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A. Giacopini, R. E. Boeri and J. A. Sikora

This investigation focuses on the study of the dissolution by annealing of carbides present in thin walled ductile iron parts. Ledeburitic carbides are usually present in the microstructure as a consequence of the rapid solidification rate induced by the small thickness. The dissolution treatment is carried out by annealing in the austenitising temperature range. The study involves unalloyed ductile irons of different equivalent carbon values that show initial amounts of free carbides that reach 40%. The results show that even very large amounts of cementite can be rapidly and easily dissolved by annealing. The dissolution rate ranges between 2 and 9% per minute. This dissolution rate is much faster than that expected from the literature data and is attributed to the particular characteristics of thin wall castings, such as the low concentration of carbide stabilising elements and the small distance for diffusion of carbon from the cementite to the nodules. The short time required for carbide dissolution implies that carbides can be completely dissolved during the austenitisation stage of many practical heat treatment cycles. MST/5751

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Introduction

Ductile irons (DI) are a family of cast alloys that cover a wide range of mechanical properties. They have been used to replace cast and forged steels in a large number of applications, with economic advantages. Therefore, the production of DI has shown a sustained rate of growth over the last three decades. Currently, DI producers continue to seek new applications. In particular, recent efforts have been aimed at introducing DI castings into the light parts market. Light parts are mostly used in vehicles, and are customarily made of low density metallic alloys or reinforced polymers. DI is not a light metallic alloy. Nevertheless, some DI grades have strength to density and elastic modulus to density ratios that approach those of cast aluminium, making it theoretically possible to apply DI in light parts.

To make full use of the comparative advantages of DI (greater stiffness and strength) parts must be light, and therefore they should have thin walls. Current technologies allow the production of sound DI parts of thickness greater than 5 mm. The production of thinner parts is limited by several restrictions. As for all grey irons, the DI microstructure is affected by the cooling rate during solidification. Larger cooling rates promote the precipitation of eutectic ledeburite, consisting of cementite and austenite. The presence of cementite in the matrix microstructure is strongly detrimental to DI mechanical properties and processing.[1] The castability of DI also becomes relevant as the wall thickness of the casting diminishes. Castability can be increased by using a higher carbon equivalent, and by increasing the pouring temperature. Moulding techniques are also of concern since, in some cases, existing moulding methodologies cannot satisfy the strict dimensional tolerances required to produce moulds for thin wall parts.

This investigation focuses on the production of irons free from ledeburitic cementite. There are two different approaches to obtain cementite free thin wall parts. The first approach would be to avoid cementite precipitation during solidification. This can be achieved by increasing the contents of Si and C, and by maximising the efficiency of inoculation. The increase in the C and Si contents changes DI into a hypereutectic composition, and improves its fluidity. On the other hand, the use of high Si reduces toughness, raises the brittle fracture transition temperature, and reduces thermal conductivity. The second approach would be to eliminate the cementite precipitated during solidification by means of a dissolution heat treatment. This second approach has not been sufficiently investigated yet, to the best of our knowledge. The conventional technical information states that once precipitated, cementite is difficult to dissolve by heat treating, requiring long holding periods at relatively high temperatures. In fact, the malleabilisation process used to dissolve carbides in white cast irons, involves the annealing of parts for periods up to 24 h, at temperatures ranging from 850 to 950 C.[2] Furthermore, the heat treatment recommended to dissolve solidification carbides in unalloyed and low alloyed ductile irons parts, involves annealing for at least 2 h at 900 C.[3–5] The relatively long time at temperature required for dissolution would indicate that this approach could not be efficiently applied industrially.

