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析氯钛基 $\text{RuO}_2-\text{Co}_3\text{O}_4-\text{TiO}_2(60)$ 涂层的研究

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摘要 用稳定极化、X射线衍射、透射电镜和扫描电镜的方法研究了钛基 $\text{RuO}_2-\text{Co}_3\text{O}_4-\text{TiO}_2(60)$ 涂层的析氯活性、导电性、使用寿命、微观结构和表面形貌, 并对其活性表面积进行了评价. 详细讨论了涂层成份、微观结构和表面形貌对涂层析氯活性和活性表面积的影响. 发现在0~10 m/o Co_3O_4 和60 m/o TiO_2 成份范围内 RuO_2 、 Co_3O_4 和 TiO_2 可形成单一金红石型固溶体, 且有优异的析氯活性、电导率和使用寿命. 以此研究为基础可改进氯碱工业广泛使用的传统 $\text{RuO}_2-\text{TiO}_2$ 阳极, 降低阳极涂层中贵金属含量, 提高阳极的电化学性能.

关键词 $\text{RuO}_2-\text{Co}_3\text{O}_4-\text{TiO}_2(60)$ 涂层, 析氯活性, 微观结构, 固溶体, 表面形貌, 欧姆极化

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A Study of $\text{RuO}_2\text{-Co}_3\text{O}_4\text{-TiO}_2(60)$ Coating on Ti-Substrate for Chlorine Gas Evolution ^①

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Abstract The chlorine gas evolution activity, electric conductivity, service life, microstructure and surface morphology of $\text{RuO}_2\text{-Co}_3\text{O}_4\text{-TiO}_2(60)$ coating on Ti-substrate were studied in 0 ~ 30 m/o Co_3O_4 range by steady-state polarization, X-ray diffraction, TEM and SEM methods. Active surface area of the coating was also evaluated. The influences of coating composition, microstructure and surface morphology on chlorine gas evolution activity and active surface area of the coating were discussed in detail. As a result, sole rutile-type solid solution of RuO_2 , Co_3O_4 and TiO_2 which showed better chlorine gas evolution activity, electric conductivity and service life was found in ca. 0 ~ 10 m/o Co_3O_4 range. Traditional $\text{RuO}_2\text{-TiO}_2/\text{Ti}$ anodes being widely used in chlor-alkali industry could be modified by a suitable amount of Co_3O_4 for the benefit of reducing content of Ru as a noble metal in the coating and improving the electrochemical properties of the anodes.

Key words $\text{RuO}_2\text{-Co}_3\text{O}_4\text{-TiO}_2(60)$ coating, Cl_2 -evolution activity, Microstructure, Solid solution, Surface morphology, Ohmic polarizaton

Since the dimensionally stable anodes (DSA) were developed by de Nora^[1], multicomponent oxide-coated anodes have aroused more and more interest in electrochemical industry for their good electrochemical properties and/or, low cost^[2]. The knowledge of coating composition, microstructure and surface morphology and their effects on electrochemical properties is essential for the design and the optimization of multicomponent active oxide coating.

There have existed various studies on RuO_2 , $\text{RuO}_2\text{-TiO}_2$, $\text{Co}_3\text{O}_4\text{-RuO}_2$ (on the Co_3O_4 -rich side) and Co_3O_4 coatings^[1~12]. Some of them, especial $\text{RuO}_2\text{-TiO}_2$ coated anode, are widely used in chlor-alkali industry. It was consistently confirmed that RuO_2 was an excellent electrochemical catalyst, and inactive TiO_2 could improve the adhesion of oxide coating with Ti-substrate. Co_3O_4 was also proved to be an electrochemical active, non-noble, material. Nevertheless, the $\text{RuO}_2\text{-Co}_3\text{O}_4\text{-TiO}_2$ coating has not been studied in detail thus far. The aim of this paper was to elucidate the behavior of such a mixed oxide system, expecting to provide some helpful information for the improvement of traditional $\text{RuO}_2\text{-TiO}_2/\text{Ti}$ anode widely used for chlorine gas evolution. Just from such a point of view

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the 60 m/o TiO_2 , a classical content in the RuO_2 - TiO_2 /Ti anode, was chosen in the mixed oxide system.

