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Fe_3Al-Fe_3AlC intermetallics for high temperature applications: An assessment

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The advantage of carbon containing dual-phase iron aluminides is that they exhibit relative improvement in high temperature strength as well as reduction in probability of hydrogen embrittlement (HE) over the single-phase iron aluminides, which were the main impediment for the commercialisation of these materials. Owing to its practical and scientific importance a study on the dual-phase Fe_3Al-Fe_3AlC intermetallics is presented, which deals with the current status of research and developments, understanding of physical metallurgy, HE, oxidation resistance and thermal stability; and its limitation and future challenges. © *2004 Kluwer Academic Publishers*

1. Introduction

In the development of materials for high temperature applications, Fe_3Al based intermetallics are considered as one of the potential candidates primarily because they constitute low cost elements, show excellent corrosion resistance at elevated temperatures and exhibit high strength to weight ratio [1, 2]. Nevertheless, these materials could not be commercialised to their full potential due to their poor room temperature ductility and inadequate high temperature strength above 550°C [2]. Considerable efforts have been dedicated over the last two decades in order to improve these properties by the addition of alloying elements such as B, Ti, Be, Cr, Mo, Zr, Hf and Nb, and through different process routes [3–6]. In parallel to this development, addition of C to Fe-Al alloys came as a most promising discovery compared to others [7–14]. Considering initial success and relatively low cost of Fe-Al-C alloys compared to other developments in this field, it is expected that these materials will keep researchers busy at least for another two decades. Additional advantages of this material are avoiding the use of strategic elements such as Cr and Ni. Despite substantial effort in this development there is no self-contained description in literature about these materials to the present. Therefore, an attempt is made here to provide an insight of Fe-Al-C alloys to the researchers working in this field based on a comprehensive review of published data in last decade. In this paper a comprehensive outline on physical metallurgy, HE and high temperature oxidation behaviour of Fe-Al-C alloys is provided.

It will be instructive to take a concise historical account before reviewing the present status of these alloys. Reported works in the late-eighties on the development of Fe-Al-C alloys appear to be contradictory. Kerr [15] reported that on reduction of C content from 500 to 50 ppm or/and elimination of carbide precipitates improved the ductility in Fe_3Al. Whereas in the work of Morris and Morris [16], a change in fracture mode of iron aluminide from cleavage fracture to ductile fracture with presence of $Fe_{63}Al_{34}C_3$ carbide was depicted. In the nineties and onwards, there have been an onset number of studies in development of carbon containing iron aluminides, especially in India [10–12, 17, 18]. A breakthrough in those studies was the improvement in high temperature strength of the alloy without affecting its ductility. In addition, it was also claimed that the dual-phase iron aluminides have more resistance to HE compared to the usual single-phase iron aluminides, though the mechanism is still under discussion. These findings continued to receive worldwide acceptance as other investigators also paid interest in the development of these materials [6–9].

2. Physical metallurgy

Within the context of physical metallurgy, a brief description on the microstructural and phase analysis of Fe-Al-C alloys are presented here, whereas detailed information about these studies is found in the Refs. [19–21]. Micrographs of Fe-16Al-0.05C alloy and Fe-16Al-0.5C alloy are shown in Fig. 1a and b, respectively to illustrate the effect of C on its microstructures. The dark contrast in the micrograph corresponds to the carbides, whereas light contrast refers to the matrix. Evidently, the size and volume fraction of the carbide increases with increasing carbon content in the alloy. On further increase in C content from 0.5 to 1%, carbides form continuous networks in the interdendritic

