

Short Communication

## Preparation of Al/TiC Nanocomposite Coatings on 304 stainless steel via Electrodeposition in inorganic Molten Salts

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The electrodeposition of nanocomposite coatings has been widely investigated in aqueous solutions and room temperature ionic liquids, but there are no literature reports of that in inorganic molten salts. In this study, Al/TiC nanocomposite coatings were successfully electrodeposited in an AlCl<sub>3</sub>-based molten inorganic salt. The electrodeposited composite was investigated using an AlCl<sub>3</sub>-NaCl-KCl electrolyte containing dispersed TiC particles with a mean size of 50 nm. The micromorphologies of the surface and cross-section of the produced nanocomposite coating were observed by scanning electron microscopy (SEM). A smooth and compact nanocomposite was coated well on the substrate. The presence of TiC nanoparticles in the Al coating was confirmed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). This method of electrodepositing nanocomposite coatings in inorganic molten salts could also be used for preparing refractory metal-based (such as W- and Ti-based) and Mg-based nanocomposite coatings.

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**Keywords:** inorganic molten salts, composite electrodeposition, Al/TiC nanocomposite coating, titanium carbide nanoparticles

### 1. INTRODUCTION

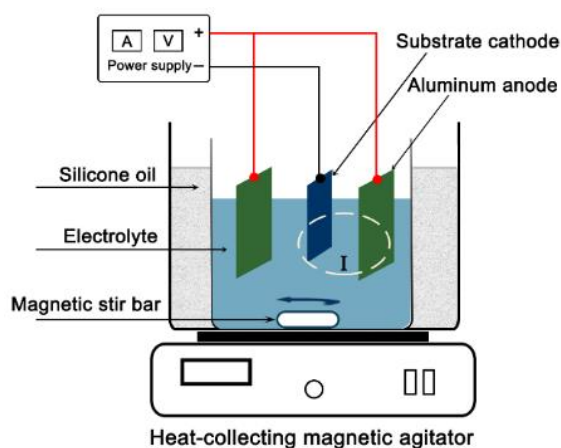
Pure Al coatings have been widely applied for protection against metal corrosion. However, they possess low hardness and corrosion resistance [1,2]. Al matrix composite coatings that contain reinforcing particles possess considerably higher hardness and wear resistance, and can protect the metal substrate from harsh environments [3-5]. Currently, Al matrix composite coatings are primarily prepared by cold spraying such as Al/Al<sub>2</sub>O<sub>3</sub> [6] and Al/SiC [7]. Although cold spraying avoids the problems that exists in thermal spraying, such as powder oxidation and high coating porosity, there are not so many types of specialized composite powders available for cold spraying. Furthermore, the spraying gas is expensive [8].

Electroplating is a surface-treatment technology where surface coatings with special properties are deposited on different substrates at low cost [9]. It is well known that nanocomposite coatings have been prepared via composite electrodeposition in aqueous solutions [10-13]. It is impossible for Al metal to be deposited in aqueous solutions. Therefore, the electrodeposition of Al matrix composite coatings should be carried out in non-aqueous solutions. They have been produced in room temperature ionic liquids, such as Al/Al<sub>2</sub>O<sub>3</sub> [14,16], Al/SiO<sub>2</sub> (SiC, TiB, BN) [16], and Al/carbon nanotubes [15]. However, there are few comprehensive studies on the cross-section and mechanical properties of these coatings.

The electrodeposition of Al coatings in inorganic AlCl<sub>3</sub>-NaCl-KCl molten salts has been widely reported. Several studies have shown that Al coatings with a certain thickness can be electrodeposited [17-20]; however, the electrodeposition of Al matrix nanocomposite coatings in inorganic molten salts has not been reported. In this study, Al/TiC coatings were prepared via composite electrodeposition in an AlCl<sub>3</sub>-NaCl-KCl molten salt containing TiC nanoparticles, and their microstructures were characterized.

