

Effects of process variables on morphology of palladium metal deposit in hydrochloric acid medium

Min-Seuk kim, Jae-Chun Lee, Won-Back Kim, Jin-Ki Jeong, Chul-Woo Nam
Korea Institute of Geoscience and Mineral Resources, Daejeon, Korea

Abstract: Palladium is widely used for several applications and recovery of palladium from secondary sources becomes increasingly important since palladium is one of maldistributed platinum group metals. Electrochemical recovery of dense palladium metal sheet from Pd leaching solution is a simple and easily controlled method. The surface morphology of the recovered Pd metal was significantly affected by current density and temperature. Dense deposit morphology was in higher stress state regardless of preparation condition under 55 °C. Rising temperature up to 70 °C had a stress releasing effect besides densification of Pd deposit.

1. Introduction

Palladium is widely used for several applications: electronics, catalyst, dental, etc [1]. Recovery of palladium from secondary sources becomes increasingly important since palladium is one of maldistributed Platinum Group Metals [1,2]. Recently, various processes have been studied to recover palladium from hydrochloric acid leaching solution [3] and electrochemical recovery of palladium from the leaching solution has a possibility to be relatively simple and easily controlled method. Palladium can be recovered directly as a metal sheet form by the electrochemical process from the leaching solution. In the case of electrochemical metal sheet formation, morphology control of metal deposit is important since the morphology controls various properties like purity and residual stress of the deposit.

The purpose of the present work is to make a systematic investigation of relationship between the deposit morphology and electrochemical process variables for recovery of dense Pd metal sheet. An attempt was also made to elucidate the morphology effect on stress of the deposit.

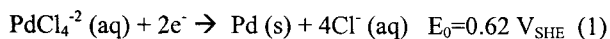
2. Experimental

Hydrochloric acid solutions containing Pd were prepared by dissolving various concentrations of PdCl₂ (Wako, 99%) in 6M hydrochloric acid solutions. Electrochemical behaviours of Pd in the solutions were examined using a three-electrode cell: Ti working electrode of 1cm², graphite counter electrode of 6cm², and saturated calomel reference electrode. The cell temperature was automatically controlled with a heating bath. Stress occurred during Pd deposition was also measured by a laser deflection technique. The laser deflection technique in this study used laser beam deflection produced by stain of electrode. Working electrode was Pt-coated glass electrode of 200um thickness. Since the stress bends the Pt-coated glass electrode during the deposition, a reflection angle of laser beam from the electrode is changed in proportion to the stress level. The deflection is a degree of strain that is directly proportional to the stress. Surface morphology of the deposit was examined by a scanning electron microscope. All electrochemical tests were done using EG&G 273 potentiostat/galvanostat.

3. Results and discussion

Electrochemical studies

Figure 1 shows liner polarization curves in 6M hydrochloric acid solutions with various Pd ion concentrations. Cathodic currents begun to flow at about 0 V. It has been reported that palladium ions make chloride complexes in the present of chloride ions that are strongly affected by pH and Cl⁻ concentration and PdCl₄⁻² anions were regarded as known major species in the solution of high chloride concentration and low pH [4-6]. Several authors have reported the electrodeposition of palladium from PdCl₄⁻² in the acid solution as follows [7,8]:



It is seen from the linear polarograms that limiting current regions were followed by hydrogen absorption reaction into palladium at -0.15V in the 6M HCl solutions. Hydrogen evolution after the absorption reaction dominates overall reaction at more negative potential. The limiting current increased linearly in proportion to Pd concentration at low Pd concentrations as shown in figure 2. Limiting current can be expressed by equation (2) and is proportional to bulk concentration (C_{bulk}) of reactant in a solution at a sufficiently high overpotential [9].

$$i_L = nFD C_{\text{bulk}}/N \quad (2)$$

A deviation from the linear relationship was observed over 0.06 M PdCl₂ and increased with Pd concentration. The deviation from the equation in the high Pd concentration seems to be caused by a change of Pd deposit morphology.

