

STUDY ON HIGHLY ALLOYED STEEL ANODE COATED BY MIXED METAL OXIDES SnO₂ - Sb₂O₃ THIN FILM AND APPLICATION IN WASTEWATER TREATMENT

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Received: 11 August 2017; Accepted for publication: 6 October 2017

ABSTRACT

In this study, thin film of mixed SnO₂ and Sb₂O₃ on Cr18Ni12Ti high alloy steel (HAS) substrate (SnO₂-Sb₂O₃/HAS) was fabricated by dip coating - pyrolysis method. The morphology and structure of the material surface was observed by scanning electron microscopy (SEM). The mechanical property was evaluated by using Vickers hardness test (HV test). The electrochemical properties of the formed film were investigated by open circuit potential measurement vs. time and potentiodynamic polarization curves in the 3.5% NaCl solution.

The results indicate that the SnO₂-Sb₂O₃/HAS electrode has high hardness and good electrochemical strength. The SnO₂-Sb₂O₃/HAS electrode was used as an anode to remove Rhodamine B (RhB) - a color dye - from wastewater. The effect of electrolysis time on treatment efficiency for RhB is studied. The UV-Vis spectra and Total Organic Carbon (TOC) analysis shows that the RhB color dye are removed from wastewater via electrochemical oxidation process.

Keywords: high alloy steel, SnO₂-Sb₂O₃/HAS electrode, Rhodamine B, degradation, electrochemical oxidation.

1. INTRODUCTION

Protection of the environment is one of the most challenging and pressing task for mankind due to industrial development. Now, the dyes industry is one of the most polluting industries in the world causing grave damage to the environment. Dyes are usually used in textile industries, paper industries, food technologies and also in agricultural research. Therefore, wastewater of these industries contain large amount of dye pigments which contain toxic material such as organic compounds and color pigments.

In the past two decades, electrochemical oxidation method has been widely application for dye wastewater treatment [1-3]. This method has high oxidation efficiency; convenient operation and environmental friendliness which make it be a very attractive alternative to the conventional processes for degrading biologically refractory organic and toxic pollutants, especially for those

hard to degradation. However, effective and economical oxidation of pollutants requires appropriate catalytic electrode materials.

Many conducting materials, such as stainless steel, graphite, noble metals, dimensionally stable anodes (DSA), conducting electro-active polymers anodes, and boron-doped diamond (BDD), have been investigated for the oxidation of refractory pollutants. DSA anodes usually are made by metal oxides coating on Ti substrate. However, Ti is expensive and prone to be inactive. Highly alloyed steel (HAS) also can be applied as substrate for DSA electrode. It has corrosion resistance but low price [4].

In this article, studies on the physical, chemical and electrochemical properties of SnO₂-Sb₂O₃/HAS were done. Application of this material as an anode for Rhodamine B color dye treatment by advanced electrochemical oxidation method.

2. MATERIALS AND METHODS

2.1 Materials and chemicals

Substrates (HAS) of 100 mm in length and 8 mm diameter are obtained commercially.

SbCl₃ (>99%, China), SnCl₄.5H₂O (> 99%, China), iso-propanol and hydrochloric acid (37%, China), NaCl (> 99%, China) are used as chemicals for preparing coating.

2.3. Methods

2.3.1. Preparation of coating

HAS were mechanically polished with 1000-grid sand paper and rinsed with distilled water. Then, the substrates were etched in 15 wt.% oxalic acid (20 %) at 98 °C for an hour. After that, the substrates were washed with distilled water.

The coating solution was prepared by dissolving 162 g.L⁻¹ SnCl₄.6H₂O and 10 g.L⁻¹ SbCl₃ in isopropanol and the pH of the solution was adjusted to 1 by hydrochloric acid.

The HAS substrates were brushed with the coating solution, and subsequently calcined at 450 °C in a muffle oven for an hour. This procedure was repeated 6 times. Finally, the electrode was annealed at 450 °C for 5 hour to induce crystallization.

2.3.2. Characterization of the prepared electrode

The crystal structure and compositions of the coating film were studied by XRD (XPRT PRO, Netherlands, using Cu-K α radiation). The surface morphology of the metal oxide coating film was observed by SEM (JEOL, JSM-7600F, US). The resistivity of the film was measured by the four probe method.

