

The electrochemical polishing behavior of porous austenitic stainless steel (AISI 316L) in phosphoric-sulfuric mixed acids

S.C. Chen, G.C. Tu, C.A. Huang*

Department Materials Science and Engineering, Chiao Tung University, Hsinchu, Taiwan, ROC

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Abstract

The electrochemical polishing of porous austenitic stainless steel (PASS), AISI 316L, in the phosphoric-sulfuric mixed acid with volume-ratio of 1:1, 2:1 and 3:1 at temperature ranging from 60 to 80 °C was studied. Electrochemical polishing of PASS was performed in the potential located in the limiting-current plateau of its anodic polarization curve using a rotating cylinder electrode (RCE). The results show that the electrochemical polishing of PASS is strongly affected by the volume ratio of the mixed acid and the polishing temperature, yet very little by the potentiostatic polishing charge. An optimal brightening and leveling surface of PASS could be achieved by polishing in 2:1 v/v mixed acid at 70 °C. Whereas, polishing in 1:1 and 2:1 v/v ratios at and above 75 °C would result in formation of enlarged pores on the PASS surface due to high dissolution rate within the pores. Pores with rounded edges in the surface morphology of PASS was shown when polishing in 3:1 v/v mixed acid at temperature ranging from 60 to 80 °C. The effects of temperature, acid volume-ratio as well as potentiostatic polishing charge on polishing behavior were discussed based on the results of electrochemical test and the polished surface morphology using scanning electron microscope (SEM).

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1. Introduction

The porous austenitic stainless steel (PASS), made by powder metallurgy (P/M) process, is generally used as a filter for solid–gas or solid–liquid separation. Due to its fabrication readiness, mechanical rigidity and thermal stability, PASS is employed recently as the porous support, on which noble metal membrane is deposited, for the application of hydrogen separation and purification engineering [1–3]. To deposit the noble metal membrane on PASS, many methods, such as chemical vaporized deposition (CVD), sputtering deposition, electrodeposition etc., were proposed [4–6]. For this application the brightening and leveling of the PASS surface with numerous mini-

mized pores are the prerequisites, such that thinner noble metal deposited membrane on polished PASS be feasible for hydrogen separation. A thinner membrane would lead to a higher permeation efficiency and lower manufacturing cost [7]. Thus, surface pretreatment by electrochemical polishing of PASS plays an important role for the successful deposition of metallic membrane on it.

It is known in practical application that austenitic stainless steel can be well electrochemically polished in concentrated phosphoric-sulfuric mixed acid at temperatures above 65 °C [8–10]. Generally, the volume ratio of mixed acid for polishing austenitic stainless steel is set between 1:1 and 3:1 [11–13]. However, scarce literature have been reported regarding the effects of volume-ratio of mixed acid, polishing temperature as well as polishing charge on the polishing behavior austenitic stainless steel; especially polishing behavior of a porous austenitic stainless steel, a typical P/M product, is still lacking and in demand. The above issues are addressed in this study.

* Corresponding author. Department Mechanical Engineering, Chang Gung University, Taoyuan, Taiwan, ROC. Tel.: +886 3 2118800x5346; fax: +886 3 2118050.

E-mail address: gfehu@mail.cgu.edu.tw (C.A. Huang).

2. Experimental procedure

Commercial porous austenitic stainless steel (PASS), purchased from Mott Metallurgical and fabricated by powder metallurgy process with a compact density of ca. 7 g/cm^3 was used in this study. The chemical composition (wt.%) of the PASS AISI 316L was 18% Cr, 8% Ni, 2% Mo, <0.03% C, bal. Fe. The as-received PASS surface morphology is shown in the SEM micrograph of Fig. 1, it displays that the PASS comprised compacted powders with average size of ca. $20 \mu\text{m}$, which were sintered together leaving many pores with sizes smaller than $10 \mu\text{m}$. Before electrochemical test and polishing, the PASS surface was mechanically ground with 200 grit emery paper. Fig. 2 shows the ground surface appearance of PASS; it reveals that most of the surface pores were eliminated by gross plastic deformation after mechanical grinding.