## 2. EXPERIMENTAL

The inorganic AlCl<sub>3</sub>-NaCl-KCl molten salt (mass ratio = 8:0.9:1.1), which is similar to that commonly used for preparing Al coatings [20-22], was used in this study. TiC nanoparticles with a mean size of 50 nm were used (Shanghai Chaowei, China).



**Figure 1.** Schematic of composite electrodeposition in AlCl<sub>3</sub>-based inorganic molten salt.

A solid NaCl-KCl salt with a uniform distribution of TiC nanoparticles was prepared to introduce TiC nanoparticles into the molten electrolyte. First, the TiC nanoparticles and ball-milled mixed salt (NaCl-KCl, mass ratio = 0.9:1.1) were uniformly mixed at a mass ratio of 1:1. The nanoparticle-containing salt was ultrasonicated in acetone for 2 h at a frequency of 100 Hz, then dried in an oven at 120 °C for 1 h.

The inorganic molten salt containing TiC nanoparticles was prepared as follows. First,  $\text{AlCl}_3$  was weighed and ground in a glove box filled with dry Ar. Second, the mixed salt was placed in a quartz crucible under Ar atmosphere. The crucible was placed in an oil bath and heated at  $180\text{ }^\circ\text{C}$  to melt the mixed salt (Fig. 1). Finally, the prepared TiC nanoparticles-containing salt was fed into the molten salt through the feeding hole with the concentration of TiC nanoparticles as 20 g/L.

As the cathode, 304 stainless steel covered with polytetrafluoroethylene tape with exposed surface of  $10\text{ mm} \times 5\text{ mm} \times 0.5\text{ mm}$  was used. As the anode, 99.999% pure Al plates were used, and the size of the plate immersed in the molten salt was  $20\text{ mm} \times 10\text{ mm} \times 3\text{ mm}$ . Prior to electrolysis, the surface of the cathode plate was pretreated as follows. It was ground with successively finer sandpaper (400#, 800#, and 1500#). The ground cathode was chemically degreased by placing it in a boiled alkaline solution containing 50-60 g/L NaOH and 60-70 g/L  $\text{NaHCO}_3$  for approximately 30 min. Subsequently, the cathode plate was immersed in 20-25% HCl for 1-2 min to remove surface oxides and activate the surface. Finally, the surface of the anode was polished and degreased with acetone. After pretreatment, the cathode and anode were arranged as shown in Fig. 1.

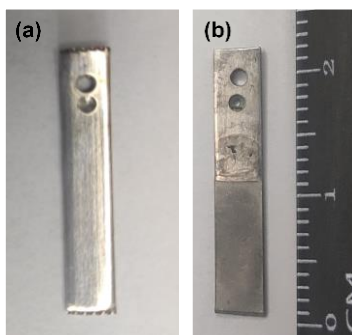
A DC power supply (HLR-3660D, Henghui) was used to maintain a constant current density of  $5\text{ A/dm}^2$ . The molten salts were stirred using a magnetic stirrer at a stirring rate of 350 rpm. After 10 min of composite electrodeposition, Al matrix composite coatings containing TiC nanoparticles were obtained.

Scanning electron microscopy (SEM; Regulus 8220, Hitachi) and transmission electron microscopy (TEM; JEM-2100, Jeol) were employed to characterize the micromorphology and microstructure of the sample. The TEM samples were prepared using a precision ion polishing system (Model 691, Gatan). The phase composition of the composite coating was analyzed using X-ray diffraction (XRD; SmartLab, Rigaku).