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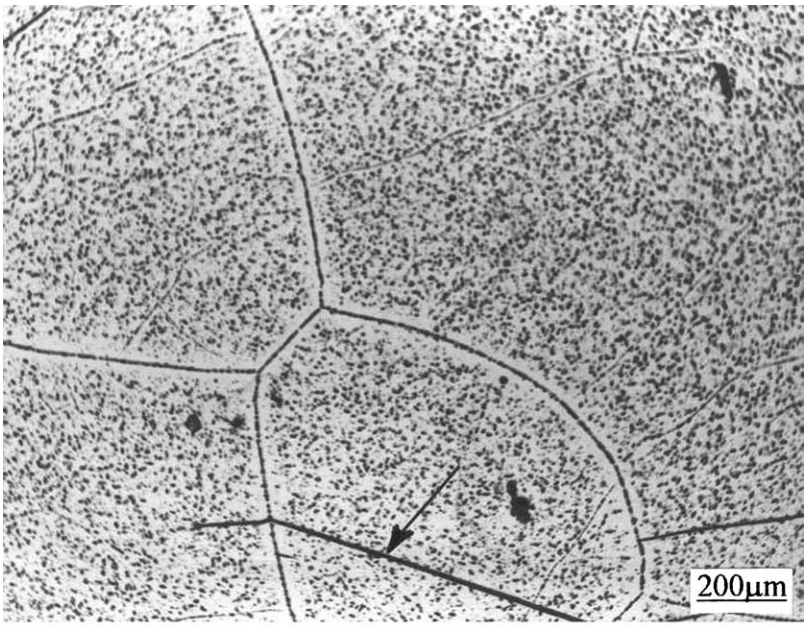
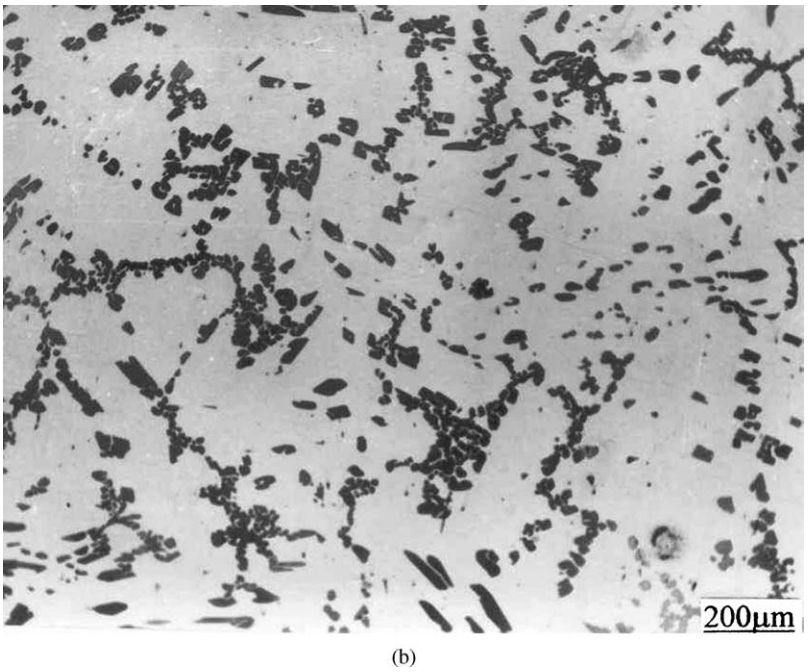


(a)



(b)

Figure 1 Optical microstructures (a) Fe-16Al-0.05C alloy and (b) Fe-16Al-0.5C alloy, shows increase in volume fraction of the carbides with increase in C content. The black arrow indicates the presence of microcrack in low-C content alloy [19].

region [19]. X-ray diffraction pattern of Fe-16Al-0.5C alloy is shown in Fig. 2, which reveals the matrix and carbide phase as Fe_3Al and $Fe_3AlC_{0.69}$, respectively. The former has a bcc ordered structure and the latter has perovskite structure. The stoichiometry of the carbide remains unchanged with variation of the C content in the alloy. On increasing the Al content from 16 to 23% the carbides convert into soft graphite, whereas on reduction of the Al content from 16 to 10%, the Fe_3Al phase converts into $\propto$ (Fe-Al) phase. Table I summarises the phases present in Fe-Al-C alloys along with the properties related to elongation with different alloy compositions. Addition of C at low concentration (<0.05%) in Fe_3Al improves its strength by solid solution strengthening due to interstitial C, whereas at high concentration by precipitation hardening, due to formation of the Fe_3AlC. As seen in the Table I tensile strength of these alloys increases with increasing C content up to 0.5%, beyond which no further increase in the strength is noticed. The interesting aspect to note is that the benefits obtained by the addition of C in iron aluminides based on Fe_3Al, could not be achieved in FeAl based iron aluminides. This is because of the precipitation of the soft graphite as against hard Fe_3AlC with increasing addition of C content in FeAl [22].

