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The Effects of Different Sealing Techniques for Anodic Film of Al-12.7Si-0.7Mg Alloys

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Al-12.7Si-0.7Mg is a novel kind of high silicon aluminum alloy and urgently in need of surface treatment technologies. Optimal processing parameters of stearic acid sealing treatment were investigated by evaluating the weight loss of anodic film. The anodic films were sealed by other four sealing methods of boiling water sealing, nickel acetate sealing, chromate sealing and cold nickel fluoride sealing in order to compare with stearic acid sealing. Surface morphology of anodic oxide films after sealing treatment showed that stearic acid sealing specimens were smooth, uniform and compact. The results of potentiodynamic polarization, phosphorus-chromium acid oxide method and alkaline etching test indicated that stearic acid sealing was more highly effective and environmentally friendly and exhibited excellent corrosion resistance.

Keywords: Al-12.7Si-0.7Mg alloy; anodizing; stearic acid; sealing; corrosion resistance

1. INTRODUCTION

High silicon aluminum alloys are widely spread applications in building field, aeronautic industry, automotive industry and naval construction, due to their prominent properties, such as high strength-to-weight ratio, outstanding castability or excellent crack resistance [1-5]. Al-12.7Si-0.7Mg is a novel kind of high silicon aluminum alloy [6,7] and urgently in need of surface treatment technologies. Anodizing techniques are the most commonly used method on the surface treatment of aluminum alloy in industry. The formation of anodic oxide films, consisting of the inner block layer and the outer porous layer, can significantly improved corrosion resistance of alloys [8-10]. However, Al-12.7Si-0.7Mg alloys contain higher content of silicon as alloy element, which are difficult to be covered and anodized during anodizing treatment. It is understood that anodic films are heterogeneous and corrosion resistance is decreased. Hence, subsequent processing of anodizing is indispensable to enhance the surface evenness and corrosion resistance.

Sealing treatment is physical or chemical process for the porous layer of anodic films in order to reduce the porosity and adsorption capacity of oxide layers and improve corrosion resistance of aluminum alloy [11]. So far, according to the previous researches [12-18], numerous of sealing methods were developed and applied, e.g. hot water sealing, steam sealing, dichromate sealing, sodium silicate sealing, nickel acetate sealing, cold nickel fluoride sealing and rare earth sealing [19,20]. Different sealing techniques had the limited conditions and exhibited different influences on corrosion resistance [21]. Additionally, heavy metals were highly toxic and not beneficial to environment. Therefore, development of green, non-toxic, low energy consumption and stable sealing method without chromium, nickel and fluorine has the great significance.

In present work, the optimal processing parameters of stearic acid sealing treatment were carried out. Four different sealing techniques were applied to anodic films, comparing with organic acid sealing. Surface morphology of anodic oxide films after sealing was examined. Alkaline etching test, phosphorus-chromium acid oxide method and potentiodynamic polarization measurement were characterized the corrosion resistance of the effect of different sealing treatment on oxide films.

2. MATERIALS AND METHODS

2.1 Materials

The material used is Al-12.7Si-0.7Mg alloy with dimensions of 32×30×3.8 mm, which was indigenously-developed in China and was provided by Key Laboratory of Electromagnetic Processing of Materials (Ministry of Education), Northeastern University. The chemical compositions were listed in Table 1. Chemical reagents were of analytical purity and deionized water was used as solvent.

Table 1. Chemical composition of Al-12.7Si-0.7Mg alloy

Element	Si	Mg	Fe	Cu	Ni	Ti	Al
Content / (wt.%)	12.7	0.7	0.3	1.5	0.3	0.3	Bal.

2.2 Preparation of anodic films

Mechanical polishing, degreasing, alkaline etching, acidic washing and desmutting were used as pre-treatment of anodic oxidation of aluminum alloy. All samples were anodized in a stirred aqueous solution of 170 $g \cdot L^{-1}$ H_2SO_4 at room temperature for 25 min, using 1.5 $A \cdot dm^{-2}$ of current density. The current supply was served by direct current (DC) stabilized power supply (RXN-305D, Shenzhen Zhaoxin Electronic Instrument and Equipment Factory, China) and graphite electrode was used as a cathode. After anodizing, all specimens were sealed, rinsed in ethyl alcohol and dried in warm air.

