Deciphering the potentiodynamic polarization curves of iron aluminides Fe₃Al and Fe₃Al + Cr

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Abstract. The potentiodynamic polarization curves of Fe_3Al and $Fe_3Al + Cr$ intermetallics obtained in aerated pH 4 H_2SO_4 acidic solution have been theoretically analyzed. The role of chromium in minimizing the hydrogen embrittlement (HE) of the intermetallic Fe_3Al (resulting in its poor ductility) has been addressed based on the analysis. In the case of the chromium-alloyed iron aluminide, calculations indicate that hydrogen liberation does not occur on the surface due to the shift of the corrosion mixed potential to a value nobler than the electrode potential for the hydrogen evolution reaction. This shift occurs due to the induction of passivity on alloying with Cr resulting in the formation of a passive film. The minimization of HE of iron aluminides on alloying with Cr can thus be understood.

Keywords. Iron aluminide; hydrogen embrittlement; potentiodynamic polarization; mixed potential theory.

1. Introduction

Iron aluminides, based on the stoichiometric compositions of Fe_3Al and FeAl, have been attracting increasing attention due to their high temperature oxidation and sulphidation resistance. They have been considered as favourable materials to replace the conventional stainless steels in coal-based energy conversion systems for this reason. However, one of the major limitation of applying iron aluminides commercially is their poor ductility at ambient temperatures, which has been attributed to hydrogen embrittlement (Liu *et al* 1990). The moisture-induced hydrogen embrittlement (HE) of iron aluminides has been the subject of several studies and the subject has been critically reviewed (Stoloff and Duquette 1993; Agarwal and Balasubramaniam 1996). One of the effective ways of minimizing hydrogen embrittlement in iron aluminides is by alloying it with Cr (McKamey *et al* 1988). Addition of Cr as low as 2% has produced significant improvements in ductility of binary iron aluminides.

The role of chromium in minimizing the room temperature hydrogen embrittlement in iron aluminides has been usually explained by Cr providing a passive film at the surface that decreases diffusion of hydrogen into the material (McKamey and Liu 1990). It has been recently proposed theoretically that Cr induces passivity in the aluminide and this reduces hydrogen evolution rates (on freshly created surfaces) to a very low value compared to unalloyed iron aluminides (Balasubramaniam 1996). The low hydrogen evolution rates on Cr-alloyed Fe_3Al results in a lower amount of hydrogen entering into the lattice, thereby minimizing embrittlement. This philosophy, which has been theoretically proposed based on the mixed potential theory, has been experimentally verified by potentiodynamic polarization studies on binary and

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Cr-alloyed iron aluminides (figure 1) (Balasubramaniam 1996). Moreover, an alloy development philosophy to produce ductile iron aluminides has been outlined, based on this theory (Balasubramaniam 1996).

Explaining the role of chromium in minimizing room temperature embrittlement due to hydrogen (Balasubramaniam 1996), the anodic polarization curves for Fe_3Al and $Fe_3Al + Cr$ were shown as exhibiting active and active–passive behaviour, respectively. The different rates of hydrogen evolution on the two materials were obained by the intersection of the cathodic reduction line with the anodic polarization curve of Fe_3Al in the active region, and with that of $Fe_3Al + Cr$ in the passive region. The cathodic reaction was implicitly assumed to be the hydrogen evolution reaction, given by

$$H^+ + e^- \rightarrow H,$$ (1)

which results in the generation of atomic hydrogen on the surface and subsequent H diffusion into the material, causing embrittlement. The role of the oxygen reduction reaction was not addressed (Balasubramaniam 1996). Oxygen can also be reduced if present in the electrolyte and the nature of the reaction would depend upon the pH of the solution. In acidic medium, this is given as

