

## Short Communication

---

# Studies on the anodic behavior of aluminum electrodes in alkaline solution

Shi Pengfei, Yin Geping, Xia Baojia and Lu Guoqi  
*Harbin Institute of Technology, Harbin 150006 (China)*

(Received August 25, 1992; accepted November 28, 1992)

### Abstract

An efficient process for developing aluminum alloys for alkaline battery anodes is described. The addition of gallium to aluminum eliminates remarkably the anisotropy of aluminum, and thus renders its electrode potential more negative. The uniform distribution of alloying elements is an essential factor for lowering the corrosion rate of the alloy. The accumulation of an alloying element at intergranular boundaries, or the formation of a secondary phase that contains the element, will result in a rise in the corrosion rate of aluminum.

### Introduction

Batteries with aluminum anodes coupled with air or silver oxide cathodes in alkaline solutions are chemical power sources of high specific energy. Aluminum/air batteries are also noted for their inexpensiveness and mechanical rechargeability, i.e., they can be used repeatedly by replacing the aluminum electrodes and refilling the electrolyte. Aluminum electrodes are interesting because of their negative potential, low electrochemical equivalent and reactivity in aqueous solutions. Nevertheless, their application in batteries is limited due to the following electrochemical properties: (i) a high corrosion rate, and (ii) a significant degree of anodic polarization.

In order to use aluminum successfully as anodes in batteries, two research objectives must be achieved. First, the preparation of aluminum alloys that have the required properties (by addition of some alloying elements to pure aluminum); second, the addition of inorganic or organic corrosion inhibitors to the electrolyte [1–6].

This paper describes the development of aluminum alloys by the process of combining electrochemical measurements with micromorphological analysis as determined by scanning electron microscopy (SEM). The alloy E-3 developed by such a process has the following properties in 4 M NaOH + 0.06 M Na<sub>2</sub>SnO<sub>3</sub> electrolyte at 50 °C:

- a rest potential of  $-1.83$  V versus Hg/HgO electrode
- a corrosion rate of  $0.98$  to  $1.80$  cm<sup>3</sup> H<sub>2</sub> cm<sup>-2</sup> min<sup>-1</sup>
- for an anodic current density is  $100$  mA cm<sup>-2</sup>, a polarization potential of  $-1.60$  to  $-1.64$  V and a corrosion rate of  $0.40$  to  $0.78$  cm<sup>3</sup> cm<sup>-2</sup> min<sup>-1</sup>

## Experimental procedure and results

### *Corrosion characteristics of aluminum in alkaline solution*

The anodic dissolution of aluminum is complex. Experiments were set up to demonstrate the effects of alkaline concentration on the anodic dissolution behavior of pure aluminum. The working electrode consisted of pure aluminum (99.99%) that was punched from a plate of 5 mm thickness with a specified die; a lead wire contact was welded to the back and shielded by epoxy resin. The apparent working area was  $0.5 \text{ cm}^2$  and this was polished with 380 mesh abrasive paper. The counter electrode was made of platinum, and a saturated calomel electrode was served as the reference electrode. In order to measure the rate of the corrosion of the aluminum electrode that is caused by the hydrogen evolution reaction, an electrolyte-filled burette with a funnel-shaped gas collector was connected to the cell immediately just above the working electrode.

The electrolyte was  $25 \text{ g l}^{-1} \text{ KCl} + x \text{ g l}^{-1} \text{ KOH}$  at  $25 \text{ }^\circ\text{C}$ . The corrosion rate, expressed as the volume of hydrogen evolved in unit time per unit area, was measured at different anodic current densities with different KOH contents. The results are given in Fig. 1.