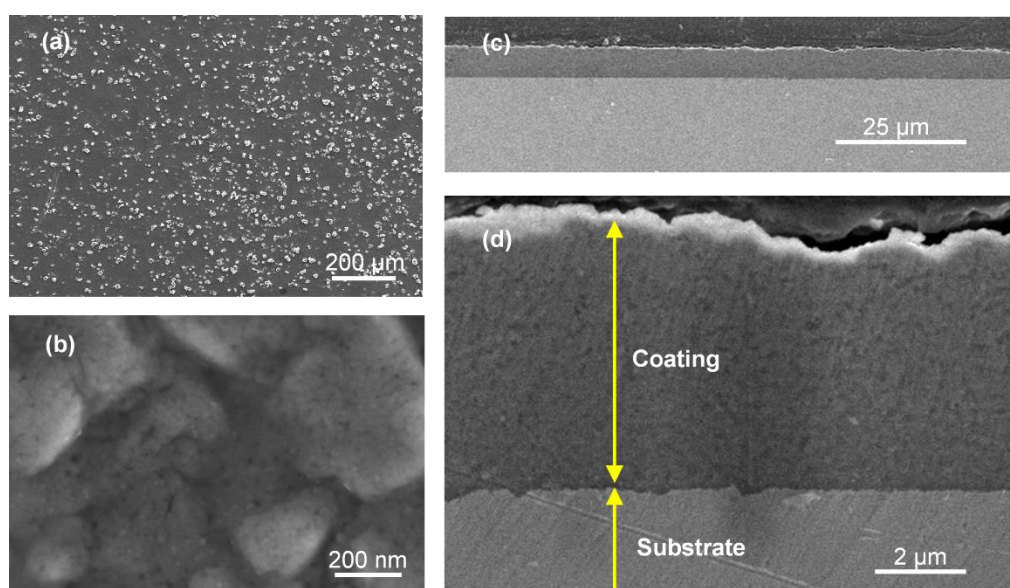
### 3. RESULTS AND DISCUSSION

The composite electrodeposition of TiC nanoparticles and Al ions was performed in the inorganic  $\text{AlCl}_3$ -NaCl-KCl molten salt. Photos of the stainless-steel cathode sheet before and after electrodeposition are presented in Fig. 2.

The surface of the Al/TiC coating was analyzed using SEM. As shown in Figs. 3a, the bright domains represent the dendritic Al metal on the surface. The morphology of the coating surface with higher magnification (electrodeposition time: 1 min) is as shown in Fig. 3b. It is almost impossible to observe the incorporated TiC nanoparticles directly. It is assumed that due to the small size (mean size = 50 nm) and diverse shapes, it is difficult to observe the particles directly using SEM. This is similar to the situation of Al/ $\text{Al}_2\text{O}_3$  nanocomposite coatings prepared via composite electrodeposition in  $\text{AlCl}_3$ -DMSO<sub>2</sub> [16]. Al metal can be directly deposited on the surface of the conductive particles and wrapped the particles, making it harder to distinguish the particles. Figs. 3c and 3d show that the cross-section of the coating is dense and smooth, with a thickness of 5-6  $\mu\text{m}$ . In addition, under this circumstance, the current efficiency for producing Al/TiC composite coating in inorganic molten salts was calculated as 85.71% and the power consumption was estimated as 2.25 kJ/g.

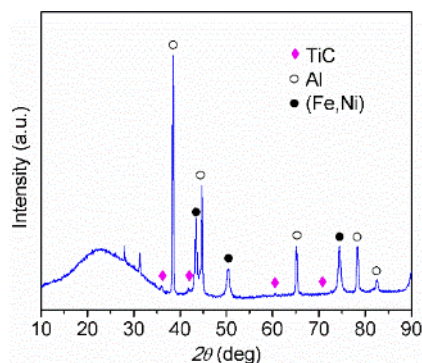


**Figure 2.** Photos of stainless-steel cathode (a) before and (b) after composite electrodeposition in  $\text{AlCl}_3\text{-NaCl-KCl}$  molten salts containing 20 g/L TiC nanoparticles at  $180^\circ\text{C}$  (current density:  $5 \text{ A/dm}^2$ , time: 10 min).



