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Relationship between amorphous structure and corrosion behaviour in a Zr–Ni metallic glass

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ABSTRACT

The effect of amorphous structure on corrosion is a long-term puzzling problem. To elucidate this relationship, a Zr_2Ni metallic glass and its single crystal counterpart were selected, in which they are both homogeneous in composition and structure. The corrosion behaviour has been evaluated in 0.1 M NaCl aqueous solution. Compared with the single crystal, the amorphous alloy presents a higher corrosion resistance. The passive film formed on the amorphous alloy contains more ZrO_2 and less NiO content. These results reflect that the amorphous structure could effectively influence the composition and compactability of passive films.

1. Introduction

Since the discovery of the extremely high corrosion resistance of the Fe–Cr-metalloid amorphous alloy in 1974 [1], the corrosion behaviour of metallic glasses has been investigated extensively, and a number of amorphous alloys with excellent corrosion resistance have been reported, e.g. Zr- [2], Fe- [3], Ti- [4], Ni-based [5] systems. The high corrosion resistance of metallic glasses is often attributed to their componential and structural homogeneity, as well as their abilities to form supersaturated solid solutions with substantial beneficial alloying elements, since the metallic glasses are prepared at an extremely rapid quench rate [6].

It is well known that the chemical composition plays an important role in the corrosion behaviour of metallic glasses [5,7]. However, how the amorphous structure affects the corrosion behaviour of alloys is a long-term puzzling problem. It is recognised that unlike crystal alloys, metallic glasses present unique structural characteristics without long-range periodic lattice. This structural variation in atom scale could theoretically induce even larger changes in their electrochemical properties [6]. To reveal the influence of this structure on the corrosion behaviour of alloys, a series of work have been performed in different metallic glass systems by comparing the corrosion behaviour between amorphous alloys and their crystallised counterparts after heat treatment. There exist various competing results in different alloy systems. Compared with amorphous samples, crystallised alloys exhibited decreased corrosion resistance in ZrCuNiTiAl [8], AlFeGd and AlNiY alloys [9], however, no distinct differences were presented in FeSiB [10] and ZrTiCuNiBe alloys [11]. Further, for ZrCr [12] and FeCuNbSiB [13] alloys, even the crystallised samples held much better corrosion resistance due to the precipitation of nanoscale phases enriched high corrosion elements.

From the above controversial results, it seems that the amorphous alloys with homogeneous and defect-free microstructure do not always present higher corrosion resistance than their crystallised samples. Although the intrinsic reason still remains ambiguous, its most possibility is related to the composite effects of compositional and structural variations rather than only the single structure role. It is noted that for most of multi-component metallic glasses, there exist the compositional redistribution and the precipitation of various phases during the crystallisation. Some studies have further proved that the differences of the kind, size, and distribution of those phases could cause different effects on the corrosion behaviour [12,14,15]. So it is difficult to change the structure independent of composition in most metallic glass systems.

To clarify the correlation between amorphous structure and corrosion, the key is to separate the structural effect from the compositional effect. Recently, Wang et al. conducted a detailed study on the corrosion behaviour of a $Ni_{50}Nb_{50}$ metallic glass, which can transform to its crystalline state *via* polycrystallisation without compositional redistribution. Noble effects of amorphous structure on the inhibition of pit initiation and early growth stage of pits were determined, however, no differences could be discerned from passive regions in polarisation curves between the amorphous and nanocrystalline samples [16,17]. After irradiating a nickel single crystal with Ni ions, Trzebiatowski et al. obtained highly defected samples towards an amorphous structure and made a comparison

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in the corrosion behaviour between the single crystal and irradiated samples [18]. From these results, it should be noted that the selected nanocrystalline $Ni_{50}Nb_{50}$ samples locate metastable state rather than crystallographic equilibrium state; on the other hand, the irradiated Ni samples are not ideal amorphous structure. Thus, an in-depth understanding of the correlation between amorphous structure and corrosion needs both an ideal amorphous sample and a much more equilibrium crystal sample.

In the present study, an attempt has been strived to understand the role of the amorphous structure on the corrosion behaviour. A Zr_2Ni metallic glass was selected as a model system. The most important reason for the selection is that the Zr_2Ni alloy can be prepared in the form of both amorphous structure and single crystal. The equilibrium state of the single crystal also has a componential and structural homogeneity without grain boundaries and second phase particles. Consequently, from the angle of the homogeneity of composition and structure, the Zr_2Ni alloy is an ideal system to reveal the structural effects on corrosion separating from a chemical composition factor. Furthermore, the high corrosion resistance of the binary Zr_2Ni alloy is beneficial to understanding the corrosion mechanism. To elucidate the relationship between the amorphous structure and corrosion behaviour, electrochemical properties of the amorphous alloy, single crystal as well as nanocrystallised samples were evaluated in 0.1 M NaCl aqueous solution. XPS analysis was performed for a better understanding of the passive films.