In order to study the polishing behavior of PASS, potentiostatic polishing was conducted at the potential located in the middle of the limiting-current plateau of its anodic polarization curve tested in the phosphoric-sulfuric mixed acid with volume ratios of 1:1, 2:1 and 3:1, respectively. A rotating cylinder electrode (RCE), 9.6 mm in diameter and 6.6 mm in length, was used. The exposing or polishing area of the RCE is 1.96 cm^2 . The rotating speed of the RCE was kept constant at 3500 rpm for each electrochemical test and polishing. The potentiostatic polishing was performed at temperatures of 60, 65, 70, 75 and $80 \text{ }^\circ\text{C}$, respectively. The polishing potential corresponding to limiting-current plateau was determined by its anodic polarization test, carried out potentiodynamically with a scan rate of 5 mV/s starting from -250 (vs. E_{corr}) to 1200 mV (vs. $\text{Ag/AgCl}_{\text{sat.}}$) with a potentiostat/galvanostat (EG & G Model 273A) in a flat cell (EG & G Model K0235). Before anodic polarization scanning or potentiostatic polishing, the RCE was immersed in the testing mixed acid for 10 min until metal/electrolyte interface reached a dynamically stable status.

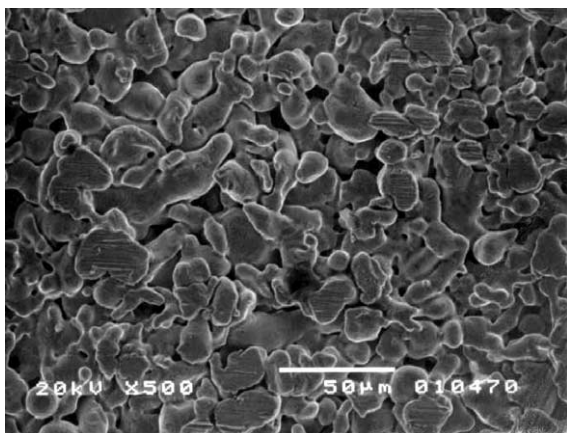


Fig. 1. SEM-micrograph showing the surface morphology of as-received PASS.

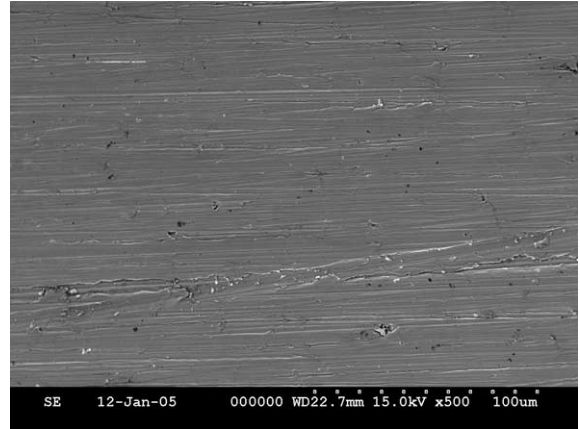


Fig. 2. SEM-micrograph showing the surface of PASS mechanical grinding with 600 grit emery paper.

To evaluate the polished morphology, specimen surface was examined with scanning electron microscope (SEM) after potentiostatic polishing.

3. Results and discussion

3.1. Anodic polarization measurement

Anodic polarization curves of the RCE in 1:1, 2:1 and 3:1 v/v mixed acids, at temperatures of 60, 70 and $80 \text{ }^\circ\text{C}$, were shown in Figs. 3–5. It can be clearly seen from Figs. 3–5 that scanning from the open-circuit potential there are three distinct regions in each anodic polarization curve, namely, active dissolution, limiting current plateau and oxygen evolution region. It is known that kinetic controlled mechanism dominates in the active dissolution region, different phases and microstructures in the exposed surface of RCE could have dissimilar dissolution rate. Thus, electrochemical polishing cannot be well performed in this potential range.

