



Improving corrosion resistance of nickel-aluminum bronzes by surface modification with chromium ion implantation



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ABSTRACT

As-cast nickel-aluminum bronze is prone to suffering selective phase corrosion in marine environments. To solve this problem, chromium was introduced via ion implantation to modify its surface microstructure, which was characterized by high-resolution transmission electron microscopy and auger electron spectroscopy. The corrosion behavior was studied by electrochemical measurements and salt spray test. It was found that the inherent selective phase corrosion in as-cast NAB was inhibited effectively when the implantation fluence was 5×10^{17} ions/cm². The improved corrosion resistance after ion implantation was believed to stem from the rapid formation of a more protective film containing chromium oxides and hydroxides.

1. Introduction

Nickel-aluminum bronze (NAB) is copper–aluminum alloy with addition of nickel and iron elements. It is widely used as pipes, valves, and pump casings in marine environments, due to the excellent combination of mechanical properties, corrosion resistance, and biofouling resistance [1–4]. This alloy exhibits an inhomogeneous microstructure in as-cast condition, containing a coarse Cu-rich α phase, retained martensitic β' phase, and four intermetallic κ phases (named κ_I through κ_{IV}) distinguished by their morphologies [5,6]. Due to the disparity in chemical composition and crystal structure, the relative nobility of each phase in corrosion medium is different from others [7,8]. Published reports have shown that β' phase and α phase at boundaries with κ precipitates were preferentially corroded in seawater environments [2,9,10]. This kind of selective phase corrosion degenerates the corrosion properties and affects the integrity of NAB alloys [11].

Considerable methods have been investigated to improve the corrosion resistance of as-cast NAB alloy. Heat treatment was adopted to homogenize the microstructure by reducing the preferential corroded β' phase [12], but it can only eliminate β' phase partly, and the inherent susceptibility to selective phase corrosion was still inevitable. Friction-stir processing reduced static immersion corrosion rate for the refined the microstructure [13–15]. However, this method introduced large residual stress and presented a decreased electrochemical corrosion resistance [16].

The microstructure and corrosion behavior of NAB alloys are highly related to the composition [17,18]. Adjusting alloying elements in cast NAB alloy can alter its microstructure and the resulting properties [19]. Previous researches have shown that increasing nickel content would improve the hardness and enhance the corrosion resistance [3,20]. Besides, adding molybdenum in NAB alloy could refine the microstructure and increase the hardness [21]. It is well known that the chromium is a beneficial alloy element for corrosion resistance. However, Cu-Cr solid solutions containing more than 1 at.% Cr cannot be manufactured by conventional metallurgical methods [22], due to their disparity in crystal structure. It is generally accepted that the corrosion behavior is mainly attributed to the surface properties, which can be modified by surface treatment technique, such as magnetron co-sputtering [23–25], chemical vapor deposition [26], and ion implantation [27]. Ion implantation is widely used to introduce different elements into the surface of materials without thermodynamic limitations pertaining to solubility and phase diagrams. It is reported that Cr ion implantation can improve the corrosion resistance of nickel [28,29] and stainless steel [30], and have beneficial effects on the localized corrosion resistance of aluminum alloy [31,32]. However, no work has been published on the effect of chromium implantation in NAB alloys.

The aim of this paper is to improve the corrosion behavior of the NAB alloy via Cr implantation. The composition and structure of the implanted layer were characterized by auger electron spectroscopy (AES), glancing angle X-ray diffraction (GAXRD) and high-resolution

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Table 1
Chemical composition of the as-cast NAB alloy.

Element	Al	Ni	Fe	Mn	Cu
Mass (wt%)	9.5	4.2	4.0	1.2	Bal.

transmission electron microscopy (HR-TEM). Electrochemical measurements and salt spray tests were used to investigate the influence of Cr implantation on the corrosion behaviors. In addition, the composition of corrosion product film formed in salt spray environment was also analyzed to study the corrosion mechanism.

2. Experimental

2.1. Materials and ion implantation treatment

A NAB cast ingot was cut into samples with a dimension of 20 mm by 20 mm by 3 mm, and polished to mirror-grade using 1 μm diamond paste. The chemical composition was determined by X-ray fluorescence spectrum, and the result is given in Table 1. After being ultrasonically cleaned in acetone and dried with a cold air blaster, the specimens were loaded onto a sample holder of a MEVVA (metal vapor vacuum arc) implanter. The vacuum level of the implantation chamber was 1.3×10^{-3} Pa, and the extracted voltage was 40 kV. Samples were Cr implanted with the influence of 1×10^{16} , 1×10^{17} , and 5×10^{17} ions/cm², named as Cr-1, Cr-2, and Cr-3, respectively. The implantation parameters are summarized in Table 2.

2.2. Surface characterization

Auger electron spectroscopy (AES, PHI-700) was employed to examine surface composition and depth profile of the implanted layer. The surface microstructure was characterized by high-resolution transmission electron microscopy (HR-TEM) performed on JEOL 2100F operated at 200 kV. Phase composition analysis of the implanted layer was conducted by glancing angle X-ray diffraction (GAXRD). The incidence angle was set as 0.5°, so that the penetration depth of X-ray was about 26 nm to investigate the top surface structure [19].

