Environmental effects in iron aluminides

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Abstract. Iron aluminides based on the stoichiometric compositions of Fe_3Al and FeAl exhibit poor room temperature ductilities due to hydrogen embrittlement (HE). The presence of surface passive films reduces HE. The reduction is due to the lower rate of hydrogen liberation on the surface of iron aluminides with a passive layer. Theoretical and experimental verification for this idea are provided. The effect of addition of passivity-inducing elements Ti, Zr, V, Nb, Ta, Cr, Mo, W, Si and Ni to Fe_3Al on the thermomechanical and electrochemical behaviour has been outlined. The Cr- and Ti-alloyed intermetallics exhibited significant room temperature ductilities. Microstructural studies of the alloyed intermetallics revealed that when the addition of passivity-inducing element results in the precipitation of brittle phases with Fe and Al, they crack during the processing operation. The addition of oxygen-active elements on the embrittlement behaviour is also discussed. The effect of these additions on the potentiodynamic polarization behaviour and high temperature oxidation behaviour is also briefly addressed. Methods to minimize HE by the addition of elements that irreversibly trap hydrogen and that prevent recrystallization have also been discussed.

Keywords. Iron aluminides; passivity; hydrogen embrittlement; structure–property–processing correlation.

1. Introduction

Iron aluminides based on the stoichiometric compositions of Fe_3Al and FeAl are candidate materials for high temperature applications due to their superior oxidation and sulphidation resistance. One of the impediments to the commercial application of iron aluminides is their poor room temperature ductility. This is due to their susceptibility to hydrogen embrittlement (HE) (Liu *et al* 1989, 1990). Several methods have been proposed to minimize HE like oxide coatings (McKamey and Liu 1990) (to minimize hydrogen pick-up from the environment), heat treatments (McKamey and Pierce 1993) (to produce a partially recrystallized microstructure) and alloying with passivity-inducing elements (Balasubramaniam 1996, 1997) (which provide a passive layer on the surface of the intermetallic that reduces hydrogen liberation rates on the surfaces and thereby minimizes hydrogen entry). Environmental effects in iron aluminides is addressed in the following sections. Although HE of iron aluminides would be focused, the communication would also address the room temperature aqueous corrosion and high temperature oxidation of Fe_3Al -based iron aluminides.

2. Relationship of hydrogen liberation rate to embrittlement

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* 1989, 1990). The moisture-induced hydrogen embrittlement of iron aluminides has been the subject of several studies and the subject has been critically reviewed (Liu and Kumar 1993; Stoloff and Duquette 1990). One of the effective ways of minimizing HE in iron aluminides is by alloying with Cr (McKamey *et al* 1988). Additions of Cr as low as 2% have 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 critically addressed. It has been theoretically proposed 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 has been theoretically explained based on the mixed potential theory as provided in figure 1 (Balasubramaniam 1996). Moreover, an alloy development philosophy to produce ductile iron aluminides has been outlined, based on this theory (Balasubramaniam 1996, 1997).

In the original paper explaining the role of chromium in minimizing room temperature embrittlement due to hydrogen (Balasubramaniam 1996), the anodic polarization curves for Fe_3Al and $\text{Fe}_3\text{Al}+\text{Cr}$ were shown as exhibiting active and active-passive behaviour, respectively. The different rates of hydrogen evolution on the two materials were obtained by the intersection of the cathodic reduction line with the anodic polarization

curve of Fe_3Al in the active region, and with that of $\text{Fe}_3\text{Al}+\text{Cr}$ in the passive region (figure 1). It can be noticed from this figure that the rate of hydrogen liberation (which is also equal to the rate of corrosion) is lower in the case of Cr-alloyed intermetallic due to the intersection of the reduction line in the passive region of the polarization curve in the case of this intermetallic. Moreover, the overpotential for hydrogen reduction reaction is much lower in the Cr-alloyed intermetallic compared to the base aluminide and this implies that the partial pressure of hydrogen that is liberated on the surface of the former is much lower than in the case of the latter. The cathodic reaction was implicitly assumed to be the hydrogen evolution reaction, which results in H entry into the material, causing embrittlement. The role of the oxygen reduction reaction was also considered in a subsequent paper and the potentiodynamic polarization curves of Fe_3Al and $\text{Fe}_3\text{Al}+\text{Cr}$ were deciphered theoretically (Mukherjee and Balasubramaniam 1996). It was seen that the oxygen reduction reaction is important in passivity induction for the Cr-alloyed iron aluminide, whereas it does not have a significant effect on the cathodic polarization curve in the case of the binary aluminide.

