Supplementary materials

S1 - SAXS analysis

The Porod invariant is defined in the Equation S1.

$$Q = \int_0^\infty q^2 I(q)dq = 2\pi^2 V_0(\Delta\rho^2) \qquad \text{Equation S1}$$

Where, $(\Delta\rho^2) = (\rho_1\text{-}\rho_2)^2\varphi_1\varphi_2$ is the contrast in binary system [53]. The ρ_1 and ρ_2 correspond to the density of both phase 1 and 2, respectively, while φ_1 and φ_2 represent the volume ratio of each phase. In other words, the beam scattering happened at the interface of the different phases. In a typical ex-situ experiment, the vacancy of porous material was filled with air [61]. So the ρ_2 is the density of air while φ_2 is the porosity of material.

The contrast $(\Delta\rho^2)$ was therefore modified in order to satisfy trinary phase system (Equation S2).

$$(\Delta\rho^2) = (\rho_1 - \rho_2)^2\varphi_1\varphi_2 + (\rho_1 - \rho_3)^2\varphi_1\varphi_3 + (\rho_3 - \rho_2)^2\varphi_3\varphi_2 \qquad \text{Equation S2}$$

Where the ρ_1 and φ_1 represent the density and volume ratio of pristine brass phase respectively; while the ρ_2 and φ_2 represent those of the vacancy phase which is filled by solution and the ρ_3 and φ_3 correspond to the ligament phase. A number of assumptions were introduced to simplify the data analysis.

The Kratky plot was calculated from Equation S3 and S4.

$$Q = \int_0^{0.2} q^2 I(q)dq \qquad \text{Equation S3}$$

Then,

$$Q(t) = \int_{0}^{0.2} q^2 I(q,t) dq \qquad \text{Equation S4}$$

In Equation S5, *t* corresponds to the duration. At $t = 0$, then $I(\mathrm{q,t}) = I_0(\mathrm{q})$, which yields the background invariant Q_0. The porous layer invariant $Q_\mathrm{p}(\mathrm{t})$ is therefore calculated by the difference between $Q(\mathrm{t})$ and Q_0.

$$Q_P(t) = Q(T) - Q_0 = \int_{0}^{0.2} q^2 \,[I(q,t) - I_0(q)\,]dq \qquad \text{Equation S5}$$

Since only the porous part will scatter in the given q range observed the difference value between $\mathrm{I(q,t)} - \mathrm{I_0(q)}$ is theoretically nill, except in the peak area. In other words, only the area under the knee is relevant and may be integrated, to further simply the system, from 0 to 0.2 Å^{-1} (Equation S6).

$$Q_P(t) = \int_{Peak\ area} q^2 \,[I(q,t) - I_0(q)\,]dq \qquad \text{Equation S6}$$

The *Q* invariant was determined from the Kratky plot data. Specifically, I”(q,t) was defined as, I”(q,t) = (I’(q,t)+I’b(t)) * $\mathrm{I_0(q)}$. Since the value interval of original $\mathrm{I_0(q)}$ is ranging from 0.003 Å^{-1} to 0.2 Å^{-1}, the $\mathrm{I_0}$’(q) was obtained by extrapolating $\mathrm{I_0(q)}$ with the Boltzmann equation, which yielded Equation S7.

$$Q_P(t) = \int_{Peak\ start}^{Peak\ end} q^2 \,[I''(q,t) - I_0'(q)\,]dq \qquad \text{Equation S7}$$

The $Q_p(t)$ is regarded as the scattering energy on the de-alloyed part of the sample if assuming the background is constant (assumption still valid in this case, largely within experimental error). Therefore, the scattering volume of the de-alloyed part was obtained by inputing the $Q_p(t)$ into Equation 4.1. Regarding the dense part of the sample, or the non-dealloyed part, which is still part of the background signal, the contrast $(\Delta\rho)^2$ can be simplified into a simple binary system, which is $(\Delta\rho^2) = (\rho_1-\rho_2)^2\varphi_1\varphi_2$.

In the Porod's law, the intensity I(q) is proportional to the scattering vector q in high q, while the relative surface area S is the coefficient (Equation S8).

$$I(q) \sim S\, q^{-4} \qquad \text{Equation S8}$$

The interval of validity of the Porod law should in theory be smaller than 0.1 Å^{-1} since the scattering features in this range would be attributed to interfaces rather than atoms or bonds. Here, the Porod's law was used to reveal the surface area of the ligaments. Therefore, the scattering vector interval of interest was taken for the Porod law outside the range of the main knee area, and close to 0.1 Å^{-1}.

