

Carbide Precipitation in the Microstructures of Austempered Ductile Irons Containing 0.48% and 4.88% Al

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Abstract

The influence of aluminium on the microstructure of austempered ductile cast iron (ADI) has been studied. The presence of well distributed graphite in the matrix, and a relatively high volume fraction of retained austenite are responsible for the good mechanical properties of the Aluminium alloyed austempered ductile irons including excellent wear resistance, higher resistance to thermal shock, better graphitising tendency and higher resistance to oxidation at high temperatures. A number of specimens of different composition have been made by green sand-casting and gravity die-casting. The transformation to a bainitic microstructure during austempering under different conditions was then examined for the most successful experimental casts. Austenitising temperature of 920°C, and austempering temperatures of 350°C at different holding times have been used. Microstructures have been examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Furthermore, it was found that isothermal transformation at 350°C for different soaking times gave a typical bainitic microstructure. Extension of isothermal transformation time leads to precipitation of carbides which also depends on the Al concentration.

Keywords: Aluminium, Austempering, Austenitising, Bainitic microstructure, Carbide precipitation.

Introduction

Carbide precipitation in ductile iron during isothermal transformation leads to a decrease in the volume fraction of high-carbon retained austenite in the fully austempered matrix, resulting in a corresponding decrease in the impact energy. Most of the time, the precipitated carbides are too small to be easily detected by conventional methods. However, carbide formation can be analysed using TEM.

The changes in microstructure of austempered ductile cast irons essentially result from the holding time at austempering temperature. Few microstructural studies of austempered ductile iron using TEM have been reported, probably due to the difficulties in thin foil preparation. The precipitation of carbides for both upper and lower bainite occurs after the formation of bainitic ferrite. The carbide precipitation may occur from supersaturated ferrite and especially from the high-carbon retained austenite which is thermodynamically unstable¹⁾. The high-carbon retained austenite decomposes to ferrite and carbide at the longer holding times of isothermal heat treatment, and the carbide precipitation commences at the austenite/ferrite interfaces and grows into the austenite²⁾.

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During isothermal heat treatment the cementite or transitional carbides precipitate within bainitic ferrite or retained austenite and exhibit different orientation relationships. Analysis of many electron diffraction patterns has revealed common or uncommon relationships between carbide precipitates and matrix.

Electron microscopy revealed that for a ductile iron austempered at 410°C, the microstructure consists of ϵ -carbide precipitation within austenite³⁾. According to Sidjanin et al.,⁴⁾ in iron containing 3.2%C, 0.3%Si, 0.6%Ni, and 2.2%Al isothermally heated at 400°C more than 3 hrs, different carbide precipitation is observed in the microstructure. They reported that orthorhombic η -carbide was found after isothermal heat treatment for 3 hrs. They also showed that after 5 hrs the microstructure consists of η -carbide in ferrite and monoclinic χ -carbide at the ferrite/austenite interface due to decomposition of the high carbon retained austenite. They also reported that during austempering at 300°C for up to 3 hrs bainitic ferrite containing ϵ -carbide together with high carbon retained austenite is produced and the amount of ϵ -carbide increases between 3 to 5 hrs. In addition, they believed that the reduction in elongation and impact energy is due to χ -carbide precipitation on the interface of ferrite and retained austenite holding at 300°C for times longer than 5 hrs.

In another study carried out by Honarbakhsh-Raouf⁵⁾, for iron containing 3.39%C, 2.3%Si, 0.15%Mn, 1.8%Ni, 1.9%Cu and 0.16%Mo, austempered at 450°C for 45 min, the possibility of carbide formation was confirmed with precipitates very close to cementite in a matrix of ferrite. In addition, the TEM micrograph of the same sample after 2 hr indicated a triclinic carbide similar to that reported for high-silicon steel. Some carbides which have similar morphology to cementite in lower bainite in steels were detected for samples austempered at 350°C for periods of more than 1 hr. A typical morphology of cementite was also observed, with an angle to the plate direction of the bainitic ferrite plates interwoven with retained austenite films, after austempering at 250°C for 2 hr and the high-carbon retained austenite was also transformed to ferrite and carbide after 200 hr.

