

# Preparation and Properties of Sn-TiO<sub>2</sub> nanocomposite coatings

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**Abstract.** Sn-TiO<sub>2</sub> nanocomposite coatings were prepared by sol-gel enhanced electrodeposition technique and the effect of c concentration on the performance of the composite coatings was investigated by adding different volumes of TiO<sub>2</sub> sol to the electrolyte. The microscopic morphology and corrosion resistance of the coatings were characterized by XRD tests, SEM tests, hardness tests and a series of electrochemical tests. From the test results, it was found that the coating had the highest hardness value and the best corrosion resistance when the TiO<sub>2</sub> sol was added at 15 mL/L; however, when the TiO<sub>2</sub> sol concentration was too large, the corrosion resistance and hardness value of the Sn-TiO<sub>2</sub> composite coating decreased significantly due to the destruction of the crystal structure and coating structure by the agglomerated TiO<sub>2</sub> nanoparticles in the coating.

**Keywords:** Nanocomposite; TiO<sub>2</sub> sol; electrodeposition; coating.

## 1. Introduction

Nowadays, with the development of the world economy, there is an increasing demand for high-performance coating materials[1-3]. How to improve the quality of coatings has become a top priority in the field of coating research. As the surface of iron and steel devices is easy to rust, this problem limits its further application in the industrial field. Generally, new coatings can be prepared on the surface of iron and steel devices by electrodeposition technology to enhance the corrosion resistance of iron and steel devices. The coatings prepared by electrodeposition technology should have good corrosion resistance and mechanical properties, such as Zn[4], Ni[5], Cu[6] and so on. Because of its good corrosion resistance and solderability, tin coating is widely used in various industrial fields as a protective coating for all kinds of metal devices. However, in a relatively harsh environment, the protective effect of a single tin coating on the metal substrate is limited, how to further improve the quality of tin coating has become a hot issue in the field of surface engineering technology. At present, most of the research is to improve the coating quality of tin coating by doping metal elements and nanoparticles. In recent years, a new TiO<sub>2</sub>-sol-enhanced electrodeposition technology has been developed, TiO<sub>2</sub> nanoparticles will be formed in situ in the process of electrodeposition, and this sol-enhanced electrodeposition technology can improve the dispersion of nanoparticles in the coating, thus can better improve the quality of the coating[7]. However, there is no research on Sn-TiO<sub>2</sub> nano-coating at present. In order to prove the potential of Sn-TiO<sub>2</sub> nanocomposite coatings, Sn-TiO<sub>2</sub>

nanocomposite coatings were prepared by TiO<sub>2</sub>-sol enhanced electrodeposition, and the effects of different concentrations of TiO<sub>2</sub> sol on tin coatings were systematically studied.

## 2. Experimental

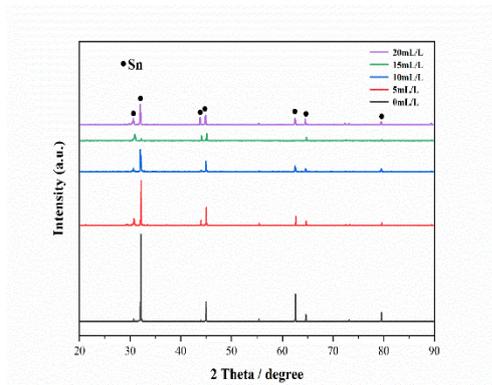
In this paper, Fe sheets were used as the substrate, and Fe substrate was acid-washed using concentrated hydrochloric acid before the preparation of the coating, with the aim of removing the corrosion products surviving on the surface of the iron sheets. In our experiments, we prepared Fe/Sn-TiO<sub>2</sub> composite coatings by DC electrodeposition method, using the methanesulfonic acid system solution as the electrolyte (the main components are MSA, MSASn and gelatin, respectively), and slowly drop a certain amount of TiO<sub>2</sub> sol into the plating solution before plating. The coating was prepared as follows: the tin plate (40 mm × 40 mm) was used as the anode of the electrolytic cell, and the treated Fe sheet was used as the cathode of the electrolytic cell, under 30 mA/cm<sup>2</sup> current density. During the electroplating process, the electrolyte was stirred at a constant speed using a magnetic stirrer, the plating temperature was controlled at 30°C, and the plating time was 20 min; the prepared samples were rinsed with anhydrous ethanol and deionized water and then transferred to a drying oven at 100°C to obtain the Fe/Sn-TiO<sub>2</sub> composite coating.

