Al-Cr-Mo Alloy Corrosion Resistant Coating For Bipolar Plates In Proton Exchange Membrane Fuel Cells

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Abstract:

The two main issues concerning large scale application of stainless steels as bipolar plates (BPP) in proton exchange membrane fuel cells (PEMFCs) are insufficient corrosion resistance and high interfacial contact resistance. In this study, an amorphous Al-Cr-Mo ternary alloy coating was developed on type316L SS using physical vapour deposition (PVD) DC magnetron sputtering technique in an attempt to increase its corrosion resistance. X-ray diffraction (XRD), scanning electron microscopy (SEM) and electrochemical techniques were used to characterize the Al-Cr-Mo coated on type 316L SS. XRD showed that Al-Cr- Mo coating was amorphous in nature. SEM images (cross section) showed its thickness to be around 3-4 μm. Electrochemical tests carried out in the simulated anode working environmentof 0.5M H_2SO_4 at 70°C (±2°C) and purged with N_2gas indicated that the current density of the Al-Cr-Mo coated sample was significantly lower thanthat of the bare type316L SS. Potentiostatic tests at -0.1V_{SCE} too showed a lower anodic current density for the coated stainless steel than that of the bare type 316L SS. Electrochemical impedance spectroscopy (EIS) study revealed about two orders of magnitude raise in polarisation resistance of the steel due to the coating. The above studies indicated that Al-Cr-Mo system can be a potential coating for bipolar plates inPEMFCs.

Keywords: BPP; PEMFC; corrosion resistance; coating; magnetron sputtering.

1. Introduction

Proton exchange membrane fuelcells (PEMFCs) have attracted great attention due to their conversion of hydrogen and oxygen into electrical energy, heat and water and high electrical energy efficiency with no pollutant emission. One of the most important components of PEMFC sare the bipolar plates(BPPs) [1-3]. The main purpose of the BPP is to evenly distribute the reactant gases, provide an electrically conductive pathway and facilitate water removal from the cell [4-7]. These BPPs have been fabricated traditionally from graphite due to their high chemical stability, corrosion resistance andelectrical conductivity. However, graphite BPPsare brittle, have poor mechanical properties and high manufacturing costs [8]. MetallicBPPs, in comparison are desired because of their good mechanical properties and high electrical conductivity [9,10]. However, the irpoor corrosion resistance in the humid and acidic environments of the fuel cell limits their application [11- 13]. Therefore, acorrosion resistant and conductive coating is necessary for the applicationof stainless steel in BPPs. Hence, in the present study, an attempt has been made to develop an Al-Cr-Mo amorphous alloy coating on type 316L SS by DC Magnetron sputtering for BPP applications and to evaluate its performance in simulated PEMFC operating conditions [14 15, 16].

2. Experimental

Type 316 LSS was chosen as the basematerial primarily because of its good corrosion resistance. The nominal chemical composition determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES)is shown in Table1.

The stainless steel samples were cut into the dimensions of 10 x 10 x 3 mm. They were polished

Table 1. Chemical composition of type 316L SS

Elements	Cr	Mo	Ni	Mn	C	Fe
Weight %	16.23	2.47	11.03	1.49	0.02	Balance

with Si Cabrasive paper starting from 220 upto 1200 grit size. They were then polished using artificial diamond pastes of 1and 0.5μm sizes. The polished samples were then ultra sonicated in acetone and distilled water to remove the grinding and polishing residues. Finally, the specimens were air dried before placing them in the DC sputtering vacuum chamber. The coating was deposited on polished stainless steel substrates by direct-current (DC)magnetron sputtering. The sputter target composed of an Al disk (99.95% purity) on which Cr (99.95% purity) and Mo (99.95% purity) disks were placed on the sputter erosion region. The sputter deposition was carried out at a working pressure of 2.2 x 10^{-2} mbar. For processing, high-purity Argas (99.99%) was used. For plas mageneration, a DC voltage with as puttering voltage of around -280 V and 0.45 A was applied to the cathode. Prior to deposition, the target was sputter-cleaned for 10 min in order to remove the surface oxides and impurities.The coated samples were examined by X-ray diffraction(XRD) PAN alytical X'pertPro machine (30 mA), operated at 40 kV with Cu-Ka radiation of the wavelength of 1.5406Å. After the coating process, the coatings were characterised via grazing incident X-ray diffraction (GIXRD) using monochromatic Cu-Ka radiation with a wavelength of 1.542 Å. The coated samples were examined by scanning electron microscopy (SEM) HITACHI S- 3400N-II.Energy-dispersive X-ray spectroscopy (EDS) analysis was carried out using Thermo Noran NSS-200.Potentiodynamic tests were carried out using deaerated 0.5M H_2SO_4 solution at 70°C to with ascan rate of 0.5 mV/sec to analyze the corrosion characteristics of both bare and coated type 316L SS. The electrochemical studies were conducted using a Gamry Potentiostat SN 05010 supported with Gamrysoftware.