The microstructure of irons with 2.02%, 2.65% and 3.31%Si for different heat treatment condition was investigated by Mallia⁶⁾. It was suggested that high levels of carbon dissolved in the bainite and retained austenite could not remain for a long time during isothermal heat treatment and thus different transition carbides such as η -carbide, χ -carbide and ε -carbide precipitated with extended holding time. In addition, it was argued that η -carbide with the chemical formula Fe_2C decomposes to $\varepsilon\text{-Fe}_{2.4-3}\text{C}$ with increasing austempering time. The Kurdjomov-Sachs orientation relationship between carbide-free bainite and retained austenite was also reported. However, the orientation relationship indicated in the presence of carbides was Nishyma-Wasserman (N-W). The η -carbide and ε -carbide exhibited Hirotsu and Nagakura type and the Jack-type orientation relationship, respectively, with bainitic ferrite (α_b).

Additional TEM observations are reported by Perez et al.⁷⁾ who showed that the microstructure for a ductile iron containing 3.7%C, 2.5%Si, 0.24%Mn, 1%Cu and 0.25%Mo, austenitised at 870°C for 2 hr and followed by isothermal heat treatment at 375°C for 24 hr, comprises a $[\bar{1}5\bar{3}]_{\alpha}$ and $[0\bar{1}1]_{\gamma}$ zone plus orthorhombic Fe_2C and Mo_2C carbides.

Boutorabi et al.,⁸⁾ have shown that in a SG Al cast iron with 2.35% Al, the austenitising and austempering temperature and time influence the morphology, distribution, volume and size of the microscopic phases. Boutorabi et al.,⁹⁾ have reported that austempering temperature determines the morphology of the bainite and the volume of retained austenite and that changes in the austenitising

temperature and austempering time have a smaller effect on transformation.

The present work is designed to study the effect of aluminium and heat treatment on the microstructure of ADI, especially on the bainite reaction¹⁰⁾.

Experimental

Experimental ductile irons with the composition range given in Table 1 were produced in a Morgan gas - fired furnace (with 25 kg capacity lift - out crucible) and a high - frequency melting plant of 20 kg capacity (with a tilting crucible). After melting, the iron was superheated at 1550°C and small pieces of solid aluminium were added by plunging into the bottom of the liquid metal. Enough time was given to dissolve the aluminium completely in the molten metal. Following aluminium treatment, FeSiMg (5%Mg) alloy was plunged into the liquid iron and splashing of molten metal during solution of magnesium was prevented by using special enclosed reaction vessels. Finally, post-inoculation of ferro-silicon containing 75%Si was carried out in the crucible. The sandwich technique was used to treat the melt of each iron with a ferro-silicon alloy containing 5%Mg at 1400°C.

The melts were cast with a pouring temperature of approximately 1350°C by both green sand moulding and gravity die casting. Standard 12.5 mm and 25 mm Y-block sand moulds and permanent moulds were used and a bottom gating introduced the metal smoothly into the mould cavity to ensure a sound casting. Quantitative measurements of the carbon content in the experimental irons were made using equipment at Swinden Technology Centre of Corus Group PLC (formerly British Steel Ltd.). Analyses were performed by an infrared absorption method after combustion in an induction furnace and oxidation to CO_2 . In order to analyse for aluminum in high-Al content ductile irons, an atomic absorption spectrophotometry (AAS) method was used by Hi-Search Technology (HIST) of Birmingham University.

The compositions selected resulted in more than 90% nodularity of graphite. Optical microscopy, SEM and TEM were used to show the microstructure of the spheroidal graphite (spherulite).

Austenitising was carried out in an electrically-heated Carbolite muffle furnace. The samples were coated with a thin layer of commercial Berkatect 32/12 to prevent decarburization and oxidation during heating. The samples were heated at 920°C for 90 min and transferred quickly into a

Table 1. Composition of irons, wt. %.

Alloy	C	Al	Si	Ni	Mn	P	S	Mg	Fe
0.48%Al	3.68	0.48	1.06	0.04	0.06	<0.005	<0.005	0.05	balance
4.88%Al	3.44	4.88	1.22	0.05	0.10	<0.005	<0.005	0.05	balance

molten lead bath. Isothermal transformation or austempering was carried out in the temperature 350°C and time range 30 sec. to 384 hours followed by quenching into water.