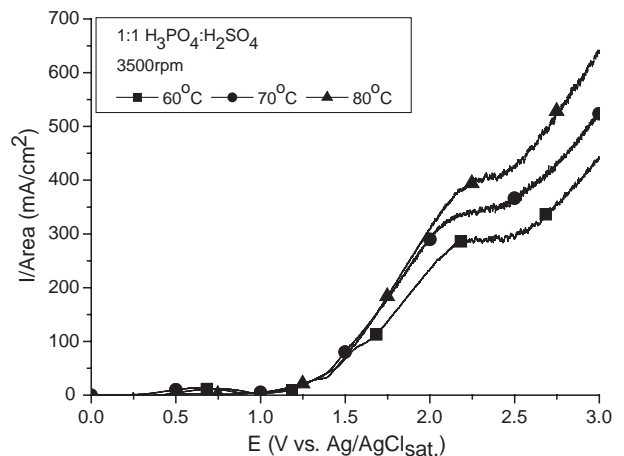


Fig. 3. The anodic polarization behavior of PASS in 1:1 v/v mixed acid at temperatures of 60, 70 and $80 \text{ }^\circ\text{C}$. (RCE at 3500 rpm).

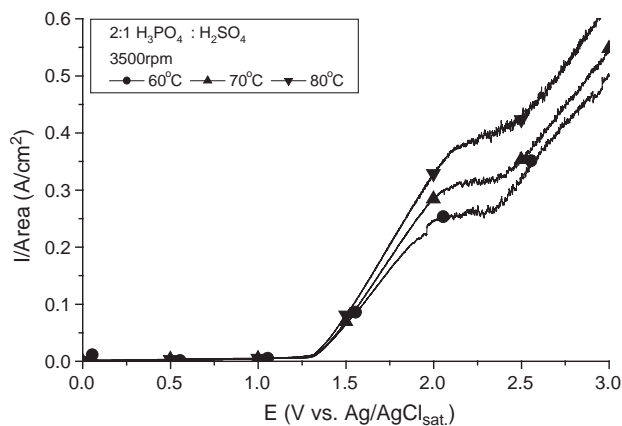


Fig. 4. The anodic polarization behavior of PASS in 2:1 v/v mixed acid at temperatures of 60, 70 and 80 °C. (RCE at 3500 rpm).

Anodic dissolution in the potential corresponding to limiting-current plateau follows mass-transfer controlled mechanism, in which leveling and brightening of an exposed electrode surface could occur simultaneously [9,13,14]. It has been accepted from several studies that electrochemical polishing can be accomplished in this potential range [9,14]. From the results of the anodic polarization tests, we found that there was an obvious limiting-current plateau in every anodic polarization curve and the potential range corresponding to limiting-current plateau lay between 2.1 and 2.5 V (vs. Ag/AgCl_{sat.}). Therefore, potentiostatic polishing in this study was performed at 2.3 V.

Anodic dissolution occurs in the potential above limiting-current plateau, which takes place apparently with oxygen evolution reaction. The simultaneously occurring oxygen evolution reaction on the porous surface would inevitably reduce the extent and quality of the electrochemical polishing.

After anodic polarization test, a shining surface of RCE was observed visually. It implies that a leveling and brightening surface of the PASS could possibly be