The Guinier analysis allows for the direct estimation of two SAXS invariants, the radius-of-gyration, Rg, and the extrapolated intensity at zero scattering angles, I(0) (Equation S9).

$$\ln \mathrm{I}(q) = \ln I(0) - \frac{{R_g}^2}{3} \cdot q^2 \qquad \text{Equation S9}$$

Where the R_g in Radius of Gyration, the q is scattering vector and I is the scattering intensity which is the function of q. The $q\cdot R_g$ should typically be smaller than 1.3 according to the most common definition of R_g [52, 62]. Since I(0) is constant, the can be simplified and converted into Equation S10.

$$\ln I(q) \sim -\frac{{R_g}^2}{3} \cdot q^2 \qquad \text{Equation S10}$$

The probed volume V_0 of the sample corresponds to the beam size multiplied by the thickness of the sample. So, the scattering volume $V_s = V_0\ \varphi_1(t)$. Therefore, as shown in Equation S11:

$$SQ \sim V_s\,(t)\varphi_2(t) \lim_{q\to\infty} (q^4 I(q)) \qquad \text{Equation S11}$$

Where,

$$\lim_{q\to\infty} (q^4 I(q)) \rightarrow constant$$

Then,

$$AQ \sim V_s(t)[1 - \varphi_1(t)] \qquad \text{Equation S12}$$

The plot A x Q against the process duration, is provided in Figure 6.

During the Au-Ag in-situ dealloying tests, the solid phase ratio increased with process progressing but the increase rate was negatively correlated to the solution temperature. The dissolution rate of atoms is proportional to the solution temperature.

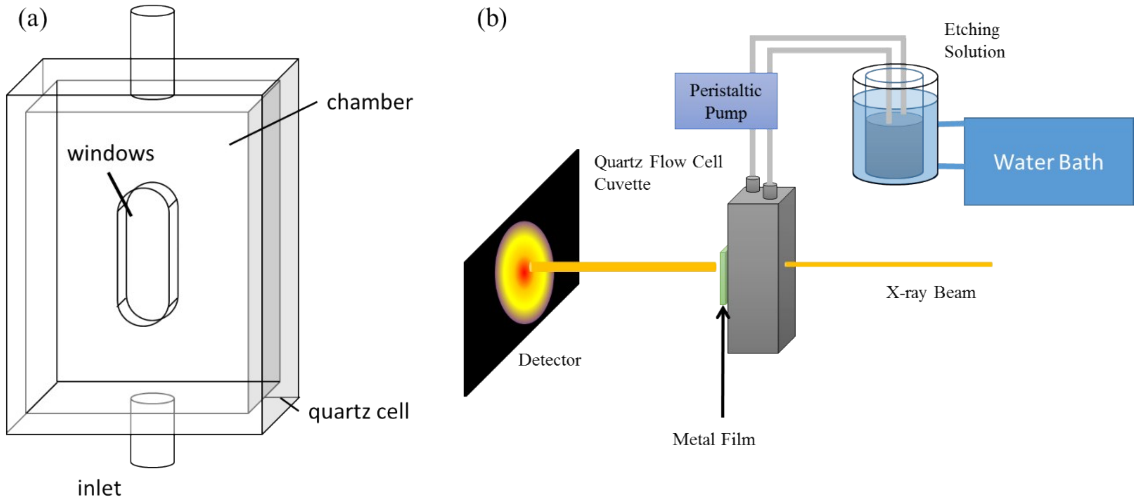


Figure S1. (a) Schematic of the flow cell and (b) schematic of the in-situ chemical DA experiment on the SAXS beam line

