Electrochemical polarization and corrosion behavior of Al–Zn–In based alloy in acidity and alkalinity solutions

CrossMark

Jingling Ma, Jiuba Wen, Quanan Li, Qing Zhang*

School of Materials Science and Engineering, Henan University of Science and Technology, Luoyang 471003, PR China

ARTICLE INFO

ABSTRACT

The corrosion behavior of Al–5Zn–1Mg–0.02In–0.05Ti–0.1Si (wt %) alloy has been investigated in different pH solutions by cyclic polarization, self-corrosion and scanning electron microscopy. The results show that the alloy undergoes two types of corrosion, including pitting in acidic solutions, relative light pitting in neutral solutions and crystallographic corrosion in alkalinity solutions with a high possibility. The difference of $\Delta E = (E_{pit} - E_{cor})$ are used as criterion for susceptibility to pitting and the hysteresis loop area as criterion for pitting propagation and repassivation of the alloy. The criterion is discussed. Corrosion morphologies of the alloy are in good agreement with corrosion parameters.

1. Introduction

Owing to the low atomic mass of aluminum, high energetic capacity (2980 Ah kg^{-1}), along with the negative value of standard electrode potential (−1.66 V vs. Normal Hydrogen Electrode), low cost, and no pollution, Al-air battery is a promising power source and energy storage device [1–3]. However currently, the Al-air battery is still not as popular as Zn–air battery [4]. The major problem is that Al anode exhibited some less attractive properties, such as the protective oxide film, which is spontaneously formed on Al surface, and the severe self-corrosion during battery discharge [5,6]. Due to presence of oxide film, the corrosion potential of Al anode is shifted in the positive direction (about −0.8 V vs.NHE), and the active dissolution of Al is slowed down considerably [7,8]. The addition of alloying elements such as In, Ga, Hg, and Sn can shift the potential toward more negative, causing the so-called activation of Al [9–11]. This wasteful self-corrosion results in severe capacity loss and low anodic efficiency. For the purpose of reducing the self-corrosion of Al anode the measures were taken: use alloying with the elements of high hydrogen over-potential such as Pb, Zn and Sn, etc [12–14]. The paper investigated the effects of Mg and Ti on microstructure and electrochemical performance of Al–Zn–In alloy [15]. The Al–Zn–In series alloys have been widely used as anode in China [16]. In order to further reduce the self-corrosion of the alloy, silicon as an alloying element is considered. This is mainly due to silicon can improve the casting characteristics, corrosion resistance and other mechanical properties of the Al alloys [17,18]. The effect of In and Si elements on the microstructure and electrochemical performance of Al–5Zn–1Mg–(0.01, 0.02, 0.03, 0.04, 0.05) In–0.05Ti–(0.05, 0.1, 0.15, 0.2) Si (wt %) anode alloys in sodium chloride solution was studied in our preliminary research. The results show that Al–5Zn–1Mg–0.02 In–0.05Ti–0.1Si (wt %) has relatively good electrochemical

* Corresponding author. Tel.: +86 379 64231846; fax: +86 379 64230597.
  E-mail address: wenjiuba52@126.com (J. Wen).

properties. The electrochemical behavior of Al–5Zn–1Mg–0.02In–0.05Ti–0.1Si alloy as anode of Al-air battery was studied in this paper.

The electrolytes used in Al-air battery have typically aqueous alkaline solution such as sodium hydroxide and neutral saline electrolytes such as sodium chloride. The high dissolution rate of aluminum in the concentrated alkaline solutions is known to stem from the attack by hydroxyl ions in the solution [19]. It has been reported that the addition of Cl^- ions to acidic and neutral solutions increases the dissolution rate of aluminum [20,21]. The solutions with acid or alkali have an important influence on corrosion behavior of aluminum alloy.

The paper investigated the corrosion behavior of Al–Zn–Mg–In–Ti–Si alloy in 3.5% NaCl solutions [22]. However, it provides little information about the anodic dissolution of the alloy in acidic and alkaline solutions. The present work will study the corrosion behavior of the alloy in acidic and alkaline solutions with different pH. The effect of the pH solutions and the potentiodynamic anodic polarization on the localized corrosion of the alloy will be considered. The goal of this paper is to give the suitable pH value of electrolyte for the Al-air battery based on Al–Zn–Mg–In–Ti–Si by researching the corrosion characteristics of the anode in acidic and alkaline solutions, which would provide some help to the development of Al-air battery.

