



Effect of cluster interface structure on the spontaneous escape behavior of silver in ion plating coatings and its inhibition mechanism



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ABSTRACT

In order to study the spontaneous escape behavior of silver in ion plating coatings and its inhibition mechanism, a series of silver-doped titanium nitride coatings were prepared by magnetron sputtering. The effect of cluster interface structure on the spontaneous escape behavior of silver in ion plating coatings were observed, and various thicknesses of homogenous silver-free barrier layers were explored to achieve the permanent retention of silver. Results showed that for silver-doped titanium nitride coatings prepared with the silver target current increased from 0.01 A to 0.2 A, more spontaneously escaped silver particles were observed at the cluster interface of the coating and were far from being crystallized into a layered structure. Approximately 500 nm pure titanium nitride surface cover could achieve the permanent retention of silver in titanium nitride coatings with a high dopant content of silver. The cluster interfaces of the titanium nitride coating interdigitated with each other to form a dendritic network structure. The interdigitated dendritic network structure blocked the spontaneous escape of silver and achieved the permanent retention of silver in the titanium nitride coating.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are considered to be the ultimate source to power new energy vehicles due to their high conversion efficiency, pollution-free nature, and quick startup [1–4]. Bipolar plates are an important part of PEMFCs and account for approximately 60%–80% of the total weight and volume of a PEMFC [5,6]. Traditional PEMFC bipolar plates are mostly 2-mm-thick graphite plates, making it difficult to meet the small size and high energy density requirements of the vehicle battery pack. Therefore, replacing each 2-mm-thick graphite plate with a metal plate of thickness less than 0.5 mm is an effective way to reduce the weight and volume of the vehicle fuel cell. However, due to the acidic working environment of the PEMFC, the surface of the metal plate can be easily passivated and corroded, resulting in an increase in surface contact resistance, thus further affecting the output power and service lifetime of the fuel cell [7–12]. Therefore, the preparation of a conductive corrosion-resistant surface coating of the metal plate has become a difficult issue to resolve in the metallization of bipolar plates of fuel cells.

Conductive corrosion-resistant coatings for the surface modification of metal plates mainly include those based on noble metals [13,14], carbon [15–19], metal nitrides and carbides [20–25]. Among them, graphite-like carbon (C) and titanium nitride (TiN) coatings have

attracted extensive attention due to their high electrical conductivity and excellent corrosion resistance. However, the presence of defects, such as micropores and microcracks, on the surface of graphite-like carbon and titanium nitride coatings prepared by physical vapor deposition methods, such as magnetron sputtering, further reduces the electrical conductivity and corrosion resistance of coatings [11,26–29]. Therefore, the researchers have tried to increase the conductivity of such coatings through the incorporation of metallic silver. However, due to the spontaneous escape of silver, methods for raising the conductivity by increasing the doping concentration of silver have been met with difficulty [30–33]. Therefore, the study of the spontaneous escape mechanism of silver and the inhibition mechanism to realize the permanent retention of silver in the coating have become research hotspots in recent years. Our previous study indicated that the silver particles escaped from the amorphous carbon coatings are mainly distributed at the cluster interface of the coating, and the silver particles that segregated at the carbon cluster interface will escape under the gas molecular extrusion from the atmosphere [34]. Thus, it is of great scientific significance to investigate the effect of cluster interface structure on the spontaneous escape behavior of silver in ion plating coatings and its inhibition mechanism.

Based on this, in this paper, a series of silver-doped titanium nitride coatings were prepared on the surface of aluminum alloys by

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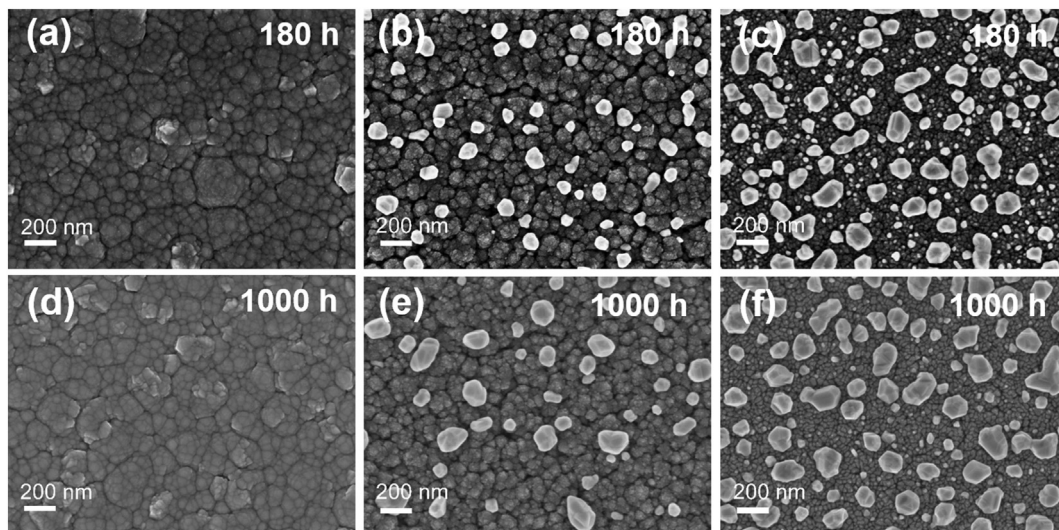


Fig. 1. Surface morphologies of silver-doped titanium nitride coatings placed in the atmosphere for 180 h and 1000 h prepared with Ag target currents of (a, d) 0.01 A, (b, e) 0.1 A, and (c, f) 0.2 A.

magnetron sputtering. The effect of cluster interface structure on the spontaneous escape behavior of silver in ion plating coatings were studied, and various thicknesses of homogenous silver-free barrier layers were explored to achieve the permanent retention of silver.