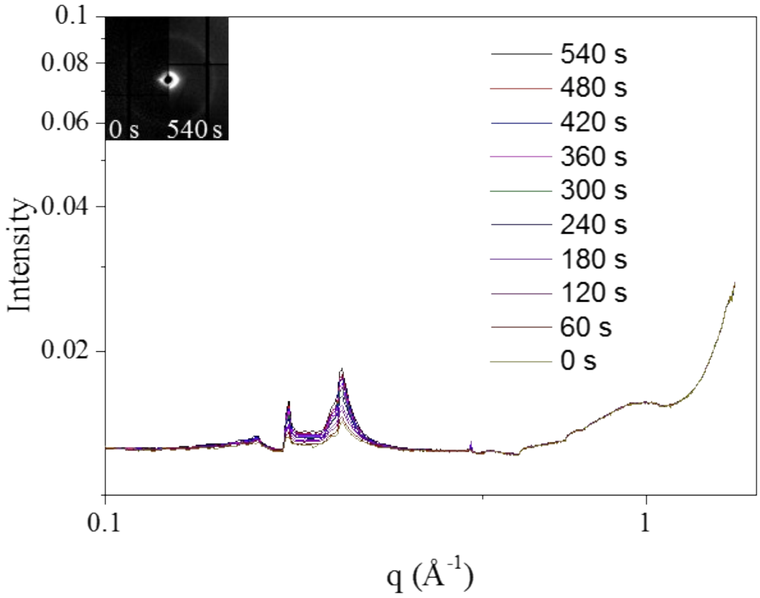


Figure S2. The SAXS patterns of in-situ dealloying test on Au-Ag alloy with 0.6 m camera lens. De-alloyed with 10% HNO_3 at 20 °C