The findings show that the corrosion rate of aluminum in KCl solution increases with increasing anodic current density, i.e., a negative differential effect. When the KOH content exceeds  $2.5 \text{ g l}^{-1}$ , however, the corrosion rate of aluminum anode decreases with increasing anodic current density, i.e., a positive differential effect. The pH value is 11 to 12 for an electrolyte that contains  $3 \text{ g l}^{-1} \text{ KOH}$ . Thus, it can be concluded that there is no evident barrier film on the aluminum surface for anodic dissolution in an electrolyte with a pH higher than 11 to 12.

### *Factors influencing the anodic behavior of aluminum*

Two kinds of quaternary aluminum alloys with different gallium contents were prepared. Alloys no. 1 and no. 2 contained 0.03 and 0.3 wt.% Ga, respectively. The individual contents of lead and bismuth were 0.15 wt.% in both alloys. The working electrodes were fabricated from these alloys and from pure aluminum by the above-mentioned process. The electrolyte was 30 wt.% KOH at  $25 \text{ }^\circ\text{C}$ . The reference electrode

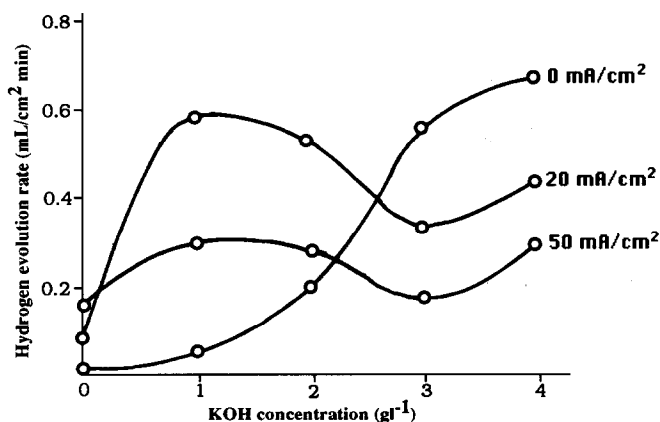


Fig. 1. Effect of KOH content ( $\text{g l}^{-1}$ ) in KCl electrolyte on the corrosion rate of aluminum anode.

was a Hg/HgO electrode. The hydrogen evolution rate (HER) and the relationship between electrode potential and duration of anodic polarization were measured under galvanostatic conditions. The results are given in Table 1. Clearly, aluminum and its alloys exhibit a positive differential effect during anodic dissolution in alkaline solution. The anodic polarization potentials of alloy electrodes are more negative than that of pure aluminum, and the corresponding corrosion rates of the alloys at rest potential are much higher. The micromorphology of the electrode surface was observed with a SEM. In particular, the composition of some spots on the surface was determined. The experimental procedure was as follows. First, the electrode sample was polished with coarse, medium and fine metallographic abrasive papers. Care was taken to avoid a temperature rise of the sample during such treatment. Next, the sample was polarized anodically in 30 wt.% KOH solution for 20 to 30 s at a given overvoltage of 200 to 300 mV. Immediately after polarization, the sample was rinsed with running water and immersed in a dilute  $H_3BO_3$  solution for neutralization. After rinsing again, it was examined promptly by the SEM. The electronmicrographs are shown in Fig. 2.

The electron micrograph for pure aluminum (Fig. 2(a)) shows clearly that the metallic crystals dissolve anisotropically during anodic polarization. Different crystal faces of aluminum display different electrochemical behavior, thus the crystal structure is manifested after anodic dissolution. By contrast, the micromorphology of the two alloys is quite different. Figure 2(b) shows alloy no. 1 after anodic dissolution. It is clear that the crystal structure is not exposed. In addition, the macrostructure of the electrode surface shows its uniform dissolution. This indicates that the addition of gallium and other elements to pure aluminum forms a solid solution, and thus the anisotropy of the pure aluminum crystals is changed. As a consequence, the anodic potential of the alloy shifts in a negative direction. The black pit is due to corrosion; it contains a white secondary phase. The composition of the latter is 52.49 wt.% Al, 0.32 wt.% Ga, 10.27 wt.% Pb and 36.09 wt.% Bi. The white spots are, therefore, enriched with the alloying elements and may be the cathodes of corrosion microcells. In such a cell, the cathode is surrounded by the anode. Anode dissolution leads to expansion of the black pits, exposure of the white spots and, finally, shedding of the white spots, as shown by point A in Fig. 2(b). Thus, whilst the addition of some alloying elements to aluminum may improve the anodic dissolution behavior, excessive amounts of these additives is not recommended as this would result in the formation of a secondary phase that provides cathodic sites for hydrogen evolution and therefore, promotes the corrosion of aluminum.

