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S. WEN*, J.A. SZPUNAR*

TEXTURE AND CORROSION RESISTANCE OF ELECTRODEPOSITED TIN COATINGS

TEKSTURA I ODPORNOŚĆ NA KOROZJĘ ELEKTROLITYCZNIE OSADZONEJ POWŁOKI CYNOWEJ

Tin electrodeposition on mild steel substrates using stannous sulfate and sulfuric acid electrolyte was studied under different current densities. The morphology, macrotexture, and the orientations and sizes of individual grains were examined by FEG-SEM, x-ray texture goniometry and orientation imaging microscopy (OIM) respectively. The corrosion resistance of electrodeposited tin coatings was measured using a standard corrosion cell kit according to the ASTM standard G3-89 (94).

It was found that tin coatings with two different texture, (100) and (301) fiber texture can be produced by electrodeposition at room temperature by varying current density. At a lower current density of 100A/m^2, (301) fibre was obtained. At the current densities of 100 and up to 400 A/m^2, only (100) fibre texture was observed. An increase in current density leads to a decrease in grain size. At a higher current density of 200 A/m^2, the deposit was dense and smooth. The corrosion resistance of tin coatings increases with an increase in current density. The results suggest that operating parameters play an important role in controlling corrosion rate of tin based coatings. par *Keywords*: Tin, electrodeposition, texture, grain size, morphology, corrosion resistance, OIM

Przedmiotem badań było osadzanie elektrolityczne cyny na stali miękkiej przy zastosowaniu elektrolitu z siarczynu cynowego i kwasu siarkowego w zależności od różnych gęstości prądu. Morfologia, makrotekstura, orientacja i wielkość pojedynczych ziaren zostały określone przy użyciu FEG-SEM, rentgenograficznych badań tekstury oraz metody OIM. Odporność na korozję elektrolitycznie osadzonej powłoki cynowej była mierzona przy pomocy standardowego zestawu do badania korozji zgodnie z normą ASTM o numerze G3-89 (94).

Wykazano, że w pokryciach cynowych z dwoma różnymi teksturami (100) i (301) włókniste tekstury mogą być uzyskane przy zmianie gęstości prądu w czasie osadzania elektrolitycznego. Przy gęstości prądu niższej od 100A/m^2 otrzymano teksturę włóknistą (301). Natomiast przy gęstościach prądu pomiędzy 100 a 400A/m^2 otrzymywano jedynie

* DEPARTMENT OF MINING, METALS AND MATERIALS ENGINEERING, MCGILL UNIVERSITY, MONTREAL, QUEBECK, CANADA, H3A 2B2

teksturę włóknistą (100). Wzrost gęstości prądu prowadził do zmniejszenia wielkości ziaren a przy gęstości powyżej 200A/m^2 depozyt był gęsty i gładki. Odporność na korozję powłoki cynowej zwiększa się wraz z podniesieniem gęstości prądu osadzania. Otrzymane wyniki sugerują, że zmiana parametrów osadzania odgrywa istotną rolę w kontroli właściwości korozyjnych powłok cynowych.

1. Introduction

A metal surface is a complex of crystal faces, edges, corners, boundaries, and disturbed layers [1]. A composite of these various types of structure, in turn, dictates the properties of the surface [2]. The driving force of a reaction is dependent on the change in free energy in going from the initial to the final state. The free energy of a solid surface varies with the crystal face due to the different arrangement of atoms for different crystal faces. The free energy of a surface also depends on the medium in which it exists. Tungsten, for instance, the ratio of free energies between faces may in some cases be as high as a factor of 5 [1]. The corrosion behavior of metallic coatings is dependent on the texture, morphology and chemical composition of the deposits [3]. In addition, grain boundary character distribution of the coating also influences the corrosion behavior [4]. Experimental evidence for the variation of corrosion resistance with crystal face has been obtained in iron, copper, nickel, and zinc. Park and Szpunar [3] have found that Zinc and zinc-iron coatings with a strong basal texture exhibit a better corrosion resistance than the deposits with a weak basal texture or texture with a pyramidal fiber component. Zinc grains possessing an {0001} orientation were found by Vlad [5] to have a higher corrosion resistance in NaOH than that of grains with other orientations.

Tinplate, steel coated with a thin layer of tin, has been used for steel cans for food preservation for decades. The corrosion resistance is obviously of critical importance since the consequences of corrosion are product contamination and loss of package integrity. However, no published work has yet been made on the influence of current density on the corrosion resistance of tin coatings.

