

Effect of alloying on aqueous corrosion and mechanical behaviour of iron aluminide Fe₃Al

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Passivity-inducing elements have been added to iron aluminide, Fe₃Al, to tackle their poor room-temperature ductility problem. The effect of alloying on the aqueous corrosion and mechanical behaviour of iron aluminides has been examined. It was found that the corrosion behaviour of intermetallic Fe₃Al–5M (M = Cr, Mo, Ta and Ti) was superior compared to that of binary Fe₃Al in electrolytes of pH 4 (H₂SO₄) and pH 8 (NaOH). The relative corrosion behaviour of these intermetallics in these electrolytes was comparable. The possible reasons for passivity enhancement have been discussed. Fe₃Al–5M₁ (M₁ = Mo, Ta, V, Nb and Si) intermetallics could not be processed thermomechanically at 1000 °C because they cracked during deformation processing. The Fe₃Al–5Cr and Fe₃Al–5Ti intermetallics could be processed up to 80% deformation at 1000 °C by rolling into thin strips. These intermetallics exhibited improved room-temperature ductilities but poor yield strengths. The improvement in ductility has been attributed to passivity and microstructural effects. The low yield strengths of these intermetallics are poorly understood.

1. Introduction

Ordered iron aluminide intermetallics of composition Fe₃Al and FeAl possess attractive properties for application as structural materials at elevated temperature in aggressive environments [1–3]. However, their poor room-temperature ductility limits their use as engineering materials because they are difficult to process into useful shapes like plates and tubes. It has been well established that the poor ductility of iron aluminides is due to hydrogen embrittlement (HE) [3].

Several methods have been proposed to improve the room-temperature ductility of iron aluminides. These methods include thermomechanical treatments [4] and alloying [5, 6]. HE can also be minimized by providing an oxide film on the iron aluminide surface [5, 7]. The role of surface films in the HE of iron aluminides has been reviewed [8]. Chromium addition to iron aluminides is effective in providing improved ductilities [5, 7]. The role of chromium in improving the room-temperature ductility of iron aluminide has been elucidated recently from an electrochemical viewpoint and, based on this, an alloy development philosophy has been suggested to develop ductile iron aluminide intermetallics [6]. According to this philosophy, addition of passivity-inducing elements (such as chromium, titanium, molybdenum, tantalum, vanadium, silicon, nickel, tungsten and niobium) should change the nature of anodic polarization curve and shift the corrosion potential into the passive range. The corrosion rate decreases significantly in alloyed iron aluminides due to passivity, leading to a corresponding decrease in the hydrogen reduction reaction rate. This reduced hydrogen liberation rate

lowers the amount of nascent hydrogen in the material and hence minimizes HE. Additionally, the passive layer would also act as a barrier to the diffusion of hydrogen into the material.

Novel iron aluminide intermetallics are synthesized on the basis of the above mentioned philosophy. The aqueous corrosion and mechanical behaviour of alloyed iron aluminides have been studied. The aim of the present work was to study the correlation between passivity and room-temperature ductilities in the alloyed iron aluminides.

2. Experimental procedure

The present study has been carried out on several Fe₃Al–5M alloys synthesized at IIT Kanpur. Fe–24Al–5M (M = passivity-inducing elements Cr, Mo, Ta, Nb, V, Si, Ni and Ti) type of intermetallics were melted in an arc furnace, using an inert argon environment. Alloying elements added had a purity of 99.99%. All these intermetallics were melted three times to minimize segregation, and were obtained in the form of buttons weighing 20 g each. (Nickel could not be alloyed because of a violent exothermic reaction on melting, which resulted in an inhomogeneous alloy button.) These buttons were homogenized at 1000 °C for 4 h to minimize segregation further. All the buttons were rolled initially at 1000 °C; only the Fe₃Al–5Cr and Fe₃Al–5Ti intermetallics could be deformed by 80%. X-ray diffraction (XRD) patterns were obtained from the rolled strips of the alloyed intermetallics in a Rich Seifert 2000D diffractometer using CuK_α radiation.