2. Experimental details

2.1. Coatings deposition

In the experiment, a series of silver-doped titanium nitride coatings were deposited on the surface of silicon and 6061 aluminum alloy substrates in constant current control mode using a magnetron sputtering system consisting of two opposite targets [34]. The high pure (99.99%) titanium (Ti) target and the silver (Ag) target with the diameter of 100 mm and thickness of 4 mm were symmetrically arranged on both sides of the cylindrical furnace chamber. The high purity (99.99%) argon (Ar) and nitrogen (N_2) were used as the sputtering gas for the growth of silver-doped titanium nitride coatings.

Prior to deposition, the substrates were dried with a blower after ultrasonic cleaning for 20 min in ethanol and acetone baths in succession, and then fixed on the sample seat in the vacuum chamber. During the deposition process, the background pressure of the process chamber was evacuated to below 3.0×10^{-3} Pa and then Ar gas with a constant flow of 30 sccm was introduced into the chamber. Then, the substrates were cleaned using plasma for 20 min with an applied current of 0.3 A to the Ti target, 0.01 A to the Ag target, and a bias voltage of -400 V on the sample substrate to remove the surface contaminations and activate the surface prior to film deposition. Subsequently, a pure Ti bottom layer was deposited on the substrate surface for 3 min with the Ti target current of 2 A and a bias voltage being -120 V to increase the binding force between the coating and the substrate. Next, a transition layer was deposited for 5 min with Ti target and Ag target opened simultaneously. Afterwards, on the top of interlayers (Ti bottom layer and transition layer), function layers (silver-doped titanium nitride coatings) were deposited with different Ag target currents of 0.01 A, 0.05 A, 0.1 A, and 0.2 A, a Ti target current of 2 A, a N_2 flow rate of 4 sccm and a bias voltage of -60 V on the substrate for a deposition time of 45 min. And then, at Ag target current of 0.2 A, after Ti and Ag were co-deposited for 45 min, a pure titanium nitride coating was deposited for 10 min, 15 min, 20 min, or 30 min on the co-deposited titanium-silver coating to inhibit the spontaneous escape of silver. In addition, a set of pure silver coatings without transition layer was deposited with different Ag target current of 0.01 A, 0.05 A, 0.1 A and 0.2 A at a bias voltage of -60 V on

the substrate for a deposition time of 45 min.

2.2. Characterization

The surface and cross-sectional morphologies of the coatings were observed by a field-emission scanning electron microscopy (SEM, JSM-6700F) operated at 3 kV accelerating voltage. The amount of silver residue in the coating was analyzed using energy dispersive X-ray spectroscopy (EDS), operating at an accelerating voltage of 10 kV for an acquisition time of 200 s on a cross-section view sample magnified by 5000. The cluster interface morphology of the coatings was observed by SEM and cross sectional transmission electron microscopy (TEM, IEM-3010) at an accelerating voltage of 200 kV. In preparing TEM samples, two cross-sectional specimens at size of $3 \text{ mm} \times 3 \text{ mm}$ were glued together face to face. Then, it was ground and polished down to about $20 \mu\text{m}$ thick. This thin specimen was attached to a Cu grid for ion milling. Ion milling was operated at 7 kV, using a single-sided sample holder with a milling angle of 6° by focused ion beam (FIB, FISCHI-ONE-1010) milling. An RTS-8 type four-probe tester was used to measure the conductivity of the coatings in sheet resistance mode.

3. Results and discussion

3.1. Effect of silver target current on the spontaneous escape behavior of silver in ion plating coatings

The surface morphologies of silver-doped titanium nitride coatings prepared under different Ag target current after being exposed to air for 180 h and 1000 h are shown in Fig. 1(a–f). From Fig. 1(a) and Fig. 1(d), it can be seen for the sample prepared with a Ag target current of 0.01 A, there was barely any silver escape observed by SEM on the surface of the titanium nitride coating after the samples, which were exposed to the atmosphere for 180 h and 1000 h. Even when the Ag target current was increased by a factor of 10 to 0.1 A and the sample was left in air for 180 h, the spontaneously escaped silver particles remained dispersed at the cluster interface of the coating. Moreover, the total area of the silver particles spreading along the surface did not exceed 15% of the surface area of the coating (as shown in Fig. 1(b)). With a further increase in the Ag target current to 0.2 A and a standing time in air of 1000 h, the diameter of the silver particles grown at the cluster interface did not exceed 200 nm, and the silver distribution was far from resembling the formation of a crystalline layer (as shown in Fig. 1(f)). The results indicate that more spontaneously escaped silver particles

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