2.3 Sealing process of anodic films

Anodizing specimens were sealed in stearic acid-isopropyl alcohol solution. Concentration ranges of stearic acid was from 30 wt.% to 100 wt.%. Sealing time range was 20-90 min and sealing temperature was 60-100 ºC, respectively. Optimal sealing condition was worked out by weight loss (mg·dm^{-2}), according to GB/T 8753.1-2005. Other four different sealing methods were applied to anodic films in order to compare with stearic acid sealing. Processing parameters of sealing techniques are given in Table 2. Figure 1 shows schematic illustration of technological process of sealing technique of anodic film.

Table 2. Processing parameters of different sealing techniques applied to anodic films

Sealing method	Processing parameters
Boiling water sealing	Deionized water, pH 5.5-6.5, 98-100 ºC, 40 min.
Chromate sealing	K_2CrO_7 50-70 g·L^{-1}, pH 6.0-7.5, 90-95 ºC, 30 min.
Nickel acetate sealing	Ni^{2+} 1.4-1.8 g·L^{-1}, acetic acid 0.5 wt.%, pH 5.5-6.0, 85-90 ºC, 40 min.
Cold nickel fluoride sealing	Sealing, Ni^{2+} 0.8-1.5 g·L^{-1}, F^- 0.4-0.6 g·L^{-1}, pH 5.5-6.5, 25 ºC, 12-18 min. Post-treatment, deionized water, pH 5.5-6.5, 60-80 ºC, 20 min.

2.4 Characterization of oxide films after sealing

Surface morphology of anodic oxide films after different sealing methods was examined by scanning electron microscope (SEM, SSX-550, Shimadzu Corporation, Japan). To characterize the corrosion resistance of the effect of different sealing techniques on oxide films, alkaline etching test (JIS H 8681-1:1999), phosphorus-chromium acid oxide method (GB/T 8753.1-2005) and potentiodynamic polarization experiment were measured.

Corrosion time was recorded by alkaline etching test. The solution of alkaline etching test was 100 g·L^{-1} NaOH. Clean the specimen, drop the alkaline etching solution on the surface of sealed samples, record the time (s) until observing uniform bubbles. The weight loss (mg·dm^{-2}) was detected by phosphorus-chromium acid oxide method. The test solution should have the following makeup: 20 g·L^{-1} of CrO_3 and 35 mL·L^{-1} of orthophosphoric acid. Potentiodynamic polarization curves were obtained using three-electrode system in 3.5 wt.% NaCl solution at room temperature on electrochemical workstation (CHI600D, Shanghai CH Instruments, China). The working electrode was 10×10 mm area of sealed specimen set in epoxy resin. The reference electrode was saturated calomel electrode (SCE) and platinum stick was used as the counter electrode. Sealed specimens were measured with the scan rate of 5 mV·s^{-1}.

