The New Methods of Graphite Nodules Detection in Ductile Cast Iron

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The properties of nodular ductile cast iron are strongly influenced by morphology, size and distribution of graphite particles. Nodular ductile irons have spheroidal graphites in the as-cast state. In this work, these nodules are characterized by means of light optical microscopy (LOM) and electron microscopy (EM). Experimental data are represented by LOM. Metallography is processed to obtain an image where the graphite nodules are clearly distinguished from the similar inclusions which make doubts in microstructure characterization; this is formed by completely unconventional procedures. EM was used to show more clear aspects of granular graphite in cast irons. These data can provide a valid support towards a more confident quality control in the ductile iron production.

Keywords Ductile iron; Echant; EM; Graphite; LOM.

INTRODUCTION

The nodular irons are relatively inexpensive, and special properties such as a high degree of ductility and shock resistance are achieved by modifying the form of the graphite. For their interesting mechanical properties, nodular graphite cast iron has been a topic of growing interest in engineering productions. The success of ductile iron means that it currently accounts for about 20 to 30% of the cast irons used in the most industrialized countries [1].

Spheroidal graphite (SG) cast iron microstructure comprises free carbon (graphite) not combined into carbides and exists as nodules of graphite dispersed into a matrix of steel type. Ductile cast iron has higher strength and toughness than grey cast iron with flake graphite form. Deviation from nodular graphite to flake graphite introduces a lower strength because the flakes act as easy crack paths and stress concentrators in the metal. By modifying the graphite to spheroidal form, a higher level of tensile strength and ductility can be achieved [2, 3].

Generally, the form of the graphite characterizes the cast iron microstructures. Changes in the shape, size, and distribution of graphite can be caused by numerous factors such as alloying elements, melting temperature, and cooling rate. Morrogh and Williams [4] reported that obtaining a nodular structure in an alloy with appreciable sulfur content is impossible. They suggested that an appropriate amount of cerium, which is a desulphuriser, should be added to the melt to ensure a nodular graphite structure. Thomas and Gruzleski [5] have suggested that the nodular form of graphite is the normal and preferred growth morphology of graphite.

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Graphite is a hexagonal-close pack form of carbon that can grow in both the liquid and solid states of iron. Theoretically, in irons above the eutectic composition of carbon, the graphite first nucleates in the liquid and then continues to grow in the solid. In irons below the eutectic composition, the graphite does not start to grow until the iron reaches eutectic temperature. As seen in a microstructure, the larger nodules are from growth initiated in the liquid, and the smaller nodules are from growth that does not start until solidification temperatures are reached.

Graphite is composed of a series of stacked parallel layer planes shown schematically in Fig. 1, with the trigonal sp^2 bonding. In Fig. 1, the circles showing the position of the carbon atoms do not represent the actual size of the atom. Each atom, in fact, contacts its neighbors [6]. Within each layer plane, the carbon atom is bonded to three others, forming a series of continuous hexagons in what can be considered as an essentially infinite two-dimensional molecule [6].

The most common stacking sequence of the graphite crystal is hexagonal (alpha) with a -ABABAB- stacking order [6]. Atoms can add much more easily in the -a- directions as compared with the -c- direction; Double and Hellawell [7] explained that if the layer lattice is rolled to a sphere, the possibility of molecular addition in the -c- direction will be increased. They believed that the hexagonal monolayer or graphone sheets freely precipitate from the molten metal solution and reported that impurities in the melt such as oxygen and/or sulfur would promote the growth of graphite sheets in the -c- direction, which leads to the flake graphite form.