CEMENTITE FORMATION IN DI SOLIDIFICATION

Both kinetic and thermodynamic factors can influence cementite formation during DI solidification.[2] Fast cooling rates increase eutectic undercooling and may cause the formation of white or mottled iron, while slow cooling favours graphite precipitation. Thermodynamic factors are related to the influence of alloying elements and its microsegregation. Graphitising elements, such as Si and Ni, increase the gap between stable and metastable eutectic temperatures, reducing the tendency to precipitate ledeburite. On the other hand, carbide forming elements (Cr, Mo, Mn, V, Ti), reduce the temperature gap and favour cementite precipitation.[2] The influence of alloying elements on the precipitation of free carbides is further enhanced by microsegregation. As solidification advances, the remaining melt becomes enriched in carbide stabilising alloy elements, and impoverished in graphite forming elements.[6–8] This greatly increases the tendency to precipitate cementite at the later stages of solidification. When cementite precipitation takes place in the very last portions of melt to freeze, the precipitates are usually called intercellular carbides. Therefore, strategies to minimise carbide precipitation involve the control of DI chemical composition, reducing the content of carbide formers to a minimum. Additionally, carbide precipitation can be reduced by improving the efficiency of inoculation, which leads to finer solidification microstructures, characterised by more dispersed microsegregation,

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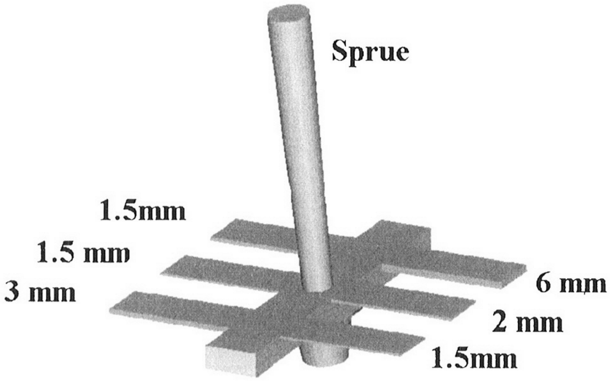


1 Experimental casting pattern, showing thin wall sections

shorter diffusion distances, and greater graphite nodule counts.

In the case of thin wall DI, the fast solidification rate imposed during solidification is the major factor promoting carbide precipitation. Nevertheless, the high solidification rate also causes favourable effects, since the solidification microstructure becomes refined as the solidification rate increases, leading to higher nodule counts and reduced microsegregation. Additionally, DI used to produce thin wall parts is generally unalloyed. The absence of significant amounts of carbide formers prevents the precipitation of the more stable alloyed carbides. Under these circumstances, characterised by the presence of a fine microstructure and the absence of alloyed carbides, the dissolution of carbides by annealing appears to be easier to attain than in conventional DI.

The objective of this investigation is to study the dissolution of carbides precipitated in thin wall unalloyed DI plates cast in sand moulds, during the austenitising step of heat treatment cycles.

Experimental

Thin wall plates were cast using the pattern shown in Fig. 1.[9] Six plates 120 × 40 mm were obtained from each casting. The plates were approximately 1·5, 2, 3 and 6 mm thick. Moulds were made of alkydic resin bonded silica sand (AFS GPN 62). Inner mould surfaces were coated with graphite paint to improve the casting surface finish. Melts were produced in a pilot plant, using a 55 kg capacity medium frequency induction furnace. The charge was made of pig iron, foundry returns, steel scrap, and ferroalloys. The melts were nodularised by using 1·4% wt-%FeSiMg (6%) and inoculated with 0·8%FeSi(75%). The chemical compositions of all melts investigated are listed in Table 1.

Cementite dissolution heat treatments were carried out in a low vacuum enclosure to prevent sample oxidation and extensive decarburisation. Five sets of samples were prepared. Each set was composed of one sample from each melt and thickness, and having dimensions approximately 10 × 8 mm. Only samples exhibiting some cementite content as cast were included. Each set of samples was placed in a quartz tube that was evacuated and closed. All sets were introduced simultaneously into a furnace held at the selected austenitising temperature, and were later removed from the furnace one by one after specified periods of time.

Table 1 Chemical composition of alloys wt-%. (trace elements in all alloys: Mo<0·006, Cr<0·037, Ni<0·018, Cu<0·035.)

Melt	C	Si	Mn	S	P	Mg
A	3·15	2·05	0·19	0·015	0·051	0·037
B	3·40	2·70	0·35	0·025	0·046	0·070
C	3·45	2·91	0·22	0·011	0·044	0·034
D	3·31	4·42	0·23	0·014	0·051	0·046

Preliminary tests were carried out in order to identify the proper annealing (or austenitising) temperature and range of holding times to be investigated. Austenitising temperatures of 850, 900, and 950°C were used. The lower temperature was insufficient to produce full austenitisation of the hypereutectic DI. The dissolution rate was fast at both 900 and 950°C. Therefore annealing tests were carried out at 900°C.