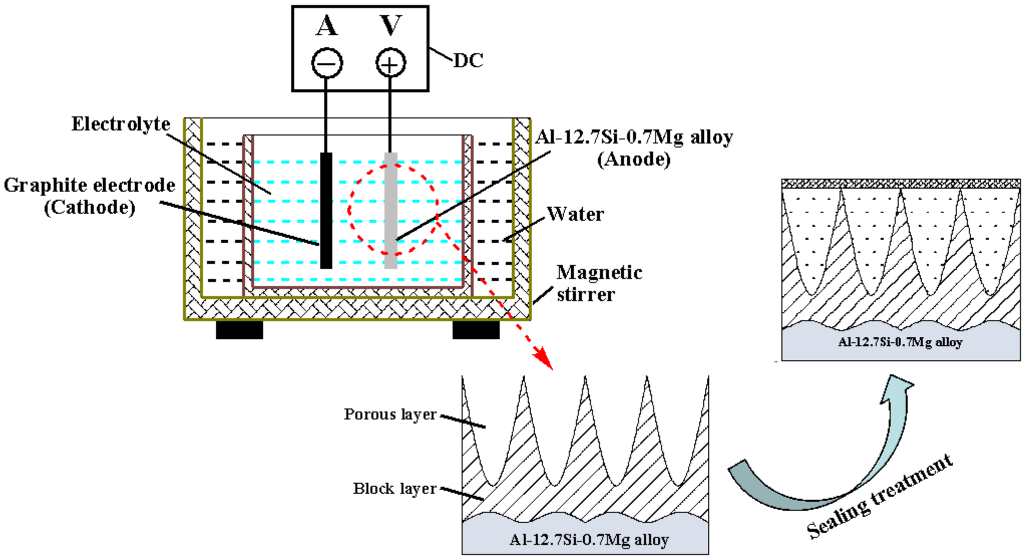

Figure 1. Schematic illustration of technological process of sealing technique of anodic film

3. RESULTS AND DISCUSSION

3.1 The optimal process conditions of stearic acid sealing

The influence of processing condition of stearic acid sealing on anodic oxidation film weight loss was investigated. The results are shown in Figure 2. The concentration of stearic acid increased from 30 % to 100% (wt.%), the values of weight loss decreased by 50%. The chemical reaction between organic fatty acid and metal or metal oxide form complex compounds, which could improve the corrosion resistance and protect metal alloy [22-26]. Stearic acid is a long-chain saturated fatty acid and is nontoxic and biocompatible. During sealing process, stearic acid transformed to a layer of fatty soaps with alumina by chemical reaction [25]. In this research, high concentration stearic acid was advantage to form aluminum soap compounds between the anodized layer and organic acid. Moreover, fatigue or stress cracking occurred on the surface of anodic films, the organic acid reacted with oxide layer to form soap, reestablishing a barrier to protect alloy [27,28]. Consequently, the porous layers of anodic films were sealed entirely and exhibited excellent corrosion resistance.

The reaction of organic acid and anodic film was incompletely when sealing time was shorter than 45 min, causing surface of anodic film uneven or the occurrence of pitting. As sealing time prolonged more than 45 min, the aging of sealing solution speeded up. It is easily to understand that sealing time of 45 min was suitable for stearic sealing processing.

As shown in Figure 2 (c), sealing temperature was at 95 ºC, weight loss presented the minimum value, about 46 $mg\cdot dm^{-2}$. Stearic acid was inadequately dissolved and reacted with anodic film slowly at low temperature. Meanwhile, aluminum soap compounds were difficultly generated. On the other hand, the stability of sealing solution was reduced and cracks were produced easily on the surface of anodic layer at high temperature. The effect of sealing was poor and corrosion resistance of alloy surface was reduced. Hence, 95 ºC of sealing temperature was the best choice.

To sum up, the optimal processing parameters of organic acid sealing treatment were as follows: 100% (wt.%) of concentration stearic acid, sealing time of 45 min and 95 ºC of sealing temperature, respectively.