A Cambridge Series 3 SEM fitted with a Link 860 series 1 EDX system and a Cambridge Series 4 SEM were used. A working distance between 20-24 mm was chosen with an accelerating voltage of 20kv and spot size between 4 - 6 nm.

The successful preparation of TEM thin foils from cast iron is more complicated than most kinds of metal alloys and steels because there are two quite different phases (iron and graphite) in cast iron. When Jet polishing is used, a dark surface due to strong oxidation and corrosion can be obtained and the detachment of large graphite nodules can take place before adequate thinning. The preparation of a thin foil from the bulk samples was only achieved by a more laborious process of mechanical polishing and ion thinning. The samples were ion beam thinned, initially under a 15° inclination angle and finally 10°, for times ranging from 2 hr to 24 hr depending on initial thickness, using a Gatan dual ion milling machine model 600 beam thinner and a Gatan precision ion polishing system model 691 PIPS™ V4.31. The thin foils were

examined using a Philips CM200 TEM operating at an accelerating voltage of 200 kv.

Results

Figure 1 shows SEM micrographs of the experimental ductile irons with 0.48% and 4.88%Al content. As can be seen, the graphite nodules are dispersed randomly in the ferritic – pearlitic matrix.

Some characteristics of the experimental ductile irons are tabulated in Tables 2 and 3, respectively. The products of the transformation depend on the composition and cooling rate. The presence of graphitising elements such as Si and Al tends to promote the formation of graphite¹¹⁻¹³.

The results given in Tables 2 and 3 show an increase in the number of graphite nodules and pearlite fraction with an increase in aluminum content. This was accompanied by a reduction in the size of graphite nodules and lower ferrite content. In addition, the higher cooling rate induced by casting in a permanent mould compared with a sand mould, probably due to the increased undercooling, also gave a similar result, i.e. an increased number of graphite nodules (Table 2) of smaller size.

