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Wettability of Nanoporous Silver Fabricated by Electrochemical Dealloying

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The wettability of nanoporous silver fabricated by dealloying was studied before and after stearic acid treatment. The dependencies of both water and glycerol contact angles on the variation of pore size as well as time were investigated. The research shows that nanoporous silver surfaces convert from hydrophilicity to superhydrophilicity as the pores increase from 70 nm to 300 nm. After modification with stearic acid, the surfaces convert from hydrophobicity to hydrophilicity as the pores increase. The nanoporous silver surfaces exhibit lipophilicity to glycerol and become oleophobicity after modification with stearic acid. The water and glycerol contact angles both decrease from maximum to minimum values with increase of the pore size. The experiment shows that the wettability to liquid of nanoporous silver surfaces can be adjusted by pore size control and stearic acid treatment.

Keywords: nanoporous silver; dealloying; wettability; stearic acid

1. INTRODUCTION

Wettability is one of the most important properties associated with a material surface, which depends on the chemical composition and roughness (geometric microstructure)[1]. It is one of the most common phenomena in nature and of great significance to study the effect of fluid on solid material surfaces, which can extend the working life and expand the application field of materials, such as oil extraction[2, 3], response switches[4, 5], waterproofing and anti-fouling[6, 7]. This area has aroused more and more attentions.

Due to its significant effect on wetting of the outermost layers of solid surfaces, the surface roughness and surface energy coating are indispensable to the wettability of a material[8]. Many strategies have been studied to alter the shape, dimensions and regularity of the surface morphology utilizing the methods such as sol-gel[9], plasma etching[10, 11], chemical deposition[12, 13], chemical etching[14], template[15], hydrothermal[16, 17], and laser machining[18, 19]. Electrochemical dealloying has been widely employed for the formation of nanostructured surfaces, either by applying a certain external potential or using the galvanic ion exchange reaction between the substrate and ions (no external potential). These methods can change the wettability of material surfaces. Nanoporous silver fabricated by dealloying can be applied to catalysts[20], electrochemical actuators[21], and electrochemical sensors[22] as well as utilized in surface-enhanced Raman scattering[23]. The surface behavior plays an important role in these applications. In this paper, nanoporous silver specimens with different pore sizes were prepared by electrochemical dealloying. The relationships between water and glycerol contact angles on nanoporous silver surfaces with different pore sizes were investigated. The changes in wettability of the nanoporous silver surfaces before and after modification with stearic acid were also examined.

2. EXPERIMENTAL

$Ag_{25}Zn_{75}$ alloy was prepared through the induction melting method under Ar protection and then annealed at 550°C for one week. The specimens were ground with sandpaper and polished with diamond paste and then ultrasonically cleaned with deionized water and ethanol. Electrochemical dealloying was conducted in a three-electrode electrochemical cell controlled with a potentiostat (LK98Ⅱ, Lanlike) at room temperature. An electrochemical potential of 0.4 V (SCE) was applied in 0.1 M H_2SO_4 solution. A Pt plate electrode, saturated calomel electrode and alloy were employed as the counter electrode, reference electrode and working electrode, respectively. Stearic acid-ethanol solution with a concentration of 0.05 mol/L was utilized in the experiment. The surface morphology and composition of the specimens were characterized by utilizing field emission scanning electron microscopy (Supra55, Zeiss) coupled with energy dispersive X-ray spectroscopy (INCA, Oxford Instruments). The contact angles were determined through the sessile drop method using a contact angle tester JC2000C1 at ambient temperature. The droplet volume used in measuring the contact angles was 2 mL. The surface moved upward at a constant speed of 3 mm/min until it contacted the droplet.