Microhardness tester was used to test the hardness of the sample, and 50g charge for 10s was applied to each indentation on the sample. The crystal structure was identified by X-ray Diffraction(XRD, D2 Phaser, Bruker, Germany) at a step size of 2°. The surface morphology was

deserved by a scanning electron microscope (SEM, Phenom proX, Netherlands). The electrochemical analyses were tested by the electrochemical workstation (CS2350H, Chenhua Instrument, Shanghai). A three-electrode system was used in the whole electrochemical test, Fe/Sn-TiO<sub>2</sub> (10mm×10mm) as working electrode, platinum plate (20mm×20mm) as counter electrode, saturated calomel electrode (SCE) as reference electrode, and the 3.5%wt NaCl solution used as electrolyte solution. In the dynamic potential scan test, the potential scan range is -0.5V~0.5V, and the scan speed is 0.5mV/s; in the electrochemical impedance test, the frequency range is 0.01~100000Hz.

### 3. Result and Discussion

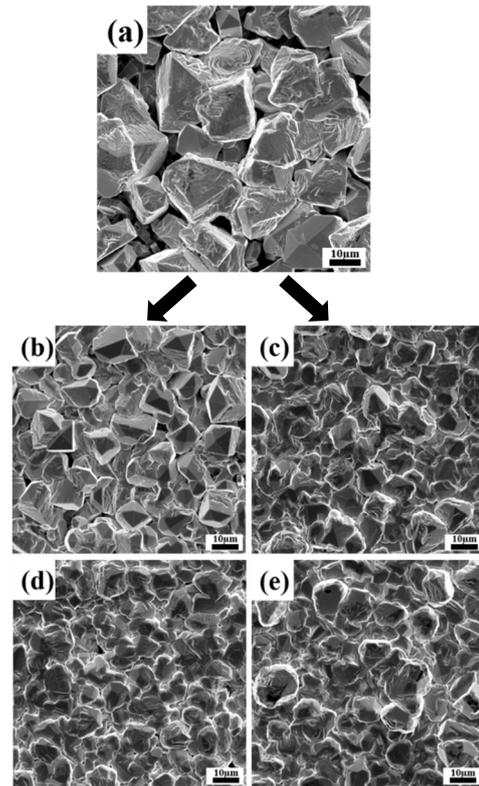
Figure 1 shows the crystal structure of the Sn-TiO<sub>2</sub> coating. The positions of all the diffraction peaks in the figure are consistent with the PDF card of the tetragonal Sn (PDF:88-2625). Due to the small amount of TiO<sub>2</sub> sol, there is no diffraction peak of TiO<sub>2</sub> in the XRD pattern. The results show that with the increase of the amount of TiO<sub>2</sub> sol, the intensity of the diffraction peak decreases and the FWHM increases, indicating that the size of the crystal decreases gradually. However, when the addition of TiO<sub>2</sub> sol exceeds that of 15mL/L, the intensity of the diffraction peak increases, indicating that the addition of excessive TiO<sub>2</sub> sol will lead to grain coarsening.



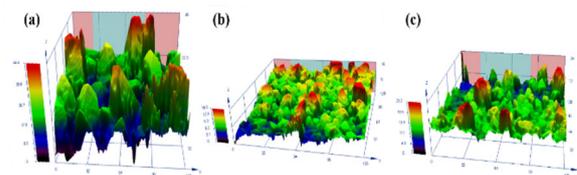
**Fig. 1.** XRD patterns of Sn-TiO<sub>2</sub> nanocomposite coatings prepared at different TiO<sub>2</sub> sol addition.

Figure 2 depicts the surface morphology of Fe/Sn coating and the coating prepared by adding different volumes of TiO<sub>2</sub> sol. It can be seen from the figure that when the addition of TiO<sub>2</sub> sol is 0mL/L, the particle size on the surface of Sn coating is larger, at the same time, the surface structure of Sn coating is loose and there are large pores. With the increase of the amount of TiO<sub>2</sub> sol, the number of pores on the coating surface decreased gradually, and the coating surface was obviously refined, this is because the dispersed TiO<sub>2</sub> nanoparticles can make up for the coating defects and improve the coating quality. When the addition of TiO<sub>2</sub> sol is 15mL/L, the particle size on the surface of the coating is the smallest and the arrangement is the most uniform. It can be seen from figure 2 (e) that when the addition of TiO<sub>2</sub> sol is further increased, the particle size on the surface of the coating is different, and the crystal clusters are easy to be found, and the quality of the coating is poor.