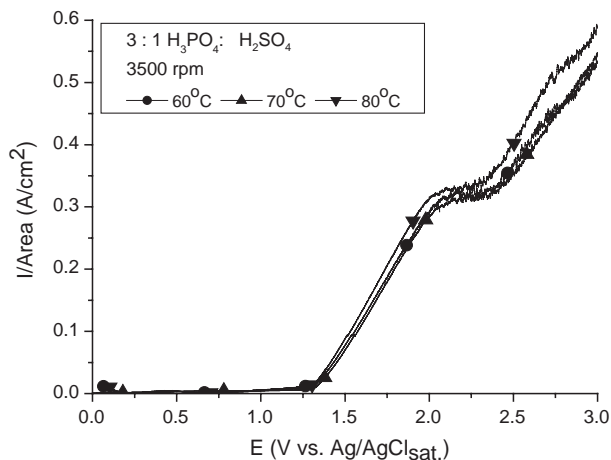


Fig. 5. The anodic polarization behavior of PASS in 3:1 v/v mixed acid at temperatures of 60, 70 and 80 °C. (RCE at 3500 rpm).

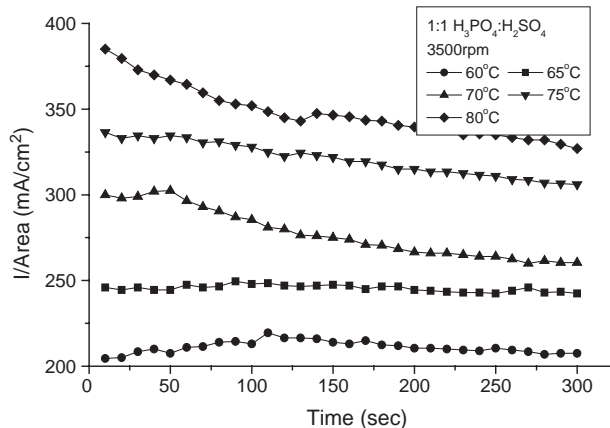


Fig. 6. The relationship between current density and polishing time of PASS potentiostatically polished in 1:1 v/v mixed acid at temperatures ranging from 60 to 80 °C. (Polarized at 2.3 V vs. Ag/AgCl_{sat.}, RCE at 3500 rpm).

achieved when electropolishing in the potential corresponding to limiting-current plateau. Details of polished surface morphology were further studied with SEM-examination.

3.2. Potentiostatic polishing

Potentiostatic polishing of PASS was performed at 2.3 V (vs. Ag/AgCl_{sat.}) as mentioned previously. The relationship between polishing current density and polishing time in 1:1 v/v mixed acids is presented in Fig. 6; the polishing current density became stable after 100 s in most conditions. This implies that stable anodic dissolution of PASS could be achieved during potentiostatic polishing in spite of its particular porous morphology and structure. The same potentiostatic polishing behavior of PASS can be found in 2:1 and 3:1 v/v mixed acids but with different stable polishing current densities. The relationships of the stable polishing current density, volume-ratio of mixed acid and polishing temperature is summarized in Fig. 7, which show

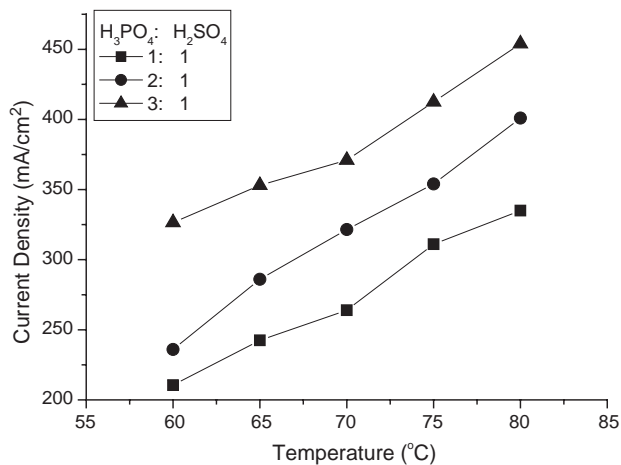


Fig. 7. The relationship between polishing current density and polishing temperature of PASS potentiostatically polished in 1:1, 2:1 and 3:1 mixed acids. (Polarized at 2.3 V vs. Ag/AgCl_{sat.}, RCE at 3500 rpm).



