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A comparison of de-alloying crystalline and amorphous multicomponent Au alloys

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Abstract: The formation of nanoporous metals by de-alloying is not fully disclosed especially in the case of complex alloys such as amorphous ones. Here a crystalline porous scaffold made of ligaments and pores must originate from a matrix of diverse structure.

In this paper a contribution to the field is achieved by pointing out differences that have been noticed comparing ligaments in de-alloyed materials obtained from either amorphous or crystalline precursors. Two multicomponent Au-based alloys in the form of ribbons, an amorphous $\text{Au}_{40}\text{Cu}_{28}\text{Ag}_7\text{Pd}_5\text{Si}_{20}$ and a polycrystalline $\text{Au}_{31}\text{Cu}_{41}\text{Zn}_{12.8}\text{Mn}_{15.2}$, have been chemically de-alloyed in same conditions. The resulting nanoporous materials have been characterized by microscopy and diffraction and the kinetics of the process have been determined. The morphology of ligaments is definitely diverse as well as the size of crystals. This is proven by the ratio, r , between the ligament size and the size of scattering domains obtained by Rietveld analysis: the ligaments formed from the amorphous precursor are constituted by several crystals ($r \approx 5$) whereas ligaments from crystalline alloys contain a single domain ($r \approx 1$). The results are discussed in terms of surface diffusion and mechanism of growth of ligaments.

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4 **A Comparison of De-alloying Crystalline and Amorphous**
5 **Multicomponent Au Alloys**
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14 Abstract

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31 growth of ligaments.
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37 **Keywords:** A) porous materials, A) metal glasses, B) corrosion, B) diffusion, D) interfaces.
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1. Introduction

De-alloying is the corrosion process, either chemical or electrochemical, in which less noble metal are selectively removed from an alloy, leading to a material made of interconnecting ligaments and pores [1]. The resulting meso/nanoporous structure is proposed for application in various field such as catalysis [2], sensors, hydrogen storage, molecular sieves, surface-enhanced Raman scattering [3] and actuators [4]. One requirement for application is a tunable ligament size made of an almost pure inert metal [5], although small amounts of impurity elements could be crucial for improving the sensing or chemical activity [2].

The de-alloying has been studied in a number of binary alloys, usually solid solutions of Au with Cu [6] and Ag [7, 8]. The main aspects of the mechanisms and the parameters for de-alloying of crystalline alloys have been identified by the studies of Erlebacher [9, 10], Pickering [11, 12] and Sieradzky [13]: the model that has been proposed takes into account surface diffusion, capillary forces and kinetics of electrochemical dissolution. On selective removal of less noble elements, the noble ones reorganize in islands by surface diffusion of adatoms on the underlying crystals forming hillocks which are then subject to undercutting, spreading ligaments and porosities into the bulk [1]. Therefore, the nanoporous material has the same crystal structure as the matrix, i. e. *fcc*, and the original grain microstructure is retained [14]. If the precursor structure has complex crystal lattice or is amorphous, the nanoporous material has again *fcc* structure, but ligaments are made of multiple crystals [15, 16, 17]. The mechanism of formation of ligaments is not yet fully disclosed and this study is aimed at elucidating some aspects of it by comparing the nanoporous gold (NPG) obtained by chemical de-alloying two Au-based multicomponent precursors: a $\text{Au}_{40}\text{Cu}_{28}\text{Ag}_7\text{Pd}_5\text{Si}_{20}$ [18] amorphous alloy whose complex composition reflects the requirement for having good glass forming ability, and a polycrystalline $\text{Au}_{31}\text{Cu}_{41}\text{Zn}_{12.8}\text{Mn}_{15.2}$ [19]. Both of them have been synthesized by rapid solidification ensuring the achievement of a single homogeneous phase.

2. Experimental

Ingots of $\text{Au}_{31}\text{Cu}_{41}\text{Zn}_{12.8}\text{Mn}_{15.2}$ and $\text{Au}_{40}\text{Cu}_{28}\text{Ag}_7\text{Pd}_5\text{Si}_{20}$ [20] were prepared by arc-melting the mixture of commercially pure elements in Ti gettered Ar atmosphere. Ribbons 25 μm thick and 2 mm wide were obtained by melt-spinning the master alloy with a linear velocity of the copper wheel of 22 m/s. The former alloy solidifies as an *fcc* solid solution, the latter as a glass.

Ribbons of the two alloys have been free corroded in 14.4 M, 10 M and 5 M HNO_3 aqueous solution for etching time of 1 month at 255 K, 24 h at 293K and 6 h at 343 K and 363 K aiming at complete de-alloying through the thickness. They have been analysed before and after etching using X-ray diffraction (XRD) in Bragg-Brentano geometry with monochromatic Cu $K\alpha$ radiation, Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS) (calibrated with a Co standard), [Transmission Electron Microscopy \(TEM\) after mechanical thinning](#).

All electrolytes have been prepared from chemical grade reagents and deionized water. Characterization of the porous structure has been performed by measuring the average ligament size using a software for image analysis and checked also with some manual tests employing the intercept method.

3. Results

3.1 Characterization and free corrosion of a multicomponent crystalline alloy

$\text{Au}_{31}\text{Cu}_{41}\text{Zn}_{12.8}\text{Mn}_{15.2}$ is a 14 carats alloy, whose composition was designed to be free of allergenic Ni, a major whitener of most commercial white golds [11]. In addition to being well characterized in the Authors' laboratory, this alloy has been selected because it is multicomponent and the amount of the most noble element, i.e. Au, is less than the parting

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4 limit for de-alloying of Au based alloys [5, 21]. The melt spun ribbon is constituted by
5 columnar grains of a *fcc* solid solution which grew from the surface in contact with the wheel
6 of the melt spinning apparatus in the direction along which heat was subtracted during the
7 rapid quenching process. High resolution SEM images of the top view of as-spun ribbons de-
8 alloyed in 14.4 M at different temperatures are shown in Fig. 1a to 1d. The porous structure is
9 similar also inside the cross section and uniform for every sample. The size of ligaments
10 increases as a function of temperature and electrolyte concentration (see Figs. S1 and S2 in
11 supporting information). The samples are fully de-alloyed as shown by the image of the cross
12 section (Fig. 1e); it is apparent that the ribbon underwent intergranular fracture and, therefore,
13 the elongated grains produced by the solidification are recognized. The average size resulting
14 from at least one hundred ligaments, is reported for all samples in Fig. 1f. The scatter
15 associated to each measurement is the standard deviation with respect to the average size.
16 Ligaments and pores coarsen on increasing the processing temperature. No significant
17 differences have been observed in ligament size between air and wheel-side of the melt spun
18 ribbon. EDS analyses show the ligaments are made of almost pure Au for samples de-alloyed
19 in 14.4 M, 10 M, and 5 M HNO₃ at the highest temperatures whereas after de-alloying at the
20 lowest temperature Cu, Mn and Zn have still been detected in the amount of ~18, 7 and 4 at
21 %, respectively.