Figure 3 shows the 3D surface topography of the coating prepared by adding different volumes of TiO<sub>2</sub> sol. When the addition of TiO<sub>2</sub> sol is 15mL/L, the coating has a smooth and dense surface structure, but when the addition of TiO<sub>2</sub> sol is too large, the surface of the coating becomes rough. This is due to the fact that when the amount of TiO<sub>2</sub> sol is appropriate, the dispersion of TiO<sub>2</sub> nanoparticles is better, and the coating quality is improved; while when the amount of TiO<sub>2</sub> sol is too large, TiO<sub>2</sub> nanoparticles are easy to agglomerate, which reduces the quality of the coating[8].



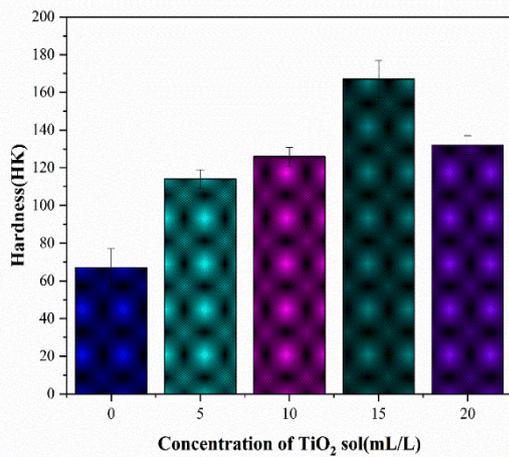
**Fig.2.** SEM images of Sn-TiO<sub>2</sub> Nano-Coatings prepared by adding different volumes of TiO<sub>2</sub> sol (a) 0mL/L (b) 5mL/L (c) 10mL/L (d) 15mL/L (e) 20mL/L



**Fig.3.** 3D images of Sn-TiO<sub>2</sub> Nano-Coatings prepared by adding different volumes of TiO<sub>2</sub> sol (a) 0mL/L (b) 15mL/L (c) 20mL/L

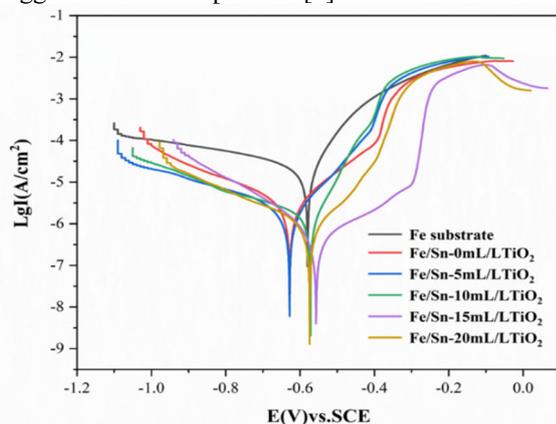
The hardness of the Sn coating prepared by adding different concentrations of TiO<sub>2</sub> sol is tested, and the results are shown in the figure 4. The results of the bar chart show that with the increase of the amount of TiO<sub>2</sub> sol, the hardness of the coating increases from 67HK (pure tin coating) to 167HK (15mL/L TiO<sub>2</sub> sol), but when the amount of TiO<sub>2</sub> sol continues to increase, the hardness of the coating decreases, indicating that excessive TiO<sub>2</sub> sol will damage the hardness of the coating. The results show

that the dispersed TiO<sub>2</sub> nanoparticles can effectively improve the hardness of tin coating.



**Fig.4.** Hardness values of different Sn-TiO<sub>2</sub> Nano-Coatings

Figure 5 shows the Tafel curve of the coating prepared by adding different volumes of TiO<sub>2</sub> sol and iron substrate. Through the fitting calculation of the polarization curve, the corrosion parameters (corrosion potential, corrosion current density and corrosion rate) are shown in Table 1. The corrosion resistance is related to the corrosion potential and corrosion current density. The coating with higher corrosion potential and lower corrosion current density has better corrosion resistance. It can be seen from the table that the corrosion resistance of Fe/Sn is obviously higher than that of Fe matrix, and the corrosion rate is up to  $4.9 \times 10^{-2}$  mm/a. With the increase of the addition of TiO<sub>2</sub> sol, the corrosion rate of the coating decreased gradually, and when the addition of TiO<sub>2</sub> sol was 15 mL/L, the corrosion potential of the coating was the highest (-0.55V), the corrosion potential was the lowest ( $6.9 \times 10^{-7}$  A/cm<sup>2</sup>), and the corrosion rate reached  $8.1 \times 10^{-3}$  mm. It is proved that the corrosion resistance of the coating is the best, and when the addition of TiO<sub>2</sub> sol continues to increase, the corrosion resistance of the coating becomes worse, which is related to a large number of agglomerated nanoparticles[9].

