Precipitation and dissolution of carbides in low alloy ductile iron plates of varied thickness

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The present work has investigated the feasibility of achieving carbide free microstructures in low alloy thin wall ductile iron (TWDI) after dissolution heat treatments. Studies were conducted using low alloy and unalloyed hypereutectic irons, obtained from thin and regular thickness blocks, cast using sand moulds. The amount of carbides present in the microstructure was measured before and after annealing heat treatments carried out at temperatures ranging between 870 and 930°C. As cast specimens contained up to 30 vol.-% of carbides. The results show that annealing heat treatments dissolved more than 90% of as cast carbides present in thinner wall specimens, while dissolution was below 30% for 13 and 25 mm Y block specimens. Chemical microanalysis demonstrated that the content of carbide stabilising elements in the carbides increased as the cooling rate during solidification diminished. Therefore, carbides present in irons solidified at a slower cooling rate are more difficult to dissolve by annealing.

Keywords: Thin wall ductile iron (TWDI), Carbides, Phase transformation kinetics

Introduction

Significant research efforts have been directed recently towards the study of several aspects relating to the production of thin wall ductile iron (TWDI). One of the key factors affecting TWDI is the precipitation of carbides caused by the fast cooling rate imposed during the solidification of thin wall castings. Most research has aimed to produce carbide free microstructures as cast. Nevertheless, Giacopini *et al.*[1] have shown that it is possible to use a different approach. Castings can be produced with significant amounts of free carbides, as cast, and these carbides can be dissolved later by annealing. Giacopini *et al.* demonstrated that this is a feasible route when ductile irons are unalloyed. They showed that very large amounts of free carbides are readily dissolved after short annealing treatments. The dissolution of carbides is facilitated by the absence of carbide stabilising elements in the alloy. Nevertheless, unalloyed ductile irons cannot be used in all applications. The use of small amounts of alloying elements is often necessary either to control the microstructure and properties, or to confer desired levels of hardenability. The behaviour of carbides in low alloy TWDI has not been studied. Therefore, the present investigation focuses on the study of the precipitation and dissolution of carbides in low alloy TWDI.

Ductile irons are multicomponent alloys that are prone to exhibiting microstructural heterogeneity, such as microsegregation of the alloying elements and the precipitation of free carbides during solidification. Both microsegregation and the precipitation of carbides in ductile iron (DI) have been extensively studied. It has been shown that the precipitation of carbides is affected by microsegregation.[2–5] In fact, as solidification advances, carbide forming elements such as manganese, chromium and molybdenum segregate to the remaining melt. As a result, by the end of solidification the last portions of melt may show a high concentration of carbide forming elements, which may induce the precipitation of carbides at these locations. These precipitates are usually known as ‘microsegregation carbides’. The tendency to precipitate carbides in the last portions of melt becomes more notable as the amount of carbide forming elements in the alloy increases. As the rate of cooling during solidification increases, the size of the microsegregated regions diminishes, and therefore these are less prone to the presence of ‘microsegregation carbides’. Nevertheless, the tendency to diminish carbide precipitation as the cooling rate increases has a limit. As a result of the increase in cooling rate, solidification of DI may take place fully or partially according to the metastable equilibrium diagram, causing transformation of the melt into ledeburite, a mixture of austenite and iron carbide. Microsegregation carbides are generally present in small amounts, while ledeburitic carbides are usually present in a relatively large quantity. The presence of either type of carbide is detrimental to the quality and properties of DI.

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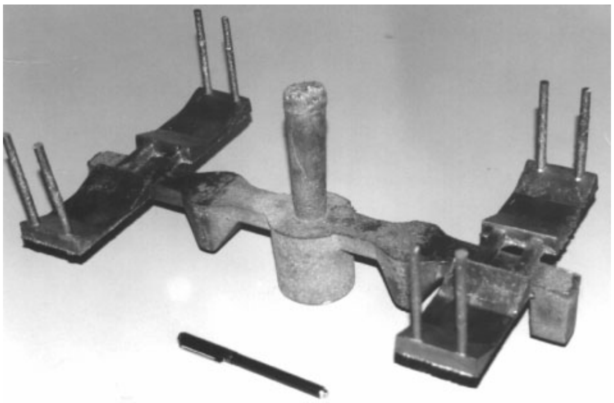