The theoretical interpretation of the polarization diagrams of the Fe_3Al and $\text{Fe}_3\text{Al}+\text{Cr}$ have been verified by potentiodynamic polarization experiments (figure 2). These results provide strong indications that the hydrogen liberation rate is the deciding factor in determining the role of surfaces on hydrogen embrittlement. In this regard, it is interesting to review some of the recent

results published in the literature on this topic. Although nickel aluminides are different from iron aluminides, a recent study by Lee *et al* (1996) provides some significant clues on the similarity of HE phenomenon in these two class of intermetallics. It has been shown experimentally by Lee *et al* (1996) that hydrogen liberation rates on the surfaces of Ni_3Al play a deciding role in the hydrogen embrittlement on these class of aluminides. They determined the rate of hydrogen liberation on both pure Ni_3Al and boron-doped Ni_3Al by fracturing the alloys in a ultra high vacuum fracture chamber attached to a Auger electron spectroscopy unit. Different low partial pressures of moisture in the fracture chamber were used in the study. It was clearly shown that the rate of hydrogen liberation was lower on the boron-doped nickel aluminide than that on the nickel aluminide. This was determined based on the height of the oxygen peak that was obtained by Auger spectroscopy. It is therefore evident that the rate of hydrogen liberation is lowered significantly in the boron-doped Ni_3Al and in this way the embrittlement due to hydrogen is reduced on boron addition. It was earlier thought that the effect of boron on improving ductility (i.e. lowering hydrogen embrittlement) was related to the lowering of hydrogen diffusivity through the grain boundaries of the boron-doped Ni_3Al due to trapping of hydrogen by boron present at the grain boundaries and also by enhancing the grain boundary cohesive strength (Liu and Kumar 1993).

In case the lower rate of hydrogen liberation is responsible for the lower degree of hydrogen embrittlement,

Figure 1. Mixed potential analysis of hydrogen liberation rates on surfaces of iron aluminide with and without Cr.

Figure 2. Experimental potentiodynamic polarization curves for iron aluminides with and without Cr.

it is possible to visualize that the effect of passivation on the ductility would be significant during initial exposure to the environment; but with continued exposure, there would be sufficient hydrogen pick-up in the material due to continued hydrogen liberation on the surface. In such a case, even a material on whose surface the hydrogen liberation rate is low would be susceptible to hydrogen embrittlement if it is exposed for a sufficient time in the environment. Therefore, it is anticipated that even Cr-alloyed iron aluminides would be susceptible to embrittlement if they are exposed to the environment for longer times. It is only when tensile testing is performed immediately that Cr-alloyed iron aluminides provide ductility, because in the short time of the tensile test the entry of hydrogen would be minimal due to low hydrogen liberation rates. In this regard, the recent experimental results of Tu *et al* (1998) are very revealing. They first completely removed hydrogen from Fe-28Al and Fe-28Al-5Cr by anodic polarization. The specimens were then immediately electrochemically charged with hydrogen and tensile tested. Their results on the ductility as a function of hydrogen charging time are presented in figure 3. It is seen that with increasing charging time, the ductility of both the Cr-containing and Cr-free iron aluminides are almost identical. The major difference is noticed only for the initial condition, i.e. for no charging. It is quite evident that when hydrogen is forced into the iron aluminide, it does not matter whether it contains the passive layer or not and in both the cases, hydrogen is able to permeate through the passive layer and enter the lattice to cause embrittlement. The beneficial effect of addition of Cr in minimizing the embrittlement is realized in testing done without hydrogen charging (i.e. when hydrogen enters the lattice by the moisture-induced oxidation of Al leading to alumina formation and sub-

sequent hydrogen generation). The increased ductility obtained with the Cr-alloyed iron aluminide can be related to the lower rate of hydrogen liberation on the surface of this aluminide. Therefore, the surface layer acting as an effective barrier to hydrogen entry can be discounted.

