Heterogeneous Nuclei and Graphite Chemistry in Flake and Nodular Cast Irons

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Nodular and flake graphite have been extracted from commercial cast irons and studied by a variety of techniques, including high voltage transmission electron microscopy. For nodular graphite the nuclei are (in these cast irons at least) 2 to 5 μm diam spherical particles of primarily CeO_2, MgO, and Fe_2O_3. In addition the nuclei contain variously Ca, Al, P, S, and Si. The composition of the nuclei is highly variable, presumably due to the highly nonequilibrium conditions under which they are formed. For flake graphite the nuclei are apparently sulfide particles, again of variable composition. They are spherical and approximately the same diameter as the nodular nuclei. Moreover, chemical analysis of flake and nodular graphites shows that there is a relatively high concentration of oxygen in solution in flake graphite but not in nodular graphite, which suggests oxygen is a growth modifier.

GRAPHITE nucleation and growth in cast irons has been the focus of an enormous amount of research in the past three decades.[1] But the physical phenomena associated with the morphological control of graphite in cast irons are not yet unambiguously demonstrated. This may be attributed to the experimental problems inherent in cast iron work, where high temperatures, complex chemistry, and intervening solid state reactions make explicit nucleation and growth data difficult to obtain.

While data on many aspects of cast iron solidification (for example the effects of composition on cooling curves, the effects of inoculants and inoculating practice on nodule counts, or the effects of various deleterious elements, Pb, As, and so forth, on graphite shape) are now abundant some very crucial aspects have scarcely been touched. Two of the latter are the chemistry of the graphite in cast irons and the morphology and chemistry of the heterogeneous nuclei for graphite formation. The heterogeneous nuclei are important because they exert a powerful influence on the solidication of the cast iron, and ultimately on the mechanical properties; this influence is exerted through the number of nucleating centers, *i.e.* the colony or nodule count, and their effect on the undercooling. (Fortunately, this aspect is also one over which the metalcaster has considerable control, as the effectiveness of the various post inoculation treatments demonstrates.) However, it is very unlikely that the heterogeneous nuclei by themselves exert any influence on the final graphite shape, which should be controlled by the graphite growth conditions. It is generally believed, and has been for some time, that growth modifiers are a very important factor in determining the graphite shape; and it is for this reason that the graphite chemistry is of interest, since it is expected that growth modifiers will be incorporated into the graphite lattice. Both of these aspects (nuclei morphology and chemistry and graphite chemistry) of cast iron solidification must be understood in detail before an accurate and full understanding of the mechanisms associated with the morphological control of graphite can be developed.

In recent years there have been several investigations in these areas. Jacobs *et al*[2] attempted to identify nodular graphite nuclei using transmission and scanning electron microscopy coupled with energy dispersive X-ray analysis (EDAX). They found foreign particles at the centers of nodules; these particles contained Mg, Al, Si, S, Ca, and Fe. They also claim to have identified the heterogeneous nuclei for graphite to be a duplex structure with a sulfide core surrounded by an oxide shell. However, they did not clearly establish the particles they identified were graphite nuclei. Lalich and Hitchings[3] used the electron microprobe and the scanning electron microscope to investigate nodular iron graphite nuclei in metallurgical cross-sections. They concluded that in their laboratory nodular irons the nuclei were primarily sulfides (Mg and Ca sulfides or rare-earth sulfides, depending on the type of inoculant), and that in cupola irons the nuclei were probably complex mixtures of sulfides and silicates. Johnson and Smartt[4] studied gray and nodular cast iron fracture surfaces using a scanning Auger microprobe. They report that sulfur and oxygen were adsorbed at graphite/metal interfaces in gray iron but that in nodular cast iron the interfaces were free of foreign elements. The validity of their conclusion, however, suffers from the fact that the graphite/metal interfaces they studied were probably formed *after* solidification, since a considerable amount of graphite precipitation occurs in the solid state in cast irons; and it is reasonable to assume a large portion and probably most of this precipitation occurs on the surfaces of the graphite formed *during* solidification. Nonetheless it is significant that their conclusions agree with those reported here.

The present investigation was designed to identify the heterogeneous nuclei for nodular and flake graphite and to determine as explicitly as possible the elements present and their distribution in the two types of graphite (exclusive of the nuclei). Commercial cast irons were studied because the flake/nodular transition can be induced in cast irons with

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such a variety of compositions, that the general features of the mechanisms of formation must be independent of the exact composition and because commercial cast irons are the ones of ultimate interest. The approach taken here, in contrast to that of most previous workers, was to examine graphite which had been extracted from the matrix, rather than examine graphite in metallurgical cross-sections or fracture surfaces. This approach was selected because it eliminates any possibility of matrix interference with the various chemical analysis techniques, because it permits transmission electron microscopy of the graphite, and because it presents the possibility of an unambiguous isolation of nuclei particles. It does however introduce the problem of chemical interference occuring during the extraction of the graphite. It has been suggested[5] the extraction process may leach out certain constituents of the nuclei or the graphite via graphite grain boundaries or pores. Transmission electron microscopy provided evidence that in the present case this leaching did not occur to a significant extent. This will be discussed fully in the Results section.

EXPERIMENTAL PROCEDURES

Specimens of nodular graphite were taken from three different types of nodular iron castings. One set of specimens came from the flash of a small (<5 kg) casting. This flash is quite uniform in dimensions, with a thickness of about 1.6 mm. The microstructure of the flash consisted of cementite, nodules, ferrite and pearlite. The nodules present in the flash were very small, due to the rapid solidification conditions, with a relatively large fraction of 10 μm diam, and an average diam of about 13 μm (optical measurement of extracted nodules). This set of specimens will be referred to as Small Regular Nodules (SRN). A second set of specimens came from various approximately square casting sections with areas in excess of 400 mm^2 across the sections. Solidification was relatively much slower for this set of specimens and consequently these nodules are larger than the SRN; the smallest nodules here are about 10 μm diameter, the largest about 50 μm, and the average about 22 μm. This set of specimens will be referred to as Large Regular Nodules (LRN). The third set of nodular specimens came from castings of approximately the same section size as the LRN, but are distinguished from the LRN by a different melt chemistry (primarily higher silicon and lower carbon) and have about the same size distribution as LRN. They will be referred to as High Silicon Large Regular Nodules (HSLRN).

Specimens of flake graphite were taken from gray iron castings uniformly ~3 mm thick. The predominant microstructure in these castings is pearlite with mostly type A and some type B graphite. In addition, on one end of the castings, in a region which cools very rapidly, nodular graphite occurs. At the very end of the castings, where cooling is most rapid, the nodules are intermixed with cementite. A small distance in from the end, where cooling is relatively less rapid, the nodules are intermixed with type D graphite. Thus specimens of flake graphite taken from this region of these castings frequently contain nodular graphite, in addition to flake colonies. These nodules will be referred to as Flake Iron Nodules (FIN), and the flake graphite as Flake (F).

The castings from which the specimens were taken were produced in a commercial foundry by standard shell molding techniques. The metal for all three types of castings was produced by induction melting in 227 kg heats.