22
23 The close-up image of ligaments and pores in Fig. 2a shows the interconnected network
24 within a single crystal of NPG. Surfaces display varied curvature with smooth transition from
25 place and pores are rounded in several locations.

26 Diffraction patterns of the samples de-alloyed in 14.4 M HNO₃ at different temperatures
27 indicate that the *fcc* solid solution in the as spun ribbon is completely de-alloyed except at
28 255 K (Fig. 3): in the former case only *fcc* reflections of almost pure gold appear, in the latter
29 low intensity reflections of the starting *fcc* solid solution are still recognized. The lattice
30 parameter, a_0 , is close to the value of pure Au ($a_0 = 4.08 \text{ \AA}$) within the experimental error for
31 all samples, except that prepared at 255 K and 5 M at low temperatures in which residual
32 percentage of other elements inside ligaments is retained. A texture effect on (111) and (200)
33 reflections is observed in patterns taken on the air side (Fig. 3, inset) confirming the crystal
34 orientation is maintained in the porous gold after de-alloying. The same behaviour has been
35 noticed for samples de-alloyed in 10 M and 5 M HNO₃ (Supporting information, Figs. S3
36 and S4). The size of scattering domains has been evaluated according to the Rietveld method
37 [22] and results of the same order as that of ligaments (data are collected in Table 1,
38 supporting information).

39 40 41 3.2 Characterization and free corrosion of a multicomponent Au₄₀Cu₂₈Ag₇Pd₅Si₂₀ 42 amorphous alloy

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44 The Au₄₀Cu₂₈Ag₇Pd₅Si₂₀ composition has been developed to improve the glass forming
45 ability of Au-based glassy alloys [23]. Glass formation in these alloys is favoured by the
46 negative enthalpy of mixing between the main components in the liquid state which implies
47 the occurrence of short range order. In glass-forming melts based on Au a preferential
48 interaction occurs between the metalloid, Si, and the metal atoms, therefore the Si is mostly
49 surrounded by metals in the glass structure, as typical for metal-metalloid systems [24].
50 Among the component elements, the Si is less noble and, therefore, its removal initiates the
51 etching process by providing sites for dissolution of the surrounding less noble metals which
52 lead to electrolyte percolation for continuing the process in the interior of the ribbon. The
53 glass structure is then disrupted and the local composition is shifted outside the glass forming
54 range. The remaining noble atoms are then left free to group by moving to short distances. A
55 large number of crystals of nanometre size having compact structure is formed as shown by
56 TEM images of samples de-alloyed for 30 s in 1 M HNO₃ [17] (Figs. S5, Supporting
57 information). After 5 minutes the crystals appear to coalesce into ligaments and with pores in
58 between (Figs. S6, Supporting information). These images were collected with samples
59 mechanically thinned before de-alloying, a measure taken to avoid any artifact in the
60 preparation of transparent samples. For longer de-alloying times significant information is
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4 provided by the SEM images (Fig. 2b) which show that ligaments have grown in multiple
5 locations to the size of hundreds of nanometre while being made of several crystals. It is
6 apparent that surface diffusion of the adatoms along the surface/electrolyte interface has
7 extensively occurred causing growth of the impinged crystals forming ligaments. The
8 reduction of surface energy has also driven the coalescence of pore. The kinetics of the
9 diffusional mechanism of de-alloying was earlier reported both in the case of potentiostatic
10 etching in 1 M HNO₃, H₂SO₄ and HClO₄ [17] and of free corrosion [20]. Since amorphous
11 alloys are corrosion resistant, complete de-alloying of the ribbon can be achieved in
12 reasonable times only at temperatures from 70 °C and above. Results on the size of ligaments
13 as a function of temperature are reported in Fig. 1f and collected in Tab. 2 of supplementary
14 information. The size is comparable to that of ligaments obtained from the crystalline alloy at
15 all temperatures. XRD patterns display broad reflections of the *fcc* phase indicating the
16 occurrence of fine scattering domains (Fig. 4). Their size was obtained from Rietveld analysis
17 and is given in Tab. 2 as well.

18
19 EDS performed on areas of the surface reveals the predominance of Au but also
20 substantial quantities of the other elements. Since the crystallization of Au implies that Si has
21 been removed from the uppermost layer, the measured overall Si content must originate from
22 the underlying glassy phase. This is 6 at % after 15 minutes de-alloying, detected at spots
23 after 30 minutes, and below the detection limit from 1 h onwards. The amount found for
24 metal elements is due to contribution of both the de-alloyed layer and of the amorphous
25 substrate. After 15 and 30 minutes the metal concentrations are, respectively: 19 and 7 at %
26 for Cu, 3 and 2 at % for Ag, 1 at % and below limit for Pd. These average values result from
27 several measurement on different parts of the surface and are affected by a scatter of the order
28 of 30%. However, they exceed those expected if the elements were contained only in the
29 amorphous part. For longer times, inspection of spectra revealed clearly traces of Cu, Ag and
30 Pd in various locations although their overall amount cannot be quantified with precision
31 [17]. It is, therefore, concluded that these elements remain trapped to some extent in the
32 protrusions and ligaments.

