

Aqueous Corrosion Behavior of Iron Aluminide Intermetallics

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Iron aluminide intermetallics based on DO_3 ordered structure are being developed for use as structural materials and cladding material for conventional engineering alloys. Aqueous corrosion behavior of iron aluminides has been studied extensively by electrochemical techniques. Studies were carried out on pure Fe (99.9%), Fe-28Al (at.%), Fe-28Al-3Cr (at.%), and AISI SS 304 so as to compare and contrast their behavior in same experimental condition. Polarization behavior under different pH conditions was examined to evaluate their performance in acidic, basic, and neutral solutions. Pitting behavior was also studied in solution containing Cl^- ions. The stability of the passive film formed was studied by current time transients and potential decay profiles. The presence of 3 at.% Cr in iron aluminides was found to improve the aqueous corrosion resistance and makes it comparable to AISI SS 304.

Keywords corrosion studies, intermetallics, iron aluminides (based on Fe_3Al), ordered structures

1. Introduction

Iron aluminides have received extensive attention as materials with good potential for industrial application because of their low cost, low density, good wear resistance, and excellent sulfidation and oxidation resistance (Ref 1-3). The lack of ductility at room temperature and decrease in strength above 873 K is one of the main drawbacks, which had retarded their development as a structural material. However, improvement in the room temperature ductility of Fe_3Al has been achieved recently by the addition of alloying elements such as Cr (Ref 4-6). Although iron aluminides were developed for high-temperature application, they can also be considered for use at low temperature if their corrosion behavior in aqueous solutions is suitable. A number of studies have been reported on the high temperature corrosion/oxidation behavior and hydrogen embrittlement in iron aluminides (Ref 7-11). However, to date, only few studies have been reported on the aqueous corrosion behavior of these materials. Buchanan and Kim (Ref 12, 13) have reported pitting behavior of DO_3 type iron aluminide in acid rain type medium. Improvement in pitting and crevice resistance was found on addition of Cr and Mo (Ref 12). Similarly, the beneficial effect of Cr and Mo addition on the passivity and its breakdown in Fe_3Al alloys has also been studied (Ref 14). Rao et al. have reported the effect of

Cr on the corrosion behavior of Fe_3Al in sulfuric acid (Ref 15, 16). Passivity of βFeAl has also been studied in detail (Ref 17, 18). The present work is undertaken to investigate the aqueous corrosion behavior of the pure Fe, Fe-28Al, Fe-28Al-3Cr, and SS 304 and the results were compared to understand the role of Cr addition on the passivity of iron aluminides.

2. Experimental

Alloys Fe-28Al (at.%) and Fe-28Al-3Cr (at.%) were prepared by induction melting followed by electrosag remelting for complete homogenization. Samples were cut of required dimensions and were heat treated at 813 K for 170 h followed by furnace cooling to obtain the desired DO_3 ordered structure. Electrochemical experiments were carried out in the conventional three-electrode cell; reference electrode, counter electrode, and working electrode. Saturated calomel electrode (SCE) was used as the reference electrode, platinum foil as the counter electrode and sample as the working electrode. The reference electrode was contained in Agar-Agar bridge (3% Agar + 30% KCl) to avoid the presence of chlorine in the electrolyte. It was connected to the electrolytic cell with a luggin capillary tip. Working electrode was rectangular in shape and was spot-welded with a steel wire for electrical connection. The electrode was set in cold mount METSET 101 and a fixed area was exposed. Corrosion studies were carried out on pure Fe (99.9%), Fe-28Al (at.%), Fe-28Al-3Cr (at.%), and AISI SS 304. The solutions were prepared from high-purity chemicals and deionized water and were deaerated with argon before use. The samples were metallographically polished to have an initial average roughness (R_a) of 0.32 μm . The polished area of the sample was exposed at open circuit conditions to the electrolytes. Once the open circuit potential (OCP) is stabilized, the potential was raised with time and the corresponding change in the current was recorded. The passive film formed on the exposed surface was analyzed by XPS technique.

