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Hydrogen in iron aluminides

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Abstract

Ordered intermetallic alloys based on the stoichiometric iron aluminide compositions of Fe_3Al and FeAl are being actively considered for high-temperature structural applications. They exhibit poor room temperature ductilities due to hydrogen embrittlement. Surface passive films reduce embrittlement by lowering the rate of hydrogen liberation on the surface. This has been explained by the mixed potential theory. The mechanism of hydrogen embrittlement in iron aluminides (namely, decohesion) has been addressed. Methods to minimize the degree of embrittlement have been discussed. These include passivity induction, addition of oxygen active elements, recrystallization inhibition and addition of irreversible hydrogen traps. The diffusion of hydrogen in iron aluminides has also been reviewed.

Keywords: Iron aluminides; Hydrogen embrittlement; Decohesion; Hydrogen diffusivity

1. Introduction

Iron aluminides are candidate high-temperature materials. The phase diagram of the Fe–Al system reveals that several intermetallic compositions exist in this system. The intermetallic alloys considered for structural applications are based on compositions centered around Fe_3Al and FeAl. The intermetallics with a higher percentage of Al are suitable for coating applications. It is also interesting to note from the phase diagram that Fe_3Al can exist in different structural modifications depending upon the temperature. At high temperatures, it exists as a disordered b.c.c. structure, which upon cooling first orders to the B2 and on further cooling, to the DO_3 structure. Both these structures are ordered b.c.c. structures.

The commercial importance of iron aluminides for high-temperature structural applications has been well established [1]. Iron aluminides contain two of the most easily available metals, namely Fe and Al. They offer low material cost, conservation of strategic materials and lower density than stainless steels. The importance of these iron aluminides is due to their excellent oxidation and sulphidation resistance. The oxidation resistance of Fe–Al alloys increases with increasing Al content. The critical amount of Al for external alumina oxide formation has been determined to be about 14 at% at 800°C [2]. The formation of a stable adherent oxide of alumina is responsible for the excellent oxidation resistance of the iron aluminides. Additionally, iron aluminides possess excellent sulphidation resistance. This is an important property as iron aluminides are candidate structural materials for fossil-based energy conversion systems, where a relatively high amount of sulfur is encountered. Other engineering applications envisaged include jet engine compressor blades and housing, structural members in aircraft, heating elements, furnace fixtures, heat exchangers, piping and tubing in automotive equipment, food handling equipment, chemical processing equipment, magnetic and electronic parts and nuclear reactor components [1].

In spite of all these inherent advantages, the binary iron aluminides suffer from certain disadvantages. Their room temperature ductility is poor. They possess relatively poor high-temperature strength and poor creep resistance. By suitable structural modifications (alloying and heat treatment), high-temperature strength and creep resistance can be significantly increased [1]. However, the poor room temperature ductility is a major concern. It has been recently recognized that the poor ambient temperature ductility is due to hydrogen embrittlement. The aim of the present paper is to provide an overview of hydrogen in iron aluminides and address some critical aspects regarding hydrogen embrittlement of iron aluminides. The diffusivity of hydrogen in these intermetallics will also be reviewed.

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2. Embrittlement by hydrogen

The embrittling effect of hydrogen in Fe_3Al has been established by tensile testing the aluminide in environments with different amount of hydrogen [3]. With increasing amount of hydrogen in the environment, there is a greater reduction in ductility, thereby proving that hydrogen is the cause of the poor ductilities. The observed ductility is small even for specimens tested in air and this has been attributed to the embrittling effect of hydrogen, produced on the surface due to the reaction of moisture with the freshly created surface of Al, according to the following equation:

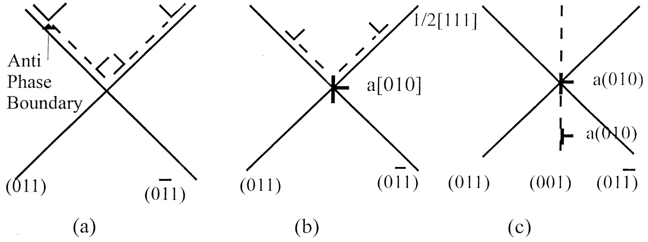
$$Al + H_2O = Al_2O_3 + 6H$$

The nascent hydrogen, which is liberated on the surface, enters the material and causes embrittlement.