3. RESULTS AND DISCUSSION

Electrochemical dealloying is a competitive process involving the selective dissolution of the active component (zinc atoms) and the formation/coarsening of the nanoporous structure caused by the diffusion of the noble component (silver atoms). Figures 1 (a)-(c) show SEM images of the nanoporous silver surfaces immersed in the 0.05 mol/L stearic acid-ethanol solution for 1 min, 5 min, and 10 min. Nanoporous silver is obtained through dealloying the $Ag_{25}Zn_{75}$ alloy for 30 min at 0.4 V in 0.1 M H_2SO_4 at a current density of 21.6 mA/cm^2. It can be observed that no distinct change occurs after immersion for 1 min. However, a layer of translucent flocculent material forms on the surface with prolonging immersion time, and eventually develops into a sheet. The number and size of the sheets both increase over time. Figure 1 (d) shows the element distribution on the nanoporous silver surface after immersion in the stearic acid-alcohol solution for 10 min. The main elements Ag, C and trace amounts of O are detected. Ag element is uniformly distributed on the surface, while C and O elements are mainly distributed on the flaky structure material. Since the H element is not in the detection range of the energy dispersive X-ray spectroscopy instrument and the chemical formula of stearic acid is $CH_3(CH_2)_{16}COOH$, it can be concluded that the substance with a sheet-like structure is stearic acid. In the following experiment, the samples in the wettability test are all immersed in the 0.05 mol/L stearic acid-ethanol solution for 1 min and subsequently dried in air.

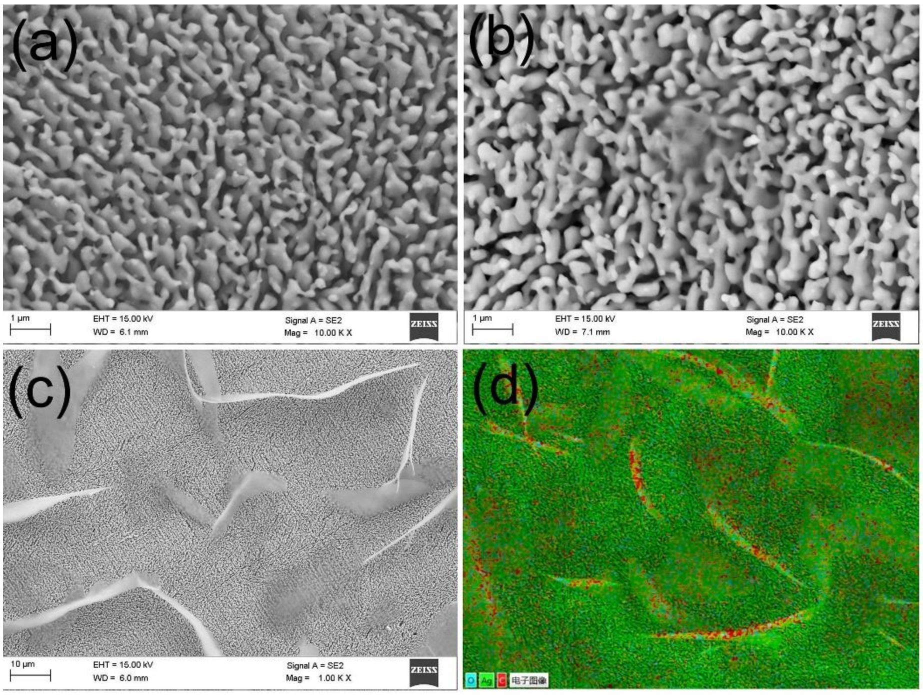

Figure 1. Surface morphologies of nanoporous silver immersed in the 0.05 mol/L stearic acid-ethanol solution for (a) 1 min, (b) 5 min, (c) 10 min, and (d) surface element distribution after immersion for 10 min. The nanoporous silver was obtained through dealloying $Ag_{25}Zn_{75}$ for 30 min at 0.4 V in 0.1 M H_2SO_4.