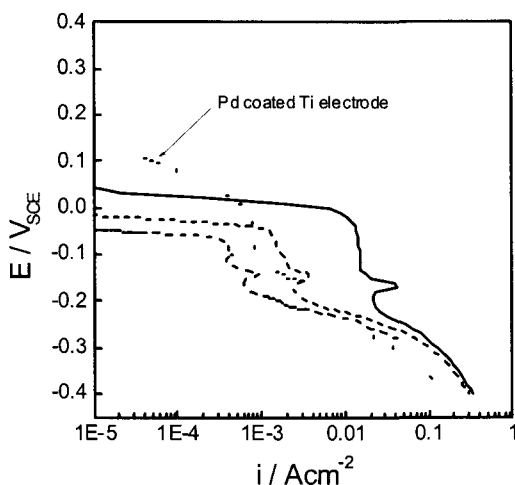


Fig 1. Polarization curves with a variation of dissolved Pd concentration in 6MHCl solution at 40°C.
(a)—— 0.1M (b)..... 0.02M (c) --- 0.01M (d)---- 0.005M

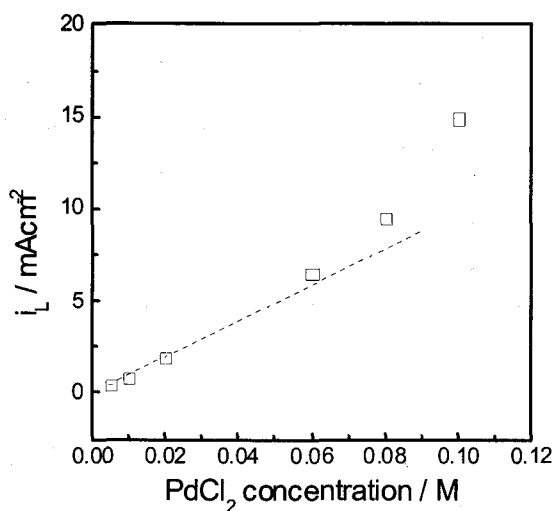


Fig.2 Limiting current density at -100mV vs. Pd concentration in 6M HCl solutions.

Deposit Morphology studies

Figure 3 shows a change of deposit morphology by increasing current density in the 6M HCl solution containing 0.1M PdCl₂ at 25 °C. An increase of the current density changed the deposit morphology from dense irregular at 0.2i_L and 0.44i_L to starfish-like porous one at 1.46i_L via acicular at 0.88i_L. It has been reported that a growth mode of metal deposit is changed from polycrystalline to powders via nodules or dendrites by increasing current density [10]. For more dense structure, it is better to lower the current density as shown in figure 3. Figure 4 shows that, at the current density of 0.88i_L in figure 3 (c), rising temperature changes the deposit morphology from the acicular to the dense irregular. Figure 5 reveals that the two dense deposits with the similar morphology in figure 3 (a) and 4 (c) are in a similar state of stress regardless of preparation condition. A positive sign of strain axis in figure 5 corresponds to tensile stress on the deposit. The stress increased with rising temperature until 55 °C and turn to decrease at 70 °C as shown in figure 6. The change of deposit morphology from the acicular to the dense irregular brings a deposit to high stress state. The increase of stress by densification was overcome by rising temperature up to 70 °C in figure 6 (d) that has a stress releasing effect besides the densification of deposit.

4. Conclusions

Electrochemical behavior of Pd in 6M hydrochloric acid solution was investigated by linear polarization method. Limiting current region was followed by hydrogen absorption reaction into palladium at -0.15V in the solution. Hydrogen evolution after the absorption reaction dominates overall reaction at more negative potential. The limiting current increased linearly in proportion to Pd content at low Pd concentrations under 0.06M Pd.

Effects of electrochemical process variables on Pd deposit morphology were examined by scanning electron microscope observation and laser deflection stress measurement technique. Increasing current density changed the morphology of Pd deposit from dense irregular to starfish-like porous one. Rising temperature showed similar effect to lowering current density on deposit morphology. The dense deposit was in higher stress state than the porous one regardless of preparation condition. The stress increased with rising temperature until 55 °C. Rising temperature up to 70 °C, however, had a stress releasing effect besides the densification of deposit.