Electrochemical properties of the formed film were investigated by open circuit potential measurement vs. time and potentiodynamic polarization curves in the 3.5% NaCl solution at room temperature. The electrochemical measurements were conducted on a three-electrode electrochemical system (Autolab PGSTAT 302N, Netherlands) with the prepared electrode served as the working electrode, Pt mesh as the counter electrode and a saturated calomel electrode as the reference electrode. The working electrode potentials were scanned from -0.3 V

to + 2 V versus open circuit potential with scanning rate of 5 mV/s in potentiodynamic polarization measurement.

2.3.3. Confirmation of the RhB degradation

The degradation of the RhB solution was done in the 20 mg.L⁻¹. The SnO₂-Sb₂O₃/HAS was used as anode and a stainless steel was used as cathode. A DC voltage was applied on the electrode bath and the electrolysis process was controlled by current density controlling at 8 mA.cm⁻².

In this study, the degradation efficiency of Rhodamine B solution was monitored by UV-visible spectrophotometer (UV-2100, Unic, Shanghai, China) at the wavelength of 555 nm. The TOC in aqueous solution was observed by Teledyne Tekmar Apollo 9000 combustion TOC analyzer (US)

3. RESULTS AND DISCUSSION

3.1. Effect of component on film structure and surface morphology on HAS

Figure 1 shows the XRD tracens of the prepared sample where appears the characteristic peak of the rutile SnO₂ at 2θ of 26.59°, 33.88°, 50.69°, 52.78°.

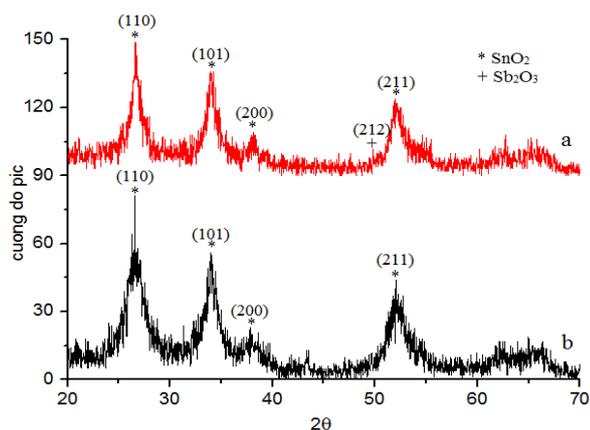


Figure 1. X-ray diffractogram of the SnO₂/HAS (a) and SnO₂-Sb₂O₃/HAS (b) after calcination at 450 °C in 1 hour.

It was shown that SnCl₄ thermally decomposed to become SnO₂. When the addition of SbCl₃ to the film forming solution, the peak of Sb₂O₃ oxide at 50.69°, indicating that Sb₂O₃ - SnO₂ mixed oxide film is formed on the HAS substrate surface. With the addition of antimony, a decrease in the peak intensities was observed.

The results of the SEM (Figure 2) show that the high-alloy steel surface significantly change between before (Figure 2a) and after (Figure 2b, c) coating. After coating of SnO₂, the surface of the substrate strongly changed from smooth surface of HAS to rugged and scratched one. When SbCl₃ was added to the film forming solution, the surface morphology was more rugged and the deposited clusters is significantly bigger. There is a mixture, dissolving between two salts on the surface of the steel. Both samples with coating on HAS are not crack-mud.