Baihe Miao et al. [8] illustrated many fanlike structures, which are aggregates of graphite platelets forming a spheroid of graphite. In addition, Baihe Miao et al. [9] suggested, based upon the Double and Hellawell model, a graphite spherulite consisting of conical helixes, in which the {0001} planes of graphite within each conical helix
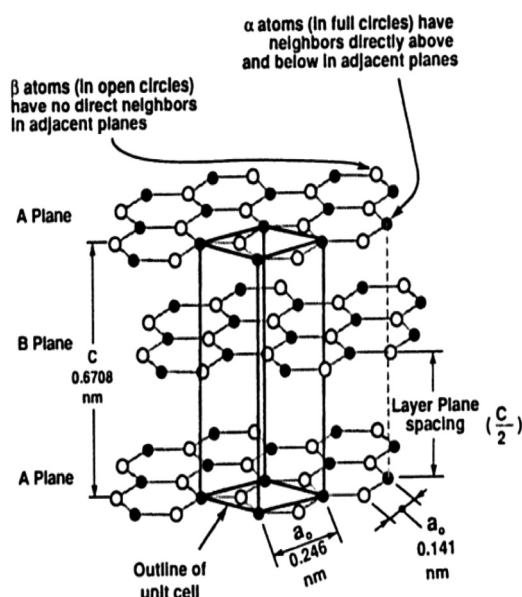
FIGURE 1.—Crystal structure of graphite showing -ABABAB- stacking sequence and unit cell [4].

grow out of the graphite platelets. They believed that crystallographic defects present in the graphite structure could change normal growth of the spherulite and lead to bending or branching of the crystal within the basal plane. The interplatelet area illustrates that the spiral growth of graphite is not perfect.

The present study has been conducted to the as-cast samples. The aim of this work is to acquire the structural information about graphite detection in experimental cast iron so there is no doubt between this kind of phases with foreign particles such as inclusions and impurities which are reported occasionally instead of graphite in the metallography of cast irons. In this article, the problem of identification and characterization of the graphite nodules has been considered, and a novel qualitative analysis procedure has been developed based on a chemical etchant technique. This is a kind of methodology for image analysis of the material metallographic specimen's pictures that provide a reliable and efficient separation of the elements of interest from the background and the evaluation of their morphological characteristics.

EXPERIMENTAL

Experimental ductile irons with the compositions given in Table 1 were produced in a Morgan gas-fired furnace and a high-frequency melting plant of 20 kg capacity. The sandwich technique was used to treat the melt of each iron with a ferrosilicon alloy containing 5% Mg at 1400°C. Finally, post-inoculation of ferrosilicon containing 75% Si was carried out in the crucible. Standard Y-block sand moulds and permanent moulds were used 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.).

The compositions selected resulted in more than 90% nodularity of graphite. Optical microscopy and scanning electron microscopy (SEM) were used to examine and delineate any variations in the microstructure. Light optical microscopes (LOM) were used to analyze metallographically prepared specimens, etched with a Nital 2% for 10 s. Furthermore, a solution containing 20 g iodine in 1000 ml of alcohol, known as iodine solution or iodine tincture, has been used to colorize graphite nodules in ductile cast iron.

For scanning electron microscopy, a Cambridge Series 3 SEM fitted with a Link 860 series 1 EDX system and a Cambridge Series 4 SEM were used. For the characterization of microstructure, a working distance between 20–24 mm was chosen, and an accelerating voltage of 20 kV and spot size between 4–6 nm.

The successful preparation of transmission electron microscopy (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 as follows:

1) Specimens were cut to sections approximately 250 μm thick, using a Struers Accutom-2 slitting machine;
2) Discs of 3 mm diameter were punched from these sections;
3) The 3 mm diameter disks were mechanically polished to 80–100 μm thickness;
4) The central specimen area was dimpled to 10–20 μm thickness using a Gatan precision dimple grinder model 656; and
5) 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.

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
1.77% Al	3.58	1.71	1.18	0.04	0.07	<0.005	<0.005	0.05	–
4.88% Al	3.44	4.88	1.22	0.05	0.10	<0.005	<0.005	0.05	–

The Gatan Model 656 Dimple Grinder is a precision instrument used for grinding circular dimples, of spherical or flat bottomed profile, in the surface of materials such as ceramics, semiconductors, and metals. The principal application is the preparation of TEM specimens.