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34 A close up view of ligaments and pores is shown in Fig. 2b. The main feature to be noted
35 is that the ligaments are made of several crystals whose boundaries are visible on the external
36 surface. The size of these grains is of the same order as that of scattering domains. This
37 microstructure indicates that each crystal grew separately until impingement with one
38 another. The shape of ligaments is less homogeneous than in Fig. 2a, containing some crystal
39 agglomerates and thinner bridged in between.

40 4. Discussion

41 4.1 De-alloying of Crystalline vs Amorphous Alloys

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45 The formation and evolution of ligaments and pores in homogeneous crystalline solid
46 solutions i.e. Au-Ag or Au-Cu, is understood according to the model put forward by
47 Erlebacher and co-workers [7] which accounts for surface diffusion of atoms and capillary
48 forces competing during the de-alloying process. The less noble metal is dissolved layer by
49 layer letting gold free to move by surface diffusion to form islands and then hills. As more
50 atoms are removed, the mounds are undercut and a skeleton of ligaments of Au is formed in
51 the bulk of the original grains of the alloy. Coarsening of ligaments due to a capillary-driven
52 mechanism, or de-roughening, occurs with time at length scales of the order of the diffusion
53 distance. The de-alloying of the multicomponent alloy employed in this work appears to
54 follow closely this mechanism in all instances. It is apparent that Au atoms diffuse on the
55 surface of the *fcc* phase and cluster to get a complete shell of nearest neighbours. Therefore,
56 the original grains to which the ligaments are bonded are progressively filled with pores.

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58 The local order in metal-metalloid amorphous alloys is represented by polyhedra which
59 contain at their centre the metalloid atom, e. g. capped trigonal prisms of metal atoms having
60 varied local distortion. The prototype Au₈₆Si₁₆ from which the glassy alloy employed in this
61 study was derived, was shown to conform to this picture [24]. Usually the density of
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4 amorphous alloys is slightly less than that of the corresponding crystals (of the order of a few
5 units percent [25]). The metal atoms then have slightly looser bonding and coordination in
6 the glassy structure with respect to the crystalline counterpart. The combination of metal
7 atoms contained in $\text{Au}_{40}\text{Cu}_{28}\text{Ag}_7\text{Pd}_5\text{Si}_{20}$ increases the glass forming tendency by reducing the
8 chance of nucleating crystals on quenching. It is reckoned the metal atoms mix randomly in
9 the coordination shell of Si of which the Au constitutes about one half. These Au first
10 neighbours are liberated by dissolution of less noble elements and move as adatoms creating
11 sites for aggregation of further noble atoms into their stable *fcc* structure. This occurs at
12 random in a large number of places so that numerous domains grow as a function of time
13 until they impinge on each other forming ligaments. The size of the crystalline domains
14 should then be of the order of the diffusion distance in the given condition of temperature and
15 electrolyte concentration. The morphology of ligaments (Fig. 2) obtained from crystalline
16 alloys are smooth and roundish while ligaments originated from amorphous precursors are
17 knobby and rough suggesting a difference in mechanism of de-alloying between crystalline
18 and amorphous precursors. This is then demonstrated by considering the ratio, *r*, between the
19 dimension of scattering domains from Rietveld analyses of the pertinent XRD patterns and
20 the ligament size as measured by high resolution SEM images (Fig. 5) which is close to one
21 for the crystalline alloy and between 4 and 5.5 for the amorphous alloy indicating that each
22 ligament is composed of multiple crystals. The decreasing trend of *r* as a function of
23 temperature is indicative of the expected coarsening of crystal domains.
24

25 A common feature of both crystalline [26] and amorphous alloys is that their de-alloyed
26 products retain amounts of less noble metal atoms which are apparently trapped in the
27 crystals by the movement of the Au atoms. [The combination of morphology and residual
28 elements occurring only in the case of de-alloying a metallic glass might be of relevance for
29 specific applications in catalysis or sensing \[6, 27\].](#)
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31 4.2 Surface Au diffusivity in free corrosion condition 32

33 Diffusion of adatoms along the surface/electrolyte interface in de-alloying is driven by
34 the decrease of interfacial energy due to the reduction of surface area analogously to
35 coalescence of particles in de-roughening of Au electrodes [28, 29]. The rate of increase in
36 radius of the coarsening particles, *r*(*t*), is given by $\frac{d(r^4)}{dt} = \frac{2\gamma a_0^4 D_s}{kT}$. The surface diffusivity, *D_s*,
37 is obtained by integrating this equation and by using the following parameters [30, 31, 32]: *k*
38 the Boltzmann constant, *T* the dealloying temperature, γ the surface energy (of the order of 1
39 Jm^{-2} for Au in contact with an aqueous solution [28]), *t* the dealloying time, *a*₀ a jump
40 distance assumed to be of the order of the lattice constant of Au (4.08×10^{-10} m), *r* is the
41 ligament size when the precursor is a crystalline alloy or the dimension of scattering domains
42 in the case of an amorphous one [20]. *D_s* values obtained for the crystalline alloy increase as a
43 function of temperature with an Arrhenius dependence and with electrolyte concentration
44 (Fig. 6, and values collected in Tab. 3, supporting information). They fall in the range of the
45 diffusivity values reported in the literature for electrode de-roughening at comparable
46 temperatures [25, 33, 34]. The activation energy for surface diffusion, *E_a*, has been obtained
47 as 78 ± 4 , 93 ± 7 and 97 ± 5 kJ mol^{-1} respectively in 14.4, 10 and 5 M HNO_3 . (Table 4,
48 supporting information). Values of *E_a* for surface diffusion of Au under an applied potential
49 fall in the range from 50 to 60 kJ/mol with decreasing trend with increasing potential [26]
50 whereas it reaches 167 kJ/mol in a vacuum. The present intermediate values look appropriate
51 for a free corrosion process although the varied *E_a*'s obtained for de-alloying in concentrated
52 HNO_3 solutions cannot be explained at the moment. The activation energy for the formation
53 of ligaments using the amorphous alloy is 76 ± 17 kJ/mol [20], close to the above values for
54 de-alloying of the crystalline alloy in consideration of the scatter in data for both cases. The
55 *D_s* values are lower for the amorphous alloy apparently because of a varied pre-exponential
56 factor which is dependent on the activation entropy [26], i. e. the difference in entropy
57 between the activated state and the initial state of the atom. As discussed for the de-
58 roughening process the pre-exponential factor vary widely according to the environment
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4 where the crystal is with higher values in contact with the vacuum and lower when the
5 moving atom interacts with an electrolyte. In the de-alloying of either crystalline or
6 amorphous alloys the activated state should involve a relevant interaction with the electrolyte
7 which will mostly determine the height of the activation barrier in both cases whereas the
8 initial state differs: the case of Au atoms on the surface of an amorphous alloy implying more
9 disorder. Care must be taken in handling these values in consideration of the scatter in data
10 for both cases.