1 Experimental

The preparation of the oxide coatings was carried out by thermal decomposition method in the following way. 20% HCl aqueous solutions with appropriate amounts of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and TiCl_3 were brushed onto Ti- substrates which were degreased with acetone and then etched in boiling oxalic acid for 5 hours, and the solvent evaporated at 150 °C for 10 min. The process was repeated in 8 ~ 12 runs, and after each run samples were fired in air for 20 min at selected temperatures, 350 °C before the fifth run, 450 °C latter. After the final run, samples were fired for another 40 min, to complete the thermal decomposition. The TiO_2 content was kept at a constant value 60 m/o, the Co_3O_4 content varied between 0 ~ 30 m/o (pre-investigation showed that, CoTiO_3 phase will exist in the coating if Co_3O_4 is more than 30 m/o). The total amount of RuO_2 , Co_3O_4 and TiO_2 in the coatings was 10^{-5} mol/cm². The amount of each metallic oxide in specific coating will be indicated in parentheses in mole percent.

For electrochemical measurements, a polymethyl methacrylate H-type cell with fritted glass (G4 type) separating the study and counter electrode sections was used as electrolytic cell and Pt sheet or graphite bar as counter electrode. Only 1 cm² area of the oxide coating was used for electrochemical studies and the rest was isolated with Araldite glue. Potentials of the study electrodes were measured against a saturated calomel electrode (SCE), via Luggine capillary with its tip (1 mm-inner diam., 1.5 mm-out diam.) located about 2 mm up from the lower coating edge and 1.5 mm away from the coating surface. A salt bridge was inserted between the reference electrode and Luggine capillary.

The anode polarization characteristics were studied by steady-state galvanostatic method at 15 °C in saturated NaCl+1 mol/L HClO_4 solution which was pre-electrolyzed under N_2 -bubbling condition prior to use and saturated by chlorine gas in measurements. The ohmic drop in solution and oxide coating was corrected by the current interruption technique.

For evaluation of the active surface area of the oxide coating, cyclically voltammetric studies were carried out in 1 mol/L H_2SO_4 solution which was deaerated by bubbling N_2 gas for 40 min., 0 ~ 600 mV vs. SCE scanning range, 15 °C.

X-ray diffraction, Transmission electron microscopy (TEM) and Scanning electron microscopy (SEM) techniques were also employed for phase, microstructure and surface morphology analyses. The TEM foils were thinned at Ti-substrate side and polished at oxide coating side by ionic thinner.

Chemicals used were all Analar grade.

2 Results and Discussion

2.1 Phase and Microstructure

The series of RuO_2 - Co_3O_4 - TiO_2 (60) coatings on flat titanium sheets were examined by fast-scan X-ray diffraction (Fig. 1). The composition of the coating varied from 0 ~ 30 m/o Co_3O_4 at 5 m/o

intervals. No un-indexed reflections were observed. For 0, 5, 10 m/o Co₃O₄ coatings, diffraction peaks could be assigned to a rutile-type structure, additional peaks corresponded to reflections expected from the titanium substrate. Combined with the diffraction peaks mentioned above, the peaks of spinel Co₃O₄ diffraction appeared in the 15, 20, 25, 30 m/o Co₃O₄ coatings and their intensity increased with Co₃O₄ content. It should be emphasized that the rutile-type peaks were relatively broad and weak, and the more Co₃O₄ content, the broader and weaker the peaks. No evidence for separate TiO₂-and RuO₂-rich phase was provided even in a more detailed analyses of the major peaks (110, 101) belonging to rutile-type structure using a slower scan rate. It was concluded that the rutile-type phase was a solid solution consisted, at least, of RuO₂ and TiO₂.