In the present work, the texture, morphology and microstructure of tin coatings obtained under different current densities were studied. The corrosion resistance of tin coatings was also measured electrochemically. This work purported to suggest the optimum operation conditions to obtain the best corrosion resistance.

2. Experimental

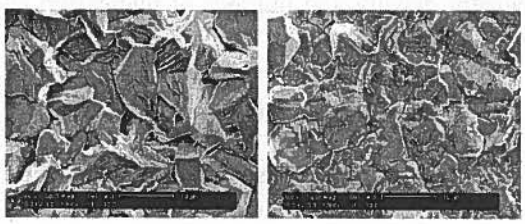
The electrodeposition experiments were carried out in a conventional two-electrode cell under galvanostatic control using an EG&G Princeton Applied Research potentiostat. The temperature was controlled by a thermostat. The substrate, a sheet of low carbon steel, was the cathode. The anode was a tin rod (99.98%) with a diameter of 12.7 mm. The steel substrate was degreased in acetone, and then pickled in 2M sulfuric

acid solution before deposition. Between every procedure, it was thoroughly rinsed in distilled water. The composition of the electrolyte used was the same as in a previous paper [6], namely, $0.2MSnO_4 + 0.3MH_2SO_4 + 0.2g/l$ gelatin. The surface morphology of tin coatings was examined by a Philips XL-30 field-emission-gun SEM. A Siemens x-ray Diffractometer was used for pole figures measurements. For every specimen, four pole figures, (200), (201), (211) and (311) were measured. And all these pole figures were used to quantitatively describe the texture in the orientation distribution function (ODF). This was done using commercially available TexTools software [7]. The microstructure was examined by a TSL orientation imaging microscope (OIM). Corrosion measurements were conducted according to ASTM standard G3 [8] in a deaerated 1M NaCl solution at room temperature using a computer-controlled VoltaLab PGZ100 potentiostat in a three-electrode cell, where the tin coating specimen was the working electrode, a spiral platinum wire the counter electrode, and a saturated calomel electrode (SCE) the reference electrode.

3. Results and discussion

3.1. Morphology

In order to investigate the influence of current density on the morphologies and texture of tin coatings, a wider range of current density was intent to choose. On the one hand, however, at a low current density, say 10 A/m^2, the covering power is poor and a complete coverage could not be produced. On the other hand, if current density is too high, such as 450 A/m^2, burnt deposit was obtained. In this study, the current densities were chosen from 50 A/m^2 up to 400 A/m^2. Figure 1 shows the morphologies of tin coatings deposited at 50 and 200 A/m^2. As can be seen, at 50 A/m^2, the deposit was rough; while at a higher current density of 200 A/m^2, it was very dense, compact and smooth.



(a) (b)

Fig. 1. The SEM images of tin deposits. (a) 50 A/m^2. (b) 200 A/m^2

3.2. Texture of tin coatings

Figure 2 shows the ODFs of tin coatings obtained at various current densities. The deposition time at different current densities was chosen to obtain the same thickness of tin coatings about 15 microns. Fig. 2a and 2b are (301) fibre texture and Fig.2c and 2d are (100) fibre texture. It is clear that (301) fibre texture evolved at lower current densities and the coating's texture changed to (100) when applied current density was 100 A/m^2 or higher.

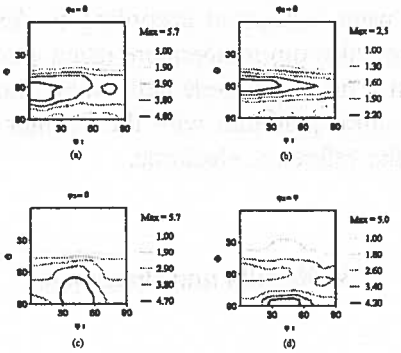


Fig. 2. The ODFs of tin coatings obtained at different current densities. (a) 10 A/m^2 for 5hr. (b) 50 A/m^2 for 1 hr. (c) 100 A/m^2 for 30 min. (d) 400 A/m^2 for 7.5 min

3.3. Microstructure of tin coatings

Figure 3 shows the OIM images of tin coatings deposited at different current densities. The orientations of individual grains can be identified using color coded maps. The grain size distribution is shown in Figure 4 and one can see that the grain size decreases with an increase in current density. The grain size of 15 μm has the highest area fraction in Fig. 4a, and in Fig. 4b, the highest fraction is observed for 7 μm grains. At a higher current density, the number of nucleation sites increased resulting in a smaller grain size.