Fig. 8. The cross-section view of PASS specimen after mechanical grinding with 200-grit emery paper.

that the polishing current density increases with the increase of the polishing temperature and the phosphoric acid content in the mixed acid.

Since the anodic dissolution of RCE in limiting-current plateau follows mass-transfer controlled mechanism, the polishing current density could be increased with raising of the polishing temperature, the concentration of chemical acceptor-limited species and the rotating velocity of RCE [13–17]. As presented in Fig. 7, the behavior of phosphoric acid content in the mixed acid suggests that H_2PO_4^- or its complex could be the chemical acceptor-limited species in these polishing conditions.

All the polished surfaces of specimens appear bright to the naked eye after potentiostatic polishing. The effects of polishing temperature and volume-ratio of the mixed acid on polishing morphology will be further examined and evaluated with SEM examination in next section.

3.3. Polished surface morphology

Fig. 8 shows the cross-section view of PASS electrode. An obvious plastic deformed layer with a thickness of ca. $3\ \mu\text{m}$ was developed on the porous specimen after mechanical grinding with 200-grit emery paper. To avoid the effect of plastically deformed layer on the electrochemical polishing behavior of PASS, potentiostatic polishing in this study is capable of dissolving a thickness at least larger than $42\ \mu\text{m}$, estimated from the lowest current density of

$210\ \text{mA}/\text{cm}^2$ in Fig. 7, away from the mechanically grinding surface.

Fig. 9 shows the SEM-micrographs of surface morphologies of specimens after potentiostatic polishing in 1:1 v/v mixed acid; it shows apparently that the polishing behavior is very sensitive to the polishing temperature. Polishing at $70\ ^\circ\text{C}$, a brightening and leveling surface (Fig. 9a) is obtained. Polishing temperature at and above $75\ ^\circ\text{C}$, some deep and enlarged pores is developed on the specimen surface (Fig. 9b); the size of enlarged pores could reach as large as $50\ \mu\text{m}$. The increase of pore size is assumably ascribed to the remarkable anodic dissolution rate taking place within the pores of PASS. In summary, the objective of electropolishing on porous surface is not achieved in 1:1 v/v mixed acid at and above $75\ ^\circ\text{C}$. However, a shining surface of PASS can still be visually observed in all the above-mentioned polishing conditions.

Surface morphologies of PASS after potentiostatic polishing in 2:1 v/v mixed acid are shown in Fig. 10, in which leveling and brightening surface of PASS was apparently accomplished. Especially, an optimal leveling and brightening surface of PASS can be clearly observed when polishing in 2:1 v/v mixed acid at $70\ ^\circ\text{C}$ (Fig. 10c). For polishing at 60 and $65\ ^\circ\text{C}$, although a leveling and brightening surface still shown yet their surface morphologies are not as smooth as that polished at $70\ ^\circ\text{C}$. The pore size of PASS does not increase for polishing under these conditions. It indicates that the brightening effect on the surface of PASS can be improved in the polishing temperature at and above $70\ ^\circ\text{C}$. In spite that a smooth brightening surface can be realized as polishing at and above $75\ ^\circ\text{C}$ (Fig. 10d), a few enlarged pores can still be observed on the surface. However, a well brightening and leveling surface can be found in the region near the enlarged pores. That is, anodic dissolution rate within the surface pores of PASS increases as polishing temperature being increased above $75\ ^\circ\text{C}$. However, the enlarged pores polished in 2:1 v/v mixed acid is visually showing a much smaller size than that polished in 1:1 v/v mixed acid; i.e. increasing the

