Effect of carbon on corrosion behaviour of Fe$_3$Al intermetallics in 0.5 N sulphuric acid

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Abstract

Electrochemical corrosion behaviour of iron aluminides, produced by electroslag remelting technique, having the compositions (1) Fe–15.6Al–0.05C, (2) Fe–15.6Al–0.14C, (3) Fe–15.6Al–0.5C and (4) Fe–15.6Al–1C were investigated in 0.5 N H$_2$SO$_4$ media. Corrosion rates of these alloys were found to increase with carbon content. This was attributed to the preferential attack of the carbide phases. These alloys exhibited typical active–passive–trans-passive behaviour. In addition, they displayed a secondary anodic current maxima during polarization. The resistance of aluminides to breakdown of passivity was assessed by varying addition of chloride ions in the same media.

Keywords: Intermetallics; Potentiostatic; Passivity; Hydrogen

1. Introduction

Iron aluminides based on Fe$_3$Al posses unique properties of high mechanical strength to weight ratio and excellent resistance to high temperature oxidation and sulphidation [1,2]. These materials could be a possible substitute for the alloys using strategic elements such as nickel and chromium. Nevertheless, poor room temperature ductility and drop in strength above 600°C did restrict their commercial applications [3]. Reviews by Mckmey et al. [4] and Stoloff [5] outlines various aspects of these materials.
Recently, iron aluminides produced by electroslag remelting process (ESR) with addition of carbon have been reported to possess relatively better room temperature ductility, than those produced by vacuum arc melting [6–8]. This is attributed to trapping of hydrogen atoms by presence of carbides. These alloys further exhibit improvement in strength above 600°C. This is possible by virtue of C exerting interstitial solid solution strengthening at low concentration and precipitation hardening at high concentration [9]. Though, these materials are mainly developed for high temperature applications, ambient temperature aqueous corrosion can also be a serious problem for its durability. This can happen when the alloys are possibly exposed to humid environments containing sulphates and/or chlorides, either during alloy processing stage or during idling time of the finished components. Much of the previous research on the iron aluminides, made through ESR, is focused on alloy development, processing and microstructural control and improving mechanical properties [7,9–11]. In view of this, understanding of aqueous corrosion behaviour of these iron aluminides is needed. Therefore, the present work is undertaken to investigate the electrochemical corrosion behaviour of the iron aluminides in sulphuric acid and to understand the role of chloride ions on their passivity. The study also enables to understand the effect of C on electrochemical corrosion behaviour of iron aluminides. Simultaneously, polarization study for pure aluminium (99.99%) and Armco iron, the major constitute elements, has been carried out for better understanding the role of alloying elements.

2. Experimental

2.1. Materials and microstructures

The nominal compositions of alloys used in the present study, in weight percentage, are: (1) Fe–15.6Al–0.05C, (2) Fe–15.6Al–0.14C, (3) Fe–15.6Al–0.5C and (4) Fe–15.6Al–1C. Iron aluminides of the above compositions were melted in a medium frequency air induction furnace of 50 kg capacity and chill cast into cast iron moulds. The ingot were tested for their soundness in a radiography unit, using a 5 Ci 60Co source. The air induction melted ingots (55 mm diameter, 360 mm long) were machined to 50 mm diameter for refining in an AC electroslag remelting furnace of 350 kVA capacity. A commercial prefused flux based on CaF2 (70%CaF2 + 15%CaO + 15%Al2O3) was used. The flux was preheated and held at 850°C for 2 h before use to remove moisture. Iron aluminide electrode was remelted under flux cover and cast into a 76 mm ingot in a water cooled steel mould. A mild steel starter plate was used, since the use of graphite starter plate led to carbon pick up. Towards the end of the operation, the power supply was gradually reduced to achieve hot topping. Further, details on process parameters and mechanical properties can be found elsewhere [10,11]. To verify their soundness, ESR ingots were also radiographed. Specimens for the oxidation studies were cut from the ingots using a high speed abrasive silicon carbide cut-off wheel.
Samples for optical microscopy was obtained by polishing them on various grade of silicon carbide emery papers starting from 220 to 1000, followed by 1 μ diamond paste and etching. The etchant consisted of 33%CH$_3$COOH + 33%HNO$_3$ + 1%HF + 33%H$_2$O by volume. Microstructures of the alloys were examined using a Leica, Recichert MeF3A optical microscope.