The heating of samples inside the quartz tube after they were placed into the furnace preheated to 900°C was recorded using a thermocouple carefully located at the centre of the set of samples, to make sure that the temperature recorded was that of the coldest point of the assembly. The time necessary for the load to reach the austenitising temperature was 2·5 min. As a consequence, 3·5 min was the minimum holding time used, which in fact means an actual holding time of 1 min. Therefore, the effective holding times were as follows: 1, 2, 4, 8, 16 and 24 min. Samples were rapidly cooled to room temperature after the desired holding time had been completed by quenching in water after breaking the quartz tube.

After heat treatment, samples were surface ground and polished metallographically.

Microstructure characterisation was aided by the use of the Image Pro Plus software. The nodule count was measured on unetched samples, while the amount of cementite was measured after etching with ammonia persulphate (10%). The reported values of nodule count and carbide content are the averages of at least five readings on each sample, at × 100 magnification.

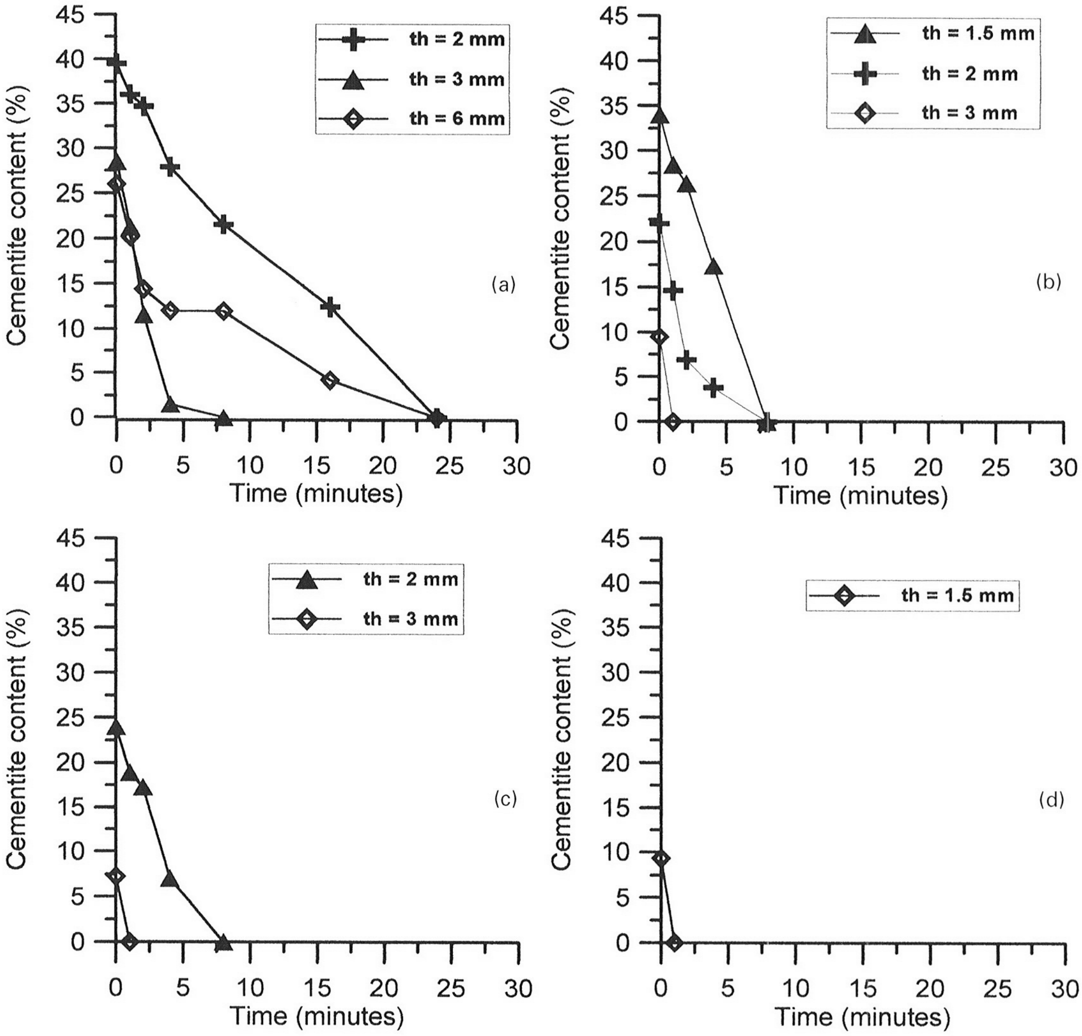
Results and discussion

Table 2 lists the as cast characteristics of all samples, including the nodule count and cementite amount. As expected, the lower the carbon equivalent of the alloy, the greater the amount of cementite present. The thinner samples of the lower carbon equivalent melt A showed approximately 40% cementite. The higher Si hypereutectic melt D, on the other hand, showed only 9% cementite in the 1·5 mm thick section, while the 2 mm plates of this melt were free from cementite.

The change in the amount of cementite as a function of annealing time for all the studied samples is shown in Fig. 2*a*–*d*.

Table 2 Carbon equivalent (CE), thickness, nodule count and cementite content (as cast), for all samples

Melt	CE, %	Thickness, mm	Nodule count, nod mm^{-2}	Cementite, %
A	3·83	6·0	495	23·0
		3·0	541	28·5
		2·0	505	39·5
B	4·3	6·0	588	0
		3·0	1039	9·0
		2·0	1380	24·0
		1·5	1311	34·0
C	4·42	6·0	854	0
		3·0	1037	7·3
		2·0	1100	24·0
D	4·78	6·0	1127	0
		3·0	1726	0
		2·0	1890	0
		1·5	2027	9·3



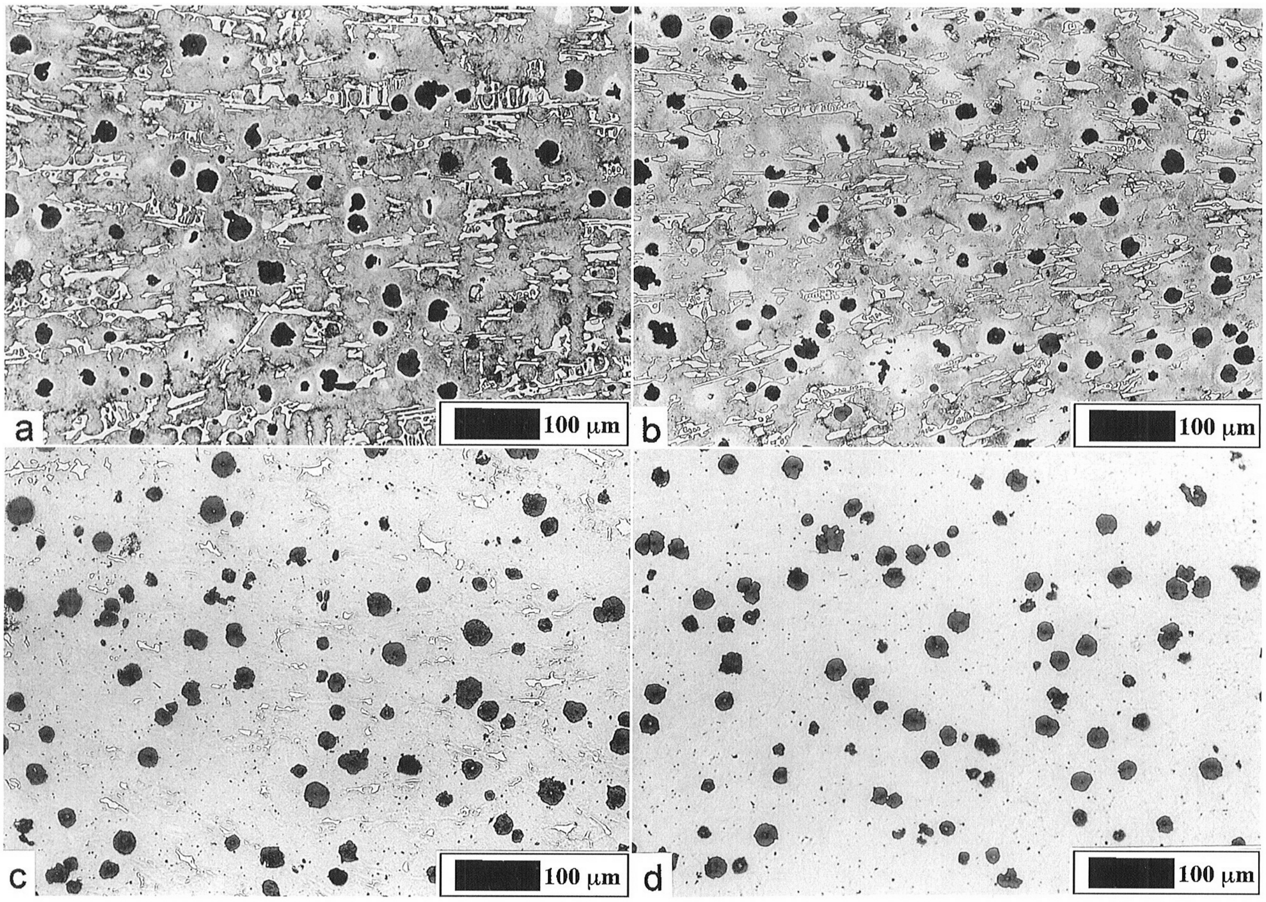
a melt A; *b* melt B; *c* melt C; *d* melt D