If specimen blanks are mechanically dimpled prior to final thinning, then the finished specimen has a larger than usual electron transparent area of a more uniform thickness and, in the case ion or neutral particle beam thinning systems, the time required for final thinning is significantly reduced. Moreover, the specimen has a relatively thick rim surrounding the thin region and is thus very robust.

A careful operator can routinely produce thickness less than 5 μm, although in the case of most metals, a final thickness between 20 μm and 50 μm is more normal since mechanical damage introduced into the specimen surface by the action of grinding must be removed. The preparation of such specimens is completed by electropolishing, ion beam thinning, etc. However, the Dimple Grinder is gentle enough and provides sufficient control over the process of dimpling.

The thin foils were examined using a Philips CM20 TEM operating at an accelerating voltage of 200 kV. Identification of the structure and the phases present in the experimental specimens was determined with a series of bright field (BF) and dark field (DF) images and the corresponding electron diffraction patterns (DP).

Results and discussions

The chemical analysis of the as-cast metal obtained in the melting furnace is given in Table 1. The nodular graphite structure was obtained in the as-cast Al-alloyed ductile irons by the use of magnesium addition and suitable inoculant (ferrosilicon). Optical microscopy and scanning and transmission electron microscopy were used to show the microstructure of the spheroidal graphite (spherulite). The nodules of graphite in the specimens were identified and characterized by means of LOM microscopy. Optical microscope images demonstrate typical microstructure of ductile cast iron with ferritic-pearlitic matrix (Fig. 2).

The free carbon (graphite) and metal phases of these materials are significantly different in characterization. Almost using analytical methods are not the useful techniques for their microstructures characterization. Direct method implies metallographic preparation procedures and a surface light 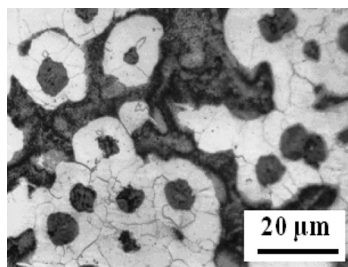optical microscope observation, usually considering a 100 × magnification. If a microstructure observation is necessary, a chemical etching is also performed before the LOM analysis. Almost using conventional analytical methods are not useful techniques for this purpose.

Considering ductile irons investigated by previous studies; images obtained by light optical microscope on metallographically prepared specimens show both graphite elements (spheroids, nodules, lamellas, etc.) and microstructure elements (ferrite grains, pearlite lamellas, etc.) and some artifacts due the preparation procedure that should be distinguished by more interesting element.

The aim of this work is to provide the expert a support to distinguish the nodules of graphite from similar inclusions and impurities of various natures which make doubts in microstructural characterization. A quality approach to the detection and characterization of the nodules morphology requires their neat separation from the background (matrix). Among various techniques, a chemical procedure with unconventional composition was preferred.

Figure 3 shows polished graphite nodules in ductile iron structure. For describing the distribution of graphite nodules in the matrix of microstructure, it is not adequate to characterize only one or two graphite particles. The presence of graphite nodules and also evaluating the nodularity, dimension, and distribution of nodules can be defined by means of this kind of LOM microscopy. An example of the result of this procedure is shown in Fig. 3.

If the etchant chosen improves the contrast between the feature of particles of interest and everything else, a selective characterization method will acquire more magnification. This etchant preferentially attacks or colors a specific phase. Etchant that reveals the graphite nodules is very important for successful determination of microstructure.

