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Comparison of corrosion behaviors between SS304 and Ti substrate coated with (Ti,Zr)N thin films as Metal bipolar plate for unitized regenerative fuel cell

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ABSTRACT

In this study, a (Ti,Zr)N coating consisting of nano-composite structure of the TiN and ZrN phases is deposited on SS304 and titanium substrates as the metal bipolar plate through the cathodic arc evaporation techniques. This improves the corrosion resistance of SS304 and Ti metal when used in a unitized regenerative fuel cell (URFC). The corrosion behaviors of these two substrates are compared. Scanning electron microscope, energy dispersive spectrometer, and X-ray diffractometer are used to characterize the microstructure, thickness, chemical composition, as well as crystalline and phase states of the deposited thin films. The potentiodynamic polarization of the (Ti,Zr)N coating is tested in a simulated URFC H_2 environment, i.e., 0.50 M H_2SO_4 with 3 ppm NaF solution purging with H_2 gas at 60 °C. Experimental results demonstrate that the (Ti,Zr)N coating improves the corrosion resistance of SS304 (about 215 times that of uncoated SS304) better than that of the Ti substrate (about 200 times that of uncoated Ti). The enhanced corrosion resistance is attributed to the nano-composite structure of TiN and ZrN, which has a dense and columnar microstructure that is impermeable to a corrosive medium. The coating of the (Ti,Zr)N layer has better corrosion resistance than the increased sheet resistance for both substrates. Therefore, the (Ti,Zr)N–SS304 and (Ti,Zr)N–Ti samples, specifically the (Ti,Zr)N–SS304 sample, are good candidates as the material for URFC H_2 side metal bipolar plate.

1. Introduction

A unitized regenerative fuel cell (URFC) is a device that functions as a fuel cell when supplying it with hydrogen and oxygen as fuel, but acts as an electrolyzer when water was used as fuel instead. When the URFC is in the fuel cell mode, the electricity is generated by an electrochemical reaction between hydrogen and oxygen. When the URFC is in the water electrolyzer mode, hydrogen and oxygen are produced by water electrolysis. URFC has many attractive advantages in the application of long-term energy sources when combined with traditional secondary batteries (e.g., Li ion and lead acid batteries). These advantages include high durability, high energy density, and low environmental impact [1–5]. However, two challenges must be addressed before this technology becomes commercially viable. The first challenge concerns the development of a highly active and stable oxygen electrocatalyst for redox reaction at the oxygen electrode [1,6–9]. The second challenge is on improving the corrosion resistance of the bipolar plate for the URFC during the two operation modes [10,11].

The bipolar plate acts as a fuel distributer, electron conductive medium, and supporting material of stack. The bipolar plate also assists in managing heat and water inside the cell [4,12]. Therefore, the plate must have high mechanical strength, high corrosion resistance, low interfacial contact resistance, lightweight, and effective manufacturability properties. Graphite, metal, and a polymer blend with carbon are three candidate materials for the bipolar plate. The dense graphite can fulfill most of the requirements of a bipolar plate. However, it has challenges with toughness, corrosion at high potential (>1.5 V) at water electrolysis mode [13,14], and poor manufacturability [15,16]. The polymer blended with carbon has an advantage on effective manufacturability, but still suffers from poor electron conductivity. Therefore, metal is a good alternate candidate for bipolar plates because it has excellent manufacturability, is non-permeable to gases and water, has high thermal and electric conductivity, and is cost-effective [17,18].

The typical material of a metal-based bipolar plate includes titanium [10,17], stainless steel [19–21], copper alloy [22,23], aluminum [24], and nickel [25]. Among these materials, titanium has been extensively investigated because it has good mechanical strength, can resist acidic corrosion, and does not corrode in high positive over-potential under-humidified conditions. However, the surface of the titanium bipolar plates reacts with oxygen to form a passive oxide layer during the fuel cell operating mode. This layer increases contact resistance between the bipolar plates and the electrode. As a result, the cell performance is significantly reduced [17,26]. Therefore, many researchers have used surface modification techniques to deposit gold or platinum thin film on the Ti surface to prevent the formation of the Ti oxide layer and improve the corrosion resistance of the Ti metal [26,27].

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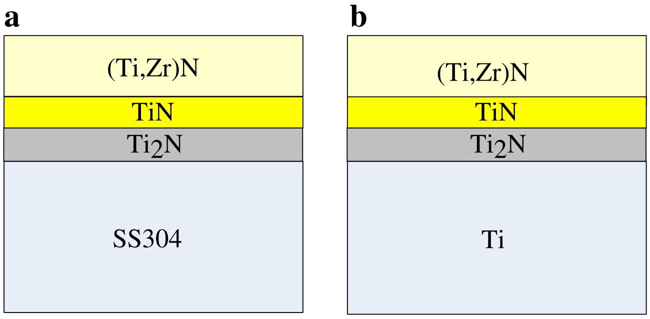

Fig. 1. Diagrams for the proposed layer structures. (a) (Ti,Zr)N coating on SS304 substrate, (b) (Ti,Zr)N coating on Ti substrate.