Tensile specimens were machined from the rolled strips of Fe₃Al-5Cr and Fe₃Al-5Ti and they were partially recrystallized at 750 °C for 1 h. The recrystallization treatment was carried out because a partially recrystallized microstructure produces better ductilities in binary Fe₃Al [9, 10]. Tensile testing was performed on an Instron Testing machine at a constant strain rate of 10⁻⁴ s⁻¹. All the tests were carried out in air at room temperature. The tensile samples were coated with silicone oil to prevent hydrogen entry into the lattice during straining [11]. All the fractured tensile specimens were examined under a scanning electron microscope (Jeol JSM 840A). Optical microscopy was carried out using a Leitz Laborlux microscope at a magnification of 100. Metallographic samples were prepared by etching in 8 parts CH₃COOH, 4 parts HNO₃ and 1 part HCl. Etching was carried out for only a few seconds (5–8 s) because greater times caused pitting.

Specimens of size 1 cm × 1 cm were machined from the rolled strip of Fe₃Al-5M (M = Cr, Ta, Ti and Mo) for electrochemical studies. Although the tantalum- and molybdenum-containing intermetallics cracked during rolling at 1000 °C, the specimens used for electrochemical studies were machined from the cracked strips such that they were free of cracks. The other intermetallics were severely cracked after deformation processing and hence could not be used for electrochemical polarization experiments. Electric contact between the sample and a (sealed) wire was maintained using sellotape and immediately mounted by cold mounting using a thermosetting resin which acted as an insulator for the other sides. Each mounted specimen was coarse ground initially with the help of an abrading belt and later polished with emery paper (1/0 through 4/0) and degreased with acetone before each experiment. The main apparatus used for the polarization experiments was a polarization cell equipped with a facility for bubbling nitrogen/air, and a potentiostat (Vibrant Potentiostat/Galvanostat VSM/PG/30) interfaced to a personal computer. One limitation of the potentiostat was that it could not measure currents below 1 μA. A round-bottomed 1 l flask, modified by the addition of various necks to permit the introduction of electrodes, gas inlet and outlet tubes, and a thermometer, served as the polarization cell. The three electrodes used were the working electrode (mounted specimen connected with a wire), the counter electrode (high-purity platinum flat stock wire), and the reference electrode (saturated calomel electrode with E⁰ = 0.242 V versus standard hydrogen electrode), as per ASTM recommendations [12]. The potential of the calomel electrode was checked at periodic intervals to ensure its accuracy.

Aqueous solutions of H₂SO₄ of pH 4 and NaOH of pH 8 were used as electrolytes. In the polarization experiments, the corrosion potential of the working electrode was continuously recorded starting immediately after immersion until a constant potential was obtained. Potentiodynamic polarization studies were conducted immediately after stabilized free corrosion potentials (FCP) were obtained. The period

for stabilization depended upon the specimen, its surface finish, and the electrolyte employed. Generally, it took 4–5 h for obtaining a constant potential. All the tests were conducted with a potential scan rate of 1 mV s⁻¹.

3. Results and discussion

3.1. Corrosion behaviour

The potentiodynamic polarization curves of binary Fe₃Al and Fe₃Al-5M (M = Cr, Mo, Ta and Ti) intermetallics in electrolytes of pH 4 and 8 are presented in Figs 1 and 2, respectively. The corrosion characteristics of these intermetallics in electrolytes of pH 4 and 8 are summarized in Tables I and II, respectively.