Phase transitions in the present alloys with respect to temperature is an important aspect both in terms of understanding the ambient temperature microstructure of the alloys as well as their oxidation behaviour at various temperatures. This aspect is briefly discussed here. Though a few authors have reviewed Fe-Al-C phase diagram [23–26], location of phase boundaries of various

TABLE I Effect of chemical composition in Fe-Al-C alloys on their phases and mechanical properties

Composition (wt%)	Phases	Condition	YS (MPa)	EL (%)	UTS (MPa)	Ref.
Fe-15.6Al-0.05C	Fe_3Al					[19]
Fe-15.6Al-0.14C	Fe_3Al, Fe_3AlC	Cast	380	3.5	447	[10, 19]
Fe-16Al-0.27C	Fe_3Al, Fe_3AlC	Cast	415	4.4	526	[10]
Fe-15.6Al-0.5C	Fe_3Al, Fe_3AlC	Cast	425	4.2	545	[10, 19]
Fe-15.24Al-1C	Fe_3Al, Fe_3AlC	Cast	416	5.4	575	[18]
Fe-11.2Al-0.5C	Fe-Al, Fe_3AlC	Cast	538	8.6	829	[17]
Fe-10.8Al-1C	Fe-Al, Fe_3AlC	Cast	565	8	940	[17, 20]
Fe-8.3Al-0.5C	Fe-Al, Fe_3AlC	Cast	440	10.0	658	[17, 20]
Fe-7.2Al-1C	Fe-Al, Fe_3AlC	Cast	430	6	540	[17, 20]
Fe-23Al-0.27C	FeAl, Fe_3AlC		590[a]	15	–	[22]
Fe-23Al-1.3C	FeAl, graphite		536[a]	19	–	[22]

[a]Compressive strength.

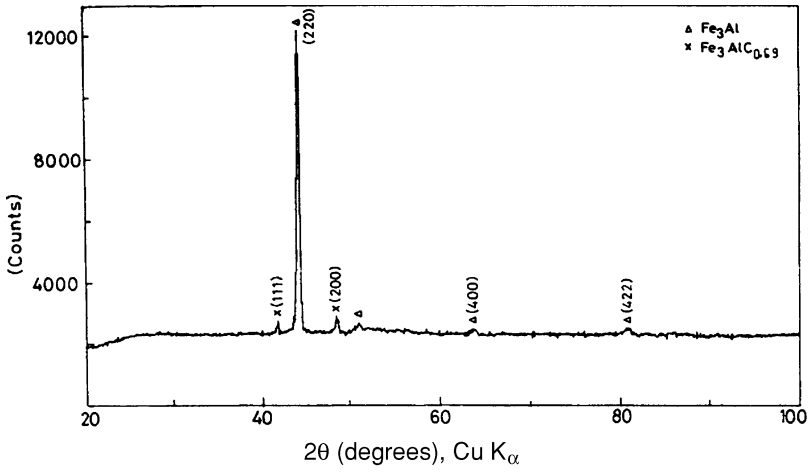


Figure 2 X-ray diffraction pattern of an Fe-16Al-0.5C alloy, showing the presence of matrix and carbide as Fe_3Al and $Fe_3AlC_{0.69}$, respectively [19].

phases at different temperatures still remains uncertain. The main reason attributed to this was the difficulty in determining the exact composition of the carbide phase and the precipitation of graphite due to poor solubility of C in Fe-Al alloys [25].

