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Corrosion behavior of niobium coated 304 stainless steel in acid solution

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ABSTRACT

The niobium coating is fabricated on the surface of AISI Type 304 stainless steel (304SS) by using a high energy micro arc alloying technique in order to improvecorrosion resistance of the steel against acidic environments. The electrochemical corrosion resistance of the niobium coating in 0.7 M sulfuric acid solutions is evaluated by electrochemical impedance spectroscopy, potentiodynamic polarization and the open circuit potential versus time. Electrochemical measurements indicate that the niobium coating increases the free corrosion potential of the substrate by 110 mV and a reduction in the corrosion rate by two orders of magnitude compared to the substrate alone. The niobium coating maintains large impedance and effectively offers good protection for the substrate during the long-term exposure tests, which is mainly ascribed to the niobium coating acting inhibiting permeation of corrosive species. Finally, the corresponding electrochemical impedance models are proposed to elucidate the corrosion resistance behavior of the niobium coating in acid solutions.

1. Introduction

In recent years, more attention has focused on the use of niobium because its high level of resistance against attack of many chemicals was realized at a relatively low weight [1–3]. For example, niobium is used in the manufacture of crucibles for diamond growth and corrosion-resistant evaporation boats. Niobium is also used in implant materials due to its high level of biocompatibility and superior corrosion resistance [4–8]. However, niobium in pure form is mechanically weak. Alternatively, the corrosion resistance of niobium can be utilized without sacrificing overall component strength by using niobium coatings [8].

However, so far, only a few researches have been performed on the application of niobium coatings because niobium coatings cannot be easily produced by the conventional methods such as electroplating or cladding. Although the ion-beam assisted deposition was also applied to make dense and protective niobium coatings at room temperature [9], the performance of the niobium coatings mainly rely on the complexity deposition conditions. The niobium coating deposited by physical vapor deposition (PVD) consisted of columnar grains with open boundaries [10,11], which impaired the performance of coating. Currently, high energy micro arc alloying technique (HEMAA) is a simple and cost-effective technique to achieve pinhole free layer and a metallurgical combination between coating and alloy matrix, which is also proved by the reference [12]. The advantage of this technique over other surface coating technique such as thermal spraying and slurry, chemical vapor deposition (CVD) and physical vapor deposition (PVD) are the possibility of achieving a diffusion layer with a minimal thermal distortion and with a high resistance to spallation. Moreover, microcrystalline or amorphous structure easily obtained through this technique beneficially improves corrosion resistance of substrate. Therefore, in this study, the HEMAA technique is used to prepare niobium coatings on the surface of AISI type 304SS stainless steel to investigate its corrosion behavior in acidic environment.

Niobium generally hinders attack from water, aqueous solutions and all non-metallic substances in addition to fluorine because the surface of niobium is naturally covered with a dense niobium oxides layer. In general, niobium oxides mainly include NbO, NbO_2 and Nb_2O_5. NbO has usually a luster and excellent electrical conductivity. However, NbO is thermodynamically unstable in acid and neutral solution, and easily oxidized to a higher oxidation state.

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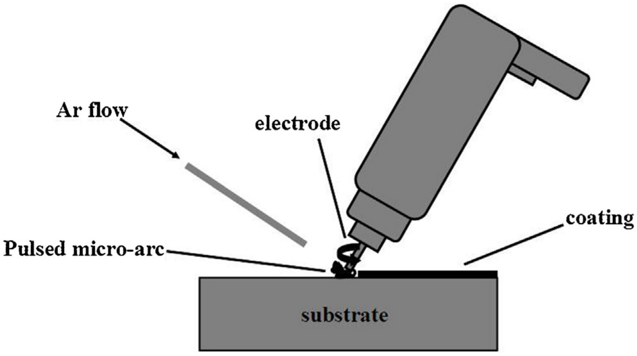

Fig. 1. A schematic diagram of highenergymicroarc alloying process.

Consequently, its corrosion resistance behavior of niobium mainly depends on the nature of the oxide layer and its stability in various conditions [13,14].

In the past few decades, many studies on corrosion of niobium have been conducted in HCl and H_2SO_4 solutions [15–19]. However, these researches mainly focused on test conditions, such as temperatures at or above the boiling point of the acid solution and solution concentration. The research reports rarely identify corrosion kinetic processes by using electrochemical methods even though corrosion reaction of niobium in acid solution is essentially the electrochemical reaction process. Therefore, it is necessary to use electrochemical techniques to reveal the corrosion process. Generally, electrochemical measurements include free-corrosion potential, cyclic voltammetry, scanning polarization, linear-polarization resistance and electrochemical impedance spectroscopy (EIS), wherein, EIS is a useful tool to elucidate the electrochemical reaction process during aqueous corrosion [20–22].