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O,$$ (2)

while in alkaline/neutral media, the oxygen reduction reaction occurs according to
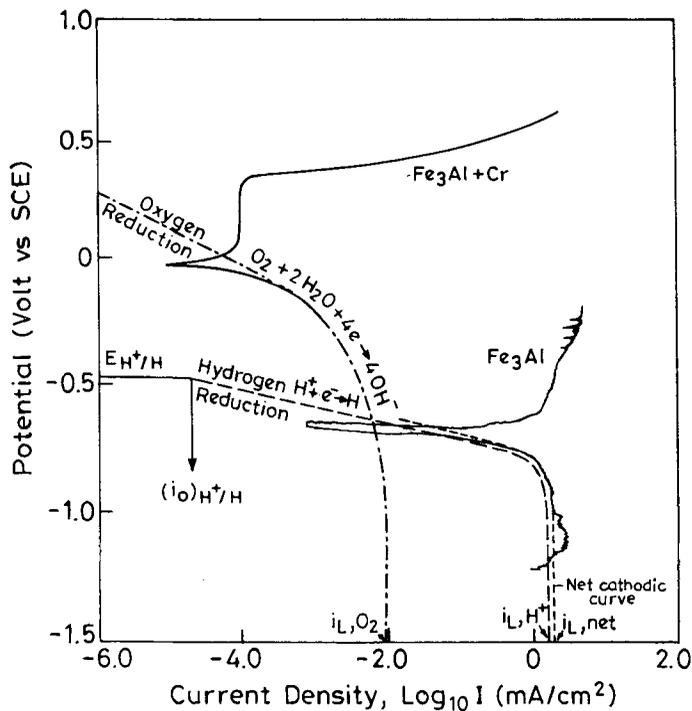
$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-.$$ (3)

Figure 1. Superposition of theoretical cathodic polarization curves on the experimental polarization curve obtained in pH 4 H_2SO_4 solution with 200 ppm Cl^- ions. Note that the hydrogen evolution reaction does not occur on the $Fe_3Al + Cr$ intermetallic.

While deciphering the actual polarization curves of binary and Cr-alloyed iron aluminides, the oxygen reduction reaction also needs to be considered in addition to the hydrogen evolution reaction (HER). This is reasonable since the potential for hydrogen evolution reaction at pH = 4 (the acid solution in which the experiment was performed), denoted as $E_{H^+/H}$ in figure 1 is lower than the zero current potential for the Cr-alloyed Fe$_3$Al. This very clearly indicates that HER cannot be the operative cathode reaction in the Fe$_3$Al + Cr system. It is therefore important to consider oxygen reduction reaction on the iron aluminide surface while deciphering the polarization curves. This would also provide insight into the hydrogen evolution process on fresh surfaces of iron aluminides. The aim of the present paper is to obtain such an understanding.

2. Analysis

In the following calculations, SCE refers to the saturated calomel (reference) electrode, and SHE to the standard hydrogen electrode. The two are related as

$$SCE = + 0.2416 \, V \text{ vs SHE}.$$

In the case of HER provided in (1) above, the electrode potential at which it occurs in a solution of pH 4 is given by the Nernst equation as

$$E_{H^+/H} = - 0.059 \, pH \quad V \text{ vs SHE},$$

$$= - 0.4776 \quad V \text{ vs SCE},$$

while for the oxygen reduction reaction, it is

$$E_{O_2/OH} = 1.229 - 0.059 \, pH + 0.015 \log p_{O_2} \quad V \text{ vs SHE},$$

$$= 0.7409 \, V \text{ vs SCE}.$$

It is assumed in the above calculation that water/moisture is aerated by atmospheric air at room temperature and therefore, the partial pressure of oxygen (p_{O_2}) is 0.2 atm (West 1970).

All further analysis is with respect to the experimental potentiodynamic polarization curves for Fe$_3$Al and Fe$_3$Al + Cr intermetallics in aerated pH 4 H$_2$SO$_4$ solution containing 200 ppm of Cl$^-$ ions (Balasubramaniam 1996). These curves are shown in figure 1 as bold lines.

