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Effect of Thermal Treatment Temperature on Lifespan of Conductive Oxide Electrode

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Dimensionally stable anodes have been widely used to cathodically protect the metallic materials in corrosive environments including concrete structure as the insoluble anode. Lifespan of the anode for concrete construction can be determined by NACE TM0294-94 method. Lifespan of conductive oxide electrode would be affected by thermal treatment condition in the process of sol-gel coatings. This work aims to evaluate the effect of thermal treatment temperature on the lifespan of the RuO_2 electrode. 450 ℃ treated conductive oxide electrode showed the excellent properties and its lifespan was evaluated to be over 88 years in 3% NaCl, 4% NaOH, and simulated pore water. This behavior was related to the formation of RuO_2.

Keywords *: conductive oxide electrode, concrete, anode, lifespan, cathodic protection, thermal treatment*

1. Introduction

All cathodic protection (CP) systems except Zn-anode using system have been used carbon as an anode in concrete. Many CP systems used carbon-anode since CP needs high stable anode and also low cost on the anode. However, carbon was not appropriate in concrete and thus carbon materials should be mixed with polymer, resin, and so on. In addition, carbon showed low electric conductivity than other metals and carbon could react in concrete and made carbon dioxide, carbonate and its salt.

Properties of the anode for cathodic protection need low overvoltage for oxygen evolution and high corrosion resistance. It is well known that dimensionally stable anode (DSA) has been the best anode ever since.[1)~6)] DSA is mainly composed of RuO_2, IrO_2, ZrO_2, Co_2O_3, and also Ta_2O_5, TiO_2, MnO_2 are added to DSA for better corrosion resistance. In recent years, 3-components or multi-components anodes (MMO, Mixed metal oxide) are studied because 2-component anodes have low corrosion resistance. These newly developed electrodes show lower overvoltage for oxygen evolution and higher corrosion resistance than 2-component anodes.

The lifetime of DSA is also one of the very important factors. Thus, RuO_2, IrO_2, RhO_2, ZrO_2 are well used for life extension, and many researches have focused on life extension by lowering oxygen evolution potential and minimizing dissolution of oxide coatings. Oxide coating usually is performing using a sol-gel method. Typical sol-gel coating on Ti plate was performed as follows; one cycle coating process consists of dip-coating, 1st drying and 2nd drying. Several cycles of coating processes are repeatedly performed and followed by the final heat treatment.[7)] Temperature of 2nd drying and final thermal treatment would affect the properties of conductive oxide electrode since temperature is high and it is final process. This study aims to evaluate the effect of thermal treatment on the lifespan of conductive oxide electrode for cathodic protection to concrete structure.

2. Experimental methods

To make stable RuO_2 sol at room temperature, ruthenium chloride hydrate ($RuCl_3 \cdot 3H_2O$, Kojima Chemical Co.) was used and its concentration was 0.097M as $RuCl_3$. Isopropanol ($(CH_3)_2CHOH$, Aldrich) was used as a solvent.

Base material to be coated used titanium plate (grade Ⅱ) and its size was 10×80×0.5 mm. After mechanical polishing using SiC paper #220, Ti plate was immersed for 30 minutes in 35% HCl solution at room temperature and rinsed. Sol-gel coating on Ti plate was performed as follows; One cycle coating process consists of dip-coating (1.0cm/min), 1st drying (130℃, 10 min.), and 2nd drying

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at different temperatures. 3 cycles of coating processes are performed and followed by the final heat treatment at same 2nd drying temperatures for 1 hr.

Polarization test (scan rate; 1 mV/sec) and cyclic polarization test (scan rate; 1 mV/sec) were performed using a Potentiostat (Model EG&G 273A) at 25℃, 1M H_2SO_4 and 25℃, 0.5 M H_2SO_4 respectively. Saturated calomel electrode was used as a reference electrode and high density graphite electrode as a counter electrode.