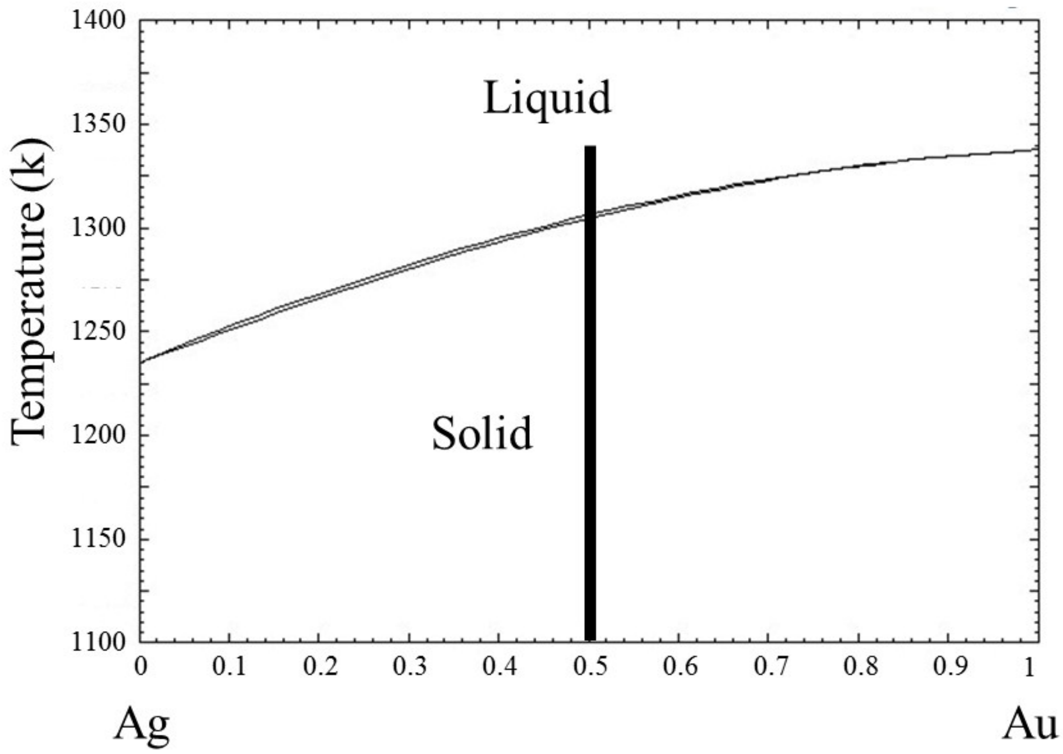


Figure S3. Phase diagram of Au-Ag (re-phase from [56]). Solid line: AuAg50

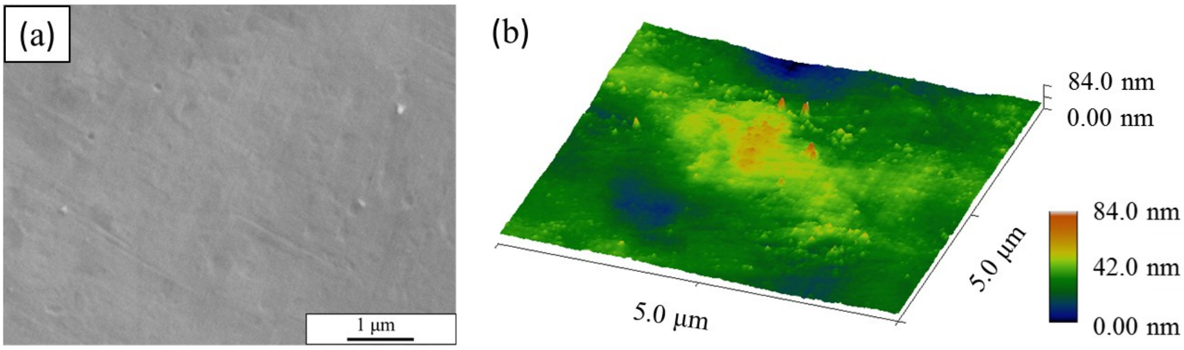
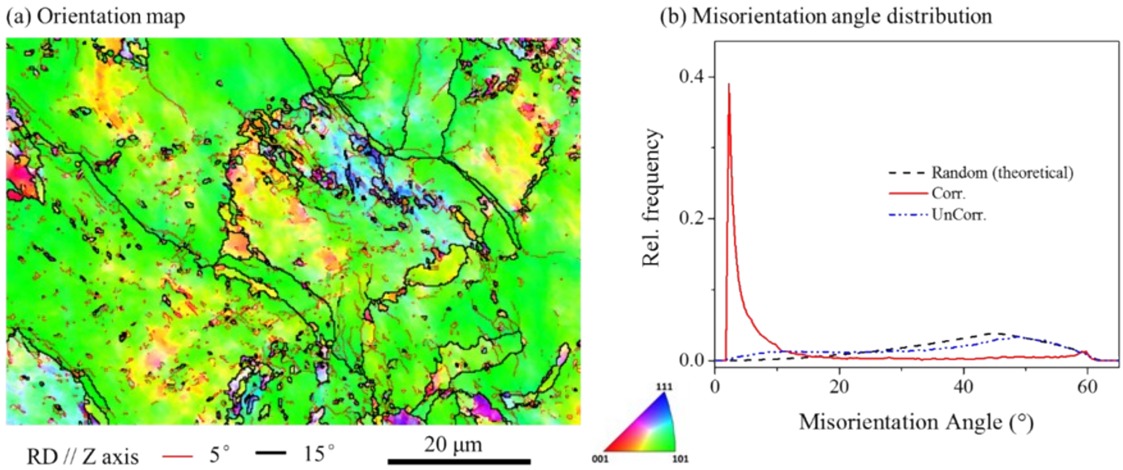


Figure S4. Surface morphology of pristine 120 nm AuAg50 ultra-thin foil. (a) SE IMAGES image; (b) AFM mapping