3. Results anddiscussion

3.1. X-ray diffractionanalysis

Fig. 1shows the XRD traces for bare and Al-Cr-Mo coated type 316L SS. The XRD trace of bare type 316L SS shows the presence of an austenitic phase as expected. Even the coated one does not reveal any features of the coating, presumably because of the thin coating. So, GIXRD was performedat 1 degree and the same is shown in Fig. 1. The X-ray diffraction pattern of the Al-Cr-Mo coated stainless steel showed a broad peak between 25 to 35 degrees of 20, indicative of the amorphous nature of the coating, which could be one of the reasons, why the normal XRD pattern of the coated alloy did not reveal any additional features.

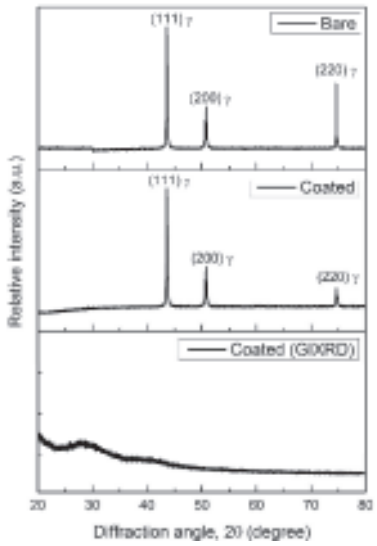
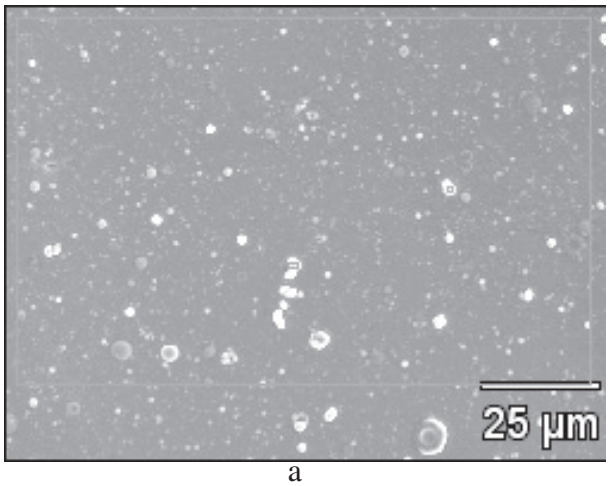


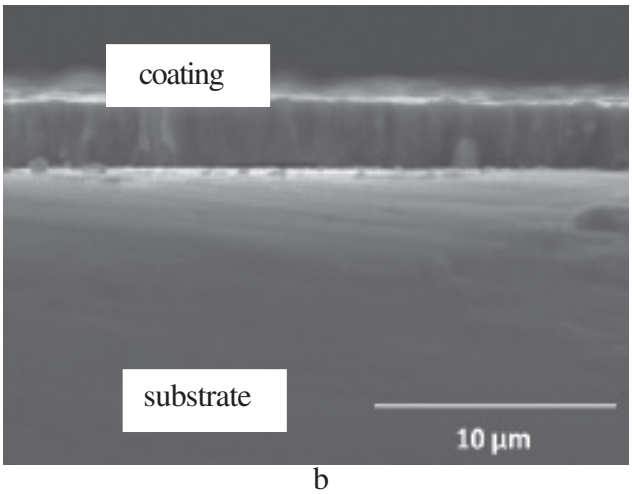
Figure 1: XRD traces for bare and coated type 316L SS (GIXRD was used for the coated sample)

