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Determination of Ligament Size Distribution of Nanoporous Gold by Scanning Electron Microscopy and Image Analysis

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A new method to quantitatively analyze the sponge-like structure of nanoporous gold (NPG) was developed. Images of NPG, acquired by a field emission scanning electron microscope (FESEM), were first binarized based on a gray threshold, and then ligaments were separated into a string of nanometer particles by an image split technique. In this way, the size distribution of these nanometer particles is equivalent to ligament size distribution. With similar approach, two addition parameters, pore width distribution and pore/ligament width ratio, were determined. And our results show a clear temperature dependence of the structure evolution of NPG.

Keywords: Nanoporous Gold, Image Analysis, Ligament Size Distribution.

1. INTRODUCTION

Nanoporous gold (NPG) prepared by selective dissolution of silver from silver–gold alloys represents a new class of nanostructured functional materials with intriguing properties. It adopts an open sponge-like structure of interconnecting ligaments and voids with tunable structure unit ranging from a few nanometers to many microns. Size distributions of pore and ligament of NPG are closely related to its preparation conditions, and are the key parameters to decide the properties of porous materials, such as catalytic, sensing and mechanical behaviors.[1,2] Microscopy and image analysis have been frequently used to determine pore width distributions of porous materials with well-defined structures. Calvo and co-workers[3,4] analyzed the sub-micron pore of several polycarbonate and alumina filters by scanning electron microscopy (SEM) and computerized image analysis. The statistical distribution of the pore areas, pore perimeters, equivalent pore diameters, and pore shape factors were studied as well. However, these conventional techniques are not applicable for determination of the ligament size distributions for a random uniform nanostructure such as NPG. Here we report that by employing an image split technique, the characteristic features of NPG can be quantitatively analyzed, including the pore/ligament size distribution and nanoporosity information. We further use this method to investigate the coarsening of NPG upon thermal annealing, and find a clear temperature dependence of the structure evolution of NPG.

2. EXPERIMENTAL DETAILS

Nanoporous gold (NPG) was prepared by free corrosion of silver from $Ag_{70}Au_{30}$ alloy sheet in concentrated HNO_3 (~67%) solution for 3 hrs. Energy dispersive X-ray (EDX) spectra collected from the nanoporous Au samples confirmed that nearly all Ag atoms were dissolved during dealloying. The nanoporous Au was divided into several small pieces, and annealed by a muffle furnace in air for 30 min at 200 °C and 300 °C, respectively.

In this work, the images of NPG samples were acquired by a FEI Sirion 200 field emission scanning electron microscope (FESEM). SIS Analysis 3.0 software (Germany) was used to process these images, and Excel 2000 software (USA) was used for both data handling and graph drawing. The procedures of image processing and measurement were combined into a macro program, by which we could process these images semi-automatically.

3. RESULTS AND DISCUSSION

As an example of SEM image, Figure 1(a) is a two dimensional array of 645×516 pixels (picture elements) with gray values from 0 to 255. To enable the system to

