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Effect of aluminum content on the passivation behavior of Fe–Al alloys in sulfuric acid solution

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The passivation behavior of Fe–Al alloys (3.4, 10.4, 18.7, 19.4, 29.5, and 41.7 at % Al) and Fe–Al alloys (19.5 and 29.0 at % Al) with 5.1 at % Cr addition in 0.1 N H_2SO_4 is reported in this paper. The behavior has been evaluated by potentiodynamic polarization measurements. The results show the Fe–Al alloys, which the Al content of alloy exceeds 19 at %, have wide passivation regions with low passivation current. However, when the Al content of Fe–Al alloys exceeds this range, the increment of Al content has slight influence on passivation behavior compared with ternary Cr addition. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

Fe–Al alloys are regarded as promising materials for high temperature applications because of their good strength to weight ratio, and excellent oxidation and sulfidation resistance [1–3]. However, they exhibit poor ambient temperature ductility because of moisture induced hydrogen embrittlement [4–10]. It had been proven that the addition of Cr (2–6 at %) can increase the room temperature ductility of Fe–Al alloys significantly [11–15]. Although Fe–Al alloys are mainly applied in facilities at high temperature, their aqueous corrosion behavior at room temperature should also be concerned. The purpose of this study is to investigate the effect of Al content form 3–40 at % on electrochemical polarization behavior of binary Fe–Al alloys in 0.1 N H_2SO_4 at room temperature. The effect of Cr additions in some Fe–Al alloys is also discussed in this study.

2. Experimental methods

The specimens of Fe–Al alloys used in this study were produced from 99.99 % Fe, 99.95 % Al, and 99.95 % Cr elements. For minimizing segregation, each alloy ingot was produced by repeated melting with vacuum induction melting (VIM) and then with vacuum arc remelting (VAR) and cast into copper mold. Detailed ingot-melting and specimen-preparation were described in previous studies [8, 9]. For comparison, the specimen of pure iron was also used in this study. The composition analyses of specimens were carried out by energy dispersive X-ray spectrometry (EDX) and listed in Table I. The crystal structure was confirmed by X-ray diffraction (XRD) using CuKα radiation.

Potentiodynamic polarization measurements were carried out in a typical three-electrode cell setup as described in previous studies [16], and all potentials were reported with respect to saturated calomel electrode (SCE). The measurements were conducted in 0.1 N H_2SO_4 solution at 25°C under atmospheric condition. The specimens were scanned potentiodynamically at a rate of 1 mV/s from the initial potential of -0.1 V versus open-circuit potential, which was recorded after 1 h immersion before measurements, to the final potential of 2.0 V_{SCE}.

3. Results and discussion

According to the results of XRD analyses and Fe–Al phase diagrams [17, 18], the crystal structures of specimens depend on Al content. Alloys A, B, C, D, and D-1 belong to α-disordered solid solution structure. Alloys E and E-1 (Fe_3Al intermetallic phase) and Alloy F (FeAl intermetallic phase) belong to imperfect B2 ordered structure, respectively.

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TABLE I. Alloy compositions and electrochemical parameters in 0.1 N H_2SO_4

	Compositions			Electrochemical parameters						
	Fe (at %)	Al (at %)	Cr (at %)	E_{corr} (V_{SCE})	i_{corr} (A/cm^2)	E_{pp} (V_{SCE})	i_{crit} (A/cm^2)	i_{pass} (A/cm^2)	E_b (V_{SCE})	$E_b - E_{pp}$
Pure iron	99.9	–	–	−0.58	1.36×10^{-4}	1.28	7.94×10^{-2}	3.29×10^{-3}	1.58	0.30
Alloy A	96.6	3.4	–	−0.59	1.53×10^{-4}	–	–	–	–	–
Alloy B	89.6	10.4	–	−0.59	4.33×10^{-4}	1.05	6.88×10^{-2}	2.60×10^{-4}	1.47	0.42
Alloy C	81.3	18.7	–	−0.59	7.49×10^{-4}	0.51	4.14×10^{-2}	1.62×10^{-5}	1.42	0.91
Alloy D	80.6	19.4	–	−0.60	6.84×10^{-4}	−0.05	1.25×10^{-2}	1.34×10^{-5}	1.42	1.47
Alloy D-1	75.4	19.5	5.1	−0.61	9.88×10^{-4}	−0.38	1.14×10^{-2}	7.15×10^{-6}	1.43	1.81
Alloy E	70.5	29.5	–	−0.60	1.06×10^{-3}	−0.23	1.77×10^{-2}	1.10×10^{-5}	1.43	1.66
Alloy E-1	65.9	29.0	5.1	−0.60	1.37×10^{-3}	−0.38	7.81×10^{-3}	9.20×10^{-6}	1.45	1.83
Alloy F	58.3	41.7	–	−0.65	1.22×10^{-3}	−0.48	7.32×10^{-3}	1.17×10^{-5}	1.45	1.93

