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THE INITIAL CORROSION MECHANISM OF α–PHASE ALUMINIUM BRONZE IN NaCl SOLUTION①

Zhu, Xiaolong②
General Research Institute for Non-Ferrous Metals, Beijing 100088, China
Li, Renshun③ Wu, Rengeng④ Zhou, Derui③
Harbin Institute of Technology, Harbin 150006, China

ABSTRACT

The polarization curves of the α–phase aluminium bronze measured in 5% NaCl electrochemically show that the corrosion process of the alloy is controlled by the diffusion of oxygen. The corrosion surface of the α–phase Al bronze in NaCl solution for a short time was analysed by X–ray Photoelectron Spectroscopy (XPS). The results indicate that the initial corrosion product of the Al bronze consists of a simple Cu_2O phase, Al and Ni are incorporated in Cu_2O lattice structure in the form of ions, and none of the aluminium compound can be detected. The authors propose that the initial corrosion mechanism of α–phase Al bronzes in NaCl solution should include oxidation, reduction and diffusion.

Key words: α–phase Al bronze, NaCl solution, initial corrosion, X–ray Photoelectron Spectroscopy

1 INTRODUCTION

The corrosion characteristics of Cu–Al alloys in NaCl solution have been investigated[1–2]. It has been found that the inhibiting effect of the increasing of aluminium content on high temperature corrosion of α–phase alloys has been well demonstrated[3–5], but there still exists controversy concerning the effciency of aluminium in the reduction of corrosion rates in aqueous media such as sea water[1, 6–8].

From potentiodynamic studies by means of polarization curves obtained in solutions of chlorides, it has been concluded that binary Cu–Al alloys present a pattern of corrosion that produces complex salts of (Cu–Cl)which are deposited over the anodes generating galvanic cells formed by this product and metallic support. Furthermore, it has also been found that the concentration of O_2 in the solutions of NaCl increases the corrosion[9].

As it applies to both the initial corrosion and the interface between the corrosion product layer and the metal substrate in long-term corrosion, the intial corrosion mechanism is helpful to clarify the corrosion resistance of the alloy. The purpose of the present work is to characterise the corrosion dynamics of α–phase Al bronzes in NaCl solution, analyse the initial corrosion product and further

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②Engineer; ③Professor; ④Associate Professor discuss the initial corrosion mechanism.

2 MATERIALS AND METHODS

The chemical compositions wt.−% of specimens were Cu 90.2, Al 7.9, Ni 1.9. The specimens were homogeneously annealed at 850 ℃ for 4 h. Polarization curves were measured by the model 351 corrosion measurement system (Princeton Applied Research, USA), cylindrical specimens (10 mm in diameter) sealed with epoxy resin were ground on SiC paper. Polarization curves began to be measured with a scanning speed of 20 mV / min after immersion for 10 min in the solution of 5% NaCl.

The specimen immersed in 5% NaCl for 24 h was studied by X−ray Photoelectron Spectroscopy (PHI 5300)to clarify the nature of the corrosion products. The exciting source was Mg K_α and the Cls peak of contamination at 284.6eV was regarded as the reference for binding energy corrosion. Argon ions bombed the specimen with 3 kV for the depth profiling.

3 RESULTS

Fig.1 shows the polarization curves of the specimen in 5% NaCl solution. The anodic dissolution does not meet any hindrance, while the cathodic process gets to the limit current of oxygen diffusion. The corrosion of the alloy in 5%NaCl solution is controlled by oxygen diffusion.

Immersed in 5% NaCl for 24 h, the surface of the specimen was covered by a red thin layer. The XPS survey of the specimen shown in Fig.2 indicates that the corrosion surface is primarily made up of Cu, O and C, with trace chlorine presented. The shapes and positions of Cu2p spectra do not appear to be different with ion bombardment, however copper is found to change from the cuprous ion to the free copper in the depth profile(Fig.3). The Al2s spectra in the outside of the film have two peaks, of which the main peak was Cu3s and the weak peak is situated at 120 eV, corresponding to Al^{3+} (Fig.4). After 12 min ion bombardment, a new peak appears (binding energy at 118.0 eV) and becomes prominent and is identified as pure aluminium from Handbook of X−ray Photoelectron Spectroscopy[10].

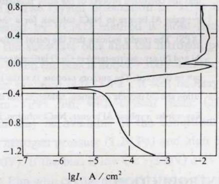

Fig.1 Polarization curves of the α−phase aluminium bronze in 5% NaCl

20 mV / min, room temperature.

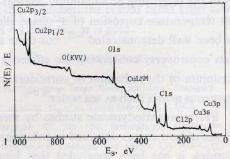

Fig.2 XPS Survey of the corrosion surface of the immersed specimen

5% NaCl, 24 h, room temp.

