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Full Length Article

Composition-controlled active-passive transition and corrosion behavior of Fe-Cr(Mo)-Zr-B bulk amorphous steels

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ABSTRACT

Various corrosive environments in daily life and industry have put forward high requirement on corrosion resistance of metals, especially steels. Unlike the strict demand in Cr content of crystalline stainless steels, amorphous steels (ASs) with lower Cr content can be endowed with outstanding corrosion resistance, while the intrinsic mechanism is not fully understood. Herein, we present a novel $Fe_{92-x-y-z}Cr_xMo_yZr_8B_z$ ($6 \le x \le 40$, $0 \le y \le 22$, and $12 \le z \le 18$) bulk amorphous steel (BAS) forming system and reveal the synergistic effect of Cr and Mo in determining the chemical stability of oxide films. It has been found the $Fe_{92-x-z}Cr_xZr_8B_z$ BASs with 1 mm in diameter display a Cr-controlling active-passive transition at the Cr threshold of ~25% in 1 M hydrochloric acid. When adding minor Mo into the BASs, the Cr threshold can be remarkably reduced by forming favorable hexavalent Mo oxides. The generation of Mo^{6+} is facilitated by atomic selective dissolution at the interface and can promote the passivation. In contrast, when the Cr content of the Mo-doped glasses exceeds 25%, few Mo^{6+} oxides would produce as the prior formation of protective passive films inhibits the further oxidation of Mo. Therefore, manipulating the active-passive transition properly is crucial to designing ASs with high stainlessness.

1. Introduction

It is well documented that economic losses caused by corrosion of metallic materials are enormous [1–3]. Exploring new metallic materials with high corrosion resistance has been important topics for a long term [4–7]. Limited by the drawbacks of crystalline structure, conventional metallic materials are susceptible to corrosion in a variety of environments [8–11]. In contrast, metallic glasses (MGs) containing elements with high electronegativity or passivation property can exhibit superior corrosion resistance owing to the random disordering in long-range and grain-boundary free structure [12–15]. Chromium, the widely used corrosion-resistant element in crystalline alloys, was also expected to play a role in amorphous alloys [16–19]. Of the numerous MGs developed to date, Cr-bearing amorphous steels (ASs) are of special interest due to their outstanding corrosion resistance and low cost [15,20–24]. Therefore, the early developed Fe-Cr-Mo-C-B based bulk amorphous steels (BASs) have drawn great attention as they possess not only excellent corrosion resistance but also high glass forming ability (GFA) and superior mechanical properties [25–27]. This kind of BASs can be used as anticorrosion instruments [28], or protective coatings on conventional steels [29,30]. Moreover, ASs with high B content have been considered as promising neutron absorbers for absorbing thermal neutrons in nuclear industry [31,32]. In view of the advantages in cost and superior properties of Cr-bearing ASs, it is of great importance to further develop Cr-bearing ASs with high GFA.

In metastable Cr-bearing MGs, Cr has strong affinity to oxygen and high chemical stability in oxidized state [26,33,34]. Thus the formation of homogeneous and protective Cr-oxide films in spontaneous passivation process is responsible for the high corrosion resistance [15,16]. In crystalline Fe-Cr alloys, 13% (mass fraction) or more Cr is required to ensure the fine corrosion resistance [35,36], which is owing to the sudden increase in chemical stability; while ASs are able to form more protective oxide films even they contain less Cr [16,20]. Commonly, the low Cr threshold is considered to be attributed to the formation of homogeneous and compact amorphous Cr-oxide films, which are expected to have high chemical stability [15,33,34]. However, it was also found that ASs with identical Cr content but different compositions might exhibit much different corrosion properties in acid solutions [23,37]. Comparing with Fe-Cr alloys, the compositions of Cr-bearing ASs, especially BASs, are much more complex, so their

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corrosion-resistance dependence on composition has not been fully studied and understood. And technically, it is difficult to prepare a single crystal or a single-phase crystalline alloy with the composition of certain Cr-bearing AS, thus the Cr threshold of crystalline stainless steels may be confined by compositions. In this regard, it is imperative to investigate the dependence of Cr threshold on multiple components and explore the nature of the super stainlessness for Cr-bearing ASs.

In this paper, we present a new Fe-Cr-Mo-Zr-B BAS forming system and study the corrosion-resistance dependence on Cr and Mo in HCl solutions. It was found that minor change in composition could lead to huge variation in corrosion resistance for the BASs. Furthermore, we revealed a specific phenomenon about the synergistic chemical effect of Cr and Mo in ensuring the stainlessness of BASs through the characterization of oxide films.

2. Experimental section

2.1. Glass preparation and examination

Alloy ingots were prepared by arc melting pure Fe (99.8%), Cr (99.9%), Zr (99.95%), and ferroboron (impurities <0.7%) alloy, ferromolybdenum (impurities <0.8%) alloy in a Ti-gettered pure argon atmosphere. Bulk alloy samples in rod form were prepared by copper-mold suction casting method. The amorphous nature of the as-cast alloys with critical diameters was ascertained by X-ray diffraction (XRD) examinations and differential scanning calorimetry (DSC) tests at a heating rate of 20 K min^{-1}. The TEM images of representative $Fe_{57}Cr_{10}Mo_7Zr_8B_{18}$ BAS were taken from a sample cut from 3-mm-diameter rod.

