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Development of PVD coatings for PEMFC metallic bipolar plates

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ABSTRACT

Metallic PEM fuel cell bipolar plate (BPP) materials such as stainless steel typically suffer from insufficient corrosion resistance and/or interfacial contact resistance (ICR). Therefore, coatings with both high corrosion resistance and low ICR are required. Closed field unbalanced magnetron sputter ion plating (CFUBMSIP) was used to produce dense and well adhered TiN, TiN + C and Graphit-iC™ coatings on an AISI316L foil substrate. The ICR of the coatings was measured before and after a potentiostatic measurement at a cathodic standby PEMFC potential of 1 V/SHE. Following the corrosion measurement only the TiN + C, Graphit-iC™ and 10 nm Au coatings met the ICR and corrosion US DoE targets of <10 mΩ cm^2 and <1 μAcm^{-2}. Potentiodynamic corrosion measurements of the applied coatings were carried out under the same conditions. The multilayer coating TiN + C showed improved corrosion resistance over single layer coatings of TiN and Graphit-iC™. Multilayer coatings and 10 nm Au coatings were identified as the best candidates for future research.

1. Introduction

The Polymer Electrolyte Membrane Fuel Cell (PEMFC) has been the focus of increasing attention due to growing environmental concerns associated with the combustion of fossil fuels. PEMFCs are capable of providing CO_2 emission-free energy in addition to having high power densities, low weight and compact size [1–4]. The bipolar plates are a multifunctional component, separating individual cells, acting as both the anode and cathode, collecting the electrical current from the fuel cells, removing heat and exhausting water which is transported away via the plates flow channels. Therefore, high interfacial electrical conductivities, corrosion resistance, mechanical strength, gas impermeability, and cost effectiveness are essential for their practical application [5,6]. Compared to graphite and composite plates, metallic bipolar plates (BPPs) for PEMFCs have many advantages due to their high strength, mechanical durability, electrical conductivity, and the minimum thicknesses resulting in weight and space savings essential for transport applications. Stainless steels have widely been researched as one of the leading bipolar plate material candidates [7–9]. However, surface engineering techniques are still required to inhibit their corrosion, and to ensure sufficient electrical functionality and adequate longevity in the aggressive electrochemical environment of the fuel cell. [2,10–12]. Thin film coatings offer the advantages of enhanced power density [kW/kg] as the mass of the coated plates is minimised, combined with easier thermal management and reduced packaging requirements, which are both especially attractive for automotive applications of PEM fuel cells. End of life considerations are also addressed by the potential for conventional re-use and ultimate recyclability of coated metallic plates.

In the literature, various physical vapour deposition (PVD) techniques have been used to deposit a range of coatings, including metal nitrides (TiN, TiAlN, CrN, and ZrN) [13,14], amorphous carbon [8] and very thin (nm) layers of Au [15] for metallic bipolar plates.

In this work TiN was selected for investigation as it is widely applied as a protective coating in the field of wear and corrosion protection [16–18]. Furthermore TiN coatings have metallic levels of electrical conductivity [19] and have been identified as a promising candidate for bipolar plate coatings [20]. A non-hydrogenated amorphous carbon coating (Graphit-iC™) [21,22] was also selected for investigation. Developed by Teer Coatings Ltd., UK, it exhibits both low friction, relevant to many engineering applications, and excellent corrosion resistance properties, and, in contrast to hydrogenated diamond-like carbon (DLC) coatings, it is electrically conductive, which is attributed to its relatively high levels of sp^2 carbon bonds. Multilayer PVD coatings have also been shown to have improved corrosion resistance over single layer coatings due to a reduced proportion of pinholes caused by the interruption of through-thickness defects [23]. Therefore a combination of a TiN and carbon coating to form a new composite, multilayer coating of TiN + C could be an effective way of improving corrosion resistance whilst maintaining a low ICR. This multilayer coating may also improve the process efficiency and economic viability by allowing thinner individual layers and therefore produce lower cost coatings for the protection of stainless steel BPPs in PEMFC. Finally, an Au coating was selected due to its excellent corrosion resistance and electrical conductivity. Although it has been historically considered to be too expensive, when deposited

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as a very thin (10 nm) film it has been suggested that only 5 g would be needed for an 80 kW stack [15], which begins to make this coating a potentially economically viable solution.

Closed field unbalanced magnetron sputter ion plating (CFUBMSIP) [24] produces dense, well adhered coatings, and both transition metal nitrides and graded, nano-composite, non-hydrogenated amorphous carbon coatings demonstrate the combination of properties required in this application. The quality of the coatings allows coating thickness to be minimised while still providing adequate functionality and longevity, and of course this is also critical to the minimisation of production costs. Ultimately this technology is compatible with low-cost manufacturing techniques similar to those already employed for serial production of many PVD coated automotive components.

Progress has been made towards the industrial production of CFUBMSIP-based coatings for the metallic BPPs, using high rate reactive magnetron sputtering, including an in-line, air-to-air, load-locked, multi-chamber coating system for future scale-up, for transition metal nitrides and carbon-based coatings. The characterisation of the coatings, in terms of their properties, relevant to the PEMFC application, is described in this study, and future developments are discussed.

2. Experimental details

2.1. Base BPP materials

All the AISI316L austenitic stainless steel foils used in the experiments were purchased from ADVENT Research Materials Ltd., UK, (Catalogue No. FE694618; Purity: Fe/Cr18/Ni10/Mo3), typical analysis (ppm) of this material is: C<300, Si<1%, Mn<2%, Ni 10–14%, Cr 16–18%, Mo 2–3%, S<300, P<450, Fe balance. The heat treatment condition for the foil was temper annealed. The AISI316L foil samples, all 0.1 mm thick, were cut into dimensions of approximately 100 mm × 100 mm. The foil surfaces were finished by the manufacturer in accordance with its standard, giving average 3D surface roughness (Sa) (ISO/DIS 25178-2 & ASME B46.1) of 0.0366 μm from 10 images at 100× magnification, as measured by an optical interferometer. The foils were cleaned with acetone and distilled water in an ultrasonic bath and dried before the PVD coating processes.

