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# Comparing Selective Corrosion of Au-based amorphous, partially amorphous, and devitrified alloys

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#### Abstract

Corrosion studies in an acidic environment have been performed for the good  $Au_{40}Cu_{28}Pd_5Ag_7Si_{20}$  glass former with emphasis on the selective dissolution (de-alloying) process. The final porous microstructures obtained from fully amorphous ribbons and ribbons containing crystals as well as composition inhomogeneity in their amorphous matrix. The results are compared by using the same etching conditions. As reference, ribbons containing different crystalline fractions produced by isothermal annealing at temperatures in the glass transition region and then de-alloyed. The results show that a different mechanism of de-alloying operates for amorphous and crystallized materials. The finer homogenous nanoporous structure occurs after de-alloying a fully crystallized ribbon.

#### 1. Introduction

Au-based amorphous alloys are possible precursors for developing homogeneous nanoporous gold structures (NPG) composed of ligaments and pores [1-9] through the process of selective corrosion (de-alloying) resulting in materials with high surface area. The NPGs have been tested as electro-catalysts [2,3] and substrates for SERS activity [4,5] showing good activity. One of the main features of NPG derived from glassy alloys is that the ligament networks deriving from Au-based amorphous alloys have a different morphology in comparison to those derived from Au-based crystalline alloys [6], because of the spontaneous germination of many crystals during de-alloying giving ligaments made of several fine crystalline domains rather than a single crystal.

The Au<sub>40</sub>Cu<sub>28</sub>Pd<sub>5</sub>Ag<sub>7</sub>Si<sub>20</sub> composition is reported as one of the best glass formers among Au-based alloys [10] and was chosen for the studies of this work. Its composition conforms to the requirements for de-alloying, i. e. the difference in the standard redox potentials among the alloy components, [11-13] and the parting limit corresponding to the maximum content of Au needed to avoid surface passivation. The Au<sub>40</sub>Cu<sub>28</sub>Pd<sub>5</sub>Ag<sub>7</sub>Si<sub>20</sub> can be de-alloyed by using the alloy as anode in an electrochemical cell in 1M HNO<sub>3</sub> at 70°C [2,3].

During the processing of glass formers by rapid solidification, minority crystalline phases, often metastable, can nucleate from the melt and remain embedded in the amorphous

matrix. On the other hand, crystals can be developed in amorphous alloy if they are devitrified by annealing.

In this work, the  $Au_{40}Cu_{28}Pd_5Ag_7Si_{20}$  alloy in the form of ribbons is studied aiming at comparing the selective corrosion in amorphous and partially or fully crystallized states. The crystalline phases formed during quenching and annealing are analyzed and their corrosion behavior determined.

#### 2. Experimental part

The Au<sub>40</sub>Cu<sub>28</sub>Pd<sub>5</sub>Ag<sub>7</sub>Si<sub>20</sub> master alloy was made by arc melting of the pure elements (Au, Ag, Cu, Pd, Si: 99.99%); a melt spinning apparatus was utilized to produce glassy ribbons with gas Ar overpressure around 0.35 bar onto a Cu wheel, rotating at a speed of 20m/s in an evacuated chamber kept under Ar pressure in the order of ~ 1bar. The resulting ribbons have silvery color, are about 30µm thick and 2mm wide. A Panalytical X'Pert X-Ray equipment was used for structural characterization with Cu K<sub> $\alpha$ </sub> ( $\lambda$ = 1.5418 A<sup> $\circ$ </sup>) radiation in Bragg-Brentano geometry ( $\theta/2\theta$ ). Samples were heated with a scan rate of 40K/min in a heat flux differential scanning calorimetry (DSC), Q-100 instrument, using aluminum pans. Progressive isothermal crystallization was obtained at 140°C, within the glass transition range (130°C to 150°C), for different time periods. Samples 15 mm in length were cut and used as an anode in a three-electrode electrochemical cell connected to a PGSTAT302N Potentiostat/Galvanostat of MetroOhm Instruments. Polarization curves with a scan rate of 5mV/sec have been collected in 1 M HNO<sub>3</sub> aqueous solution at 70°C de-aerated with Ar gas. De-alloying at the potential of 1.1 V vs Ag/AgCl using a Pt grid cylinder as a counter electrode was performed in the same conditions which were previously shown to produce a continuous and homogeneous nanoporous network [2,4,6-9].