2.2. Electrochemical measurements

$Fe_{92-x-y-z}Cr_xMo_yZr_8B_z$ BASs with 1 mm in diameter were used to evaluate the corrosion properties in 1 M HCl. The electrolytes were prepared from reagent grade chemical and distilled water. The electrochemical measurements were conducted in a three-electrode cell using a platinum counter electrode and a saturated calomel electrode (SCE). The anodic polarization curves were measured with a potential sweep rate of 60 mV min^{-1} scanning from open circuit potential at 298 K. Prior to electrochemical measurements, the specimen ends were ground through successive grades of SiC papers up to 2000 grade, polished using 2 μm diamond suspension, ultrasonically cleaned in deionized water, dried and exposed in air for 24 h. The specimens were tested after they were stabilized in 1 M HCl for 30 min. The electrochemical measurements were performed at least twice for each specimen to confirm reproducibility.

2.3. Immersion tests

The cylindrical $Fe_{92-x-y-z}Cr_xMo_yZr_8B_z$ specimens with 1 mm in diameter for weight-loss tests were cut into about 8 mm in length. Prior to the immersion tests, the specimen ends were ground through successive grades of SiC papers up to 5000 grade. Then the specimens were ultrasonically cleaned in deionized water, ultrasonically degreased in acetone, dried and exposed in air for 24 h. After immersion tests, the amorphous rods were first ultrasonically cleaned in deionized water for 5 min, ultrasonically degreased in acetone for 5 min to wash off possible oxide products, then dried in air. Due to the decrease in mold-filling capacity in casting processes when increasing Mo content in the alloys, glassy rods with length larger than 5 mm were difficult to be prepared by using Cu-mold casting method, amorphous ribbons were used to measure the corrosion rates in 12 M HCl. The ribbons of 30–50 μm thick and 1.5–3 mm wide were prepared by single-roller melt spinning. The weights of the specimens were measured using an analytical balance in a DSC (Netzsch STA 449C) with a reliable precision of 1 μg. All the specimens were immersed in 10 milliliters corrosive solutions in glass tubes with cocks. And the corrosion rate for each MG was estimated by the weight loss and immersion time, averaged from three tests in HCl solutions open to air at 298 K for 168 h. The 316L SS ($Fe_{67.5}Ni_{10.5}Cr_{18}Mo_{1.5}Mn_{1.5}(Si,C)_1$, at.%) and Hastelloy C-22 ($Ni_{61.4}Cr_{25.5}Mo_9W_{1.1}Fe_3$, at.%) rods were prepared by copper-casting method using commercial alloys. Scanning electron microscopy (SEM) was employed to examine the morphological features of BAS samples.

2.4. X-ray photoelectron spectroscopy (XPS) analysis

XPS tests were performed using a photoelectron spectrometer with Al-$K\alpha$ excitation ($h\nu$ = 1486.8 eV). The air-exposed $Fe_{92-x-y-z}Cr_xMo_yZr_8B_z$ specimens were exposed in air for at least 24 h after sample preparation. The immersed samples in weight-loss tests were used to detect components of oxide films. Two groups of samples were detected to ensure repeatability. Photoelectron signal collecting areas were chose at the lateral faces of the cylindrical specimens. The binding energies were calibrated by using carbon contamination with C 1 s peak value of 284.8 eV.

3. Results and discussion

3.1. Glass formation in Fe-Cr(Mo)-Zr-B system

The $Fe_{92-x-y-z}Cr_xMo_yZr_8B_z$ (the contents are in atomic percentage in the following context) ASs were designed based on ternary Fe-Cr-B system near the eutectic points [38]. Although it has been reported that Fe-Cr-B can form glasses, the GFA is known to be marginal [22–24]. In this work we find that, by adding Mo and Zr, the BASs with high GFA can be achieved, as displayed by the contour map shown in Fig. 1a. The map with composition variation along 2 dimensions, x and y, was constructed on the basis of more than 130 alloys. The inset shows the dependence of B content (z) on Cr content (x), and the optimal B content shows obvious downtrend with the increase of Cr content. The B content was set at the optimal value in terms of optimal GFA *via* experimental method when Cr content was fixed. Representative XRD pattern for the $Fe_{57}Cr_{10}Mo_7Zr_8B_{18}$ alloy within the contour map is shown in Fig. 1b. The pattern exhibits typical amorphous halo hump without visible crystal diffraction peak, indicating the disordered atomic structure of the alloys. The amorphous structure was further confirmed by transmission electron microscope (TEM) characterizations (Fig. 1c). The clear glass transition in the DSC curve in Fig. 1d demonstrates the glassy nature. As displayed in Fig. 1a, ASs in bulk form can be obtained over an extensive composition range, *i.e.*, 6–40% for Cr, 0–22% for Mo, and 12–18% for B. The best GFA can be achieved in the range of 7–11% for Cr, 4–12% for Mo, and 16–18% for B. It can also be seen from the contour map that GFA decreases more rapidly at the lower-left corner, indicating that glass formation in the $Fe_{92-x-y-z}Cr_xMo_yZr_8B_z$ system is sensitive to Cr and Mo contents, especially when the Cr content is less that 6%.

3.2. Corrosion behavior in HCl solutions

The corrosion properties of $Fe_{92-x-y-z}Cr_xMo_yZr_8B_z$ BASs were investigated using HCl solutions. The alloys are denoted by C*x*M*y* in the following context for convenience according to the Cr and Mo contents. Cr content determines the B content (see Fig. 1a) so that Mo content can be calculated, *e.g.*, C10M0 stands for $Fe_{64}Cr_{10}Zr_8B_{18}$. In order to understand the relation between corrosion