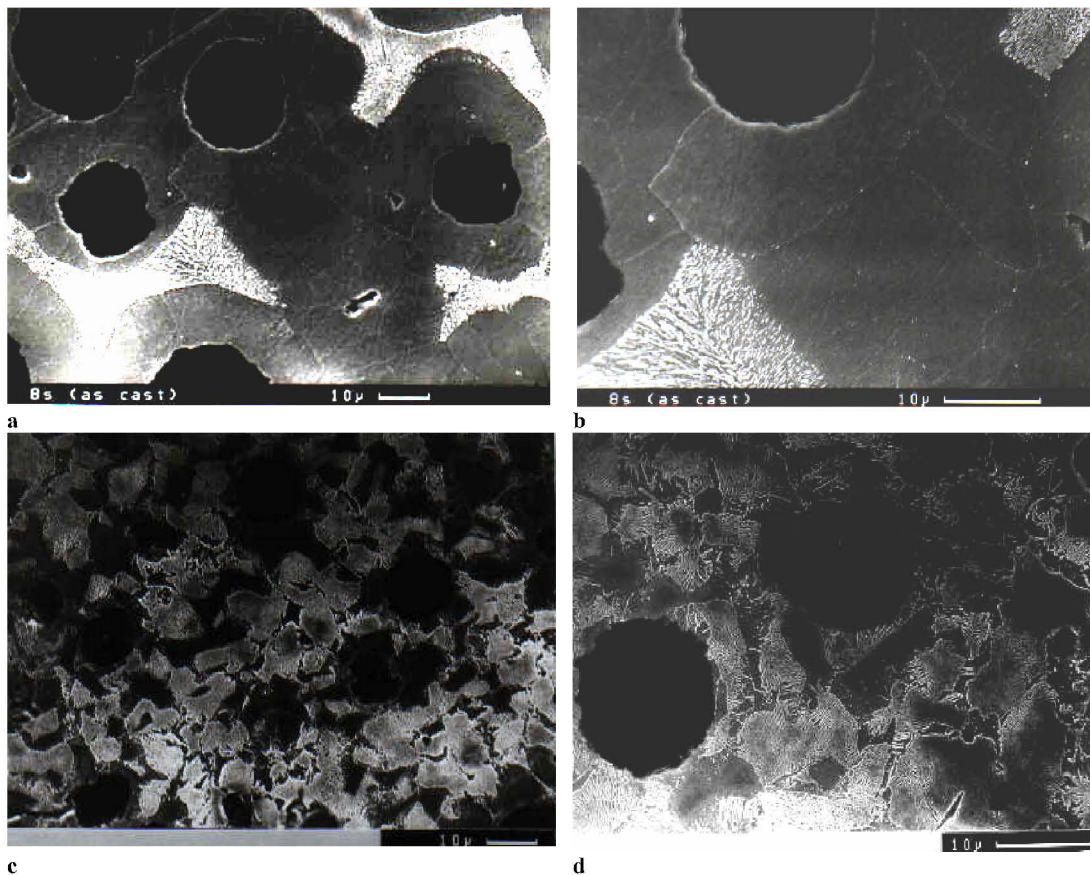


Fig. 1. SEM micrographs of initial microstructure of two ductile irons at two different magnifications. Graphite, ferrite and pearlite are present in the structure (etched 2% nital); a and b, 0.48% Al and c and d, 4.88% Al.

Table 2. Characteristics of as-cast experimental irons cast in different moulds.

Alloy	Nodule count / mm ⁻²		average nodule size (µm)		Hardness (HV 50)	
	S	P	S	P	S	P
0.48% Al	339	438	29.4	25.0	197.8	288.5
4.88% Al	472	563	17.2	14.4	246.9	341.2

S: Sand mould casting P: Permanent mould casting

Table 3. Structure and phases for Al - alloyed iron cast in different moulds.

Alloy	Sand mould casting			Permanent mould casting		
	Graphite, %	Ferrite, %	Pearlite, %	Graphite, %	Ferrite, %	Pearlite, %
0.48% Al	13.9	75.8	10.3	13.0	45.3	41.7
4.88% Al	9.9	10.5	79.6	7.6	8.4	84.0

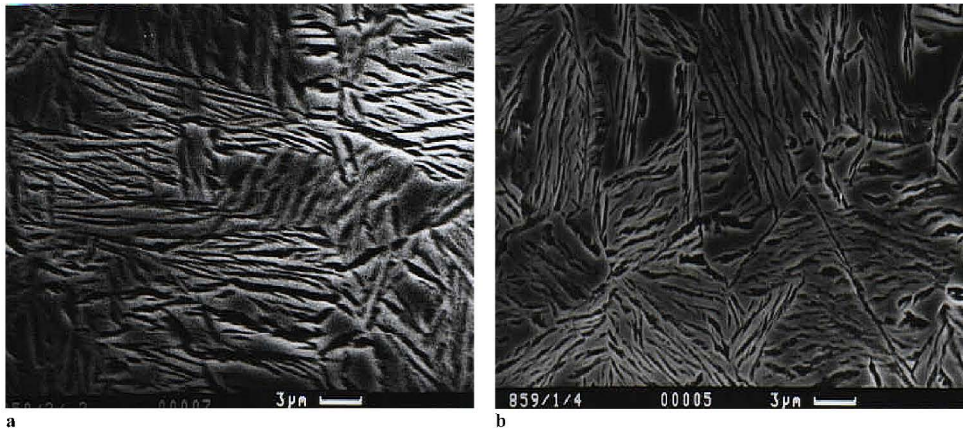


Fig. 2. SEM micrographs of Al ductile cast irons austenitised at 920 °C for 90 min and austempered at 350 °C for 16 days; a) 0.48%Al, b) 4.88%Al.

The as - cast microstructures that are shown in Figure 1 consist of graphite nodules in a ferrite-pearlite matrix. The structures and phases for Al-alloyed iron with different mould casting are given in Table 3. It has been found that as the amount of aluminium decreased, a bulls - eye structure formed. In agreement with the present study, Walson¹⁴⁾ reported a pearlite-type matrix in Al - alloyed grey iron with a range between 2 to 5 wt.% Al, but this is contrary to reports in another study by Smickley and Rundman¹⁵⁾. They believed that the free ferrite content in the structure of grey cast iron shows an increase with additions of 0.6%, 1.02% and 1.5% aluminium.