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3. Results and Discussion

Polarization studies were conducted on pure Fe, Fe-28Al (at.%), Fe-28Al-3Cr (at.%), and SS 304 in 1 M H₂SO₄, 1 M Na₂SO₄, and 1 M NaOH at scan rate of 0.5 mV/s. The polarization curve of Fe, Fe-28Al (at.%), Fe-28Al-3Cr (at.%), and SS 304 in 1 M H₂SO₄ is shown in Fig. 1(a). This plot showed that all these alloys exhibit passivation; however, they differ in nature of transition from active to passive state. Fe showed sudden transition from active to passive state after considerable active dissolution, whereas iron aluminides and SS 304 showed typical active passive transition. Critical current density (I_c) and passive current density (I_p) were found to be lowest for SS 304. Notably, the presence of Al and Cr in iron aluminides showed a drastic reduction in active-passive currents as compared to Fe. The presence of Al and Cr in Fe-28Al was found to reduce its I_p as compared to pure Fe. It has been well-reported that at low potential, the spontaneous passivation tendency of Al present in Fe-28Al reduced the active dissolution by formation of an Al₂O₃ film, whereas at higher potential the presence of Fe₂O₃ provided additional resistance to the passage of current with Al₂O₃ (Ref 16). Thus, current density of Fe-28Al in the passive region was lower than that of Fe. Similarly, the presence of Cr in Fe-28Al-3Cr showed beneficial effect by reducing I_p further as compared to Fe-28Al. Compared to iron aluminides, SS 304 showed very small active passive current. However, the transpassive potential (T_p) at which the passivity is lost, was found to be high for iron aluminides as compared to SS 304. The behavior of Fe and iron aluminides was found to be same in the transpassive region.

The polarization behavior of Fe, Fe-28Al, Fe-28Al-3Cr, and SS 304 in 1 M Na₂SO₄ is compared in Fig. 1(b). The OCP varied over a large-potential range and gradually shifted in the positive direction from Fe to Fe-28Al-3Cr. The critical current density (I_c) and passive current density (I_p) were found to be low in these materials as compared to that in sulfuric acid. There was a sudden transition from active to passive state in Fe and Fe-28Al alloy, whereas Fe-28Al-3Cr showed relatively slow active to passive transition. SS 304 showed passivity just above OCP and the current was found to be as low as ~1.4–1.8 $\mu\text{A}/\text{cm}^2$. The transpassive potential for Fe, Fe-28Al, and Fe-28Al-3Cr was found to be quite high as compared to SS 304. Transpassive potential, in general decreased in sodium sulfate solution compared to that in sulfuric acid as expected from the potential pH diagram (Ref 19).

Figure 1(c) showed polarization behavior in 1 M NaOH. In general, the OCP was found to be lowest in this medium than that in the other two media studied. Both critical current and passive current were lower in this medium as compared to other two solutions. Fe-28Al showed higher critical current than Fe but lower passive current above -50 mV. SS 304 showed passivity and low-passive current as compared to Fe-28Al-3Cr, Fe-28Al, and Fe. A summary of electrochemical parameters derived from polarization tests is given in Table 1.

As clear from the polarization studies there was definite improvement in the aqueous corrosion behavior of Fe-28Al and Fe-28Al-3Cr over Fe in all the three solutions. The presence of Cr in iron aluminides showed further improvement in corrosion properties by reducing the active and passive currents. The aqueous corrosion behavior of iron aluminides was compared with SS 304 because the motivation behind the development of iron aluminides is to replace stainless steels in aqueous

