

# *In situ* TEM/STEM of the Coarsening of Nanoporous Gold

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## Abstract

Nanoporous gold (NPG) is usually fabricated by the selective electrolytic dissolution (dealloying) of Ag from a binary Ag-Au alloy, or sometimes from a ternary alloy such as Ag-Au-Pt. The resulting ligament-pore structure is bicontinuous and has many interesting properties and potential applications [1].

Coarsening of NPG after dealloying can alter its catalytic and functional properties considerably. Driven by curvature, Au atoms diffuse quickly along step edges, acting to smoothen the freshly formed surface [2]. Understanding the structural and morphological changes that occur during this process is vital to define the thermal and chemical environments where NPG can be utilized most successfully.

The results reveal how the presence of Pt causes a significant change in the coarsening mechanism, thermal onset of coarsening, and coarsening rate. The distinction between the two main coarsening mechanisms observed, Migration and Coalescence, and Ostwald Ripening, is shown for NPG.

**Keywords:** dealloying, nanoporous gold, coarsening, ostwald ripening, in situ TEM

## 1 Introduction

Several notable studies demonstrated the significance of surface diffusion of Au in the coarsening of ligaments within NPG at temperatures as low as 200 °C [3][4]. However, the presence and/or formation of voids and vacancies during coarsening adds to the complexity of the multi-faceted mechanism involved [5][6].

The effect of the addition of small amounts of Pt to NPG precursors has been proven not only to limit the size of ligaments during dealloying, but to also limit the coarsening of NPG post-dealloying in certain environments [2][7]. The atomistic action of Pt is not understood, beyond the likelihood that slowly diffusing Pt atoms accumulate at step edges.

In an effort to provide a more in-depth understanding on this topic, we have carried out a comparative in situ TEM/STEM study of the morphological evolution of nanoporous layers with different precursors during thermal coarsening. An atmosphere of hydrogen has been used to

ensure a reductive environment, as oxygen causes adsorbate induced segregation of platinum, which totally inhibits coarsening [7]. Effects of sample size and initial pore size-to-ligament size ratio on the coarsening behaviour will also be discussed.

## 2 Experimental

Rectangular samples with the nominal surface areas of ~0.2 cm<sup>2</sup> were cut out of a 25 μm foil made from cold-rolled 200 μm sheet of Ag<sub>77</sub>Au<sub>23</sub> & Ag<sub>77</sub>Au<sub>19</sub>Pt<sub>4</sub> (at.%) from Goodfellow Metals, Cambridge, UK. The samples were annealed at 925 °C for 15 h in H<sub>2</sub>-Ar atmosphere. The samples were then soldered to a copper electrical wire from one end (taking care not to alter the active surface area to be dealloyed). A fine coating of Microshield TM lacquer supplied by SPI was applied to the solder-copper-sample junction to insulate it from the solution used.

All solutions were prepared with 18 MΩ cm de-ionized water and de-aerated by high-purity nitrogen purging (min purity: 99.998%). The samples were dealloyed (separately) potentiostatically in a solution of 0.5 M HClO<sub>4</sub> from Analar grade HClO<sub>4</sub> (Alfa-Aesar, 62 %), at a potential of 550 mV vs. MSE (Mercury/Mercurous Sulfate Electrode/sat. K<sub>2</sub>SO<sub>4</sub>), until the removal of 7 C/cm<sup>2</sup>. The dealloyed samples were then immersed in de-ionized water for approximately 1 h to remove residual acid.

Small particles were detached mechanically on to filter paper and then on to TEM hardware. After mounting the samples on Norcada MEMS heating chips, UV cleaning was done for twenty minutes on the Hitachi TEM holder to ensure the surfaces of the samples are clean.

The pressure of hydrogen flow into the system is set exactly at 1 Pa, which was allowed into the system 10 mins before heating to allow for the pressure all over the chip to equilibrate. Higher pressure of hydrogen was not used as it would accelerate the degradation of the beam current.

In a Hitachi HF-3300 environmental TEM/STEM, the temperature was increased gradually from 25 °C to 600 °C while particles of different sizes, at different areas of the chip are observed in situ using SE (Secondary Electron), BF (Bright Field) and DF (Dark Field) modes at the same time.

## 3 Thermal Coarsening of NPG (AgAu)

Pore sizes measured before heating were measured to be at an average of 8.8 nm, while average ligament sizes were

18.2 nm. Figure 1 shows (encircled in red) the voids formed during dealloying. Such voids are much smaller than pores and can be differentiated from pores as they do not appear in the SE images, showing they are enclosed inside ligaments rather than neighbouring them.