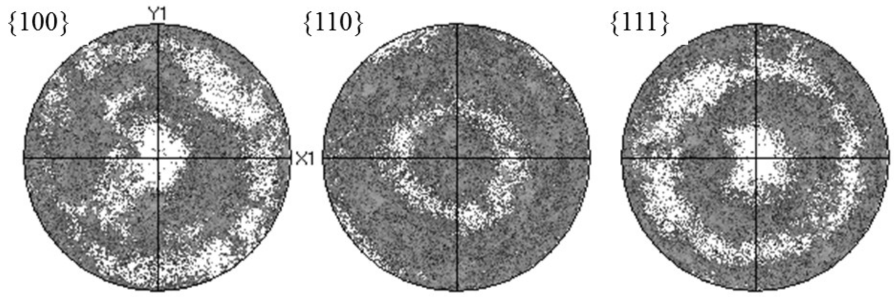


(a) Orientation map

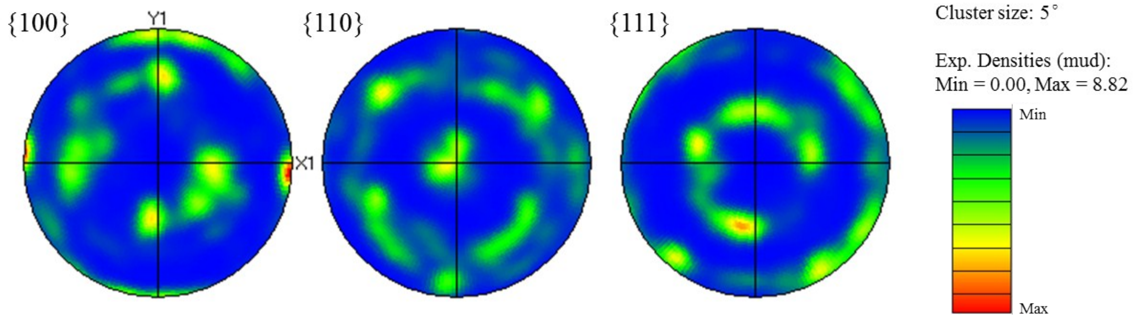
(b) Misorientation angle distribution

Figure S5. (a) EBSD orientation map of pristine 120 nm AuAg50 ultra-thin foil; (b) Misorientation angle distribution

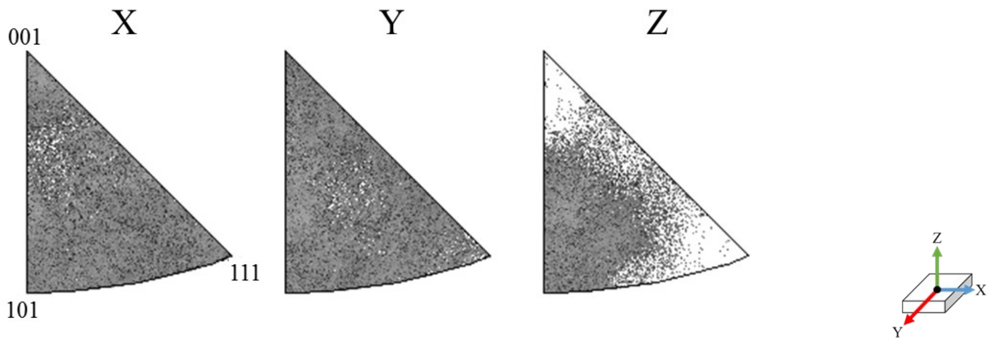
(a) Pole figure



(b) Pole figure – contoured



(c) Inverse pole figure



(d) Inverse pole figure –contoured

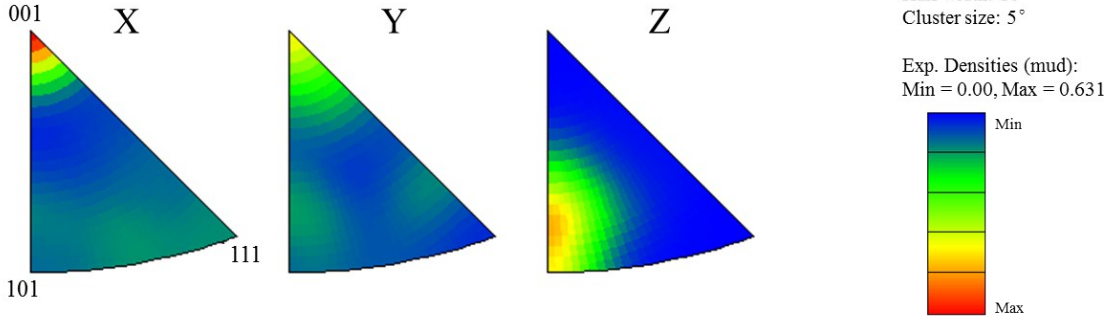
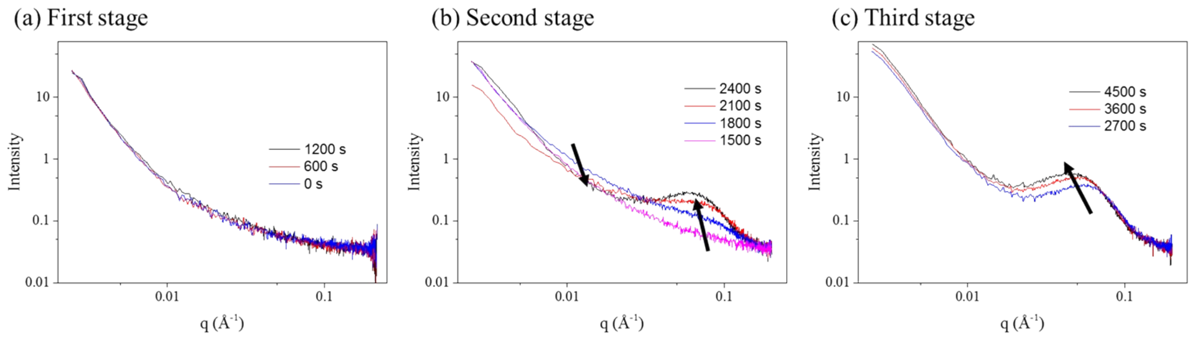


