A nanocrystalline zirconium carbide coating as a functional corrosion-resistant barrier for polymer electrolyte membrane fuel cell application

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HIGHLIGHTS

- A ZrC coating exhibits a dense, homogeneous microstructure.
- The corrosion resistance of the coating is higher than that of Ti6Al4V substrate.
- The ZrC coating exhibits good hydrophobic and low interfacial contact resistance.

ARTICLE INFO

ABSTRACT

A ZrC nanocrystalline coating is engineered onto a Ti–6Al–4V substrate using a double cathode glow discharge technique in order to improve the corrosion resistance and long-term stability of this alloy. The new coating exhibits an extremely dense, homogeneous microstructure composed of equiaxed grains with an average grain size of ~12 nm and is well adhered on the surface of the substrate. The corrosion behaviour of the coating is systematically investigated using various electrochemical methods, including potentiodynamic, potentiostatic polarizations and electrochemical impedance spectroscopy (EIS), in a simulated polymer electrolyte membrane fuel cell (PEMFC) operating circumstances under different temperatures. The results show that with rising temperature, the corrosion potential (E_{corr}) decreases and the corrosion current density (i_{corr}) of the ZrC coated specimen increases, indicating that the corrosion resistance decreased with increasing temperature. However, at a given temperature, the ZrC-coated Ti–6Al–4V alloy has a higher E_{corr} and lower i_{corr} as compared to the bare substrate. The results of EIS measurements show that the values of the resistance for the ZrC coated Ti–6Al–4V alloy are three orders of magnitude larger than those of Ti–6A1–4V in the simulated PEMFC environment.

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1. Introduction

As an energy-producing device, fuel cells can directly convert the chemical energy of fuel and oxidant into electrical energy via an electrochemical reaction. They are designed to operate at high efficiencies over a wide range of operating conditions with water as the only byproduct, and thus, have received extensive attention as one of the cleanest and most sustainable solutions to meet future energy needs [1]. Among the many types of fuel cells, the polymer electrolyte membrane fuel cell (PEMFC) is one of the most promising candidates for automobile and portable power applications, due to its high efficiency of energy conversion, low temperature operation, quick start-up time and environmentally friendly, near-zero emissions [2]. Bipolar plates, as one of the major components in the PEMFC stacks, constitute approximately 80% of the total weight, 30% of the total cost and almost all of the volume in a typical fuel cell stacks [3]. Bipolar plates perform multiple functions; that is, conducting currents between cells, supporting the cell stack, managing the heat and water of the cells, and

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distributing the cathodic and anodic reactant gases uniformly. Ideally, bipolar plates should have excellent corrosion resistance in the PEMFC environment, high electrical conductivity to reduce resistive losses, suitable surface properties for water removal, low gas permeability, light weight with good mechanical strength, and low manufacturing cost etc. [4,5]. Owing to their excellent corrosion resistance and electrical conductivity, graphite and graphite composite have been widely used in the manufacture of bipolar plates [6]. Nevertheless, their commercial application is plagued by some complex problems, including poor barrier to reactant gases, insufficient mechanical strength and high manufacturing cost. In comparison, metals have a significant advantage over graphite-based materials in terms of cost, mechanical strength, ease of manufacture and specific volumetric power density. Therefore, metallic bipolar plates, particularly those fabricated from different grades of stainless steels, have received much attention, and are considered to have the greatest potential as an alternative material for the widely used non-porous graphite [7,8]. When applying stainless steels to bipolar plates for PEMFCs, the passive film formed on their surfaces in the highly acidic environment of the fuel cell acts, in part, as an electrical insulator and, thus, increases the contact resistance between the electrode and the bipolar plate, resulting in a decrease in cell performance [9]. In addition, due to their insufficient corrosion resistance, the release of metallic ions, e.g. Fe, Cr and Ni ions from stainless steel, leads to contamination of the polymer electrolyte and Pt catalyst [10]. As compared to stainless steel, titanium and its alloys are a better alternative for the fabrication of metallic bipolar plates for portable applications, because they can produce higher volumetric power densities when assembled into stacks [11]. Surface modification by the deposition of a protective coating is commonly used to improve and control the corrosion resistance of metals without changing the bulk properties of the metal substrate. Therefore, in recent studies, various types of thin, noble metal coatings, such as gold and platinum, have been employed to protect bipolar plates made of titanium and its alloys from the formation of oxide layers with a high resistivity in the PEMFC environment [12–15]. For example, Wang et al. [13] found that the cell performance of the gold-plated bipolar plates is close to, and often superior than, the PEM fuel cells with graphite and uncoated titanium bipolar plates. It is worth noting that in addition to good corrosion protection, low electrical contact resistance, high mechanical strength, excellent adhesion between the coating and the substrate and low fabrication cost are also key factors to the application of a protective coating on these metallic bipolar plates. However, the corrosion resistance of these noble metal coatings has not been systematically investigated. Further, the cost of these noble metals is prohibitive for commercial application in PEMFCs, even in the form of thin coatings.