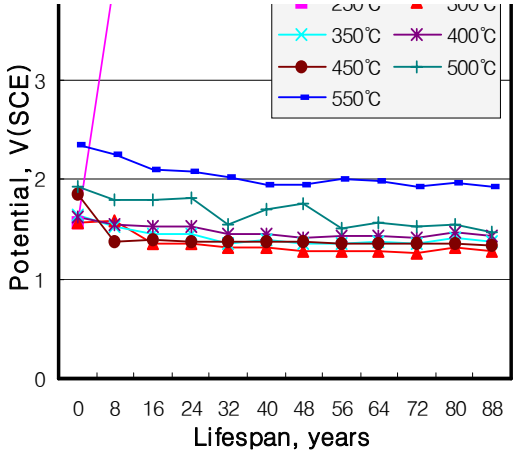
Lifespan was evaluated according to NACE Standard TM 0294-94[8] in 3% NaCl, 4% NaOH, and simulated pore water (0.20% $Ca(OH)_2$ + 3.20% KCl + 1.00% KOH + 2.45% NaOH + 93.15% H_2O). Applied current was constantly 320 mA/cm^2 and the experiment was continued before electrode potential reaches 4 V(SCE).

3. Results and discussion

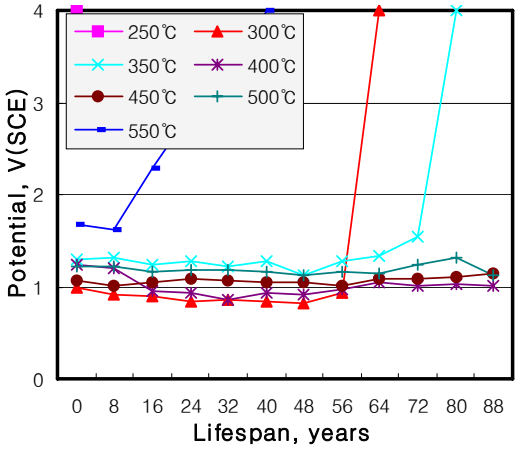
Coating process of RuO_2 single component was as follows; after dipping in sol solution - 0.097M as $RuCl_3$, 1st drying was done for 10 minutes at 130℃ and then 2nd drying was performed for 1 hour at 250, 300, 350, 400, and 450℃ respectively and this process repeated 3 times. Also, final thermal treatment was subjected to the dried specimen for 1 hour at the temperature as same as 2nd drying temperature.

Fig. 1 shows the effect of 2nd drying and final thermal treatment temperature on the lifespan of conductive oxide electrode (3 cycles coating using 0.097M as RuCl3); (a) is in 3% NaCl, (b) is in 4% NaOH, (c) is in simulated pore water. In case of 3% NaCl, specimen treated at 250℃ showed very short lifespan below 10 years, but the others had the lifespan over 88 years. However, anode potential during the test of 550℃ treated specimen revealed near 2V(SCE). Specimen treated at 300~450℃ represented very stable potential. In case of 4% NaOH, specimens treated at 250 and 550℃ showed very short lifespan below 8 years, but 300℃ treated specimen revealed the lifespan of 56 years and 350℃ treated specimen represented the lifespan of 72 years. However, 400~500℃ treated specimens showed the lifespan over 88 years and stable potential. In case of simulated pore water, only 450℃ treated specimen showed the lifespan over 88 years, but the others revealed relatively short lifespan below 64 years. Therefore, it should be noted that optimum thermal treatment temperature was 450℃.

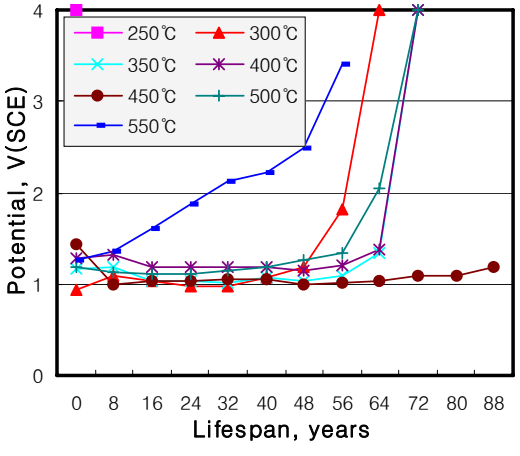
Fig. 2 shows the effect of 2nd drying and final thermal treatment temperature on the polarization behavior of conductive oxide electrode (3 cycles coating using 0.097M as $RuCl_3$) in 1 M H_2SO_4 at room temperature. Scanning rate was 1 mV/sec. 250℃ treated specimen showed very



(a)



(b)



(c)

Fig. 1. Effect of 2nd drying and final thermal treatment temperature on the lifespan of conductive oxide electrode (3 cycles coating using 0.097M as $RuCl_3$); (a) 3% NaCl, (b) 4% NaOH, (c) Simulated pore water