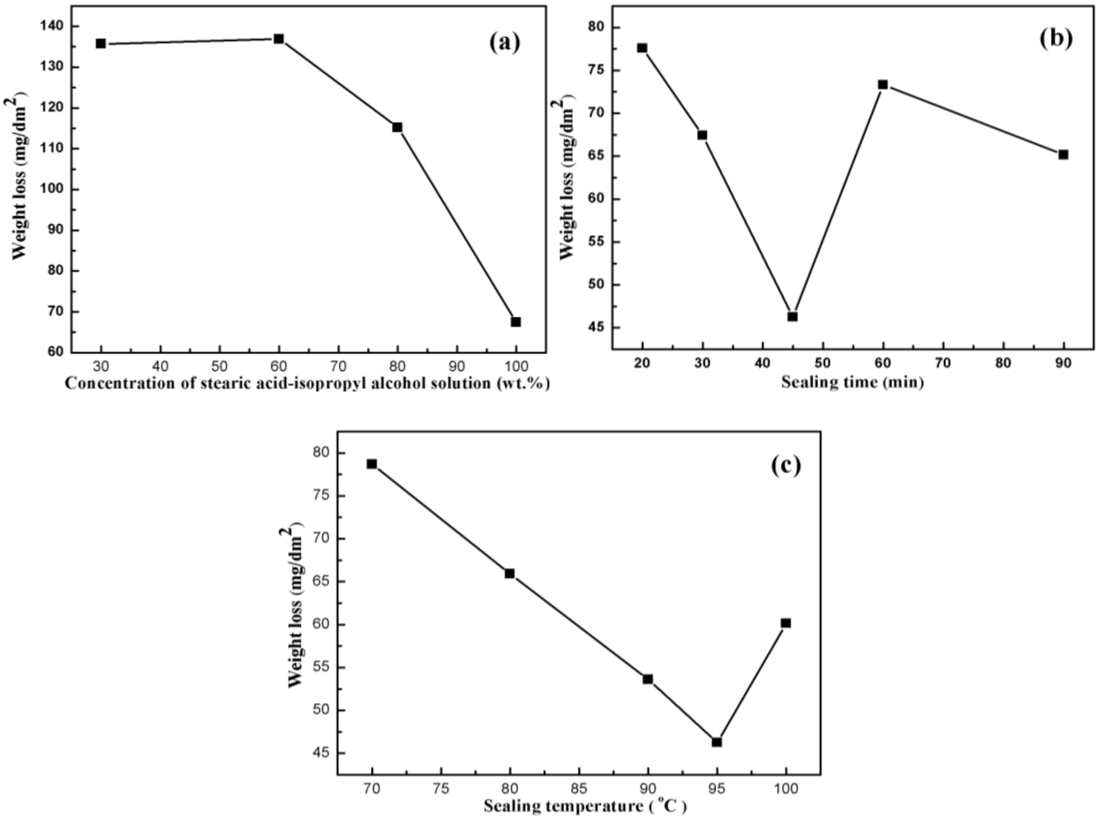

Figure 2. The influence of processing parameters of stearic acid sealing on anodic oxidation film weight loss ((a) Concentration of stearic acid (wt.%), (b) Sealing time (min), (c) Sealing temperature (ºC)). Anodic oxidation parameters were 170 g·L^{-1} H_2SO_4 at room temperature for 25 min, using 1.5 A·dm^{-2} of current density.

3.2 Surface morphology of anodic films

To observe the surface morphology of anodic oxide films with different sealing methods, SEM micrographs of samples are presented in Figure 3. As comparison, anodic film with unsealing is showed in Figure 3 (f). White granules were silicon as alloy element and distributed evenly in alloy substrate [6]. Alloy elements were difficult to be anodized during anodizing processing [11]. Addition of silicon particles in Al-12.7Si-0.7Mg alloy could cause the continuity of anodic oxide film poorly. The pitting on the surface of alloy was readily occurred. Thus, the corrosion resistance of anodizing aluminum alloy was reduced. As shown in Figure 3, the surface of anodizing samples after sealing treatment was more smooth, uniform and compact than that of unsealing. Silicon granules were embedded in the anodic layer closely. The porous layer of anodic films was sealed to avoid the occurrence of pitting. Compared to other sealing treatment, boiling water sealing and stearic acid sealing exhibited more excellent flatness and uniformity and the sealing effect was best. Moreover, silicon granules were almost completely covered after stearic acid sealing treatment, as shown in Figure 3 (d). Stearic acid sealing method could markedly improve the corrosion resistance of Al-12.7Si-0.7Mg alloy.