The microstructure of ductile irons with 0.48%Al and 4.88%Al have been investigated after austempering at 350 °C for different time following austenitising at 920 °C for 90 min. Optical microscopy, SEM and TEM were used to study the changes during austempering¹⁰⁾.

Figure 2 illustrates the SEM micrographs obtained following austempering of 0.48% Al at 350 °C for 16 days (384 hours). The micrographs show a matrix consisting of alternate laths of bainitic ferrite and high carbon retained austenite. The structure also showed regions of blocky retained austenite. The amount of martensite decreases with increasing isothermal transformation time. The high carbon retained austenite can change to ferrite and

carbide/carbides at longer periods of transformation time. These results are in agreement with a number of studies. For example, Honarbakhsh-Raouf⁵⁾ reported that for a 2.3% Si ductile iron austempered at 350 °C, the matrix consists of thin laths of bainitic ferrite, retained austenite and martensite at short times, and the amount of martensite decreases with increasing time. It is reported that after 200 hrs austempering at 350 °C of Si-SG iron, some retained austenite was still present in the microstructure.

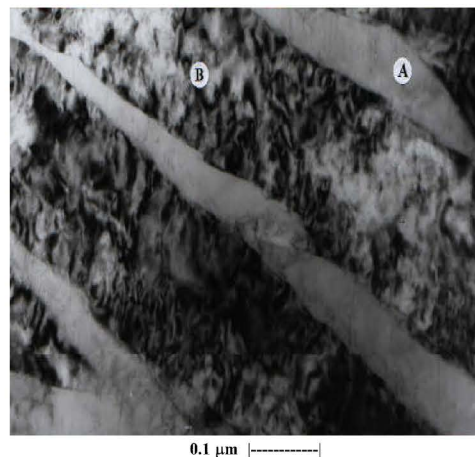


Fig. 3. Typical microstructure of 0.48%Al ductile iron austenitised at 920 °C for 90 min and austempered at 350 °C for 16 days.

Figure 3 shows the TEM micrographs for the 0.48%Al ductile iron for an isothermal heat treatment of 16 days at 350°C. Of great importance is the stability of retained austenite after long austempering time and the microstructure shows only a little change. Bhadeshia and Edmonds¹⁶⁾ [1983] have argued that the major part of high carbon retained austenite obtained during austempering has a blocky morphology. In addition, it has been illustrated that the film austenite formed during the early stage of isothermal transformation is more stable than the retained austenite with a blocky morphology.

Figures 4 is another TEM micrograph of the same sample. Small carbide particles were also observed in the bright field image (Figure 4a) which are shown in the corresponding dark field image (Figure 4b).

The dark field image reflected from the $[0\bar{2}\bar{1}]_{Fe_3C}$ from the SADP are illustrated in Figure 4 (c). As can be observed in Figure 4d, the corresponding SADP was indexed as bainitic ferrite, high carbon retained austenite and carbide. This carbide proved to be cementite. The dark field image (Figure 4b) suggests that the carbides are present within the bainitic ferrite, and possibly at the previous interfaces of bainitic ferrite and retained austenite. Mallia⁶⁾ [1998] reported that carbide precipitated in the microstructure after 100 minutes reduced the stability of the retained austenite with the result that the remaining austenite continuously transformed to ferrite and carbide with further isothermal heat treatment.

