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Study of the characteristics and corrosion behavior for the Zr-based metallic glass thin film fabricated by pulse magnetron sputtering process

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ABSTRACT

Two sets of source target which consist of ZrCuAlNiV and ZrTiAlNiV, respectively were selected as the target materials for preparing a series of thin film coatings on the 304 stainless steel substrate by DC pulse magnetron sputtering process. The microstructures of these as-prepared ZrCuAlNiV and ZrTiAlNiV thin films were examined by X-ray diffraction and TEM observation. In parallel, the characteristic analysis of these ZrCuAlNiV and ZrTiAlNiV alloy thin films including surface roughness, and corrosion resistance were analyzed by atomic force microscopy (AFM), and tested by electrochemical method as well as salt spray testing, respectively. The results showed that the ZrCuAlNiV thin film exhibits a typical amorphous microstructure and smooth surface with average roughness about 1 nm. The ZrCuAlNiV thin film performs similar corrosion resistance to 304 stainless steel according to the result of salt spray testing in 5% NaCl solution. Additionally, the AC impedance value of ZrCuAlNiV is 20 times than 316L stainless steel and 4 times than ZrTiAlNiV, implying that the ZrCuAlNiV thin film has better corrosion resistance than the others owing to its amorphous state.

1. Introduction

Currently, the graphite bi-polar plate is the major material for applying in the fuel cell world wide because of its high conductivity and better corrosion resistance. However, inherent from the weakness on mechanical strength and the flexibility of the graphite, the brittle crack of graphite bi-polar plate often occurs while in assembly and utilization. Therefore, the bi-polar plate with robust form would be favored for design applications. Besides, the high manufacturing cost of bi-polar plate based on the graphite raw material due to the time consuming process and low yielding rate (the unit price of producing bi-polar plate using graphite as raw material is over US$100/piece) directly affects the application development of the fuel cell. Industrial advanced nations actively engaged in this subject and invest in the research and development of manufacturing the high conductivity plastic carbon plate, carbon nano-tube, graphite bi-polar plate and metallic bi-polar plate. Among these bi-polar plates, the metallic bi-polar plate possesses the advantages of: (1) higher selectivity for alloy materials, lower cost, high chemical stability and better corrosion resistance, (2) high strength and thinability, and (3) better electrical and thermal conductivity, (4) availability for the mass production processes with low cost and high production rate such as stamping, embossing, rolling, etching, etc. The metallic bi-polar plate has been focused as preferable for research and development direction by advanced international organizations such as the NREL (National Renewable Energy Laboratory) of USA. However, beside the advantages which are being described above, there still exist some drawbacks for the metallic bi-polar plate to be applied on the full cell, including: (1) operation under severe corrosion environment, such as wet and damping conditions, electrical chemical reaction at 80 °C and pH 2–3, small amount of fluoride leaching from proton exchange membrane and the halides/SO_x/NO_x exist in the air, (2) the surface metal oxides possess excellent corrosion resistance. However, the contact resistance increased, and (3) the metal ions generated from corrosion contaminate the proton exchange membrane. Therefore, the development of surface treatment technologies for corrosion resistance and the selection of metallic bi-polar plate are equally important in the development of bi-polar plate.

Zr-based metallic glasses have been reported to exhibit good mechanical properties for engineering applications [1–7]. The tensile fracture strength, the Vickers hardness, and the density of the Zr-based metallic glasses can reach ultimate tensile strength about 1800 MPa, Hv of 500–600, and density of 5.9–6.7 Mg/m^3, respectively at room temperature [8,9]. In addition, the Zr-based metallic glass has good fracture toughness and impact fracture energy as well as the attractive corrosion resistance [10–12]. In this study, we approach with the 340 stainless steel, ZrAlCuNiV and ZrTiCuNiV amorphous films in examining their characteristics, which include the surface roughness, wetting

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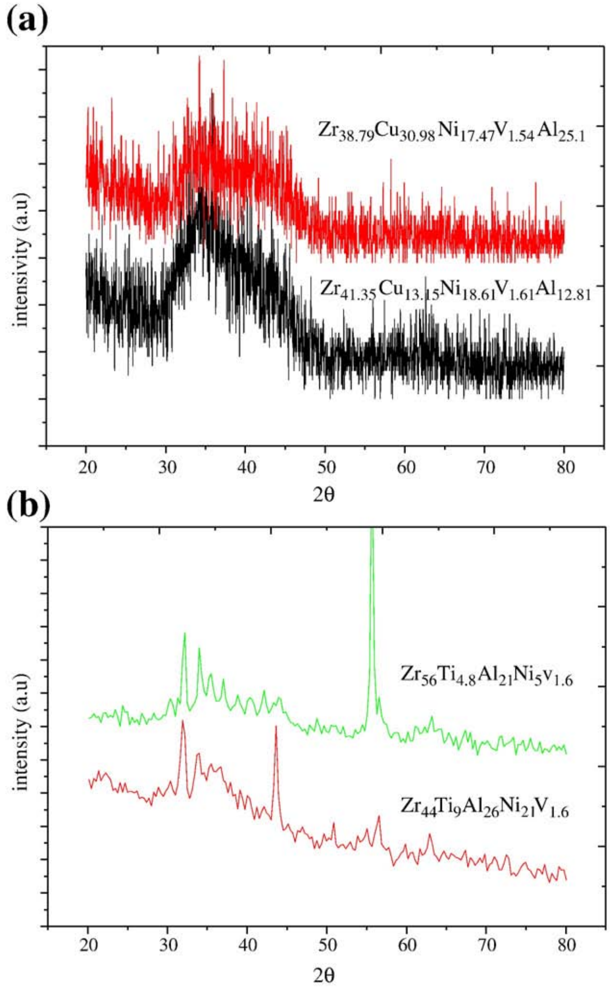

Fig. 1. X-ray diffraction patterns of the as-deposited ZrCuAlNiV and ZrTiAlNiV thin films.

ability and the corrosion resistance capability. The objective of this work was to study the electrochemical corrosion behaviors of the Zr-Base alloy thin films in the bi-polar plate of fuel cell.