Figure 2(c) shows the micromorphology of alloy no. 2. The composition of the grain surface is 99.774 wt.% Al and 0.226 wt.% Ga, and that of the intergranular

TABLE 1

Effect of alloy composition on the anodic behavior of aluminum electrodes

Electrodes	$i=0$		$i=100 \text{ mA cm}^{-2}$	
	Rest potential (V)	HER ( $\text{cm}^3 \text{ 10 min}^{-1} \text{ cm}^{-2}$ )	Potential (V)	HER ( $\text{cm}^3 \text{ 10 min}^{-1} \text{ cm}^{-2}$ )
Alloy no. 1	-1.44	5.44	-0.87	0.002
Alloy no. 2	-1.45	6.60	-0.98	0.020
Pure aluminum	-1.36	2.50	-0.81	0.100

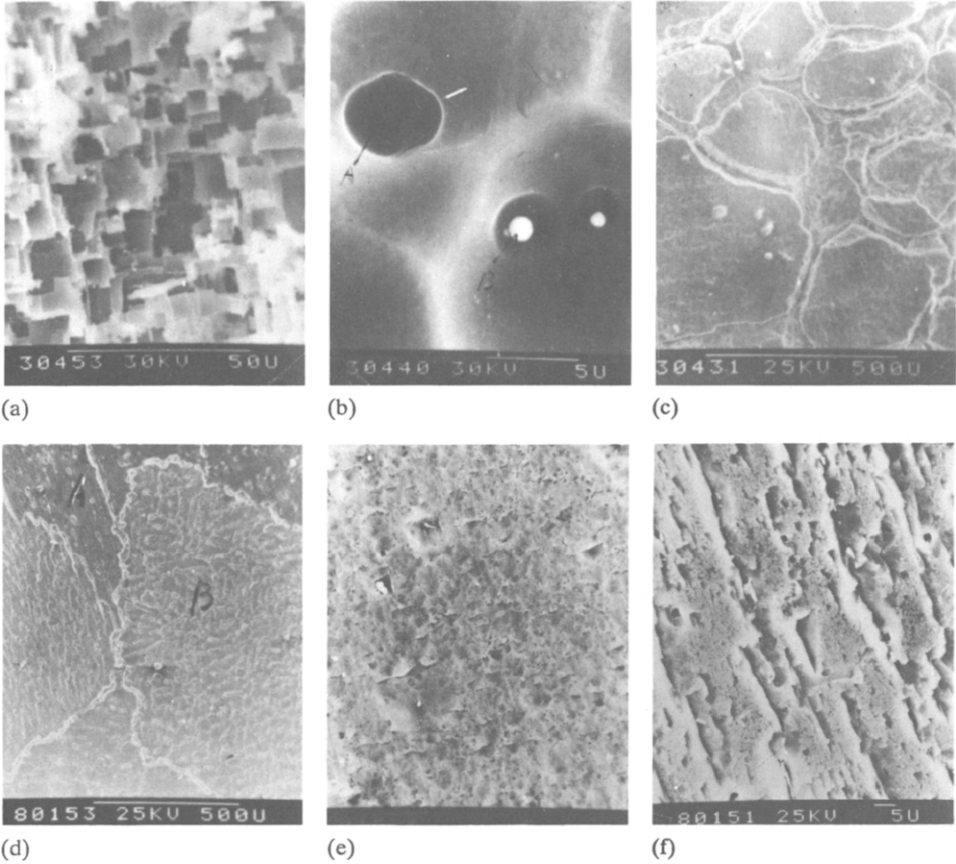


Fig. 2. Scanning electron micrographs for: (a) pure aluminum; (b) alloy no. 1; (c) alloy no. 2; (d)–(f) alloy E-3.