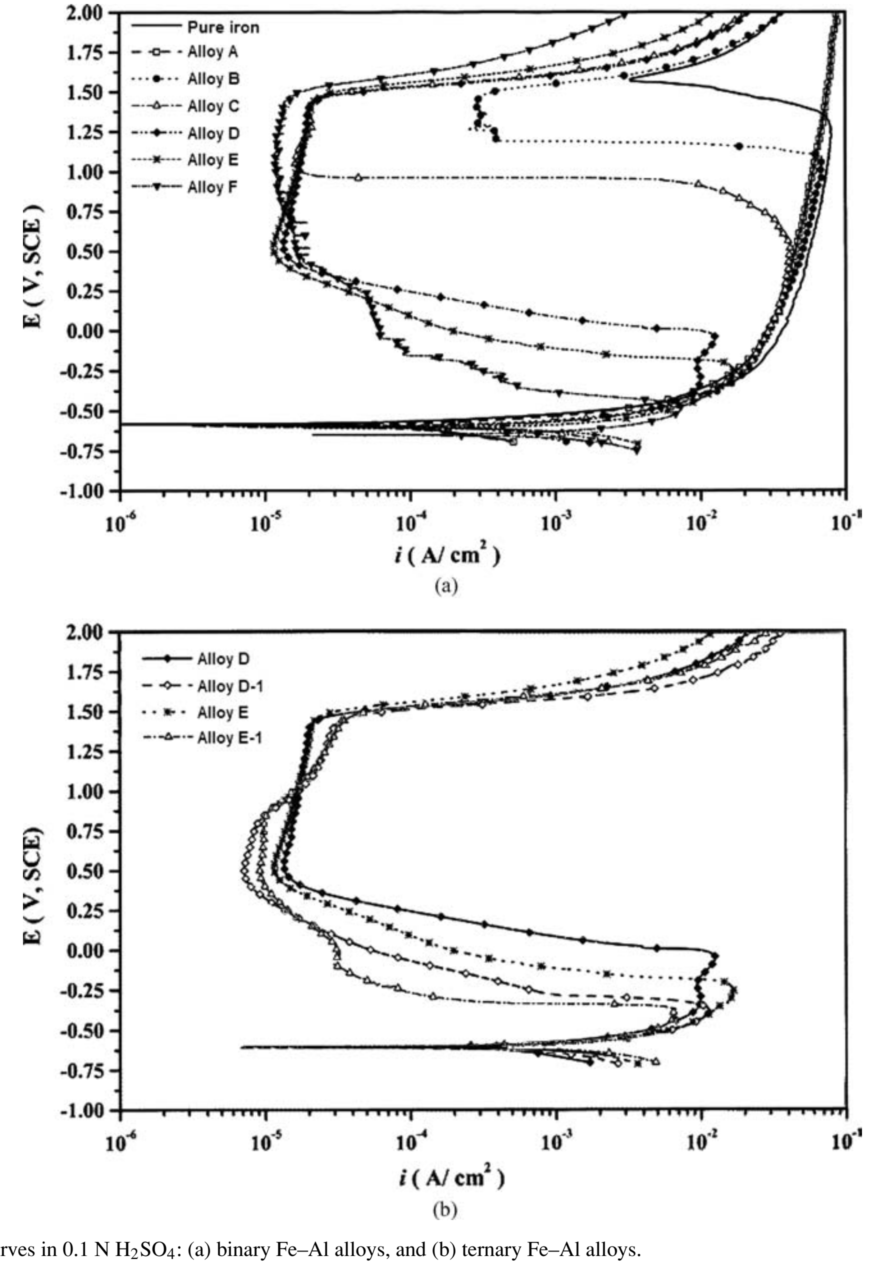

Figure 1 Polarization curves in 0.1 N H_2SO_4: (a) binary Fe–Al alloys, and (b) ternary Fe–Al alloys.