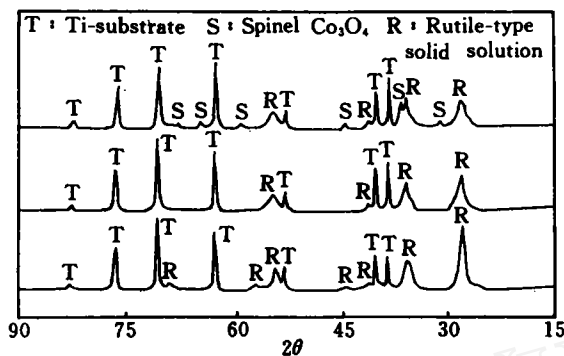


Fig. 1 X-ray diffraction patterns of RuO₂(40)-TiO₂(60) (a), RuO₂(30)-Co₃O₄(10)-TiO₂(60) (b), and RuO₂(25)-Co₃O₄(15)-TiO₂(60) (c) coatings on Ti-substrates

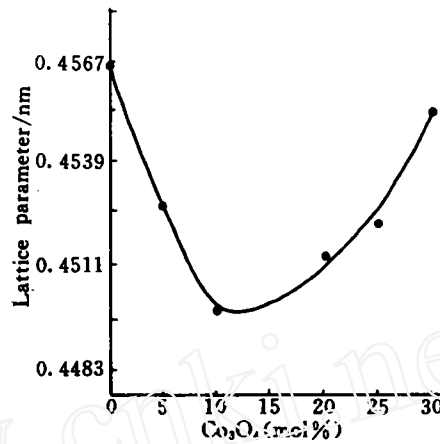


Fig. 2 Variation of lattice parameter a of rutile-type phase in the RuO₂-Co₃O₄-TiO₂(60) coating with Co₃O₄ content

Lattice parameter a of rutile type phase was measured precisely (Lattice parameter c could not be measured precisely due to the influence of diffraction peaks belonging to Ti-substrate and Co₃O₄). With the increasing of Co₃O₄ content in the coating, lattice parameter a of rutile type phase decreased rapidly and reached a minimum value at about 12 m/o Co₃O₄ composition before its obvious increasing (Fig2). Lattice parameter a of TiO₂ (rutile-type) is bigger than that of RuO₂. If the rutile type phase was a dual-component solid solution of RuO₂ and TiO₂, its lattice parameter a would increase monotonously, according to L. Vegard's law, with more TiO₂ in the solid solution as Co₃O₄ content increased in the coating. No doubt the abnormal variation of lattice parameter a resulted from the existence of Co₃O₄ as the third component in the rutile-type solid solution.

TEM inspection and micro-electron-bundle diffraction showed that the microstructure of RuO₂-

Co_3O_4 - TiO_2 (60) coating was very similar to that of RuO_2 (40)- TiO_2 (60) coating (sole rutile-type solid solution(Fig. 1)) as Co_3O_4 content was not more than 10 m/o, no spinel Co_3O_4 were found. As Co_3O_4 content higher than 10 m/o, distinguishable spinel Co_3O_4 phase appeared in the coating. The higher the Co_3O_4 content, the bigger the size of the spinel Co_3O_4 .

Evidently the RuO_2 - Co_3O_4 - TiO_2 (60) coating concerned in this paper should be of sole rutile-type solid solution of RuO_2 , Co_3O_4 and TiO_2 in ca. 0~10 m/o Co_3O_4 range. Spinel Co_3O_4 only emerges in the coating as Co_3O_4 content exceeds ca. 10 m/o, and its size increases remarkably with Co_3O_4 content increasing.

2.2 Surface Morphology and Active Surface Area

Typical surface morphologies taken by SEM are shown in Fig. 3. The surface of the coating which consisted of sole solid solution exhibited long net-like cracks. The more dissolved Co_3O_4 , the