A Bruker-Atomic Force Microscope Dimension Icon (AFM) was used to examine the sample topography in tapping mode with a scanning rate of 75 Hz. A Si tip on a nitride cantilever (Scanasyst-Air) was employed with a resonance frequency of 78 kHz. The AFM data analysis was made by means of the WSxM5.0 Develop 7.0 software. An Inspect F<sup>TM</sup> FEG Scanning Electron Microscope (SEM) was also used for checking the morphology of the samples that have been de-alloyed.

X-rays Photoelectron spectroscopy (XPS) investigations were performed with a PHI 5600 XPS system using monochromatic AI  $K_{\alpha}$  X-rays (350 W). For profiling samples in the depth, Ar<sup>+</sup> ions were used with an energy of 3.5 keV and an angle of around 30 degrees to the surface normal. The sputtering rate was 0.7 nm/min measured with SiO<sub>2</sub> reference and the pressure in the XPS analysis chamber was 1·10<sup>-8</sup>Pa. Auger Electron Spectroscopy (AES) measurements were made with a JEOL JAMP 9500F Scanning Auger Microprobe, which had a hemispherical analyzer, a chamber pressure of 10<sup>-7</sup>Pa (without sputtering) and a Schottky field emission source. The analyzer was operated setting the constant retarding ratio (CRR) mode at 0.32, resulting in a relative energy resolution of 0.5%. The electron beam conditions were at 10keV and 10nA. Direct spectra were used for evidencing the presence of elements and differential spectra for concentration calculations. The ribbons were sputtered with 2keV Ar<sup>+</sup> ions with a sputtering rate of 5nm/min for 30secs, to remove any possible surface contamination. The chemical analysis was performed on both air and wheel side of the de-alloyed ribbons. Data analysis was

made by means of PHI-MULTIPAC software package, V.9.3, ULVAC-PHI, (1994-2011) for both AES and XPS results [14].

### 3. Results and discussion

### 3.1 Crystallized ribbons produced by isothermal annealing.

The crystallization of ribbons annealed at 140°C isothermally starts after 45 minutes and is complete after 90 minutes. The DSC trace displays a single exothermal event (see Fig. SI.1 in supplementary information). The XRD patterns of samples containing different amount of crystalline fraction (Fig.1 (a)) have limited number of reflections of increasing intensity compatible with a cubic structure of large lattice constant. They do not correspond to those of known compounds found in other alloys of this family [15]. In fact, the crystallization on both continuous heating and isothermal conditions of the Au<sub>49</sub>Cu<sub>26.9</sub>Pd<sub>2.3</sub>Ag<sub>5.5</sub>Si<sub>16.3</sub> amorphous alloy results in a different metastable phase of a complex cubic structure, whereas the alloy at equilibrium close to the eutectic melting temperature is made of a Au-rich silicide, a Cu-rich silicide, small fractions of Pd<sub>3</sub>Si, free Si, and (Au-Ag-Cu) solid solution [15]. Comparing the occurrence of phases in the patterns Au<sub>40</sub>Cu<sub>28</sub>Pd<sub>5</sub>Ag<sub>7</sub>Si<sub>20</sub>, alloys with varying Au and Cu content, namely of Au<sub>30</sub>Cu<sub>38</sub>Pd<sub>5</sub>Ag<sub>7</sub>Si<sub>20</sub>, and Au<sub>20</sub>Cu<sub>48</sub>Pd<sub>5</sub>Ag<sub>7</sub>Si<sub>20</sub>, some common reflections can be identified. Table 1 reports a list of reflections for all phases in S.I. In summary, reflections of a Cu-rich silicide increase in intensity with increasing Cu content as well as those of the (Au-Ag-Cu) solid solution, while those of the Au-rich silicide decrease in intensity with decreasing Au content. The XRD patterns and the single DSC trace indicate that the crystallization of  $Au_{40}Cu_{28}Pd_5Ag_7Si_{20}$  occurs polymorphically to a metastable phase.