The regular nodular iron and the high silicon nodular iron (SRN, LRN, and HSLRN graphite samples) were inoculated with 5.9 kg/heat of a rare earth bearing magnesium-ferrosilicon alloy (46 pct Si, 3.5 pct Mg, 2 pct rare earths-primarily Ce) and 1.4 kg/heat of 75 pct ferrosilicon using the pour-over technique. Typical analyzed compositions of the finished castings are 2.7 pct Si, 3.6 pct C, 0.3 pct Mn, 0.3 pct Cu, 0.015 pct S, 0.02 pct P, and 0.03 pct Mg for the regular nodular iron and 4.0 pct Si, 3.2 pct C, the remainder similar, for the high silicon nodular iron.

The flake iron was inoculated with 1.2 kg/heat of Inculoy 63 (Foote Mineral Company Tradename) and 1.4 kg/heat of 75 pct ferrosilicon. Typical analyzed composition of the finished castings is 2.7 pct Si, 3.60 pct C, 0.5 pct Mn, 1 pct Cu, 1 pct Ni, 0.2 pct Cr, 0.1 pct Mo, 0.02 pct S, and 0.02 pct P.

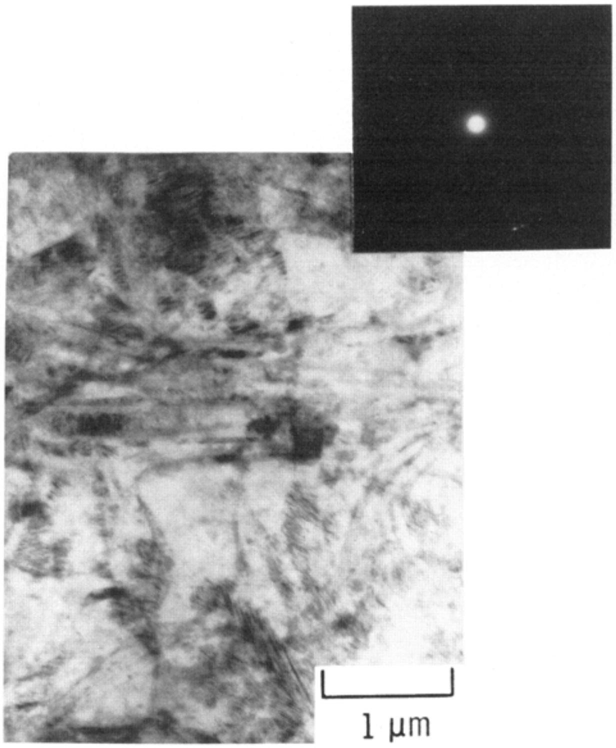
Graphite specimens were extracted from the castings by dissolving the matrix in a concentrated solution of either $H_3PO_4 + H_2O_2$ or $HNO_3 + H_2O_2$ (acid: H_2O_2 about 2 : 1, but not critical). The resulting deposit contained a variety of compounds in addition to graphite. These compounds were dissolved by repeatedly (5 to 15 times) washing the deposit with concentrated HF. In addition repeated washing with concentrated HNO_3 was sometimes necessary. Specimens were washed until visible discoloration of the washing solution ceased to occur. Once the acid wash yielded a colorless solution, specimens were washed several times with distilled water and then with pure ethanol.

A centrifuge was used throughout the washing process to facilitate separation of the graphite from the washing solution. Polypropylene centrifuge tubes were used since the HF reacted with glass tubes and in subsequent washing operations SiO_2 would precipitate.

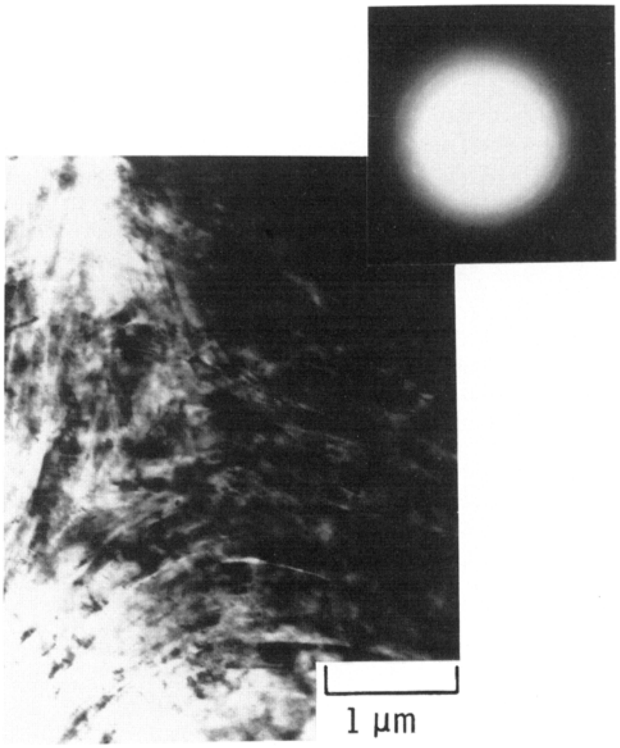
The cleanliness of the first few specimens was very carefully determined by examining the specimens in an optical microscope and in a SEM with the aid of EDAX. A considerable amount of debris was always present even when specimens were "clean." This debris was graphite and probably was exfoliated during the HF wash. X-ray diffraction patterns of samples washed with HF and samples not washed with HF were identical (except for lines due to deposits in the unwashed samples), so the HF wash was not causing major microstructural changes in the graphite. The cleanliness of later samples was checked optically only, with the exception of a few spot checks using SEM and EDAX.

Specimens for TEM were mounted on evaporated carbon films. These films were prepared by first slightly softening replicating tape and then placing a drop of ethanol, with the graphite dispersed in the ethanol, on the softened tape. The tape was then coated with carbon and the carbon films collected by regular techniques. Presoftening of the tape allowed the graphite to partially embed in the tape and ensured good contact with the evaporated film.

Specimens of SRN were also microtomed for subsequent examination by TEM and SEM. These specimens were mounted in Epon epoxy and cut approximately 0.5 μm thick with a diamond knife.

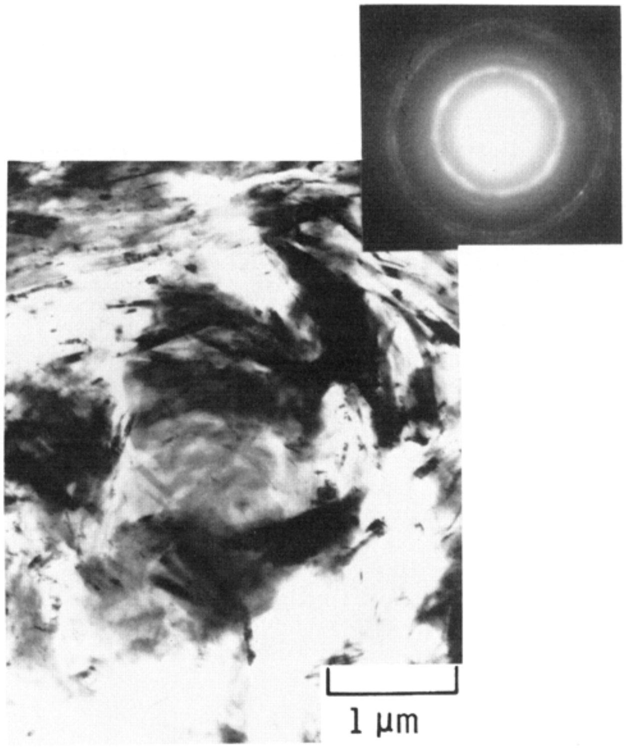


(a)



(b)

Fig. 1—TEM micrographs of flake and nodular graphite: (*a*) Flake graphite characterized by rotation faults, (*b*) Flake graphite with uncharacterized faulting similar to that in (*c*), (*c*) Microtomed nodular graphite with typical faulting.