As a transition metal carbide, ZrC exhibits both ceramic and metallic characteristics including a very high melting point (>3540 °C), high hardness, excellent corrosion resistance and high electrical and thermal conductivities [16–18]. The unique combination of these physical and chemical properties makes it a potential coating material for the PEMFC application. To date, however, transition metal nitride or carbide coatings fabricated by various deposition techniques (such as e-beam evaporation and sputtering) have been of poor quality due to the presence of defects, such as pinholes, pores and macro-droplets, which severely reduce their corrosion resistance [19,20]. To address this issue, a double glow discharge plasma technique has been utilized for hard coating synthesis in our recent work, which yielded thick, dense coatings on titanium alloy substrates, which are strong and effective in combating corrosion attack [21].

In this study, the application of ZrC as a functional protective coating for PEMFC bipolar plates is explored. To so do, a ZrC nanocrystalline coating was deposited onto a Ti–6A1–4V substrate using a double glow discharge plasma technique. The microstructure of the as-deposited coating was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM). The mechanical properties and adhesion strength of the as-deposited coating were measured using nanoindentation and scratch testing. Considering that the bipolar plates operate in a wide range of temperatures in PEMFC, the corrosion behaviour of the ZrC coating in simulated PEMFC environments was investigated using electrochemical techniques at three solution temperatures of 25, 55 and 70 °C. Furthermore, the interfacial contact resistance and surface wettability of the ZrC coated specimen were measured and compared with the uncoated Ti–6A1–4V alloy.

2. Experimental details

2.1. Preparation of ZrC nanocrystalline coating

The ZrC nanocrystalline coating were deposited onto a Ti–6A1–4V substrate using a double cathode glow discharge apparatus. In the process of double cathode glow discharge, one cathode serves as the target fabricated from the desired sputtering materials, and the other cathode as the substrate material, as described elsewhere [21]. When two different voltages are applied to the two cathodes, glow discharge occurs. In this work, a ZrC disk with dimensions $\Phi 80 \times 4$ mm was used as the sputtering target. It was fabricated from ball-milled Zr (300 mesh, >99.9% purity) and C powders (graphite, 500 mesh, >99.9% purity) by employing cold compaction under a pressure of 600 MPa. Disk-shaped substrates, 40 mm in diameter and 3 mm thick, were machined from a commercial Ti–6Al–4V alloy rod. The nominal composition of this alloy in weight percent is: Al, 6.04; V, 4.03; Fe, 0.3; O, 0.1; C, 0.1; N, 0.05; H, 0.015 and the balance Ti. Before sputter deposition, the polished substrates were ultrasonically cleaned in acetone, alcohol, distilled water and then dried. The detailed deposition parameters can be described as follows: the base pressure, 5×10^{-3} Pa; working pressure, 35 Pa; target electrode bias voltage with direct current, −750 V; substrate bias voltage with impulse current, −350 V; substrate temperature, 650 °C; target/substrate distance, 10 mm and treatment time, 2 h.

2.2. Phase and microstructure characterization

The phase composition of the as-deposited coating was characterized using X-ray diffraction (XRD) (D8ADVANCE using Cu Kα radiation), with the instrument operating at 35 kV and 40 mA. X-ray data were collected using a 0.1° step scan with a count time of 1 s. Atomic force microscopy (AFM; Veeco Nanoscope V) was used to characterize the surface features and to determine roughness values of the as-deposited coating. Both the cross-sectional and corroded surface morphology of the as-deposited coatings were studied by scanning electron microscopy (SEM, Quanta200, FEI Company). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were performed using a JEOL JEM-2010 operating at an accelerating voltage of 200 kV. Thin-foil specimens for TEM observation were prepared by single-jet electropolishing from the untreated side of the substrate. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Kratos AXIS Ultra ESCA System using an Al Kα X-ray source with energy of 1486.71 eV. The accelerating voltage and emission current of the X-ray source were kept at 12 kV and 12 mA, respectively. The base pressure of the sample analysis chamber was maintained at ~10^{-10} Torr. The pass energy was selected to be 80 eV