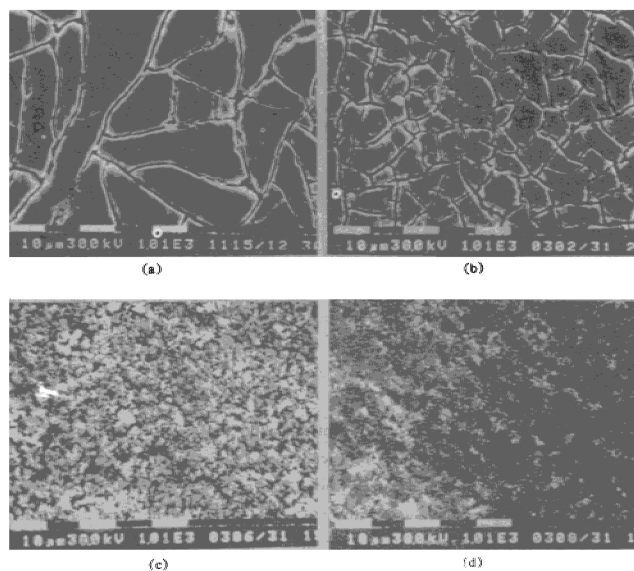


Fig. 3 Surface morphology of RuO_2 (30)- Co_3O_4 (10)- TiO_2 (60) (a), RuO_2 (25)- Co_3O_4 (15)- TiO_2 (60) (b), RuO_2 - Co_3O_4 (25)- TiO_2 (60) (c), and RuO_2 (10)- Co_3O_4 (30)- TiO_2 (60) (d), coatings on Ti-substrates.

more narrow cracks. As spinel Co_3O_4 emerged in the coating, the number of cracks increased critically. The coating of higher Co_3O_4 content appeared to be more compact and homogeneous but very porous. Clearly the roughness of $\text{RuO}_2-\text{Co}_3\text{O}_4-\text{TiO}_2(60)$ coating is enhanced by spinel Co_3O_4 .

The active surface area of the oxide coating was evaluated by double layer capacitance value. Cyclic voltammograms of the oxide-coated electrode in N_2 -saturated 1 mol/L H_2SO_4 were recorded at varying scan rate in 0~600 mV vs. SCE range. The double layer capacitance value was determined from the slope of linear plot, charging current vs. scan rate. The coating with a little of spinel Co_3O_4 showed higher active surface area in accordance to its roughness. But the active surface area decreased linearly with Co_3O_4 content increasing as more spinel Co_3O_4 emerged in the coating, in spite of the increasing of coating roughness (Fig. 4). This implies that the active surface area changes from roughness sensitive to composition sensitive. In other words, the average amount of active sites in the oxide coating decreases overwhelmingly with more emerged spinel Co_3O_4 .

2.3 Chlorine Gas Evolution

Anodic polarization curves for chlorine gas evolution at $(\text{RuO}_2-\text{Co}_3\text{O}_4-\text{TiO}_2(60))$ -coated titanium electrodes in saturated $\text{NaCl}+1$ mol/L HClO_4 solution pre-saturated with chlorine gas are shown in Fig. 5. The $\text{RuO}_2-\text{Co}_3\text{O}_4-\text{TiO}_2(60)$ coating, in a wide composition range, are more active for chlorine gas evolution than the $\text{RuO}_2(40)-\text{TiO}_2(60)$ coating (similar to the composition of industrial anodes). With increasing Co_3O_4 content of the coating, the chlorine gas evolution rate increased almost vertically to a maximum value at the maximum solubility point of Co_3O_4 in the rutile-type solid solution after a slow increase, then took a sudden turn and developed rapidly prior to a relatively slow decrease. This is directly illustrated in Fig. 6 where current densities at specific overpotentials are given with respect to oxide composition.

Obviously, the chlorine gas evolution activity of the $\text{RuO}_2-\text{Co}_3\text{O}_4-\text{TiO}_2(60)$ coating is composition- and microstructure-sensitive. This should be critically attributed to the effect of crystal defects. The crystal structure of Co_3O_4 is far different from that rutile-type RuO_2 and TiO_2 . When Co_3O_4 dissolves in the rutile-type solid solution of RuO_2 and TiO_2 , as the quantitative X-ray diffraction analyses has proved, severe crystal defects are introduced into the coating, and the more dissolved Co_3O_4 , the more severe crystal defects. No doubt the severe crystal defects will greatly enhance the activities of RuO_2 and Co_3O_4 which are active components in the coating. So, the rutile-type solid solution of RuO_2 and TiO_2 saturated by Co_3O_4 will show best chlorine gas evolution