1 Plates of 2, 3 and 4 mm thickness cast using horizontal mould designed earlier[14]

Extensive research efforts have been aimed towards studying the solidification of cast irons according to both stable and metastable equilibrium diagrams.[6–13] Lacaze[11] studied the effects of the microsegregation of silicon on the solidification of DI. He observed that the patterns of distribution of silicon are very different, depending on whether solidification has proceeded according to the stable or the metastable diagram. Irons solidified in part according to the metastable diagram, usually termed mottled irons, show less heterogeneity in silicon distribution. Lacaze *et al.*[12] also studied the chemical composition of ledeburitic carbides precipitated in mottled irons. They found that as the amount of ledeburite increases, the ledeburitic carbides show lower concentrations of carbide forming alloying elements. This is in agreement with the proposal of Giacopini *et al.*[1] These studies suggest that microsegregation in irons solidified as mottled and later subjected to a carbide dissolution heat treatment will be less intense than that found in irons solidified according to the stable equilibrium diagram. Of course, this will be only applicable if the carbides can be effectively dissolved by heat treatment.

The precipitation of carbides in white and mottled irons has been analysed by Gundlach *et al.*,[6] Nastac and Stefanescu[9] and Zhao and Liu.[10] They propose that a fully white microstructure will show the presence of only ledeburitic carbides, while mottled irons will show both microsegregated and ledeburitic carbides. If this is the case, the dissolution behaviour of both types of carbides may be different, as microsegregated carbides will exhibit a higher content of carbide stabilising elements, and thus will be more stable.

The objective of the present study is to assess the feasibility of achieving carbide free microstructures in low alloy TWDI after carbide dissolution heat treatments. The efficiency of dissolution heat treatments is analysed and related to the chemical composition of the carbides.

Table 1 Chemical composition* of melts, wt-%

Melt†	C	Si	Mn	Cr	Mo	Mg	CE	Fe
LA	3·62	3·21	0·72	0·37	0·38	0·066	4·69	Bal.
UA	3·60	3·02	0·23	···	···	0·036	4·60	Bal.

*CE is carbon equivalent.
†LA is low alloy, UA is unalloyed.

Experimental methods

Melts were prepared in a medium frequency induction furnace of 50 kg capacity. They were superheated to 1540°C before tapping. Nodularisation was carried out using the sandwich method and 1·5% of Fe–Si–Mg (6%Mg). The melts were inoculated with 0·6% Fe–Si (75%Si) in stream.

Experimental castings included plates of 2, 3 and 4 mm thickness, shown in Fig. 1, that were cast using a mould designed earlier,[14] and Y blocks of 13 and 25 mm thickness (ASTM standard A395).

The chemical composition of the melts is listed in Table 1. The melts were hypereutectic to obtain the castability required to fill the thin wall moulds. Melt LA (low alloy) showed significant amounts of carbide stabilising elements, such as manganese, chromium and molybdenum. This alloy was not designed for industrial application. The level of alloying was chosen deliberately to accentuate any detrimental effect caused by the carbide stabilising elements.

Small specimens were cut from plates and Y blocks of every section of melt LA. Several sets of specimens were prepared. All sets included one specimen of each thickness. Various annealing treatments were carried out on the sets, consisting of austenitising stages at different temperatures and times, followed by water quenching. These treatments were carried out in a high carbon potential enclosure, to prevent decarburisation. Graphite and carbides were measured and characterised using routines developed for Image Pro Plus software. The nodule count was measured on unetched polished specimens, while the amount of carbides was measured on specimens etched with ammonium persulphate (10%). Reported values are the average of at least five fields.

The chemical composition of the carbides was measured in specimens of melt LA as cast, using a microprobe. Reported concentrations of silicon, manganese, chromium and molybdenum are the average of at least four readings on each specimen.