11 It is finally noted that in addition to de-roughening and coarsening of ligaments, the
12 surface tension drives a further phenomenon: i. e. grain boundary grooving. Grooves form
13 where the external surface meets grain boundaries by atomic movement away from the
14 junction. The flux of atoms is described in an way analogous to de-roughening but in
15 opposite direction [35]. Applying this concept to the present case of formation of ligaments
16 by de-alloying an amorphous alloy, it is then expected that the flattening of the surface of
17 ligaments ceases when local equilibrium at the triple junction is reached. The images in Fig. 2
18 may be representative of the different behaviour with respect to crystalline alloys due to the
19 occurrence or absence of grain boundaries in the two cases although the process was
20 conducted in the same conditions and to the same extent.
21

22 Conclusions

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24 Two multicomponent Au-based alloys having respectively a crystalline and an
25 amorphous structure have been de-alloyed by free corrosion in the same conditions leading to
26 NPG. The morphology and size of ligaments and pores have been studied by XRD, Rietveld
27 analysis and SEM images showing the coarsening of ligaments as a function of temperature
28 and electrolyte concentration.
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30 By comparing the ligament morphology between NPG from crystalline or amorphous
31 precursor, differences in the de-alloying mechanism have been revealed: while for the
32 crystalline alloy the etching retains the original grains on removing the less noble elements,
33 in amorphous alloy the progressive removal of less noble elements liberates adatoms of Au
34 that form aggregates with other noble atoms moving by surface diffusion. These domains
35 grow as a function of the time until they impinge with other domains forming ligaments
36 composed of several crystals. The morphology of ligaments is then dependent on the nature
37 of the matrix from which it derives. In addition to the surface appearance of ligaments this is
38 proven by the parameter r , defined as the ratio between the size of ligaments and scattering
39 domains, which in the case of amorphous alloys is of the order of 5 while in the case of
40 crystalline alloys is close to one. Furthermore, the surface diffusivity D_s and the activation
41 energy for diffusion E_a have been discussed using a surface diffusion model of de-roughening
42 Au electrodes: D_s result in the range found in literature, the activation energy is somewhat
43 higher in comparison with de-alloying processes performed with an applied electrochemical
44 potential, and the pre-exponential factor is lower for the amorphous alloy in relation to
45 differences in entropy between the activated state and the initial state of the moving atom.
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51
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Table 1

Conc. (M)	Temp. (K)	Ligament size (D)/(nm)	Scattering Domains (S_d)/(nm)	r D/ S_d
5	255	22±6	25±1	0.69±0.21
	293	37±9	47±1	0.63±0.16
	343	116±28	115±2	1.00±0.26
	363	166±66	136±1	1.69±0.65
10	255	26±4	48±1	0.54±0.09
	293	41±11	60±1	0.48±0.14
	343	132±33	132±1	0.93±0.25
	363	168±43	156±3	1.21±0.35
14.4	255	46±12	45±1	1.03±0.30
	293	66±17	65±1	0.76±0.20
	343	139±32	107±1	1.39±0.33
	363	155±40	207±4	0.69±0.20

Tab.2

Concentration [M]	Temp. (K)	Ligament size (D)/(nm)	Scat. Domains (S_d)/(nm)	r D/ S_d
10	293	77±17	14±1	5.66±1.29
	313	81±17	17±1	4.82±1.04
	343	92±21	19±1	4.77±1.19
	363	142±43	38±1	3.78±1.16

Table 3

Temperature K	Electrolyte concentration		
	14.4 M	10 M	5 M
255	$7.1 \cdot 10^{-21}$	$7.0 \cdot 10^{-22}$	$3.4 \cdot 10^{-22}$
293	$9.9 \cdot 10^{-19}$	$1.5 \cdot 10^{-19}$	$1.0 \cdot 10^{-19}$
343	$9.3 \cdot 10^{-17}$	$7.4 \cdot 10^{-17}$	$4.5 \cdot 10^{-17}$
363	$1.5 \cdot 10^{-16}$	$2.0 \cdot 10^{-16}$	$2.0 \cdot 10^{-16}$

Table 4

Reference	Structure of the starting alloy	Sample	Electrolyte	E_a kJ mol ⁻¹
[29] Z. Zhang	Crystalline	Al ₂ Au	20 wt.% NaOH	60.1±2.9
[27] J.M. Dona	Crystalline	Au	0.5 H ₂ SO ₄	55.1-14.3
[28] C. Alonso	Crystalline	Au	0.5 H ₂ SO ₄	59
[28] C. Alonso	Crystalline	Pt	0.5 H ₂ SO ₄	79
[30] L.H. Qian	Crystalline	Ag ₆₅ Au ₃₅	70% HNO ₃	74±3
[20] F. Scaglione	Amorphous	Au ₄₀ Cu ₂₈ Ag ₇ Pd ₅ Si ₂₀	10 M HNO ₃	76±17

