Effect of cerium addition on microstructures of carbon-alloyed iron aluminides

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Abstract. The effect of Ce addition on the microstructure of carbon-alloyed Fe₃Al-based intermetallic has been studied. Three different alloys of composition, Fe–18.5Al–3.6C, Fe–20.0Al–2.0C and Fe–19.2Al–3.3C–0.07Ce (in at%), were prepared by electroslag remelting process. Their microstructures were characterized using optical and scanning electron microscopies. Stereological methods were utilized to understand the observed microstructures. All the alloys exhibited a typical two-phase microstructure consisting of Fe₃AlC carbides in an iron aluminide matrix. In the alloy without Ce addition, large bulky carbides were equally distributed throughout the matrix with many smaller precipitates interspersed in between. In the alloy with Ce addition, the carbide grain sizes were finer and uniformly distributed throughout the matrix. The effect of Ce addition on the carbide morphology has been explained based on the known effect of Ce in modifying carbide morphology in cast irons.

Keywords. Iron aluminide; Fe₃Al; Ce addition; microstructure; stereology.

1. Introduction

Iron aluminides, based around the stoichiometric compositions, Fe₃Al and FeAl, offer excellent resistance to oxidation and sulphidation at high temperatures, with low material cost and density than austenitic and ferritic stainless steels (Liu *et al* 1990a; Liu and Kumar 1993). They contain enough aluminium to form a thin film of aluminium oxide (in oxidizing environments) that is often compact and protective. They possess relatively high specific strengths and suitable mechanical properties at elevated temperatures. They have, therefore, undergone extensive development, in the recent past, exclusively for high temperature applications. However, their potential use as structural materials at elevated temperatures has been hindered by limited ductility at room temperature and sharp drop in strength above 600°C. It is well established that the poor room temperature ductility of iron aluminides is due to hydrogen embrittlement (Liu *et al* 1990b, 1996), with hydrogen causing embrittlement arising out of the interaction of atmospheric moisture with Al as per $2\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{H}$ (Zhu *et al* 1996). Considerable efforts have been put to understand and improve their mechanical properties. Addition of passivity-inducing alloying elements has been one of the methods suggested to improve ductility of iron aluminides (McKamey and Liu 1992; Balasubramaniam 1996, 1997). These alloying

additions modify surface condition such that hydrogen diffusion into the material is hindered, thereby reducing the propensity to hydrogen embrittlement. Microstructural control leads to further enhancement in ductilities. These include refinement of grain structure, enhancement of grain boundary cohesion, control of grain shape and adjusting the recrystallization condition (McKamey and Pierce 1993; Lin *et al* 1994).

It has also been shown recently that carbon additions may be beneficial in improving the room temperature ductility of iron aluminides (Baligidad *et al* 1997a,b). The main benefit of carbon-alloyed iron aluminide is its cheap cost (by using steel scrap) and its robust processing by the electroslag remelting (ESR) process (Baligidad *et al* 1994). The addition of carbon even in small amounts, however, drastically modifies the microstructure because carbon results in the precipitation of Fe₃Al_xC_y carbides in the microstructure (Baligidad *et al* 1997a,b). The size, shape and distribution of these carbides are influenced by alloy composition and thermomechanical processing conditions (Baligidad and Radhakrishna 2000). Improvements in ductility have also been observed in carbon-alloyed aluminides and it has been suggested that carbon additions lowered the degree of hydrogen embrittlement by hindering hydrogen diffusion due to precipitated carbide (Sen and Balasubramaniam 2000) as well as interstitial carbon (Prakash and Sauthoff 2001). Lower hydrogen diffusivities have, in fact, been measured in carbon alloyed iron aluminides (Parvathavarthini *et al* 2002).

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Yangshan *et al* (1995) reported that small addition of Ce to Fe₃Al-based alloys enhanced ductility and strength of Cr-alloyed iron aluminides at ambient temperature. Moreover, they also observed improvements in tensile properties and creep resistance at 600°C. Improvements were also observed in the case of Ce addition along with molybdenum, zirconium and niobium in iron aluminides. Ce addition resulted in a finer grain size material.

The aim of the present study was to understand the effect of Ce addition on the microstructure of carbon-alloyed iron aluminides. The microstructures were analysed by stereological methods (Underwood 1970). Quantitative stereology is efficient in finding means for measuring familiar geometric quantities as well as discovering parameters that can be useful in establishing geometric relationships among the properties of alloys.