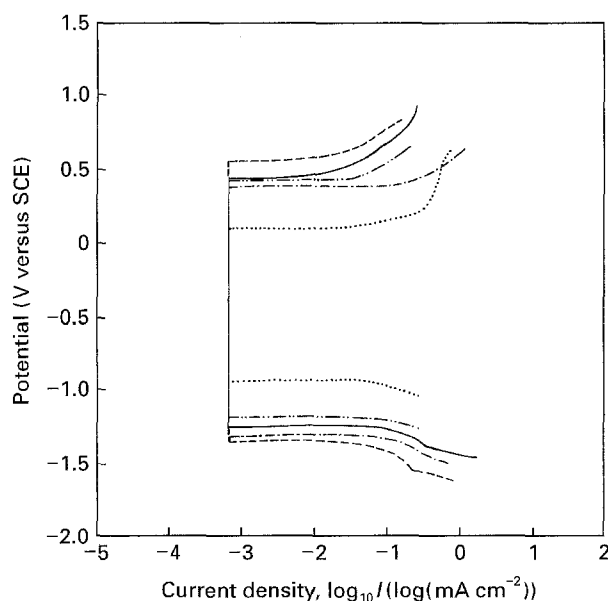


Figure 1 Potentiodynamic polarization curves Fe₃Al-5M (M = (— · —) Cr, (---) Mo, (—) Ta and (— · —) Ti) intermetallics in H₂SO₄ electrolyte of pH 4, without Cl, at 298 K. (···) Fe₃Al.

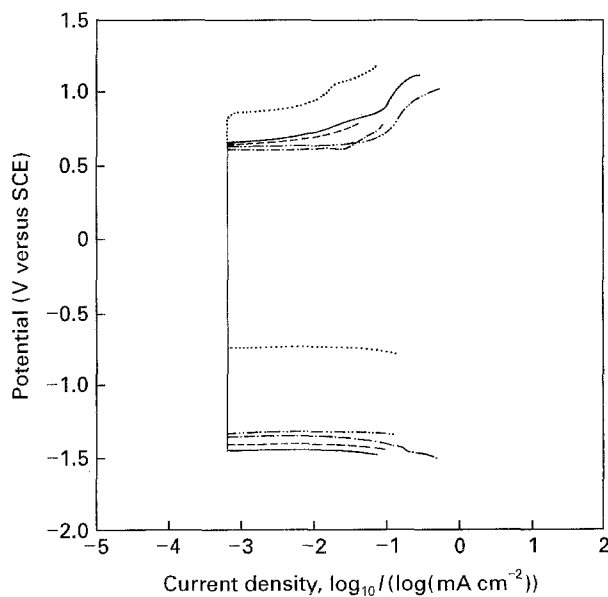


Figure 2 Potentiodynamic polarization curves Fe₃Al-5M (M = (— · —) Cr, (---) Mo, (—) Ta and (— · —) Ti) intermetallics in NaOH electrolyte of pH 8, without Cl, at 298 K. (···) Fe₃Al.

TABLE I Corrosion characteristics of Fe₃Al-5M and binary Fe₃Al in electrolyte of pH 4

Sample	Free corrosion potential (mV versus SCE)	Complete passivation potential (mV versus SCE)	Pitting potential (mV versus SCE)	Passivity range (mV)
Fe ₃ Al	-363	-950	100	1050
Fe ₃ Al-Cr	-330	-1333	400	1733
Fe ₃ Al-Ti	-350	-1196	444	1640
Fe ₃ Al-Mo	-334	-1360	585	1945
Fe ₃ Al-Ta	-293	-1264	454	1718

TABLE II Corrosion characteristics of Fe₃Al-5M and Fe₃Al in electrolyte of pH 8

Sample	Free corrosion potential (mV versus SCE)	Complete passivation potential (mV versus SCE)	Pitting potential (mV versus SCE)	Passivity range (mV)
Fe ₃ Al	-272	-750	850	1600
Fe ₃ Al-Cr	-180	-1381	634	2015
Fe ₃ Al-Ti	-180	-1357	664	2021
Fe ₃ Al-Mo	-187	-1435	690	2125
Fe ₃ Al-Ta	-141	-1480	700	2180

Incidentally, the corrosion behaviour of the binary Fe₃Al has been investigated in a variety of electrolytes and this has been discussed elsewhere [13]. The following comparative observations could be made for Fe₃Al-5M intermetallics and binary Fe₃Al. The FCP of Fe₃Al-5M intermetallics were noble compared to binary Fe₃Al in both the electrolytes (pH 4 and 8). The complete passivation potentials, E_{cp} , were more negative for Fe₃Al-5M intermetallics compared to binary Fe₃Al, thereby indicating that it should be easier to passivate Fe₃Al-5M compared to Fe₃Al. The pitting potentials, E_{pit} , were noble for Fe₃Al-5M intermetallics compared to binary Fe₃Al in the electrolyte of pH 4 indicating that they retain passivity to much higher potentials without pitting. However, the reverse was the case in the electrolyte of pH 8, where Fe₃Al showed a noble pitting potential compared to the Fe₃Al-5M intermetallics. The passivity range was larger for Fe₃Al-5M intermetallics compared to binary Fe₃Al in both the electrolytes. The above observations could be explained as follows.