2.2. Polarization studies

Passivation behaviour of iron aluminides was studied using potentiodynamic polarization technique with a scan rate of 0.5 mV/s. The set-up consisted of a PARC, EG&G potentiostat/galvanostat Model 273 driven by M352 software and an electrochemical corrosion cell. The cell used for the polarization studies was a glass vessel similar to ASTM G5 with 500-ml capacity. Pt foil as counterelectrode, saturated calomel (SCE) as a reference electrode and specimen as a working electrode were employed. Specimens were mounted using cold setting resin with one end soldered to a copper wire. Mounted specimens were polished in a similar manner that was done for optical microscopy. These samples were further cleaned with distilled water and methanol before commencement of the experiment. 0.5 N H$_2$SO$_4$ acid solution with and without chloride additions and freely exposed to air were chosen as environments. Electrolyte was prepared by dissolving AR grade H$_2$SO$_4$ and NaCl in distilled water. Experiments were conducted in duplicates to check for reproducibility in results. After completion of each experiment, specimen was rinsed with distilled water and dried. Later on, they were viewed under a scanning electron microscopy (SEM) to examine the nature of attack.

3. Results and discussion

3.1. Microstructures

The variation in microstructures of the alloys as seen in optical microscope for the addition of different carbon contents is brought out in Fig. 1. Two distinct phases are seen in the micrographs. The X-ray diffraction patterns can be indexed based on the joint committee powder diffraction standards (JCPDS) card no. PDF #06-0695 and #03-0965, which correspond to the Fe$_3$Al and Fe$_3$AlC$_{0.69}$ respectively. While the Fe$_3$Al phase is dominant and forms the matrix with light contrast, the carbide phase (Fe$_3$AlC$_{0.69}$) is seen as dark particles. It is noted that the size and volume fraction of the carbides increase with the increasing carbon content. The alloy-1 containing low level of carbon, 0.05%, exhibits fine distribution of carbide phase in the matrix (Fig. 1(a)). Even in alloy-2, with a carbon content of 0.14%, the carbide phase remains relatively fine (Fig. 1(b)). The microstructure of alloy-3 containing 0.5% carbon (Fig. 1(c)) displays elongated particles of carbide. Close examination of microstructures reveals further information. Alloy-1 displays grains and subgrains, and along both the sides of these grains the population of carbides is found to be less. On deep etching (in set of Fig. 1(b)) alloy-2 also shows fine grains. No such grains are visible in
Fig. 1. Optical microstructures: (a) alloy-1, fine distribution of carbide particles, black arrow mark shows microcrack; (b) alloy-2, relatively fine distribution of carbide particles; in set of this figure displays grains (c) alloy-3, elongated carbide particles (d) alloy-4, a network of carbide phase.

alloy-3. The carbide phase forms a net work when the carbon content is raised to 1% as exhibited by the alloy-4 (Fig. 1(d)). Notably, all the carbides are located at interdendritic regions. In addition, the alloy-1 having low carbon is found to be susceptible to microcracking as a result of etching (as shown by an arrow in Fig. 1(a)), while the other alloys are found to be free from cracking.

3.2. Potentiodynamic polarization in 0.5 N \( \text{H}_2\text{SO}_4 \)

Potentiodynamic polarization curves of all the four alloys are compared in Fig. 2(a). Anodic and cathodic curves close to corrosion potential \( (E_{\text{corr}}) \) are expanded and brought out in Fig. 2(b) to show that they follow Tafel behaviour. These alloys exhibit a broad active–passive–transpassive behaviour. Notably, the anodic polarization curves of all these alloys display a secondary anodic current peak at \(-0.14\) V, before reaching the broad passive zone. To understand the role of Fe and Al, on the corrosion behaviour of the present aluminides, polarization curves of Al and Fe are obtained and compared with alloy-1 (Fig. 3). The electrochemical kinetic parameters
Fig. 2. (a) Potentiodynamic polarization curves of alloys 1–4 obtained in 0.5 N H₂SO₄. (b) Expanded region of anodic and cathodic polarization curves close to corrosion potential from Fig. 2(a) shows the Tafel behaviour of the alloys.

decide the corrosion behaviour of alloys. Hence these values, namely, $E_{\text{corr}}$, corrosion current density ($i_{\text{corr}}$), passive current density ($i_{\text{pass}}$), critical current density ($i_{\text{crit}}$), passive potential ($E_{\text{pass}}$), cathodic Tafel slope ($\beta_c$), anodic Tafel slope ($\beta_a$) and exchange current density for hydrogen equilibrium ($i_{\text{H}^+/\text{H}_2}$) for these alloys are derived from the curves and are summarized in Table 1.