2. Experimental

The nominal compositions of alloys used in the present study, in atomic percent, were Fe–20.0Al–2.0C, Fe–18.5Al–3.6C and Fe–19.2Al–3.3C–0.07Ce. The compositions of these alloys, in weight percent, were Fe–11.0Al–0.5C, Fe–10.5Al–0.9C and Fe–10.5Al–0.8C–0.2Ce, respectively. The iron aluminides were melted in a medium frequency air induction furnace of 50 kg capacity and chill cast into cast iron moulds. The air induction melted ingots (55 mm diameter, 360 mm long) were machined to 50 mm diameter for refining in an a.c. electro slag remelting (ESR) furnace of 350 kVA capacity. A commercial prefused flux based on CaF₂ (70%CaF₂ + 15%CaO + 15%Al₂O₃) was used. The flux was preheated and held at 850°C for 2 h before use to remove moisture. The iron aluminide electrode was remelted under this flux cover and cast into 76 mm ingot in a water cooled steel mould. Towards the end of the process, the power supply was gradually reduced to achieve hot tapping. Further details on process parameters and mechanical properties of iron aluminides can be found elsewhere (Baligidad *et al* 1994). The ingots were then forged to a reduction ratio of 70%.

Specimens for microstructural studies were cut from the forged strips using a high speed abrasive silicon carbide cut-off wheel. The as-received microstructures in all the three sections (rolling (RD), long transverse (LT) and short transverse (ST)) were obtained by etching the polished surfaces (final polish with 1 µm diamond paste) using 33%CH₃COOH + 33%HNO₃ + 1%HF + 33%H₂O (by volume). Microstructures were examined in all the three directions using an optical microscope (Axiolab A, Ziess, Germany) and a scanning electron microscope, SEM (JEOL JSM 840A).

Stereological analysis was performed using an image analysis software (Image-Pro Plus, version 4.1, Media Cybernetics, USA). The rolling plane was analysed in the stereological studies because the available area for analy-

sis was larger for the rolling plane. Each sample was observed at 30 different locations (fields of view). The 95% confidence interval, which is a measure of the sampling error, has also been estimated.

In order to estimate the volume fraction, V_V , of the carbides, a 10 × 10 grid was used and the sample was observed at 500×. The total number of intersection points between the crossed grid of the test lines and the carbides in each field of view were calculated manually and divided by the total number of points. The result provided the volume fraction. The size of the grains were calculated by imposing 8 random test lines, each of length 2300 µm, on the image taken at a magnification of 50×. The total number of intersection points between the test lines and the grain boundaries was counted and the measured grain size is given by

$$G_z = (n L/P), \quad (1)$$

where G_z represents the grain size, n the total number of grid lines, L the length of a grid line and P the number of intersection points between the test lines and grain boundaries.

Surface area of exploded carbides per unit volume provides an understanding of the space occupied by the carbides in the matrix (Underwood 1970). For the purpose of calculating the surface area of the exploded carbides per unit volume and the contiguity parameters (to be discussed below), 10 test lines, each of length 206 µm, were drawn on the optical micrograph and the readings taken. The surface area of exploded carbides per unit volume is given by the relation

$$(S_V)_C = (2P/L), \quad (2)$$

where $(S_V)_C$ is the surface area of the exploded carbides per unit volume, P the number of intersection points between the test lines and the partition line of carbides, and L the total length of the test lines. During the calculation of $(S_V)_G$, 2 is multiplied with P because when a test line intersects the boundary of two grains, the number of intersection points were counted as one.

Contiguity is a measure of the fractional surface area of each feature occupied by other features of the same type (Underwood 1970). Contiguity of carbides is calculated using the equation

$$C_G = 4P_{L\alpha\alpha}/(4P_{Laa} + 2P_{Lab}), \quad (3)$$

where C_G is the contiguity of carbides, P_{Laa} the number of intersection points between the test lines and the partition line of two adjoining carbides divided by the unit length of the test line and P_{Lab} the number of point intersections between the test lines and the partition line of grains and carbides divided by the unit length of the test line.

3. Results and discussion

The microstructures of the as-received iron aluminide alloys were analysed in all the three directions. The opti-

cal micrographs of Fe-18.5Al-3.6C obtained from the rolling plane, longitudinal and short transverse sections of the as received plate are given in figure 1, while the scanning electron micrographs for the same are provided in figure 2. In a similar fashion the optical and scanning electron micrographs for Fe-20.0Al-2.0C are presented in figures 3 and 4, respectively, while those for Fe-19.2Al-3.3C-0.07Ce in figures 5 and 6, respectively. All the alloys possessed recrystallized grains. This was expected because the thermomechanical processing of the alloys was performed at a high temperature (550–600°C) where dynamic recrystallization had taken place (Baligidad *et al* 1997a,b).