For Ni2p spectra(Fig.5), nickel exists

respectively in the form of Ni^{3+}, Ni^{2+} and Ni^0 with the depth of ion bombardment.

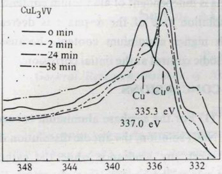

Fig.3 CuL_3VV spectra with ion−bombardment for the immersed specimen

5% NaCl, 24 h, room temp.

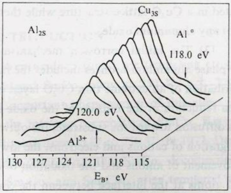

Fig.4 Ion etch sequence for A12s spectra of the immersed specimen (each step = 4 min).

Hat separate phases presented in the corrosion product layer must be ascertained by the oxygen peak. Fig.6 shows that the oxygen peak in the outer surface displays obvious asymmetry, the part of lower binding energy (531.7 eV), after peak-fitting, is found to be in agreement with that of the oxygen peak of Cu_2O, so it can be concluded that Cu_2O exists, while the part of higher energy is that of atomic oxygen from the combination of quantitative analyses with other results[11] With the time of ion bombardment, the Ols peak becomes a little weaker and symmetrial, which indicates the amount of the atomic oxygen decreases and Cu_2O gradually disappears. Haber et al reported[12] that the binding energy of Ols combined with Ni^{3+} and Ni^{2+} is respectively 529.3 eV and 529.8 eV, however Fig.6 does not provide the evidence of any nickel oxide.

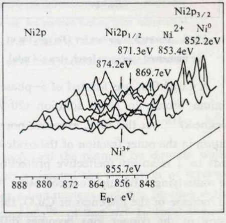

Fig.5 Ion etch sequence for Ni2p spectra of the immersed specimen (each step = 4 min).

4 DISCUSSION

The corrosion resistance of aluminium bronzes is generally believed to be attributed to a layer of the aluminium compound on the surface. Sury, P. and Oswarld, H. R.[12] applied X−ray diffraction and electron microscopy to study the corrosion product layer of α−phase aluminium bronzes in NaCl solution and did not find the existence of any aluminium oxide, therefore they proposed that the corrosion product consists of a single and porous layer of Cu_2O coped with Al^{3+}. The above results confirm their model. Aluminium and nickel are incorporated in Cu_2O lattice structure in the form of ions, so that the corrosion resistance of the alloy depends on the protective characteristics of the Cu_2O.

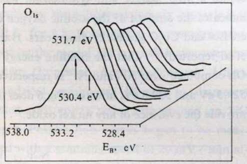

Fig.6 Ion etch sequence for Ols spectra of the immersed specimen (each step = 4 min).

A Cu_2O film was formed of α–phase aluminium bronze in NaCl solution (20 Å in thickness)[13]. At this time, excessive pore formation in the outer fraction of the oxide layer leads to a relatively ineffective protection of the underlying substrate from corrosion. With the increase of the thickness of Cu_2O, the diffusion of the copper ions becomes difficult through the oxide, and is carried out only through pores of Cu_2O, meanwhile the electron conductivity of the P–type semiconductor Cu_2O is kept at a relatively high value and electron transportation is by means of the interchange of Cu^+ and Cu^{2+}. This enables O_2 to be reduced at the outer oxide surface. At the interface between Cu_2O and the metal substrate, metal atoms change into metal ions by losing electrons. Oxygen continually diffuses inwards under the gradient of the concentration. The aluminium and nickel ions are incorporated in Cu_2O by either occupying a cation vacancy or substituting for a Cu^+. In the first case, both ionic and electronic resistance would increase while in the second way only the electronic resistance would increase, they both produces a higher overpotential of O_2 reduction. Although the anodic reaction at electrodes free of secondary corrosion products is independent of aluminium content, the dissolution rate of the α–phase is decreased with higher aluminium contents because of cathodic control at the initial corrosion.

5 CONCLUSIONS

(1) For the α–phase aluminium bronze in 5% NaCl solution, the anodic dissolution does not meet any hindrance while the cathodic part gets to the limit current of oxygen diffusion, so that the corrosion process of the alloy is controlled by the diffusion of oxygen.

(2) The initial corrosion product of the α–phase aluminium bronzes in NaCl solution is Cu_2O, and Al^{3+}, Ni^{2+} and Ni^{3+} are incorporated in a Cu_2O lattice structure while there is not any aluminium oxide.

(3) The initial corrosion mechanism of α–phase aluminium bronzes includes the rapid formation of an extreme thin Cu_2O layer, oxygen reduction in the outside of the oxide and its diffusion toward the substrate, the outward migration of cations and electrons, the inward movement of anions and the oxidation of metal atoms at the interface betweenn the corrosion product and the substrate.

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(To be continued on page 76)