The changes of water contact angles on the nanoporous silver surfaces with different pore sizes before and after stearic acid modification are shown in Figure. 2. Here, the nanoporous silver specimens with different pore sizes were obtained by dealloying $Ag_{25}Zn_{75}$ alloy for 5 min, 10 min, 30 min, 60 min and 120 min in 0.1 M H_2SO_4 solution at an applied voltage of 0.4 V. The contact angles on the surfaces before and after modification both decrease monotonouslly along with increase of the pore sizes. For the surface with a pore size of 70 nm, the water contact angle increases from 43.5° to 130° after modification. The surface surprisingly changes from hydrophilicity to hydrophobicity, which indicates that low surface energy material modification can notably change the wettability of nanoporous silver surfaces. For the surface with a pore size of 300 nm, a water droplet dropped onto it spreads very quickly, exhibiting superhydrophilic behavior. The water contact angle increases from 0° to 87.5° after stearic acid modification. It is assumed that air could be easily trapped into such nanopores after modification, which can prevent water from intruding into the interspaces among the microstructure. In the dealloying process, the pores formed in the initial moment, then the pore size and ligament size will grow and coarsen with dealloying time[24]. It is worth noting that no microstructure is present on the coarsened ligaments[25], and the specific surface area will decrease with increasing dealloying time. Along with increase of the pore size, the nanopores of the solid surface layer not only extend toward the interior of the solid but also form an irregularly bicontinuous structure. Hence, the contact portion of the droplet with the solid surface will extend to the outside. Due to the capillary effect of the nanopores of the surfaces[26], it is impossible to establish an "air cushion" between the droplet and solid. For nanoscale materials, due to atomic coordination imperfection on the surface or interface, the surface or interface energy will decrease with decrease of the pore size[27]. This can explain why the contact angles on the surfaces of the nanoporous silver both before and after steric acid modification tend to decrease with increase of the pore size. This indicates with increasing the dealloying time, the nanoporous silver surface will become more hydrophilic.

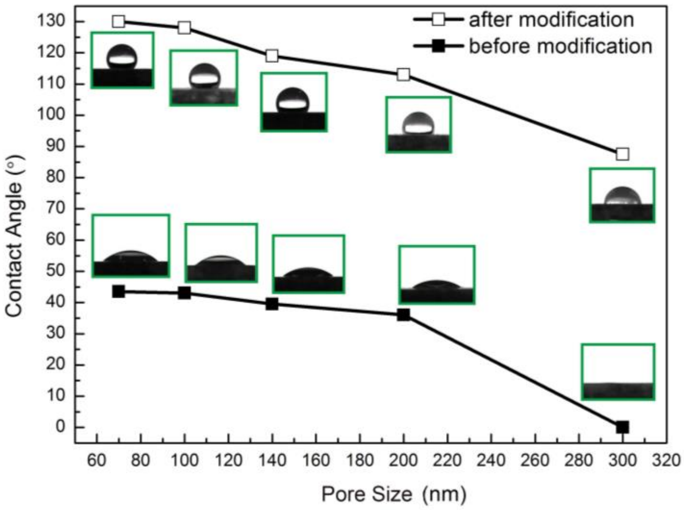

Figure 2. Variation of water contact angles on the nanoporous silver surfaces as a function of pore size. Dealloying time: 5, 10, 30, 60 and 120 min; electrolyte: 0.1 M H_2SO_4; applied voltage: 0.4 V; immersion time in the stearic acid-ethanol solution: 1 min.