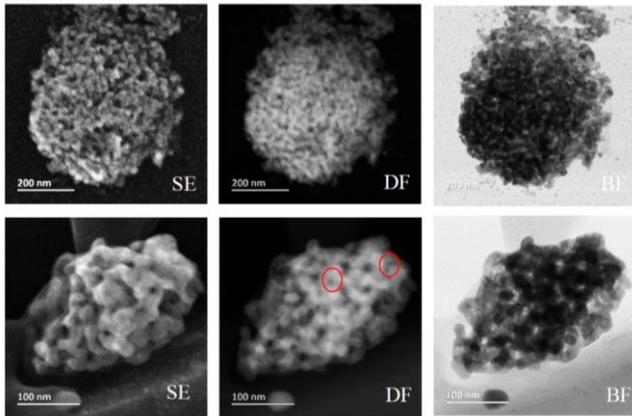


Figure 1: STEM images of as-dealloyed NPG, before heating. Particulates of different sizes are present.

As soon as the temperature is increased to 200 °C, ligaments grew in size by coalescing, at the surface and in the layers of ligaments beneath (evident from the DF images in figure 2).

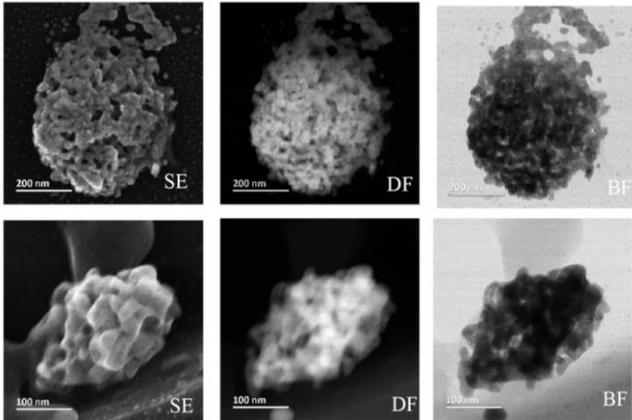


Figure 2: STEM images of as-dealloyed NPG, after heating at 200 °C. Particles of different sizes are shown.

Figure 2 also shows how the smaller sized particle had a faster elimination of porosity.

Voids start moving at 250 °C to the surface and to ligament/ligament interfaces formed by coalescence. Figure 3 shows an example of a void observed in situ as it moves from a ligament centre to a ligament/ligament interface.

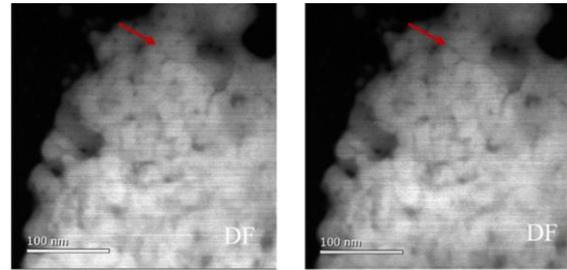


Figure 3: Void moving to ligament /ligament interface

At 300 °C and above, the surface of the bigger particle begins sintering considerably. Ligament coalescence is faster and pores start moving to the surface, beginning the densification process, yet not fully densifying.

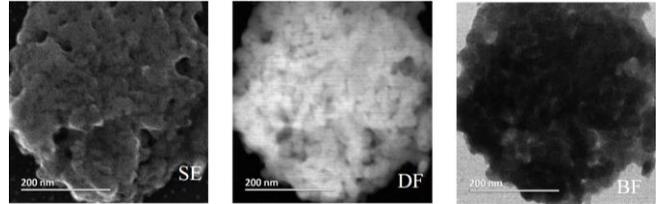


Figure 4: NPG at 350 °C

As we reach higher temperatures, ligaments coalesce more until reaching 400 °C where it appears that most of the sample went into densification. Some of the voids remain in ligaments at this point, while all of the pores moved to the surface of the bigger sample.

At higher temperatures, approximately 600 °C, the porous particles are fully consolidated into restructured grains (figure 5) with features such as twin boundaries and grain boundaries that can be seen in figure 6.

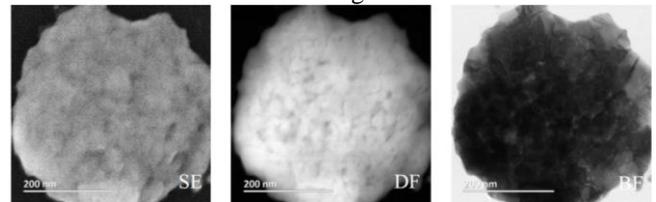


Figure 5: Fully densified particle at 600 °C.