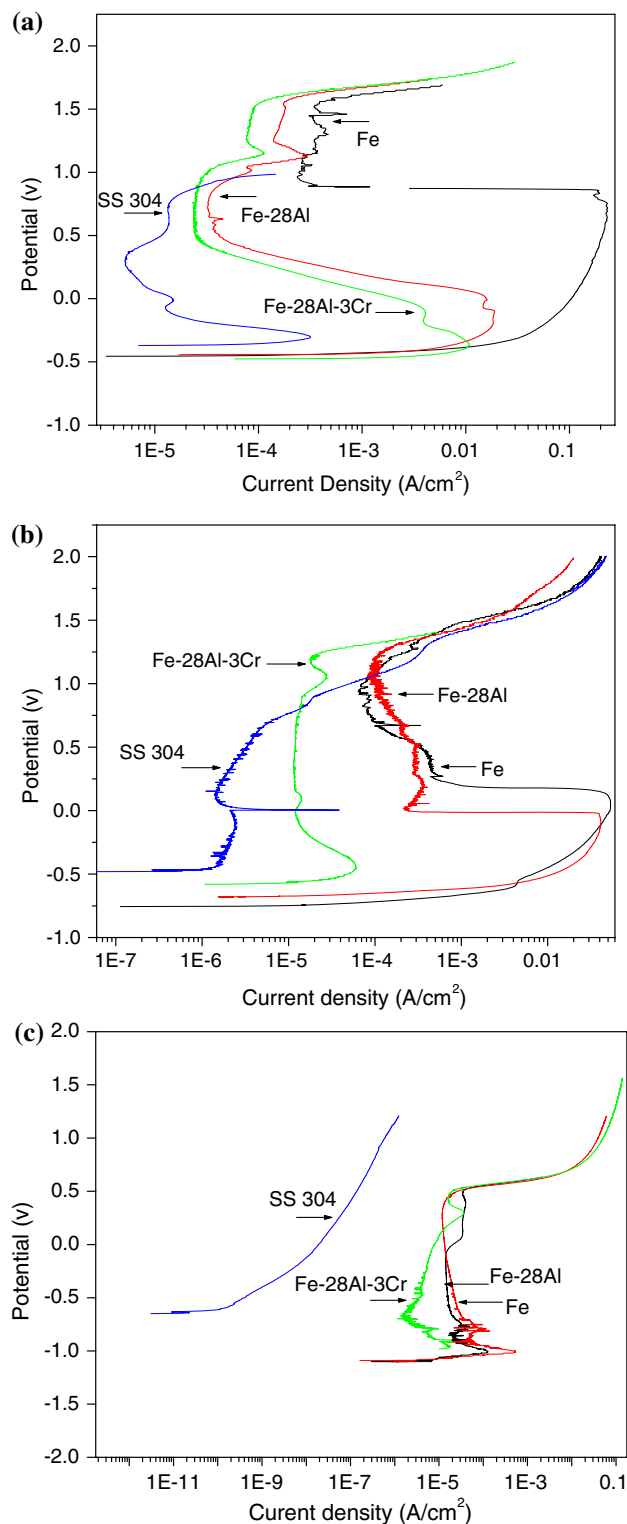


Fig. 1 Polarization of Fe, Fe-28Al, Fe-28Al-3Cr, and SS 304 in (a) 1 M H₂SO₄ (Ar), (b) 1 M Na₂SO₄ (Ar), (c) 1 M NaOH (Ar); at a scan rate of 0.5 mV/s

environment applications. Electrochemical data obtained from the respective polarization curve showed that critical current density, which is an important parameter to assess the dissolution tendency of an alloy, was lowest for SS 304 compared to Fe-28Al-3Cr. While comparing both alloys in their

passive regions it was found that Fe-28Al-3Cr has noble passive potential and at the same time the passive region is much wider compared to SS 304, but its passive current density is about one order higher than that of stainless steel. However, SS 304 showed lower transpassive potential as compared to iron aluminides. Transpassive potential and current slope of Fe and Fe-28Al were found to be similar. As the current rise slope was similar, this showed that similar film formed on the surface of Fe and Fe-28Al. In case of SS 304, transpassivity is due to film breakdown, which is a factor of chromium content. The oxide layer, which was present on the surface of SS, has Cr^{3+} oxidation state. With the increase in potential Cr^{3+} state transform to Cr^{6+} state, becomes unstable and start dissolving at the onset of the transpassive region. Transpassivity in iron and iron aluminides was due to evolution of oxygen instead of film breakdown.

Figure 2 depicts the pitting behavior of Fe, Fe-28Al, Fe-28Al-3Cr, and SS 304 in a 0.05 M $\text{Na}_2\text{SO}_4 + 500$ ppm NaCl solution. Fe and Fe-28Al showed very high currents in the active region, tending to a limiting current indicating uniform

Table 1 Electrochemical parameters for Fe, Fe-28Al, Fe-28Al-3Cr, and SS 304 derived from polarization curves

Electrochemical parameter	Fe	Fe-28Al	Fe-28Al-3Cr	304 SS
1 M H_2SO_4				
OCP, mV	-481	-484	-491	-378
I_c , mA/cm^2	232	190	10.8	0.32
I_p , $\mu\text{A}/\text{cm}^2$	356	64	31.9	8.28
T_p , mV	1478	1539	1539	748
1 M Na_2SO_4				
OCP, mV	-756	-638	-596	-352
I_c , mA/cm^2	53.4	40.95	0.061	...
I_p , $\mu\text{A}/\text{cm}^2$	20.5	12.1	9	1.4
T_p , mV	1351	1357	1345	634
1 M NaOH				
OCP, mV	-981	-859	-779	-725
I_c , $\mu\text{A}/\text{cm}^2$	120	53	4	...
I_p , $\mu\text{A}/\text{cm}^2$	12	9	0.5	...
T_p , mV	450	485	497	...