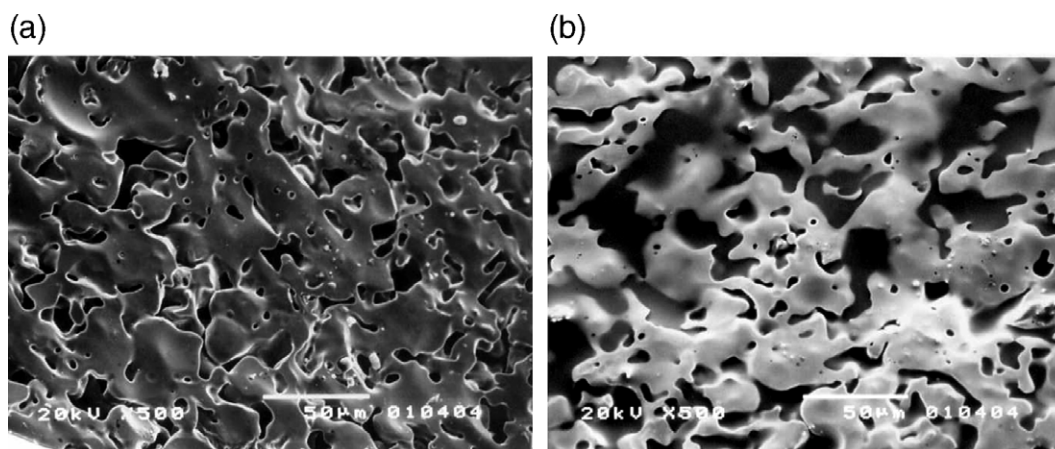


Fig. 9. SEM-micrograph showing the surface morphology of PASS after potentiostatic polishing in 1:1 v/v mixed acid at (a) $70\ ^\circ\text{C}$ and (b) $75\ ^\circ\text{C}$.