The passive layers on iron aluminides have not been characterized in detail. However, Yangshan *et al* (1996) performed X-ray photoelectron spectroscopy (XPS) and determined the surface oxide composition of iron aluminides with and without Ce. It was clearly shown that the constituents of the scale were chromia, iron oxide and alumina in both the cases. With the addition of Ce, the percentage of chromia and alumina in the scale increased and this is due to the addition of Ce, an oxygen active element which changes the oxide composition and properties. We shall later address the addition of oxygen active elements on the environmental degradation behaviour of iron aluminides. However, the purpose of the above discussion is to show that the oxides that form on the surface of iron aluminides are stable oxides and it cannot be reduced by electrochemically charging with hydrogen. The alloy tested by Tu *et al* (1998) also contained Ce in addition to Zr and B. This implies that the passive layer on the surface of the iron aluminide do not provide hindrance to the entry of hydrogen into the lattice and if at all they do, it could be significant only in the initial stages. The oxides on the surface of the iron aluminides at high temperatures are relatively open with cracks in them (Babu 1998). Although this behaviour may not be the same on room temperature exposure, it nevertheless provides a clue that the cracks in the oxides on the surface of iron aluminides could provide short diffusion paths for hydrogen to enter the lattice. Moreover, the diffusivity of hydrogen has been determined by several investigators. The diffusivity of hydrogen in Fe₃Al (Banerjee and Balasubramaniam 1998b) is higher than in FeAl (Banerjee and Balasubramaniam 1997). This could possibly be related to the higher Al content in the FeAl lattice, providing anti-trapping sites thereby reducing hydrogen diffusivity. Therefore, it is important to note that the deciding factor in determining the effect of alloying is the way it affects the hydrogen liberation rates on the surface of the aluminides.

All the above discussions are equally applicable to FeAl-based intermetallics. However, there is one major difference in their mechanical response when compared to Fe₃Al-based intermetallics. The grain boundaries of FeAl are inherently weak and therefore these intermetallics fail by brittle intergranular failure. This factor overrides the environmental effect in the case of binary FeAl aluminides. However, when the grain boundaries are strengthened by B additions, the environmental effect due to hydrogen is realized (Liu and George 1990).

Figure 3. Variation of ductility of Fe-25Al and Fe-28Al-5Cr as a function of hydrogen charging time (Tu *et al* 1998).

3. Alloy development efforts

Some salient features of iron aluminide alloy development activities pursued at IIT, Kanpur would be discussed in the following sections.

3.1 Passivity induction

We had earlier described that alloying additions that induce passivity in iron aluminides could be added to induce ductility. In such a case, the passive surface layer that forms in the environment would lower hydrogen liberation rates and thereby minimize hydrogen embrittlement. In view of the beneficial effect of surface passive films in lowering HE of iron aluminides (Agarwal and Balasubramaniam 1996a), an alloy development philosophy was proposed wherein it was stated that elements that induce passivity in iron when added to Fe_3Al would inhibit hydrogen reduction and also its entry by maintaining a passive layer (Balasubramaniam 1996, 1997).

Several passivity-inducing elements ($M = \text{Ti, Zr, V, Nb, Ta, Cr, Mo, W, Si}$ and Ni) were alloyed to the base Fe_3Al intermetallic (to produce Fe-24Al-5M intermetallics) in order to test the ductility enhancement philosophy (Agarwal *et al* 1996b). Ni could not be alloyed due to a violent reaction with the intermetallic on mixing, which is possibly due to the large exothermic heat of mixing between Ni and Al (Sikka 1994). Electrochemical polarization studies of the alloyed intermetallics in acidic $0.05 \text{ mol/l H}_2\text{SO}_4$ solution indicated that the alloyed intermetallics generally induced passivity to the base iron aluminide (Agarwal *et al* 1996b; Banerjee and Balasubramaniam 1999). The base iron aluminide exhibited active corrosion in this medium. Therefore, passivity enhancement due to the addition of these elements has been verified. The base Fe_3Al (Agarwal *et al* 1996a) and the alloyed intermetallics (Agarwal *et al* 1996b) were thermomechanically processed at 1000°C by multi-pass rolling after a homogenization treatment. It was observed that only the Fe-25Al , Fe-24Al-5Cr and Fe-24Al-5Ti intermetallics could be rolled successfully to 80% deformation in multiple passes at 1000°C . The Fe-24Al-5Ta intermetallic cracked after 50% deformation and the Fe-24Al-5Nb intermetallic cracked after 40% deformation. The Fe-24Al-5Mo , Fe-24Al-5Si and Fe-24Al-5V could not be rolled as they cracked in the first rolling pass itself. Thermomechanical processing of the intermetallic is also an important aspect of alloy development as the material should be amenable to deformation processing from a commercial angle. Therefore, although the alloy additions induced passivity in the base intermetallic, they were not effective in enhancing ductilities. The poor thermomechanical response of the intermetallics alloyed with Ta, Nb, Mo, Si and V was investigated. X-ray diffraction analysis of the alloyed