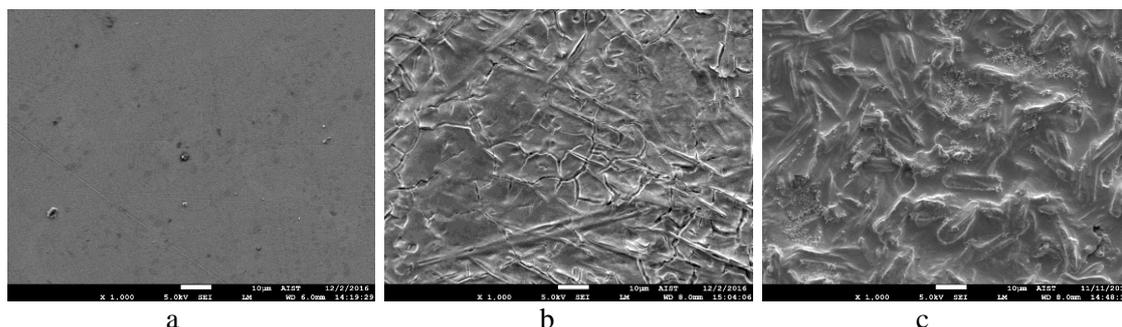


Figure 2. Scanning electron microscope image of the HAS (a), SnO_2 coating on HAS (b) and $\text{HAS/SnO}_2\text{-Sb}_2\text{O}_3$

3.2. Effect of component on film mechanical properties on HAS

The effect of Sb doping on resistivity of deposited films was studied by four probe method and shown in the Table 1. The results show that the film resistivity decreases when Sb is added to the film forming solution. It was also reported that the initial resistivity reduction was due to the replacement of Sn^{4+} with Sb^{5+} in the SnO_2 network because the ionic radius of Sb^{5+} was greater than Sn^{4+} , which acts as a donor and hence there will increase carrier concentration [5].

Table 1. Resistivity and hardness of high alloyed steel before and after film forming.

| Material | Resistivity ($\Omega\cdot\text{cm}$) | HV Hardness (kG/mm^2) |
|--|--|----------------------------------|
| HAS | $5,4 \cdot 10^{-7}$ | 239 |
| HAS/SnO_2 | $2,2 \cdot 10^3$ | 289 |
| $\text{HAS/SnO}_2\text{-Sb}_2\text{O}_3$ | $4,3 \cdot 10^{-2}$ | 475 |

Table 1 also shows the effect of adding Sb to the hardness of the film. The hardness of the SnO_2 film lightly increases, around $\text{HV} \approx 300 \text{ kG/mm}^2$. But when the solution is supplemented with SbCl_3 , the hardness of the $\text{SnO}_2\text{-Sb}_2\text{O}_3$ film is doubled higher compared to HAS. The conductivity and hardness of the studied material is fixed with the requirements of the anode material.

3.2. Effect of component on electrochemical properties of film on HAS

The dependence of corrosion potential of HAS $\text{SnO}_2\text{-Sb}_2\text{O}_3/\text{HAS}$ electrode in 3.5 % NaCl solution on time are illustrated in Figure 3.

Figure 3 shows that corrosion potential of HAS are quite negative, significantly change for ten hours (in the range of $-40 \text{ mV} \div -120 \text{ mV}$ vs. SCE) and then remained unchanged from 10 to 100 hours (corrosion potential is about -100 mV vs. SCE). In the case of $\text{SnO}_2\text{-Sb}_2\text{O}_3/\text{HAS}$ electrode, the corrosion potential is much more positive than HAS (about 160 mV) in all of immersion time from 0 to 100 hours. The more positive of corrosion potential of the material, the more electrochemical durability of the electrodes.

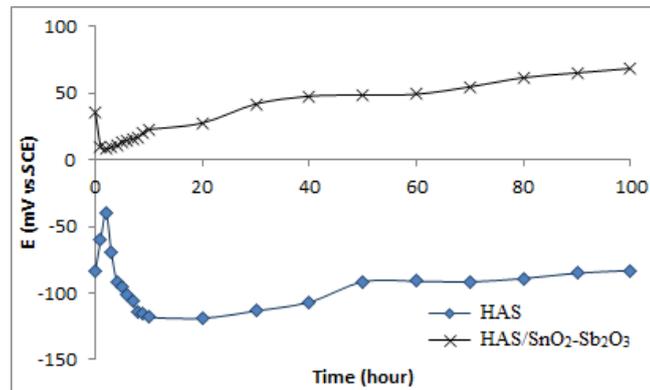


Figure 3. The dependence of corrosion potential of HAS and HAS is coated $\text{SnO}_2\text{-Sb}_2\text{O}_3$ mixed oxides thin film in 3.5 % NaCl solution on time.