DSC scans show that the crystallization peak is reduced in size for the 50min annealed ribbons, and disappears entirely for the 90min annealed ribbons (see Fig. SI.2 supplementary). The crystallization temperature  $T_x$  is shifted to a lower temperature for the 50min annealed ribbon with respect to that of the amorphous sample, since it already contains a crystalline fraction. More peaks are seen in all traces, which correspond to transformations of the metastable phase to more stable phase mixtures.

Polarization curves in 1 M HNO<sub>3</sub> at 70°C for the 90 min annealed (red) and the amorphous ribbon (black) are reported in Fig. 1 (b). It is observed that the corrosion potential,  $E_{corr}$ , of the amorphous ribbon is 0.75V, as shown earlier [6,9], and shifts to lower values with increasing crystalline fraction: 0.28 V for 50% crystalline fraction and 0.18 V for fully crystallized.

SEM-EDS analyses performed on both sides of the amorphous and crystallized samples prove that the composition of the amorphous ribbon is homogeneous and close to the nominal value, while the back-scattering SEM images of a 50mins annealed ribbon shows some protrusions on the surface (see Fig. SI.3 supplementary). EDS analysis of the central area of these protrusions (indicated by an arrow), reveals the occurrence of a Curich silicide: Cu 55.7%, Au 25.5 %, Si 14.8% and Pd 4.0% at. %. The same protrusions also appeared for a 90mins annealed sample. The negative shift of  $E_{corr}$  can be related to the increase in surface fraction (exposed surface area) of these Cu-based crystals, since the redox potential of Cu is more negative than that of Au. Moreover, the fully amorphous sample exhibits active dissolution of the less noble elements from around 0.8V with steep

slope in the polarization curve, prior to a passive transition (black curve Fig. 1 (b)). In the curve of the fully crystallized alloy (red in Fig. 1 (b)), the slope is still pronounced ending in a current density plateau of ~20  $\mu$ A/cm<sup>2</sup>. This should be related to the metastable phase formed polymorphically by crystallization. Previous potentiodynamic experiments in 1 M HNO<sub>3</sub> at 70°C and applied potential of 1.1V vs Ag/AgCl (corresponding to the maximum of the current density (1mA/cm<sup>2</sup>) of the anodic branch) resulted in dissolution of less noble elements, forming NPG with remaining traces of Pd and Ag at around 0.5-0.7% at. [2]. It is noted that the anodic branch of the potentiodynamic curve of the annealed ribbon shows a hump at 1.1V, indicating the possibility of selective etching at this potential also for these materials.

#### 3.2 Melt spun ribbons containing crystals

A ribbon resulting brittle and dull after rapid solidification provided the XRD pattern shown in Fig. 1(a) (blue curve), which shows an amount of crystals formed during the solidification. The crystalline phases have been identified as silicides rich in Cu and Au since they give XRD reflections identical to those of equilibrated master alloys.

The corrosion potential for this ribbon is close to 0.3V vs Ag/AgCI (the sample is named S2 here for simplicity, Fig. 1 (b), blue curve). The constituents displaying more negative redox potentials than Au could be responsible for the low corrosion potential similarly to the case of ribbons crystallized by annealing. On the other hand, the anodic part of the polarization curve shows a current density one order of magnitude lower compared to the fully amorphous sample around 1.1V, indicating passive behavior. This can be explained by considering the surface topography of the sample (see Fig. SI.4 supplementary). It was previously found that Au<sub>40</sub>Cu<sub>28</sub>Pd<sub>5</sub>Ag<sub>7</sub>Si<sub>20</sub>, amorphous ribbons are covered by a surface layer of SiO<sub>2</sub> [9]. When the de-alloying process starts, the electrolyte penetrates through the cracks of the layer and the less noble elements are dissolved. (Fig. 2 (a)). The patches of SiO<sub>2</sub> in S2 are wider than those on the fully amorphous sample [9], while the XPS depth profile also indicates that the  $SiO_2$  layer is thicker (about 5-6 nm) and rougher. Furthermore, the amount of copper is more on the surface of S2. The Cu enrichment is confirmed by EDS results as well, and may contribute to the lowering of the corrosion potential. The thick SiO<sub>2</sub> layer enhances the anodic passivation in HNO<sub>3</sub> around 1.1 V. The surface oxidation of Si has very likely promoted the formation of crystals during melt spinning, although the solidification parameters, such as wheel rotating speed, overpressure etc. were the same for the two samples.