Voids that were stable at temperatures as high as 400 °C were fully eliminated by bulk diffusion.

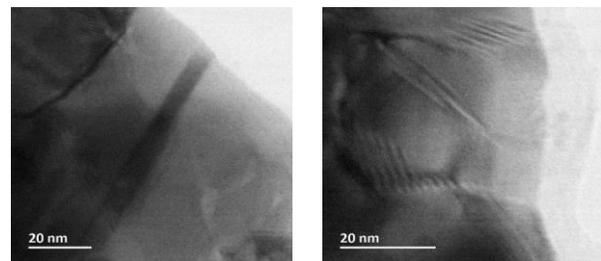


Figure 6: BF images of twin boundaries and grain boundaries formed due to restructuring at 600 °C.

## 4 Thermal Coarsening of NPG-Pt (AgAuPt)

NPG-Pt formed by the dealloying of the ternary alloy precursor had significantly refined ligament/pore sizes (figure 7), down to 3.2 nm in average, while the pore sizes are strikingly similar at 3.2 nm. Until reaching a temperature of 200 °C, no coarsening is observed. At 250 °C the ligaments and pores start increasing in size (figure 8).

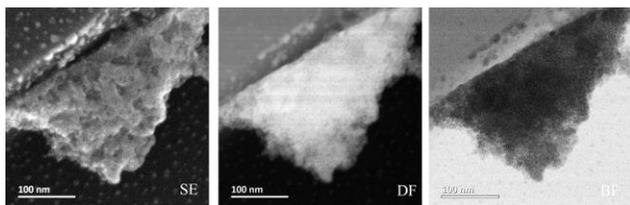


Figure 7: STEM images of as-dealloyed NPG-Pt.

At each temperature above 240 °C, the rate of coarsening would plateau eventually, reaching a quasi-equilibrium. This may, however, be due to the apparent plateau effect inherent in  $t^{0.25}$  coarsening kinetics.

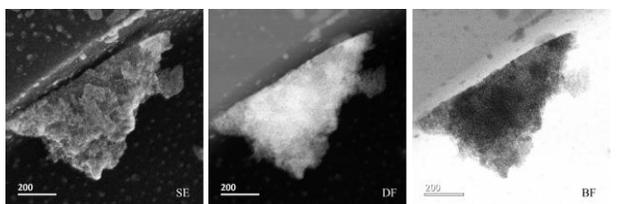


Figure 8: STEM images of NPG-Pt, after heating at 250 °C.

The rate of surface area loss, judging qualitatively from the porous area of the sample, is less than that observed for NPG in section 3.

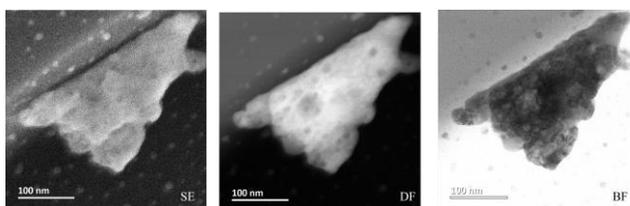


Figure 9: STEM images of NPG-Pt, after heating at 400 °C.

Figure 9 shows how porosity at 400 C is not yet fully annihilated, unlike the case with NPG. Bigger pores would increase in size at the expense of smaller ones, until the ligament in between gets too small, leading to sudden ligament collapse into the neighbouring ligament causing the two neighbouring pores to coalesce into one (visible in available videos). One of the many examples seen in situ is shown in figure 10.

Densification in NPG-Pt is facilitated at temperatures higher than 400 °C; pores that are larger in size and closer

to the surface would just emerge at the surface as shown in figure 11.

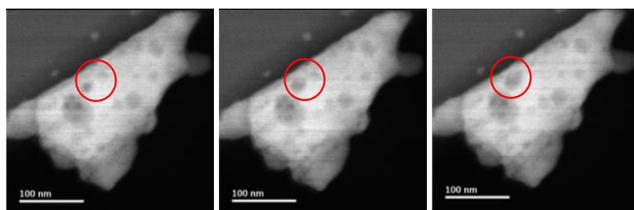


Figure 10: DF- STEM images of NPG-Pt at 500 °C showing the process of ripening that leads to growth of one pore at the expense of another and consequential ligament collapse.