Alloying with an element that readily passivates into a metal or alloy causes the metal or alloy to develop, either fully or partially, the passive properties of the introduced material [14]. Therefore, alloying Fe₃Al with passivity-inducing components chromium, titanium, tantalum and molybdenum, enhanced the passive behaviour of binary Fe₃Al, as obtained in the present study. The passivating effect of such alloying elements can be attributed to the following reasons. Firstly, the enrichment of stable passive atoms in the surface of the alloy, by the formation of ordered structures with the alloying component, would result in enhanced passive behaviour. This could be the case on alloying with tantalum and molybdenum because the XRD patterns of Fe₃Al-5Ta and Fe₃Al-5Mo revealed

the presence of additional phases (see Section 3.2). Secondly, a change in the internal electronic structure of the atoms by the formation of solid solutions could result in enhanced passivity [15]. This could be the case on alloying with chromium and titanium as they exist in solid solution in Fe₃Al and, moreover, the vacancies in the 3d electron levels of titanium and chromium allow electron transfer from iron and aluminium, thereby rendering them into passive states, as has been shown for chromium alloyed to iron [15]. Thirdly, it is possible that there is a gradual enrichment in the surface layer of the Fe₃Al-5M intermetallics with atoms of a more stable/passive component due to the corrosion process. This increase in the concentration of the passivity-inducing component of the alloy could lead to the formation of either new surface structures (intermetallic compounds), or even a surface layer of the alloyed component. This process should confer additional passivity. In this regard, it was earlier observed that the corrosion of FeAl in NaOH solution resulted in surface enrichment of iron due to preferential dissolution of aluminium [16]. It is reasonable to assume that in the present intermetallics, the concentration of the passivity-inducing elements (i.e. the alloying elements) would have been enhanced in the surface layers, resulting in the superior passivation behaviour of the alloyed Fe₃Al-5M intermetallics. This is indirectly verified by the experimental result obtained in the present study that the free corrosion potentials of the alloyed intermetallic were noble to that of binary Fe₃Al in both the electrolytes. The E_{pit} of binary iron aluminide in the electrolyte of pH 8 was very high (noble) which appears to be due to a favourable protective surface layer. Therefore, further alloying by a passivity-inducing element did not have any effect on the E_{pit} , although it did help in

enhancing the passivity range by shifting the E_{cp} in the active direction.

3.2. Mechanical behaviour

It was observed that only the $Fe_3Al-5Cr$ and $Fe_3Al-5Ti$ intermetallics could be rolled in multiple passes at $1000^\circ C$ to 80% deformation. Therefore, tensile specimens could be machined only from the

$Fe_3Al-5Cr$ and $Fe_3Al-5Ti$ strips. The $Fe_3Al-5Ta$ intermetallic cracked after 50% deformation, and the $Fe_3Al-5Nb$ intermetallic cracked after 40% deformation. $Fe_3Al-5Mo$, $Fe_3Al-5Si$ and Fe_3Al-5V could not be rolled, because they cracked in the first rolling pass itself. This could be due to formation of brittle intermetallics in ternary iron aluminides. X-ray diffraction (XRD) studies (Fig. 3) on these intermetallics revealed that additional peaks corresponding to new phase