3.2. Surfacemorphology

The surface morphology,locations of the chemical analysis and cross-section of the Al-Cr-Mo sputter deposited coatingobserved using SEM is shown in Figs. 2(a) and (b), respectively. The coating thickness was determined by cutting the sample by wire cutter.The coating revealed distinct tiny spots. Corresponding EDS values are summarized in Table 2.



a



b

Figure2: SEM micrographs (SE mode) of (a) longitudinal section and (b) transverse section of the coated sample

Assuming the deposition rate is constant during the deposition, the Al-Cr-Mo coating thickness is estimated to be about 3.5 µm. The thickness was achieved by carrying out the sputter deposition for around 1h.Based on the data provided in the Table 2, the chemical composition of the coating can be suggested to be Al-44Cr-11Mo.As seen from the table, not much variation in the chemical composition between these regions is seen. Hence,the occurrence of these tiny white spots could not be corroborated with the presence of any particular element in thealloy.

3.3. Potentiodynamicpolarization

Fig. 3 represents the potentiodynamic results for coated and bare type316L SS. The open circuit potential of the bare alloy is "0.3V_{SCE}, while that of the coated sample increased to -0.16V_{SCE}. Comparing the two curves, it can be said that the base 316L SS shows active, passive and transpassive regions in the anodic curve, indicating that spontaneous passivity is not possible in the fuel cell environment. However, the corrosion curve for coated specimen showed no visible active-passive transition region indicating a spontaneous passivation. The corrosion current density (i_{corr}) value of the bare sample was around 3 x 10^{-5} A.$cm^{-2}$and that of the coated sample was around 2 x10^{-7} A.cm^{-2}showing a two orders of magnitude increase in the corrosion resistance due to the coating. For a typical coating thickness of 3.5 µm, we can calculate that the life of the coating is around 3years i.e around 26000 hours.

Table 2. Alloy composition from EDS analysis

Sample	Al		Cr		Mo		Fe	
Area	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%
Point 1	44.08	25.92	44.74	50.71	11.18	23.37	-	-
Point 2	43.34	25.40	44.54	50.36	11.01	22.92	1.05	1.28
Point 3	44.82	26.47	43.99	50.05	11.19	23.48	-	-
Point 4	43.70	25.53	44.68	50.31	11.62	24.25	-	-

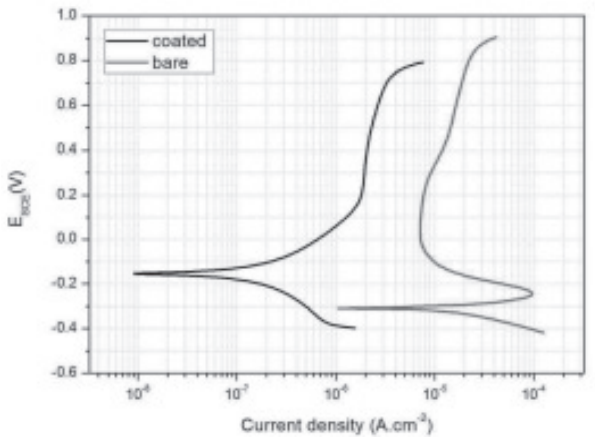


Figure3: Potentiodynamic polarization curves of baretype 316L SSand Al-Cr-Mo coated specimen in deaerated 0.5M H_2SO_4 solution at 70°C ± 2°C.

4. Conclusion

Al-44Cr-11Mo ternary alloy coating with a thickness about 3.5µm was developed ontype 316L SS through DC Magnetron sputtering. XRD analysis showed that the coating formed on the substrate was amorphous in nature. The corrosion resistance of the coating was evaluated in simulated PEMFC anode environments usingDC polarization and electrochemical impedance studies showed that the Al-44Cr-11Mo coated type 316L SS displayed two orders of higher corrosion resistance than that in the bare condition. The above studies indicate that Al-Cr-Mo system can be a potential coating for BPPs in PEMFCs. However, further studies to characterize the contact resistance are essential.

5. Acknowledgements

One of the authors Avinash Ingleexpresses his gratitude to Prof. D.S. Patil, Metallurgical Engineering and Materials Science Department, Indian Institute of Technology Bombay and former scientistat Bhabha Atomic Research Centre (B.A.R.C.) for hisassistance and showing keen interest in this work.

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