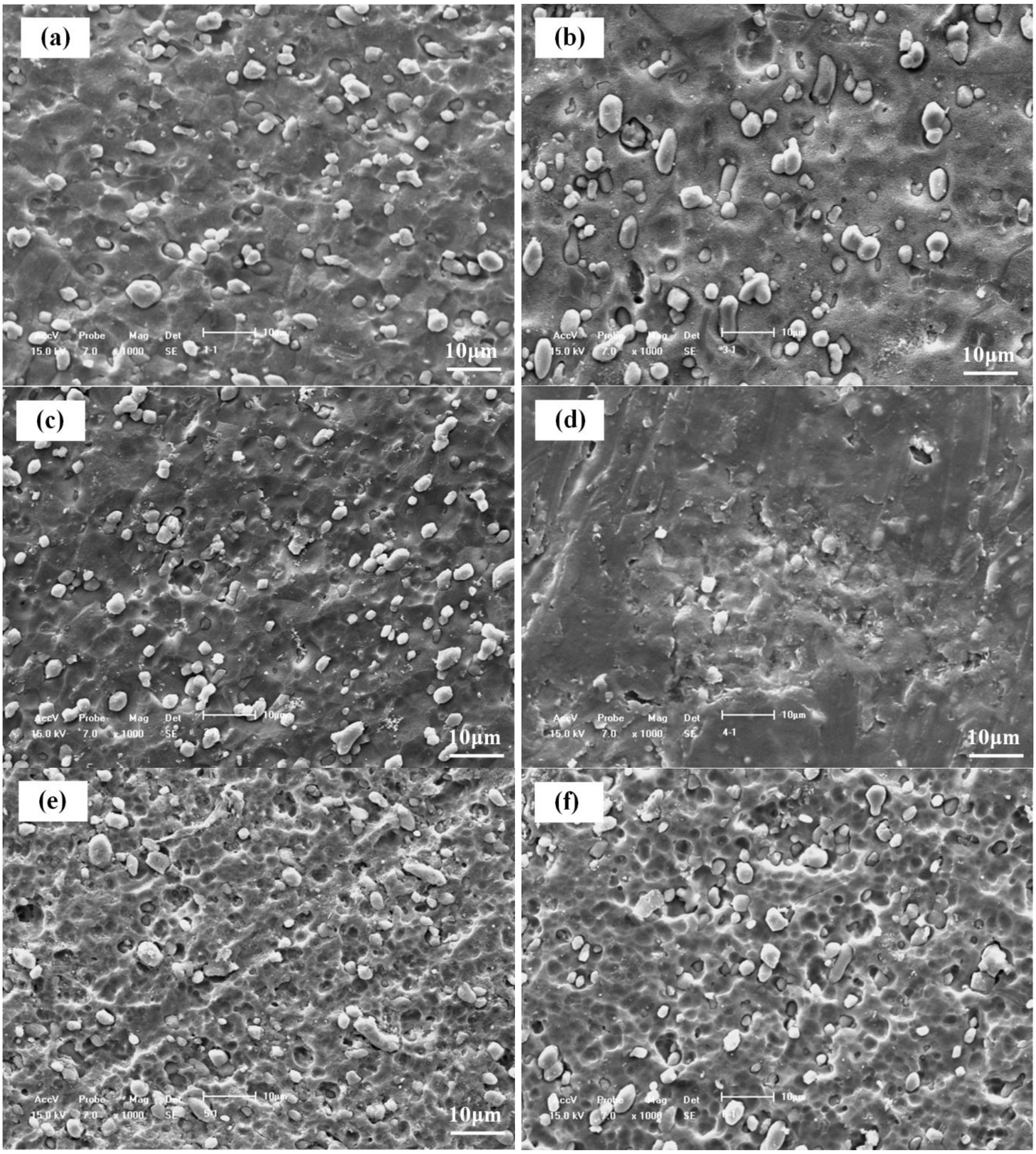

Figure 3. SEM micrographs of surface morphology of anodic oxide films with different sealing methods ((a) Boiling water sealing, (b) Nickel acetate sealing, (c) Cold nickel fluoride sealing, (d) Stearic acid sealing, (e) Potassium bichromate sealing, (f) Unsealing).

3.3 Corrosion resistance research

To investigate the corrosion resistance of anodizing specimens with different sealing techniques, potentiodynamic polarization, alkaline etching test (JIS H 8681-1:1999) and phosphorus-chromium acid oxide method (GB/T 8753.1-2005) was studied.

