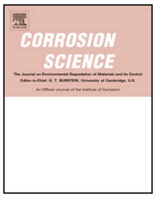
Corrosion Science xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci



Study of corrosion inhibition of coupled Al_2Cu–Al and Al_3Fe–Al by cerium cinnamate using scanning vibrating electrode technique and scanning ion-selective electrode technique

Hongwei Shi[a,*], En-Hou Han[a], Fuchun Liu[a], Tao Wei[a], Zhengwang Zhu[b], Daokui Xu[a]

[a] *Key Laboratory of Nuclear Materials and Safety Assessment, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China*
[b] *Shenyang National Laboratory for Materials Sciences, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China*

ARTICLE INFO

Article history:
Received 18 December 2014
Accepted 12 May 2015
Available online xxx

Keywords:
A. Alloy
A. Aluminium
B. Galvanostatic
B. SEM
C. Neutral inhibition

ABSTRACT

The galvanic corrosion of the coupled Al_2Cu and Al as well as Al_3Fe and Al in 0.005 M NaCl in and without the presence of cerium cinnamate was studied. Scanning vibrating electrode technique and scanning ion-selective electrode technique were used to measure the distribution of current densities and pH. The results indicate that cerium cinnamate played inhibiting effect on the coupling corrosion of Al_2Cu–Al and Al_3Fe–Al. For Al_2Cu–Al, the inhibition was mainly influenced by the production of cerium oxide/hydroxide on Al_2Cu surface. However, for Al_3Fe–Al, the inhibition was mainly influenced by the adsorbed cerium cinnamate on the Al_3Fe surface.

1. Introduction

Aluminium alloys are successfully used in many modern applications because of their light weight, high strength and good corrosion resistance. High strength age-hardenable aluminium alloys, such as AA 2024-T3, are widely used as structural material in aeronautical industries [1–3]. Because of the high susceptibility of AA2024-T3 to corrosion, the corrosion behaviour of this alloy has been extensively studied in literature [4–22]. The alloying of Cu, Mg, Fe and Mn in AA 2024-T3 improves the mechanical properties of the alloy, but leads to localized corrosion attack due to the intermetallic (IM) particles. The coupling between the IM particles and the surrounding matrix accelerates the localized corrosion of the matrix and the IM particles themselves when exposed to aggressive media.

The corrosion potentials of IM phases drive their corrosion in a sequence. Buchheit et al. have compiled a list of corrosion potentials of the IM phases in aluminium alloys in typical NaCl solutions, in which the second phases of AA2024-T3 were included [12,13]. Among the IM phases, Al_2CuMg is the most active one and contributes the most to corrosion. Some authors also reported the role of the noble phases, such as Al_2Cu, Al_3Fe and $Al_6(Cu, Fe, Mn)$ [14,15]. Birbilis et al. reviewed the corrosion characteristics of a population of second phases of AA 2024-T3. They also used macro-cells to characterize and compare the corrosion potentials and current densities of these IM phases. They pointed out that noble particles, such as Al_2Cu and Al_7Cu_2Fe, promoted peripheral pitting [17]. Zhu et al. investigated the corrosion of second phase particles of 2024-T3, finding that only a slight trench was observed in the Al matrix around $Al_6(Cu, Fe, Mn)$, which was due to the high anode-to-cathode ratio [16]. Recent works by Hughes et al. [19–22] presented the hierarchy of localized corrosion attack from different isolated IM particles of AA 2024-T3. There was progressive attack upon the S-phase, then the AlCuFeMn-phase and finally the $(Al,Cu)_x(Fe,Mn)_ySi$-phase.

As mentioned above, many studies in literature have described the corrosion behaviour of IM particles embedded inside the AA 2024-T3 surface. However, since the sizes of IM particles are very small (usually 1–30 μm), it is almost impossible to accurately measure the potentials and currents directly from the alloy [18]. The study of the galvanic coupling corrosion between single model IM phases and aluminium is informative in understanding particle-induced pitting in aluminium alloys. Moreover, it provides a suitable way to study the efficiency of corrosion inhibitors or conversion coatings on aluminium alloys. The following works have reported on the corrosion behaviour of the pure IMs of AA 2024-T3. Juffs et al. used the couplings of Al_3Fe, Cu_2FeAl_7, and Al_2Cu with aluminium to study the deposition of chromate conversion coatings [23]. Scholes and Birbilis et al. investigated the corrosion inhibition of Al_2CuMg, Al_7Cu_2Fe, Al_2Cu and Al_3Fe phases by cerium dibutyl

---

[*] Corresponding author. Tel.: +86 24 23915897; fax: +86 24 23894149.
E-mail address: hwshi@imr.ac.cn (H. Shi).

http://dx.doi.org/10.1016/j.corsci.2015.05.019
0010-938X/© 2015 Elsevier Ltd. All rights reserved.

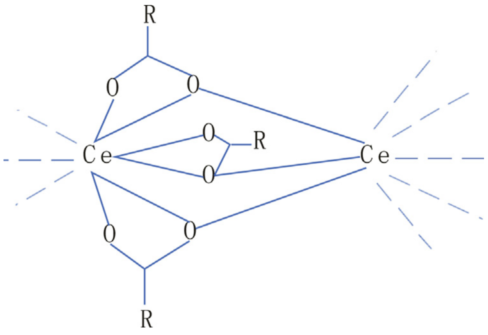


Fig. 1. Schematic of $Ce(cin)_3$, where R is $CH{=}CH{-}C_6H_4{-}H$.

phosphate [24,25]. Although there were some works focused on the corrosion inhibition of independent second phases of AA 2024-T3, the mechanism of the coupling corrosion between the IM phases and the Al matrix still needs to be explored.