(c)

All TEM work was at 650 KV accelerating voltage.

X-ray diffraction analysis employed a Debye-Scherrer camera and a Cu tube with a Ni filter, operated at 40 kV and 18 mA.

RESULTS

1. Graphite Microstructure

All of the graphite samples studied were examined for major microstructural differences. No major differences were found. X-ray diffraction analysis showed all samples to be hexagonal graphite (Strukturbericht A9) structure with $a_o = 0.246$ nm and $C_o = 0.670$ nm. LRN and HSLRN samples appeared to have some rhombohedral graphite also present, but in barely detectable amounts ($\lesssim 2$ pct).

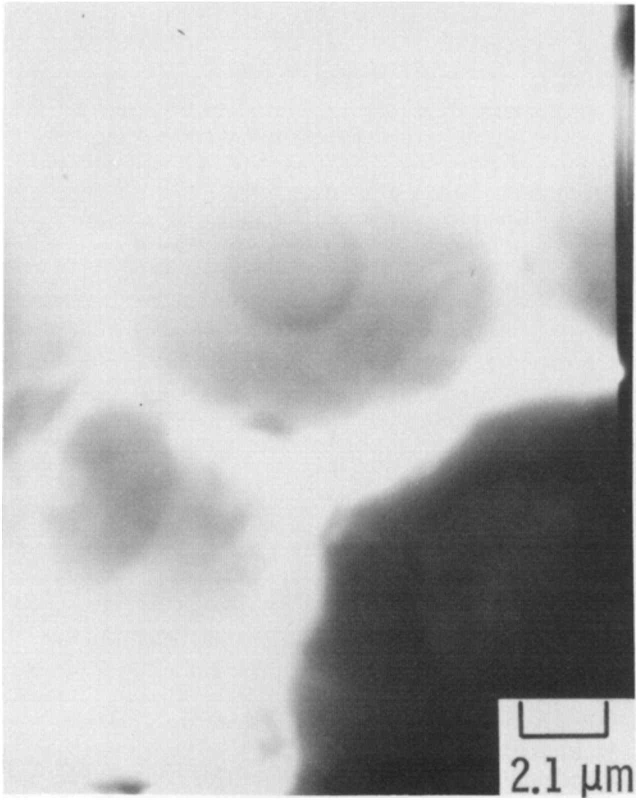
While it was not the purpose of this work to determine the microstructural characteristics of the graphite samples, a few observations about both flake and nodular graphite microstructures were made which help to characterize the graphites studied. Figure 1 shows electron micrographs of flake graphite. These two types of microstructure are typical of the structures observed. The microstructure in Fig. 1(*a*) is similar to that observed by Double and Hellawell.[6] It appears to be characterized by rotation faults of 28 deg. The nature of the faulting in Fig. 1(*b*) is not understood, but is very similar to that observed in microtomed nodular graphite, shown in Fig. 1(*c*). In both cases the graphite appears to be almost fibrous. This structure is so general in the microtomed nodular graphite specimens that it is probably representative of the graphite structure and is not a structure introduced by the passage of the knife through the graphite. It is not known whether the graphite sections in these micrographs were formed by growth from the melt or by deposition from austenite onto graphite grown from the melt. These observations suggest, but it has by no means been proven, that there are some microstructural differences between flake and nodular graphites.

While the microstructure of the graphite is almost certainly closely related to the details of growth from the melt and a study of the microstructure might yield important clues to the processes of growth from the melt, it is not currently possible to draw any conclusions about the growth mechanisms of graphite from the above observations. However, further work in this area might prove to be very interesting.

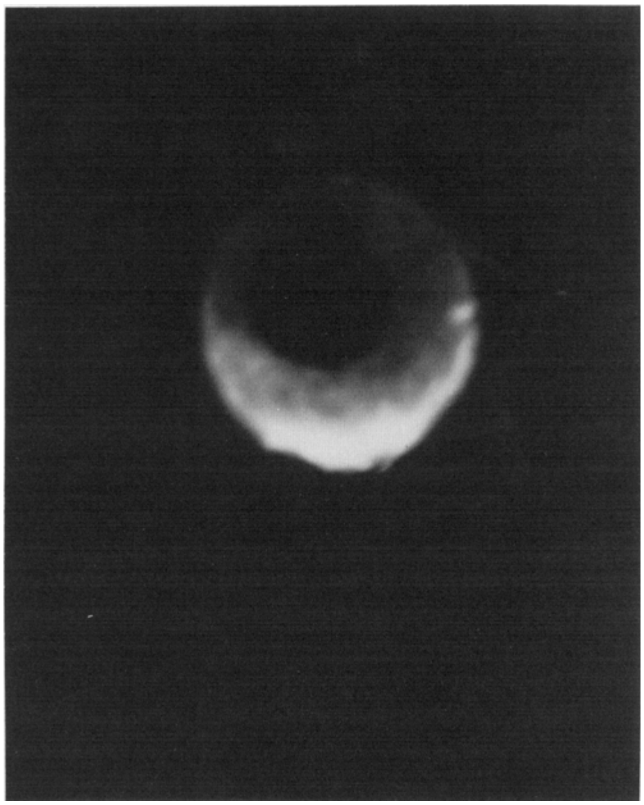
2. Heterogeneous Nuclei for Graphite

TEM provided clear evidence of heterogeneous particles present at the center of nodules, as shown in Fig. 2. These 2 to 5 μm diam particles were frequently observed in bright field images of whole nodules <10 μm in diam. Because of the high background level of scattered electrons, contrast was generally very poor and these particles were usually visible only when an intermediate field aperture was inserted. It was not possible to image nuclei particles for flake graphite as the flake colonies were too thick.

It should be noted that particles were not *always* visible in the center of nodules <10 μm in diam. In view of the fact that electron diffraction of microtomed nodules shows the particles are not highly polycrystalline, it is expected that particles would not be *readily* observed in all nodules. Rather they would be observed only when oriented for strong diffraction. Thus the fact that particles were not always visible should not be construed as evidence they are not always there.