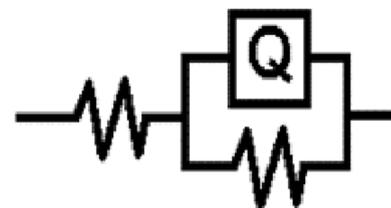
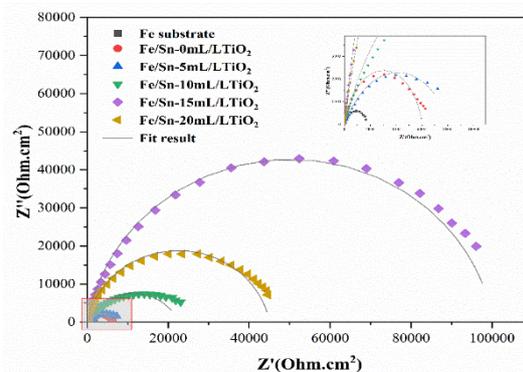


**Fig.5.** Tafel curve of Sn-TiO<sub>2</sub> Nano-Coating

**Table 1** Tafel fitting results of Sn-TiO<sub>2</sub> Nano-Coating

Sample name	E <sub>corr</sub> (V)	I <sub>corr</sub> (A/cm <sup>2</sup> )	Corrosion rate(mm/a)
Fe substrate	-0.58	$3.13 \times 10^{-5}$	$3.68 \times 10^{-1}$
Fe/Sn-0mL/LTiO <sub>2</sub>	-0.63	$4.17 \times 10^{-6}$	$4.9 \times 10^{-2}$
Fe/Sn-5mL/LTiO <sub>2</sub>	-0.63	$2.0 \times 10^{-6}$	$2.4 \times 10^{-2}$
Fe/Sn-10mL/LTiO <sub>2</sub>	-0.57	$1.42 \times 10^{-6}$	$1.7 \times 10^{-2}$
Fe/Sn-15mL/LTiO <sub>2</sub>	-0.55	$6.9 \times 10^{-7}$	$8.1 \times 10^{-3}$
Fe/Sn-20mL/LTiO <sub>2</sub>	-0.57	$9.2 \times 10^{-7}$	$1.1 \times 10^{-2}$

Figure 6 shows the Nyquist images of iron substrates and different coatings in 3.5%wt NaCl solution. The capacitive rings in the image show different ring radii, which is related to the change of polarization resistance in the corrosion process. The larger the ring radius is, the higher the charge transfer impedance is and the better the corrosion resistance of the coating is. The equivalent circuit can be fitted according to the Nyquist image, as shown in figure 6. R<sub>s</sub> and R<sub>ct</sub> are solution impedance and charge transfer impedance respectively, and CPE is the original of constant phase angle. The results show that the R<sub>ct</sub> value increases gradually with the increase of TiO<sub>2</sub> sol addition, and when the TiO<sub>2</sub> sol addition is 15 mL/L, the R<sub>ct</sub> value is the highest (100.3kΩ/cm<sup>2</sup>), indicating that it can better resist the corrosion of the external environment.



**Fig.6.** Nyquist image of Sn-TiO<sub>2</sub> Nano-Coating and Equivalent circuit diagram

#### 4. Conclusion

In this study, a method for the preparation of Sn-TiO<sub>2</sub> composite coatings by sol-gel enhanced electrodeposition was pioneered. It is concluded that with the increase of TiO<sub>2</sub> sol addition, the grain refinement occurs and the

coating structure is more dense and flat, and when the TiO<sub>2</sub> sol addition is 15 mL/L, the hardness of the coating is the highest and the corrosion resistance is the best; however, when too much TiO<sub>2</sub> sol is added, it leads to more defects in the coating, which is not conducive to the improvement of the mechanical properties and corrosion resistance of the coating.

## References

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