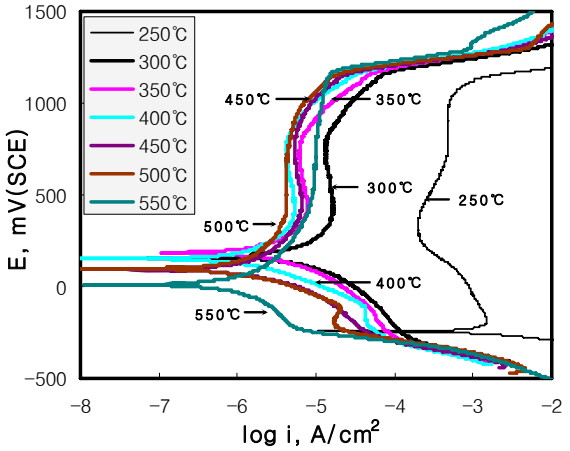


Fig. 2. Effect of 2nd drying and final thermal treatment temperature on the polarization behavior of conductive oxide electrode (3 cycles coating using 0.097M as $RuCl_3$) in 1 M H_2SO_4 at room temperature

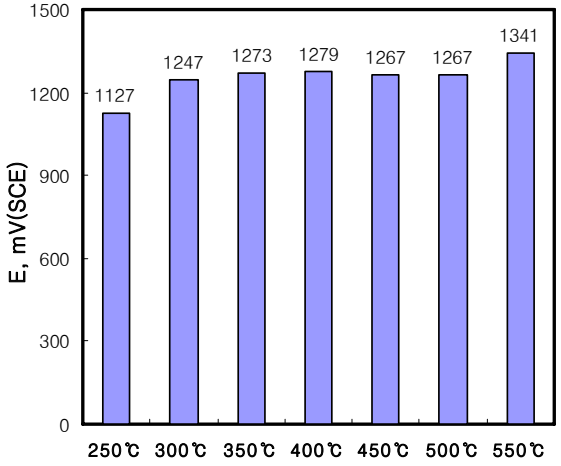


Fig. 3. Effect of 2nd drying and final thermal treatment temperature on the oxygen evolution potentials of conductive oxide electrode (3 cycles coating using 0.097M as $RuCl_3$) determined in 1 M H_2SO_4 at room temperature

low corrosion potential and large passive current density. 550℃ treated specimen revealed relatively low corrosion potential and 300℃ treated specimen represented relatively large passive current density. The others showed excellent passivation behavior.

Fig. 3 shows the effect of 2nd drying and final thermal treatment temperature on the oxygen evolution potentials of conductive oxide electrode (3 cycles coating using 0.097M as $RuCl_3$) determined in 1 M H_2SO_4 at room temperature. In this work, oxygen evolution potential was defined as the potential showing the current density of 10^{-3} A/cm^2. 250℃ treated specimen revealed the lowest