(a)



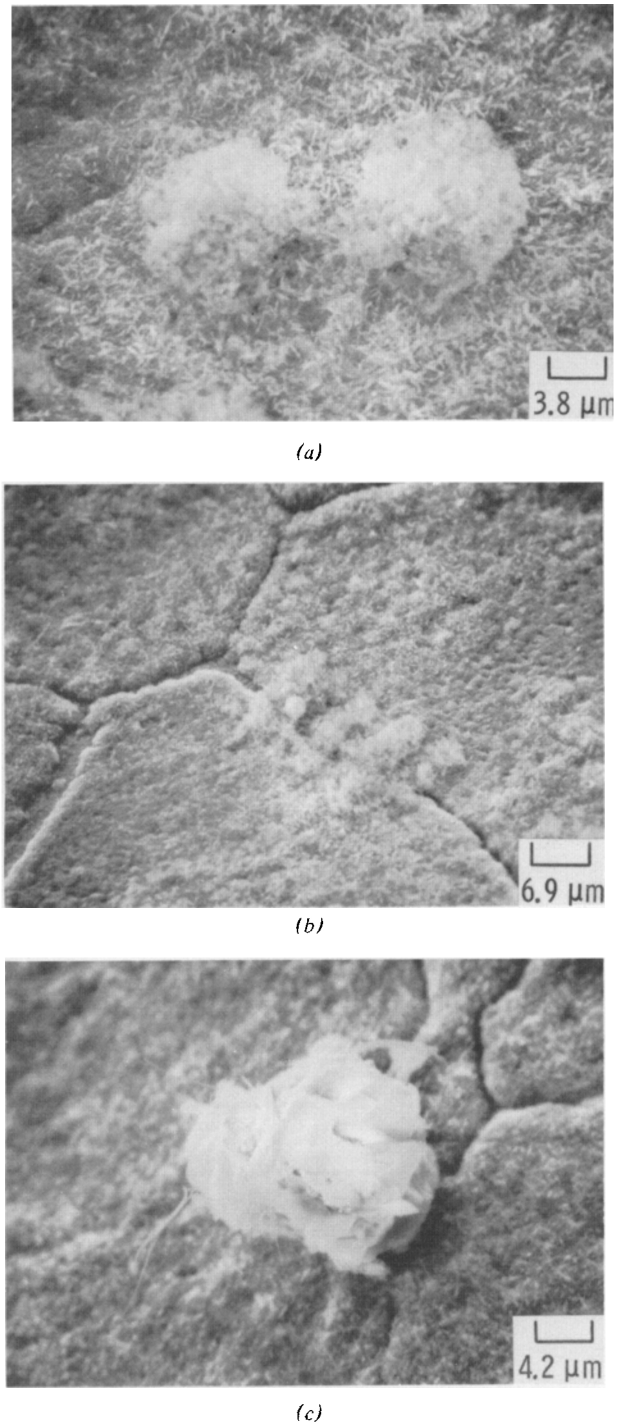
(b)

Fig. 2—TEM micrograph of whole SRN nodule with heterogeneous nucleus particle in the center: (*a*) Without intermediate aperture, (*b*) With intermediate aperture.

From the viewpoint of nucleation theory it is expected that the graphite will always nucleate on a heterogeneous nucleus; evidence was obtained which suggests all the nodules studied did have a round particle at their center and that this particle is the heterogeneous nucleus for nodular graphite.

Specimens of SRN were dispersed on a clean, polished stainless steel slab. The specimens and slab were held at 873 K for two h in air. The residue was then examined by SEM. Each nodule leaves an identifiable residue, as shown in Fig. 3(*a*). This residue is from the oxidation of elements present in the graphite or in interstices in the graphite. A round particle was invariably associated with each observed clump of residue from a burned nodule as shown by the typical example in Fig. 3(*b*). Note that in order to reveal the particles it was necessary to press a clean glass slide on the stainless steel surface; if performed very carefully, this maneuver exposed the particles without destroying the identification of each particle with its accompanying residue.

Attempts to use the same technique to demonstrate the universal presence of particles in flake graphite were not conclusive, as so little residue was left after burning that the particles present could not be clearly identified with each flake colony. A typical example is shown in Fig. 3(*c*). EDAX analysis showed this particular particle to be CaS, but as discussed later the composition of these particles is variable. The identification of flake graphite nuclei as sulfides is consistent with numerous accounts, Patterson[7] for example, of the importance of sulfur in effective inoculation. The reason for the peculiar surface structure of this particle is not known; it may be that the surface "leaves" are graphite which had not been completely oxidized during the two h at 873 K. Presumably FIN graphite nucleates on the same particles. It should be noted that transmission electron microscopy of whole FIN graphite reveals round particles at the center which are morphologically indistinguishable from those found in nodular iron graphite.



(a)

(b)

(c)

Fig. 3—SEM micrographs of: (*a*) Burned SRN specimen on stainless steel slab. The two "fluffy" clumps in the center of the micrograph are the residue of two nodules, (*b*) A round heterogeneous nucleus associated with the "fluff", (*c*) A flake graphite particle, presumably a nucleus, on a slab. EDAX showed this particle to be primarily CaS. The reason for the peculiar surface structure is not known, it may be unburned graphite.

The immediate question is whether or not the particles observed in the center of the nodular graphite are heterogeneous nuclei for the graphite. The preceeding evidence strongly suggests these particles *are* the heterogeneous nuclei for the following reasons:

a) Transmission electron microscopy *always* showed the particles to be at the growth center of the nodule where they are expected to be under conditions of radially symmetric growth. For spherical nodules they were at the center of the sphere. In the two cases in which nonspherical nodules were observed, the shape of the nodules and the particles at their centers were *closely related;** an oval nodule had an oval particle, and a wishbone shaped nodule had a wishbone shaped particle (the result of two particles touching in the melt). This is exactly the morphological relationship we expect from heterogeneous nuclei; conversely it is not the morphological relationship we expect between the graphite and an inclusion which was incorporated during growth (irrespective of whether the inclusion was solid or liquid at the time).

b) Examination of burned nodules always disclosed *one* round particle, approximately 2 to 5 μm in diam, per nodule. It is most unlikely that inclusions would be incorporated, during growth, with such a precise frequency. Similarly it is most unlikely that these particles are the product of interdendritic infiltration of melt into the growing graphite, since a number of such particles per nodule would then be expected. One particle per nodule is, however, precisely what we expect to find if that particle is a heterogeneous nucleus. Furthermore, the apparently universal presence of these particles in nodules precludes other nucleation mechanisms, such as carbon clusters, from significant contribution to the total nodule count.

c) The severe acid wash precludes mistaking a matrix inclusion particle (which had actually been an inclusion in the *metal*) for a heterogeneous nucleus particle. Any particles not protected by the graphite were dissolved and washed away in the acid wash. Careful examination of numerous unburned samples by SEM verified that no foreign particles were present, prior to burning or microtoming.

Thus there is substantial evidence that the observed particles are the heterogeneous nuclei for nodular graphite in the nodular irons examined. Therefore, for the balance of this paper it will be assumed these particles are the heterogeneous nuclei for nodular graphite.