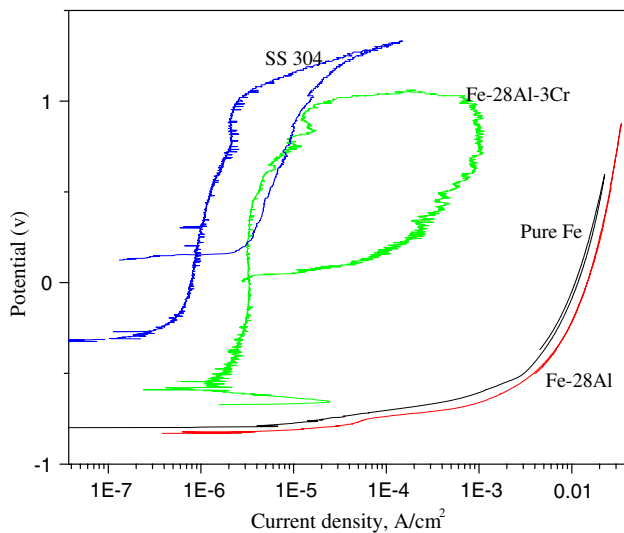


Fig. 2 Polarization curve showing the pitting behaviors of Fe, Fe-28Al, Fe-28Al-3Cr, and SS 304 in 0.05 M $\text{Na}_2\text{SO}_4 + 500$ ppm NaCl (Ar), scan rate 0.166 mV/s

dissolution. However, Fe-28Al-3Cr and SS 304 exhibited comparable pitting behaviors. Pitting potential (E_{pit}) and protection potential (E_{prot}) values for the Fe-28Al-3Cr alloy were found to be 940 and 153 mV, respectively. Similarly, SS 304 showed a E_{pit} value of 990 mV and E_{prot} of 210 mV. Both these alloys showed almost the same difference between the E_{pit} and E_{prot} values. However, once a pit formed, it propagated at a faster rate in the Fe-28Al-3Cr alloy as compared to SS 304, as indicated by the higher-active current value in the former. Buchanan and Kim (Ref 12, 13) have reported that the cyclic anodic polarization testing in a H_2SO_4 solution (pH 4, containing 200 ppm Cl^- ions) indicates the occurrence of passivation, but with a relatively low-breakdown potential for E_{pit} and E_{prot} lower than the OCP. In the present study, however, a high value of E_{pit} and E_{prot} above OCP was found for the Fe-28Al-3Cr alloy. This difference could be due to the different testing conditions used in the two studies. Overall, the results obtained indicated that the presence of Cr increased the resistance of Fe-28Al-3Cr alloy to a localized corrosion.

The stability of the film formed on the exposed surfaces of Fe, Fe-28Al, and Fe-28Al-3Cr was examined by studying potentiostatic current-time transients and potential decay profiles. Figure 3(a) depicts the current-time transients obtained for Fe-28Al-3Cr in 1 M Na_2SO_4 at two different holding potentials