The zero current potential (ZCP) of Fe$_3$Al (E_{ZCP}/Fe$_3$Al) is $- 0.6786$ V vs SCE, while that for the alloyed Fe$_3$Al + Cr (E_{ZCP}/Fe$_3$Al + Cr) is $- 0.0357$ V vs SCE (figure 1). As indicated earlier, it is obvious that $E_{H^+/H}(= - 0.4776$ V vs SCE) is less than ZCP for Fe$_3$Al + Cr. Therefore, the HER cannot be the cathodic reaction at the mixed corrosion potential for the Fe$_3$Al + Cr intermetallic in pH 4 H$_2$SO$_4$ solution.

In order to decipher the polarization curves, two distinct cathodic reaction lines are drawn to the experimental curves (figure 1). For Fe$_3$Al, the cathodic line is drawn as an extrapolation of the linear portion of the cathodic curve, from which the corrosion rate (i_{corr}) is estimated to be 53.4×10^{-6} A/cm^2 and the Tafel slope (β_c) $- 0.05$ V/decade. Using this extrapolated straight cathodic line, and extending it up to $E_{H^+/H}$, the exchange current density (i_0) for HER on Fe$_3$Al under the experimental conditions is estimated as 10^{-8} A/cm^2. For comparison, the reported values of i_0 for HER on Fe in

$2 \mathrm{N} \, \mathrm{H}_2 \mathrm{SO}_4$ is $10^{-6} \mathrm{A/cm^2}$, while that on Al in $2 \mathrm{N} \, \mathrm{H}_2 \mathrm{SO}_4$ is $10^{-10} \mathrm{A/cm^2}$ (Fontana 1986). Therefore, the estimated exchange current density of the HER on $\mathrm{Fe}_3 \mathrm{Al}$ appears reasonable. Notice from the polarization curve that the cathodic reaction for $\mathrm{Fe}_3 \mathrm{Al}$ appears to be under concentration polarization at large overpotentials, from which the limiting current density ($i_{\mathrm{L.net}}$ in figure 1) is estimated as $1 \cdot 75 \times 10^{-3} \mathrm{A/cm^2}$.

In the case of the Cr-alloyed $\mathrm{Fe}_3 \mathrm{Al}$, the experimental polarization curve reveals that the intermetallic is passivated on immersion in the electrolyte. Consequently, the corrosion current density is given by the passive current density and this is $10^{-7} \mathrm{A/cm^2}$. The cathodic curve possesses a Tafel slope (β_c) of approximately $-0 \cdot 16 \mathrm{V/decade}$. Assuming this line to be the oxygen reduction line, we use the value of β_c to estimate the value of exchange current density for O_2 reduction $i_{0(\mathrm{O}_2/\mathrm{OH}^-)}$ on $\mathrm{Fe}_3 \mathrm{Al} + \mathrm{Cr}$ as $1 \cdot 62 \times 10^{-12} \mathrm{A/cm^2}$. Such a low value of $i_{0(\mathrm{O}_2/\mathrm{OH}^-)}$ in aqueous solutions is quite reasonable. Exchange current densities for O_2 reduction are usually very low, being of the order of $10^{-14} \mathrm{A/cm^2}$ on Fe and are maximum of the order of $\sim 10^{-10} \mathrm{A/cm^2}$ on Pt (West 1970). This is due to the low limiting rates of oxygen diffusion in water/aqueous solutions and also due to the presence of a surface oxide film resulting from chemical bonding with the initial oxygen (adsorbed) monolayer. There is, therefore, no simple metal-electrolyte double layer and electrode kinetics are suitably modified by the electrical conducting properties of the film of oxide, which is several atomic layers thick (West 1970).

Thus so far, the deciphering of the cathodic polarization curves reveals that the effect of Cr addition is to induce passivity such that the mixed (unpolarized) potential of the alloy is at a noble value such that it exceeds $E_{\mathrm{H}^+/\mathrm{H}}$. Hence, the hydrogen evolution reaction is not the cathodic reaction for $\mathrm{Fe}_3 \mathrm{Al} + \mathrm{Cr}$ system. On the other hand, HER is indeed the predominant cathodic reaction on unalloyed $\mathrm{Fe}_3 \mathrm{Al}$, due to which hydrogen entry into the intermetallic and subsequent embrittlement is likely.