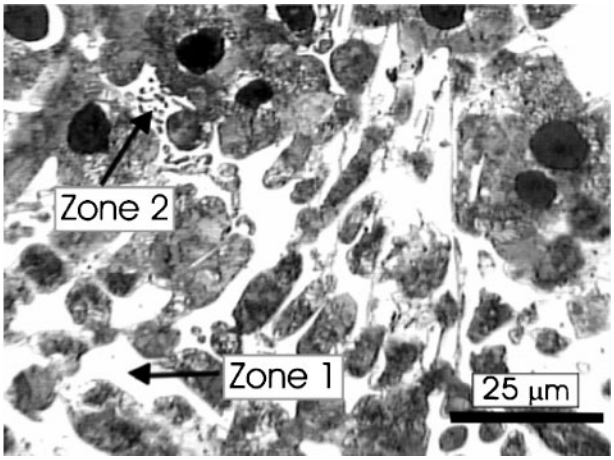
Sets of specimens were ferritised by annealing at 900°C for 3 h, followed by a cooling stage in the furnace down to 700°C, where they were held for 1 h, and later cooled to room temperature in the furnace. This heat treatment led to practically fully ferritic matrixes. These specimens were used to identify the microsegregation patterns by applying a colour metallography technique developed earlier.[15]

Results and discussion

Table 2 lists the microstructural characteristics of specimens of melt LA as cast. The results show that as the thickness of the plates increases, which involves a decrease in cooling rate, both the amount of carbides and the nodule count diminish. The thin wall specimens

Table 2 Microstructural characterisation of melt LA

Thickness, mm	Nodule count, mm^{-2}	Carbide content, %
2	1148	30
3	896	24
4	758	19
13	328	1·6
25	161	2

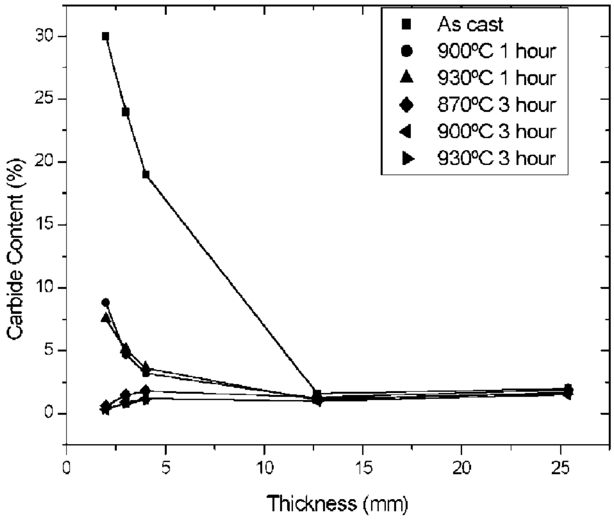


2 Microstructure of 2 mm thickness specimen of melt LA (low alloy) as cast: zone 1 plate shaped carbides, zone 2 ledeburitic carbides

(thickness from 2 to 4 mm) exhibit carbide contents an order of magnitude larger than those found in the thicker specimens. Additionally, nodule counts are 2–3 times greater for the thinner specimens.

Figure 2 shows the microstructure of a 2 mm thickness specimen of melt LA as cast. Although the morphology of the carbides is quite irregular and complex, two distinctive shapes can be identified: plates, marked as zone 1 in Fig. 2; and ledeburitic shapes, marked as zone 2. These carbide morphologies were found in all specimens of thin wall. Gundlach *et al.*,[6] Nastac and Stefanescu[9] and Zhao and Liu[10] have proposed that both ledeburitic and microsegregation carbides may be present in mottled ductile iron. If this is the case in the present specimens, the chemical composition of the two types of carbides could be different. As a result, their dissolution rates could also be different. Therefore, it becomes relevant to characterise the chemical composition of both types of carbides observed in the specimens. Table 3 lists the chemical composition measured for carbides of zone 1 and zone 2 of thin wall specimens of melt LA. For specimens of the same thickness, differences in chemical composition were small, and judged to be irrelevant. This suggests that both carbide morphologies are formed from the same melt, and should show similar dissolution behaviour. This is further supported by the observation that portions of the matrix that were free from carbides showed dendritic morphology, while carbides were always precipitated at the interdendritic regions. This indicates that, in the present case, all carbides originated from the interdendritic melt.