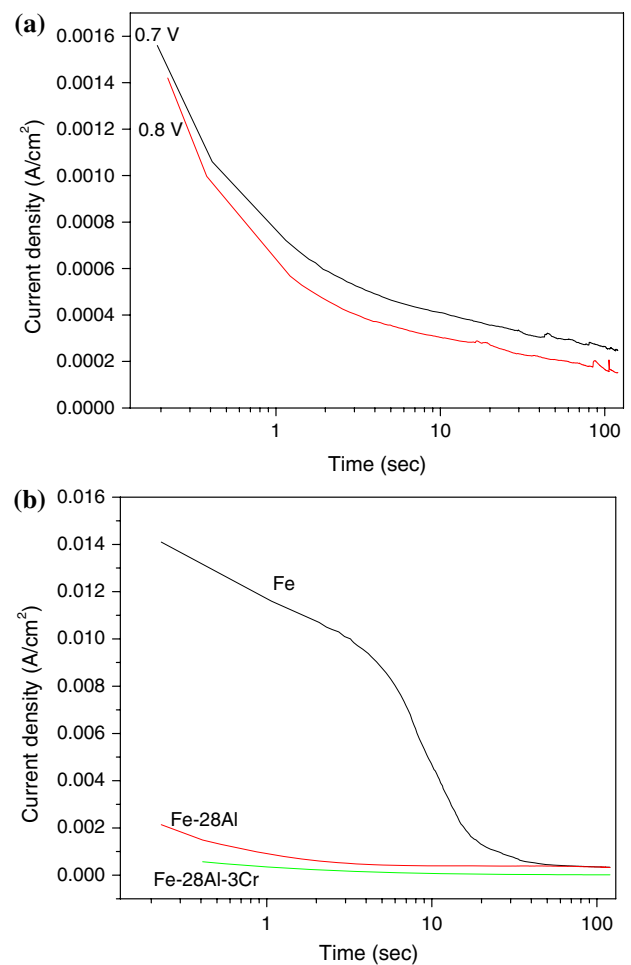


Fig. 3 Current-time transients for film formation on the (a) Fe-28Al-3Cr alloy in 1 M Na_2SO_4 (Ar) at different holding potential; (b) Fe, Fe-28Al, and Fe-28Al-3Cr in 1 M Na_2SO_4 (Ar) at 0.8 V, pH 6

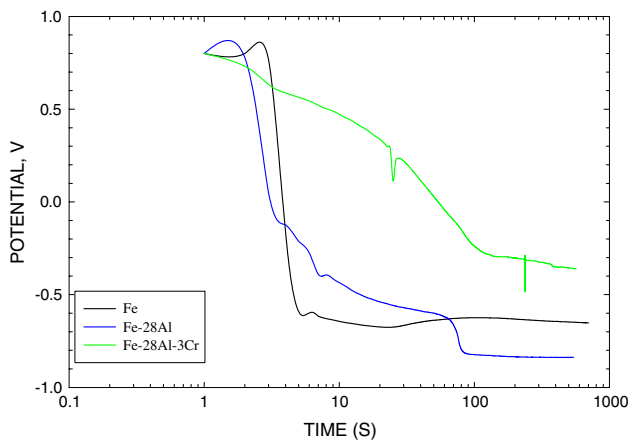


Fig. 4 Potential decay transient for film breakdown on Fe, Fe-28Al, and Fe-28Al-3Cr in 1 M Na₂SO₄ (Ar) 0.8 V, pH 6

(0.7 and 0.8 V). The plot showed a decrease in the current density with time, indicating passive film formation on the surface. Also, an increase in the holding potential from 0.7 to 0.8 V increased the passivation rate. Figure 3(b) shows current-time transients for Fe, Fe-28Al, and Fe-28Al-3Cr in 1 M Na₂SO₄. Fe showed a slow-film formation rate during the initial 5 s, and then the film formed rapidly and the process was completed in 25 s. In the case of Fe-28Al and Fe-28Al-3Cr alloys, stable films formed almost instantly showing a steady current after very short time. This showed that film formation on iron aluminides was very rapid as compared to the case of elemental Fe. The current density for Fe-28Al-3Cr was found to be lowest, indicating a high-passivation tendency of the alloy.

The potential decay profile for film breakdown was also studied for Fe, Fe-28Al, and Fe-28Al-3Cr. Figure 4 shows that the film formed on Fe broke down in single step in 10 s with one break at -528 mV. In Fe-28Al showed film breakdown occurred in two steps, with one break at -482 mV (4 s) and other at -797 mV (72 s). Fe-28Al-3Cr also showed a two-step breakdown with one potential arrest at 126 mV (28 s) and another at -350 mV (200 s). This result showed that the film formed on Fe-28Al-3Cr was stable and took relatively more time for final breakdown than Fe and Fe-28Al.

For examining the compositions of the films formed on the exposed surfaces of the Fe-28Al and Fe-28Al-3Cr alloys, samples of these alloys were anodically held in 1 M Na₂SO₄ solution (under deaerated condition) at room temperature for 45 min. This allowed the formation of passive films on the exposed surfaces. XPS studies were then performed on these exposed surfaces. The Fe-28Al-3Cr alloy showed XPS peaks at 74.3 eV corresponding to presence of Al³⁺ (as Al₂O₃), 575.8 eV indicating the presence of Cr³⁺ as Cr₂O₃ and 710.6 eV indicating the presence of Fe³⁺ (as Fe₂O₃), shown in Fig. 5(a-c). These results showed that the passive film formed on Fe-28Al-3Cr alloy was a mixed oxide of Al₂O₃, Cr₂O₃, and Fe₂O₃. These results thus confirm that the addition of Cr in iron aluminides is beneficial for its aqueous corrosion resistance.

4. Conclusions

The aqueous corrosion behavior of Fe-28Al and Fe-28Al-3Cr was studied in comparison to pure Fe and SS 304.