In NaCl solution, the anodic and cathodic reactions occurring on the IM particles and the Al matrix are associated with the pH change in the local area. The role of chemical reactions of IM particles is very important, which is closely related to the pH change on the particles. In this sense, the measurements of the current densities on the galvanic coupling between IM particles and the alloy matrix, as well as the pH distribution, provide the possibility to simulate the corrosion or inhibition process of IM phase particles in AA 2024-T3. As it is commonly known, the selection of effective corrosion inhibitors for an alloy is an important issue. The selection of the inhibitors is usually achieved by studying the efficiency of inhibitors on the whole alloy surface using electrochemical tests, such as electrochemical impedance spectra (EIS) or polarization tests. The overall corrosion inhibition of the alloys can be evaluated using these methods. However, the corrosion inhibition mechanism of the independent IM phases is not clear. If the inhibitors are used in a corrosive medium and the inhibiting effects are proved to be effective in the coupling of IM phase with Al, it can be assumed that the inhibitors are also effective in inhibiting the corrosion of the alloy, since IM phase particles are often the sites of corrosion initiation. Therefore, the efficiency of the corrosion inhibitor on an alloy can be evaluated. Additionally, the type of corrosion inhibition, i.e. “anodic inhibition” or “cathodic inhibition” is expected to be identified by detecting the current density on the anodic and cathodic electrodes. The above information can be further used to screen the effective inhibitors for an alloy.

In our previous work, an ingot of the Al_2CuMg phase was coupled with an Al wire to study the role of this phase in the corrosion

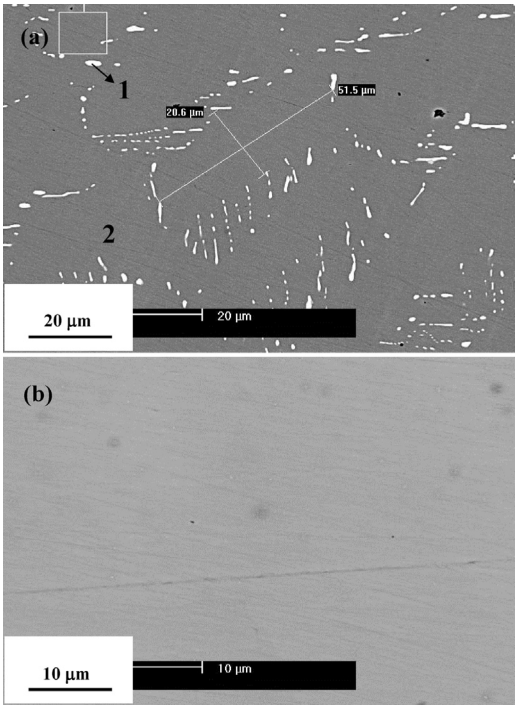


Fig. 2. SEM images of the obtained (a) Al_2Cu and (b) Al_3Fe phases material.

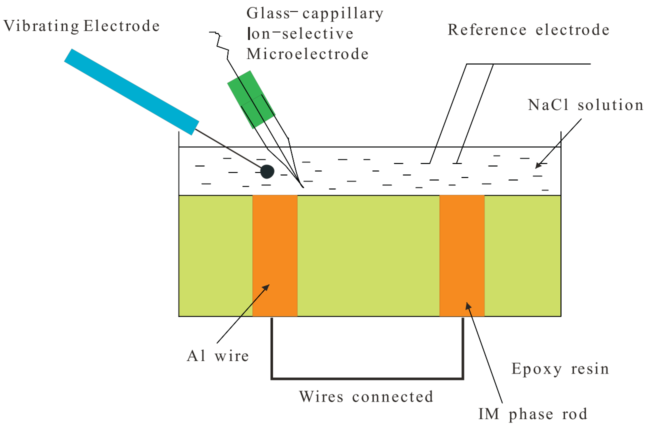


Fig. 3. Simple SVET/SIET schematic diagram.

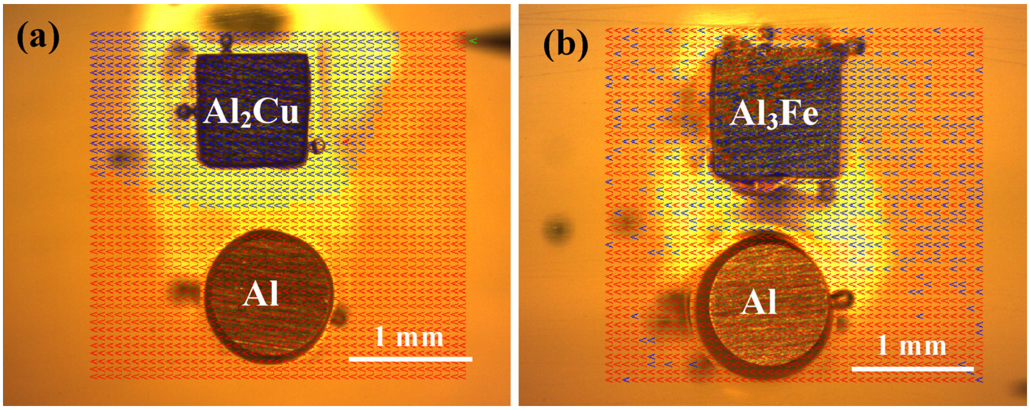


Fig. 4. Photographs of top view of the scanned area showing the current points for (a) coupled Al_2Cu–Al and (b) coupled Al_3Fe–Al embedded in an epoxy sleeve.

Please cite this article in press as: H. Shi, et al., Study of corrosion inhibition of coupled Al_2Cu–Al and Al_3Fe–Al by cerium cinnamate using scanning vibrating electrode technique and scanning ion-selective electrode technique, *Corros. Sci.* (2015), http://dx.doi.org/10.1016/j.corsci.2015.05.019