



Surface morphology, crystal structure and orientation of aluminium coatings electrodeposited on mild steel in ionic liquid

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ABSTRACT

Galvano-static electrodeposition was used to electrodeposit aluminium on mild steel in $\text{AlCl}_3/[\text{bmim}]\text{Cl}$ (1-butyl-3-methylimidazolium chloride) ionic liquid at variable temperatures (308–328 K). Effects of variations in current density and temperature on surface morphology and crystal orientations were systematically studied. Results show current density certainly caused changes in the morphology and deposit microstructure, and the type of deposit microstructure changed rapidly as a function of temperature, especially at higher current density. It was indicated that all of the electrodeposits exhibited a strong preferred (200) crystallographic orientation. Compared with the (200) reflection, the preferred (222) orientation was relatively weak for most samples, and under higher temperature and current density it disappears. The (111), (220), and (311) reflections were relatively weak.

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1. Introduction

Interest in the preparation of aluminium coatings has steadily increased due to its excellent corrosion resistance, decorative-ness and physicochemical properties. Several procedures can be employed for coating of Al on various substrates—mainly on steels—such as hot dipping [1,2], thermal spraying [3], sputter deposition [4,5], vapor deposition [6,7], etc. These techniques are rather expensive and often impractical, and the main disadvantages of them are the uneven surfaces, impossibility of controlling the thickness and quality of the layer, and possible damage of the specimen at employed high temperatures. On the contrary, the electrodeposition method is a valuable technology due to its advantages such as mild conditions, easy operation, uniform thickness distribution, adjustable microstructure of the deposited layers and unlimited substrates (including arbitrary shapes or complex geometries).

Electrodeposition of Al from aqueous solutions is impossible owing to a massive hydrogen evolution at the cathode caused by the rather negative standard potential of Al/Al(III) couple (−1.67 V vs. NHE). Essentially, two types of aprotic electrolytes are eligible: organic solvents and molten salts. There are three typical kinds of organic solvents used for electrodeposition of Al: aromatic hydrocarbons [8,9], dimethylsulfone [10,11] and ethers [12,13]. At present, only two commercial processes based on organic solvents are available for electroplating of Al: SIGAL [8] and REAL [14,15]. The main

disadvantages of such processes are the flammability and volatility of the electrolytes. High temperature inorganic molten salts, such as NaCl–KCl [16], AlCl_3 –NaCl [17] and AlCl_3 –NaCl–KCl [18] have been extensively studied for the electrodeposition of Al. However, the high temperature and their highly corrosive natures bring great difficulties for finding container materials that can withstand chemical attack by the melts.

Over the last decades, aluminium plating in the room temperature molten salts (also called room temperature ionic liquids—RTILs), has received considerable attention. As a new and novel generation of solvents, RTILs exhibit many attractive properties, including excellent chemical and thermal stability, low melting points with negligible vapor pressure, high electrical conductivity and solvent transport properties, wide range of operational liquid temperature, ability to dissolve various organic, inorganic, and organometallic compounds and large electrochemical window of about 4.0 V. These properties give RTILs a certain potential to play a vital role in the electrochemistry field. Electrodeposition of Al from AlCl_3 based ILs were intensively and systematically studied from the 1980s, seeing for example [19–26]. These ILs exhibit adjustable Lewis acidity depending on the molar ratio of AlCl_3/IL [27]. Electrodeposition of Al can only be performed under the Lewis acidic condition, in which the Al_2Cl_7^- precursor, the dominant species in the electrolyte, can be electrochemically reduced to the metallic form according to the following reaction [28]:



A lot of progresses have been made and the electrodeposition was performed on various substrates such as platinum [20,29], tungsten

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[20,21], gold [30,31], copper [32,33], glass carbon [20] and mild steel [34]. However, little information has been reported in the literature about the systematic study of the relationships between deposit appearance, surface morphology and current efficiency with current density and temperature, respectively. Moreover, there is a lack of published reports describing the effects of current density and temperature on the crystal structure and orientation of Al electrodeposited from RTILs. In this work, we describe comprehensive and detailed investigation of surface morphology and crystal orientation of Al coatings electroplated on mild steel substrates in Lewis acidic $\text{AlCl}_3/[\text{bmim}]\text{Cl}$ ILs by galvanostatic technique. Temperatures were determined in the range from 308 K to 328 K based on our parallel study, where smoother, denser and brighter deposits were obtained.

2. Experimental

The electrolyte preparation and subsequent electrodeposition were both conducted in an electrolytic cell with a jacket under a dry nitrogen atmosphere. $[\text{bmim}]\text{Cl}$ was synthesized in our laboratory. Anhydrous AlCl_3 (powder) obtained from Beijing Chemical Reagents Company, without further purification, was used as the initial source of Al. The Lewis acidic electrolyte (with 2.0:1 molar ratio of $\text{AlCl}_3/[\text{bmim}]\text{Cl}$) was carefully prepared by mixing precise quantities of AlCl_3 and $[\text{bmim}]\text{Cl}$. The obtained electrolyte was continuously stirred for several hours to ensure uniformity. Moreover, the electrolyte was used without further purification so that the electrodeposition of Al could be investigated in the conditions easily transferable to the industry.