Accordingly, graphite is considered as an isotope of carbon, and we can produce colored compounds by considering possibility of carbon interaction with other elements. In the matter, carbon interaction with halogens particularly iodine is more important. Iodine composition with carbon is known as carbon tetraiodide that is produced from the following reaction:

$$C \text{ (Graphite)} + I \rightarrow CI_4. \tag{1}$$

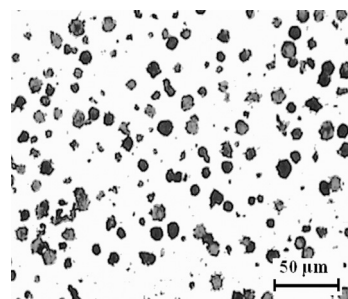Figure 2.—A typical LOM microstructure of ductile cast iron with ferritic-pearlitic matrix.

Figure 3.—Shape, size, and distribution of graphite nodules produced in the cast iron microstructure; unetched, light micrograph.

TABLE 2.—Some physical properties of carbon tetraiodide and iodoform.

Molecular formula	Molar mass	Appearance	Density	Melting point	Crystal structure
CI_4	519.63 g/mol	Red crystals	4.32 g/cm^3	171°C	Monoclinic
CHI_3	393.73 g/mol	Yellowish crystals	4.008 g/cm^3	123°C	Hexagonal

The carbon tetraiodide (CI_4) is a tetrahalomethane. Being bright red, it is a relatively rare example of a highly colored methane derivative. CI_4 is slightly reactive towards water, giving iodoform and I_2. Otherwise, it is soluble in nonpolar organic solvents. It is decomposed by hot alcohol, giving iodoform and iodine. The compound iodoform (CHI_3) is a pale yellow, crystalline, and volatile substance. Some physical properties of carbon tetraiodide and iodoform are listed in Table 2.

A typical light microscopy (LM) micrograph of cast iron microstructure after detection of graphite by tincture of iodine at room temperature for 5 minutes is shown in Fig. 4. According to Eq. (1), carbon in the form of graphite nodules changes to carbon tetraiodide and appears bright red.

The specimen was then immersed in container containing hot tincture of iodine for 5 minutes. The solution temperature was around 65°C. During this time, graphite particles in ductile iron interacted with hot iodine solution and produced carbon tetraiodide. This compound is not stable in hot alcohol and is decomposed to iodoform with pale yellow color (Fig. 5). This procedure may be useful for distinguishing graphite from similar particles or inclusions such as MnS in iron structures.

It is evident that the graphite nodules are apparent by quite different color in the darker background. The resultant images show that hot tincture of iodine solution is a suitable etchant for clarifying the graphite nodules in the microstructure (Fig. 5). For the as-cast cast iron, a gradual appearance of graphite is observed while the solution of etchant remains in contact with samples for longer etching time.

The experimental results are completed by electron microscopy (SEM and TEM images) that let us consider more than one technique for better judgments.

The microscopic observation showed that the microstructure normally consists of nodular graphite in a ferritic-pearlitic matrix. Figure 6 show a typical

FIGURE 5.—A typical LM micrograph of cast iron microstructure after detection of graphite by hot tincher of iodine.

microstructure of the iron containing 1.71% Al, in which the volume fraction of graphite present in the iron is about 12%. Figure 7 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 microstructure (Fig. 3).

Some previous studies [10, 11] gave a description of the microstructure of the spheroids. Conventional methods used in structural metallurgy have been associated to electron microscopy which is a powerful testing method for determination of the graphite in these irons.

Figure 8 shows TEM micrographs from the ductile iron at two different magnifications. Figure 8(a) illustrates three graphite nodules at low magnification. Some nodule cross-sections were thin enough for TEM examination of the graphite structure. Based on TEM observations, formation of spheroidal or plate-like particles morphology of graphites nodules is presented. A bright field image of a section at high magnification is shown in Fig. 8(b). The structure of the spherulite is built up by aggregation of graphite platelets to produce a fanlike structure. This structure consists of graphite platelets and interplatelet regions. This observation is consistent with previous studies performed on two kinds of nodular silicon irons [8, 9]. Figure 9 shows another TEM micrograph of the cross-section of a graphite nodule. The bright field image illustrates the layered morphology of the
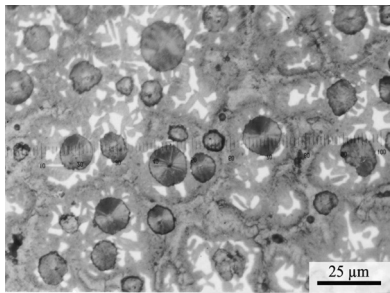