Anodic layers after sealing by different methods were measured in 3.5 wt.% NaCl solution after immersion for 30 min. Potentiodynamic polarization curves of specimens are presented in Figure 4. According to Tafel extrapolation method [29,30], the corrosion potential (E_{corr}), corrosion current density (I_{corr}), corrosion rate (V_{corr}), anodic Tafel slope (b_a) and cathodic Tafel slope (b_c) are calculated and all values are listed in Table 4. In a typical polarization curve, a lower I_{corr} or a higher E_{corr} corresponds to a lower corrosion rate and a better corrosion resistance [31]. It can be observed that the corrosion potential of anodic film with stearic acid sealing was about -2.2 mV vs. SCE, corrosion current density and corrosion rate was 2.88×10^{-9} A·cm^{-2} and 3.37×10^{-5} mm·a^{-1}, respectively. The anodic oxide film with stearic acid sealing exhibited very low corrosion rate, a 20-fold decrease from unsealing sample, 4-fold decrease from nickel acetate sealing. Compared with other four sealing methods, stearic acid sealing with a higher corrosion potential and a lower corrosion current density showed excellent corrosion resistance.

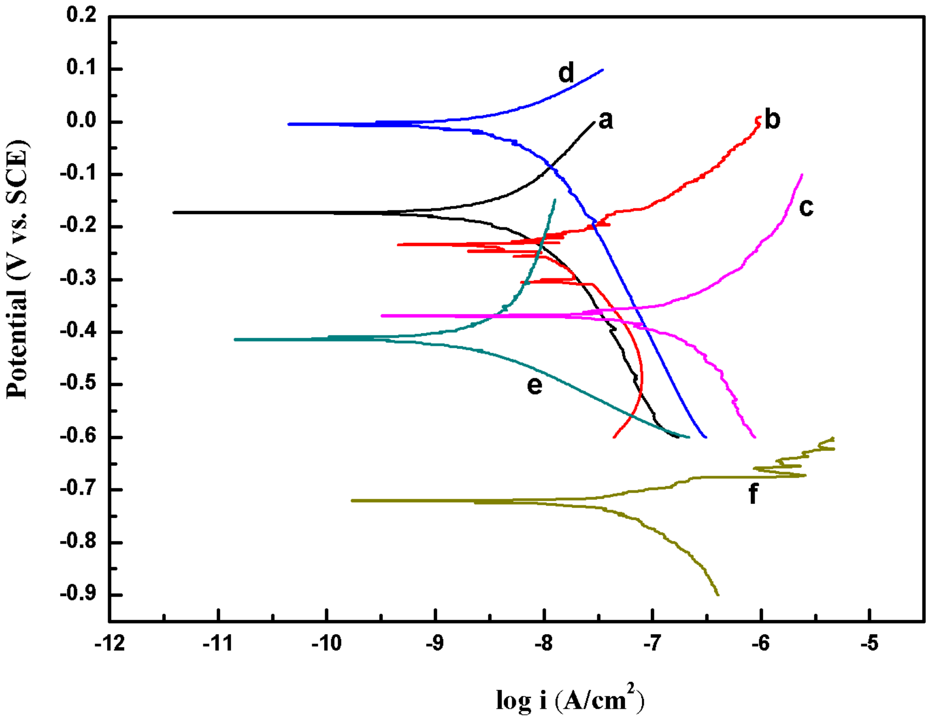

Figure 4. Potentiodynamic polarization curves of anodizing specimens with different sealing methods in 3.5 wt% NaCl solution at room temperature ((a) Boiling water sealing, (b) Nickel acetate sealing, (c) Cold nickel fluoride sealing, (d) Stearic acid sealing, (e) Potassium bichromate sealing, (f) Unsealing).

Table 3. Corrosion potential, corrosion current, corrosion rate of anodizing specimens with different sealing methods.

Sample	b_a (V·dec^{-1})	b_c (V·dec^{-1})	E_{corr} (mV vs.SCE)	I_{corr} (A·cm^{-2})	V_{corr} (mm·a^{-1})
Boiling water sealing	0.187	0.168	-173	3.85×10^{-9}	4.50×10^{-5}
Nickel acetate sealing	0.092	0.187	-243	1.01×10^{-8}	1.18×10^{-4}
Cold nickel fluoride sealing	0.097	0.096	-378	7.08×10^{-8}	8.28×10^{-4}
Stearic acid sealing	0.076	0.145	-2.2	2.88×10^{-9}	3.37×10^{-5}
Potassium bichromate sealing	0.422	0.102	-418	3.05×10^{-9}	3.57×10^{-5}
Unsealing	0.057	0.126	-722	5.88×10^{-8}	6.88×10^{-4}

b_a (V·dec^{-1})-anodic Tafel slope; b_c (V·dec^{-1})-cathodic Tafel slope; E_{corr} (mV vs.SCE)-corrosion potential; I_{corr} (A·cm^{-2})-corrosion current density; V_{corr} (mm·a^{-1})- corrosion rate.