Stainless steel is a cheap and widely used material. The material is easily machined to thin bipolar plates to reduce the stack volume. Unfortunately, the corrosion resistance of this material is poor when it is operated at high potential and current. Many surface modification methods such as nitrogen surface treatment, electrochemical deposition, physical vapor deposition (PVD), and chemical vapor deposition [28–32] have been used to deposit TiN/ZrN multilayers [33–35] or a ZrN [36,37], TiN [28,38], TiC [39], or Cr-based multilayer [40] on the stainless steel surface to improve the corrosion resistance. Yan Wang and coworkers [38] coated TiN on SS316L with PVD technology and tested the surface in a simulated proton exchange membrane fuel cell environment. They showed that the TiN coating improved the corrosion resistance while increasing the open circuit potential of the uncoated SS316L by 1.60 V. Other researchers observed that a zirconium nitride (ZrN) coating on stainless steel could enhance the corrosion resistance and hardness of the substrate [36,37]. The coating of composite TiN/ZrN multilayers has been demonstrated as having excellent hardness and mechanical properties [33–35]. However, the corrosion resistance of these composite TiN/ZrN multilayers has not been studied further in the application of URFC.

This study aims to improve the corrosion resistance of the SS304 and Ti substrates in a rigorous H_2 environment in URFC by depositing a (Ti,Zr)N layer comprising a nano-composite of TiN and ZrN on the SS304 and titanium substrates via cathodic arc evaporation physical vapor deposition (CAE-PVD) techniques. The designed structure of the thin film is shown in Fig. 1. The influences of the microstructure and potentiodynamic polarization parameters on corrosion resistance are studied. The proposed mechanism of enhanced corrosion resistance is also investigated.

2. Experiment

2.1. Specimen preparation

Commercial SS304 stainless steels and titanium plates were selected as the substrates in this study, and the materials' chemical composition is listed in Table 1. All specimens were cut into 20 mm × 30 mm × 1 mm and were polished with silicon carbide papers ranging from 240# to 2400# grit on a grinder and then with 0.05 μm Al_2O_3 powder on rubbing fur. The specimens were then thoroughly degreased, ultrasonically cleaned with detergent, rinsed with deionized water, and finally dried in a hot oven.

2.2. Preparation of thin film

The CAE-PVD technology was used to deposit (Ti,Zr)N/TiN thin films on the SS304 and titanium substrates. The CAE-PVD system consisted of a stainless steel chamber, vacuum system, arc generation system, DC source system, and control system. The high-purity titanium and zirconium targets served as the cathode, and the substrates, i.e., Ti or SS304, served as the anode. The substrates were placed at the same rotated holder located between the Ti and Zr targets at a distance of 170–180 mm. To obtain different compositions of the thin films, we fixed the targets' power and controlled the targets' power-on time and the amount of reactive N_2 gas.

Before the coating process, the chamber pressure was vacuumed to 5×10^{-2} Pa. The substrate surface was cleaned with argon-plasma with substrate bias of −800 V for 20 min and followed by titanium ion bombardment with substrate bias of −400 V for 1 min. To obtain the thin film structure shown in Fig. 1, the substrate bias and chamber pressure were fixed at −120 V and 1–2 Pa to obtain the first layer, Ti_2N. The TiN second layer was obtained by controlling the deposition time and chamber pressure. Finally, the (Ti,Zr)N layer was deposited on the TiN layer by adjusting the substrate bias and chamber pressure to −80 V and 3–4 Pa, respectively. The process temperature was set from 150 to 200 °C, and the rotation speed of specimen holder was about 3 rpm. The coating sample with the SS304 substrate is denoted as (Ti,Zr)N–SS304, while the sample with the Ti plate substrate is denoted as (Ti,Zr)N–Ti.

2.3. Surface analysis

The microstructure, thickness, and chemical composition of the deposited thin films were examined with a field-emission scanning microscope (FE-SEM) (model: JSM 7000 F, JOEL) under operation voltage of 15 kV, a transmission electron microscope (TEM) (model: JSM 2100, JOEL) operated at an acceleration voltage of 200 kV and an energy dispersive spectrometer (EDS) (model: INCA x-sight 7557, OXFORD INSTRUMENTS). The samples conducted with EDS analyses were measured at working distance of 10 mm and magnification of 5000 times under operation voltage of 15 kV. The TEM samples were prepared by a dual beam-focused ion beam using an FEI Quant 3D FEG system. Due to the automatic control of the ion beam, this system can accurately cut the sample into the required dimension, i.e. thickness of 100–150 nm.

The crystalline and phase states of the coatings were analyzed with an X-ray diffractometer, BRUKER, D8 Discover. The X-ray diffraction (XRD) patterns were received using Cu Kα radiation from a rotating anode source operating at 30 kV and 15 mA. The specimens were scanned at 3°/min in continuous scan mode in the range of 20° to 100°.

2.4. Electrochemical test

An electrochemical polarization test such as the potentiodynamic measurement is the method most frequently used to observe the corrosion behavior of the coatings and substrate for bipolar plates in a

Table 1
Chemical compositions of SS304 and titanium substrates (wt.%).

Alloy	Chemical composition (wt.%)									
	C	Mn	Si	Ni	Cr	N	S	P	Fe	Al	Ti
SS304	0.08	2.0	0.75	8.0–12.0	18.0–20.0	0.1	0.03	0.045	Balance	–	–
Ti	0.008	0.012	–	–	–	0.003	–	–	0.02	0.02	Balance