The polarization curves of Fe–Al alloys and pure iron in 0.1 N H_2SO_4 are compared in Fig. 1. The curves show the passivation regions can be obviously observed when the Al content is higher than 10 at %. The electrochemical parameters of alloys are derived from polarization curves and summarized in Table I, that is, corrosion potential (E_{corr}), corrosion current density (i_{corr}), primary passivation potential (E_{pp}), critical passivation current density (i_{crit}), passivation current density (i_{pass}, minimum current density in passivation region), and breakdown potential (E_b). The relationship between the E_b-E_{pp} and Al content are also summarized in Table I. From the viewpoint of E_b-E_{pp}, the greater the E_b-E_{pp}, the broader the passivation region.

The curves and parameters indicate that when Al content is added to exceed above 18 at %, Fe–Al alloys, at higher anodic potential, tend to form the relatively stable passive film with low passivation current density. This result shows the increment of Al content can enhance the stability of passive film. The shift in E_{corr} (open circuit potential) is not significant in all specimens. In Table I as comparison with Alloy C, Alloy D shows more pronounced reduction in the E_{pp} and more pronounced increment in E_b-E_{pp}, although the Al content of Alloy D is slightly higher than that of Alloy C. It could be explained by the basis of electron configuration theory: the minimum Al content needed to fill the Fe atomic level d in order to modify the Fe surface properties is about 20 at % [19]. When the Al content exceeds about 19 at %, the passivation behavior shows significant difference between Alloy C and Alloy D.

Table I and Fig. 1(b) indicate Fe–Al alloys with 5 at % Cr (Alloys D-1 and E-1) have the tendency to broaden the passivation region in comparison with those without 5 at % Cr (Alloys D and E). Table I also indicates these alloys with 5 at % Cr, at higher anodic potential, tend to form relatively more stable passive film with slight lower passivation current density. It is also noted that the passivation behavior of Alloy D-1 is even better than that of Alloy E. Therefore, the passivation behavior of these alloys can be improved with Cr addition, especially in Alloy D. Because Al tends to form porous oxide film (separate oxide phase) in H_2SO_4 and cause galvanic attack in weaker and more porous oxide region, the Cr, is regarded as a strong oxide film-forming element, can give Fe–Al alloys an additional resistance to the passage of metal ions through Al oxide film, and can further improve the passivation behavior by the formation of a film composed of $Cr(OH)_3$ and Cr_2O_3 in alloys with higher Cr content [20–23]. However, when the Al content is higher in alloys, the beneficial effect of less Cr addition (5.1 at %) on passivation is not obvious as expectation [24]. Also from Fig. 1(b), it can be found the anodic polarization curve of Alloy D-1 is similar with that of Alloy E-1, although they have different Al content and crystal structure. Some studies suggested the crystal structure of Fe–Al alloys has slight influence on passivation properties [25, 26].

In this work, it indicates that in 0.1 N H_2SO_4, when the Al content of Fe–Al alloys exceeds about 19 at %, the increment of Al content has slight influence on passivation behavior in comparison with ternary Cr addition.

4. Conclusions

The results of this study have highlighted the passivation behavior of Fe–Al alloys in 0.1 N H_2SO_4. The results are summarized as follows:

1. When the Al content of Fe–Al alloys exceeds about 19 at %, the passivation behavior of alloys can be improved significantly. However, the influence on passivation behavior of Fe–Al alloys becomes less beneficial when the Al content exceeds this range.
2. The Cr addition in Fe–Al alloys causes the tendency to form relatively more stable passive film with slightly lower passivation current density, irrespective of their Al content and crystal structure. However, when the Al content is higher, the beneficial effect of Cr on passivation behavior in case of Alloys E and E-1 is not as obvious as is expected.
3. The corrosion resistance of Fe–Al alloys in aqueous solutions needs further study to improve by alloying elements or other techniques to make their application more feasible.

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