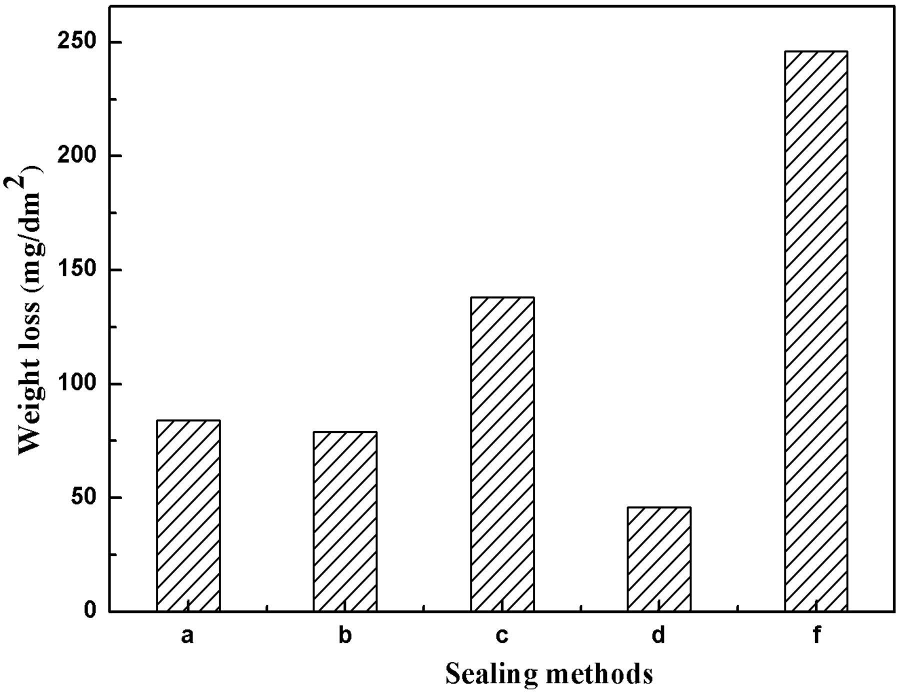

Figure 5. Weight loss (mg·dm^{-2}) of anodic oxide films with different sealing methods by phosphorus-chromium acid oxide method ((a) Boiling water sealing, (b) Nickel acetate sealing, (c) Cold nickel fluoride sealing, (d) Stearic acid sealing, (f) Unsealing). The test solution as follows: 20 g·L^{-1} of CrO_3 and 35 mL·L^{-1} of orthophosphoric acid.

Phosphorus-chromium acid oxide method was used to examine the quality of anodic films after sealing. However, this method was not applicable to the anodic oxide sample with potassium bichromate sealing. The comparison experiment was without potassium bichromate sealing in this part. The test solution of phosphorus-chromium acid oxide method was 20 g·L^{-1} of CrO_3 and 35 mL·L^{-1} of orthophosphoric acid. All samples were immersed in solution for 15 min at (38±1) ºC. Values of weight loss (mg·dm^{-2}) were calculated and showed in Figure 5. The weight loss of stearic acid sealing was 46 mg·dm^{-2}, presenting the minimum value of weight loss, only about one fifth of that of unsealing sample (246 mg·dm^{-2}), about one third of that of Cold nickel fluoride sealing (138 mg·dm^{-2}) and about a half of that of boiling water sealing (84 mg·dm^{-2}). The values of weight loss of samples with four sealing methods were lower than unsealing sample.