The parameters are calculated by extrapolation method from Tafel polarization curve (Figure. 4), including corrosion current densities (i_c) and polarization resistances (R_p) are summarized in Table 2.

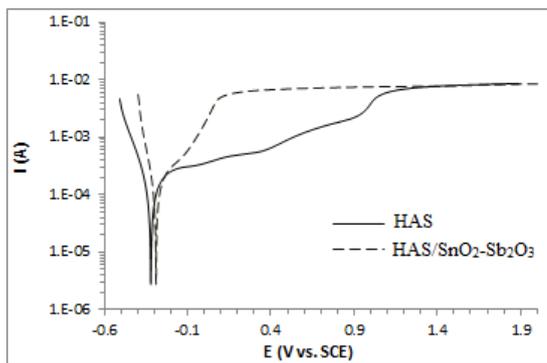


Figure 4. polarization curve of HAS and $\text{SnO}_2\text{-Sb}_2\text{O}_3/\text{HAS}$ in 3.5 % NaCl solution.

Table 2. Corrosion characteristics of samples in 3 % NaCl solution.

| Material | i_c ($\mu\text{A}/\text{cm}^2$) | R_p ($\Omega.\text{cm}^2$) |
|---|--|-----------------------------------|
| HAS | 0.301 | 370.52 |
| $\text{SnO}_2\text{-Sb}_2\text{O}_3/\text{HAS}$ | 0.128 | 895.02 |

Results in Figure 3 and Table. 2 indicate that i_c value of $\text{SnO}_2\text{-Sb}_2\text{O}_3/\text{HAS}$ coating is considerably lower and R_p is higher than the respective value of HAS. The i_c value decreases 2.35 times and the R_p value increases 2.41 times after highly alloyed steel is coated $\text{SnO}_2\text{-Sb}_2\text{O}_3$ mixed oxides film.

3.3. Application of research electrode for Rhodamine B treatment

The effect of electrolytic time (from 5 to 40 minutes) on the color change of RhB solution when electrolyzed at $8 \text{ mA}.\text{cm}^{-2}$ current density was illustrated in Figure 4.

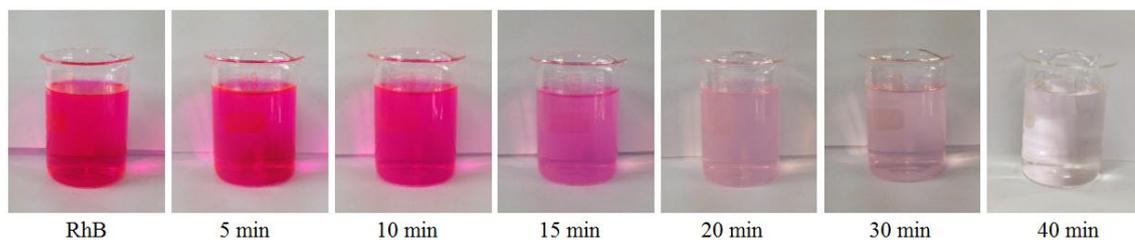


Figure 4. The color change of the 20 mg/L Rhodamine B solution over time with SnO₂-Sb₂O₃/HAS electrode.

The color of RhB solution changes with time of electrolysis. The longer the electrolytic time, the lighter the color of the solution. After 40 minutes, the solution is colorless.

In order to study on the mechanism of electrochemical oxidation with SnO₂-Sb₂O₃/HAS electrode, the data of UV-Vis spectra of RhB solution at different reaction time was recorded and showed in Figure 5.

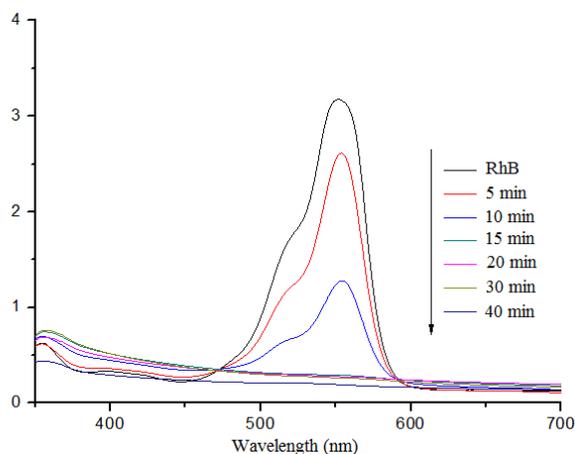


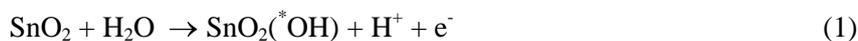
Figure 5. The UV-vis spectra of RhB solution changes with the reaction time.