Examination of the samples corroded at open circuit potential reveals preferential attack of the carbide phases as exemplified in Fig. 4. As the addition of C enhances the carbide content of aluminide, a gradual increase in corrosion rate of these alloys with C is expected. However, the unusually higher corrosion rate of alloy-1 compared to alloy-2 can be possibly attributed to the presence of microcracks in the
Fig. 3. Potentiodynamic polarization curves of alloy-1, iron and aluminium, obtained in 0.5 N H₂SO₄.

Table 1
Electrochemical parameters of alloys 1–4, Fe and Al derived from polarization curves in 0.5 N H₂SO₄

<table>
<thead>
<tr>
<th>Alloy</th>
<th>E&lt;sub&gt;corr&lt;/sub&gt; (V(SCE))</th>
<th>i&lt;sub&gt;corr&lt;/sub&gt; (mA cm&lt;sup&gt;-2&lt;/sup&gt;)</th>
<th>i&lt;sub&gt;pass&lt;/sub&gt; (μA cm&lt;sup&gt;-2&lt;/sup&gt;)</th>
<th>i&lt;sub&gt;crit&lt;/sub&gt; (mA cm&lt;sup&gt;-2&lt;/sup&gt;)</th>
<th>E&lt;sub&gt;pass&lt;/sub&gt; (V(SCE))</th>
<th>β&lt;sub&gt;e&lt;/sub&gt; (V/decade)</th>
<th>β&lt;sub&gt;a&lt;/sub&gt; (V/decade)</th>
<th>i&lt;sub&gt;0H⁺/H₂&lt;/sub&gt; (mA cm&lt;sup&gt;-2&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>−0.574</td>
<td>2.26</td>
<td>34.25</td>
<td>20.4</td>
<td>0.46</td>
<td>0.21</td>
<td>0.03</td>
<td>2.5 x 10⁻²</td>
</tr>
<tr>
<td>2</td>
<td>−0.565</td>
<td>1.02</td>
<td>38.00</td>
<td>20.32</td>
<td>0.46</td>
<td>0.17</td>
<td>0.02</td>
<td>4.3 x 10⁻²</td>
</tr>
<tr>
<td>3</td>
<td>−0.564</td>
<td>5.31</td>
<td>52.48</td>
<td>21.87</td>
<td>0.46</td>
<td>0.23</td>
<td>0.08</td>
<td>50.1 x 10⁻²</td>
</tr>
<tr>
<td>4</td>
<td>−0.523</td>
<td>10.11</td>
<td>85.11</td>
<td>18.41</td>
<td>0.46</td>
<td>0.25</td>
<td>0.28</td>
<td>1.78</td>
</tr>
<tr>
<td>Fe</td>
<td>−0.505</td>
<td>0.23</td>
<td>57.54</td>
<td>240</td>
<td>0.55</td>
<td>–</td>
<td>–</td>
<td>2.0 x 10⁻³</td>
</tr>
<tr>
<td>Al</td>
<td>−0.918</td>
<td>0.02</td>
<td>316.0</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>7.9 x 10⁻⁷</td>
</tr>
</tbody>
</table>

alloy-1 (Fig. 1(a)). These cracks are expected to promote alloy dissolution. The addition of carbon marginally raises the E<sub>corr</sub> values of aluminides towards noble direction. The E<sub>corr</sub> values of these alloys are found to be well below the equilibrium potential (of −0.278 V(SCE), which was calculated based on the measured pH of 0.6 and assuming H₂ partial pressure of 1 atm) for 2H⁺ + 2e = H₂ equilibrium. Hence, hydrogen evolution is considered to be a dominated cathodic reaction. Indeed, hydrogen gas is found to evolve on the specimen at open circuit potentials. Hence, the values of i<sub>0H⁺/H₂</sub> of these alloys become very important. It has been found from the Table 1 that aluminides posses much higher i<sub>0H⁺/H₂</sub> than that of either Al or Fe. This in turn causes higher dissolution of these alloys compared to pure Fe. Even among these aluminides the changes in exchange current density seems to influence i<sub>corr</sub>. This becomes obvious because of the fact that alloy-4 shows higher i<sub>corr</sub> value in spite of having larger β<sub>e</sub> and β<sub>a</sub> values in comparison with of the other alloys. Notably, in a recent work Frangini has also reported that the corrosion rate of FeAl aluminides is higher than that of Fe [12].
Fig. 4. SEM micrograph of alloy-4 after immersion in 0.5 N H₂SO₄, shows preferential dissolution of carbide phase.