Fig.1

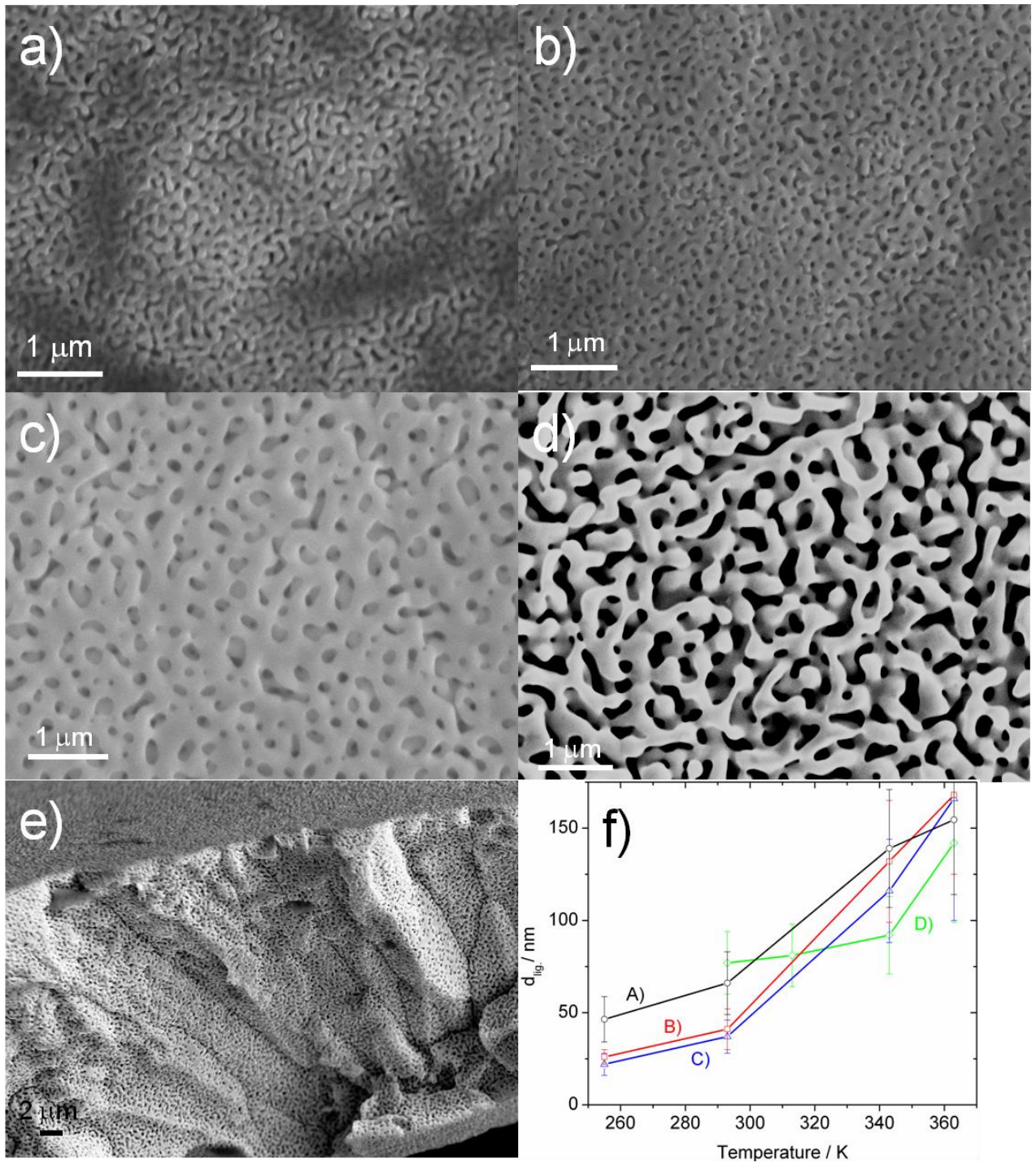


Fig. 2

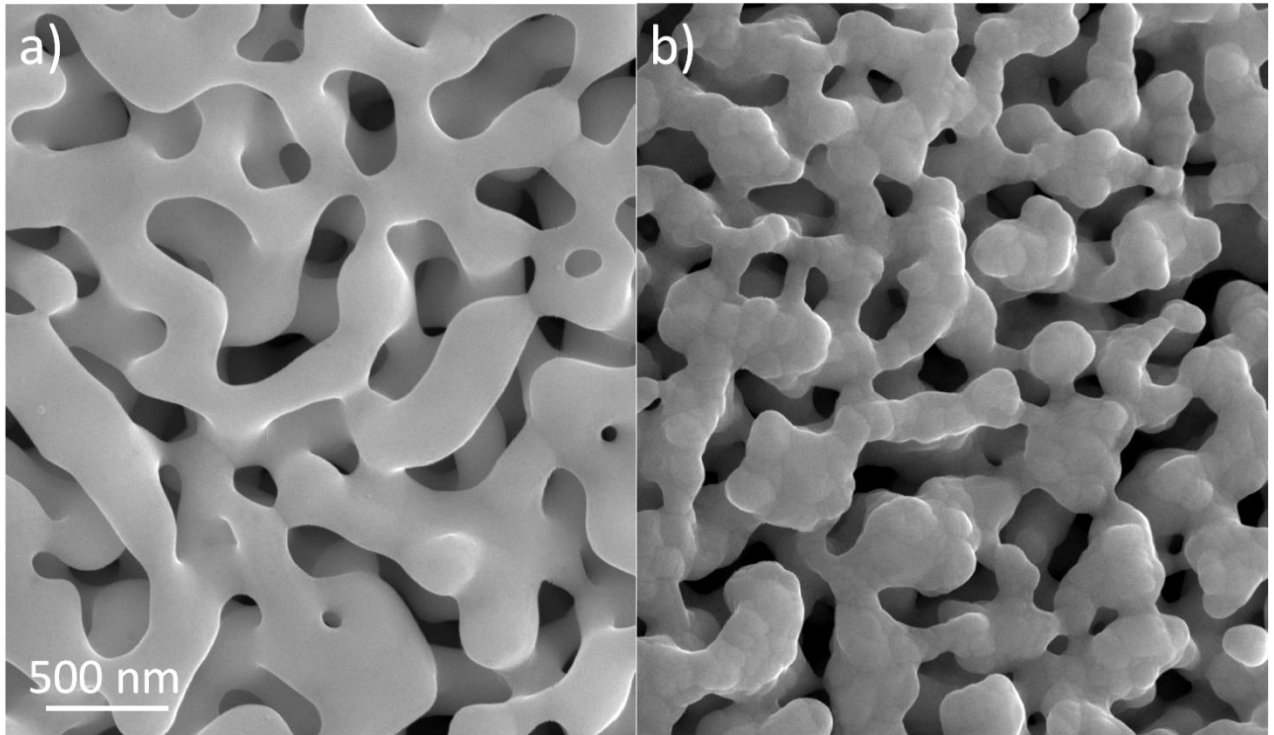


Fig.3

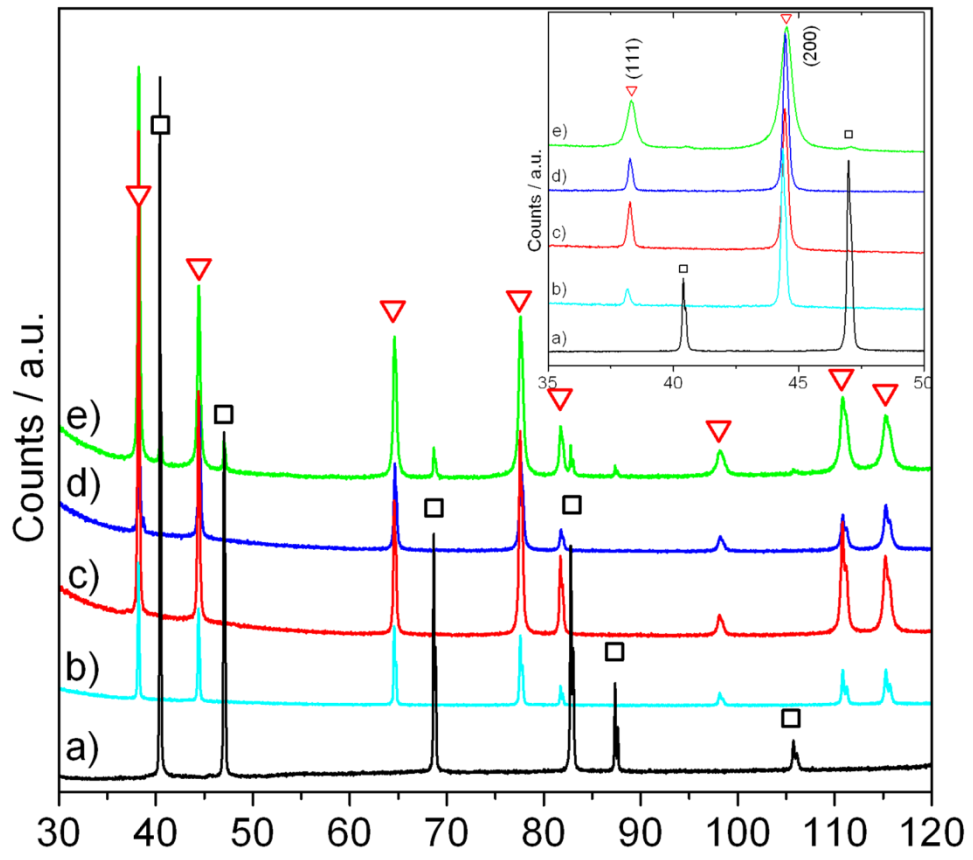


Fig.4

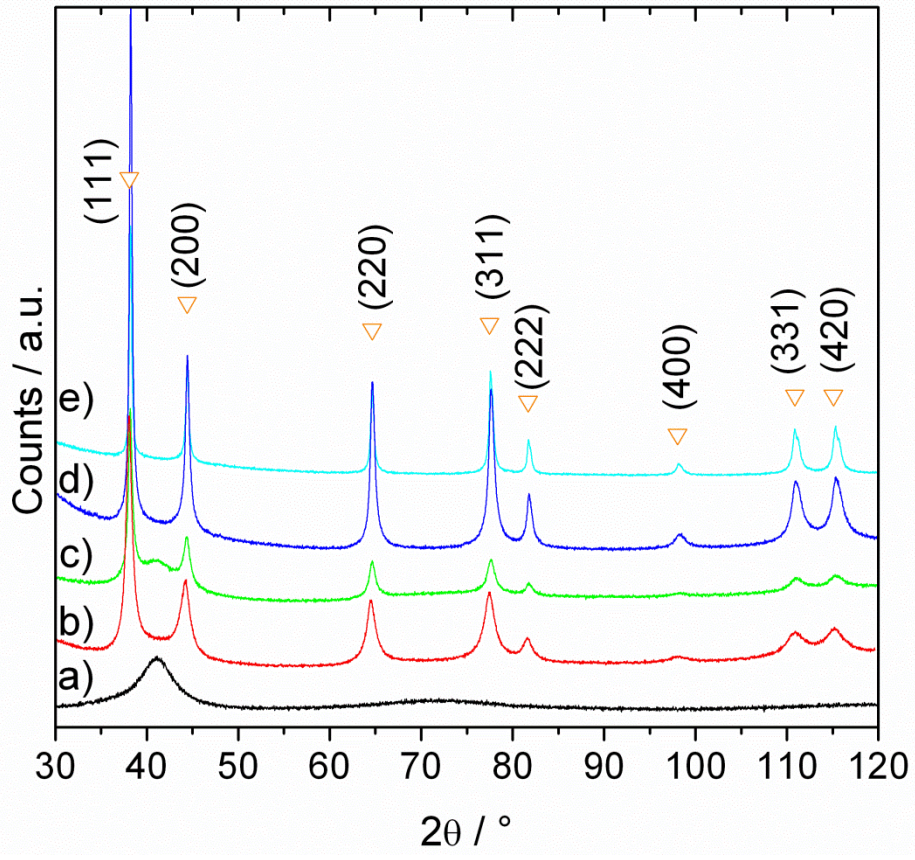


Fig.5

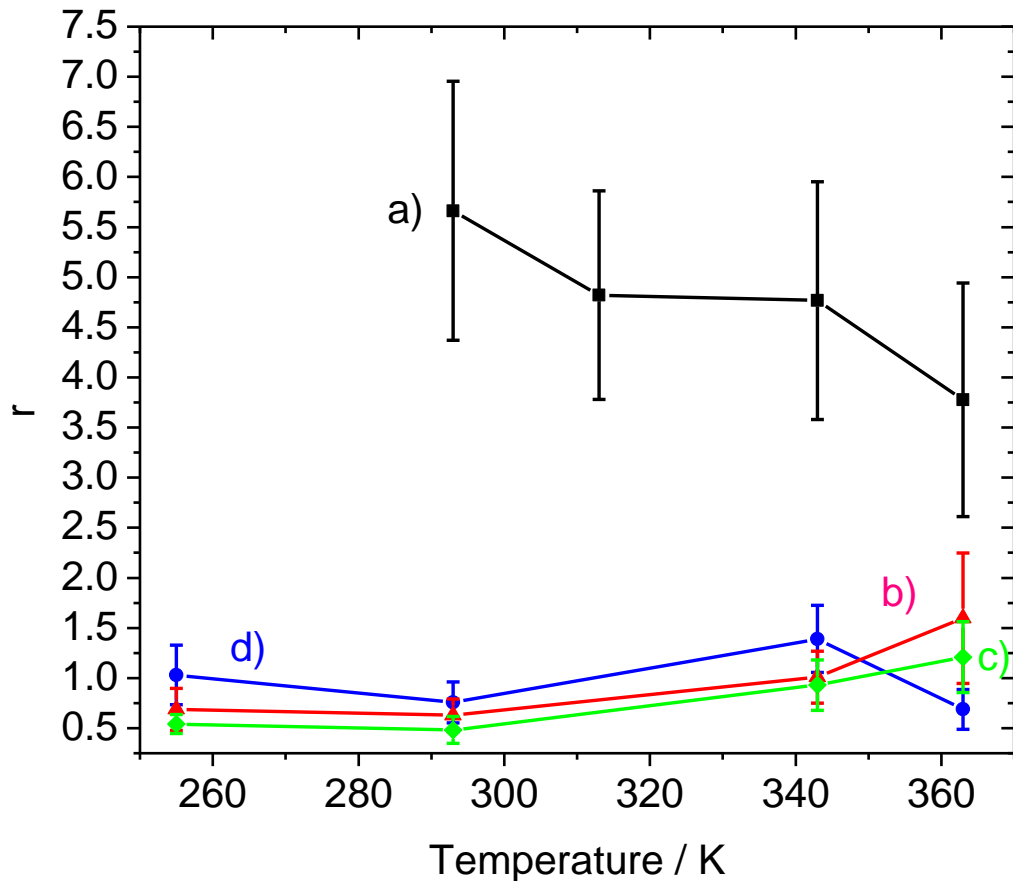
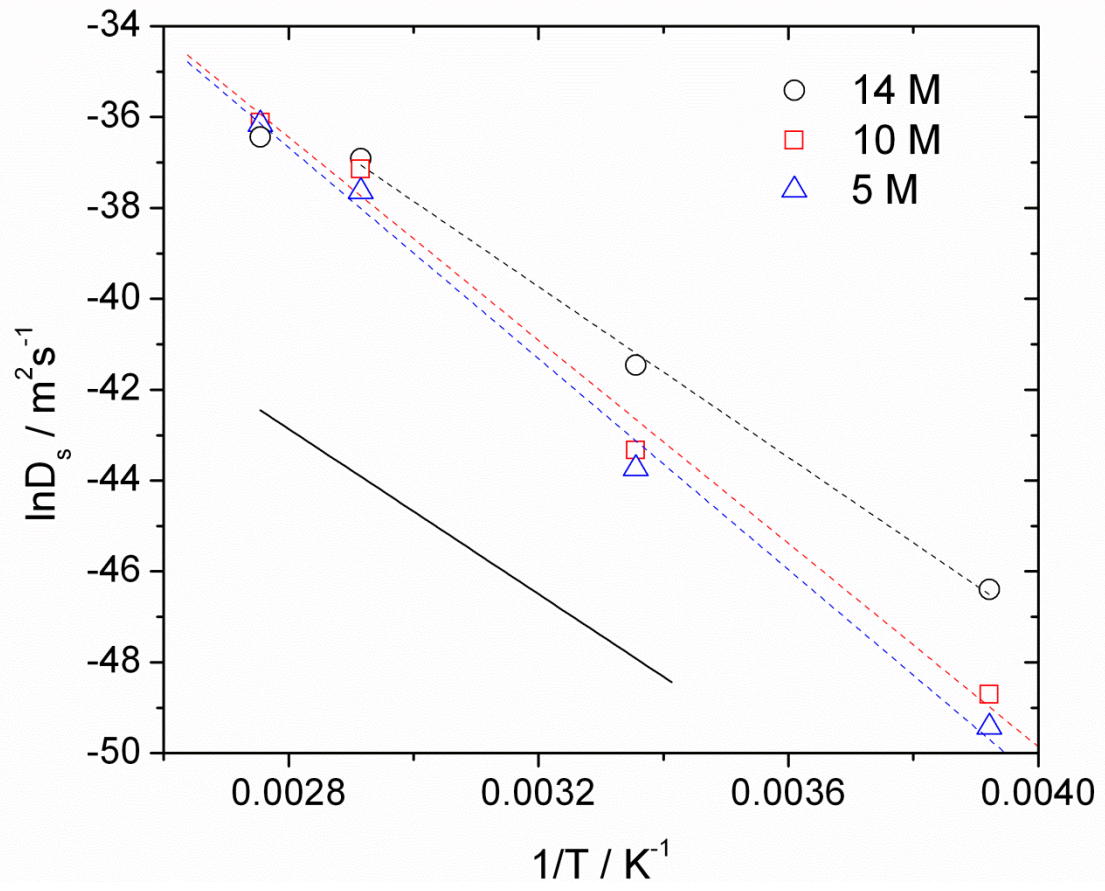


Fig.6



Highlights

- 1) NPG made by free corrosion of a crystalline and an amorphous Au-based alloys
- 2) Coarsening of ligaments as a function of temperature and electrolyte concentration
- 3) Difference in de-alloying mechanism in crystalline or amorphous precursor outlined
- 4) Ligaments morphology changes with the matrix from which they derive
- 5) Kinetics of de-alloying determined

Images captions

Fig.1. Top view of the $\text{Au}_{31}\text{Cu}_{41}\text{Zn}_{12.8}\text{Mn}_{15.2}$ crystalline alloy after free corrosion in 14.4 M HNO_3 at a) 255 K, b) 293 K, c) 343 K, d) 363 K, e) 363 K, cross section. In f) the average size of ligaments is reported as a function of temperature in A) 14.4 M, B) 10 M, C) 5 M HNO_3 . Data marked D) are for de-alloying in 10 M HNO_3 the $\text{Au}_{40}\text{Cu}_{28}\text{Ag}_7\text{Pd}_5\text{Si}_{20}$ amorphous alloy.