intermetallics revealed that Cr and Ti additions to binary Fe_3Al enter into solid solution without forming any new phase(s) or precipitates (Agarwal and Balasubramaniam 1996b). The ductility enhancement obtained with these additions is due to both passivity enhancement and the elements remaining in solid solution when compared to other alloyed Fe_3Al intermetallics. A tenacious surface film was noticed in the Ti -alloyed intermetallic (figure 4). Detailed fractographic and microstructural studies of the alloyed intermetallics revealed the precipitation of brittle phases on alloying Ta, Mo, V, Nb and Si to Fe_3Al (Agarwal and Balasubramaniam 1996b). These intermetallics could, therefore, not be thermomechanically processed at high temperatures.

The specific example of Ta addition to iron aluminide Fe_3Al is addressed below. Passivity enhancement by the addition of Ta is confirmed by potentiodynamic polarization behaviour of Fe-24Al-5Ta in $0.05 \text{ mol/l H}_2\text{SO}_4$ solution (figure 5). The base intermetallic exhibited active behaviour in this electrolyte. The addition of Ta should result in a passive layer which could inhibit the entry of hydrogen into the iron aluminide matrix and thus prevent the degradation of mechanical properties by hydrogen. However, the Ta -alloyed iron aluminide could not be thermomechanically processed into thin strips by multi-pass rolling at 1000°C as it cracked after 50% deformation. In order to understand the poor thermomechanical response of the intermetallic, a detailed microstructural examination of the intermetallic was carried out. The X-ray diffraction patterns obtained from the base Fe_3Al and the Ta -alloyed intermetallics were analyzed. The additional peaks in the pattern of Ta -alloyed intermetallic have been identified to belong to Fe_3Ta_3 . The Fe-24Al-5Ta specimen was microstructurally examined in a scanning electron microscope and a characteristic microstructure is presented in figure 6a. The precipitation

Figure 4. Tenacious surface film on the surface of Fe-24Al-5Ti .

of Fe_5Ta_3 phase in the intermetallic is confirmed. The fracture morphology of these intermetallic (figure 6b) indicates that the fracture is essentially transgranular in nature with crystallographic secondary cracks. The crack propagates by cleavage and the river line markings on the fracture surface indicate that the origin of fracture was at the grain boundaries, possibly induced by the precipitates at the grain boundaries. This results in overall brittle fracture of the intermetallic. Therefore, the addition of Ta to Fe_3Al , although beneficial from passivity enhancement angle, results in poor thermomechanical response due to the brittle nature of the precipitated phase Fe_5Ta_3 . Although hydrogen entry into the lattice would be restricted by the passive layer, there is no benefit to be gained because of the deleterious effect of the brittle phase precipitation. Therefore, the amount of Ta to be alloyed should be maintained below the solid solubility limit to prevent Fe_5Ta_3 precipitation.

It is important that the addition of passivity-inducing elements should not lead to brittle intermetallic precipitation. If this is taken into account, then the hydrogen embrittlement (HE) could be minimized and higher room temperature ductilities can be achieved with these alloying additions. Moreover, the element(s) would provide additional solid solution strength to the base intermetallic. For example, alloying with Mo, Zr, Nb, Ti and TiB_2 increases the high temperature strength of Fe_3Al and FeAl (Liu and Kumar 1993).

