ELSEVIER

Journal of Alloys and Compounds 253–254 (1997) 148–151

Journal of ALLOYS AND COMPOUNDS

Alloy development to minimize room temperature hydrogen embrittlement in iron aluminides

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Abstract

Iron aluminides based on the stoichiometric compositions Fe_3Al and FeAl exhibit poor room temperature ductilities due to hydrogen embrittlement (HE). The presence of surface passive films reduces HE. Passivity-inducing elements Ti, Zr, V, Nb, Ta, Cr, Mo W, Si and Ni have been alloyed with Fe_3Al and these aluminides have been characterized for their thermomechanical and electrochemical behavior. All the alloying additions, except V, enhanced the passivity of the base intermetallic. The base Fe_3Al, Cr- and Ti-alloyed intermetallics could be rolled to 80% deformation at 1000 °C whereas the other alloyed intermetallics cracked during deformation processing. 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. Cracks initiate from the precipitated brittle phases, propagate into the matrix and result in poor thermomechanical behavior. Therefore, the amount of passivity-inducing element addition should be kept below the solid solubility limit. This would enable the development of ductile iron aluminides. The addition of elements for irreversible hydrogen trapping and to prevent recrystallization is also 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 these materials is their poor room temperature ductility. This is due to their susceptibility to hydrogen embrittlement (HE) [1]. HE of iron aluminides is caused even in the presence of moisture. Several methods have been proposed to minimize it like oxide coatings [2] (to minimize hydrogen pick-up from the environment), heat treatments [3] (to produce a partially recrystallized microstructure) and alloying with passivity-inducing elements [4] (which provide a passive layer on the surface of the intermetallic that reduces the hydrogen liberation rates on the surfaces and thereby minimizes hydrogen entry). The alloy development methodology to be adopted to produce ductile iron aluminides is outlined in the following sections.

2. Alloy development methodology

In order to obtain the desired properties of metals, alloying with additional elements is generally attempted. The type of alloying addition would depend upon the property that is being addressed. For providing strength, elements that lead to solid solution strengthening or to the precipitation of age-hardenable phases are added. The strength could also be increased by adding elements that refine the grain size and hence provide grain strengthening. Where the corrosion resistance of the metal has to be enhanced, passivity-inducing elements should be added. It should be emphasized that the alloying element that is added should not lead to deterioration in some property where it is not intended. For example, if an element primarily added to enhance passivity, leads to the precipitation of ternary brittle intermetallics, especially at the grain boundaries, the property of strength would be very severely affected. Therefore, the possible deleterious effects of alloying should also be understood.

2.1. Passivity induction

The most effective alloying addition that results in ductility enhancements in aluminides is Cr. Even Cr additions as low as 2% have been reported to be effective in providing improved ductilities [5]. The role of Cr in minimizing embrittlement has been elucidated electro-

0925-8388/97/$17.00
PII S0925-8388(96)02940-4

chemically by the mixed potential theory [4], according to which the induction of passivity by the addition of Cr reduces hydrogen liberation rates on the surfaces of Cr-alloyed iron aluminides when compared to the base intermetallic. The potentiodynamic polarization curves of base Fe_3Al and Cr-alloyed Fe_3Al have been theoretically deciphered and it was shown that on alloying with Cr, the mixed potential of the intermetallic is established in the passive region at a potential noble to the reversible hydrogen potential [6]. Moreover, the passive layer would also hinder hydrogen entry into the lattice. In view of the beneficial effect of surface passive films in lowering the HE of iron aluminides [7], 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 its entry by maintaining a passive layer [4].

Several passivity-inducing elements (Ti, Zr, V, Nb, Ta, Cr, Mo, W, Si and Ni) have been alloyed to the base Fe_3Al intermetallic (to produce Fe_3Al–5M intermetallics) in order to test the ductility enhancement philosophy [8]. 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 [9]. Electrochemical polarization studies of the alloyed intermetallics in acidic 0.05 mol l^{-1} H_2SO_4 solution indicated that all the intermetallics, barring the V-alloyed one, induced passivity to the base iron aluminide [10]. The base iron aluminide exhibited active corrosion in this medium. Therefore, passivity enhancement upon addition of these elements has been verified.