3.4. Corrosion resistance of tin coatings

The Tafel plots of tin coatings are shown in Figure 5. The corrosion current densities and the corrosion potentials were measured on the polarization curves by using the Tafel extrapolation method. The corrosion current densities in Fig. 5 were determined to be 0.2 μA/cm^2 for coatings deposited at 200 A/m^2 and 0.5 μA/cm^2 for coatings deposited at 50 A/m^2. It is evident that the applied current density influences the corrosion resistance of tin coatings. The corrosion resistance of tin coatings increases with an increase in deposition current density. A smooth, compact deposit has a

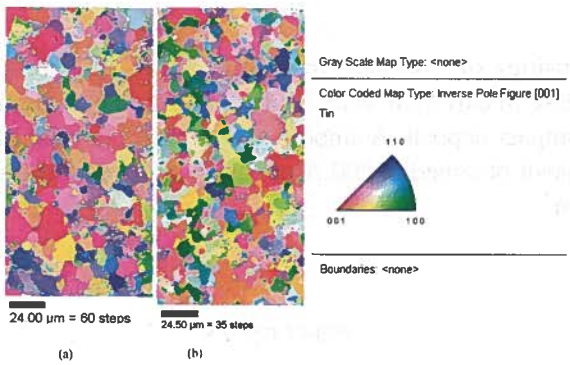


Fig. 3. EBSD maps of tin coatings obtained at different current densities. (a) 50 A/m^2. (b) 200 A/m^2. The color code indicates which crystallographic direction is parallel to ND

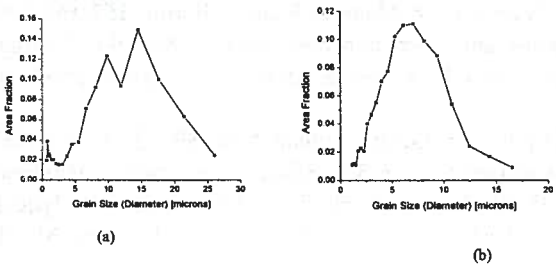


Fig. 4. Grain size distributions of tin coatings deposited at different current densities. (a) 50 A/m^2. (b) 200 A/m^2

higher corrosion resistance. How the texture and grain size contribute to the corrosion resistance is currently under investigation.

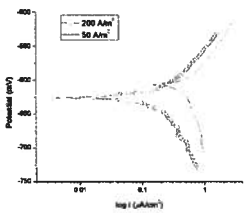


Fig. 5. The Tafel plots of tin coatings deposited at different current densities

4. Conclusions

Tin coatings with two different texture, (100) and (301) fiber texture was produced by electrodeposition. At a lower current density of 100A/m^2, (301) fibre was obtained.

At the current densities of 100 and up to 400 A/m^2, only (100) fibre texture was observed. An increase in current density leads to a decrease in grain sizes, resulting in a smoother, more compact deposit. A smooth and compact deposit has a better corrosion resistance. The deposit obtained at 200 A/m^2 has a better corrosion resistance than that obtained at 50 A/m^2.

REFERENCES

[1] A.T. Gwathmey, "Effect of Crystal Orientation on Corrosion", The Corrosion Handbook, H. H. Uhlig, ed., Wiley & Sons, Inc., 33, 1948.

[2] J.W. Dini, Electrodeposition: the Materials Science of Coatings and Substrates, Noyes Publications, Westwood, NJ, U.S.A., 169 1993.

[3] H. Park, J.A. Szpunar, Corrosion Science **40** (4/5) 525 (1998).

[4] H.M. Kim, J.A. Szpunar, Material Science Forum **157-162** 1997 (1994).

[5] C.M. Vlad,"Texture and Corrosion Resistance of Metallic Coatings", Directional Properties of Materials, Editor H. J. Bunge, DGM Informationsegesellschaft mbH, Oberursel, Germany, 1988.

[6] S. Wen, J.A. Szpunar, Electrochimica Acta, **50**, 12, 2393 (2005).

[7] H. Li, TexTools software version 3.0, Resmat Corporation, Montreal, Quebec, Canada.

[8] ASTM standard G3-89 (1999), Metals Test Methods and Analytical Procedures. Annual book of ASTM standards (volume 03.02 Wear and Erosion; Metal Corrosion), ASTM, 1999.

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