2 Change in the amount of cementite as a function of holding time at annealing temperature

Figure 3 exemplifies the sequence of cementite dissolution as a function of annealing time, for the 6 mm thick plate of melt A. This hypoeutectic sample was chosen since it shows a slower dissolution rate, allowing the process to be observed in detail. Cementite dissolves progressively. Rounding of the particles was not marked.

The rate of carbide dissolution was very fast, and for all cases the dissolution was completed after much shorter periods than estimated on the basis of literature recommendations.[3–5] For example, the 2 mm thick sample of hypoeutectic melt A, that showed the highest initial cementite content of all samples (39·5%), became free from cementite after a holding time of only 24 min. These dissolution rates are much faster than values given in the literature. Galarreta *et al.*[10] reported that a heat treatment cycle involving an austenitising step at 910°C for 60 min was insufficient to dissolve 2% of free carbides present in samples taken from a 1 inch 'Y' block of a low alloyed ductile iron casting. The chemical composition (wt-%) of the melt was: C=3·15, Si=2·63, Mn=0·96, Cu=0·88, Cr=0·27, Mg=0·04, S=0·017 and P=0·004 and the free carbides were located at the last to freeze zones.[10]

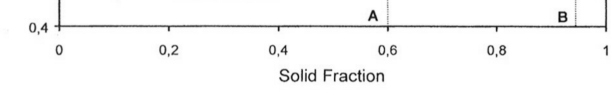
The very fast rate of dissolution of carbides observed in the thin wall plates, as compared to the dissolution of small amounts of carbides in regular thickness castings, may result from the contribution of a number of factors. The cementite in the thin samples used in this study, even when present in large amounts, was not heavily alloyed. This is not the case for regular alloys obtained after solidification in relatively thicker sections, where the small amounts of carbides precipitated in the last to freeze regions commonly show high levels of carbide stabilising alloying elements. This is explained schematically in Fig. 4. It has been shown that the microsegregation in DI can be represented with good approximation by Scheil's equation and using measured partition coefficients.[6,7] Figure 4 shows the prediction of the solute concentration of a given solute element in austenite as the solidification advances, based on Scheil's equation, and assuming that the average concentration of the solute is 1 wt-%, and its effective partition coefficient is 0·7. The concentration of solute in the remaining melt can be calculated, for a given solid fraction, as the ratio of the solute content in the austenite over the partition coefficient. This gives a good approximation when the solidification proceeds according to the stable equilibrium. In some cases, when the rate of heat extraction is large, solidification can initiate according to the stable equilibrium diagram, but it may later change to metastable solidification, as a result of the supercooling of the remaining melt. This is typical in mottled irons, where solidification initiates following the stable diagram, but finishes according to the metastable diagram. When this transition from stable to metastable solidification takes place in DI, the remaining melt transforms into ledeburite. If this transition takes place early during solidification, as indicated by point of solid fraction A in Fig. 4, the average content of carbide stabilising solute