The base Fe_3Al [11] and the alloyed intermetallics [8] were thermomechanically processed at 1000 °C by multipass rolling after a homogenization treatment (in order to make the composition of the buttons uniform). It was observed that only the Fe_3Al, Fe_3Al–5Cr and Fe_3Al–5Ti intermetallics could be rolled successfully to 80% deformation in multiple passes at 1000 °C. The Fe_3Al–5Ta intermetallic cracked after 50% deformation and the Fe_3Al–5Nb intermetallic cracked after 40% deformation. The Fe_3Al–5Mo, Fe_3Al–5Si and Fe_3Al–5V could not be rolled as they cracked in the first rolling pass. 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 perspective. Therefore, although the alloy additions induced passivity in the base intermetallic, the poor thermomechanical response of the intermetallics alloyed with Ta, Nb, Mo, Si and V has to be understood in order to decide the criterion for alloying.

The specific example of Nb addition to iron aluminide Fe_3Al is addressed below. Passivity enhancement by the addition of Nb is confirmed by potentiodynamic polarization behavior of Fe_3Al–5Nb in 0.05 mol l^{-1} H_2SO_4 solution (Fig. 1). The base intermetallic exhibited active behavior in this electrolyte. Therefore, the addition of Nb should result in a passive layer which would inhibit the entry of hydrogen into the iron aluminide matrix and thus prevent the degradation of mechanical properties by hydrogen. However, the Nb-alloyed iron aluminide could not be thermomechanically processed into thin strips by multipass rolling at 1000 °C as it cracked after 40% deformation.

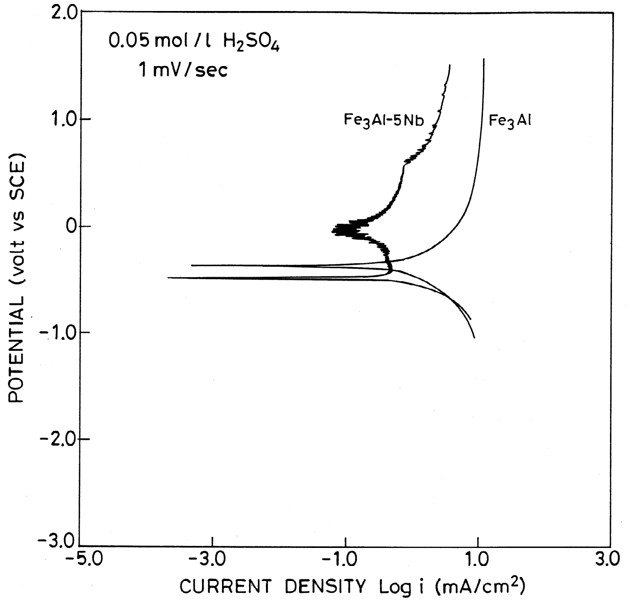

Fig. 1. Potentiodynamic polarization curves for Fe_3Al and Fe_3Al–5Nb intermetallics in 0.05 mol l^{-1} H_2SO_4 solution using a scan rate of 1 mV s^{-1}.

In order to understand the poor thermomechanical response of this intermetallic, a detailed microstructural examination of the intermetallic was carried out. The x-ray diffraction patterns obtained from the base Fe_3Al and the Nb-alloyed intermetallics were analyzed. The additional peaks in the pattern of Nb-alloyed intermetallic have been identified to belong to Fe_2Nb. The precipitation of Fe_2Nb is not surprising because it has been reported earlier that, in the Fe–28Al–2Nb intermetallic, the precipitation of this phase at high temperatures results in age-hardening of the intermetallic [12]. The Fe_3Al–5Nb specimen was microstructurally examined in a scanning electron microscope and a characteristic microstructure is presented in Fig. 2. The precipitation of Fe_2Nb phase in the intermetallic is confirmed. Notice that some of the precipitates (on the left side of the micrograph) have cracked and the crack extends into the matrix. The fracture morphology of these intermetallic (Fig. 3) indicates that the fracture is essentially transgranular in nature with intermittent brittle facets. This indicates that the crack propagates through the precipitated phases in a brittle manner while it propagates through the inter-precipitate region of the matrix in a ductile manner. This results in overall brittle fracture of the intermetallic. Therefore, the addition of Nb to Fe_3Al, although beneficial