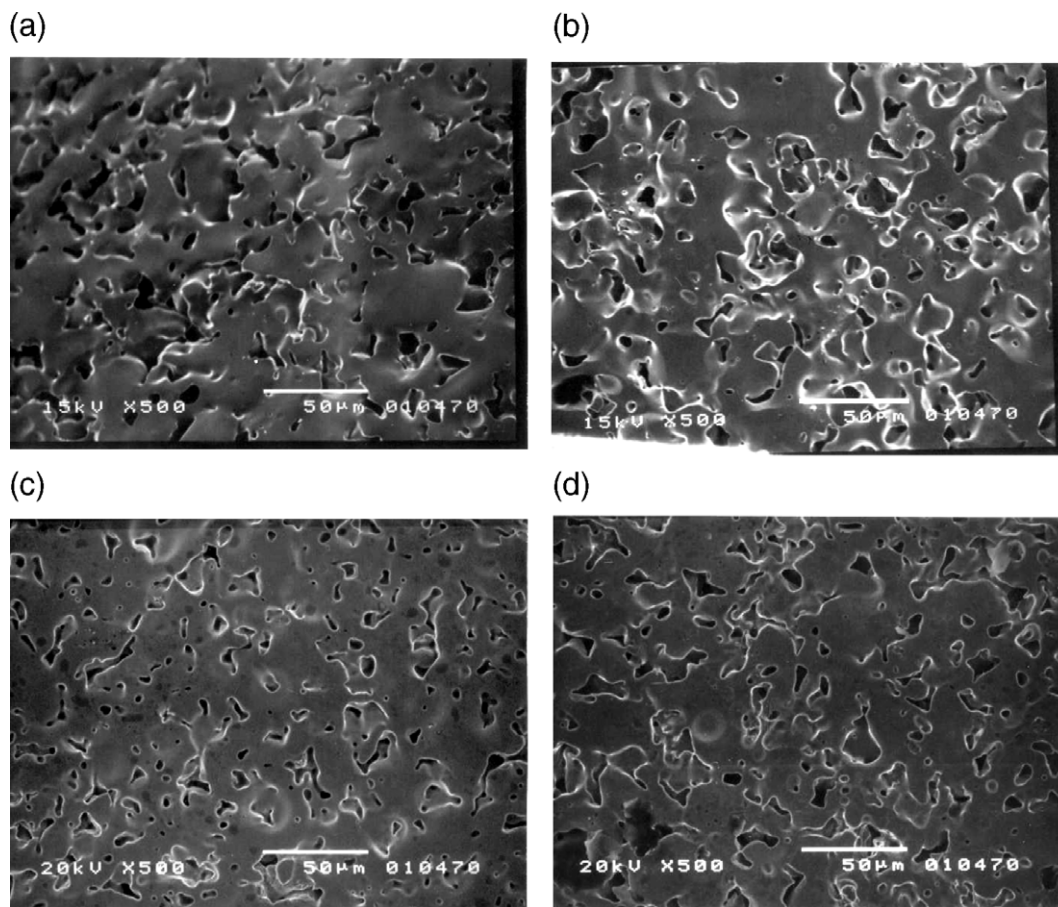


Fig. 10. SEM-micrograph showing the surface morphology of PASS after potentiostatic polishing in 2:1 v/v mixed acid at (a) 60 °C, (b) 65 °C, (c) 70 °C, and (d) 75 °C.

phosphoric acid content in the mixed acid can impede the dissolution rate within the pores.

Contrary to the polishing behavior in 1:1 and 2:1 v/v mixed acids, there is no obvious difference in surface appearance after polishing in 3:1 v/v mixed acid at temperatures ranging from 60 to 80 °C (Fig. 11). This indicated that the electrochemical polishing behavior in 3:1 v/v mixed acid is not sensitive to the polishing temperature.

Those enlarged pores are not found any more, but special feature of rounded edges surrounding the surface pores of PASS can be clearly observed. It implies that a relatively high dissolution rate may take place at the edges surrounding the surface pores. This phenomenon could be caused by the high current density concentrated at the sharp edge. This process is also regarded as leveling process, in which smoothing the rough surface is resulted from the

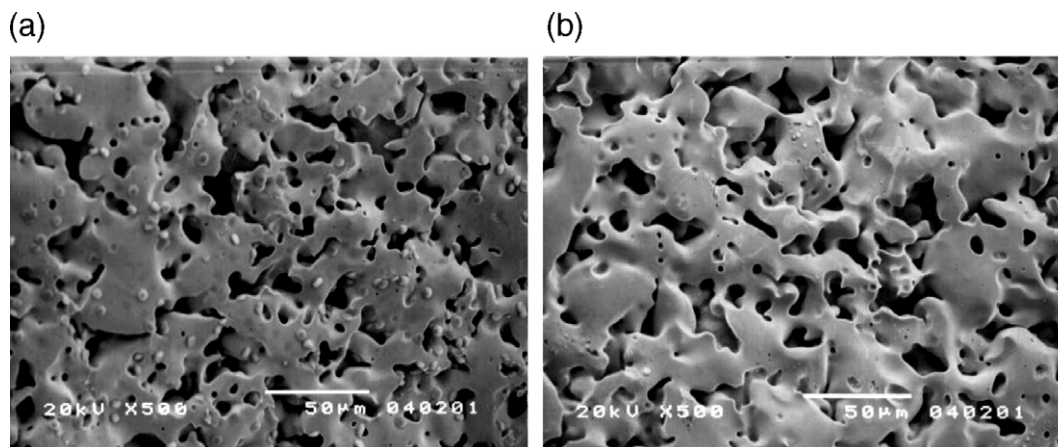


Fig. 11. SEM-micrograph showing the surface morphology of PASS after potentiostatic polishing in 3:1 v/v mixed acid at (a) 60 °C and (b) 80 °C.