2. Experimental

The Zr_2Ni (at.%) master alloy ingots were prepared by arc-melting the mixture of nickel and zirconium under a Ti-gettered argon atmosphere (Ni: 99.96%, Zr: 99.8%). The ingots were inducting-remelted in a quartz crucible under an argon atmosphere, and then the amorphous Zr_2Ni ribbons with a cross section about 2.0 mm $\times$ 0.04 mm were prepared by ejecting the melting onto a copper wheel with a rotating speed of 40 m/s. Crystallised samples were produced by annealing the amorphous ribbons encapsulated in a quartz crucible with vacuum of 10^{-4} Pa, at the temperature of 703 K for 30 min. The temperature for heat treatment was chosen from the differential scanning calorimeter (DSC). The single crystal specimens were produced in an optical floating-zone furnace (FZ-T-12000-X-VP-S, Crystal System Inc.) under the protection of flowing argon, with a growth rate of 20 mm/h and a shaft rotating rate of 15 r/min. Before the single crystal growth, the master alloy ingots were cast into cylindrical specimens about 9 mm in diameter and 60 mm in length. A single crystal Ni-based superalloy about 9 mm in diameter was prepared for the seed-crystal rod. All samples were examined by X-ray diffraction (XRD) using a Rigaku D/max 2400 diffractometer (Tokyo, Japan) with monochromated Cu-Kα radiation (λ = 0.1542 nm). The thermal stability of the amorphous ribbons was analysed in a Neztsch DSC 404C at a heating rate of 0.33 K/s under a flowing argon atmosphere. The microstructures of the samples were confirmed using a JEOL JEM-2010/2100 transmission electron microscope (TEM), operated at 200 kV. Thin foils were prepared by a standard twin-jet electropolishing using an electrolyte of methanol (70 vol.%) and nitric acid (30 vol.%), at the temperature of 243 K. Surface morphologies of the samples before and after polarisation were characterised by scanning electron microscopy (SEM) (JMS-6301).

Prior to electrochemical measurements, all kinds of samples were ground with 2000-grit SiC papers, followed by ethanol and distilled water ultrasonic clearing. The undesired dull sides of the ribbons were sealed by a mixture of paraffin and colophony. As for the single crystal, the samples connected to a copper wire were wrapped with resin, leaving an exposed working area. In electrochemical experiments, a conventional three-electrode cell was employed, using a platinum plate as the counter electrode and a saturated calomel reference electrode (SCE). All electrochemical measurements were conducted using a PAR2273 Electrochemical Measurement System (EG&G Princeton Applied Research). Potentiodynamic polarisation curves were measured with a potential sweep rate of 0.33 mV_{SCE}/s in 0.1 M NaCl aqueous solution after immersing the samples for about 30 min, when the open-circuit potential almost reached a steady state. Electrochemical impedance spectroscopy (EIS) measurements were conducted in the frequency range of 10 kHz to 10 mHz, with a sinusoidal potential perturbation of ±10 mV_{SCE}. EIS results were calculated based on a suitable fitting of an equivalent circuit using Z-view software. The Mott–Schottky plots were carried out with a step rate of 10 mV_{SCE} at the frequency of 1 kHz. Prior to the measurement of EIS curves and Mott–Schottky plots, the electrodes were polarised at -150 mV_{SCE} for 10,000 s in 0.1 M NaCl aqueous solution to form stable passive films. All the potentials mentioned in this work were all referred to SCE. Each electrochemical measurement was tested at least five times for repeatability. Only typical curves from an average of all measurements are presented in results.

Surface films of samples after mechanical polishing and 24 h immersing in 0.1 M NaCl aqueous solution were analysed by X-ray photoelectron spectroscopy (XPS), using an ESCALAB250 photoelectron spectrometer with Al-Kα ($h\nu$ = 1486.6 eV) radiation. Depth profiles of metal elements in the alloy surface were achieved by *in situ* argon ions beam sputtering with ion energy of 2 kV, at a sputtering rate of about 0.2 nm/s by adjusting the spot area. The standard binding energy of zirconium, nickel, oxygen, chlorine core levels were according to NIST XPS database. Deconvolution of the peaks was done using XPS peak 4.1 software with Newton's iteration method and quantitative information was calculated from the survey spectra using standard Scofield sensitivity factors [14].

3. Results

3.1. Structure characterisation

Fig. 1 presents the XRD patterns of the as-prepared Zr_2Ni binary alloys. The appearance of a broad halo at the angle of $2\theta = 36^\circ$ and the absence of any diffraction peaks associated with crystalline phases indicate that the amorphous structure formed in the as-quenched Zr_2Ni ribbons (see Fig. 1a). Upon heating, there exhibits only one exothermic reaction at the temperature of 669 K in the DSC curve (inset in Fig. 1a). XRD pattern of the as-crystallised ribbons in Fig. 1b reflects that only Zr_2Ni intermetallics precipitated. For the as-prepared single crystal Zr_2Ni rod, only one group of planes (002) and (004) were detected by XRD as shown in Fig. 1c, and no additional peaks were presented in the scanned range. Furthermore, the fully amorphous structure was identified in the as-quenched ribbons by a high-resolution transmission electronic microscopy (HRTEM) and selected area electron diffraction (SAED) in Fig. 2a. For the crystallised ribbons, as shown in Fig. 2b, there exhibit an average grain size of 20–30 nm and no residual amorphous regions. High magnification of the as-cast rod is shown in Fig. 2c by HRTEM, indicating its uniform structure. The corresponding SAED pattern exhibiting only one set of diffraction spots demonstrates the single crystalline nature of the as-cast rod.

3.2. Potentiodynamic polarisation

Fig. 3 shows the typical potentiodynamic polarisation curves for the Zr_2Ni ribbons and rod samples in 0.1 M NaCl aqueous solution. The corrosion current densities (i_{corr}) were derived approximately using Tafel extrapolation method by linear fitting of strong polarised zone (i.e. the potential is above ±100 mV_{SCE} from the