Figure S6. Pole figures and Inverse pole figure of pristine 120 nm AuAg50 ultra-thin foil for fibre texture analysis. (a) PF; (b) contoured PF; (c) IPF; (d) contoured IPF



(a) First stage (b) Second stage (c) Third stage

Temperature	Start	End
5 °C	1500 s	2400 s
20 °C	450 s	900 s
40 °C	30 s	240 s
60 °C	0 s	180 s

Figure S7. Example of three stages of in-situ test shown in SAXS pattern. The sample SAXS pattern is the 5 °C de-alloyed AuAg50 leaf, de-alloyed with 10% HNO3. The arrow displayed on (b) and (c) shown to the trend of intensity change with process progressing. The table shows the boundaries of transformation period for each sample.

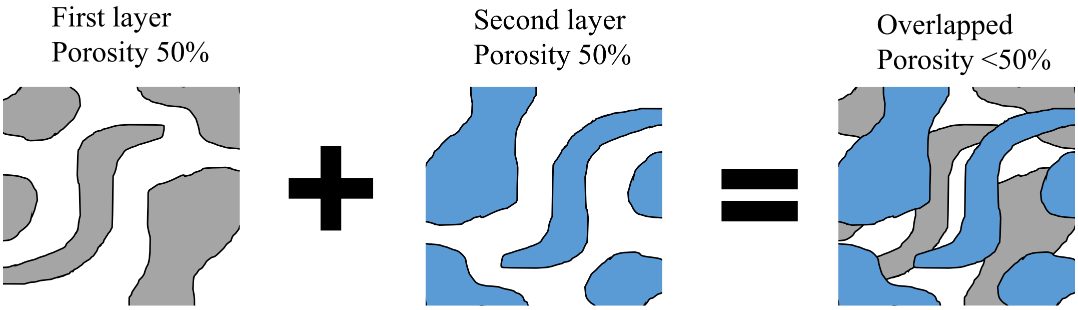
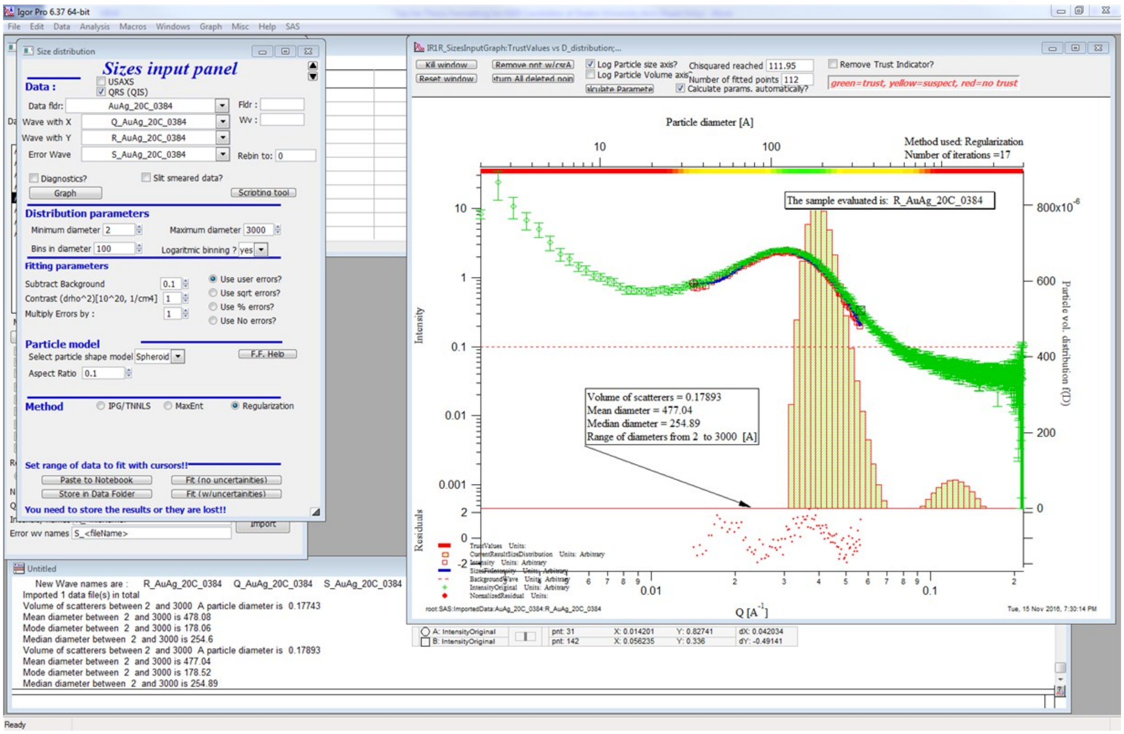