Experimental verifications of hydrogen embrittlement are available. Zhu et al. [4] have provided direct evidence for the production of hydrogen by the reaction of moisture with iron aluminide Fe–36Al (all compositions in atom percent) surfaces. They utilized a laser desorption mass spectrometric method to detect the presence of hydrogen after contact of iron aluminide with water. Moreover, with the aid of pulsed-laser material removal, they were also able to obtain three-dimensional distribution of trapped hydrogen atoms as a function of depth from the surface. Indirect evidence is also available based on the variation of mechanical properties in the presence of hydrogen. There is a reduction in embrittlement when iron aluminide surfaces are covered with either an oxide coating [5] or with Ni or Cu coating prior to tensile testing. These surface barriers are presumed to hinder entry of hydrogen into the material and thereby lower the degree of embrittlement [6]. Hydrogen embrittlement is also minimized by lowering of the hydrogen partial pressure in the environment [3]. Further proof is provided by the reversible nature of embrittlement in both Fe–25Al [7] and Fe–35Al [8] aluminides. Hydrogen embrittlement can be minimized by a baking treatment, which is an effective method of removing hydrogen from the material. These experimental observations conclusively prove that the poor ductility of iron aluminides is caused by hydrogen.

The mechanism of hydrogen embrittlement would be now considered. Hydrogen that is produced on the surface should diffuse into the material to cause embrittlement. Hydrogen has to first diffuse through the surface layer, that would invariably be present in these Al-containing intermetallics. The oxide surface scale is relatively thin on alumina-forming systems at ambient temperatures. As the surface layer is relatively thin, it is reasonable to assume that diffusion of hydrogen through the surface scale would not be the limiting factor in the embrittlement process. Once hydrogen enters the lattice in the atomic form, it has to diffuse and accumulate in critical regions in the material in order to cause embrittlement. The ductility of the samples tested in air is relatively low, of the order of a few percent. Most of the tensile testing studies have been conducted at a standard strain rate of 10^{-3} per second. Therefore, the time taken for completion of each test is small. As the diffusivity of hydrogen in iron aluminides is relatively small (of the order of 10^{-13} m^2/s [9]) compared to pure iron, it is difficult for hydrogen to be transported to the interior of the specimens in order to initiate failure. Therefore, hydrogen is transported either through fast diffusion paths during tensile testing or through cracks that are initiated in the near-surface regions and propagate with relative ease through the rest of the matrix.

The initiation of cracking and the effect of hydrogen on cracking can be explained by considering hydrogen transport through fast diffusion paths. In the b.c.c. ordered structures of iron aluminide, the glissile dislocations are of the type $a\langle 111\rangle$, which glide normally on $\{110\}$ slip planes. These dislocations are generally dissociated into partials of the type $a/2\langle 111\rangle$, separated by an antiphase boundary [10]. It is possible for the leading partials (and also the trailing partials) gliding on two different slip planes to interact to form a dislocation of type $a\langle 001\rangle$, as schematically depicted in Fig. 1. The formation of $\langle 001\rangle$ dislocations would result in transgranular cleavage across the $\{100\}$ planes [10]. The role of hydrogen in this locking mechanism is also significant. In the presence of hydrogen, it has been shown that twice the normal amount of hydrogen can be transported by the mobile dislocations [11]. When the mobile dislocations are locked, hydrogen content on the $\{100\}$ planes increases and this provides conditions favorable for initiation of cracking. The accumulation of hydrogen on the $\{100\}$ planes of the aluminide would lead to initiation and propagation of cracking in planes closely associated with the $\{100\}$ planes [12]. It has been observed experimentally that cracking in



(a) (b) (c)

Fig. 1. Schematic illustration of formation of sessile dislocations of type $a<001>$ by locking of partials of the glissile dislocations of type $a<111>$ [10]: (a) Two $a<111>$ dislocations each consisting of $a/2<111>$ partials glide on intersecting $\{011\}$ planes. (b) The leading $a/2<111>$ partials react to form $a<001>$ dislocation, and (c) the trailing $a/2<111>$ partials also interact to form a second $a<001>$ dislocation.