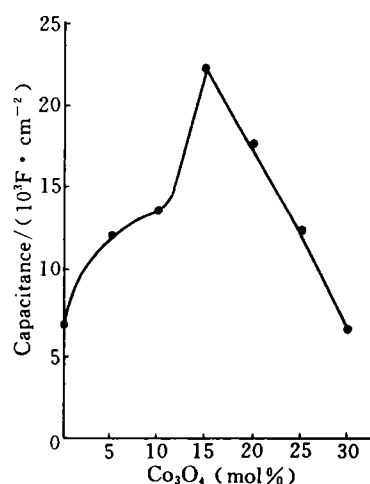


Fig. 4 Effects of Co_3O_4 content on the double layer capacitance of the $(\text{RuO}_2-\text{Co}_3\text{O}_4-\text{TiO}_2(60))$ -coated electrode in 1 mol/L H_2SO_4 at 15 C

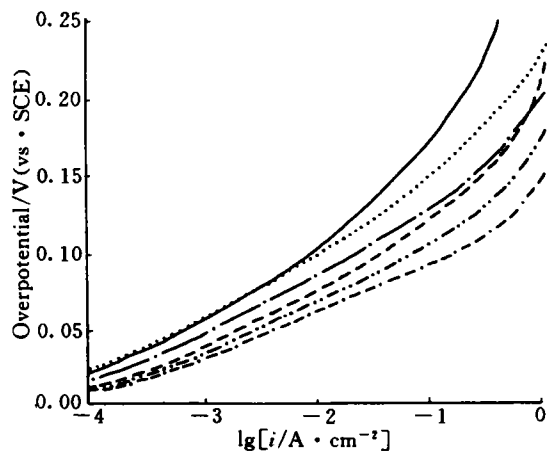


Fig. 5 Galvanostatic polarization curves for chlorine gas evolution at (RuO₂-Co₃O₄-TiO₂(60))-coated electrodes in saturated NaCl+1 mol/L HClO₄ solution (Cl₂ saturated) at 15 °C. Data corrected for ohmic drops. ····; RuO₂(40)-TiO₂(60), ····; RuO₂(35)-Co₃O₄(5)-TiO₂(60), ····; RuO₂(30)-Co₃O₄(10)-TiO₂(60), ····; RuO₂(25)-Co₃O₄(15)-TiO₂(60), ····; RuO₂(15)-Co₃O₄(25)-TiO₂(60), ····; RuO₂(10)-Co₃O₄(30)-TiO₂(60)

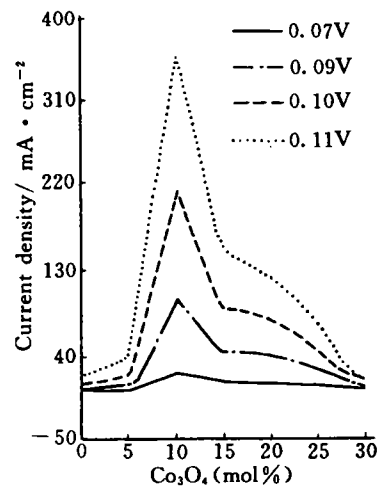


Fig. 6 Effect of Co₃O₄ content on the rate of chlorine gas evolution at (RuO₂-Co₃O₄-TiO₂(60))-coated electrode at a number of specific overpotentials (same operating conditions as given in Fig. 5)

activity though the activity of pure Co₃O₄ is inferior to that of RuO₂. As soon as spinel Co₃O₄ emerges, the amount of crystal defects in the coating would decrease remarkably. The more Co₃O₄ content, the bigger the size of the spinel Co₃O₄ and the less the crystal defects. And the activity of the coating in high Co₃O₄ range (more than 10 m/o) will deteriorate. However, the coating with a little of spinel Co₃O₄ possesses higher active surface area, because the present of spinel Co₃O₄ greatly enhances the coating roughness. It is not obscure to see a shoulder after the current peak in Fig. 6.

It was noticed, in the investigation of steady-state polarization, that the ohmic polarization value in the coating and solution showed a slight decrease before its increase with more Co₃O₄ content in the coating. A minimum value was observed at the maximum solubility point of Co₃O₄ in the solid solution(Fig. 7).