layer is 98.986 wt.% Al and 1.014 wt.% Ga. The micromorphology shows no enrichment of lead or bismuth, i.e., gallium improves the solubility of lead and bismuth in aluminum. Moreover, the higher concentration of alloying elements eliminates the anisotropy of aluminum so that the dissolved electrode surface is smooth instead of 'hill-like', and the electrode potential decreases further. The accumulation of gallium in the intergranular layer does, however, result in rapid dissolution of the layer. It is evident from the higher corrosion rate of alloy no. 2 that the gallium accumulated in the layer acts as the anodes of corrosion microcells, and accelerates the corrosion of aluminum electrodes. Hence, an appropriate content of the alloying elements should be found to eliminate, as far as possible, the anisotropy of aluminum and the resulting anodic polarization. At such an appropriate level, the elements do not accumulate at the crystal surface nor develop a secondary phase, and hence the corrosion rate of aluminum would be lowered.

#### *Micromorphology of alloy E-3*

Alloy E-3 was prepared successfully in consideration of the above results. Its micromorphology is shown in Figs. 2(d) to 2(f). From Fig. 2(d), it can be seen that

there is neither a secondary phase formed, nor accumulation of elements in the intergranular layer. These features demonstrate that appropriate values have been chosen for the contents of alloying elements. All the crystal faces dissolve uniformly. The anisotropy of aluminum is eliminated by the alloying elements, thus the anodic dissolution behavior of different crystal faces is similar. Figs. 2(e) and 2(f) are magnified images of the crystal faces A and B in Fig. 2(d). A difference in morphology is observed after anodic dissolution. Analysis shows that the contents of the alloying elements are different. For example, the content of gallium at B is twice that at A, while the content of bismuth at B is 80% of that at A. The contents of other elements at A and B are also different. This indicates that the anisotropy is not fully eliminated.

## Conclusions

These studies have yielded the following information:

- (i) aluminum and its alloys display a positive differential effect during anodic dissolution in alkaline solution;
- (ii) elimination of the anisotropy of aluminum crystals provides a means to lower the electrode potential of aluminum, and
- (iii) lowering or avoiding the accumulation (formation of a secondary phase or enrichment at the intergranular layer) of alloying elements will reduce significantly the corrosion rate of aluminum.

## References

- 1 A. Maimoni, *Proc. 20th Intersoc. Energy Conv. Eng. Conf., Miami Beach, FL, USA, Aug. 18–23, 1985*, Vol. 2, p. 2–14.
- 2 D. D. MacDonald and C. English, *J. Appl. Electrochem.*, 20 (1990) 405.
- 3 J. F. Copper, R. V. Homsy and J. H. Landrum, *Proc. 15th Intersoc. Energy Conv. Eng. Conf., Seattle, WA, USA, Aug. 18–22, 1980*, Vol. 2, p. 1487.
- 4 G. M. Scamans, B. O'Callaghan and N. P. Fitzpatrick, *Proc. 21st Intersoc. Energy Conv. Eng. Conf., San Diego, CA, USA, Aug. 25–29, 1986*, Vol. 2, p. 1057.
- 5 I. J. Albert, *J. Appl. Electrochem.*, 19 (1989) 547.
- 6 A. S. Homa and E. J. Rudd, *Proc. 24th Intersoc. Energy Conv. Eng. Conf., Washington, DC, USA, Aug. 6–11, 1989*, Vol. 3, p. 1331.