Table 4 lists the average concentration of alloying elements in the as cast carbides for specimens of different thickness of melt LA. As the content of



3 Carbide content as function of section size for specimens of melt LA as cast and heat treated

carbides in the thin wall specimens increases, the concentration of carbide stabilising elements in the carbide phase diminishes. This is in agreement with the reports of Lacaze *et al.*[12] The magnitude of the change in concentration of alloying elements is significant. For example, the 4 mm specimens exhibit carbides that have 56% more chromium and 150% more molybdenum than those of the 2 mm specimens. It is also important to note that, in contrast to carbides in the thin wall specimens, those present in specimens from the 13 and 25 mm Y blocks are microsegregation carbides. This may also indicate that different types of carbides are being formed. As a result, these thicker specimens show concentrations of chromium about one order of magnitude greater than those of the thin specimens, and concentrations of molybdenum two orders of magnitude greater, in agreement with the results of other authors.[4,5]

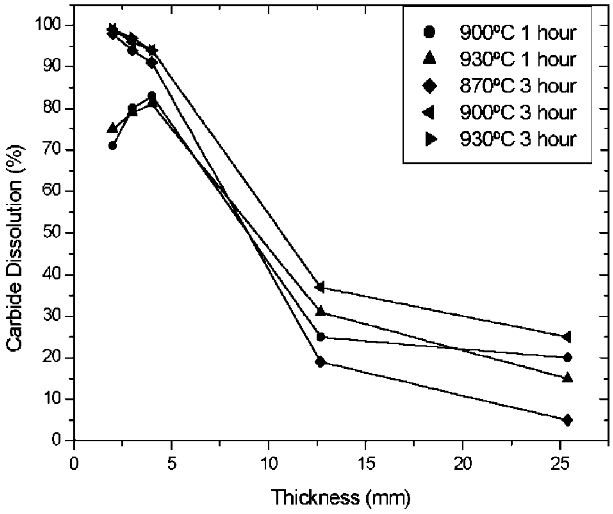
Figure 3 shows the amount of carbides as a function of the section size, for specimens of melt LA as cast, and specimens that underwent dissolution treatments. Figure 4 shows the fraction of carbides dissolved by the heat treatment cycles. The dissolution treatments carried out at 900 and 930°C for 1 h caused the dissolution of ~80% of the large amount of carbides present as cast in the thin wall specimens. Meanwhile, the same heat treatment caused the dissolution of only 25% of the smaller amount of carbides precipitated in the Y block specimens. As the holding time at the dissolution temperature was extended to 3 h, practically all carbides present in the 2 mm specimens were dissolved, while small amounts remained in the 3 and 4 mm specimens, as well as in the thicker specimens. The results show that for the 3 h holding time, advanced

Table 3 Average chemical composition of carbides in zones 1 and 2 measured in melt LA as cast, wt-%

Thickness, mm	Zone 1				Zone 2			
	Si	Mn	Cr	Mo	Si	Mn	Cr	Mo
2	0·77	1·27	0·78	<0·3	0·31	1·52	1·04	<0·3
3	0·69	1·39	0·97	0·68	0·51	1·6	1·11	0·78
4	0·6	1·88	1·51	0·77	0·49	1·66	1·34	0·74

Table 4 Average composition of as cast carbides of melt LA, wt-%

Thickness, mm	Si	Mn	Cr	Mo
2	0·54	1·39	0·91	<0·30
3	0·60	1·49	1·04	0·73
4	0·54	1·77	1·42	0·76
13	0·91	1·92	5·14	45·0
25	0·85	1·99	6·25	49·8



4 Fraction of carbides dissolved by heat treatment cycles for specimens of melt LA

dissolution exceeded 90% for the thin wall specimens, while it was below 30% for the thicker Y block specimens.