The tip of Luggine capillary was precisely located at 1.5 mm away from the coating surface, so the ohmic drop in solution was a constant value at the same current. Practically Fig. 7 shows the relative variation of ohmic polarization value in the coating and indicates that Co₃O₄ in rutile-type solid solution will improve the electric conductivity of RuO₂-Co₃O₄-TiO₂(60) coating and reduce ohmic drop in it. But as soon as spinel Co₃O₄ emerges in the coating, its electric conductivity will drop

sharply. This seems to be also related to the crystal defect effects introduced by the Co₃O₄ dissolved in the rutile-type solid solution which are mentioned above.

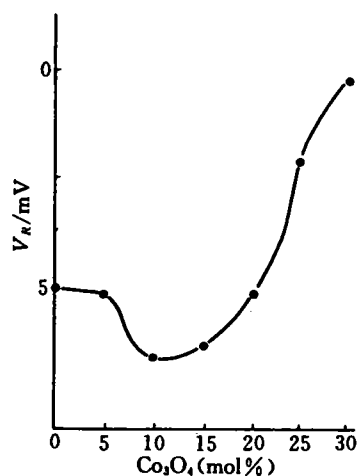


Fig. 7 Plot of ohmic drop in coating and solution at 100 mA/cm² against Co₃O₄ content (same operating conditions as given in Fig. 5)

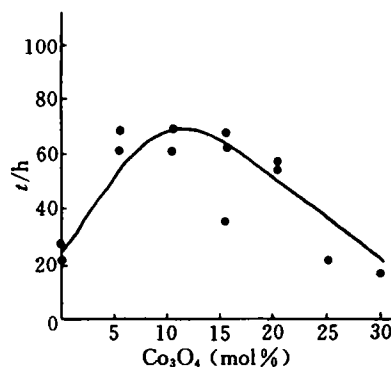


Fig. 8 Effect of Co₃O₄ content on the service life(t) of RuO₂-Co₃O₄-TiO₂(60)/Ti anode in 6 mol/L NaOH(80 °C, 1 A/cm²)

2.4 Service Life

Service life value of the RuO₂-Co₃O₄-TiO₂(60)/Ti anode, operated under severe conditions (6 mol/L NaOH, 80 °C, 1 A/cm², Pt counter electrode), were determined by recording the cell voltage as a function of time during electrolysis under galvanostatic conditions. The service life value was the time before cell-voltage increased sharply.

Also, the severe service life test results indicated that the service life of (RuO₂-Co₃O₄-TiO₂(60))-coated electrode varied in a similar way to the chlorine gas evolution rate (Fig. 8). It increased with Co₃O₄ in rutile-type solid solution and deteriorated with spinel Co₃O₄.

These results implied that traditional RuO₂-TiO₂/Ti anode being widely used in chlor-alkali industry could be replaced by RuO₂-Co₃O₄-TiO₂/Ti anode in which Co₃O₄ content should be so high as to reach, or exceed slightly, its maximum solubility point in the rutile-type phase. Thus, not only the content of noble ruthenium in the coating is to be reduced to a relatively lower extent, but also the anode chlorine gas evolution activity, service life and ohmic drop of the coating, etc., will be improved.

3 Conclusion

Sole rutile-type solid solution of RuO₂, Co₃O₄ and TiO₂, and spinel Co₃O₄ and the solid solution exist in ca. 0~10 and 10~30 mol% Co₃O₄ range respectively in the RuO₂-Co₃O₄-TiO₂(60) coating

system. The chlorine gas evolution activity, electric conductivity and service life of the coating increase with more Co_3O_4 in the rutile-type solid solution until Co_3O_4 is saturated. These properties deteriorate with the emerging of spinel Co_3O_4 . Both the roughness and the active surface area of the coating are greatly enhanced by a little of spinel Co_3O_4 . In a relatively wide composition range, the rate of chlorine gas evolution, electric conductivity and service life of $(\text{RuO}_2\text{-Co}_3\text{O}_4\text{-TiO}_2(60))$ -coated electrodes are higher compared with the $(\text{RuO}_2(40)\text{-TiO}_2(60))$ -coated electrodes. Evidently $\text{RuO}_2\text{-TiO}_2$ coated anodes could be modified by adding a suitable amount of Co_3O_4 .

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