2.3. Electrochemical techniques

Electrochemical measurements were carried out through a CHI 660E electrochemical system in a neutral 3.5 wt% NaCl solution at 25 °C, with a platinum plate and a saturated calomel electrode (SCE) served as the counter electrode and reference electrode. Samples were sealed by paraffin, leaving an area of 1 cm² exposed. Then they were immersed in the NaCl solution for 4000 s to attain a steady open circuit potential (E_{OCP}). Electrochemical impedance spectroscopy (EIS) measurements were carried out at E_{OCP} in the frequency ranging from 10 MHz to 100 kHz with a sinusoidal voltage excitation of 5 mV amplitude. Afterwards, linear potentiodynamic sweep was performed in the range of ± 5 mV_{OCP} at a rate of 0.33 mV/s to determine the polarization resistance (R_p). Subsequently, potentiodynamic polarization curves were measured at a rate of 0.5 mV/s to obtain the anodic and cathodic Tafel slopes (b_a and b_c , respectively). Then corrosion current density (i_{corr}) was calculated by the Stern-Geary relation [33].

Table 2
Processing parameters for Cr ion implantation.

Samples	Beam current density (mA)	Fluence (ions cm ⁻²)	Temperature (°C)
Cr-1	1	1×10^{16}	100
Cr-2	3	1×10^{17}	240
Cr-3	3	5×10^{17}	240

$$i_{corr} = \frac{b_a b_c}{2.303 \times R_p (b_c - b_a)} \quad (1)$$

All of the electrochemical measurements have been repeated for least three times to ensure the reliability of the testing data.

2.4. Salt spray test

Salt spray tests were carried out to evaluate the corrosion resistance of as-cast and Cr implanted NAB alloys, following the ASTM D117-97 standard. The specimens were placed in a chamber, and sprayed by a 5 wt% NaCl solution at 35 °C for different time up to 288 h. Samples were taken out after different spray periods, and the corroded morphologies were recorded by a digital camera and a scanning electron microscope (SEM, S4800, Hitachi) fitted with an energy dispersive spectroscopy analyzer. The corrosion products were investigated by photoelectron X-ray spectroscopy (XPS) using a Kratos Axis Ultra^{DL}D spectrometer (Kratos Analytical-A Shimadzu Group Company), and the XPS spectra processing was carried out by a commercial CasaXPS software package.

3. Results and discussion

3.1. Characterization of surface microstructure

The elemental depth profiles of NAB alloys after chromium implantation are depicted in Fig. 1. The result shows that a chromium-rich layer with a Gaussian-like distribution formed at the surface of the alloy. The depth of the layer increased gradually with the increasing implantation fluence, being 40 nm, 100 nm and 110 nm, corresponding to fluence of 1×10^{16} , 1×10^{17} and 5×10^{17} ions/cm², respectively. In addition, the peak concentrations of chromium were approximately 4 at.%, 24 at.% and 36 at.%, respectively.

Fig. 2 shows the GAXRD patterns obtained from the top surface of as-cast and Cr implanted NAB alloys. No peak associated with the formation of a new phase was observed after implantation, indicating that chromium was a solid solution in the matrix. However, the sharp Bragg peak at the degree of 44° became broader after implanted with 1×10^{16} ions/cm² Cr, and finally almost disappeared as the fluence became higher. According to G. Chang, this phenomenon can be explained to the disorder of atomic arrangement induced by radiation damage and cascade collisions between atoms during ion implantation [34].

The cross-sectional HR-TEM images of the specimen implanted with the fluence of 5×10^{17} ions/cm² are shown in Fig. 3. Fig. 3a shows the general view of the implanted region, and the high-resolution lattice image of the outside part is presented in Fig. 3b. According to the Fast Fourier transform (FFT) corresponding to the marked area, both the halo ring from a trace of amorphous and diffraction spots from the crystalline structures were found. The disorder of atomic arrangement is attributable to the accumulation of defects during the implantation, which coincides with the analysis in the GAXRD results.

3.2. Electrochemical results

Fig. 4 shows the electrochemical measurement of as-cast and Cr implanted NAB alloys with different fluences. After being immersed in 3.5 wt% NaCl solution for a certain time, E_{OCP} reaches a steady value as shown in Fig. 4a. It can be seen that E_{OCP} shifted positively after implantation, and reached the maximum value at the fluence of 5×10^{17} ions/cm² (Cr-3). Potentiodynamic polarization curves for the specimens are presented in Fig. 4b, and the corresponding corrosion potential (E_{corr}) and Tafel slopes (b_a , b_c) are listed in Table 3. The polarization resistance (R_p) was determined from the slopes of linear polarization plots shown in Fig. 4c. Then corrosion current density (i_{corr}) was calculated according to Eq. (1), and the values are listed in Table 3.

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