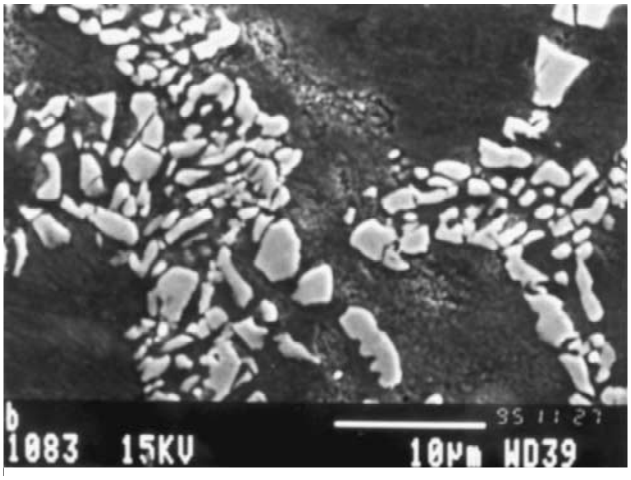

Fig. 2. Scanning electron micrograph of the Fe_3Al–5Nb intermetallic showing the presence of precipitates.

from passivity enhancement angle, results in a poor thermomechanical response due to the brittle nature of the precipitated phase Fe_2Nb. 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 Nb to be alloyed should be maintained below the solid solubility limit to prevent Fe_2Nb precipitation. X-ray diffraction analysis of the other alloyed intermetallics revealed that Cr and Ti additions to binary Fe_3Al enter into solid solution without forming any new phase(s) or precipitates [8]. 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 detailed fractographic and microstructural study of the other alloyed intermetallics revealed the precipitation of brittle phases on alloying Ta, Mo, V, Nb and Si to Fe_3Al [13]. These intermetallics could, therefore, not be thermomechanically processed at high temperatures. It is thus important that the addition of passivity-inducing elements should not lead to brittle intermetallic precipitation. If this is taken care of, 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.

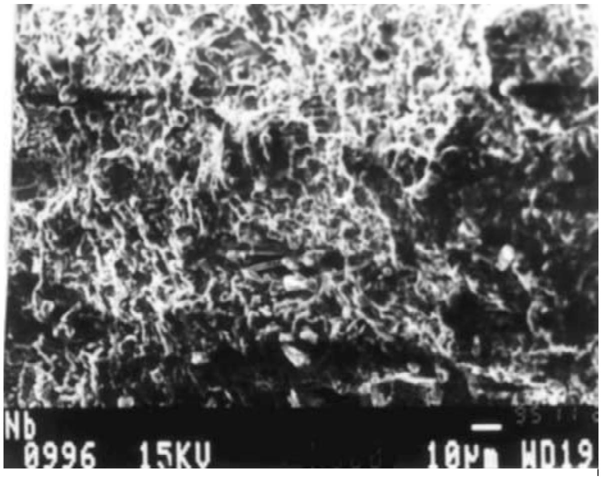

Fig. 3. Scanning electron micrograph of the fracture surface of the Fe_3Al–5Nb intermetallic showing transgranular failure with intermittent brittle facets.

2.2. Irreversible hydrogen traps

It is well know that certain elements/compounds when present in alloys act as irreversible trap sites for hydrogen, for example TiC in steels [14]. If these traps are finely and homogeneously distributed throughout the matrix, there is a good likelihood that hydrogen would be irreversibly trapped by these sites and therefore cannot accumulate in 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. It has been recently reported that addition of 0.15% Ce to iron aluminides leads to a significant increase in ductility [15], although the reason for the increase has not yet been postulated. The same study also indicated that the grain boundaries were covered with an intermetallic phase rich in Ce and Fe. It is reasonable to assume that the Ce-containing phase acts as irreversible traps for hydrogen and, therefore, lowers the amount of hydrogen present in the material, 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–28A1–2Cr alloy without Ce addition. Therefore, the presence of strong hydrogen trapping compounds, homogeneously distributed through out the iron aluminide matrix, would also be beneficial in improving ductilities.

2.3. 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 [3]. It has been hypothesized that this is due to the unrecrystallized grains disrupting the diffusion of hydrogen [3]. This may not be the reason as hydrogen can diffuse with relative ease in the iron aluminide matrix and at grain boundaries. 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⟨111⟩ partials joined by an anti-phase boundary [16].