# 4. Selective corrosion process (De-alloying) of ribbons either amorphous or containing crystals.

In this part, the selective corrosion process is explored for amorphous and rapidly quenched samples containing crystals under the same de-alloying conditions. The dealloying process lasts for 6h in 1M HNO<sub>3</sub> at 70°C [6-8]. For the amorphous sample, the current density at 1.1 V is around 1.5 mA/cm<sup>2</sup>, while it is around 0.3 mA/cm<sup>2</sup> for the samples containing crystals. The de-alloyed ribbons have different morphology. The one formerly amorphous is fully de-alloyed from both air and wheel side (see supplementary Fig. SI.5) with ligament size of 200 ± 40nm, constant throughout the ribbon thickness, confirming previous studies [6-9]. When a ribbon contains crystals, hilly features having usually volcano-looking shapes with pits and cracks, are found after de-alloying. The ligaments in these hemispherical zones have radial direction as evidenced in cross-section (marked as zone 1 in Fig. 2 (b)). According to AES and EDS analyses, these are Au-Si rich regions (Au: 59.3 at% and Si: 32.8 at% on average). Note also that the de-alloying occurred in more depth in comparison to neighboring regions, originally amorphous, where ligaments display their common morphology (marked as 2 in Fig. 2(b)). The same results were obtained after electrochemical de-alloying in 1M  $H_2SO_4$ , proving that the final inhomogeneous structures are not related to the electrolyte solution but to the initial state of the ribbon. Apparently, the selective corrosion occurs differently in the two regions. The structure of region 1 in Fig. 2 (c) appears originated by a eutectic lamellae microstructure with one phase fully etched. The eutectic mixture of silicides formed locally during rapid quenching. The Au-rich phase remains unetched, whereas the Cu-rich one is corroded. The fraction of Au contained in the latter compound is likely added to the remaining crystals.

Dealloying experiments have also been performed on Au<sub>20</sub>Cu<sub>48</sub>Pd<sub>5</sub>Ag<sub>7</sub>Si<sub>20</sub> ribbons whose XRD patterns indicate the presence of crystals. The resulting microstructure is inhomogeneous with cracks and hilly features composed of ligaments with radial direction like those in Fig. 2 (c) (see Fig. SI.6 supplementary). The presence of cracks on de-alloyed surfaces was reported in the literature in relation to local composition gradients in thin films. The length and the number of cracks appearing during de-alloying were a function of the initial film composition: the lower the Au content the more cracks are observed [15]. Here, it is noted that in samples containing crystals (e. g. Au<sub>40</sub>Cu<sub>28</sub>Pd<sub>5</sub>Ag<sub>7</sub>Si<sub>20</sub> and Au<sub>20</sub>Cu<sub>48</sub>Pd<sub>5</sub>Ag<sub>7</sub>Si<sub>20</sub>) hilly features usually having volcano-looking shapes with pits and cracks are found after dealloying, because of local demixing and composition variation, independently of the nominal composition although smaller ligaments derive from alloys containing a lower amount of Au.