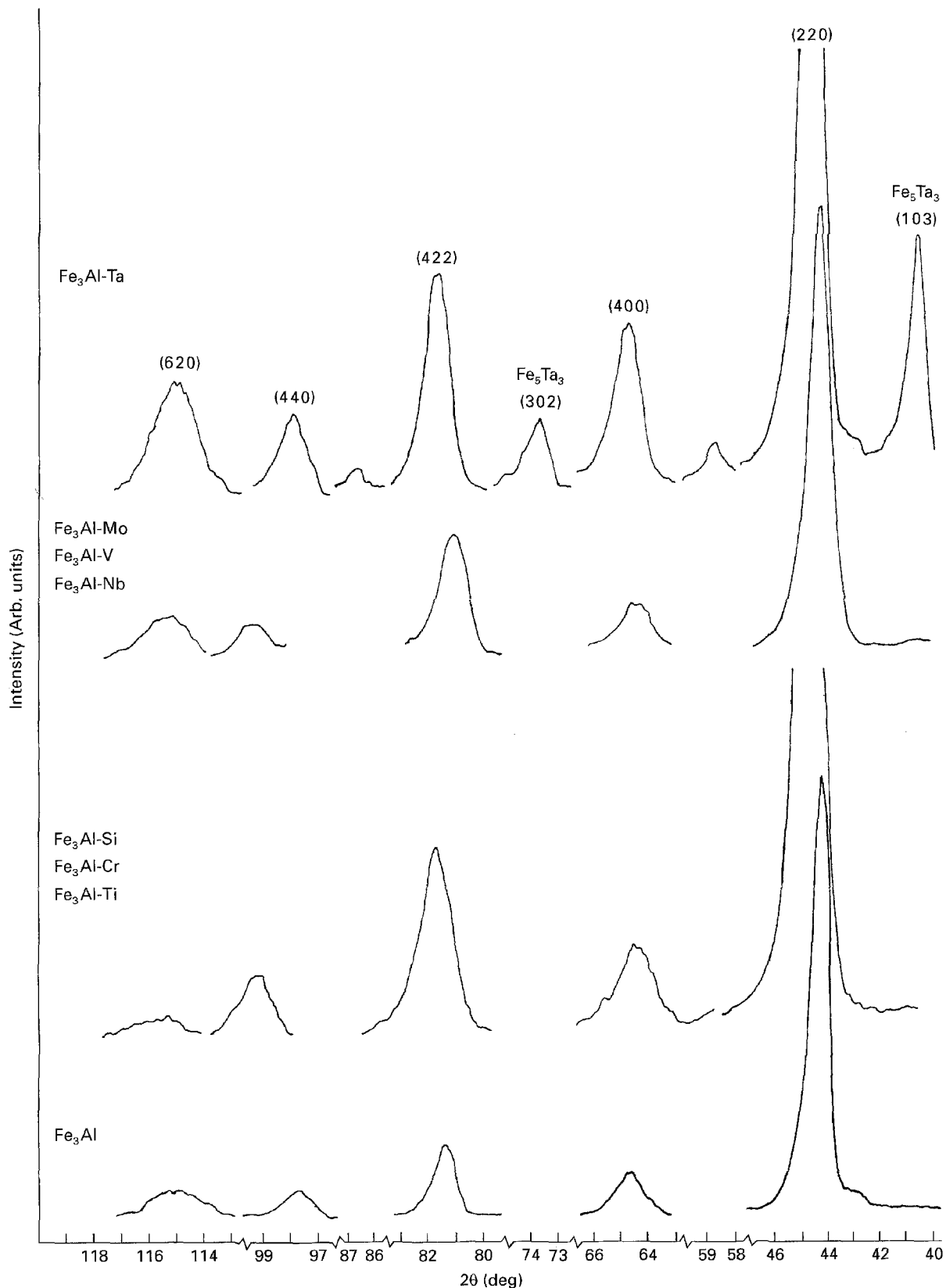


Figure 3 XRD patterns of Fe_3Al-5M intermetallics.

Fe_3Ta_3 could be unambiguously indexed in the Fe_3Al -5Ta intermetallic. All the other intermetallics exhibited reflections corresponding to the binary Fe_3Al and some additional peaks that could not be indexed. It is quite possible that the additional phase(s) in the other intermetallics are present in low volume fractions and hence could not be revealed by XRD. It has been reported that chromium and titanium have large solubilities in iron aluminides whereas niobium, tantalum, molybdenum, silicon and vanadium have limited solid solubilities and result in precipitation of brittle intermetallics [17]. For example, the phase Fe_2Nb is reported to precipitate in the Fe-25Al-2Nb intermetallic [18]. It is, therefore, reasonable to state that the Fe_3Al -5M (M = Nb, Ta, Mo, Si and V) could not be processed to 80% deformation at 1000 °C due to the presence of brittle intermetallics. A detailed microstructural characterization of these intermetallics is underway to elucidate their thermomechanical response.