While similar identification of the heterogeneous nuclei for flake graphite was attempted, it was not totally successful because the crucial link of one particle per flake colony could not be made, and also because it was not possible to image the flake nuclei in the transmission electron microscope (because of the thickness of the center region of the flake colony). Nonetheless, the severe acid wash of the extracted

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*This is not a contradiction of previous statements that growth conditions alone will control final graphite shape. These nodules were very small and under uniform radial growth as assumed here small nodules would naturally mirror the nucleus shape. But the growth conditions in the melt establish the uniform radial growth. The shape of *large* nodules will not necessarily mirror the nucleus shape.

graphite again strongly implies that the sulfide particles revealed by burning the graphite are the heterogeneous nuclei for flake graphite. As mentioned previously, this is consistent with the known importance of sulfur in flake iron inoculation.[7]

Some observations have also been made with regard to the structural relationships between the nucleus and the graphite.

Consider the micrographs of microtomed SRN nodules shown in Fig. 4(*a*) and (*b*). These micrographs show sections of two different nodules each of which contains a nucleus. These particles were positively verified as nuclei by comparing EDAX analysis (for the SEM micrograph) and diffraction analysis (for the TEM micrograph) with the chemistries discussed elsewhere in this article. The important point here is that these micrographs suggest the effective graphite growth is in the ⟨001⟩ direction from the beginning of growth, since the basal planes of the graphite adjacent to the nucleus appear, in each micrograph, to be tangent to the surface of the nucleus. This is a tentative conclusion since the microtome knife clearly disturbs the graphite and since the nucleus may have moved during the passage of the knife. However, if the above point is true it means the growth theories[6] calling for a transition from predominately pyramidal to predominately basal plane growth are clearly wrong, since basal plane growth (per above) occurs from the very beginning of graphite formation. This conclusion is also consistent with the fact that the many microtomed cross sections examined never displayed structures suggesting such a transition, and that the relatively large size of the nuclei makes the operation of a transition mechanism such as suggested by Double and Hellawell[6] very unlikely.

As mentioned in the Introduction, it has been suggested[5] the technique used to extract graphite from the metal may leach out certain constituents of the nuclei, via graphite grain boundaries or pores. TEM of whole nodules provides evidence that this does not occur to a significant extent. Examination of numerous nodules in which nuclei were visible in the center region, such as in Fig. 2, never showed evidence of a hollow region between the nucleus and the graphite. Such a hollow region would show in electron micrographs as a light halo around the nucleus. Furthermore, the size and morphology of nuclei observed by TEM and that observed by SEM of burned nodules are consistent with each other. Thus any dissolution of the nucleus, if it occurs, is restricted to a small portion of the nucleus volume, and is not likely to significantly affect the results reported here.

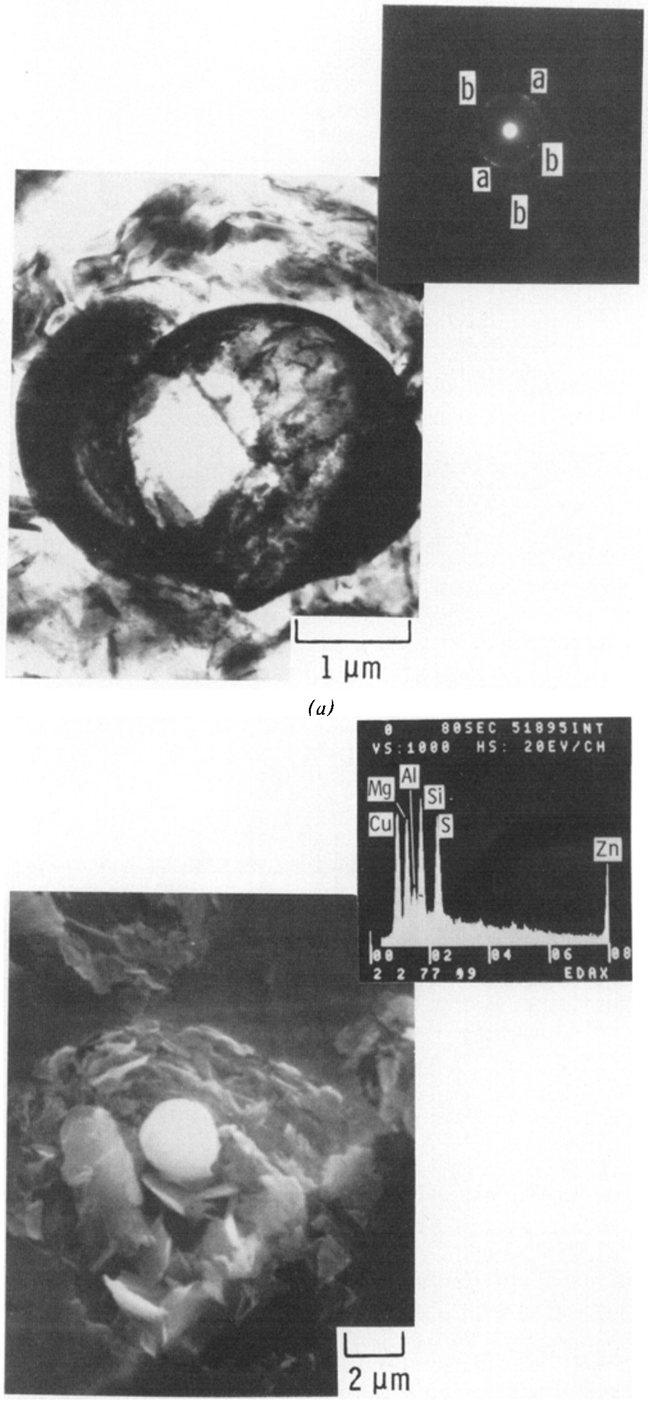
3. Graphite and Nuclei Chemistry

The chemistry of the graphite itself and of the associated heterogeneous nuclei has been studied extensively using X-ray diffraction, electron diffraction, EDAX, and standard chemical analysis techniques.

SRN, LRN and F samples were chemically analyzed by a commercial laboratory. Oxygen, phosphorous, and sulfur were determined by wet chemical analysis, the remainder of the elements detected were determined by semiquantitative emission analysis. These analyses are shown in Table I, along with estimates of the uncertainties involved. It should be noted that no cerium was detected for LRN and F samples (but was detected for SRN samples). However the detection limit for cerium is 0.1 pct, and for LRN samples, at least, cerium is clearly present as shown by X-ray diffraction analysis.

There are several important features of these analyses:

1) The Si (except for F samples) and O contents are very high.



(*a*)

(*b*)

Fig. 4—(*a*) TEM micrograph of microtomed SRN nodule showing nucleus particle in the center. The intermediate aperture image shows the region from which the diffraction pattern was taken. The diffraction spots marked "a" index to CeO_2 and those marked "b" to Fe_2O_3, (*b*) SEM micrograph of different microtomed SRN nodule with attached nucleus. The Cu and Zn lines are from the specimen support.