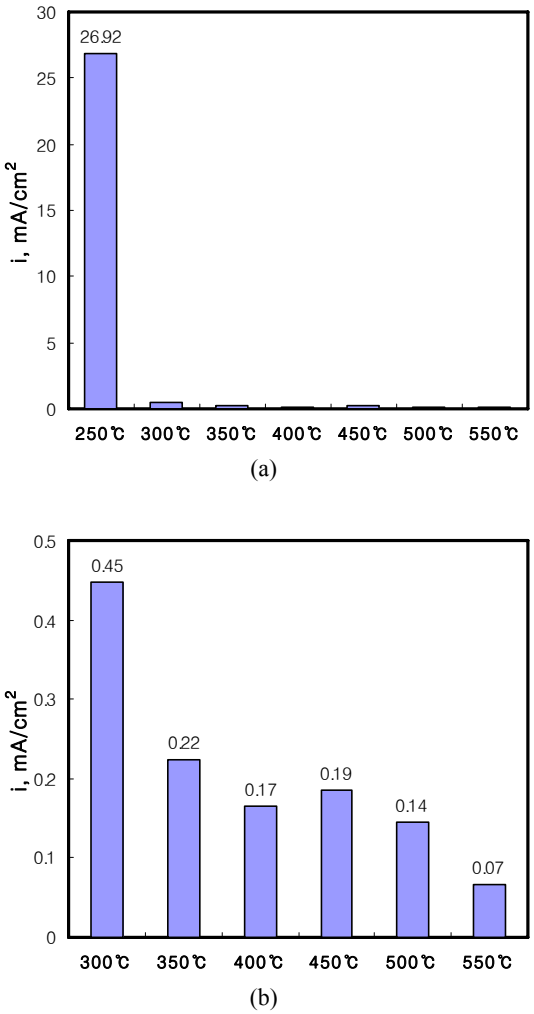


Fig. 4. Effect of 2nd drying and final thermal treatment temperature on the oxygen evolution current density of conductive oxide electrode (3 cycles coating using 0.097M as $RuCl_3$) determined in 1 M H_2SO_4 at room temperature; (a) 250~550℃ (b) 300~550℃

potential and 550℃ treated specimen represented the highest potential among the specimens. Increasing thermal treatment temperature, oxygen evolution potential increased.

Fig. 4 shows the effect of 2nd drying and final thermal treatment temperature on the oxygen evolution current density of conductive oxide electrode (3 cycles coating using 0.097M as $RuCl_3$) determined in 1 M H_2SO_4 at room temperature ; (a) 250~550℃ (b) 300~550℃. In this work, oxygen evolution potential was calculated theoretically from the pH of the solution and then its current density was determined at calculated potential. 250℃ treated specimen revealed very large current density than the others. Also, when treatment temperature increased, oxygen evolution current density reduced.

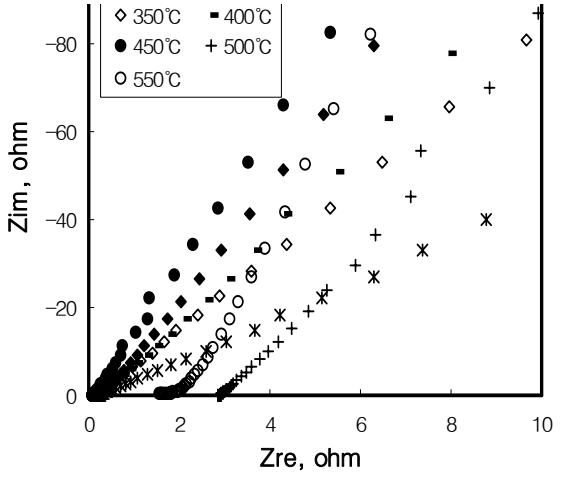


Fig. 5. Effect of 2nd drying and final thermal treatment temperature on the AC impedance of conductive oxide electrode (3 cycles coating using 0.097M as $RuCl_3$) in 1 M H_2SO_4 at room temperature

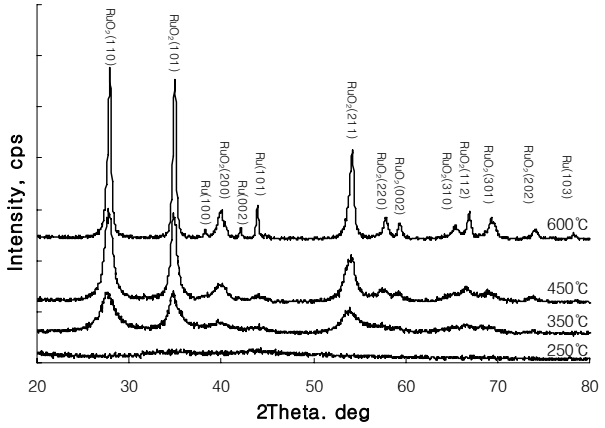


Fig. 6. Effect of 2nd drying and final thermal treatment temperature on the structure of conductive oxide electrode (3 cycles coating using 0.097M as $RuCl_3$) determined by XRD

Fig. 5 shows the effect of 2nd drying and final thermal treatment temperature on the AC impedance of conductive oxide electrode (3 cycles coating using 0.097M as $RuCl_3$) in 1 M H_2SO_4 at room temperature. 450℃ treated specimen showed the largest impedance and the others did not reveal the trend depending upon the thermal treatment temperature.