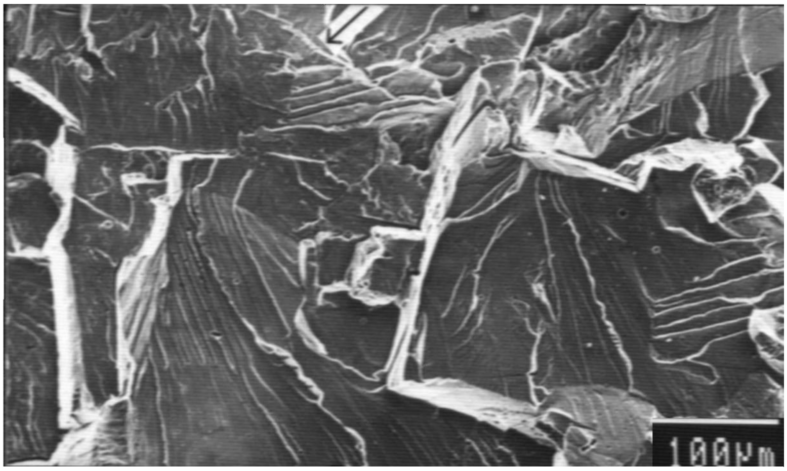


Fig. 2. Cleavage fracture observed in Fe_3Al-based intermetallics. Notice typical river line markings on the cleavage fracture surface.

iron aluminides is of transgranular cleavage-type (Fig. 2) with the cleavage planes being of the {100} type [13]. Interestingly, the cracking observed in the entire cross-section of the binary Fe_3Al aluminide is cleavage type. First, this can be due to the material being quite weak along the {100} planes and therefore susceptible to cleave along these weak planes. Secondly, it can be due to initiation of cleavage failure by hydrogen and propagation of failure by fast diffusion of hydrogen down the crack path. Therefore, hydrogen seems to initiate cracking along the weak {100} planes and propagation occurs easily as the material itself is weak along these planes. The reasons for the weakness of the material along the {100} planes is not well understood and this must be related to the type of bonding that exists across the {100} planes [12].

There is a major difference in the mechanical response of FeAl-based intermetallics when compared to Fe_3Al-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 the FeAl-based intermetallics. However, when the grain boundaries are strengthened by the addition of B, the environmental effect due to hydrogen is realized [14].

3. Minimization of hydrogen embrittlement

It is important to minimize the degree of hydrogen embrittlement in order to render these intermetallics suitable for commercial exploitation. One of the earliest methods of minimize embrittlement was by the addition of Cr [15]. The specific role played by Cr in minimizing embrittlement was not well understood initially. The effect of Cr addition on embrittlement can be explained by mixed potential analysis (Fig. 3) [12]. The rate of hydrogen liberation on the passivated surface of the Cr-alloyed iron aluminide is much lower than that on the binary aluminide. This idea has also been verified by deciphering the experimentally observed potentiodynamic polarization curves [16]. A lower rate of hydrogen liberation implies a lower rate of hydrogen absorption and therefore a delay in the onset of embrittlement. Therefore, it should be possible to engineer the surface to lower hydrogen liberation rates and thereby, hydrogen embrittlement of iron aluminides can be minimized. A thick passive film would additionally delay hydrogen entry into the material. Therefore, induction of stable passivity by the addition of alloying elements would prove beneficial to increasing ductilities [12,17].

Of course, it must be realized that the hydrogen embrit-

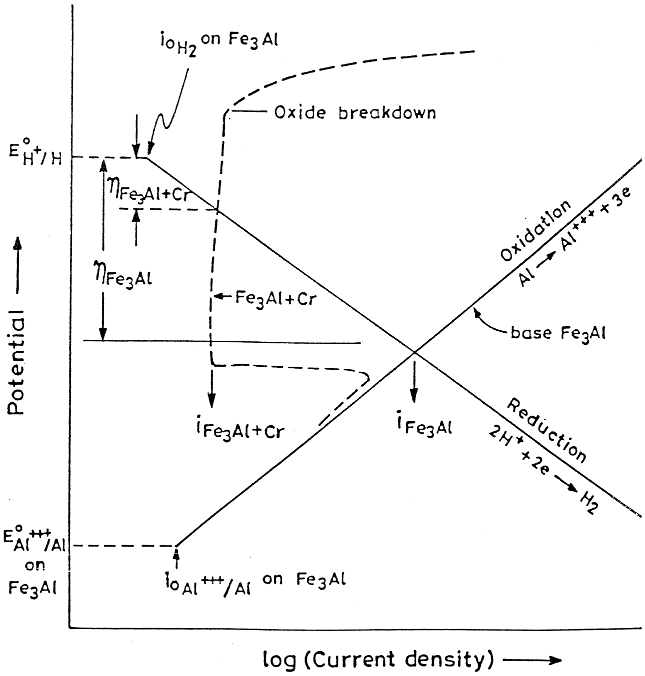


Fig. 3. Mixed potential analysis showing the lower rate of hydrogen reduction on the surface of the Cr-alloyed intermetallic when compared to the binary intermetallic [12].