2. Experimental details

The as-polished 304 stainless steel alloy plates with dimensions of 40 mm × 40 mm × 1 mm and surface roughness of 12.5 nm were used as the substrates for this study. ZrCuAlNi and ZrTiAlNi alloy thin films were deposited by means of the reactive DC plus magnetron sputtering (DC pulse could avoid the problems of the accumulation of the positive charges) method on the surface of the 304 stainless steel alloy substrate, respectively. The operating conditions for the DC plus magnetron sputtering system were set at a base pressure of 6×10^{-6} Torr, working pressure of 4 mTorr, argon (Ar) flow rate of 35 sccm, target to substrate distance of 6 cm, substrate temperature of 100 °C,thin film thickness of 0.5 mm, sputtering time of 30 min, respectively and varying the sputtering powers of 30 W. Microstructure analysis of the ZrCuAlNiV and ZrTiAlNiV thin films were examined by a Scintag X-4000 X-ray diffractometer (with Cu–Kα, $\lambda = 0.15402$ nm) and a FEI Tecni G^2 transmission electron microscopy (TEM) operated at 200 kV. The films were analyzed by scanning electron microcopy (SEM) using a Hitachi S-4700 scanning electron microscope with EDX. The surface morphology was analyzed by an atomic force microscope (AFM, Nanoscope E, Digital Instrument, USA). The capability of corrosion resistance for the bare and coated samples at 298 K was measured by salt spray testing method based on ASTM B117-07 specification. Salt spray test was done in 5% NaCl solution for 24 h. During test, the temperature was kept below 35 °C and with a PH value 7.1. The measurements for potential dynamic polarization were carried out in a 1 M H_2SO_4 solution, the ratio of H_2SO_4 solution volume to sample area was 400 ml/cm^2. After an initial delay for 1 h, scanning was conducted at a rate of 10 mV/min from −0.25 V versus open-circuit potential (OCP), in a more noble direction up to +0.25 V Three identical samples were used for each polarization curve measurement.

3. Results and discussions

Fig. 1 shows the X-Ray of diffraction pattern of ZrCuAlNiV and ZrTiAlNiV alloy deposited thin films ,respectively .There is no resolvable crystalline peak in the 2□ range of 20°–80°, but only a broad diffuse peak is observed in the range of 30°–50° for the ZrCuAlNiV thin film. This

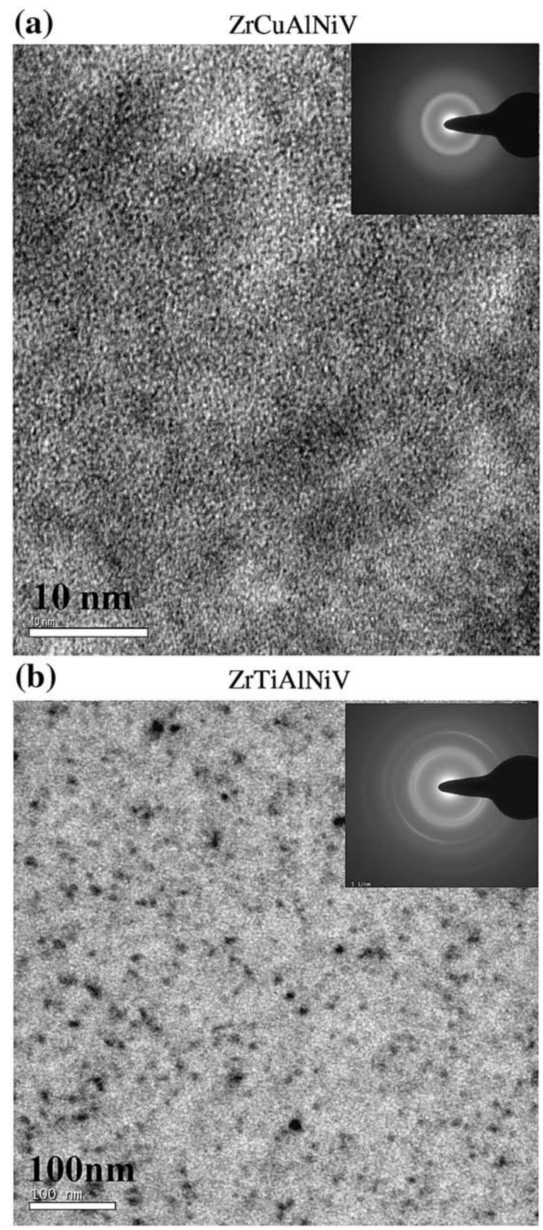

Fig. 2. Bright field TEM images with selected area diffraction pattern of the (a) ZrCuAlNiV, (b) ZrTiAlNi V thin films.