2.2. Coating design and parameters

All the coatings were deposited using a Teer UDP 650 Closed Field Unbalanced Magnetron Sputter Ion Plating (CFUBMSIP) system. This system enables coating deposition to be carried out using a high density of low energy bombarding ions, resulting in very dense, non-columnar coating structures with low internal stresses. Prior to coating, the BPP samples were ultrasonically cleaned in acetone for 15–20 min and then removed from the solvent and warm air dried or wiped dry with lint-free tissue. They were placed into the coating chamber which was then pumped down to a pressure of typically 2.7 to 4.7 Pa (2.0 to 3.5×10^{-5} torr). At the start of the coating process, argon gas was admitted, via a mass flow controller, typically operating in the range 15–25 sccm, allowing the chamber to reach a pressure between 0.107 Pa (8.0×10^{-4} torr) and 0.27 Pa (2.0×10^{-3} torr) depending on the coating required. The typical substrate temperatures reached during the deposition processes were in the 250°C to 300°C range and no auxiliary process heating was required.

The substrate for TiN coatings was first ion cleaned, applying a pulsed DC bias voltage of approximately −400 volts, and then reactively sputtered in a mixture of argon and nitrogen using four titanium rectangular magnetron targets (270 mm × 175 mm). During ion cleaning the magnetrons were all operated at 0.4 A, to intensify the ion cleaning plasma but without creating a significant coating flux, and this was increased to 6 A during the deposition phase, during which the pulsed DC bias was reduced to −60 V. The closed magnetic field arrangement is shown on Fig. 1. The coating compositions were controlled by the sputtering power applied to the Ti targets and the flow of the reactive gas (nitrogen) was controlled using an OEM (Optical Emission Monitor) control unit by monitoring the intensity of titanium optical emission line [25], i.e. the N_2 flow rate was automatically controlled to maintain a constant amplitude of the signal arising from the chosen emission line. Dynamic control of the reactive gas flow by monitoring the main metal emission line allows stable operation across a wide range of magnetron target conditions. The deposition time was varied to obtain coatings with total thickness in the range between 0.4 and 1.0 μm, verified by the subsequent ball crater taper section thickness measurements. It was also proven that similar TiN coatings could be reactively deposited in an industrial in-line, load-locked, air-to-air, twin deposition chamber coating equipment. Two pairs of magnetrons were directly opposed, in the closed-field configuration, across the rectangular deposition chamber, enabling an area of approximately 450 mm × 500 mm to be simultaneously coated from both sides. This equipment provides a route to future semi-continuous production for the coatings described here.

Two chromium targets and two graphite targets were used in the Graphit-iC™ coating process. The magnetic field arrangement was also shown in Fig. 1. During the process the sample was held at a bias voltage value of −350 V (i.e. an average voltage, achieved with pulsed DC bias) for the ion cleaning step, then −50 V for the deposition process steps. The ion cleaning step employed low magnetron target currents of 0.3 A on each Cr target and 0.2 A on each C target. A thin (approximately 100 nm) Cr metallic adhesion layer was then deposited with 4 A supplied to each of the Cr targets. A graded interface was created by reducing the current supplied to the Cr target(s) and increasing simultaneously the current supplied to the carbon targets, from 0.2 A to 3.5 A. The remaining bulk of the coating, extending to the surface, was then deposited and consisted of carbon, or carbon doped with <10 at.% metal (i.e. Cr).

TiN + C multilayer coatings were deposited in a single process using two titanium targets and 2 graphite (C) targets in the process, also shown in Fig. 1. During the process the samples were held at a bias voltage value between −400 V and −50 V, which was deliberately varied depending on the process step. The first step of the process was again ion cleaning with low target currents of 0.4 A on each Ti magnetron target. A thin (typically 100 nm) metallic Ti adhesion layer was then deposited with 4 to 7 A supplied to each Ti target. A TiN layer was created by introducing N_2 to the coating chamber, the flow of the reactive gas being controlled via the OEM system, described above, in order to achieve and maintain a required level of stoichiometry in the reactively deposited TiN coating. A thin intermediate TiN layer

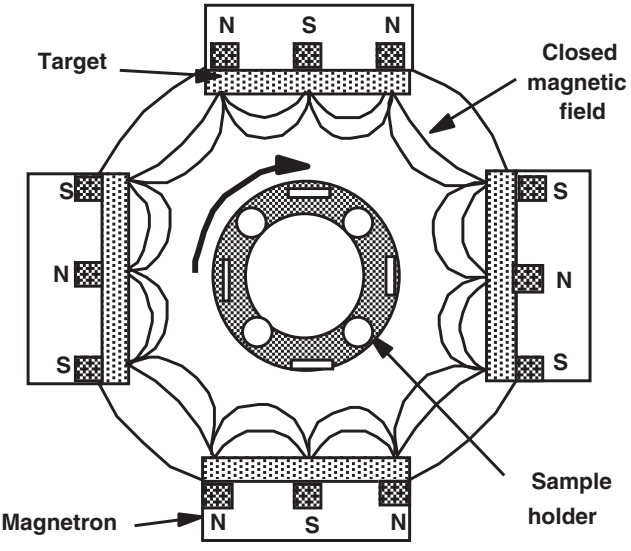

Fig. 1. Magnetron configuration of the PVD coating process.