Table 3. Parameters of Rhodamine B solution before and after electrolysis.

| Color | Unit (Pt-Co) |
|--------------------|--------------|
| Initial value | 495 |
| After electrolysis | 29 |
| QCVN 13:2015 | 50-75 |

The concentration of Rhodamine B solution (20 mg.L⁻¹) was removed rapidly and reached 93.9 % for the oxidation on the SnO₂-Sb₂O₃/HAS anode after 40 minutes of electrolysis. This result shows that RhB dye in the solution is effectively removed by electrolysis method with SnO₂-Sb₂O₃/HAS anode.

The degradation process of RhB color dye by electrochemical oxidation occurs to the following equations [3, 4, 6, 7]:



The $\cdot\text{OH}$ radicals can excitedly react with the specific molecules of organic substance adsorbed on the anode surface to cause the oxidation reaction. Therefore, to increase the dyes degradation efficiency, the radical formation need to be increased. The OH^{\cdot} radical formation strongly depends on the oxygen evolution potential of the anode. In the previous studies, the oxygen evolution potential of the SnO_2 is 1.9 V [8]. The $\text{SnO}_2\text{-Sb}_2\text{O}_3$ electrode oxygen evolution potential is 1.75 V [9, 10]. Therefore, the OH^{\cdot} radical was formed easily on $\text{SnO}_2\text{-Sb}_2\text{O}_3$ and the color dyes degradation strongly happened. The $\text{SnO}_2\text{-Sb}_2\text{O}_3$ electrode with high overpotential can efficiently extend the lifetime of $\cdot\text{OH}$ ion on the surface of the $\text{SnO}_2\text{-Sb}_2\text{O}_3/\text{HAS}$ anode.

The mineralization of RhB can be determined by performing TOC analysis. The TOC removal can be used to indicate the mineralization of the dye. It was found that after 20 min reaction, the treated solution contained 9.7 mg/L TOC (approximately 11.8 % of initial TOC that is 1.3 mg/L, was removed during the process); The mineralization percentage could have been higher with the increase of reaction time. 69.1 % of TOC was removed after 30 min reaction time at the current density of 8 mA/cm².

Table 3 shows that the color dye of the solution decreases from 495 Pt-Co to 29 Pt-Co after 40 minutes of electrolysis at 8 mA.cm⁻² current density (94 % the color are reduced), which is lower than the level (TCVN) for release to the environment.

Thus, the oxidation on the $\text{SnO}_2\text{-Sb}_2\text{O}_3/\text{HAS}$ can reduce the color of the Rhodamine B solution. The highest color removed efficiency of the electrochemical oxidation in electrolysis of 8 mA/cm² current density in 40 minutes.

4. CONCLUSIONS

SnO_2 and Sb_2O_3 mixed oxides coating layer is successfully prepared on highly alloyed steel Cr18Ni12Ti by dipping - thermal decomposition method from the solution of SnCl_4 and SbCl_3 with isopropanol and HCl medium. The changing of phase structure, morphology, resistivity, HV hardness and corrosion resistance of coating layer depend on the concentration of SbCl_3 .

Highly alloyed steel materials coated $\text{SnO}_2\text{-Sb}_2\text{O}_3$ mixed oxides are used as the anode for the electrochemical oxidation to degrade the RhB color dye. The results show that the 20 mg/L Rhodamine B solution was treated by electrolysis under 8 mA/cm² current density for 40 minutes. 93.9 % color dye is removed. TOC content decreases from 11 mg/L to 3.4 mg/L after 30 minutes of electrolysis. The waste water after treatment meets the requirements for surface water.

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