Supposing the water contact angle is 180° for air and θ for the solid surface, the nominal contact angle θ_c derived from the modified Cassie-Baxter model[28] is as follows:

$$\cos\theta_c = f_1(\gamma_{SG}-\gamma_{SL})/\gamma_{LG} - f_2 = f_1\cos\theta - f_2 \qquad (1)$$

where f_1 and f_2 are the liquid-solid contact fraction and liquid-gas contact fraction (i.e. $f_1+f_2=1$), respectively. This clearly shows that θ_c increases with decreasing f_1, which means that θ_c increases as the fraction of air trapped in the nanopores in the surface increases during the tests. A schematic of a water droplet in the Cassie-Baxter state on a rough solid surface is shown in Figure 3(a). The water contact angle on smooth silver measured in the experiment is approximately 79°, as shown in Figure 3(b), which exhibits hydrophilic behavior. The result is much the same as that reported by Safaee and Gu[29, 30]. For the nanoporous silver surface with a pore size of 70 nm immersed in the stearic acid-ethanol solution for 1 min, θ_c is 130°, and f_2 can be calculated to be 0.7, which indicates that the achievement of the hydrophobicity is mainly a result of the air trapped in the rough surface by combining nanoporous structures with the coating of stearic acid.

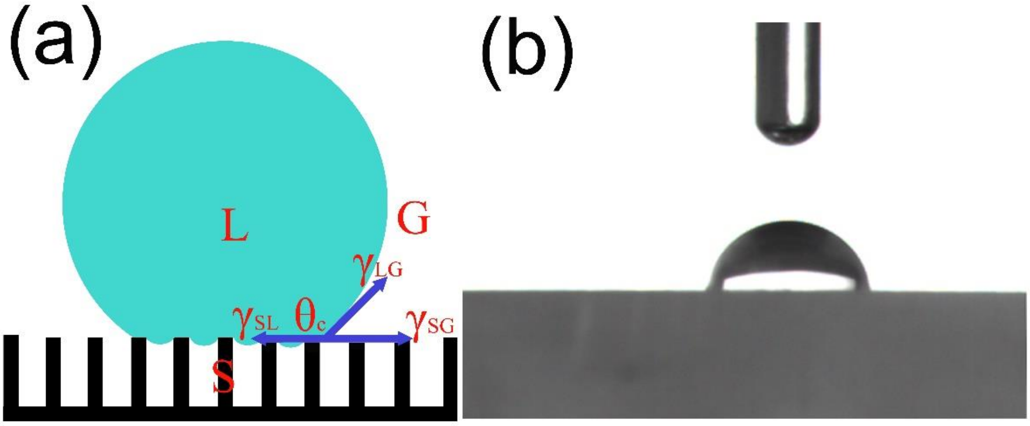

Figure 3. (a) Schematic of a water droplet in the Cassie-Baxter state on a rough solid surface, (b) a water droplet with a contact angle of 79° on the smooth silver surface.

Figure 4(a) reveals that all water contact angles decrease monotonically from maximum to minimum values over time. For the surface with a pore size of 300 nm, the water contact angle decreases sharply from 0-20 s and then reaches 0°, indicating that the water droplet has completely spread on the surface. For the surfaces with pore sizes of 200 nm and 140 nm, the water contact angles reach 0° after 120 s and 240 s, respectively. After 300 s, the water contact angles on the surfaces with pore sizes of 70 nm and 100 nm decrease from 45° to 23° and 20°, respectively. It indicates that the surface roughness has a major influence on the wettability of nanoporous silver. After modification by stearic acid, the water contact angles on the surfaces with pore sizes smaller than 200 nm all remain stable over time except for a slight decrease. In addition, the water contact angles decrease with the increase of the pore size, from 130° to 110° along with pore size increases from 70 nm to 200 nm, as shown in Figure 4(b). These results indicate that the wettability of the surface can be changed by simply varying the features of the geometrical microstructure. This also demonstrates that the hydrophobicity of nanoporous silver surfaces has a good long-term stability in air. However, the water contact angle on the surface with a pore size of 300 nm exhibits a declining tendency in the whole process, with the value dropping from the initial 90° to 10° after 300 s. It demonstrates that the coating of low energy materials and the size of bicontinuous nanopores that distribute across the surface both play a very important role in the stability of the water contact angles.