The chemical composition and relative stability of the carbides can be explained as follows. The observed increase in concentration of carbide stabilising elements in the carbides as the thickness of the casting increases is caused by the concentration of alloying elements in the melt that originates the carbides. The solidification of cast iron initiates with the precipitation of austenite dendrites and graphite; later, as a result of the fast cooling rates imposed on thin wall castings during solidification, the supercooling increases, causing the remaining melt, which is fairly enriched in alloying elements that segregate to the liquid, to solidify according to the metastable eutectic system, resulting in the formation of interdendritic ledeburitic carbides. As the size of the section increases, the cooling rate decreases and the transition from stable to metastable solidification takes place at a later stage of solidification. Therefore, smaller amounts of ledeburite are present. Nevertheless, carbides in this ledeburite are formed from remaining melt that has a larger concentration of carbide stabilising elements, causing them to be more alloyed and more stable. A further decrease in the cooling rate will lead to a solidification process that takes place almost entirely in accord with the stable equilibrium diagram. For the alloy used in the present study, which has relatively large amounts of carbide stabilising elements, microsegregation carbides are present in the very last portions of melt to solidify. This very last melt is highly concentrated in chromium, molybdenum and manganese, and will therefore originate a small amount of alloyed carbides which are more stable and difficult to dissolve than the ledeburitic carbides precipitated in the thin wall specimens. An additional factor that helps to accelerate carbide dissolution in the thin wall specimens is the high nodule count.[1,16] Graphite nodules act as carbon sinks during carbide dissolution. As the graphite count increases, the average distance between nodules diminishes, facilitating carbon migration from the carbides to the nodules.

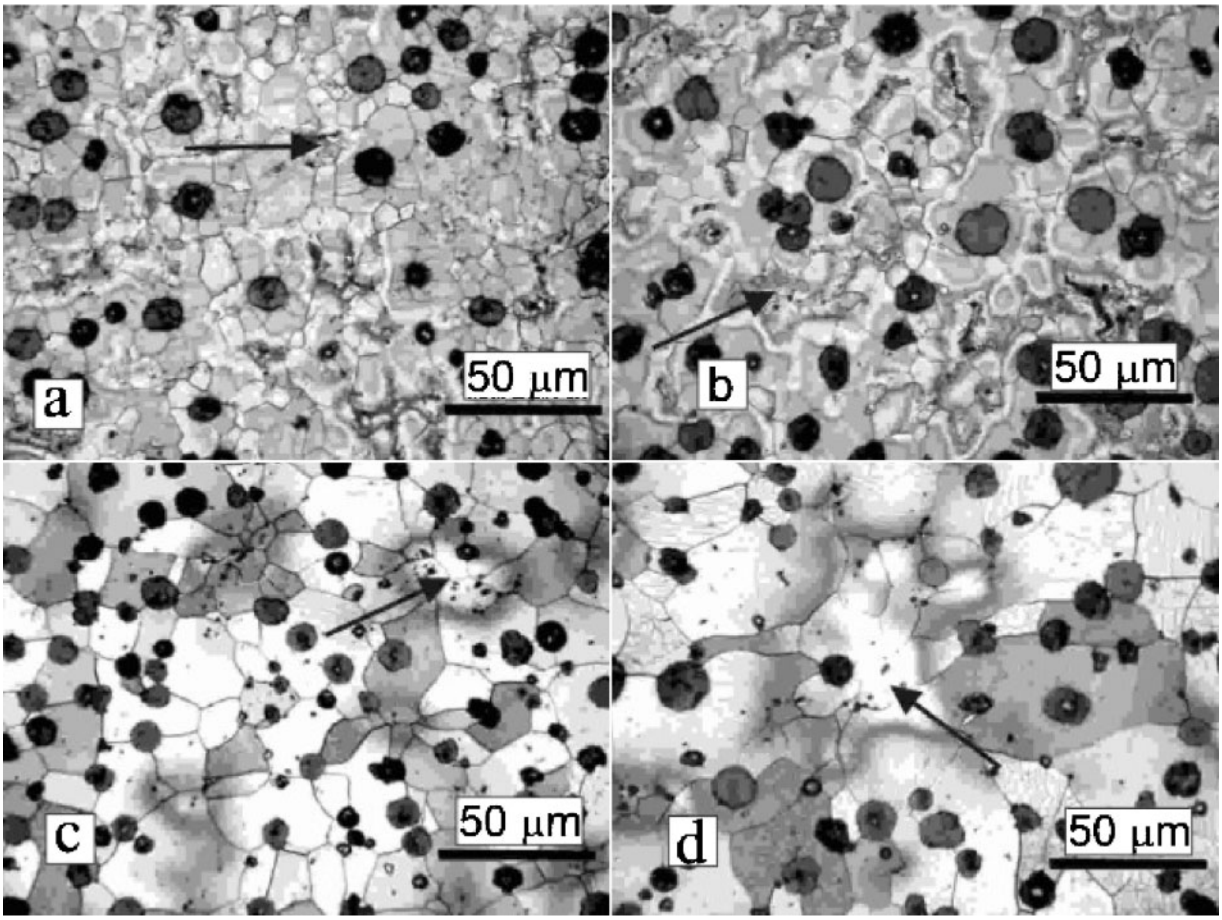
The results of the present study demonstrate that large amounts of carbides present in low alloy thin wall DI parts can be dissolved by heat treatment. The next step is to characterise the microsegregation pattern for the low alloy TWDI specimens that were heat treated to dissolve carbides, and to compare it with the pattern found in unalloyed TWDI specimens that were free from carbides as cast. The pattern of microsegregation in the different specimens was revealed by colour etching of ferritised specimens. Earlier work has shown that the colour etching technique reveals microsegregation patterns qualitatively.[15] The last regions to solidify are highlighted by the etching. These regions show the highest concentration of carbide forming alloying elements, such as chromium, molybdenum and manganese, and the lowest concentration of silicon, copper and nickel.[15] Figure 5*a* and *b* shows, in monochrome, the results of colour etching 2 and 4 mm thickness plates of melt LA. Figure 5*c* and *d* shows a typical microsegregation pattern of melt UA (unalloyed) in cast plates of 2 and 4 mm thickness. The highly microsegregated portions of the matrix appear as light grey patches (marked by arrows) in Fig. 5. Microsegregation is more notable and coarser in the unalloyed specimens. This indicates that, as predicted, TWDI specimens that solidify as mottled and are heat treated to dissolve the carbides show a greater degree of homogeneity than specimens of the same dimensions that are free from carbides as cast.