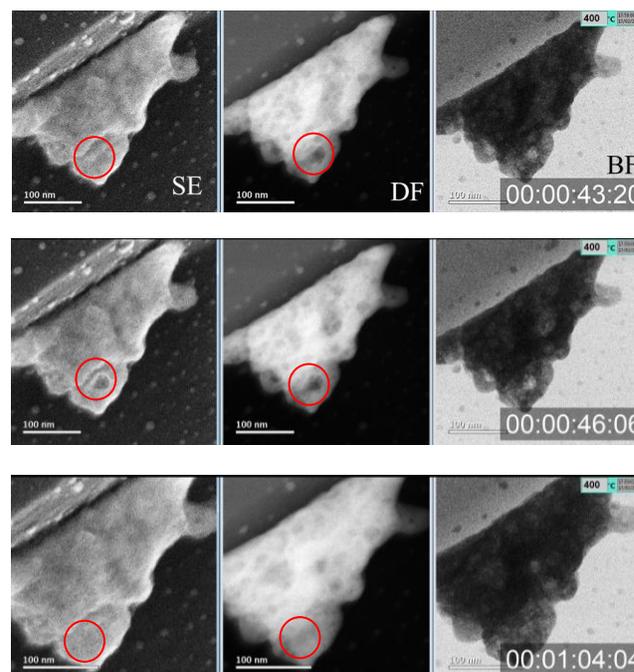


Figure 11: Series of STEM images showing the process of porosity annihilation due to pores emerging to the surface in realtime.

## 5 Discussion

It can be inferred from the direct comparison presented above how different are the coarsening pathways for NPG and NPG-Pt. It is very clear that the presence of Pt in trace amounts causes a significant change in the coarsening mechanism and its onset. The onset of coarsening was delayed by the addition of Pt from 200 °C to 240 °C. Furthermore, the refining effect of Pt on the as-dealloyed ligament size alters the coarsening mechanism. In the case of NPG, it is clear from the sharp decrease in number of ligaments that coalescence is favourable to occur, causing faster elimination of the material's porosity [8]. Whereas for NPG-Pt, the bigger pore sizes relative to ligament sizes

might contribute to Ostwald ripening being more favourable.

While it can be asserted that the coalescence and Ostwald ripening were caused by surface diffusion at temperatures as low as 200 °C, a full explanation as to the distinction in mechanism is not yet developed. The initial refinement caused by Pt alloying however, must be an indirect cause for such change in coarsening.

The Pt concentration on the surface in such a reductive environment must be very low due to its tendency to desegregate. Thus, a confident assumption can be made that the surface in both NPG and NPG-Pt is mostly comprised of Au atoms, excluding the possible contribution of the surface chemistries [9].

For NPG-Pt, localized plasticity was the likely cause of several clear observations of ligament collapse. This was explained previously due to rate of plastic work exceeding rate of surface energy reduction [10]. It is safe to propose that Ostwald ripening happens readily until ligaments get so thin they collapse, giving rise to the continuous observations of pores getting bigger on the expense of smaller ones.

There also appears to be no alteration of the onset of densification, which is 400 °C. This is probably due to the activation of bulk diffusion of Au, and residual Ag where present, at such a relatively higher temperature. There was a difference in the densification onset temperature between the large and smaller particles for NPG, which might be very well explained by the higher surface to volume ratio of the smaller particle, that makes it facile for pores to arrive faster to the surface at lower temperatures. The difference in sizes of particles, however, does not affect the mechanism of coarsening [11].

Pores very near to the surface were eliminated by simply moving to the surface; this is predicted by the LSW (Lifshitz-Slyozov-Wagner) theory that pictures the surface as the largest vacancy sink. That might have been also the reason as to why the surface sintered faster than the bulk of the sample [12]. Voids reported previously were observed to be formed after dealloying [6].

## 6 Conclusions

The addition of Pt does not only act to refine the initial porosity and surface area of NPG. This refinement acts to change the coarsening mechanism from simple coalescence of ligaments to Ostwald ripening. The direct observation of the coarsening enabled the identification of such a distinction. The role of Pt in inhibition of Au surface diffusion was limited by introducing a reductive atmosphere that ensures Pt desegregation. At best, the Pt would act to slow down Au surface diffusion at low temperatures, rather than altering the coarsening mechanism.

The ability to view the surface and the bulk of the samples simultaneously enabled the identification of voids formed in as-dealloyed NPG, and in identifying events where large pores tend to move to the surface.

## 7 Acknowledgments

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