The solution of 100 g·L^{-1} NaOH was used in alkaline etching test and Corrosion time was recorded. All results presented in Figure 6. The corrosion time of sealing specimens were higher than unsealing sample. Stearic acid sealing specimen with the maximum of corrosion time exhibited excellent corrosion resistance. Additionally, the corrosion time of anodic film with stearic acid sealing was nearly equivalent to that of potassium bichromate sealing. Actually, stearic acid sealing was suitable to use in sealing the anodic film, owing to toxicity and environmental problems of hexavalent chromium.

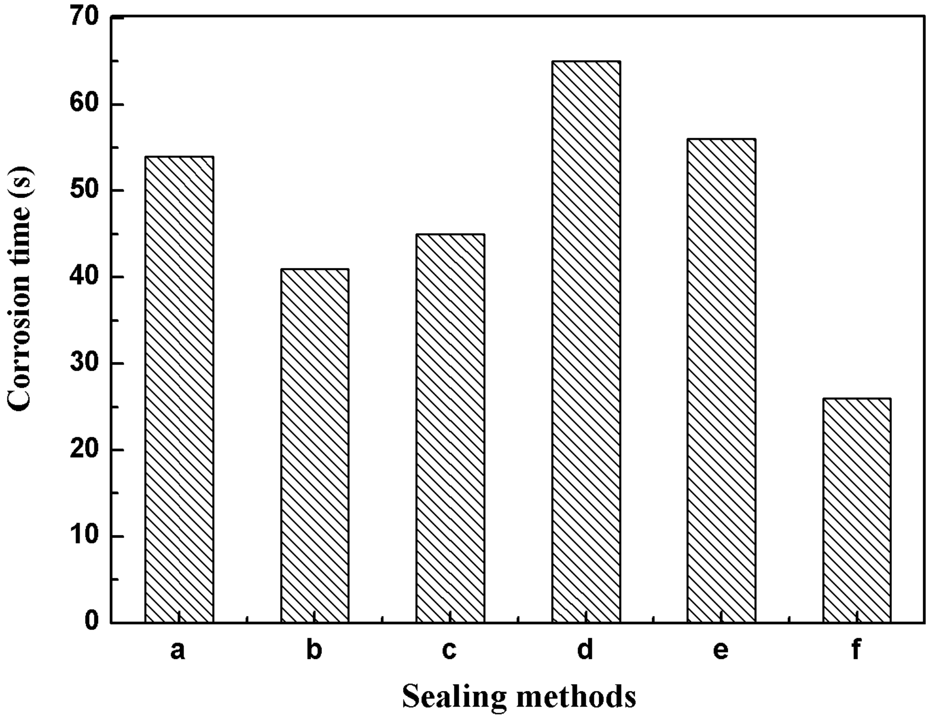

Figure 6. Corrosion time (s) of anodic oxide films with different sealing methods by alkaline etching test ((a) Boiling water sealing, (b) Nickel acetate sealing, (c) Cold nickel fluoride sealing, (d) Stearic acid sealing, (e) Potassium bichromate sealing, (f) Unsealing). The test solution was 100 g·L^{-1} NaOH.

According to the results of potentiodynamic polarization, phosphorus-chromium acid oxide method and alkaline etching test, different sealing techniques had different influences on the corrosion resistance. Sealing techniques could significantly improve the corrosion resistance of anodic films of Al-12.7Si-0.7Mg. Compared with other sealing methods, stearic acid sealing was more highly effective and environmentally friendly.

4. CONCLUSIONS

On the basis of values of weight loss, the optimal processing parameters of stearic acid sealing treatment were as follows: pure stearic acid, sealing time of 45 min and sealing temperature of 95 ºC. Surface morphology of anodic oxide films after different sealing methods showed that boiling water sealing and stearic acid sealing exhibited more excellent flatness and uniformity and the sealing effect was best. Potentiodynamic polarization, phosphorus-chromium acid oxide method and alkaline etching test were used to characterize the corrosion resistance of the effect of different sealing techniques on oxide films. The results indicated that different sealing techniques exhibited different influences on the corrosion resistance. Stearic acid sealing method was more effective for improving corrosion resistance of anodic film of Al-12.7Si-0.7Mg alloy.

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