3.2 Irreversible hydrogen traps

It is well known that certain elements/compounds when present in alloys act as trap sites for hydrogen. Traps

can be classified as either reversible or irreversible based on the binding energy of traps with hydrogen. For example, Ti in steels acts like a reversible trap while incoherent TiC precipitates in steels are irreversible traps (due to trapping at the inclusion/matrix interface) (Pressouyre 1979). If the irreversible traps are finely and homogeneously distributed throughout the matrix, there is a good likelihood that hydrogen would be irreversibly trapped at these sites and hydrogen cannot accumulate at critical regions to cause embrittlement. Therefore, addition of elements which can act as irreversible traps for hydrogen could also be envisaged to improve the ductility of iron aluminides. However, this may not be promising route because there would be sufficient accumulation of hydrogen, with time, at these locations and once the hydrogen concentration exceeds the critical concentration for embrittlement, the material would be susceptible to embrittlement. It should

Figure 5. Potentiodynamic polarization curve for Fe-24Al-5Ta in 0.05 mol/l H_2SO_4 solution using a scan rate of 1 mV/s.

Figure 6. Scanning electron micrographs of (a) the Fe-24Al-5Ta intermetallic showing the presence of precipitates and (b) the fracture surface showing transgranular failure with crystallographic secondary cracks.

be noted that hydrogen appears to be generally trapped reversibly in both Fe–25Al (Kasul and Heldt 1991) and Fe–35Al (Kasul and Heldt 1993) based on the reversible nature of embrittlement (i.e. recovery of ductility on baking treatments). The improvement in ductility on C addition to iron aluminide (Baligdad *et al* 1997) must be related to irreversible hydrogen trapping at the Fe_3AlC precipitates.

3.3 Addition of oxygen active elements

It has been recently reported that addition of 0.15% Ce to iron aluminides leads to a significant increase in ductility (Yangshan *et al* 1996), although the reason for the effect has not yet been clearly understood. The same study also indicated that the grain boundaries contained an intermetallic phase rich in Ce and Fe. One possibility for the enhancement in ductilities due to Ce addition could be the irreversible trapping of hydrogen at the Ce-containing phase, thereby minimizing embrittlement. Interestingly, the addition of Ce had also changed the composition of the surface passive film. With the addition of Ce, the surface layer contained a larger amount of Al_2O_3 and Cr_2O_3 and a lower amount of Fe_2O_3 than the Fe–28Al–2Cr alloy without Ce addition. Therefore, the presence of oxygen active element Ce does have a strong effect on the nature of the scale formed on the surface of the material and this would affect hydrogen liberation rates as well as hydrogen diffusion through the surface layer. Another effect noticed with the addition of Ce was that the recrystallized grain size was much finer, which resulted in a concomitant increase in strength. The grain size would also play a role in the diffusion of hydrogen through the material although its relative significance is not known at present. Grain size also affects the strength of iron aluminides. Fe–25Al was found to obey Hall-Petch rule (Agarwal and Balasubramaniam 1997).

In view of the beneficial effect of Ce addition on the mechanical properties, we added Mm (a mixture of rare-earth elements with the major constituent being Ce) in Cr- and Ti-alloyed iron aluminides. The processing route described above in the case of the alloyed iron aluminides was similarly employed in this case. The rolled specimens did not exhibit any ductility and this was explained on the basis of segregation of the elements that constituted Mm to the grain boundaries of the aluminide, thereby weakening them (Banerjee and Balasubramaniam 1998a). Moreover, precipitation of additional phases rich in Al, Ce and Fe was also noticed on some cleavage planes. Therefore, addition of Mm was not successful in inducing ductility. Critical control of Mm (or the oxygen active element) addition is therefore crucial to impart ductility. We simultaneously undertook a detailed study of the effect of Mm additions on the

aqueous corrosion and high temperature oxidation behaviour of the iron aluminides. Some interesting results of this study are summarized below.