Table I. Chemical Analysis of Graphite Ash

	SNR		LRN		F		Estimated
	Wt Pct	At Pct	Wt Pct	At Pct	Wt Pct	At Pct	Accuracy, Pct
O	2.1	1.6	0.47	0.35	0.46	0.35	±10
P	0.12	0.0046	0.010	0.0039	0.012	0.0046	±10
S	0.082	0.031	0.028	0.010	0.067	0.025	±10
Si	2.5	1.1	0.50	0.21	0.015	0.0064	±20
Fe	0.40	0.086	0.30	0.065	0.08	0.017	±20
Al	0.035	0.016	0.025	0.011	0.01	0.004	±50
Ce	0.1	0.009	–	–	–	–	±50
Mg	0.08	0.04	0.03	0.015	0.008	0.004	±50
B	0.010	0.010	0.015	0.017	0.030	0.033	±50
Cu	0.025	0.0047	0.001	0.0002	0.003	0.0006	±50
Ti	0.008	0.002	0.003	0.0008	–	–	±50
Zr	0.01	0.0013	–	–	–	–	±50
Ni	0.003	0.0006	–	–	–	–	±50
Ca	0.015	0.0045	0.015	0.0045	0.005	0.0015	±50
Cr	0.003	0.0007	–	–	0.003	0.0007	±50
Ba	0.002	0.0002	0.015	0.0013	0.002	0.0002	±50
Mn	0.003	0.0007	0.001	0.0002	0.002	0.0004	±50
Totals:	5.3	2.9	1.4	0.7	0.7	0.45	

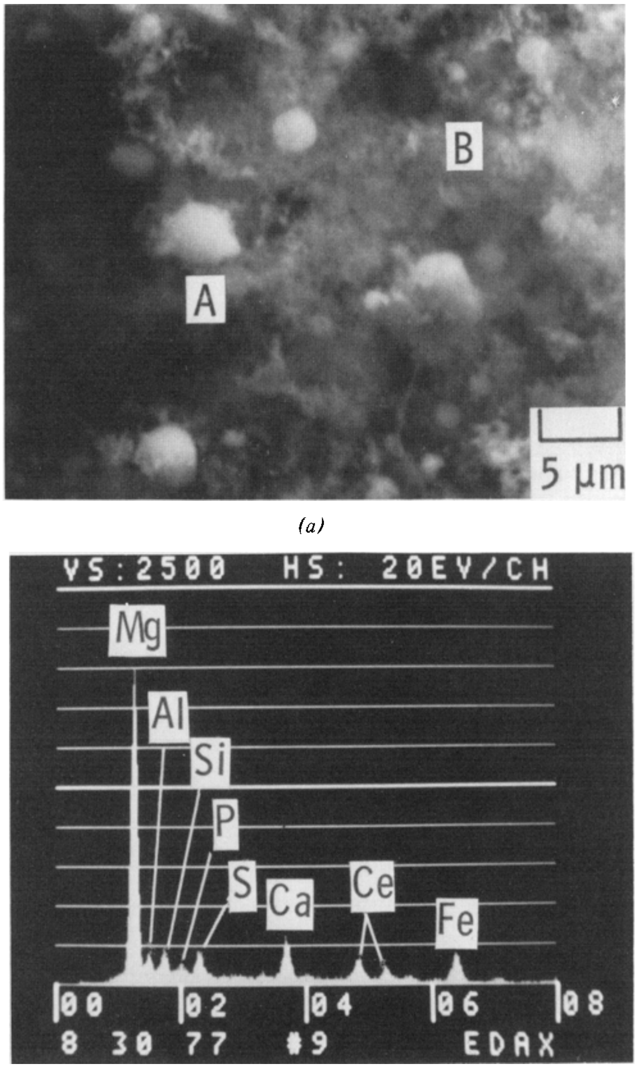
However, in the case of SRN and LRN samples these numbers are reasonable as the following simple calculation shows. The average diam of the nuclei particles is in the range of 4 to 5 μm. Therefore, the average ratio of nucleus volume to graphite volume will be in the range 3 to 6 pct for SRN samples and 0.6 to 1.2 pct for LRN samples. Assuming approximately equal densities for the graphite and the nucleus this means the total solute content of the graphite should be about 3 to 6 wt pct for SRN samples and 0.6 to 1.2 wt pct for LRN samples. These are approximately the observed ranges of total solute content.

There may, in the case of SRN and LRN, also be some silicate contamination, despite the previously mentioned efforts to obtain "clean" samples. However for the F samples there clearly was not any appreciable silicate contamination, as the Si level here is quite low, and this suggests contamination would also be low for SRN and LRN samples. EDAX of nodules and ash of nodules confirmed the presence of Si but this microanalysis was not quantitative, and hence does not provide a check on the Si levels. In the remainder of this paper I assume that the high Si and O levels are truly representative of the graphite + nuclei and are not due to silicate contamination. There is ample reason for believing this to be so, but further work will be necessary to thoroughly substantiate this belief.

2) The high O level in F samples is not balanced by a comparable level of oxide forming elements. In fact the oxide forming elements present account for <0.1 at. pct of oxygen. Thus there must be approximately 0.25 at. pct O in the graphite itself. This is a very striking fact as it means oxygen, rather than sulfur, *may* be the principal growth modifier. Johnson and Smartt[4] also suggest oxygen is a growth modifier.

Also most, if not all, of the remaining elements are present primarily in the graphite. This may be deduced as follows: The F samples consist primarily of flake colonies. These colonies are generally >100 μm in diam, with an average diam of 200 to 300 μm. If we assume a 200 μm diam colony and equilibrium freezing during the formation of the colony, then the mass of the graphite colony will be $\sim 5 \times 10^{-7}$ g. If the nucleus for the colony is 2 μm diam with a density of ~ 4 g/cc then the mass of the nucleus is $\sim 2 \times 10^{-11}$ g and the nucleus contributes ~0.004 wt pct to the mass of the colony. The total wt pct of elements present in the graphite of F samples is 0.7, and most of this must clearly be present in the graphite as the elements in solution, not oxides, and so forth, in the nucleus.

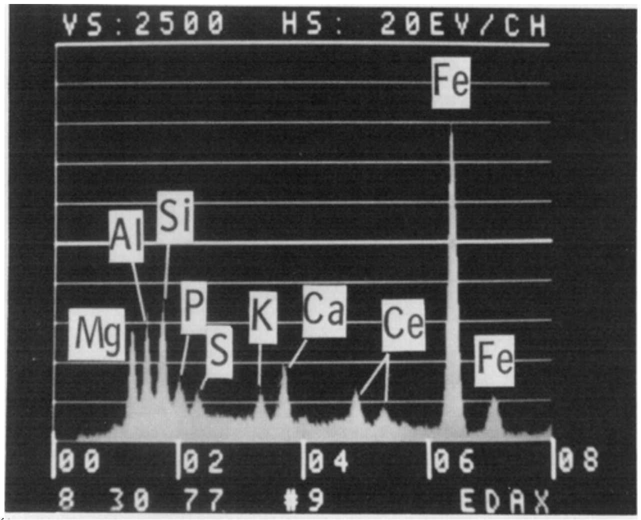
3) The analysis of two nodular graphite samples with a factor of ~2 difference in average diameters provides evidence of the dominant location of the various elements within the nodule. For SRN samples those elements which are *predominantly* located in the nucleus should be present in amounts approximately four times greater than in LRN samples. Thus, O, S, Si, Mg, Cu, Ti, and Mn appear to be present primarily in the nucleus and the remaining elements primarily in the graphite (for nodular samples). Presumably Ce behaves similarly to Mg, and occurs primarily in the nucleus also. This distribution is consistent with information obtained by EDAX and X-ray



(a)

(b)

Fig. 5—(*a*) SEM micrograph of ash of SRN nodules, burned in air at 1023 K for 1 1/2 h. The round particles are nuclei. The "fluff" between the particles is the actual residue from the graphite, (*b*) EDAX of particle at A, showing a high Mg content, (*c*) EDAX of "fluff" at B, showing a high Fe content.