The tensile stress-strain curves of Fe_3Al , Fe_3Al -5Cr and Fe_3Al -5Ti are presented in Fig. 4. Table III presents the results of tensile testing of these alloyed iron aluminides. The Fe_3Al -5Ti intermetallic exhibited a higher UTS value than the Fe_3Al -5Cr intermetallic. The fracture morphologies of these intermetallics are shown in Fig. 5a-c. Fe_3Al and Fe_3Al -5Cr exhibited a transgranular cleavage kind of fracture surface, whereas Fe_3Al -5Ti (Fig. 5c) showed a mixed mode of

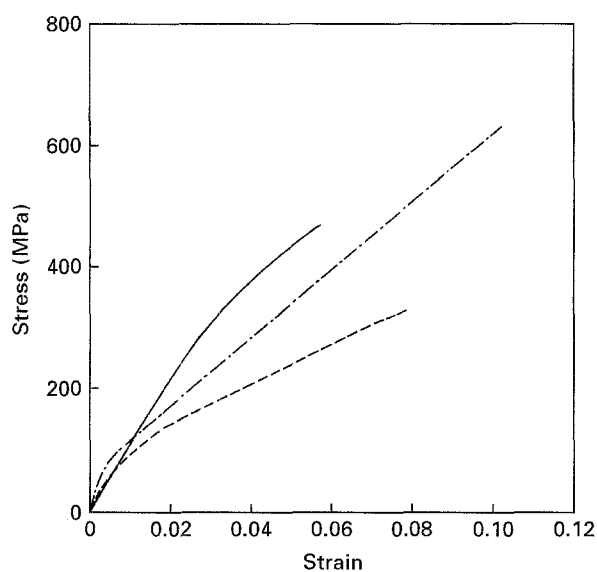


Figure 4 Stress-strain behaviour of (—) Fe_3Al , (---) Fe_3Al -5Cr and (-·-) Fe_3Al -5Ti.

TABLE III Room-temperature tensile properties of Fe_3Al , Fe_3Al -5Cr and Fe_3Al -5Ti intermetallics

Sample	Yield strength (MPa)	UTS (MPa)	Ductility (%)	Fracture type
Fe_3Al	380	460	1.4	TG
Fe_3Al -5Cr	160	310	4.9	TG
Fe_3Al -5Ti	114	629	6.8	TG + IG

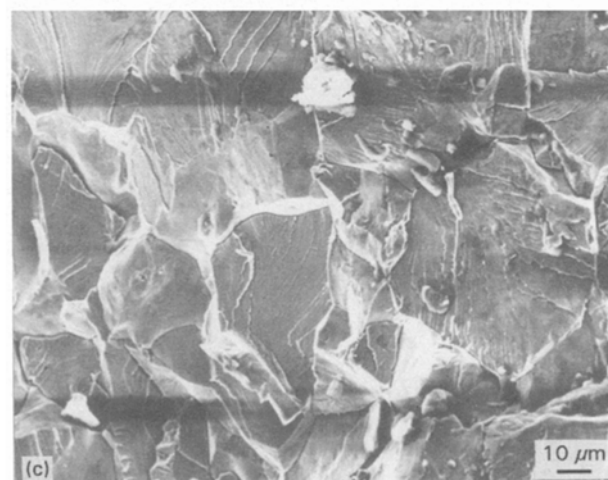
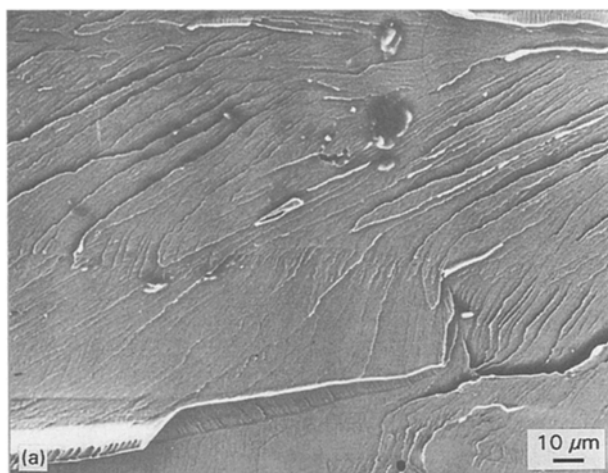