tlement problem can be delayed but cannot be entirely eliminated even in the case of aluminides with a stable passive layer. This is evident from the experimental results of Tu et al. [18] who found that with increasing hydrogen contents, both the binary and Cr-alloyed intermetallics were embrittled to the same degree; although a higher ductility was observed for the Cr-alloyed intermetallic as compared to the binary intermetallic when tensile testing was performed immediately after removal of all hydrogen from the material. The Cr-alloyed intermetallic will pick up sufficient hydrogen with time, eventually resulting in failure. Therefore, additional methods have to be envisaged to minimize embrittlement. Several passivity-inducing elements (Ti, V, Nb, Ta, Cr, Mo, W, Si and Ni) were added to the binary Fe_3Al intermetallic and it was found that Ti and Cr were effective in producing ductilities [19]. The other intermetallics failed due to precipitation of brittle phases [20]. Therefore, it is important that the addition of passivity-inducing elements does not lead to precipitation of deleterious phases.

As regards alloying addition, the beneficial aspect of adding oxygen-active elements on ductility has been documented. For example, addition of 0.15% Ce to iron aluminide significantly increased the ductility [21]. Addition of Ce resulted in a finer grain size (thereby resulting in concomitant increased strength) and moreover, changed the composition of the 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, passivation properties are significantly modified by the addition of even a small amount of the oxygen-active element. This has a beneficial influence in lowering hydrogen entry into the material. Potentiodynamic polarization experiments conducted on iron aluminides alloyed with mischmetal (a mixture of rare earth elements with the major components being La and Ce) clearly revealed the beneficial effect of Ce addition on the passivation of Cr-alloyed iron aluminide [22]. However, the addition of Mm did not provide sufficient ductility because it weakened the grain boundaries by segregating to these locations [23]. Therefore, there is an optimum amount of addition of oxygen-active elements which has to be determined by extensive experimentation.

It has also been shown that a partially recrystallized microstructure is more resistant to embrittlement [13,24]. Complete recrystallization leads to a drastic reduction in strength and therefore not a viable alternative. The improvement in ductility upon recrystallization could be due to the lowering of dislocation density in the intermetallic [25], rather than the grain boundaries offering resistance to hydrogen diffusion [24]. Interestingly, alloying addition like Ce produces a fine grain size upon recrystallization [21] and therefore a significant amount of strength is retained after recrystallization. Addition of elements that inhibit recrystallization results in minimization of embrittlement. Interestingly, iron aluminides obey the Hall–Petch relationship [26], which implies that their mechanical properties can be tailored by controlling the grain size.

Finally, the improvement in ductility by the addition of irreversible traps can also be envisaged. Traps for hydrogen can be either reversible in nature or irreversible in nature depending on the binding energy of the traps with hydrogen. If irreversible hydrogen traps are homogeneously distributed throughout the matrix, hydrogen would be trapped at these sites and it would take longer times for hydrogen to accumulate at critical regions to cause embrittlement. Therefore, the addition of irreversible hydrogen traps would also improve ductility. The improvement in ductility upon addition of TiB_2 in iron aluminide [1] or carbon in iron aluminide [27] is due to the trapping of hydrogen at the precipitate–matrix interfaces in the material. The effect of hydrogen on carbon-alloyed intermetallics has been recently studied in detail. Baligidad et al. have reported that addition of carbon in the range of 0.14 to 0.50 wt% significantly increased the room temperature strength of Fe–28Al alloys [27]. These alloys also exhibited good room temperature ductility. Addition of carbon to Fe_3Al-based intermetallics results in the precipitation of the carbide Fe_3AlC [27]. The improvement in ductility on C addition to iron aluminide stems from irreversible hydrogen trapping at the Fe_3AlC–matrix interfaces. The trapping of hydrogen at the carbide–matrix interfaces has been verified by hydrogen diffusivity measurements [28]. These carbon-alloyed iron aluminides, however, did not exhibit significant ductilities after hydrogen charging + baking experiments because cracking was initiated at the carbide–matrix interfaces [29].