All these aluminides, irrespective of the carbon content, show passivity in the same potential range between 0.46 and 1.46 V. The $i_{\text{pass}}$ value increases with increasing carbon content, much the same way $i_{\text{corr}}$ follows with the carbon. It seems therefore that the preferential dissolution of carbides causes higher passive current density and as its volume increases, $i_{\text{pass}}$ increases. It is also interesting to note that the alloy having the lowest carbides exhibit better passivation stability in the passive regions. Above the transpassive potential ($E_{\text{tp}}$), gases are found to evolve on the specimen surface. Since, the $E_{\text{tp}}$ value is well above the equilibrium potential of 0.96 V (SCE) for $\text{H}_2\text{O} = 1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}$ equilibrium, the evolved gas could correspond to O₂. Although, these iron aluminides display a wide passivity zone, with a low passive current density, its anodic critical current density is too high for them to self-passivate in aerated condition because the limiting current density for O₂ reduction is around 100 $\mu$A cm⁻² [13].

The SEM micrographs exhibiting the nature of attack of alloy-3 and alloy-4 after subjecting to anodic polarization, are brought out in Figs. 5 and 6, respectively. They show that carbides are preferentially attacked. A plausible explanation for the preferential attacks of carbides is that passive film formed on carbide phase is less tenacious than that formed on the matrix. In addition, it is possible that carbon in the carbides get oxidized to carbon dioxide at more noble potentials, as the transpassive potential of these alloy are well above the potential for oxygen evolution.

Analysis of anodic polarization curves of Fe and Al provides clue to their possible role on the passivation behaviour of iron aluminides. As shown from Fig. 3, between Fe and Al, the former has lower $i_{\text{pass}}$ value than the latter. However, later has a wider passive range compared to former. Combined effects of Fe and Al seem to benefit
Fig. 5. SEM micrograph of alloy-3 after polarization in 0.5 N H₂SO₄ reveals dissolution of carbides.

Fig. 6. SEM micrograph of alloy-4 after polarization in 0.5 N H₂SO₄, showing preferential dissolution of carbide phase.

iron aluminides. Thus assisted by Al, aluminides undergo less active dissolution due to formation of Al₂O₃ film, than iron before they passivated and once they reach the passive state, the presence of iron oxide provide an additional resistance to the passage of current through aluminium oxide film (it is know that Al forms porous
oxide film in sulphuric acid). Similarity in the anodic polarization curves of Fe and aluminides in the transpassive region, suggests that iron oxide/hydroxide play important role in the passive region of iron aluminides. Passivation behaviour of FeAl along with Fe and Al has been reported by Frangini et al. in 1 N H$_2$SO$_4$ [14] and 0.5 N H$_2$SO$_4$ [15]. Their studies show that the alloys exhibit similar passivation behaviour, irrespective to the concentration of acid. However, the difference between their studies and with the present study lies with respect to Fe. They have reported the $i_{\text{pass}}$ value of Fe is higher than that of Al, which is contrary to the present study. Nevertheless, the present value of $i_{\text{pass}}$ is well in agreement with that reported by Steigerwald and Greene for Fe (99.94%) [16].

Furthermore, the $i_{\text{pass}}$ value of FeAl has reported around 20 $\mu$A cm$^{-2}$ [14,15]. While, the $i_{\text{pass}}$ value of present alloys varies from 34.25 to 85.11 $\mu$A cm$^{-2}$. It should be noted that in the absence of heterogeneity in the alloy-1 such as carbides and microcracks, $i_{\text{pass}}$ value would be expected to be further lowered and become close to the value of FeAl. It appears that, though FeAl having much higher Al content (24.4 wt.%) than that of Fe-Al, there is a little transition in their passivation behaviour. In yet another study, Derfancq, has reported the $i_{\text{pass}}$ value of Fe–25.74Al–1.92C alloys in 1 N H$_2$SO$_4$ as 200 $\mu$A cm$^{-2}$ [17]. Notably, though this alloy having higher Al content than the present alloys, even it shows higher $i_{\text{pass}}$ value compared to alloy-4 (85.11 $\mu$A cm$^{-2}$), which is apparently due to higher carbon content in this alloy than that of alloy-4. It corroborates the present results, that the increase in carbon content increases the $i_{\text{pass}}$ value. In addition, comparison of these studies brings out the fact that the variation in carbon content has much stronger effect in their passivation behaviour than the change in Al content in the aluminides.