Figure S8. Schematic of the different overlapping dealloyed layers constituting the material. This aspect of the structure is rationalized to explain the difference in surface porosity calculated from the SE IMAGES analysis

Table S1. Analysed results of de-alloyed Au-Ag for both image analysis and Irena size distribution of pores

	R_g (nm)	ImageJ analysing		Irena modelling
		average radius (nm)	average diameter (nm)	mean diameter (nm)
5 ºC	10.5	15.4	30.7	30.96
20 ºC	15.8	17.1	34.2	34.56
40 ºC	17.3	21.7	43.4	47.82
60 ºC	24	27.3	54.5	54.90



Data :

☐ USAXS
☑ QRS (QIS)

Data fldr: AuAg_20C_0384
Fldr :
Wave with X: Q_AuAg_20C_0384
Wv :
Wave with Y: R_AuAg_20C_0384
Error Wave: S_AuAg_20C_0384
Rebin to: 0

☐ Diagnostics?
☐ Slit smeared data?

Distribution parameters

Minimum diameter: 2
Maximum diameter: 3000
Bins in diameter: 100
Logaritmic binning ? yes

Fitting parameters

Subtract Background: 0.1
Contrast (drho^2)[10^20, 1/cm4]: 1
Multiply Errors by : 1

● Use user errors?
○ Use sqrt errors?
○ Use % errors?
○ Use No errors?

Particle model

Select particle shape model: Spheroid
Aspect Ratio: 0.1

Method ○ IPG/TNNLS ○ MaxEnt ● Regularization

Set range of data to fit with cursors!!

You need to store the results or they are lost!!

Error wv names: S_<fileName>

☑ Log Particle size axis?
☐ Log Particle Volume axis?
Chisquared reached: 111.95
Number of fitted points: 112
☑ Calculate params. automatically?
☐ Remove Trust Indicator?
green=trust, yellow=suspect, red=no trust

Method used: Regularization
Number of iterations =17

The sample evaluated is: R_AuAg_20C_0384

Volume of scatterers = 0.17893
Mean diameter = 477.04
Median diameter = 254.89
Range of diameters from 2 to 3000 [A]

root:SAS:ImportedData:AuAg_20C_0384:R_AuAg_20C_0384
Tue, 15 Nov 2016, 7:30:14 PM

○ A: IntensityOriginal pnt: 31 X: 0.014201 Y: 0.82741 dX: 0.042034
☐ B: IntensityOriginal pnt: 142 X: 0.056235 Y: 0.336 dY: -0.49141

Untitled

```
   New Wave names are :    R_AuAg_20C_0384   Q_AuAg_20C_0384   S_AuAg_20C_0384
 Imported 1 data file(s) in total
 Volume of scatterers between 2  and 3000  A particle diameter is  0.17743
 Mean diameter between  2  and 3000 is 478.08
 Mode diameter between  2  and 3000 is 178.06
 Median diameter between  2  and 3000 is 254.6
 Volume of scatterers between 2  and 3000  A particle diameter is  0.17893
 Mean diameter between  2  and 3000 is 477.04
 Mode diameter between  2  and 3000 is 178.52
 Median diameter between  2  and 3000 is 254.89
```

Figure S9. Screen-shot of modelling with Irena