All the experiments were conducted using a three-electrode system: Al plate (Beijing Chemical Reagents Company, $\geq 99.0\%$), mild steel plate and ultra-pure Al wire (Beijing Mountain Technical Development Center for Non-Ferrous Metals, 99.999%) were used as counter electrode, working electrode, and reference electrode, respectively. The distance between the cathode and the anode was ca. 2.0 cm. Al plate was dipped in NaOH, rinsed with deionized water, followed by acetone and then dried before use; mild steel was immersed in boiling NaOH, dipped in 20–30% HCl (by volume), washed with deionized water and finally dried. Prior to use, the working electrodes were mechanically polished with sand paper, treated with a dilute mixture of hydrochloric acid (37%) and sulfuric acid (98%), rinsed with deionized water, and finally immersed into dichloromethane for degreasing. After completing the pre-treatments, the electrodes were assembled for immediate use. The depositions were carried out under a predetermined experimental temperature for 0.5 h with a constant stirring speed. Following each deposition experiment, excess IL was removed from the sample by washing in absolute alcohol; then the sample was rinsed with deionized water and dried with cool air.

Electrochemical measurements were performed using a CHI660C Electrochemical Workstation controlled with a personal computer. Surface morphology of the films was examined with emission scanning electron microscope (SEM, JSM-6700F). The compositional analysis of the deposits was confirmed by energy dispersive analysis by X-ray (EDAX, Oxford INCA300). The crystal structure was studied on a X'Pert PRO (PANalytical) X-ray diffractometer with $\text{Cu K}\alpha$ radiation.

3. Results and discussion

3.1. Effect of current density on the surface morphology

Current density usually has an important effect on the deposit brightness, thickness distribution, current efficiency and microstructure of the electrodeposits. Herein the effect of cur-

rent density was investigated from 8 mA/cm^2 to 24 mA/cm^2 at 308 K, from 8 mA/cm^2 to 26 mA/cm^2 at 318 K and from 8 mA/cm^2 to 32 mA/cm^2 at 328 K in 2.0:1 $\text{AlCl}_3/[\text{bmim}]\text{Cl}$ for 0.5 h in galvanostatic mode (the supreme current density is enhanced with the temperature increasing). All of the Al-deposited samples were dense, adherent and homogeneous and the surface coverage was quite satisfactory.

At 308 K, the deposits formed at 12–24 mA/cm^2 are quite smooth and bright, and thus the optimum current densities were determined in this range. The current efficiency decreases with increase in the current density in the range of 96.1–78.5%. The current efficiency decreases to be ca. 78.5% at 24 mA/cm^2 . As the current density increases the total charge though the cell increases, hence the theoretical amount deposited also increases. However, the actual weight deposited does not follow a similar trend as that of current density due to the current loss (polarization effects) involved in electrolysis process. Therefore, lower current efficiencies can be attributed to the above phenomena. The surface morphologies of the Al-coated mild steel substrates were further examined by SEM. Fig. 1 shows the SEM micrographs of the deposits obtained in 2.0:1 $\text{AlCl}_3/[\text{bmim}]\text{Cl}$ at 308 K for 0.5 h as a function of the current density (from 12 mA/cm^2 to 24 mA/cm^2). The deposits obtained at 12 mA/cm^2 , 16 mA/cm^2 and 20 mA/cm^2 display similar microstructures (Fig. 1a–c) and the deposited layer appeared quite dense and uniformly covered the entire mild steel substrate. Relatively scattered surface with smaller clusters of particles is observed on the deposits obtained at 24 mA/cm^2 (Fig. 1d). From the SEM analysis of the deposit microstructure at 308 K, it appears that the morphology of deposits was relatively independent of current density.

However, deposit microstructure obtained at higher temperature (318 K) of the electrolyte revealed interesting features as a function of current density. Fig. 2 shows the SEM micrographs of Al coatings with a current density of 12–24 mA/cm^2 at 318 K. The deposits obtained at 12 mA/cm^2 display continuous and dense microstructure with some nodules (Fig. 2a). At higher current densities a compact layer of deposit microstructure with spherical particles was observed as seen in Fig. 2b and c, except that the latter (Fig. 2c) is much denser and more homogeneous with smaller particles. With the highest current density in Fig. 2d the deposit morphology reveals a dense and compact layer containing non-spherical particles formed as small clusters. It can be seen from the above microstructures that at 318 K, the type of deposit microstructure changed obviously as a function of current density. Unlike the case of low temperature (308 K) where the deposit microstructure is relatively independent of current density, at 318 K, the influence of current density is clearly seen on the deposit microstructure. The influence of increased temperature seems to lead to a nucleation-controlled microstructure. Current efficiencies decrease with increase in the current density in the range of 94.8–80.6%. Compared with the one gained at 308 K, the relationship between the current efficiency and current density at 318 K seems to be the same as that of 308 K.

Fig. 3 shows the SEM images of the deposits obtained in 2.0:1 $\text{AlCl}_3/[\text{bmim}]\text{Cl}$ for 0.5 h with various current densities at much higher temperature (328 K). In Fig. 3a, deposits with homogeneous spherical particles in an average size of 10 μm can be observed where some amount of agglomeration of particles appears to have taken place. In Fig. 3b, the deposit morphology reveals a non-continuous layer containing squama particles formed as small clusters with an average size of 8 μm . At higher current densities a compact layer of deposit microstructure with spiculate particles was observed as seen in Fig. 3c and d, except that particles in Fig. 3d are a little smaller, more homogeneous and much denser than those in Fig. 3c. It can be seen from the above microstructures that at 328 K, the type of deposit microstructure also changed apparently

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