4. Diffusivity of hydrogen

The diffusion of hydrogen at ambient temperatures in iron aluminides must also be considered. Hydrogen diffusivity in iron aluminides generally decreases with increasing amount of Al in the intermetallic. For example, the diffusivity of hydrogen was estimated by Hosada et al. [30] in two binary iron aluminides based on hardness increase after exposing the alloys to different environments. It was shown that diffusivity in Fe–18Al was 10^{-11} m^2/s while it was 10^{-12} m^2/s in Fe–25Al. Hydrogen diffusivity in Fe–25Al determined by the technique of subsurface microhardness profiling [9] is similar. Increasing the Al concentration further lowers diffusivity. Kasul and Heldt [8] showed the reversibility of hydrogen embrittlement by estimating the ductility after baking a hydrogen-charged Fe–35Al polycrystal. The rate of ductility recovery provided the room temperature diffusivity of hydrogen in this intermetallic as 4×10^{-16} m^2/s. Yang and Hanada [31] studied hydrogen absorption in ordered Fe–40Al and estimated the hydrogen diffusivity at room temperature to be 4×10^{-13} m^2/s. The higher hydrogen diffusivity measured in absorption compared to that in desorption may suggest differences in the diffusion mechanism between absorption and desorption [31]. Based on the three-dimensional hydrogen distribution of hydrogen reported by Zhu et al. [4] for Fe–36Al, the diffusivity of hydrogen was estimated to be 2.4×10^{-15} m^2/s [32]. Alloying the binary Fe_3Al intermetallic with Cr, Ti or Mm resulted in lower hydrogen diffusivity [9]. Diffusivity is also lowered when irreversible hydrogen traps are homogeneously distributed in the matrix. For example, the diffusion of hydrogen in carbon-alloyed intermetallics is lower than in the base binary intermetallic (Fig. 4) due to irreversible trapping at the carbide–matrix interfaces [28].

Hydrogen diffusivity is higher in Fe_3Al-based intermetallics than in FeAl-based intermetallics. This is also in agreement with the theoretical prediction that activation energy for interstitial diffusion is higher in FeAl [33]. Hosada et al. [30] attributed the lower diffusivity in the iron aluminide containing higher Al due to the anti-trapping tendency of Al which reduces the effective hydrogen diffusivity. It is difficult to imagine anti-trapping behavior leading to lower diffusivity and it should rather be trapping due to the presence of Al that results in lower hydrogen diffusivity [9]. Similarly, the lower diffusivity obtained on alloying could be due to the trapping by the alloying additions.

In a study of the environment-sensitive cracking of Fe–28Al–5.0Cr–0.5Nb–0.5Mo–0.2C–0.2B–0.1Zr, Chiu et al. determined the room temperature diffusivity of hydrogen in the intermetallic by the time lag technique to be 1.6×10^{-9} m^2/s [34]. They concluded that the reported value of hydrogen diffusivity was reasonable as it was of the same order of magnitude as that for hydrogen diffusivity in b.c.c. metals like α-Fe, V and Nb [35]. This is the only anomalous high diffusivity value reported for alloyed Fe_3Al-based iron aluminides.

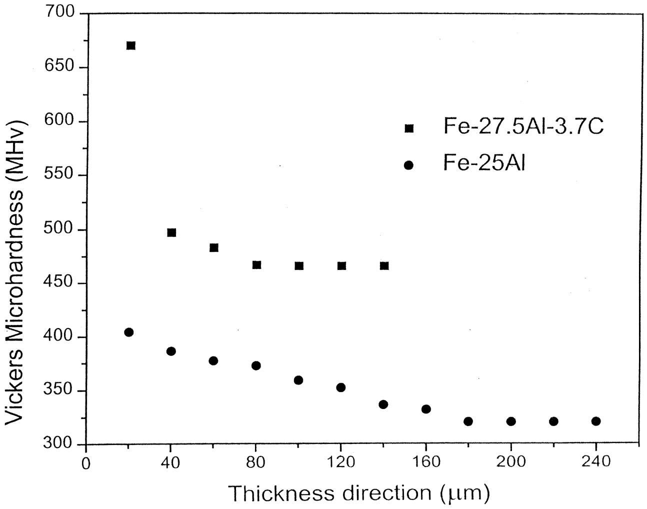


Fig. 4. Microhardness profiles for the binary and a carbon-alloyed iron aluminide along the thickness direction after cathodic hydrogen charging for 12 h at 10 mA/cm^2 in 0.05 mol/l H_2SO_4 solution. Hydrogen diffusivity in the carbon-alloyed iron aluminide is lower.

5. Conclusions

The behavior of hydrogen in iron aluminides has been discussed. The embrittlement of the intermetallics due to hydrogen has been addressed wherein the mechanism of embrittlement has been provided. Methods to minimize embrittlement have also been outlined. Finally, the diffusivity of hydrogen in iron aluminides has been reviewed.

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