Raghavan [23] outlined the reaction schemes for the Fe-Al-C system with various possibilities, however, exact temperature of the carbide formation is still not known. The nature of phase formation can be examined using the vertical section of the Fe-Al-C phase diagrams, which are shown in Fig. 3a and b. Fig. 3a, corresponding to 15 wt% Al provides solidification behaviour of the Fe_3Al based intermetallics [26]. Alloys in which C content is less than 1.9 at%, the carbide phase is formed from a solid to solid phase transformation and this transient temperature increases with increasing C content. In alloys having 3.9 at% C (corresponding to 1 wt%) formation of the carbide takes place from the liquid phase. This direct solidification of the carbide from the melt causes the dendritic network of carbides in the alloy as mentioned earlier [19]. On reducing the Al content from 16 to 10% solidification behaviour of low-C content alloys (<0.5C) remains the same, whereas solidification of the alloy with 1 wt% C follows a different route that is, from a solid-state transition [26]. On the other hand, examination of the vertical section of Fe-Al-C phase diagram corresponding to 0.4 wt% C (Fig. 3b) explains the solidification behaviour of alloys with variation of Al content [26]. In these alloys the carbide seems to be formed by a solid-state transition. Notably, this transient temperature sharply decreased with decrease in Al content and thus reducing Fe_3AlC domain in the phase diagram. Carbides are compositionally the same in all these alloys; nevertheless, their stability depends on the overall Al content of the alloy. It is worthwhile to mention that the addition of C also affects the order-disorder transformation temperature in the Fe_3Al, and it is reported to increase with addition of C [25].

3. Hydrogen embrittlement (HE)

Extensive studies have been conducted to understand the HE behaviour of iron aluminides [4, 27, 28]. This happens because the alloy picks up hydrogen due to the reaction between the highly active Al and water vapour ($2Al + 3H_2O = Al_2O_3 + 6H \uparrow$), and a direct manifestation of HE is the loss of ductility in iron aluminides, such phenomena are well known.

We will therefore limit our discussion to the effect of C/carbides on the HE of iron aluminides. There have been several evidences about the improvement in HE resistance of the iron aluminide due to addition of C in the Fe_3Al alloy [29]. Nonetheless, the mechanism behind the improvement of HE of iron aluminides due to presence of carbides in the matrix is still a subject of discussion [7, 10, 30–32]. Baligidad *et al.* [10] suggested that this is due to the reduction in probability of H atoms in the lattice due to trapment of H atoms at the carbide matrix interface. Subsequently, Pang and