Fig. 6 shows the effect of 2nd drying and final thermal treatment temperature on the structure of conductive oxide electrode (3 cycles coating using 0.097M as $RuCl_3$) determined by XRD. XRD peaks were obtained for the powder that made by 1st drying (130℃) of sol solution of 0.097M as $RuCl_3$) and then thermally treated at 2nd drying and final temperature respectively. 250℃ treated powder revealed amorphous, but the degree of crystalline increased as thermal treatment temperature increased. Thus, 600℃ treated powder showed the crystal structure and Ru peak in addition to RuO_2 peak also was observed. It should be considered that structure of conductive oxide by thermal treatment affected the lifespan of the anode.

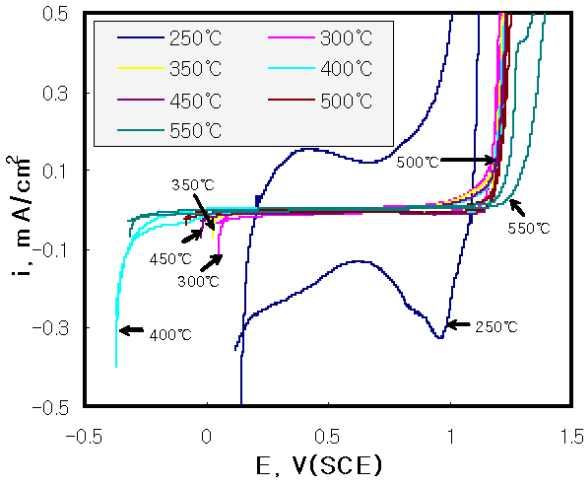


Fig. 7. Effect of 2nd drying and final thermal treatment temperature on the cyclic polarization behavior of conductive oxide electrode (3 cycles coating using 0.097M as $RuCl_3$) in 0.5 M H_2SO_4 at room

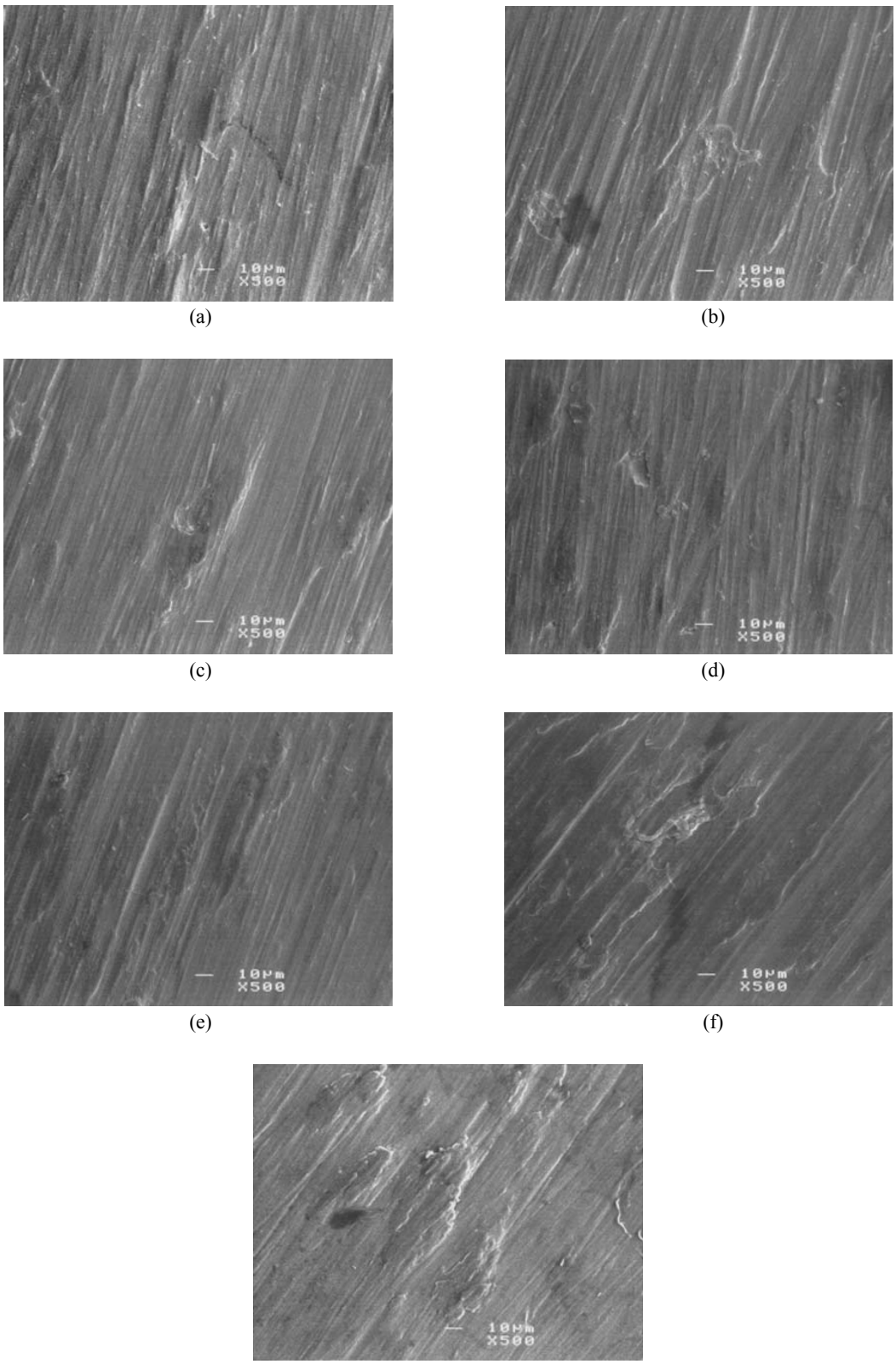
Fig. 7 shows the effect of 2nd drying and final thermal treatment temperature on the cyclic polarization behavior of conductive oxide electrode (3 cycles coating using 0.097M as $RuCl_3$) in 0.5 M H_2SO_4 at room temperature. Scanning rate was 1 mV/sec. 250℃ treated specimen revealed the largest anodic and cathodic current density and this means the dissolution of conductive oxide and finally showed very short lifespan. However, the others represented the excellent cyclic polarization behavior.