The present study has shown that even for ductile iron alloys having low contents of chromium, molybdenum and manganese, the carbides precipitated in thin wall parts can be successfully dissolved by heat treatment. The study does not attempt to recommend the use of alloying elements in TWDI unless necessary. The results of the present study also indicate that, in those cases in which TWDI parts are to be heat treated, the chemical composition of the melt may include relatively large amounts of carbide formers. This decreases restrictions on the use of scrap and returns in the furnace charge. Additionally, the study has shown that the presence of large amounts of carbides in the as cast microstructure is not necessarily a reason for rejection. These two factors may involve reductions in the cost associated with the production of TWDI.

Future studies will aim to compare the mechanical properties of TWDI plates obtained after carbide dissolution heat treatments with those of plates that are free from carbides as cast. It is foreseen that the material cast with a mottled microstructure will show better mechanical properties after dissolution heat treatment owing to its more homogeneous matrix. A more homogeneous matrix should also contribute to obtaining a better response to strengthening heat treatments, such as austempering.

Conclusions

A hypereutectic ductile iron containing 0·37%Cr, 0·38%Mo and 0·72%Mn was cast as thin wall plates and 13 and 25 mm Y blocks. With this composition, plates of 2 mm exhibited 30% carbides, while the amount of carbides decreased as the thickness of the thin plates increased, reaching 19% carbides for plates of 4 mm. The 13 and 25 mm Y blocks exhibited ~2% carbides.



a 2 mm, LA; *b* 4 mm, LA; *c* 2 mm, UA; *d* 4 mm, UA

5 Results of colour etching for low alloy (LA) and unalloyed (UA) plates of given thickness

Dissolution heat treatments carried out at temperatures between 870 and 930°C caused the dissolution of more than 90% of the carbides present in thin wall specimens as cast, while the extent of dissolution was lower than 30% for 13 and 25 mm Y blocks.

Energy dispersive X-ray microanalysis showed that carbides precipitated during solidification had higher contents of carbide stabilising elements as the cooling rate during solidification diminished. This caused the higher stability observed for carbides formed in the Y blocks.

The results suggest that in those cases in which TWDI parts are to be heat treated involving austenitisation, the presence of relatively large amounts of carbide stabilising elements can be acceptable. In addition, large amounts of carbides can be tolerated in the original casting, since these can be dissolved by heat treatment.

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