In this work, several ribbons were examined, which were produced from different master alloys of the same nominal composition. Although some samples appear fully amorphous according to their XRD pattern, from an electrochemical point of view their  $E_{corr}$  in 1M HNO<sub>3</sub> at 70°C was shifted to values lower than 0.75V which is the  $E_{corr}$  of fully amorphous ones [6,9]. These samples display local composition inhomogeneities, which give rise to varied features on their de-alloyed surfaces (Fig. 3). A significant example is provided by regions on the wheel side, circular and hilly, which are preferentially de-alloyed, while the neighboring zones are un-etched. In these passivated zones, the amount of Au and Pd found by AES is 65.7 at% and 12.6 at % respectively (area 1 in Fig. 3), i. e. the Au content is above the parting limit. This proves that the ribbon is chemically inhomogeneous and that there are regions with a different composition from the nominal one, which, however, became amorphous. Although the surface morphology is different from one hilly feature to another, the elemental composition is only slightly different with spots richer in Pd or Si. (Fig. 3). It can be considered that the polarization curve of a sample can be used as a better tool to evaluate the amorphicity compared to the XRD pattern.

So far, results were reported for ribbons containing crystals formed during solidification of the melt. In the following, fully amorphous samples are compared with samples crystallized

on purpose by thermal annealing. Fig. 4 shows the cross section of de-alloyed amorphous and crystallized samples: it is apparent that ligaments evolve in a different way. While dealloying proceeds from the outside to the inner part of the originally amorphous ribbon, the ligaments have the same average size of around 200±40 nm (Fig. 4 (a)) remaining constant throughout. The ligaments (Fig. 4 (b)) are smaller for the crystallized ribbon. The size is 96±28 nm in the external part, de-alloyed earlier, and 20 to 40 nm in the interior of the sample close to the still uncorroded portion. Since the external part has been in contact with the electrolyte for longer time, the coarsening effect is more evident.

It was already reported in previous studies [9] that at the beginning of the dealloying process of amorphous alloys, crystals are formed and grow inside an interlayer, which is around fifty nanometers thick, between ligaments and amorphous part. The crystals grow because of supply of Au atoms during dealloying, and then impinge onto each other resulting in rough ligaments [9]. On the other hand, the mean value of the crystalline domains in the crystallized ribbon before dealloying was calculated as 17±3 nm from XRD reflections using the Scherrer equation. Since the fine crystallized grains have complex structure, on de-alloying fcc Au crystals must germinate from each of them. On average, the size of ligaments remains small despite some coarsening which appears due to crystal impingement as in the case of the fully amorphous sample.

#### Conclusions

In this work, the existence of some crystals in the amorphous matrix is examined, as well as their influence on the final de-alloyed product. Some other parameters such as the surface oxide layer and local inhomogeneities are considered. These parameters along with the presence of crystals can affect the final de-alloyed structure, forming regions with bumps and cracks, while some other regions are passivated. The results show that ribbons containing crystals display lower corrosion current and potential compared to fully amorphous ones. After 6hr of dealloying the fully amorphous ribbon is fully dealloyed contrary to the ribbons containing crystals. An homogeneous de-alloyed structure is found only in the case of the fully as-spun amorphous ribbons. Also, it is observed that the ligaments forming from dealloying amorphous alloys show a steady size value on average, while the crystallized samples show a size variance from the external to the internal part due to delayed coarsening. The finer homogenous nanoporous structures occur after de-alloying of fully crystallized ribbon.

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#### **Figures Captions**

Figure 1: The XRD patterns (a) and the polarization curves in 1M HNO<sub>3</sub> at 70°C for a scan rate 5mV/sec (b). In all cases, the samples are the amorphous (black), partially crystallized ribbons containing crystals forming during solidification of the melt (blue) and almost fully crystallized (red) after thermal annealing for 90mins.

Figure 2: SEM images of a dealloyed sample in  $1M HNO_3$  containing an amount of crystals after electrochemical de-alloying. Top view (a) and cross section (b), and the region 2 in a higher magnification (c).

Figure 3: The wheel side of a de-alloyed sample that was used for AES analysis. The analysis has been performed on different zones.

Figure 4: Cross section SEM images of an amorphous (a) and annealed ribbon for 90min (b), after de-alloying in 1M HNO<sub>3</sub> at 70°C, for 3h and 6h respectively.

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