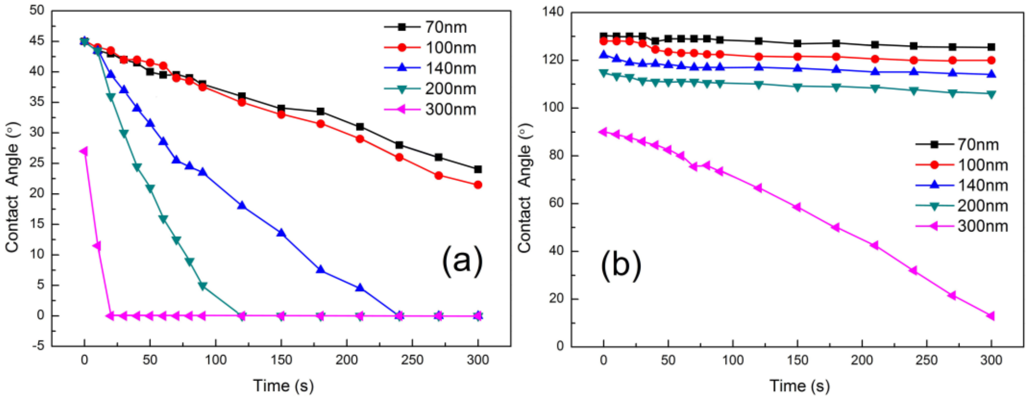

Figure 4. Variation of water contact angles on the nanoporous silver surfaces before and after treatment with stearic acid. Dealloying time: 5, 10, 30, 60 and 120 min; electrolyte: 0.1 M H_2SO_4; applied voltage: 0.4 V; immersion time in the stearic acid-ethanol solution: 1 min.

In addition, the wettability to an oily liquid of the nanoporous silver surface was also investigated. Here, we selected glycerol for the test. Figure 5(a) shows the variation of the glycerol contact angles on the nanoporous silver surfaces with different pore sizes. It is evident that the nanoporous silver surfaces all exhibit lipophilic properties. From 0-20 s, the contact angles decrease rapidly over time. For the surface with a pore size of 70 nm, the contact angle decreases from the initial 60° to 48° until stabilizing. For the other surfaces, the contact angles changes are in a range of about 4 °. From 20-80 s, the contact angles declined slightly. After 80 s, the contact angles remain basically unchanged. In addition, the contact angles all decreased significantly with increase of pore size during the same period. Figure 5(b) shows the contact angles of glycerol on the surface modified by stearic acid. Compared with Figure 5 (a), the glycerol contact angles over time show the same tendency as before modification, but reach a value range from107-137 ° after stabilization, indicating that an oleophobic surface has already been formed.