FIGURE 4.—A typical LM micrograph of cast iron microstructure after detection of graphite by tincture of iodine at room temperature for 5 minutes. According to Eq. (1), carbon in the form of graphite nodules changes to carbon tetraiodide and appears bright red.
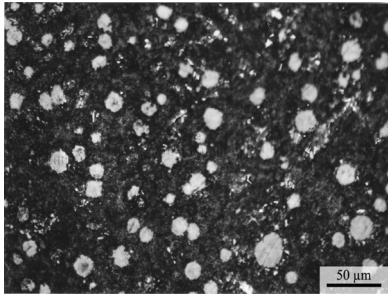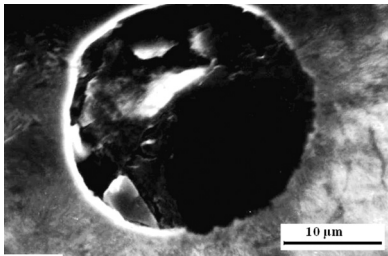

FIGURE 6.—A typical SEM micrograph of the spheroid morphology in the as-cast state of cast iron. The sample etched by nital 2%.
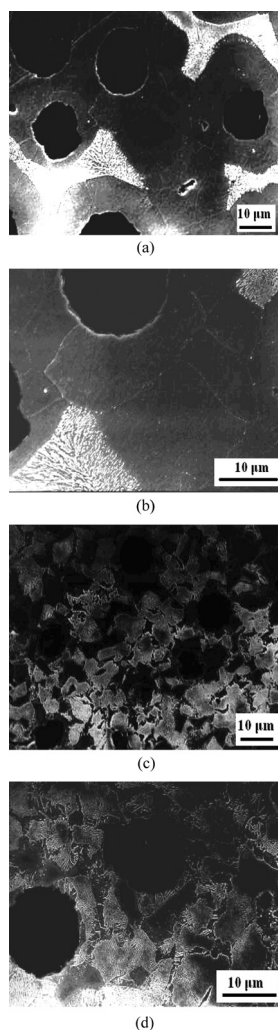
(a)

(b)

(c)

(d)

FIGURE 7.—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.
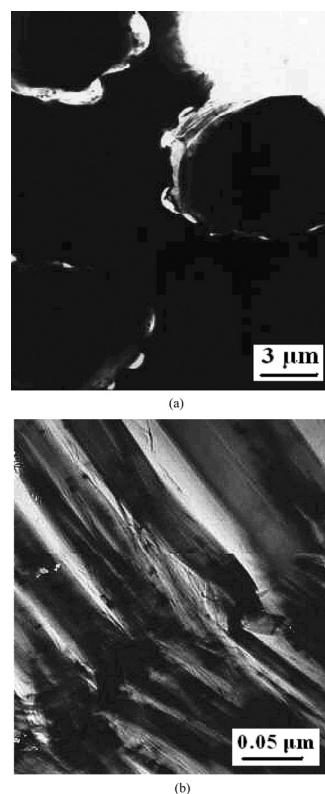

(a)

(b)

FIGURE 8.—TEM bright field images of graphite spherulites in 4.88% Al ductile iron at different magnification: (a) three graphite nodules are illustrated at low magnification and (b) typical structure observed inside the graphite nodule shown in (a).

graphite. The corresponding dark field image indicates that the layers are in similar orientation.

The crystal structure of graphite is hexagonal. Semi-infinite hexagonal layers, which are sometimes named "graphene," are stacked with -ABAB- order. Hellawell [12] explained that if the layer lattice is rolled to a sphere, the possibility of molecular addition in the -c- direction will be increased. They believed that the hexagonal monolayers or graphene sheets freely precipitate from the molten metal solution and reported that impurities in the melt such as oxygen and/or sulphur would promote the growth of graphite sheets in the -c- direction, which leads to the flake graphite form.