Therefore, in this study, the electrochemical corrosion performance of the niobium coatings produced by HEMAA technique is investigated to evaluate its suitability as a candidate coating for metallic bipolar plates of proton exchange membrane fuel cells (PEMFC). The corrosion behavior of the coating has been analyzed by electrochemical polarization and EIS tests in an acidic environment, which is to simulate the typical environment of PEMFC. Furthermore, the surface and cross-sectional morphology of the coatings were characterized using scanning electron microscopy (SEM) with energy dispersion spectroscopy (EDS), and the crystalline structure of the niobium layer was investigated through X-ray diffraction (XRD) to obtain a better understanding on the degradation mechanism of the niobium coated steel in the simulated PEMFC solution.

2. Experimental

The AISI Type 304 stainless steel was used as the substrate. The actual component for the AISI Type 304 stainless steel is as followed: 0.08C, 2.0Mn, 0.045P, 0.030S, 1.0Si, 19.90Cr, 10.00Ni, balance of Fe (at.%). The stainless steel were first cut into sheet-shaped samples, and then followed by the grinding with 1000-grit SiC paper and degreasing with acetone. In this study, the pure niobium rod was used as the electrode for the deposition of niobium coating. The schematic of the apparatus for producing Nb coating is shown in Fig. 1. During the deposition process, a succession of pluse discharge depositing operation under the conditions of low voltage and high frequency was conducted, at the same time, the substrate was kept by a strong jet of argon gas with goal to avoid oxidation of niobium. The resulting Nb coating exhibits high resistance to spallation owing to the metallurgical bonding between the coating and substrate.

Finally, the alloy specimens with and without niobium coating were embedded in epoxy resin with the exposed area of 1 cm^2 for the electrochemical measurement. The corrosion resistance of the niobium coatings was studied through potentiodynamic polarization curves and EIS tests. A conventional three-electrode system was used for the electrochemical measurements in the current study. A saturated calomel electrode (SCE) and high-purity (99.99 at.%) platinum sheet were used as the reference (RE) and counter electrodes, respectively. The above samples with 1 cm^2 exposed area were used as a working electrode (WE). The electrochemical behavior of all samples was measured in acid media corresponding to a 0.7 M H_2SO_4 solution at room temperature about 25 °C with a PAR 2273 Potentiostat/Galvanostat. Potentiodynamic polarization was undertaken with a potential scan rate of 10 mV/min after 0.5 h immersion in 0.7 M H_2SO_4 solution. During the acquisition of the open circuit potential (E_{OCP}) versus time, the samples were first kept in the solution for 0.5 h without any polarization while E_{OCP} was recorded. Three samples are selected as a group for each electrochemical examination. The electrochemical parameters such as corrosion potentials and corrosion current densities, Tafel coefficient are obtained by fitting each anodic and cathodic polarization curves. In order to ensure reliability of the data, each electrochemical parameter is taken from the mean value of three samples. After the specimen reached a stable E_{OCP}, electrochemical impedance tests were performed by applying a sinusoidal voltage of 5 mV at the frequencies range from 0.01 Hz to 100 kHz in the acid solution. In order to evaluate corrosion resistance and obtain the details about the surface state, the samples were analyzed before and after polarization and electrochemical impendence spectroscopy (EIS) tests by SEM and EDS. The XRD spectra were recorded in a typical Bragg-Brentano geometry with the sample on a horizontal plane.

3. Results and discussion

3.1. Characterization of niobium coating

Fig. 2 shows the typical surface and cross-sectional morphology of niobium coating deposited on the 304SS alloy through HEMAA technique. As can be observed in Fig. 2a, the surface morphology of the niobium coating exhibited the typical molten appearance, which was mainly associated with the characteristics of the HEMAA process. The dense and compact niobium coating was approximately 20 μm thick or less and almost free from pinholes and cracks (Fig. 2b). The metallurgical bonding was achieved between the coating and substrate and no obvious flaws were detected. The EDS analysis confirmed the presence of niobium coating on stainless steels. Fig. 3 further presented the XRD patterns for the niobium-coated alloy. It is observed that the (1 1 0) diffraction peak was the strongest, indicating the preferential orientation of niobium coating in the $\langle 1\,1\,0 \rangle$ direction.

3.2. Tafelpotentiodynamic polarization measurements

Fig. 4 shows the results for the potentiodynamic tests that were performed on the bare SS304 substrate and one with niobium coating in 0.7 M H_2SO_4 aqueous solution, respectively. Table 1 shows a summary of electrochemical parameters for the Tafel equations by fitting potentiodynamic curves. From the results, it can be concluded that the niobium coated 304SS substrates exhibited greater corrosion resistance than the bare steel based on the lower corrosion current density (I_{corr}) and higher values of corrosion potential (E_{corr}) observed for the niobium coating. Firstly, it can be observed that E_{corr} of the niobium coated 304SS increased by approximately 110 mV, compared to that of the bare substrate. In particular, I_{corr} of the niobium coated steel was lower than that of the bare alloys