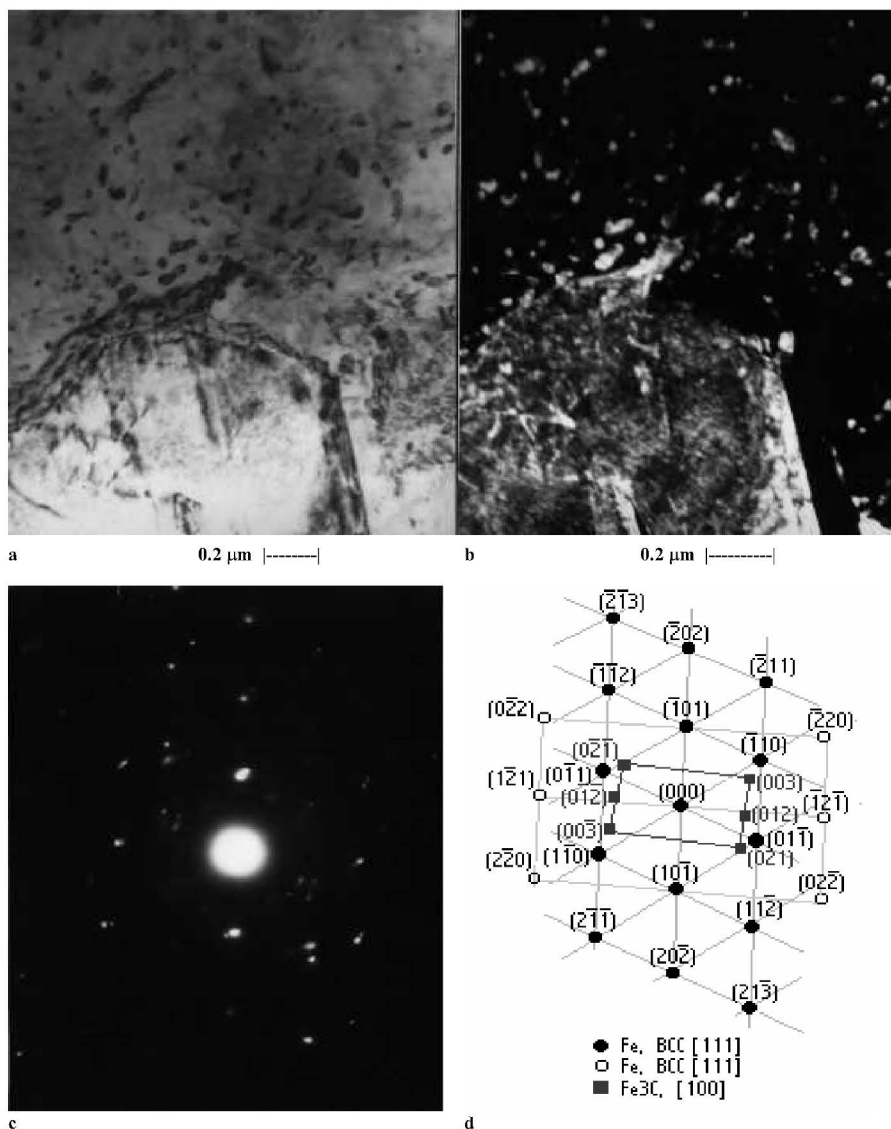


Fig. 4. Typical microstructure of 0.48%Al ductile iron austenitised at 920 °C for 90 min and austempered at 350 °C for 16 days; a) bright field image, b) dark field image from the $[0\bar{2}\bar{1}]_{Fe_3C}$, c) the corresponding SADP and d) indexed SADP.