2. Experimental

2.1. Material preparation

Raw materials are commercial pure aluminum, zinc, magnesium ingots, indium particle (>99.9%), Al–10% wt Ti master alloy, monocrystalline silicon for casting the experiment alloy. The nominal composition of the experiment alloy is 5% wt Zn–1% wt Mg–0.02% wt In–0.05% wt Ti–0.1% wt Si–Al. Raw material ingots were cut, dried, weighed the required amount of materials and melted in a corundum crucible in ZGJL0.01–4C–4 vacuum induction furnace under argon atmosphere at 760 ± 5 °C. The molten alloy was poured in a preheated cast iron dye. The ultimate composition of the alloy was analyzed by direct reading spectrometer, and the result is shown in Table 1.

2.2. Electrochemical measurements

The electrochemical tests were carried out with three electrodes system at room temperature (25 ± 2 °C) by CHI660C electrochemical test system (CHI Company, USA). A saturated calomel electrode (SCE) served as the reference electrode and a Pt sheet was used as the counter electrode.

The solutions used in this study were 4 mol/L NaOH, 0.6 mol/L NaCl and 1 mol/L HCl. All solutions were prepared

with distilled water and analytical grade reagents. NaCl, NaOH and HCl were added to the distilled water in requisite amount to make a solution with concentration 0.6 M NaCl, 4 mol/L NaOH and 1 mol/L HCl. The concentration and density of HCl density used is 36.5 wt% and 1.17 g/ml, respectively. The pH of the solutions was adjusted by using NaOH, 1 mol/L HCl and 0.6 M NaCl. All of the pH measures were made by mean of pH-meter. Table 2 shows the different solutions preparation in this study.

The working electrodes of open circuit potential (OCP) measured with an exposed area of 1 cm^2. The samples were ground with emery paper (grade 400–800–1000–2000) and then cleaned with triply distilled water. Measurements were performed in different solutions for 1 h.

The potentiodynamic cyclic polarization was measured at a scan rate of 1 mV s^{-1} after OCP measurement. The scan direction was reversed when the electrode potential reached the pre-set anodic potential and then the potential were scanned back to the initial potential.

2.3. Self-corrosion

The samples of self-corrosion tests were cut to ¢ 11.4 mm × 5 mm, then ground with emery paper (grade 400–800–1000–2000) and immersed in different solutions for 24 h except 4 mol/L NaOH solutions. The immersion time is 30 min in 4 M NaOH solutions. The weight of the samples before and after immersion was measured after cleaning the corrosion products formed on the sample surface. The corrosion products were clean-out in solutions of 2% CrO_3 and 5% H_3PO_4 at 80 °C for about 5 min, then rinsed by distilled water and ethanol.

The corrosion rate was calculated using the formula:
Corrosion rate = Weight loss/surface area/time of immersion (mg $cm^{-2}min^{-1}$)

The samples surface after self-corrosion and polarization was examined using JSM-5610LV scanning electron microscope (SEM).

3. Results and discussion

3.1. Open circuit potential

Fig. 1 shows the OCP vs. time curves obtained with the samples immersed in different solutions. Several OCP tests were

Table 1 – Chemical compositions of the studied alloy (wt %).

Element	Zn	Mg	In	Ti	Si	Fe	Cu	Al
Composition	5.062	1.010	0.021	0.049	0.092	<0.001	0.015	Remainder

Table 2 – Different solutions preparation.

Solutions	1 mol/L HCl(1L)	pH 4(10L)	pH 7 0.6 mol/L NaCl(1L)	pH 9(10L)	pH 11(10L)	4 mol/L NaOH(1L)
NaCl (g)	–	–	34.80	–	–	–
HCl (ml)	85.47	–	–	–	–	–
NaOH (g)	–	–	–	0.004	0.4	160
0.6 mol/L NaCl (L)	–	9.99 L	–	10 L	10 L	–
1 mol/L HCl (ml)	–	10 ml	–	–	–	–