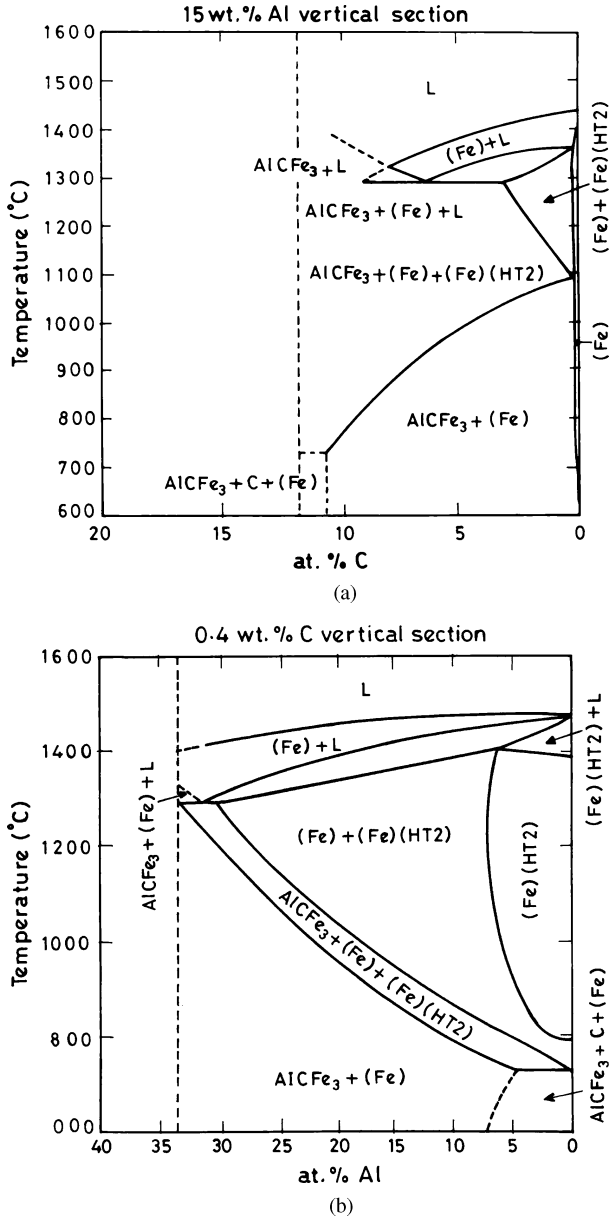


Figure 3 Vertical section of the Fe-Al-C phase diagram at (a) constant Al content of 15 wt% and (b) at constant C content of 0.5 wt%. The symbols (Fe) and (Fe) (HT2) are notations for ferrite allotropic, whereas $AlCFe_3$ denotes as carbide [26].

Kumar [7] based on slow strain rate test presented a similar view that the presence of the carbides in the matrix causes delay in the arrival of critical H to the crack tips and is the main reason for improvement in embrittlement resistance of Fe-Al-C alloys. Sen and Balasubramaniam [30] calculated the diffusivities of H in binary Fe-25 at%Al intermetallic and carbon alloyed intermetallics Fe-28Al-2.1-3.7C (at%), by subsurface microhardness profile after cathodic charging. They found that the H diffusivity in carbon containing alloys was lower than the pure binary alloy. The lower hydrogen diffusivity in the carbon-alloyed intermetallics was related to irreversible hydrogen trapping at the carbide-matrix interface. The work of Parvathavarthini *et al.* [31] provides another explanation for the improved probability for HE resistance in C containing intermetallics. According to them presence of carbides in Fe-16Al-1C alloy reduces the permeability and diffusivity of H atom in the alloy. In a most recent work, it was proved that the addition of carbon in Fe_3Al increases its hydrogen exchange current density in acid environments, which causes increase in the corrosion rate [32]. Hence, it was suggested that the addition of carbon should be as low as possible for their better corrosion resistance even so it improves the HE resistance.

4. High temperature oxidation behaviour

As these alloys are primarily developed for high temperature applications, a brief account of this study is summarised here. The effect of C (0.05–1%) on the long-term oxidation behaviour of Fe-16Al alloys was investigated in the temperature range between 700–1000°C [19]. This effect was less obvious on the oxidation resistance up to 800°C as all these alloys performed equally well irrespective of their C content. Whereas, at 900°C and above oxidation resistance of these alloys decreased with increase in C content. Nevertheless, oxidation resistance of these alloys was found better than the 310 stainless steel.

The effect of temperature on oxidation behaviour of Fe-16Al-0.14C alloy is illustrated in Fig. 4. It is evident that with increase in temperature from 700 to 900°C the oxidation tendency of the alloy increases, whereas with a further raise in temperature to 1000°C oxidation tendency of the alloy marginally decreases. This unusual decrease in oxidation tendency with rise in temperature has been explained based on Fe-Al-C phase diagram (Fig. 3a) and attributed to the reduction in volume fraction of the carbide at high temperature. However, with increase of C content to 1% in alloy this inversion of oxidation disappears. A detailed discussion on this can be found in the referred work [33].

Effect of Al on the oxidation behaviour of Fe_3Al-Fe_3AlC intermetallics was investigated between 700–1000°C [20, 21]. On reduction of Al content from 16 to 10% in above alloys oxidation resistance of the alloy was less affected, however, further reduction of the Al content down to 8% resulted in a steep rise in oxidation tendency of the alloy. Moreover, low-Al content alloys suffer from inversion in oxidation due to preferential oxidation of the Al at 800°C. It should be noted that the critical Al concentration for oxidation resistance in Fe-Al-C alloys is higher than that of the binary Fe-Al alloys. This is due to reduction of Al content