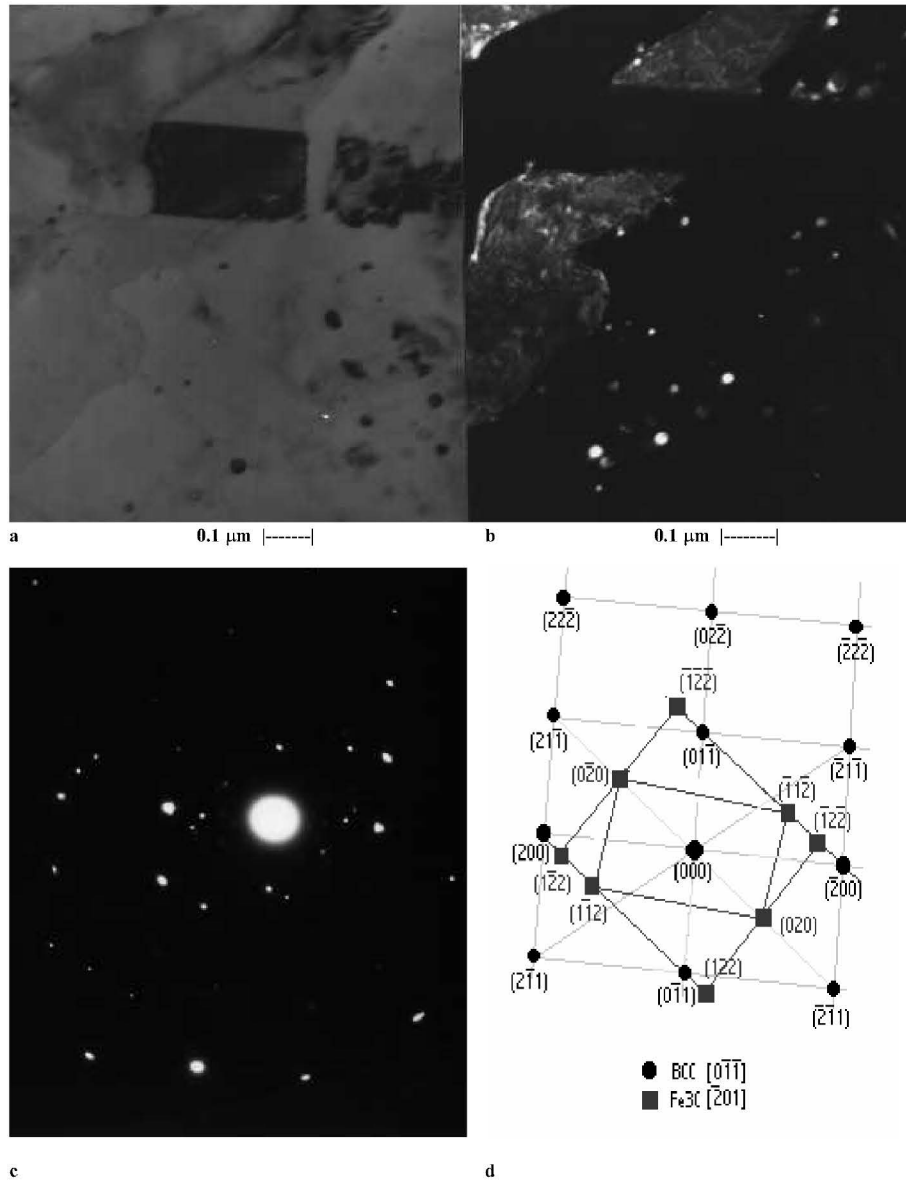


Fig. 5. Typical microstructure of 4.88%Al ductile iron austenitised at 920 °C for 90 min and austempered at 350 °C for 16 days; a) bright field image, b) dark field image from the $[1\ 2\ 2]_{Fe_3C}$, c) the corresponding SADP and d) indexed SADP.

Figure 5 shows the TEM micrographs for the 4.88%Al ductile iron for an isothermal heat treatment of 16 days at 350°C., the bright field image shows that some particles are present within the ferrite as can be seen in Figure 5a. Figure 5b shows a TEM dark field image obtained by selecting a $(1\ \bar{2}\ 2)_{Fe_3C}$ reflection. It clearly reveals the presence of particles which appear with a bright contrast. It also shows particles with different sizes distributed randomly in the matrix. Figure 5c shows the SADP of the area observed in Figures 5a and b, which was indexed as $\langle 0\ 1\ 1 \rangle_{\alpha}$ ferrite and $\langle \bar{2}\ 0\ 1 \rangle_{Fe_3C}$ cementite zones (Figure 5d).

The amount of bainitic ferrite obtained by isothermal transformation at 350°C for various times was also examined. It seems that transformation at lower times gives more bainitic ferrite formation for higher Al contents. This is in agreement with a study performed by Boutorabi¹⁷⁾.

Discussion

The structure and properties of as-cast irons are dependent on numerous factors, one of the most important being composition which must be controlled during melting. Also, the form and distribution of graphite are associated with the

composition^{18,11}). In producing the experimental ductile cast irons careful control was necessary to achieve graphitisation and to keep the variation of elements within the required range. It is well known that deviation from a spheroidal graphite shape leads to a serious reduction in the properties of irons such as tensile strength and impact resistance.