Figure 5 Fracture morphology of (a) Fe_3Al , (b) Fe_3Al -5Cr and (c) Fe_3Al -5Ti.

fracture (transgranular + intergranular). Intergranular boundaries can be clearly delineated in the fractograph of Fe_3Al -5Ti. Moreover, river-like patterns, indicative of cleavage fracture, can be seen within the grains. It can be concluded from this fracture morphology that addition of titanium possibly enhances the cleavage strength, resulting in mixed mode fracture. The enhanced ductility of the titanium-alloyed intermetallic could partly be related to the mixed

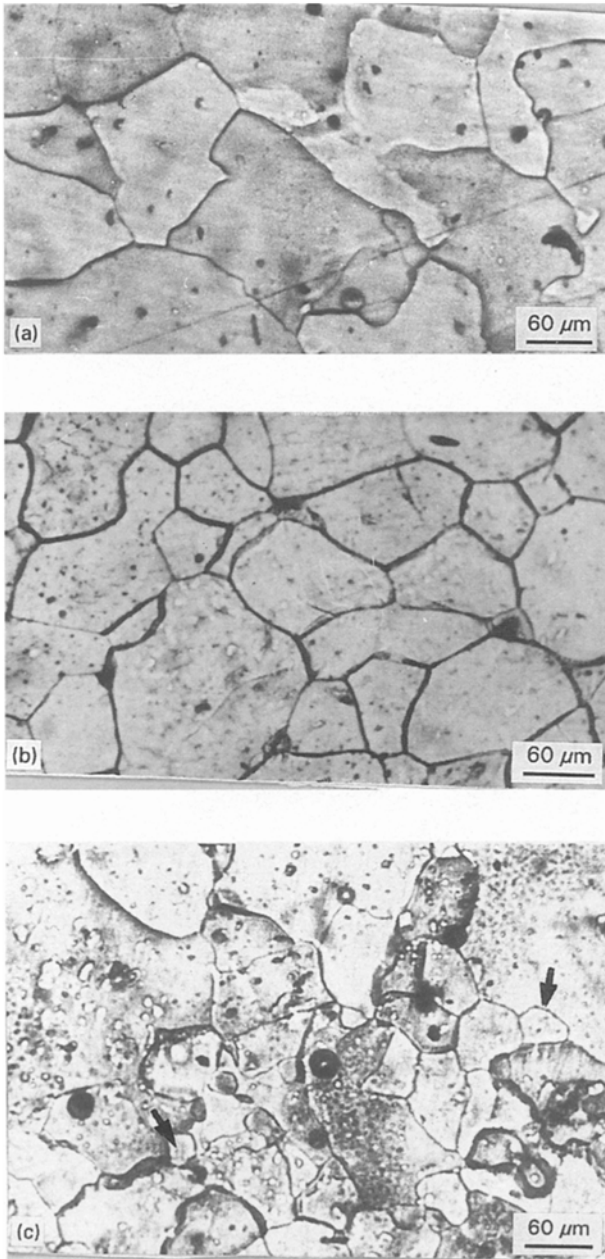


Figure 6 Optical micrographs of (a) Fe_3Al , (b) $\text{Fe}_3\text{Al-5Cr}$ and (c) $\text{Fe}_3\text{Al-5Ti}$ after 80% deformation at 1000°C and recrystallization at 750°C for 1 h.

mode of failure. However, the enhanced ductility of the chromium-alloyed intermetallic cannot be ascribed to fracture mode.