a as cast; *b* 4 min; *c* 16 min; *d* 24 min

3 Micrographs showing advance of carbide dissolution as a function of annealing time at 900°C, of a melt A 6mm plate

elements in the melt at that moment is small, as indicated by C1, and the resulting ledeburitic carbides will not be heavily alloyed. On the other hand, if the imposed solidification conditions allow the solidification to proceed according to the stable equilibrium up to the point where most liquid has disappeared, as indicated by point B in Fig. 4, the remaining melt will be highly enriched in carbide stabilising elements, as shown by point C2. As this solute rich melt turns into ledeburite, highly alloyed cementite forms. This alloyed cementite has a lower free energy than unalloyed cementite, and is therefore much more difficult to dissolve by annealing.



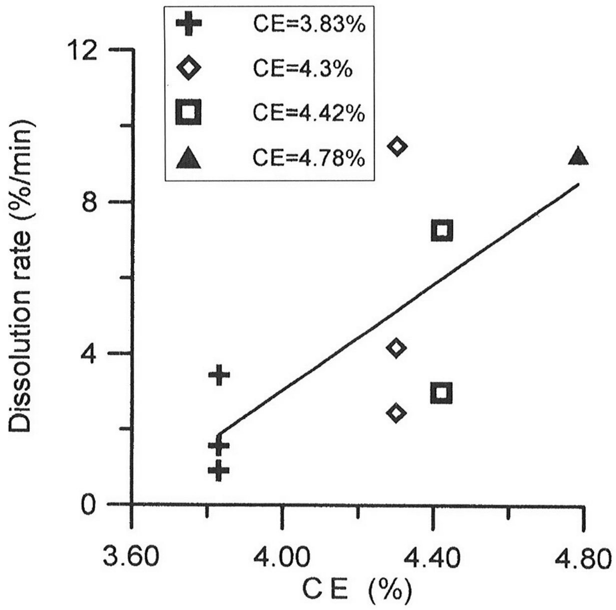
4 Prediction of solute concentration in the solid as a function of the solid fraction, according to Scheil's equation. Points C1 and C2 show the average solute concentration in the melt after solidification has advanced to solid fractions A and B respectively

The particular characteristics of the microstructure of rapidly solidified DI can also favour the cementite dissolution during annealing. In fact, rapidly solidified DI shows higher nodule count and finer or more dispersed ledeburitic regions than DI solidified at a normal rate. Graphite particles act as carbon sinks during annealing. A large nodule count will decrease the distance for diffusion of the C from the cementite to the nodules, increasing the graphitisation rate.[8]

The rate of dissolution of cementite R_d was calculated as the absolute value of the slope of the best fit straight line obtained for each dissolution experiment. The values of R_d were plotted as function of chemical and microstructural characteristics of the samples investigated, in order to identify whether some of these features play a major role in controlling the dissolution process. Figs. 5 to 7 show R_d as a function of carbon equivalent (CE), nodule count, and as cast cementite content, respectively. Figure 5 shows that R_d values are scattered, ranging approximately between 1 and 9% min^{-1}. In particular, near eutectic and hypereutectic alloys show dissolution rates larger than 2% min^{-1}. The number of experimental points decreases as CE increases, since higher CE melts only show carbides at the thinner wall samples. Therefore, the value of R_d listed for melt D (CE: 4·78%) is conservative and the actual dissolution rate may be greater.