In the light of the above analysis, it is clear that the cathodic curve for $\mathrm{Fe}_3 \mathrm{Al}$ must actually be the net sum of two reduction reactions, the HER and O_2 reduction curves. The issue is resolved rather easily, however, by considering that in an aqueous solution, despite the activation polarization for O_2 reduction, the hydrogen evolution reaction would still be the dominant cathodic reaction. This is reasonable as the rate of diffusion of O_2 to the metal surface in water is several hundred times lower than that of H^+ ions (West 1970) and due to the ready availability of H^+ ions in a pH 4 acidic solution as compared to the limited solubility of O_2 in water. The cathodic line for $\mathrm{Fe}_3 \mathrm{Al}$ is a net reduction curve, being the sum of two reduction reactions, the HER and O_2 reduction. In order to obtain the contribution due to the O_2 reduction reaction, it is to be noted that the oxygen reduction curve in aqueous solutions exhibits concentration polarization at high overpotentials. Available literature suggests that the O_2 curve must show a limiting current density. The non-linear portion of the cathodic polarization curve for $\mathrm{Cr} + \mathrm{Fe}_3 \mathrm{Al}$ system is extrapolated, from which the limiting current density for oxygen ($i_{\mathrm{L.O}_2}$ in figure 1) is estimated as $10^{-5} \mathrm{A/cm^2}$. A comparable value of $i_{\mathrm{L.O}_2} = 6 \times 10^{-5} \mathrm{A/cm^2}$ is reported for the case of iron in aerated water at room temperature (West 1986).

Once the nature of the O_2 reduction cathodic curve in the electrolyte has been deciphered, the HER curve is obtained keeping in mind that the cathodic reduction curve for $\mathrm{Fe}_3 \mathrm{Al}$ is the sum of the two reduction reactions. The position of the HER curve is graphically plotted by taking the difference between the total net curve and that due to O_2 reduction. These curves are also shown in figure 1. From the HER curve, the

Tafel slope is estimated as $\beta_c = -0.06$ V/decade and the limiting current density for HER (i_{L,H^+}) on iron aluminide as 1.74×10^{-3} A/cm^2. Note that the limiting current density for HER under concentration polarization is orders of magnitude greater than that for oxygen reduction under similar conditions, as reported in the literature (West 1970). The estimated Tafel slope of 0.06 V/decade is an indication of the reduction reaction involving a single electron, and this indirectly implies the HER.

Finally, the partial pressure of H generated on the surface of iron aluminide can be estimated from the Nernst equation and it is found to be of the order of 10^6 atmospheres. The generation of nascent hydrogen on the surface of the base binary aluminide at such high pressures can account for the easy entry of H into the lattice of the aluminide, leading to its subsequent embrittlement.

3. Conclusions

The potentiodynamic polarization behaviour of binary Fe_3Al and Cr-alloyed Fe_3Al intermetallics has been explained using mixed potential theory by considering both hydrogen and oxygen reduction cathodic reactions. In the case of the chromium-alloyed iron aluminides, the improvement in ductility can be attributed to the passivating effect of Cr additions, such that the zero current potential is nobler than the electrode potential of the hydrogen evolution reaction. The oxygen reduction reaction is the cathodic reaction for the Cr-alloyed intermetallic and hydrogen embrittlement is minimized in these intermetallics as hydrogen is not generated on the surface upon immersion in the electrolyte or when moisture condenses on the surface. In the case of Fe_3Al, the hydrogen evolution reaction is the dominant reduction reaction, leading to the generation of high pressure nascent atomic hydrogen on its surface. The above analysis also clarifies the role of Cr additions to iron aluminides in improving their ductility (Balasubramaniam 1996).

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