(c)

Fig. 5—Continued.

Table II. Debye-Scherrer Diffraction Spots for SRN and HSLRN Samples

	d-spacing, nm									
Observed	0.314	0.267	0.250	0.229	0.185	0.154	0.137	0.127	0.119	0.112
CeO_2	0.312	0.271	0.251	0.220	0.183	0.156	0.135	0.124	0.121	0.110
α-Fe_2O_3		0.269	0.251	0.220	0.183	0.156	0.135	0.126	0.121	

diffraction, as will be discussed shortly. It is also consistent with the observation that larger nodules of both LRN and SRN samples are ferromagnetic* (undoubtedly because of the presence of small clumps of Fe imbedded in the graphite) which suggests relatively large amounts of Fe are distributed in the graphite. In the case of F samples elements present in the graphite *must* be in solution. However for SRN and LRN samples it is not possible to discern which elements are in solution in the graphite and which elements are in "clumps" (*i.e.*, Fe) distributed throughout the graphite.

4) The chemical analysis suggests there is a "deficiency" of oxygen in both SRN and LRN samples. For SRN and LRN samples the oxide forming elements require respectively 2.3 and 0.48 pct O to be present as oxides only, whereas only 1.6 and 0.35 at. pct O respectively are actually present. This suggests that for these samples virtually all of the oxygen is present as oxide in the nucleus, that the graphite itself has a low oxygen concentration, in contrast to the flake graphite, and that some of the oxide forming element (*i.e.*, Fe, and so forth) must be present in the graphite. It must be emphasized, however, that this is a tentative conclusion since the estimated error bands of the oxygen and oxide forming elements do overlap.

EDAX of whole nodules from SRN and LRN samples confirmed the presence of Ce, Mg, Al, Si, S, Ca, and Fe, but did not yield any information on the location of these elements. However, EDAX of ash of these samples clearly shows that Ce is concentrated *primarily* in the nucleus and Fe *primarily* in graphite as

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*Ferromagetism of nodules has been frequently noted in the literature.

Table III. X-Ray and Electron Diffraction Analysis of SRN

		X-ray										
SRN		CeO_2		α-Fe_2O_3		MgO		α-Fe		Graphite*		TEM
d, nm	I/I_0	*d*, nm	I/I_0	*d*, nm	I/I_0	*d*, nm	I/I_0	*d*, nm	I/I_0	*d*, nm	I/I_0	*d*, nm
0.365	5			0.366	25							0.366
0.348	5											
0.335	5									0.336	100	0.333
0.314	100	0.312	100									
0.270	50	0.271	29	0.269	100							0.275
0.251	30			0.251	50							0.250
												0.230
0.220	1			0.220	30							0.220
0.210	10					0.211	100					0.209
0.203	30			0.202	2			0.203	100	0.203	10	0.201
0.192	75	0.192	51									0.191
0.184	1			0.183	40							0.183
0.175	5											0.176
0.169	1			0.169	60					0.168	20	0.168
0.164	40	0.163	44	0.163	4							
0.157	<1	0.156	5									0.158
0.148	10			0.148	35	0.149	52					0.150
0.145	1			0.145	35			0.143	20			0.145
0.136	5	0.135	5	0.135	4							0.138
0.125	10	0.124	15	0.126	8							0.128
0.122	5	0.121	6			0.122	12					
0.111	1	0.110	12					0.117	30			0.117
0.106	<1											
0.105	1					0.105	5					
0.096	<1					0.097	2					
0.092	1					0.94	17					
0.091	<1	0.091	13									0.090
0.088	<1											
0.086	<1	0.086	7			0.86	15					

*Intensities and *d*-spacings from this investigation.

shown in Fig. 5. In fact, EDAX of a number of nuclei particles consistently confirms that Mg and Ce are primarily in the nuclei and Fe is primarily in the graphite. This is consistent with the chemical analysis as discussed previously. Furthermore, EDAX of many SRN and LRN nuclei particles reveals a highly variable composition. Some particles are mostly Ce and Fe. (This is not inconsistent with the above conclusion that Fe is primarily in the graphite. Most of the *total* amount of Fe present (in nodules) *is* in the graphite, even though the concentration of Fe in the nuclei may be relatively large.) Others may have in addition Mg, Ca, Al, Si, P, and S in various amounts.

EDAX of ash of F samples was also revealing. Particles present in the ash are primarily S and Si, with variously Mg, Ce, Ca, Mn, and Fe. As discussed earlier these particles are probably the heterogeneous nuclei for flake graphite.

4. X-Ray Diffraction Analysis

SRN and HSLRN samples were also examined by X-ray diffraction to determine, if possible, the compounds present in the nuclei (and in "clumps" in the graphite, when present). Normal powder diffraction techniques were used, except the samples were not rotated. Because of the polycrystalline nature of the nodular graphite, no noticeable graininess was introduced into the graphite lines by this technique. At the same time, because of the small size of the nodules and therefore the large number of nodules (and nuclei) present, it was possible to obtain diffraction spots from the nuclei. These spots are consistent with those expected from α-Fe_2O_3 and CeO_2 for both samples, as shown in Table II.

In addition, the ash of SRN, LRN, and F samples was examined by X-ray diffraction. The results are shown in Table III for the SRN sample only. The SRN sample clearly contained mostly CeO_2 and smaller amounts of Fe_2O_3 and MgO, and probably some graphite and α-Fe. The LRN sample contained mostly Fe_2O_3, and a smaller amount of CeO_2, and probably some rhombohedral graphite. Some of the lines for LRN have not been identified. The F sample contained Fe_2O_3 and some unburned graphite. No other lines were observed for F samples.

These results are consistent with the chemical analyses. Moreover, analysis of diffraction spots from TEM of burned and microtomed samples is consistent with the above X-ray analysis, as shown in Table III. It is particularly notable that sulfides must be present in rather small amounts, as none have been identified.

It is not clear why SiO_2 was not detected by X-ray diffraction in any samples. Presumably, there is a considerable amount of SiO_2 present as glass.

DISCUSSION

For many years it has been generally assumed sulfur was the growth modifier responsible for the shape transition of graphite in cast iron. The chemical analyses reported here, however, suggests that oxygen is also a growth modifier. Johnson and Smartt[4] likewise suggest this to be the case (but as discussed earlier the data upon which their suggestion is based is inconclusive). Also some time ago Iwase and Homma[8] studied the effect of oxygen content of the melt on graphite morphology and concluded that oxygen has a powerful effect, with low oxygen levels producing nodular graphite and normal oxygen levels producing flake graphite. Thus there is corroborative evidence that oxygen is a growth modifier for the graphite.