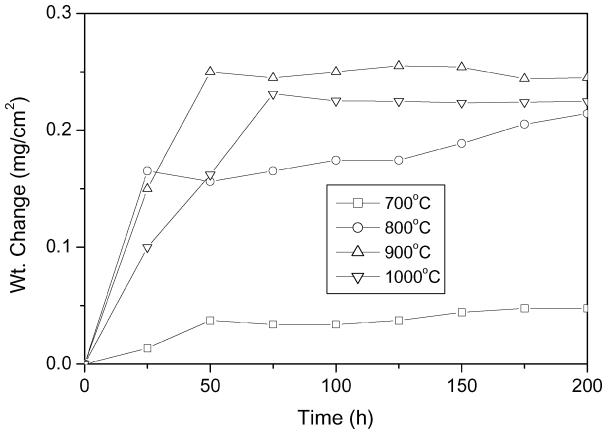


Figure 4 Oxidation kinetics of Fe-16Al-0.05C alloy from 700 to 1000°C in air [33].

from the matrix during carbides formation in Fe-Al-C alloys. Stability of the carbides was also investigated, 16% Al content alloys were found resistant to decarburisation whereas low-Al content alloys suffer from decarburisation.

In a recent study it was shown that the oxide film formed during initial stages of oxidation on the carbide phase is about four times thicker than that of the matrix [34]. Despite the difference in oxide layer thickness, the oxide formation on both the phases follow a similar pattern i.e., the inner layer consists of Al_2O_3 whereas the outer layer has Fe_2O_3 [34]. The high oxidation resistance of the matrix phase compared to that of the carbide phase was attributed to its high Al content (17%) compared to that of the carbide phase (11%). On reduction of Al content in this alloy from 16–10% the scenario becomes reverse i.e., the oxidation resistance of the matrix becomes inferior compared to carbide phase. This is because on reducing the Al content from the alloy Al is reduced from the matrix phase rather than the carbide phase in order to maintain its stoichiometry, $Fe_3AlC_{0.69}$. A full account of the high temperature oxidation behaviour of Fe-Al-C alloys related to oxidation mechanism of carbide as well as matrix phase with its oxidation model can be found in the Ref. [35].

5. Limitation & future challenging

Most of the reported works on Fe-Al-C alloys are confined to laboratory scales. Published information for bulk productions of these alloys is scanty. The mass production of these alloys by air induction melting resulted extensive gas porosity, although it was suggested that this could be minimized by argon purging of the melt [36]. Many papers dealt that on reducing the grain size of iron aluminide its oxidation resistance increases in addition the critical Al concentration for oxidation resistance decreases [36]. Extending the same technology in C containing iron aluminides will be an advantage for governing the development of these duplex iron aluminides. Refractory metal additions such as Re in ternary Fe-Al-C systems are supposed to be very promising as these elements possess excellent high temperature properties. Plus it may enhance the ductility; high ductility of W-Re alloy compared to unalloyed Re is well known. In context of the recent developments, special emphasis is needed on reviewing the Fe-Al-C phase diagram for better understanding of the solidification behaviour of Fe-Al-C alloys. Solubility of C in FeAl system and the stability of carbide phase has to be enhanced, as these carbides were not very stable at temperature above 900°C, though some work has been initiated with alloying element addition such as B, Mo and Nb [37, 38]. In spite of concentrated effort there is room for understanding the mechanism governing the improvement in HE of iron aluminides with addition of carbon. Due to its low cost these materials have also been considered for possible use in room temperature applications and some investigations have been made to test reliability of these alloys in aqueous corrosion environment [32]. These results indicate the passivation behaviour of iron aluminide is comparable to stainless steels in acid environment. However, its corrosion rate is higher than that of the stainless steels. Hence much more work is needed before extending these materials to room temperature applications.

6. Summary

Dual-phase Fe_3Al-Fe_3AlC intermetallics have emerged as a credible alternative to high temperature materials due to enhancement in high temperature strength and reduction in probability of HE over the single-phase iron aluminides. Further, these dual-phase iron aluminides possess other attractive properties which are shared by the single-phase iron aluminides. Nevertheless, the selections of C addition and Al concentration in Fe-Al-C alloys are critical factors. The former affects the mechanical properties while the later is responsible for high temperature corrosion resistance. Alloys with 16 wt% Al and (0.14–0.5 wt%) C compositions are most desirable, still special care should be taken while dealing with the specific requirements in practical applications. This material undoubtedly is promising as the next generation material in the filed of high temperature applications and should aid their entry in commercial market.

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