The potentiodynamic polarization curves for Fe–25Al, Fe–28Al, and Fe–28Al–2Cr, with and without Mm addition, in 0.05 mol/l H_2SO_4 solution are presented in figure 7 (Babu 1998). It is interesting to note that the Fe–28Al intermetallic shows a distinct active–passive transition where it is not clear in the case of Fe–25Al. This could probably be the reason why the latter is more ductile compared to the former. The Cr-alloyed aluminides also exhibit active–passive behaviour. Addition of Mm has resulted in a decrease in the passive current density, with the other parameters remaining almost similar to the Cr-alloyed intermetallic. This implies that Mm additions have a beneficial effect by modifying the passive layer on the iron aluminide. Therefore, addition of oxygen active elements are beneficial to the passivation properties of the iron aluminides. Mm addition also improved the passive film formation properties of the Ti-alloyed iron aluminides (Babu 1998; Banerjee and Balasubramaniam 1999). The effect of these additions on the high temperature oxidation of iron

Figure 7. Potentiodynamic polarization curves for Fe–25Al, Fe–28Al, Fe–28Al–2Cr and Fe–28Al–2Cr–0.15 Mm in 0.5 mol/l H_2SO_4 solution using a scan rate of 1 mV/s.

aluminides was also studied. It was earlier reported by Smialek *et al* (1988) that the addition of oxygen active elements like Hf, Zr and B in iron aluminide (Fe-40Al) resulted in slight improvements in the isothermal and cyclic oxidation behaviour. We studied the effect of Mm addition on the isothermal oxidation behaviour of Fe-28Al-Cr. The weight gain curves for Fe-28Al, Fe-28Al-2Cr and Fe-28Al-2Cr-0.15 Mm after oxidation in pure oxygen at a temperature of 1330 K in figure 8 indicate that parabolic kinetics were followed (Babu 1998). The parabolic rate constant can be determined from the slopes of the plots provided in figure 8. The oxidation resistance of Fe-28Al-2Cr is lower than that of Fe-28Al and this is due to the fast rate of oxidation in the initial stage for the Cr-alloyed intermetallic when compared with Fe-28Al. This can be easily understood by analyzing the instantaneous rate constant (k_p') of the various alloys which is provided in figure 9 (Babu 1998). The instantaneous rate constant can be determined by mathematical analysis of the weight gain curves (Roy *et al* 1996). On alloying with Mm, the initial rapid rate was not observed in the Cr-alloyed intermetallic and the oxidation rate of the Cr-alloyed aluminide with Mm was comparable to that of Fe-28Al. This clearly brings out

the beneficial effect of addition of Mm on the high temperature oxidation of iron aluminides. The addition of oxygen active elements, especially rare earth elements, in optimum amounts, leads to improved scale adhesion and resistance to oxidation (Moon 1989). In aluminides, rare earth additions are believed to decrease the stress concentration at the metal-oxide interface and consequently reduce the convolution and spallation (Prescott and Graham 1992). A tentative proposal for the increased oxidation resistance of the Mm-alloyed intermetallic is that the segregated rare earths at the grain boundaries (Banerjee and Balasubramaniam 1998a) can influence oxidation by pegging, with the rare earth oxide dispersoids acting like pegs (Babu 1998). Mm additions therefore also affect the high temperature environmental degradation behaviour. Interestingly, it was also observed that the addition of these elements which had segregated to the grain boundaries in the iron aluminides also retarded the diffusivity of hydrogen (Banerjee and Balasubramaniam 1998b), thereby showing that there is a certain amount of irreversible hydrogen trapping also associated with Mm addition.

It has been reported recently that addition of small amounts of B and Zr were very beneficial to the ductility

Figure 8. Isothermal oxidation weight gain curves for Fe-28Al, Fe-28Al-2Cr and Fe-28Al-2Cr-0.15 Mm at 1330 K in pure oxygen. Notice that oxidation behaviour obeys parabolic kinetics.

Figure 9. Instantaneous rate constant as a function of oxidation time for Fe-28Al, Fe-28Al-2Cr and Fe-28Al-2Cr-0.15 Mm at 1330 K in pure oxygen.

of iron aluminides (Broglio and Stoloff 1997). The microstructure of the alloy plays an important role in enhancing the ductility of these alloys and only under certain heat treatment conditions, does the enhanced ductilities obtain with the addition of B and Zr (Liu and Stoloff 1998). The beneficial role of alloying these elements has not yet been specifically understood. Choi *et al* (1997) have shown that Zr additions were beneficial to the cyclic oxidation resistance while Smialek *et al* (1988) reported that Hf additions were better than Zr additions. Interestingly, B additions, like TiB_2 additions, cause hot cracking and reduces the weldability while C additions are beneficial in this regard (Liu and Kumar 1993). The behaviour of iron aluminides containing C has been recently studied by Baligdad *et al* (1997).