The results obtained in the present work show that there is a significant increase in the graphite nodule number with an increase in Al content (Table 2). The above finding is similar to those in Al-SG (ductile irons)¹⁷. It is reported that large nodule number in SG Al iron can be attributed to the combination of a highly effective inoculants used and to the relative difference in the rate of diffusion of carbon in liquid iron associated with aluminium.

The microscopic observation revealed that for austempered times up to about 100 min the matrix consisted of a mixture of carbide-free bainitic ferrite and carbon enriched retained austenite. At short holding times, martensite was produced during cooling, probably due to the low residual content of carbon in austenite that is not sufficient to stabilise at room temperature.

The results of the present investigation demonstrate that the amount of bainitic ferrite and retained austenite increase with an increase in isothermal holding times during the first stage of transformation. During this period of isothermal phase transformation, there was no evidence of carbide precipitation for different levels of Al content.

TEM microscopy revealed that the microstructure of experimental irons actually consisted of a combination of carbide-free bainitic ferrite and high carbon retained austenite for times to about 100 min. Detailed electron microscopy of this bainite indicated that a Kurdjumov-Sachs orientation relationship existed between bainitic ferrite and retained austenite. The corresponding DP shows $[11\bar{1}]_{\alpha}/[10\bar{1}]_{\gamma}$ and $(011)_{\alpha}/(111)_{\gamma}$ expected for this type of relationship¹⁰. These results are consistent with previous studies in austempered ductile irons with various alloying element additions^{4-6, 19}.

Extending the isothermal heat treatment at 350°C produced a combination of bainitic ferrite and carbon-enriched residual austenite with carbide precipitation. It is believed that carbide-free bainitic ferrite and high-carbon retained austenite are not in equilibrium with other below the B_s temperature, and carbide precipitation can occur within the microstructure during longer times of isothermal heat treatment¹. Therefore, the isothermal transformation during the austempering consists of carbide precipitation in carbon-enriched austenite followed by more equilibrium phase production. It is expected that the formation of carbides during the bainite reaction could lead to some changes in mechanical

properties. Generally, lower mechanical properties of austempered ductile irons result from micro-inhomogeneity of the matrix and any carbide present in the microstructure. The influence of carbide formation is more important and is the main reason for lower ductility, toughness and also strength properties.

Depending on the aluminium content and heat treatment condition, different microstructures are found. By austempering ductile iron with low Al contents in comparison with higher Al, it is found that cementite formed at shorter times of austempering in 0.48%Al ductile iron whereas this type of carbide-precipitation is indicated only after very long periods of holding time (16 days) for 4.88%Al. This different behaviour may be caused by the high graphitisation tendency of aluminium that tends to retard the carbide formation in ADI. Results of previous investigations indicate that Al significantly affects the bainite reaction and that carbide precipitation shifted to longer austempering time compared with Si-containing austempered ductile irons¹⁷.

Conclusions

- 1- Placing the graphitizer agent in a special chamber in the running system gave more effective spheroidization and higher nodularity for the experimental irons. At the different concentrations of Al employed, more than 90% nodularity was achieved with the nodules dispersed randomly in the microstructure.
- 2- The addition of aluminium decreased the extent of bulls-eye structure to give a higher volume fraction of pearlite in the matrix.
- 3- The following results were obtained from the isothermal bainitic transformation after austenitising at 920°C for 90 min and austempering at 350°C for different holding times which were found to be consistent with heat treatments used in previous studies.
- 4- Electron diffraction analysis for 0.48%Al and 4.88%Al iron austempered at 350°C after different holding time indicated a K-S orientation relationship between bainitic ferrite and retained austenite phase after the shorter times of isothermal heat treatment in two aluminium-containing irons.
- 5- At short austempering time carbides could not be detected in the microstructures for different Al-alloyed irons and the matrix of both irons consisted of aggregated layers of carbide-free bainitic ferrite and high carbon retained austenite. It is believed that the strong effect of Al graphitisation helped to suppress formation of the carbides.
- 6- A part of the high carbon retained austenite was changed to ferrite and carbide at longer periods of transformation time, and the carbides were identified as cementite.

Acknowledgments

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