The increase in ductility of the $\text{Fe}_3\text{Al-5Ti}$ intermetallic could also be partly attributed to the microstructure of the recrystallized intermetallic. The microstructures of Fe_3Al , $\text{Fe}_3\text{Al-5Cr}$ and $\text{Fe}_3\text{Al-5Ti}$ are presented in Fig. 6. The partially recrystallized microstructure of $\text{Fe}_3\text{Al-5Ti}$ (new grains have been marked with an arrow in Fig. 6c) should lessen the severity of HE. Earlier, it was shown that partially recrystallized microstructures minimize HE in iron aluminides and improve the ductility [9, 10]. However, the structure of $\text{Fe}_3\text{Al-5Cr}$ consists of coarse grains, suggesting grain growth after the recrystallization process (Fig. 6b). McKamey and Pierce [9] had earlier concluded that the recrystallization processes in iron aluminides vary greatly with several variables

such as alloying additions and fabrication technique. Recrystallization at 750°C for 1 h results in grain growth for the chromium-alloyed intermetallic. Therefore, the higher ductility of the chromium alloyed iron aluminide cannot be solely attributed to the microstructure. It seems reasonable that chromium minimizes HE of iron aluminides by inducing passivity [9].

The increase in ductility of the $\text{Fe}_3\text{Al-5Cr}$ and $\text{Fe}_3\text{Al-5Ti}$ intermetallics over the binary Fe_3Al confirms the alloy development philosophy suggested by Balasubramaniam [6]. Although it is seen that passivity can be enhanced in iron aluminides by addition of several elements (Section 3.1), chromium and titanium additions prove very effective in causing ductility enhancements as they exist in solid solution in the matrix and do not precipitate brittle intermetallics with iron and aluminium, unlike the other alloying additions.

The chromium- and titanium-alloyed iron aluminides exhibited low yield strengths. It has been suggested that yield strength decreases due to solid-solution softening on alloying with chromium [5, 7]. However, the low yields strengths of $\text{Fe}_3\text{Al-5Ti}$ and $\text{Fe}_3\text{Al-5Cr}$ intermetallics are poorly understood, as some other investigators have mentioned that chromium should lead to solid-solution strengthening [18, 19].

4. Conclusions

1. The corrosion behaviour of $\text{Fe}_3\text{Al-5M}$ ($M = \text{Cr}, \text{Mo}, \text{Ta}$ and Ti) was better than that of binary Fe_3Al in electrolytes of pH 4 and 8 as the alloying element M induced additional passivity in the intermetallic $\text{Fe}_3\text{Al-M}$. Possible reasons for the enhancement of passivity by these alloying additions have been discussed.

2. $\text{Fe}_3\text{Al-5Cr}$ and $\text{Fe}_3\text{Al-5Ti}$ intermetallics could be deformed by 80% by rolling in multiple passes at 1000°C without cracking. $\text{Fe}_3\text{Al-5Ta}$ could be rolled to 50% deformation, while $\text{Fe}_3\text{Al-5Nb}$ could be rolled to 40% deformation prior to cracking. $\text{Fe}_3\text{Al-5Si}$, $\text{Fe}_3\text{Al-5Mo}$ and $\text{Fe}_3\text{Al-5V}$ cracked in the first rolling pass itself. The poor thermomechanical behaviour of the iron aluminides containing tantalum, niobium, silicon, molybdenum and vanadium has been attributed to the formation of brittle intermetallics. The presence of Fe_5Ta_3 in $\text{Fe}_3\text{Al-5Ta}$ has been confirmed by XRD. Intermetallics alloyed with chromium and titanium could be processed because of their large solid solubilities in iron aluminide.

3. $\text{Fe}_3\text{Al-5Cr}$ and $\text{Fe}_3\text{Al-5Ti}$ intermetallics exhibited relatively high ductilities at room temperature. The enhancement of passivity on the surface minimizes HE in these intermetallics, thus confirming the alloy development philosophy proposed to yield ductile iron aluminides [6]. However, the $\text{Fe}_3\text{Al-5Cr}$ and $\text{Fe}_3\text{Al-5Ti}$ intermetallics exhibited low yield strengths. This has been attributed to solid-solution softening, which is poorly understood.

4. Fracture characteristics revealed that addition of titanium to iron aluminide increased the cleavage

strength of this intermetallic and this resulted in mixed mode fracture. In contrast, Fe₃Al and Fe₃Al-5Cr exhibited transgranular cleavage.

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