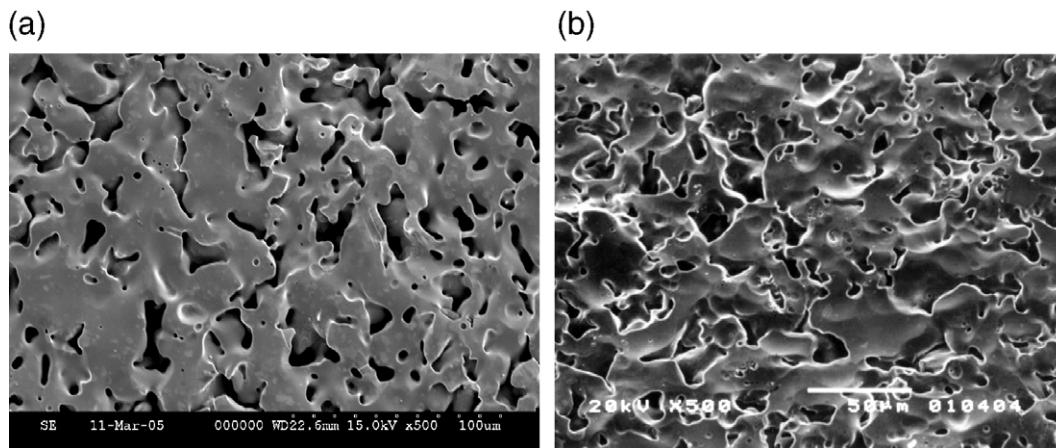


Fig. 12. SEM-micrograph showing the surface morphology of PASS after 100 C/cm² polishing (a) in 2:1 mixed acid, 60 °C for 444 s and (b) in 1:1 mixed acid, 75 °C for 303 s.

distribution of primary current density, by which the concentrated current density results in higher dissolution rate [9,15].

3.4. Effect of polishing charge

Since all experiments in this study was potentiostatically performed for 300 s, but the current densities were not always the same and so the charge passed varied. One may question about the effect of charge on resulting surface structure. When potentiostatic polishing in 3:1 v/v mixed acid, it has been shown that the polishing behavior of PASS is not sensitive to the temperature ranging from 60 to 80 °C in spite of polishing with obviously different charges (Figs. 7 and 11). However, the pore size on the polished surface increased considerably when polishing was conducted in 1:1 and 2:1 v/v mixed acids at and above 75 °C. These polishing behaviors all indicate the important roles played by the volume ratio of mixed acid and the polishing temperature, rather than by the polishing charge. To further clarify the query of charge effect, two experiments with polishing charge of 100 Coul/cm², which is the charge for optimal polishing in 2:1 v/v acid at 75 °C for 300 s, were conducted under (a) 2:1 v/v mixed acid at 60 °C for 444 and (b) 1:1 v/v mixed acid at 75 °C for 303 s conditions. The surface morphologies in both the above-mentioned specimens show little difference from those obtained respectively under the same polishing conditions yet for 300 s (Fig. 12).

It has been well known that austenitic stainless steel can be electrochemically polished in the mixed-acid above 65 °C. However, the effect of the volume ratio of the mixed acid on the electropolishing behavior is still not fully investigated. In this study it is confirmed that the volume ratio of the mixed acid and the polishing temperature are the key factors for electropolishing PASS. Polishing at high temperature (>75°C) and in low H₃PO₄-content mixed acid tends to enlarge the pore size of PASS. Nevertheless, the pore enlargement of those pores can be significantly

prevented by increasing the H₃PO₄-content in the mixed acid. Polishing in 3:1 v/v mixed acid, the polishing behavior of PASS is independent of polishing temperatures.

4. Conclusions

The electrochemical polishing behavior of porous austenitic stainless steel (PASS) is significantly affected by the polishing temperature and the volume-ratio of the H₃PO₄-H₂SO₄ mixed acid; the potentiostatic polishing charge seems to play an important role. An optimal brightening and leveling surface of PASS could be achieved when polishing was conducted in 2:1 v/v mixed acid at 70 °C. Due to the high dissolution rate taking place within the pores, the pore size on the polished surface increased considerably when polishing was conducted in 1:1 and 2:1 v/v mixed acids at and above 75 °C. In 3:1 v/v mixed acid, the polishing behavior is not sensitive to the temperature ranging from 60 to 80 °C.

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