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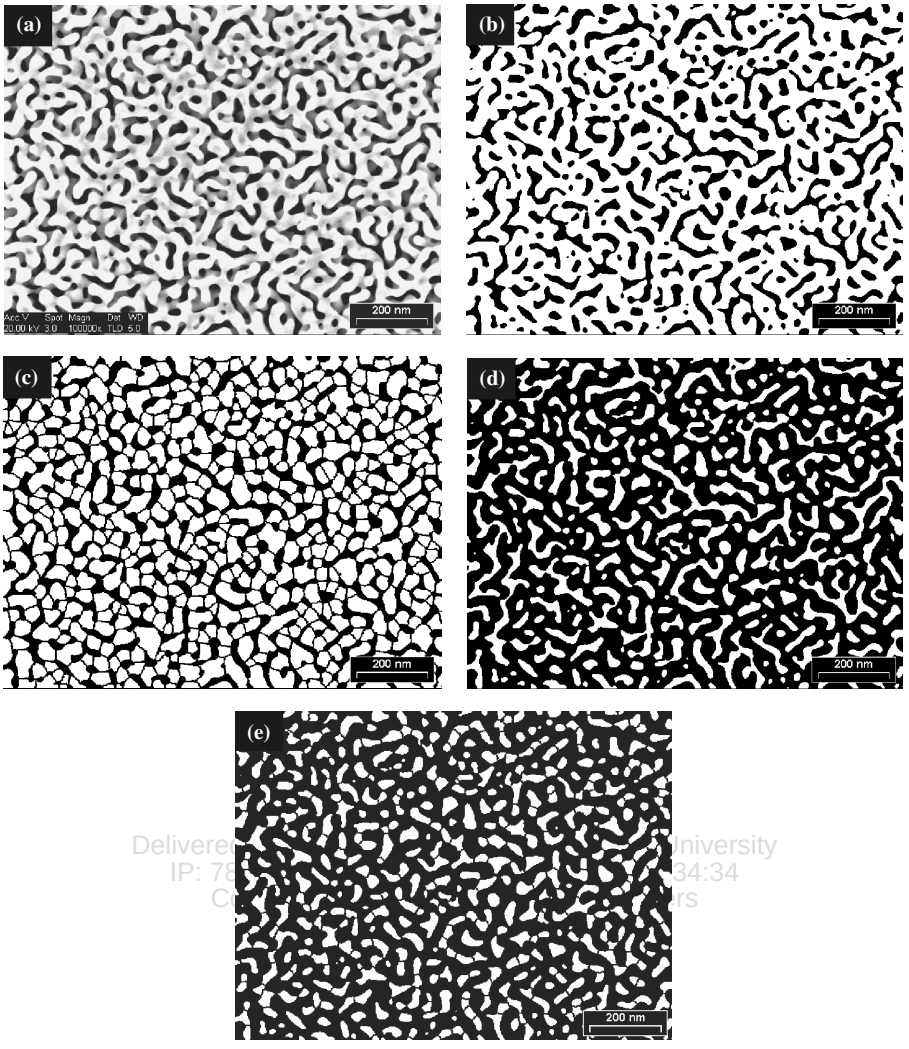

Fig. 1. NPG-1 prepared by selective dissolution of silver from silver–gold alloys. (a) FESEM image; (b) Binary images obtained using the binary threshold Tl of (a), in which the NPG ligaments in white were distinguished from the NPG pores; (c) Image derived from (b), in which the ligaments have been separated by the SIS Separate Particles Filter. The size of these nanometer particles is equivalent to the ligament width; (d) Binary images obtained using the binary threshold Tp of (a), in which the NPG pores in white were distinguished from the NPG ligaments; (e) Image derived from (d), in which the pores have been separated by the SIS Separate Particles Filter. The size of these nanometer particles is equivalent to the pore width.

distinguish the NPG ligaments from the NPG pore during the measurement, a gray value threshold (Tl) was selected so that pixels of the ligaments were in the range and pixels of the pores were out of it. And then the gray-value image was transformed into a binary image with only two gray values, 0 (black for pores) and 255 (white for ligaments), as shown in Figure 1(b). It is difficult to describe and measure the size of the net-like ligaments according conventional methods.[3,4] Thus, ligaments were separated into a string of nanometer particles by an image split technique (Fig. 1(c)). Most of these nanometer particles are close to cube. So the size of these nanometer particles is equivalent to the ligament width. All particles cut by the image border were excluded because their images did not have integrity. Equivalent circle diameters of these nanometer particles were then determined which were statistically equal to the ligament sizes of NPG.

Another gray threshold (Tp) was selected so that the NPG pores were in white, and ligaments were in black (Fig. 1(d)). Because NPG has a bi-continuous structure, within which the pore and ligament take similar structures, the same processing method described above can thus be taken to treat nanopores in order to get the pore structure and distribution information (Fig. 1(e)). This treatment is appropriate because our purpose is to analyze the whole structure, not the individual ligaments or pores. Commonly, an average number of at least 500 particles are recommended.[5] In this study, the determination of mean values and distributions was based on 10 SEM images, i.e., more than 2000 ligaments or pores were analyzed. The mean value and distribution of a large number of ligaments or pores were used to characterize the NPG structure. Upon processing, the mean ligament and pore widths of NPG-1 were determined to be 38 nm and 31 nm, respectively, with

Table I. Mean width of ligament (L) and pore (P) of original and annealed NPG-1 samples.

Sample	Mean width L	Mean width P	Mean ratio P/L
NPG-1	38	31	0.82
NPG-1 annealed at 200 °C	131	99	0.76
NPG-1 annealed at 300 °C	226	165	0.73

a mean pore/ligament ration of 0.82 (Table I). And the corresponding distribution information was shown in Figure 2.

