 °C was chosen in order to have current densities of the order of 1 mA cm⁻² (4.3×10^{-3} A cm⁻², 4.2×10^{-4} A cm⁻², 1.7×10^{-4} A cm⁻² for HNO₃, H₂SO₄ and HClO₄, respectively) which allows extensive etching of ribbon samples in times of a few hours as previously demonstrated [13]. Moreover, at 70 °C and 1.05 V (vs Ag/ AgCl) no fracture of samples due to stress corrosion cracking [14–16] was observed. On the contrary, for Au₄₀Cu₂₈Ag₇Pd₅Si₂₀ samples dealloyed in the transpassive zone at various temperatures and at potentials in excess of 1.6 V, where high current densities are acting, an extended phenomenon of stress corrosion cracking was always observed.



Fig. 1. Polarization curves of the amorphous alloy at various temperatures in 1 M $\rm H_2SO_4$ and at 70 °C in 1 M HNO_3 and 1 M HClO_4.



Fig. 2. XRD patterns of the as-spun ribbon and samples after 6 h of dealloying a 70 °C and 1.05 V (vs Ag/AgCl) in 1 M H_2SO_4 , 1 M $HCIO_4$ and 1 M HNO_3 .

3.2. Dealloying morphologies and mechanism of dealloying

Diffraction patterns of samples dealloyed in different solutions (Fig. 2) show that the amorphous halo disappears and reflections of an fcc phase based on Au occur. Rietveld analysis [17] of diffraction patterns indicate that the lattice constant (a_0) for all samples is always compatible with pure Au within the experimental error and that the size of the crystalline domains is 48 ± 4 nm, 49 ± 4 nm and 61 ± 6 nm for the samples dealloyed in 1 M HClO₄, 1 M H₂SO₄ and 1 M HNO₃, respectively.

Secondary electrons SEM images of dealloyed samples are reported in Fig. 3. As can be seen from cross section images, all samples were completely dealloyed. The size of pores and ligaments appears homogeneous on both surfaces (air and wheel-side) and within the cross section of each sample showing that the dealloying mechanism remains the same on the surface and in the inner part of the sample. Ligaments and pores appear finer in the sample dealloyed by perchloric and sulfuric acid than those obtained in nitric acid. The average ligament sizes are 98 ± 24 nm, 91 ± 22 nm and 131 ± 34 nm for 1 M HClO₄, 1 M H₂SO₄ and 1 M HNO₃ respectively. EDS analysis shows that ligaments are made of Au in all samples and that the other elements are below the detection limit of the instrument, confirming the inference from lattice constants. The produced nanoporous ribbon is a free standing material that can be bent without cracking.

In order to determine the morphology and microstructure in the initial stages of the process a Au₄₀Cu₂₈Ag₇Pd₅Si₂₀ sample was dealloyed for 30 s in 1 M HNO₃ and then observed by TEM. From High Resolution images (HRTEM) it is apparent that rounded nanocrystals of average size of 5 nm are formed, oriented in different directions (Fig. 4, HRTEM) and small nanopores appears on the surface of the sample. From HRTEM lattice fringes, the interplanar spacing of the (111) plane was determined to be 2.24 ± 0.03 Å, value slightly lower than pure Au. Therefore, the presence of other elements in solid solution with Au at this stage can be envisaged. When dealloying is performed for 300 s, a similar morphology appears with crystals roughly doubled in size, showing that crystal growth occurs immediately when Au atoms, freed of their local environment, move by surface diffusion from the inner layers of the ribbon. At this stage, the interplanar spacing of the (111) plane determined from HRTEM was 2.26 ± 0.04 Å, confirming the formation of an Au based solid solution. When the dealloying process is performed for longer times, progressive leaching with consequent nucleation of crystals in the inner part of the sample occurs as soon as pores become available to allow penetration of the electrolyte to reach the underlying amorphous alloy. It can be expected that, at Download English Version:

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