It is worthwhile to examine as to what causes the appearance of the so-called secondary anodic peak during anodic polarization of the iron aluminides. Though, Frangini et al. [14,15] did not report the existence of secondary anodic peak in FeAl, several such observation are made in literature with respect to stainless steels [18–21]. Rockel discusses in detail the possible causes for the appearance of secondary anodic peak in sensitized chromium steels in 1 N H$_2$SO$_4$ [18]. One or more factors, nickel enrichment in the surface, chromium depletion as result of carbide precipitation, accelerated grain boundary dissolution and hydrogen oxidation are considered to be responsible for this. While, Parvathavarthini et al. have attributed the second anodic peak to secondary passivation in 9%Cr–1%Mo steel in 0.5 N H$_2$SO$_4$ [19]. They observed that, addition of As$_2$O$_3$ to the electrolyte inhibit the anodic reaction during polarization, which in turn causes decreases in critical current density and so as secondary passivation peak disappears. The appearance of secondary anodic peak on the ferritic stainless steels containing Cu, in sulphuric acid is reported by Masahiro et al. [20]. Anodic dissolution of metallic Cu (Cu = Cu$^{2+} + 2\mathbf{e}^{-}$) has been attributed to the secondary anodic peak. In a more recent work, Hermas et al. have shown that P and Cu poison hydrogen evolution reaction on AISI 304 stainless steels in sulphuric acid. This facilitates the hydrogen absorption in steel and during subsequent anodic polarization it gets oxidized to secondary anodic peak [21].

The present results support the view that hydrogen oxidation is responsible for secondary anodic peak. The first support to the suggestion on oxidation of absorbed
hydrogen around secondary anodic peak stems from the fact that the peak potential (−0.14 V) is above the hydrogen equilibrium potential of −0.278 V as mentioned previously. The second indirect evidence in support of this view arises out of the experimental data based on cathodic charged samples. Fig. 7 brings out the change in secondary anodic peak of the uncharged and precharged (1 h, 2 h at −0.8 V) samples of alloy-1. The magnitude of secondary anodic peak increases in the order of uncharged <1 h precharged <2 h precharged. The raise in secondary anodic peak on the charged samples is possible due to higher probability of hydrogen absorption. Secondary anodic peak to the hydrogen oxidation is correlated indirectly to through yet another perception. It is reported by Gehrmann et al. that the carbides in the steel trap the hydrogen atoms and reduces it tendency for hydrogen embrittlement [22]. In a similar way, carbides in aluminides seem to act as trap sites for hydrogen atoms and there by reduces the diffusible hydrogen available for oxidation during anodic polarization. Hence, with increase in carbide content, the amount of free hydrogen in the sample decreases leading to the low secondary anodic peak. Thus alloy-1 exhibits higher secondary anodic peak than the other alloys. But the reduction in trapping sites, in terms of amount of carbide phase, allows more free hydrogen and makes the alloy susceptible to cracking. This proposition lends credence from the fact that iron aluminides are known to be very susceptible to hydrogen embrittlement [4,8].

3.3. Polarization studies in 0.5 N H₂SO₄ + NaCl

Since, these alloys exhibit passivity, their ability to pitting resistance is examined by adding 10–100 ppm chloride ions to the solution. Typical polarization behaviour of these alloys in 0.5 N H₂SO₄ containing 50 ppm chlorides is shown in Fig. 8 for illustration. There have been no perceptible changes are observed in secondary anodic current maxima peak due to the chloride ions. The passivation behaviour in
all these alloys deteriorates more or less in a similar way. Addition of chlorides up to 25 ppm in solution, do not have much influence in the anodic polarization behaviour of alloys. At 50 ppm, the current density within the passive range increases and enhance the dissolution tendency of carbide phase. This aspect has been brought out through alloy-4 as shown in Fig. 9. On further increasing the chloride concentration to 100 ppm, passivity of the alloys is lost and pits start forming in all the alloys (Fig. 10).

Fig. 8. Potentiodynamic polarization curves of alloys 1–4 obtained in 0.5 N H$_2$SO$_4$ + 50 ppm chloride ions.

Fig. 9. SEM photograph of alloy-4 after polarization in 0.5 N H$_2$SO$_4$ + 50 ppm chloride ions, showing enhancement in dissolution tendency due to chloride ions.
Fig. 10. SEM image of alloy-3 after polarization in 0.5 N H₂SO₄ + 100 ppm chloride ions, showing formation of pit.

4. Conclusions

1. Addition of carbon to iron aluminides promotes formation of carbide phase Fe₃AlC₀.₆₉.
2. Carbides in the iron aluminides suffer selective dissolution.
3. The corrosion resistance and passivity deteriorate with increase in carbon content.
4. The appearance of secondary anodic peak in these alloys is attributed to hydrogen oxidation.
5. Presence of carbides reduces the microcracks in the iron aluminides.
6. Addition of chloride content beyond 50 ppm destroys passivity and causes pitting.

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