There is a lot of scope, therefore, for tailoring the iron aluminide by the addition of oxygen active elements and by this process obtain a surface layer that is advantageous as regards hydrogen liberation rate and hydrogen entry are concerned. It is envisaged that the addition of these elements should be pursued with greater zeal in order to reduce the embrittling effect of hydrogen on these materials.

3.4 Recrystallization inhibition

Alloying additions to iron aluminide could also be added for preventing recrystallization during high temperature stress-relieving annealing treatments, which are generally carried out after severe deformation processing. The HE susceptibility is lower for a stress-relieved unrecrystallized structure (McKamey and Pierce 1993). This has been hypothesized to be due to the recrystallized grains disrupting the diffusion of hydrogen (McKamey and Pierce 1993). A possible reason for enhancement of ductility due to the unrecrystallized structure could be the reduction in dislocation density during stress relief annealing treatment. The gliding $a\langle 111 \rangle$ dislocations in Fe_3Al are composed of two $a/2\langle 111 \rangle$ partials joined by an anti phase boundary (Baker *et al* 1991). Hydrogen is transported primarily by these partial dislocations deep down into the material. Further, the partial dislocations can be locked as immobile $a\langle 100 \rangle$ dislocations by the Friedel mechanism. It has been shown that hydrogen promotes the formation of locked $\langle 100 \rangle$ dislocation and twice the normal amount of hydrogen can be absorbed by these locked dislocations (Li and Liu 1992). According to all theories of hydrogen embrittlement, the concentration of hydrogen should exceed a critical amount to cause embrittlement and this critical concentration is achieved in the $\{100\}$ planes due to the above reason (Balasubramaniam 1996). Once the critical concentration is achieved, hydrogen causes decohesion of the matrix and this is verified by cleavage fracture observed in this class of iron aluminides (Agarwal and Balasubramaniam

1996b). Moreover, etch-pit studies have indicated that the cleavage facets are of the $\{100\}$ type (Agarwal *et al* 1996a), further confirming the above mechanism. The improvement in ductility upon stress relieving the microstructure could therefore be due to the reduction in the number of $a/2\langle 111 \rangle$ dislocations in the structure during the annealing treatment. With a lower amount of $a/2\langle 111 \rangle$ partials in the microstructure, the local accumulation of hydrogen and the locking of partials would be less severe and hence this would result in some ductility, as observed experimentally (McKamey and Pierce 1993; Agarwal *et al* 1996a).

There is a sacrifice in strength upon the recrystallization treatment. Complete recrystallization leads to a large decrease in strength (McKamey and Pierce 1993) and therefore, not a viable alternative. The exception to the above would be when the alloying addition produces a fine grain size after the recrystallization anneal in which case the strength would not decrease drastically. Interestingly, Ce additions to iron aluminide produce a fine grained recrystallized structure unlike the large grain size obtained for the iron aluminide without Ce addition. There is no degradation of strength for the Ce-alloyed iron aluminide even in the recrystallized condition (Yangshan *et al* 1996). Mn additions also produce a fine grained structure after recrystallization (Banerjee and Balasubramaniam 1998a). Therefore, the addition of elements to inhibit recrystallization would also be beneficial in improving the room temperature strength and ductility of iron aluminides.

4. Conclusions

Environmental effects in iron aluminide have been reviewed. The importance of hydrogen liberation rates on the surfaces of iron aluminide in determining their embrittling behaviour has been described. Experimental verification for the role of hydrogen liberation rates on the HE behaviour has also been provided and discussed. The alloy development efforts to produce ductile iron aluminides are outlined. Induction of passivity in the iron aluminides is advantageous in minimizing HE. However, the alloying additions should not be added above the solid solubility limit as otherwise the material is inherently brittle due to the precipitation of brittle ternary phases. The role of oxygen active elements in affecting HE behaviour has also been addressed. The addition of such elements is generally advantageous for corrosion and high temperature oxidation. Finally, the mechanism of HE in iron aluminides has been discussed while addressing the role of the microstructure in affecting embrittlement. It is also envisaged that addition of elements that prevent complete recrystallization would be beneficial to the ductility of iron aluminides.

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