The alloy, Fe-18.5Al-3.6C, exhibited a typical two-phase structure (figures 1 and 2) consisting of carbides dispersed in the iron aluminide matrix. According to Baligidad *et al* (1997a,b), the matrix phase is based on Fe_3Al and the precipitates are $\text{Fe}_{4-y}\text{Al}_y\text{C}_x$ carbides possessing perovskite structure. The carbides were distributed uniformly throughout the matrix of iron aluminide. The compositional analysis of the matrix for a alloy of similar composition revealed, for these category of alloys, the atomic ratio of iron and aluminium in the matrix, in the order of 3 : 1, thereby suggesting that the stoichiometric formula of the matrix phase as Fe_3Al (Laha *et al* 2004). XRD studies conducted on the present alloys confirmed the formation of Fe_3AlC carbides.

The carbides seen in the alloy, Fe-18.5Al-3.6C, on the rolling and longitudinal planes were of two distinct sizes. Larger bulky carbides were equally distributed throughout the matrix with many smaller precipitates interspersed in between (figure 1). The situation was similar in all the observed planes (figures 1a through 1c). However, the distribution of carbides in short transverse section (figure 1c) was slightly different in that the bulky carbides were smaller in size compared to that seen in other planes and were more closely spaced. Smaller precipitates were dispersed around the bulky carbides in a similar fashion to that seen in the other planes. This resulted due to thermomechanical processing.

In the case of Fe-20.0Al-2.0C alloy, similar bulky carbides were observed in the rolling, long transverse and short transverse planes (figures 3 and 4). Similarly, the smaller nodular precipitates were distributed around the bulky carbides. The distribution of carbides was uniform throughout the matrix. The carbon content in Fe-20.0Al-2.0C was lower than in Fe-18.5Al-3.6C. This resulted in higher volume fraction of carbide and lower spacing between the bulky carbides in the latter alloy. In all the cross sections of Fe-20.0Al-2.0C, the inter-carbide spacing was higher when compared to the Fe-18.5Al-3.6C alloy. Examination of these microstructures using stereological methods confirmed that the volume fraction and the exploded surface area per unit volume of the carbides in the alloy Fe-18.5Al-3.6C was higher than the alloy Fe-20.0Al-2.0C (to be discussed below).

The addition of Ce modified the morphology of carbides (figures 5 and 6). The carbide grain sizes were finer and, moreover, the carbides were uniformly distributed throughout the matrix. Therefore, addition of Ce to iron aluminides affected the morphology and size of the carbides.

Figure 1. Optical micrographs of Fe-18.5Al-3.6C alloy in the (a) rolling plane, (b) long transverse, and (c) short transverse directions.

The differences in carbide morphologies in the three iron aluminides under study were clearly revealed at higher magnifications in the SEM (figure 7).

The microstructures were analysed for obtaining information on the carbide particle distribution (the carbide particle size and its surface area per unit volume). The

grain size and the mean volume fraction ($\bar{V}_V$) of the bulky carbides in the three alloys are reported in table 1. It was not possible to reveal the grain boundaries in the microstructure of Fe-19.2Al-3.3C-0.07Ce by etching. The surface area of exploded features per unit volume (S_V) and the contiguity for the bulky carbides are

Figure 2. Scanning electron micrographs of Fe-18.5Al-3.6C alloy in (a) the rolling plane, (b) long transverse, and (c) short transverse directions.

Figure 3. Optical micrographs of Fe-20.0Al-2.0C alloy in the (a) rolling plane, (b) long transverse, and (c) short transverse directions.

presented in table 2. The 95% confidence interval, which is a measure of the sampling error, is provided besides the individual measurements. As the Fe-18.5Al-3.6C and Fe-19.2Al-3.3C-0.07Ce alloys possessed higher carbon

content than Fe-20.0Al-2.0C, these alloys exhibited a higher exploded surface area per unit volume of the carbide particles. The small-sized carbides of all the samples were uniformly distributed. Noticeable differences were observed only in the shape and size of the bulky carbides. Therefore, in estimating the above parameters, the finer particles of the carbides were neglected and the analysis was performed on bulky carbides. This provided a qualitative picture of the distribution of the larger carbide particles.

Figure 4. Scanning electron micrographs of Fe-20.0Al-2.0C alloy in the (a) rolling plane, (b) long transverse, and (c) short transverse directions.

Figure 5. Optical micrographs of Fe-19.2Al-3.3C-0.07Ce alloy in the (a) rolling plane, (b) long transverse, and (c) short transverse directions.