Similarly, for annealed NPG-1 samples, the SEM images were acquired and shown in Figure 3. Significant coarsening was observed for NPG-1 samples upon annealing at elevated temperatures while the sponge-like structure remains unchanged. In order to have similar pixel information in SEM images, the magnification for original NPG-1 sample was 100,000, and for annealed samples, it was 20,000.

The mean values of these three samples are shown in Table I, and their distributions are included in Figure 2. With increasing annealing temperature, the mean widths of ligaments and pores increase, and pore/ligament ratio decreases gradually. For the original NPG-1, the distributions of ligament and pore are narrower; however, for annealed samples the distributions are wider. These results demonstrated that there is a clear temperature dependence of the structure evolution of NPG. Detailed studies are currently underway to clarify the underlying mechanisms of these processes.

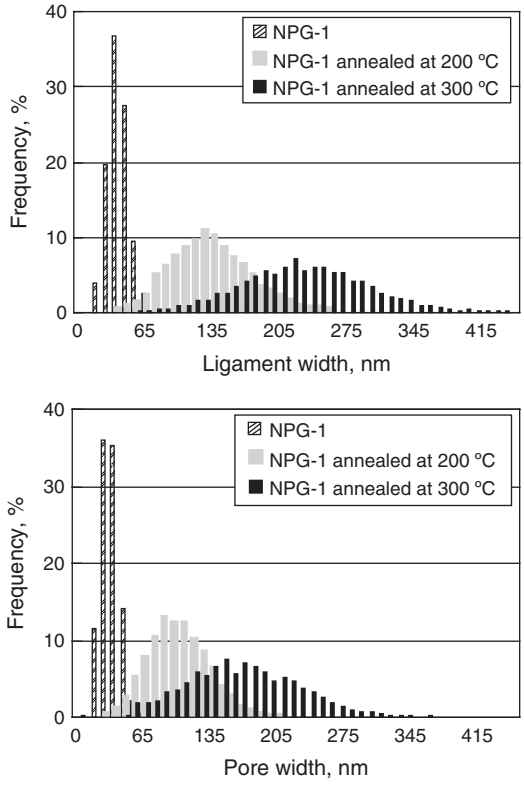

Fig. 2. (a) Ligament and (b) Pore width distributions of original and annealed NPG-1 samples.

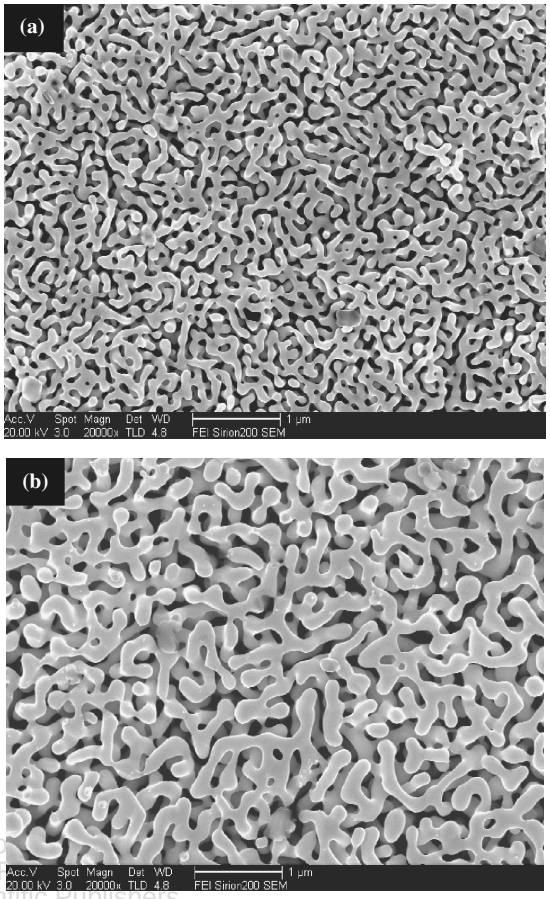

Fig. 3. FESEM images of NPG-1 samples annealed (a) at 200 °C for 30 min; and (b) at 300 °C for 30 min.

4. CONCLUSIONS

Base on FESEM image analysis, a new method was developed to analyze the ligament and pore width of sponge-like structure of nanoporous gold (NPG). Ligaments and pores were separated into a string of nanometer particles by an image split technique. The size distribution of these nanometer particles is equivalent to ligament width distribution. With similar approach, two addition parameters, pore width distribution and pore/ligament width ratio, were determined. With increasing annealing temperature, the mean widths of both ligament and pore increased, and their distributions became wider.

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