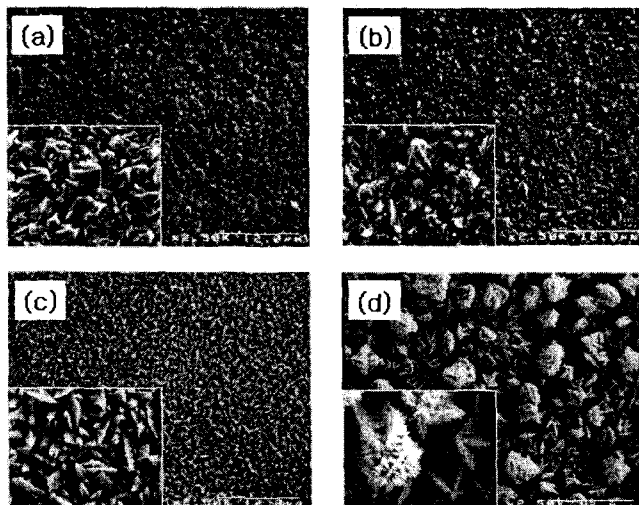


Fig. 3. Change of deposit morphology by increasing current density (mA/cm^2) in 6M HCl solution with 0.1M PdCl_2 at 25°C. Total charge $Q=2.58\text{C}$
 (a) 2.07 (b) 4.43 (c) 8.85 (d) 14.75

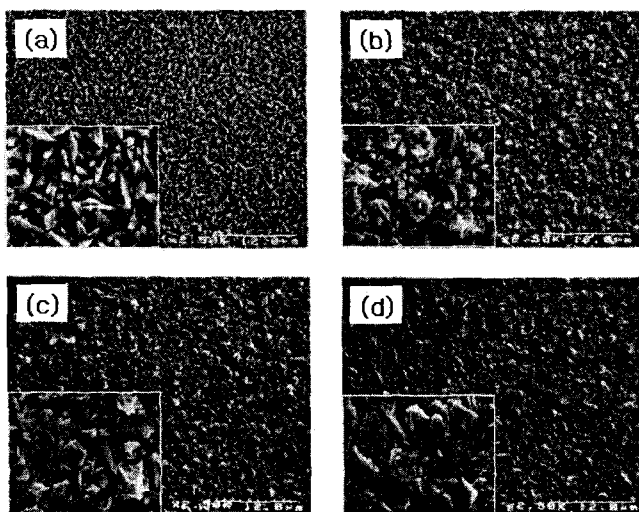


Fig. 4. Change of deposit morphology by increasing temperature at $8.85\text{ mA}/\text{cm}^2$ in 6M HCl solution with 0.1M PdCl_2 . Total charge $Q=2.58\text{C}$
 (a) 25 °C (b) 40 °C (c) 55 °C (d) 70 °C

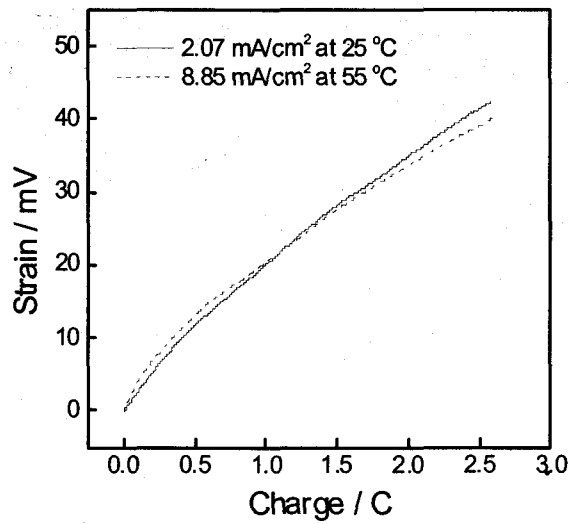


Fig.5. Strain vs. charge of two deposits with dense irregular morphology prepared by different conditions.

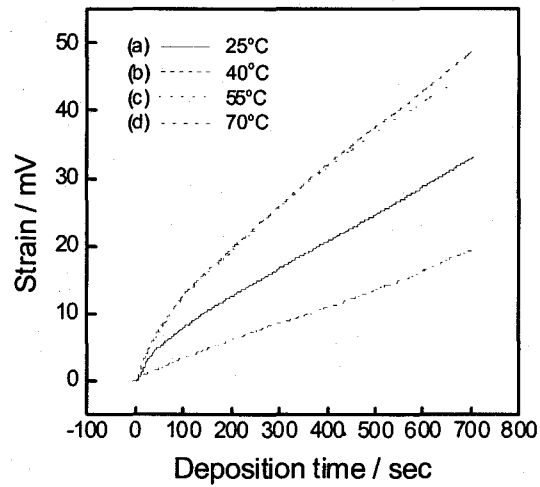


Fig.6. Strain vs. deposition time according to deposition temperature at 8.85 mA/cm² in 0.1M PdCl₂-6M HCl. (a) 25 °C (b) 40 °C (c) 55 °C (d) 70 °C

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