Hydrogen is transported primarily by these partial dislocations deep down into the material. Further, the partial dislocations can be locked as immobile a⟨100⟩ dislocations by the Friedel mechanism. It has been shown that hydrogen promotes the formation of locked ⟨100⟩ dislocation and twice the normal amount of hydrogen can be absorbed by these locked dislocations [17]. According to all theories of hydrogen embrittlement, the concentration of hydrogen should exceed a critical amount to cause enbrittlement and this critical concentration is achieved in the {100} planes due to the above reason [4]. 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 [13]. Moreover, etch-pit studies have indicated that the cleavage facets are of the {100} type [11], 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⟨111⟩ dislocations in the structure during the annealing treatment. With a lower amount of a/2⟨111⟩ partials in the microstructure, the local accumulation of hydrogen and the locking of partials would be less severe and hence this would result in enhanced ductilities, as observed experimentally [3,11].

There is a sacrifice in strength upon the recrystallization treatment. Complete recrystallization would lead to a large decrease in strength [3] and is not therefore, 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 and there is no degradation of strength for the Ce-alloyed iron aluminide even in the recrystallized condition [15]. Therefore, the addition of elements to inhibit recrystallization would also be beneficial in improving the room temperature ductility of iron aluminides.

3. Conclusions

The room temperature ductility of iron aluminides can be enhanced by the addition of passivity-inducing elements to the base iron aluminide. Ti and Cr additions are effective in enhancing passivity and also in provided higher ductilities. They exist in solid solution in the iron aluminide. The addition of passivity-inducing elements (Zr, Nb, Ta, Mo, W and Si) results in brittleness, although these additions enhance the passivity of the base intermetallic. These elements precipitate brittle phases with Fe and Al in the intermetallic leading to the poor thermomechanical response. Significant room temperature ductilities can therefore be expected in iron aluminides in which the amount of passivity-inducing elements is maintained below their solid solubility limit. Reducing the susceptibility to HE by the addition of elements which irreversibly trap hydrogen and which prevent recrystallization have also been discussed.

References

[1] N.S. Stoloff and D.J. Duquette, *J. Metals, 45* (1990) 30.

[2] C.G. McKamey, J.A. Horton and C.T. Liu, *Scripta Metall., 22* (1992) 1679.

[3] C.G. McKamey and D.H. Pierce, *Scripta Metall. Mater., 28* (1993) 1173.

[4] R. Balasubramaniam, *Scripta Mater., 34* (1996) 127.

[5] C.G. McKamey and C.T. Liu, *Scripta Metall. Mater., 24* (1990) 2119.

[6] S. Mukherjee and R. Balasubramaniam, *Bull. Mater. Sci., 19* (1996) 831.

[7] A. Agarwal and R. Balasubramaniam, *Bull. Mater. Sci., 19* (1996) 91.

[8] A. Agarwal, M.J. Akhtar and R. Balasubramaniam, *J. Mat. Sci., 31* (1996) 5207.

[9] V.K. Sikka, in J.H. Schneibel and M.A. Crimp (eds.) *Processing, Properties and Applications of Iron Aluminides*, TMS, Warrendale, 1994, p. 3.

[10] S. Astha and R. Balasubramaniam, (1996) to be published.

[11] A. Agarwal, R. Balasubramaniam and S. Bhargava, *Met. Mater. Trans A*, *27A* (1996) 2985.

[12] M. Mendiratta, S. Ehlers, D. Dimiduk, W. Kerr, S. Mazdiyasni and H.A. Lipsitt, *Mater. Res. Soc. Symp., 81* (1987) 393.

[13] A. Agarwal and R. Balasubramaniam, *Practical Metallography*, *33* (1996) 453.

[14] G.M. Pressouyre and I.M. Bernstein, *Metall. Trans A*, *9A* (1978) 1571.

[15] S. Yangshan, Y. Zhengjun, Z. Zhonghua and H. Haibo, *Scripta Mater.*, *33* (1996) 811.

[16] I. Baker, P. Nagpal, F. Liu and P. Munroe, *Acta Metall. Mater.*, *39* (1991) 1637.

[17] J.C.M. Li and C.T. Liu, *Scripta Metall. Mater., 27* (1992) 1701.