Fig.2. Close-up image of ligaments and pores obtained from de-alloying of a) the $\text{Au}_{31}\text{Cu}_{41}\text{Zn}_{12.8}\text{Mn}_{15.2}$ crystalline and b) the $\text{Au}_{40}\text{Cu}_{28}\text{Ag}_7\text{Pd}_5\text{Si}_{20}$ amorphous alloy.

Fig.3. XRD patterns taken on the wheel side of the as-spun $\text{Au}_{31}\text{Cu}_{41}\text{Zn}_{12.8}\text{Mn}_{15.2}$ ribbon a) and on samples de-alloyed in 14.4 M HNO_3 at 363 b), 343 c), RT d) and 255 K e). A detail of patterns showing the texture on the air side is given in the inset. Symbols: \square as-spun and ∇ de-alloyed.

Fig.4. XRD pattern of the $\text{Au}_{40}\text{Cu}_{28}\text{Ag}_7\text{Pd}_5\text{Si}_{20}$ amorphous alloy a) as spun and after de-alloying in 10 M HNO_3 at b) 293 K, c) 313 K, d), 343 K c) and d) and 363 K.

Fig.5 The ratio of the size of scattering domains to that of ligaments vs T for a) $\text{Au}_{40}\text{Cu}_{28}\text{Ag}_7\text{Pd}_5\text{Si}_{20}$ free corroded in 10 M HNO_3 and $\text{Au}_{31}\text{Cu}_{41}\text{Zn}_{12.8}\text{Mn}_{15.2}$ free corroded in b) 5 M, c) 10 M and d) 14.4 M HNO_3 .

Fig.6. Arrhenius plot of $\ln D_s$ vs. T^{-1} . Dashed lines are fits to the data for the de-alloyed $\text{Au}_{31}\text{Cu}_{41}\text{Zn}_{12.8}\text{Mn}_{15.2}$ crystalline alloy in 5, 10 and 14.4 M HNO_3 ; full line is from fitting the data for the de-alloyed $\text{Au}_{40}\text{Cu}_{28}\text{Ag}_7\text{Pd}_5\text{Si}_{20}$ amorphous precursor in 10 M HNO_3 [20].

Supporting information captions

Fig.S1 SEM images of pores and ligaments after free corrosion of $\text{Au}_{31}\text{Cu}_{41}\text{Zn}_{12.8}\text{Mn}_{15.2}$ in 10 M HNO_3 at 255, 293, 343 and 363 K, surface-view and cross section details.

Fig.S2 SEM images of pores and ligaments after free corrosion of $\text{Au}_{31}\text{Cu}_{41}\text{Zn}_{12.8}\text{Mn}_{15.2}$ in 5 M HNO_3 at 255, 293, 343 and 363 K, surface-view and cross section details.

Fig.S3. XRD patterns taken on the wheel side of the as-spun $\text{Au}_{31}\text{Cu}_{41}\text{Zn}_{12.8}\text{Mn}_{15.2}$ ribbon a) and on samples de-alloyed in 10 M HNO_3 at 363 b), 343 c), RT d) and 255 K e). A detail of patterns showing the texture on the air side is given in the inset. Symbols: \square as-spun and ∇ de-alloyed.

Fig.S4. XRD patterns taken on the wheel side of the as-spun $\text{Au}_{31}\text{Cu}_{41}\text{Zn}_{12.8}\text{Mn}_{15.2}$ ribbon a) and on samples de-alloyed in 5 M HNO_3 at 363 b), 343 c), RT d) and 255 K e). A detail of patterns showing the texture on the air side is given in the inset. Symbols: \square as-spun and ∇ de-alloyed.

Fig.S5. HRTEM image of a sample of amorphous $\text{Au}_{40}\text{Cu}_{28}\text{Ag}_7\text{Pd}_5\text{Si}_{20}$ de-alloyed for 30 s in 1 M HNO_3 . Lattice fringes due to random fine crystals of nanometer size are widespread in the viewing area.

Fig.S6. HRTEM image of a sample of amorphous $\text{Au}_{40}\text{Cu}_{28}\text{Ag}_7\text{Pd}_5\text{Si}_{20}$ de-alloyed for 5 min in 1 M HNO_3 . Lattice fringes due to random crystals are seen. Coalescence of crystals into ligaments and pores starts becoming apparent.

Table 1. Ligament size, scattering domains and their ratio r for the $\text{Au}_{31}\text{Cu}_{41}\text{Zn}_{12.8}\text{Mn}_{15.2}$ crystalline alloy after de-alloying treatment. Ligaments have been evaluated from high resolution SEM images while scattering domains from Rietveld analyses of the relative XRD patterns.

Table 2. Ligament size, scattering domains and their ratio r for $\text{Au}_{40}\text{Cu}_{28}\text{Ag}_7\text{Pd}_5\text{Si}_{20}$ the amorphous alloy after de-alloying treatments. Ligaments have been evaluated from hi resolution SEM images while scattering domains from Rietveld analyses of the relative XRD patterns. Data reported from literature [20].

Table.3 Surface diffusion coefficients obtained for the de-alloyed $\text{Au}_{31}\text{Cu}_{41}\text{Zn}_{12.8}\text{Mn}_{15.2}$ crystalline alloy at different condition of free corrosion de-alloying. Coefficients are expressed in m^2s^{-1} .

Table.4 Values of E_a obtained for crystalline and amorphous Au-based alloys from the literature.