doi:10.1017/S1431927618010218
Microsc. Microanal. 24 (Suppl 1), 2018

In situ STEM/SEM study of Thermal Coarsening of Pt-modified Nanoporous Gold in Oxygen and Hydrogen

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Nanoporous gold (NPG) is formed by the selective dissolution of Ag from a homogenous AgAu solid solution, forming a nanoporous 3D open-pore network [1]. The addition of 1-3 at. % Pt (forming NPG-Pt) to the precursor was shown to have a refining effect on the ligament and pore sizes [2]. Furthermore, the effect of Pt on the thermal coarsening of NPG depends on the chemical environment. Vega and Newman previously reported the inhibition of coarsening of NPG-Pt in air, due to the cosegregation of Pt and O [3].

Understanding the coarsening behavior of NPG and NPG-Pt helps in determining and optimizing their functionality. Monitoring the evolution of surface area at elevated temperatures in reductive and oxidative environments will clarify further the mechanisms involved in the coarsening phenomena. Building upon a previous investigation [4], coarsening of NPG and NPG-Pt is observed *in situ* by STEM/SEM, using a Hitachi HF3300 environmental TEM equipped with simultaneous secondary electron (SE) and transmitted electron (TE) imaging. A Hitachi Blaze heating holder and Norcada MEMS-based chips are used for heating samples at temperatures up to 600 ^{o}C in 1 Pa H_2 and 1 Pa O_2.

The operating coarsening mechanism in H_2 was found to be altered due to the Pt-refining effect. At temperatures as low as 200 ^{o}C, coalescence of ligaments was observed *in situ* for the relatively coarser NPG (Figure 1). However, coarsening of NPG-Pt was controlled by Ostwald ripening of ligaments, as large ligaments increase in size at the expense of smaller ones. As a result, very thin ligaments would collapse (Figure 2). A higher thermal threshold of coarsening was also observed for NPG-Pt. Complete annihilation of pores upon moving to the surface was also observed at temperatures higher than 400 ^{o}C leading to full densification of NPG-Pt at 600 ^{o}C.

In O_2, the complete inhibition of NPG-Pt coarsening was observed as expected, while the coarsening of NPG was similar to observations in 1 Pa H_2. The ligament pore sizes did not change until densification. At temperatures above 400^{o}C, Pt segregates were observed to emerge at the surfaces of NPG-Pt samples (Figure 3). At 600 ^{o}C and above, direct densification occurs, due to facilitated bulk diffusion. To study the mechanism of segregation in more detail, the surface coverages of Pt, Au and Ag are being studied at different temperatures using *in situ LEIS* (Low Energy Ion Scattering) in 1 Pa oxygen and 1 Pa hydrogen environments. Using the *in situ* characterisation methods explained above, this investigation identifies further the mechanisms of coarsening in NPG, and the effect of Pt. Events that lead to coarsening and changes in nanoligament chemical compositions are recorded *in situ* at high resolution [5].

References:

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[5] Electron microscopic studies were carried out at the Ontario Centre for the Characterisation of Advanced Materials (OCCAM), University of Toronto. The authors acknowledge support by an NSERC Discovery Grant (RGPIN-2014-03995) and Accelerator Supplement (RGPAS 462039-14) awarded to R.C. Newman.

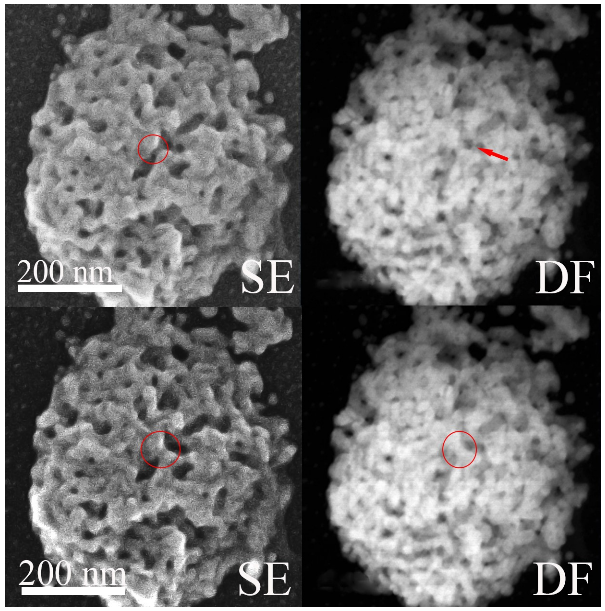

Figure 1. Coalescence of ligaments captured during the heating of NPG at 200 ^{o}C in 1 Pa H_2.

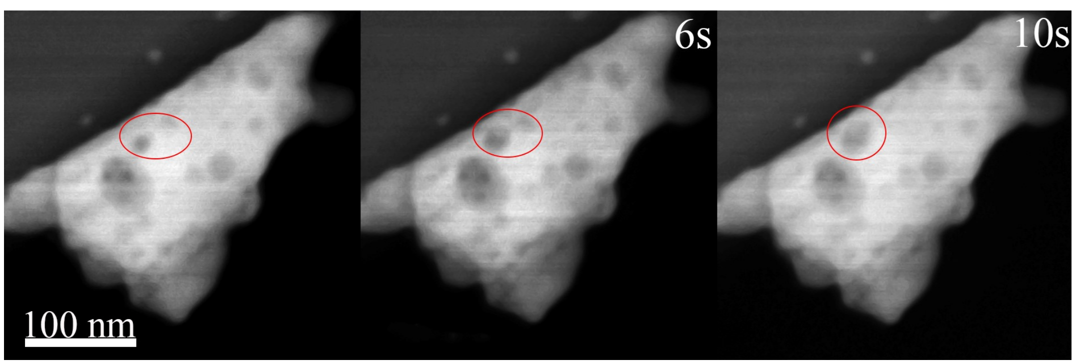

Figure 2. DF-STEM images of NPG-Pt at 500 ^{o}C showing the process of ripening that leads to growth of one pore at the expense of another and consequent ligament collapse in 1 Pa H_2.

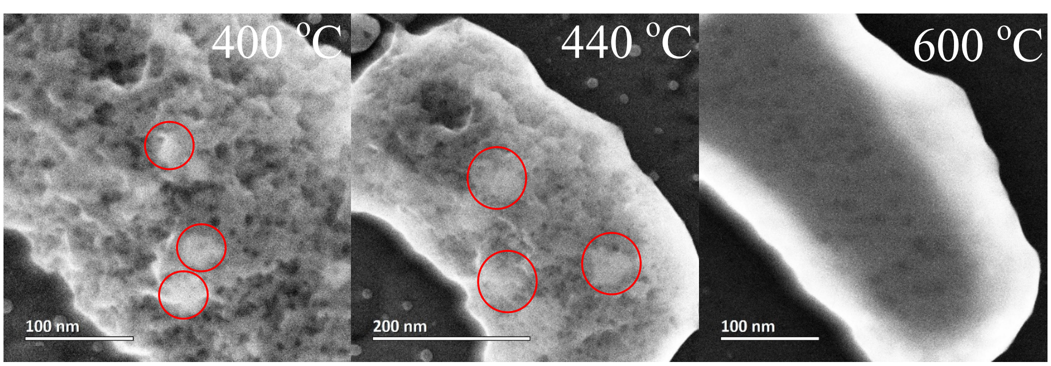

Figure 3. SE images showing Pt-segregates, circled in red, at elevated temperatures in 1 Pa O_2.