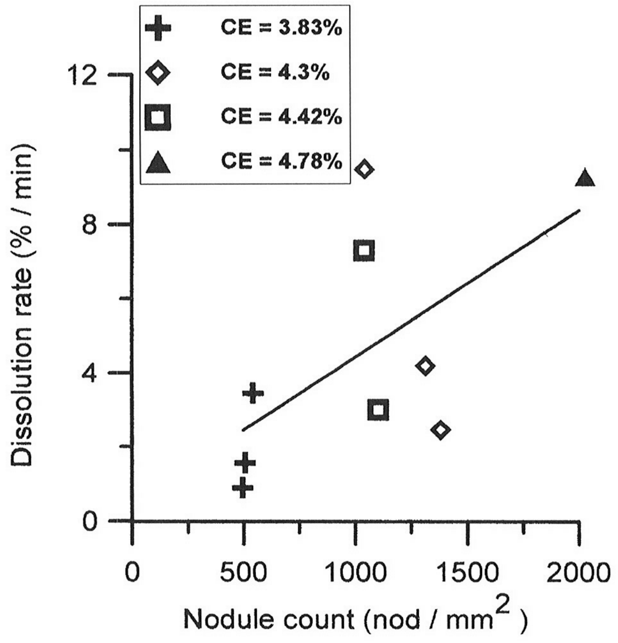
Figure 6 shows that, similar to the effect of CE, an increase in nodule count causes an increase in R_d. On the other hand, Fig. 7 shows that an increase in the amount of as cast cementite causes a noticeable decrease in R_d.

Based on the results shown in Figs. 5 to 7 , it is not possible to ascertain which of the factors is in fact controlling the dissolution process. Nevertheless, it has been

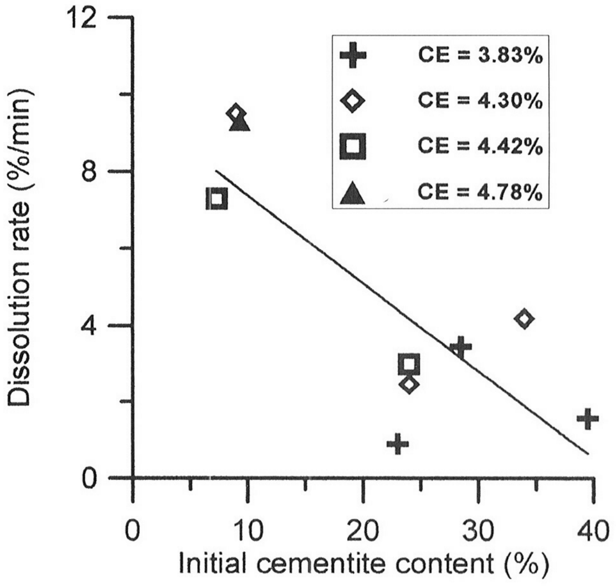


5 Change of dissolution rate as a function of CE

clearly shown that carbide dissolution is favoured by high nodule counts and elevated carbon equivalent. Dissolution takes place rapidly at a temperature of 900°C, in all cases. The high dissolution rate suggests that any regular austenitising cycle, which usually involve holding periods greater than 30 min, will lead to the complete dissolution of carbides present in thin wall unalloyed DI parts. For example, regular heat treatments, such as supercritical ferritising, normalising, quenching, or austempering, can be carried out on cementite containing thin wall DI parts without any special care. This result suggests that the production of thin wall DI parts does not necessarily require processes to be developed to obtain carbide free parts in the as cast condition, but could make use of the austenitising step to dissolve as cast carbides.



6 Change of dissolution rate as a function of nodule count



7 Change of dissolution rate as a function of as cast cementite content

Conclusions

1. Cementite, precipitated due to rapid solidification in thin wall unalloyed ductile iron parts, dissolves rapidly at austenitising temperatures.

2. Cementite dissolution rates have been measured and range between approximately 2 and 9% min^{-1}.

3. The kinetics of cementite dissolution in thin wall unalloyed DI are much faster than the values expected from recommendations in the literature.

4. The very fast rate of dissolution of carbides observed in the thin wall plates, may result from the contribution of a number of factors: (a) when a large amount of cementite is formed, its concentration of carbide stabilising elements is very small; (b) rapidly solidified DI shows higher nodule count and finer ledeburite than the material solidified at a regular rate. A large nodule count decreases the distance for diffusion of the C from the cementite to the nodules; (c) Smaller cementite volumes will disappear more rapidly during annealing. Nevertheless, the results of this study do not allow the principal factor controlling dissolution to be identified.

5. The short time required for carbide dissolution implies that, for practical heat treatment cycles involving austenitisation, cementite will dissolve fully during the high temperature holding stage.

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