Fig. 8 shows the effect of 2nd drying and final thermal treatment temperature on the appearance of conductive oxide electrode (3 cycles coating using 0.097M as $RuCl_3$) by SEM; (a) is for 250℃, (b) is for 300℃, (c) is for 350℃, (d) is for 400℃, (e) is for 450℃, (f) is for 500℃, and (g) is for 550℃. Appearance of conductive oxide anode was not affected by thermal treatment temperature.

4. Conclusions

(1) 450℃ treated conductive oxide electrode showed the excellent properties and its lifespan was evaluated to be over 88 years in 3% NaCl, 4% NaOH, and simulated pore water. This behavior was related to the formation of RuO_2.

(2) When the conductive oxide electrodes were ther-



(a) (b) (c) (d) (e) (f) (g)

Fig. 8. Effect of 2nd drying and final thermal treatment temperature on the appearance of conductive oxide electrode (3 cycles coating using 0.097M as $RuCl_3$) by SEM; (a) 250℃, (b) 300℃, (c) 350℃, (d) 400℃, (e) 450℃, (f) 500℃, (g) 550℃

mally treated below or above the optimum temperature (near 450℃), amorphous or crystal RuO_2 and metallic Ru were formed and thus the lifespan was decreased. However, thermal treatment temperature did little affect the appearance of coated outer surface.

References

1. K. M. Kim, K. Y. Hwang, H. C. Ko, and T. W. Yeu, *Hwahak Konghak*, **38**, 3 (2000).
2. K. S. Chae, J. H. Ahn, H. K. Choi, and Y. S. Song, *J. Corros. Sci. Soc. of Korea*, **30**, 1 (2001).
3. K. W. Kim, E. H. Lee, J. S. Kim, J. G. Choi, K. H. Shin, S. H. Lee, and K. H. Kim, *Hwahak Konghak*, **38**, 6 (2000).
4. S. K. Yen, *J. Electrochemical Society*, **146**, 4 (1999).
5. K. Darowicki and S. Janicki, *J. Electrochemical Society*, **148**, 3 (2001).
6. K. C. Sohn, H. Y. Chang, and Y. S. Kim, "Lifetime of insoluble anode for cathodic protection on concrete construction", The 12th Asian-Pacific Corrosion Control Conference, October 8-12, 2001, Seoul, Korea
7. Y. R. Yoo, H. Y. Chang, S. Take, and Y. S. Kim, *Corrosion Science and Technology*, **5**(2), 45 (2006).
8. NACE international standard test method TM0294-94, "Testing of embeddable anodes for use in cathodic protection of atmospherically exposed steel-reinforced concrete", NACE (1994)