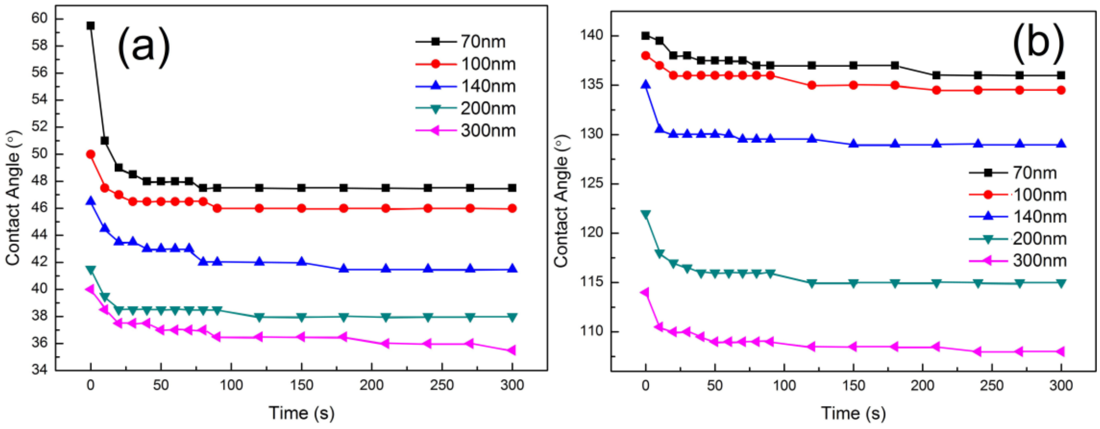

Figure 5. Variation of glycerol contact angles on the nanoporous silver surfaces before and after treatment with stearic acid. Dealloying time: 5, 10, 30, 60 and 120 min; electrolyte: 0.1 M H_2SO_4; applied voltage: 0.4 V; immersion time in the stearic acid-ethanol solution: 1 min.

Figure 6 (a) compares the trends of the water and glycerol contact angles with the pore size. For the pore sizes smaller than 200 nm, they both decrease with increase of the pore size, and the water contact angles are smaller than those of glycerin. For the surface with a pore size of 300 nm, the variation trend of the glycerin contact angle tends to be gentle while the water contact angle drops sharply to 0°. After stearic acid modification, they exhibit the same tendency. However, the surfaces change from lipophilicity to oleophobicity. The surfaces with pore sizes smaller than 200 nm exhibit hydrophobicity and convert into hydrophilicity when the pore size increase to 300 nm, as shown in Figure 6 (b). The results indicate that the pore size and coating of stearic acid are both important to wettability of water and glycerol of the nanoporous silver surfaces.

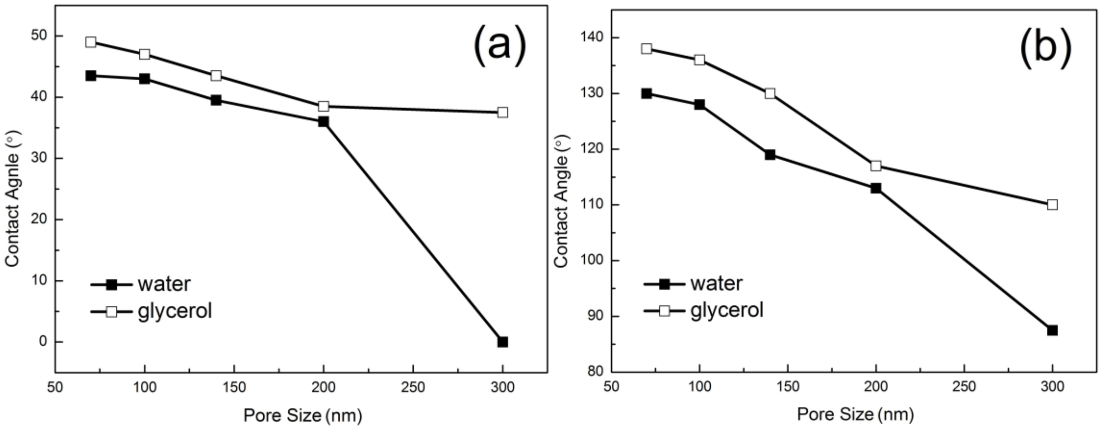

Figure 6. Variation of the water and glycerol contact angles on the nanoporous silver surface before and after stearic acid modification as a function of pore size.

4. CONCLUSIONS

In summary, bicontinuous nanoporous silver surfaces with different pore sizes are fabricated by the dealloying method. The wettability research shows that the obtained nanoporous silver surfaces convert from hydrophilicity to superhydrophilicity as the pores increase from 70 nm to 300 nm. After modification with stearic acid, the surfaces convert from hydrophobicity to hydrophilicity as the pores increase. The nanoporous silver surfaces exhibit lipophilicity and turn into oleophobicity after being modified with stearic acid. The contact angles of water and glycerol both decrease from maximum to minimum values with increase of the pore size. The experiment shows that the wettability to liquid of the surface of nanoporous silver can be adjusted by controlling the surface pore size and modifying the surface by stearic acid.

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