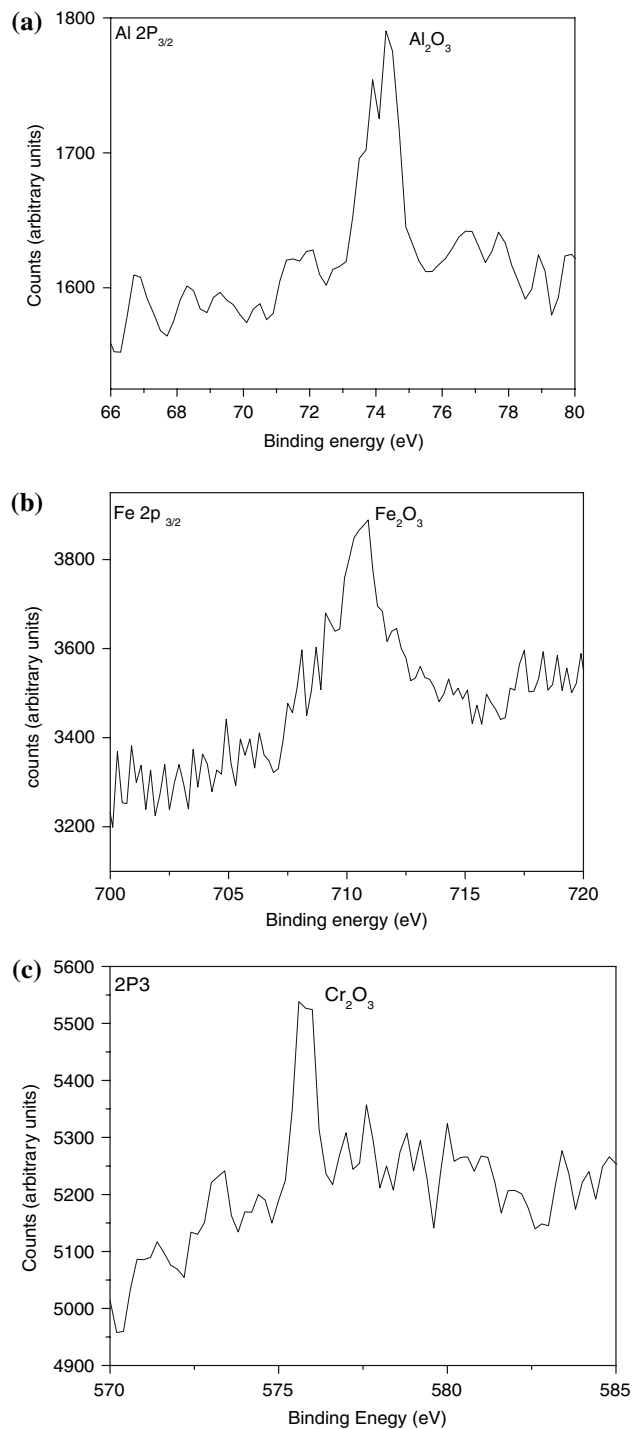


Fig. 5 XPS spectra for (a) Al 2p_{3/2} and (b) Fe 2p_{3/2} (c) Cr 2p₃ for Fe-28Al-3Cr alloy, passivated in 1 M Na₂SO₄, at 1 V_{SCE}, pH 6

1. Polarization behavior of Fe-28Al, Fe-28Al-3Cr, pure Fe, and SS 304 has been studied in 1 M H₂SO₄, 1 M Na₂SO₄, and 1 M NaOH solutions. The presence of Al in Fe-28Al alloys was found to improve the corrosion resistance of the alloy in comparison to pure Fe. Addition of Cr in Fe-28Al-3Cr alloy was found to further improve the aqueous corrosion resistance in comparison to Fe-28Al alloy. However, the critical current and passive current was found to be lowest for SS 304.

2. The pitting behavior was studied in 0.05 M Na₂SO₄ + 500 ppm NaCl solution. Fe and Fe-28Al alloy showed uniform dissolution with high-active currents. However, pitting behavior of Fe-28Al-3Cr was found to be comparable to SS 304.
3. The current time transients and potential decay profiles showed that the passive film form more rapidly on the Fe-28Al-3Cr as compared to pure Fe and Fe-28Al. Potential decay profiles showed that the passive film formed was more stable on Fe-28Al-3Cr alloy as compared to Fe-28Al and pure Fe. The XPS studies showed that the passive film on the exposed surface to be mixed oxide of Al, Cr, and Fe for Fe-28Al-3Cr alloy.

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