Double and Hellawell [13] explained that during solidification, the initial hexagonal monolayers or graphene sheets, which are carbon precipitated from molten metal, can undergo further development. They believed that in a clean iron, the extension of graphene leads to tangles, or wrapping convolutions, resulting in spherulitic graphite. The wide range of possibilities in folding, wrapping, and

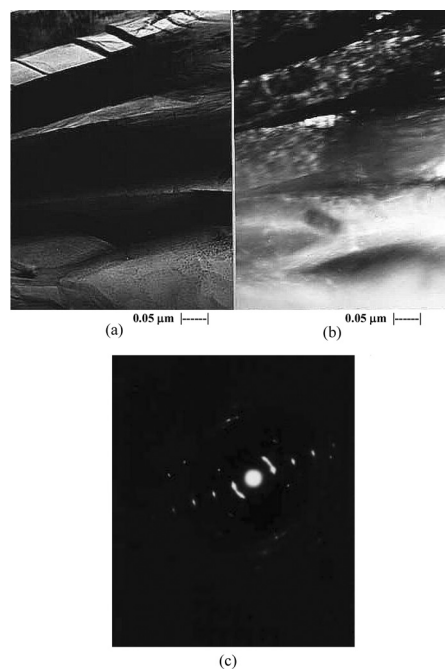(a)   (b)

(c)

FIGURE 9.—TEM micrographs of graphite spherulite and the corresponding diffraction pattern: (a) BF image; (b) DF image; and (c) corresponding diffraction pattern.
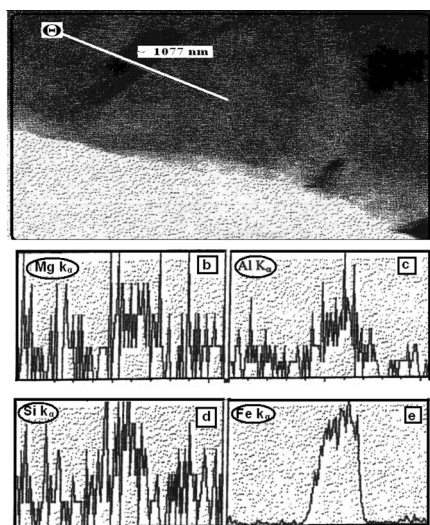
FIGURE 10.—Electron micrograph in a 4.88% Al content ductile iron and the corresponding elemental EDX line scan in this area: (a) the microstructure of a section of graphite spherulite with several inclusions in the spherulite and (b); (c); (d); (e) the magnesium, aluminium, silicon, and iron elemental energy-dispersive X-ray spectroscopy (EDX) line scans.
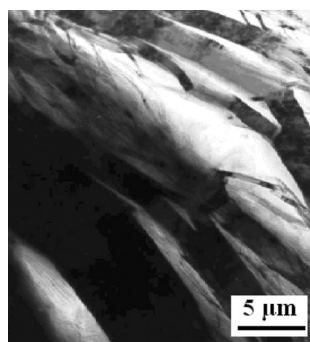

FIGURE 11.—Bright field TEM micrograph of the graphite in the as-cast state of cast iron. Spheroid exhibits regularly spaced particles. Etched by nital 2%.

FIGURE 12.—Bright field TEM micrograph of the graphite in the as-cast state of cast iron. Spheroid exhibits regularly spaced particles. Etched by nital 2%.
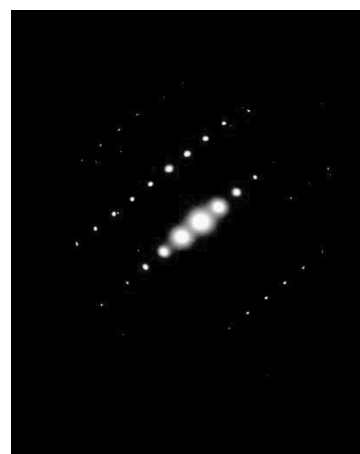

FIGURE 13.—Selected area diffraction pattern (SADP) performed on the zones shown in Fig. 12.

branching of the layers can determine the different graphite forms reported.