The contiguity of the bulky carbide phases is reported in table 2. The results show that the second phase carbides in the samples, Fe-18.5Al-3.6C and Fe-19.2Al-3.3C-0.07Ce, are more contiguous and proximate than the carbides in Fe-20.0Al-2.0C. This is due to the higher amount of carbon in Fe-18.5Al-3.6C and Fe-19.2Al-3.3C-0.07Ce. Moreover, in case of the Ce added sample, Fe-

19.2Al-3.3C-0.07Ce, the role played by Ce in producing a finer and uniform distribution of carbides can be the reason for the observed higher contiguity in the Fe-19.2Al-3.3C-0.07Ce sample.

It is well known that Ce is generally added in cast iron to act both as an inoculant and as a nodulariser (Kay *et al* 1975). Ce ties up the trace elements such as Pb, As, Bi,

Figure 6. Scanning electron micrographs of Fe-19.2Al-3.3C-0.07Ce alloy in the (a) rolling plane, (b) long transverse, and (c) short transverse directions.

Figure 7. Scanning electron micrographs of (a) Fe-20.0Al-2.0C, (b) Fe-18.5Al-3.6C and (c) Fe-19.2Al-3.3C-0.07Ce observed at higher magnification.

Table 1. Grain size and mean volume fraction ($\bar{V}_V$) of the bulky carbides distributed in the rolling plane of samples Fe–20.0Al–2.0C, Fe–18.5Al–3.6C and Fe–19.2Al–3.3C–0.07Ce samples.

Composition	Grain size		Volume fraction of bulky carbides	
	Mean (μm)	95% confidence interval	Mean	95% confidence interval
Fe–20.0Al–2.0C	480.48	54.10	0.20	0.0353
Fe–18.5Al–3.6C	574.91	85.90	0.33	0.0406
Fe–19.2Al–3.3C–0.07Ce	–	–	0.35	0.0457

Table 2. Exploded surface area per unit volume and contiguity of the carbides distributed in the rolling plane of Fe–20.0Al–2.0C, Fe–18.5Al–3.6C and Fe–19.2Al–3.3C–0.07Ce samples.

Composition	Exploded surface area per unit volume		Contiguity	
	Mean (μm^{-1})	95% confidence interval	Mean	95% confidence interval
Fe–20.0Al–2.0C	0.230	0.0364	0.065	0.0201
Fe–18.5Al–3.6C	0.247	0.0146	0.160	0.0317
Fe–19.2Al–3.3C–0.07Ce	0.237	0.0146	0.114	0.0344

Sb, Sn, Al, Cd and Ti, which have a negative influence on the structure of graphite. Additionally, Ce reacts with both dissolved oxygen and sulphur in the cast iron melt and forms sulphide or oxide inclusions which are of the type X_2Y_3 and XY_2 , where X is Ce and Y is either sulphur or oxygen. These inclusions act as nuclei for the nucleation of graphite and hence reduce the undercooling necessary to initiate eutectic solidification. This increase in the nucleation rate of the graphite nodules in the ductile cast iron results in the formation of graphite nodules. This eventually produces the so-called ductile cast iron. The morphology of graphite is changed from flakes to nodules in case of Ce alloyed cast iron (Kay *et al* 1975) because Ce chemically combines with sulphur and oxygen. Based on this well known effect, it is reasonable to conclude a similar effect for Ce in the case of carbon-alloyed iron aluminides.

4. Conclusions

Microstructural observations indicated that the alloys, Fe–18.5Al–3.6C, Fe–20.0Al–2.0C and Fe–19.2Al–3.3C–0.07Ce (in at%), exhibited a typical two-phase structure consisting of carbides dispersed in a iron aluminide matrix. The matrix contained recrystallized grains. In the case of the alloys, Fe–18.5Al–3.6C and Fe–20.0Al–2.0C, larger bulky carbides were equally distributed throughout the matrix with many smaller precipitates interspersed in between. However, in case of the Ce added alloy, Fe–19.2Al–3.3C–0.07Ce, the carbide grain sizes were much finer and they were more uniformly distributed throughout the matrix. Addition of Ce affected morphology and

size of the carbides. Stereological analysis, carried out on the rolling plane of the alloys confirmed that the alloys possessing higher carbon content, i.e. Fe–18.5Al–3.6C and Fe–19.2Al–3.3C–0.07Ce, exhibited higher volume fraction of carbide and higher exploded surface area per unit volume, when compared to the lower carbon alloy, Fe–20.0Al–2.0C. Contiguity studies revealed that the second phase carbide phases in the samples, Fe–18.5Al–3.6C and Fe–19.2Al–3.3C–0.07Ce, were more contiguous and proximate than the carbides in Fe–20.0Al–2.0C. The effect of Ce addition on the modification of the carbide structure has been explained based on the well-known effect of Ce addition in modifying the carbide/graphite morphology in cast irons.

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