By the same token it is clear that sulfur is also a growth modifier for graphite. What is the relative importance of these two growth modifiers in controlling the transition from flake to nodular graphite? There are good reasons for believing oxygen plays the dominant role here; This belief is consistent with the observed correlation between vacuum melting and nodular graphite formation.[4,9] It is also consistent with the thermodynamics of the inoculating elements Mg and Ce in the cast iron melt, since in these circumstances their affinity for oxygen is much greater than for sulfur, and with the fading observed in inoculated melts, where oxygen continues to be absorbed after inoculation but sulfur is not. It is also suggested by the fact that in the present investigation the amount of oxygen in solution in flake graphite appears to be significantly larger than the amount of sulfur in solution, and by the fact that for the cast irons studied here the heterogeneous nuclei for nodular graphite are partly Ce and Mg oxides. The implication is that oxygen in the melt modifies graphite growth such that the flake form predominates; but when the oxygen getters Ce and Mg are added the oxygen concentration is reduced to a sufficiently low level such that the nodular form presominates. The dominance of oxygen is further suggested by the aggregate results of several investigators which indicate lower measured oxygen levels (in solution in the melt) in nodular cast iron than in flake cast iron.[10-15]

However it may well be that *both* oxygen and sulfur are important. Patterson,[16] for example, points out that there is an optimum sulfur level in nodular cast iron of 0.005 to 0.015 pct; sulfur less than 0.004 pct in the base iron leads to irregular nodules. The possibility that sulfur and oxygen both have important (and presumably different) roles in graphite growth is very intriguing.

Equally intriguing is the fact that nodules can and do grow (under the specific conditions discussed earlier) in commercial cast irons which normally produce only flake graphite (*i.e.*, have not been inoculated with nodularizers). This is a regular occurrence in the particular flake cast iron studied here, and is consistent with a variety of other observations, such as the production of nodules in Fe-C-Si alloys directionally solidified at high growth rates.[17] This fact is very important. It means the nodular morphology may be produced by two separate means: removal of growth modifiers in the case of Mg or Ce inoculated melts, and growth under appropriate solidification conditions in other melts. From this viewpoint Mg and Ce inoculations are of value because they greatly expand the solidification conditions which produce nodules. It appears that high undercooling, high gradient solidification conditions promote the nodular morphology. The reason for this is not known. It may be that under these extreme conditions the normal semicooperative growth mechanism associated with the flake morphology breaks down. It should be noted that the presence of nodules in a flake cast iron has been frequently attributed to residual Mg or Ce. The presence of these elements in significant quantities after prolonged exposure to air during melt preparation is however extremely unlikely, particularly in an induction melter. In these circumstances the oxygen concentration will be controlled entirely by the silicon and carbon reactions in the melt.

Since removal of the growth modifiers yields the nodular shape it appears this is the favored growth form in the absence of modifiers. The formation of nodules in flake cast iron indicates this to be the case also. Some time ago Tiller[18] suggested, on the basis of calculated growth velocities in the absence of modifiers, that the nodular form would dominate the freely growing flake form under normal growth conditions. However his calculations do not predict the dominance of the nodular form over the flake eutectic form under the growth conditions discussed in the previous paragraph. Presumably treatment of the eutectic growth as semicooperative rather than cooperative would rectify this discrepancy, since semicooperative growth must in the limit approach free flake growth.

If the present view is correct, that in the absence of modifiers the dominant form under normal growth conditions is nodular, the presence of modifiers must (as suggested by numerous investigators) reduce the graphite growth velocity in the $\langle 001\rangle$ directions relatively more than in the $\langle 1\bar{1}0\rangle$ type directions. Since growth in $\langle 001\rangle$ occurs by motion of ledges across the $\{001\}$ planes growth modifiers must retard this ledge motion relatively more than pyramidal face growth. This shifts the relative growth rates in favor of the flake graphite, semicooperative growth mechanism. However many details of the modification mechanisms (or indeed of unmodified graphite growth) need to be known but are not. Thus we do not know the required concentrations of oxygen and sulfur, ledge densities, ledge sources, and so forth, in short many facets of the interface kinetics which are required for a thorough understanding of graphite growth in cast iron melts. Moreover our understanding will (hopefully) eventually extend to As, Pb, and so forth—those impurities deleterious to nodular graphite growth which are also growth modifiers but ones that are not so easily removed by the nodularizing inoculants.

Identification of the heterogeneous nuclei for graphite is also very important to our understanding of graphite precipitation in cast iron melts, for reasons discussed in the Introduction. In the nodular cast irons studied here these nuclei appear to be created by interaction of the inoculating species Ce and Mg with oxygen in the melt. This is indicated by their composition—CeO_2, Fe_2O_3 and MgO with, presumably, some type of silicate, and is certainly not surprising in view of the role of Ce and Mg as oxygen scavengers. However it is unclear whether or not these nuclei should be considered universal. Lalich and Hitchings[3] found rare earth sulfides to be the nuclei in their laboratory melts, which suggests there may be considerable variation in the nuclei composition in different melts. In addition, because of the extremely rapid formation of nuclei in the melt nuclei composition may vary widely *within* a melt. If this is true it is unclear how such a variety of nuclei can effectively catalyze the precipitation of graphite. However evidence does point in this direction: for in addition to Lalich and Hitchings[3] results, the present investigation suggests sulfides are the nuclei for flake graphite and presumably also for the nodules that are found in the flake cast iron. It is, furthermore, not clear what interaction occurs between the nodularizing inoculants, or their products, and the ferrosilicon introduced during postinoculation; the practice of postinoculation suggests some crucial interactions may occur here.

CONCLUSIONS

1) The heterogeneous nuclei for the commercially produced Mg + rare earth inoculated nodular irons studied here are round particles 2 to 5 μm in diameter.

2) These nuclei are *primarily* CeO_2 and Fe_2O_3 with some MgO. Presumably some silicates are also present, but it was not possible to identify any. The composition of these nuclei is highly variable with Si, Ca, Al, P, and S also being variously present.

3) There is a high concentration (~0.25 at. pct) of oxygen in solution in the flake graphite, but very little sulfur. In nodular graphite oxygen and sulfur were not found in solution in the graphite. This strongly suggests oxygen is a growth modifier in addition to sulfur, and that nodular graphite is produced by Mg and Ce largely because of their strongly deoxidizing properties.

4) Nodular graphite may also be produced by high gradient, high undercooling solidification conditions. This may be due to a complete breakdown, under these growth conditions, of the normal cooperative growth mechanism. It appears that the nodule producing inoculants ultimately work by greatly expanding the solidification conditions under which the nodular form is favored.

5) Flake graphite in commercially produced cast iron probably nucleates on sulfide particles. The composition of the sulfides is apparently variable since Mg, Ce, Ca, Mn, and Fe have all been variously detected in the particles which are apparently nuclei for flake graphite. These sulfide particles are ~1 to 3 μm in diam.

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