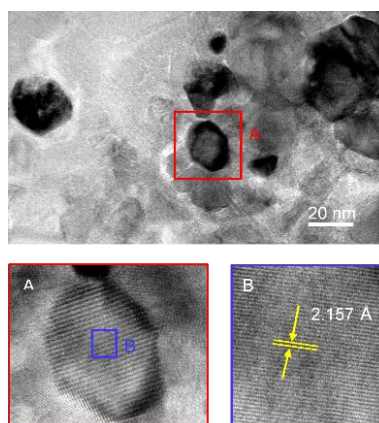
**Figure 3.** SEM images of surface ((a),(b)) and cross-section ((c),(d)) of electrodeposited Al/TiC nanocomposite coating in  $\text{AlCl}_3\text{-NaCl-KCl}$  molten salts containing 20 g/L TiC nanoparticles at  $180^\circ\text{C}$  (current density:  $5 \text{ A/dm}^2$ , time: 10 min for (a),(c),(d) and 1 min for (b)).

Fig. 4 shows the XRD pattern of the produced Al/TiC nanocomposite coating. The diffraction peaks of (Fe,Ni) are observed owing to the use of 304 stainless steel as the substrate. In addition, there are distinct diffraction peaks of Al and TiC, which indicate that the nanoparticles were successfully incorporated in the Al coating.



**Figure 4.** XRD pattern of the Al/TiC nanocomposite coating obtained from  $\text{AlCl}_3\text{-NaCl-KCl}$  molten salts containing 20 g/L TiC nanoparticles at  $180^\circ\text{C}$  (current density:  $5 \text{ A/dm}^2$ , time: 10 min).

TEM analysis was performed to confirm the existence of nanoparticles in the Al/TiC nanocomposite coating. The TEM image in Fig. 5 clearly verifies that nanoparticles, with an interplanar spacing of  $2.157 \text{ \AA}$ , corresponding to the (200) crystal plane of TiC [23], are embedded in the Al substrate. This proves the presence of the TiC nanoparticles.



**Figure 5.** TEM of the Al/TiC nanocomposite coating obtained from  $\text{AlCl}_3\text{-NaCl-KCl}$  molten salts containing 20 g/L TiC nanoparticles at  $180^\circ\text{C}$  (current density:  $5 \text{ A/dm}^2$ , time: 10 min), A and B are the magnified red and blue areas, respectively.

These experimental results confirm the successful preparation of the Al/TiC nanocomposite coating via nanocomposite electrodeposition in an  $\text{AlCl}_3$ -based inorganic molten salt. The mechanism for nanocomposite electrodeposition in an  $\text{AlCl}_3$ -based inorganic molten salt is similar to that for composite electrodeposition in an aqueous solution [24,25]. The mechanism can be mainly divided into three processes: (1) TiC nanoparticles are suspended and uniformly distributed by stirring in a molten salt; (2) nanoparticles are transported to the cathode surface via convective movement; (3) TiC nanoparticles that are adsorbed at the cathode are entrapped within the Al metal deposit.

The Al/TiC nanocomposite coating was successfully obtained via composite electrodeposition in the inorganic AlCl<sub>3</sub>-NaCl-KCl molten salt. This method could also be used to prepare nanocomposite coatings for refractory metals (such as W and Ti) and Mg-based nanocomposite coatings.

#### 4. CONCLUSIONS

In this study, composite electrodeposition was performed by adding TiC nanoparticles to an AlCl<sub>3</sub>-based inorganic molten salt for the first time. The conclusions are as follows:

(1) TiC nanoparticles can be electrodeposited with Al ions in an inorganic AlCl<sub>3</sub>-NaCl-KCl molten salt, accompanied by stirring, to obtain Al/TiC coatings.

(2) The Al/TiC coating obtained on 304 stainless steel via composite electrodeposition is dense and smooth.

#### ACKNOWLEDGEMENTS

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