A cross-section of a graphite spherulite is shown in Fig. 10. Particles can be observed within the spherulite which must have entrapped during growth of the graphite from liquid iron. The growth of the spheroid is limited after envelopment by austenite [3]. Based on TEM observations, formation of spherical or plate-like particles morphology of graphite nodule is presented (Fig. 11).

The bright field image shows that the orientation of the graphite planes inside the cone is not really constant (Figs. 11, and 12). Selected area diffraction pattern (SADP) performed on these zones are given in Fig. 13.

CONCLUSIONS

1. In this work, an image production is proposed for identification and characterization of the graphite nodules in experimental cast iron. A new identification method is proposed to distinguish the nodules from the metallic matrix.
2. An alternative metallographic method was explored for assessment of particles detection in nodular graphite cast iron. Pictures of the metallographic sections acquired by means of a LOM are processed in order to obtain a clearer image representation where only the nodules of graphites are white objects over a different color background.
3. Electron microscopy was applied for evaluation of nodular graphite ductile cast iron. Experimental results by means of SEM and TEM demonstrated a good correlation with previous studies. This work is also focused on improvement of the conventional methods.

ACKNOWLEDGMENTS

REFERENCES

1. Hughes, I.C.H. Ductile iron. In *Metals Handbook, Casting*, 9th Ed., Vol. IS; BClRA International Center for Cast Metals Technology: South Yorkshire, UK, 1988; 647–666.

2. Angus, H.T. *Cast Iron, Physical and Engineering Properties*; ButterWorths and Co. (Publishers) Ltd.: London, 1978.

3. Elliot, R. *Cast Iron Technology*; ButterWorths and Co. (Publishers) Ltd.: London, 1988.

4. Morrogh, H.; Williams, W.J. The production of nodular graphite structures in cast iron. JISI **1948**, *March*, 306–322.

5. Thomas, P.M.; Gruzleski, J.E. The nucleation and growth of graphite: The modification of cast iron. J. Iron Steel Inst. **1973**, *211*, 426.

6. Pierson, H.O. *Handbook of Carbon, Graphite, Dimond, and Fullerenes Properties, Processing and Applications*; Published by William Andrew Inc., 1993; 44–45.

7. Double, D.D.; Hellawell, A. The structure of flake graphite in Ni-C eutectic alloy. Acta Metallurgical **1969**, *17*, 1071–1083.

8. Miao, B.; Fang, K.; Bianan, W.; Liu, G. On the microstructure of graphite spherulites in cast irons by TEM and HREM. Acta Metall. Mater. **1990**, *38*, 2167–2174.

9. Miao, B.; North Wood, D.O.; Bian, W.; Fang, K.; Fan, M.H. *Structure and growth of platelets in graphite spherulites in cast iron*. Journal of Materials Science **1994**, *29*, 255–261.

10. Kiani-Rashid, A.R. The influence of aluminum and heat treatment conditions on austempered ductile irons. Ph.D. Thesis, University of Leeds, UK. 2000.

11. Kiani-Rashid, A.R.; Edmonds, D.V. Int. Journal of Engineering, Transactions B: Applications **2002**, *15* (3), 261–272.

12. Double, D.D.; Hellawell, A. The nucleation and growth of graphite, The modification of cast iron. Acta Metall. Mater. **1995**, *43* (6), 2435–2442.

13. Double, D.D.; Hellawell, A. The structure of flake graphite in Ni-C eutectic alloy. ACTA Metallurgica Aug. **1969**, *17*, 1071–1083.