The mechanism of formation of nodular graphite in cast irons remains the most debatable issue of materials science. Competition of several dozen hypotheses of the formation of nodular graphite and modern technologies of computer simulation have not designed a single universally accepted theory up to now. This is probably due to a large number of factors that affect this process: the nature of the charge materials, the presence of impurities, melting conditions, inoculation, etc.

Detection of the mechanism of formation of nodular graphite will contribute to the development of the general theory of inoculation of cast iron, it will open vast opportunities for the control of its structure and properties, and will make it possible to design effective technological processes for obtaining castings for various purposes from ductile cast iron.

Attaining new data on the structure of the inclusions of nodular shaped graphite, obtained by new modern research methods and laboratory equipment, is an urgent task to solve this problem.
2. Analysis of scientific literature and the problem statement

There are already several tens of hypotheses of the formation of nodular graphite. The development of new modern research methods, expanded abilities of research equipment and computer simulations create conditions to confirm or refute the existence of this or that particular hypothesis.

The paper [1] sets out modern views on the mechanism of formation of nodular inclusions of graphite in cast iron and the prospects of further research of this phenomenon.

According to the authors of the paper [2], the formation of nodular shaped graphite in cast iron is related to the purification of surface-active elements and their neutralization. Primarily, from sulphur, oxygen and other impurities. This version finds a growing number of supporters now.

However, from the moment of obtaining the nodular graphite in cast irons, the dominant theory was that of “gas bubbles” which are formed by vapours of magnesium, hydrogen or other gases. As is correctly pointed out in the paper [3], this is probably due to the apparent attractiveness and identity of the form of a gas bubble and nodular graphite inclusion. That is why the attempts at theoretical justification of this hypothesis have been made up to present [4]. So there are attempts to link the bubble theory with new experimental data, for example, discovery of a new modification of carbon – fullerenes and their detection in iron-carbon alloys [5, 6].

According to the version of the authors [7, 8], the gas that contributes to the formation of nodular graphite in ductile cast iron is carbon monoxide – CO. Such strong deoxidizing agents as magnesium or rare earth metals (yttrium, cerium, lanthanum, etc.) effectively react with oxygen. For example, by an established reaction:

\[
\text{Mg}_{\text{gas}} + \text{CO}_{\text{gas}} \rightarrow \text{MgO}_{\text{solid}} + \text{C}_{\text{solid}}.
\]  

(1)

It is noted [7] that at temperatures of liquid cast iron this reaction occurs from left to right, very intensively and almost to the end. As a result of the two gaseous bodies forming two solid bodies with high strength and high melting point, the areas with vacuum are created in many places of the liquid iron. The initial bubbles of magnesium are reduced from 2 mm to 2–3 μm as a result of the reaction, while the hydrogen diffuses inside simultaneously, and the carbon delays on the surface section, with the solubility decreased in iron and the temperature reduced. Thus, the growth of graphite occurs from the periphery to the centre.

Paper [9] assumes that the formation of cavities that are filled with graphite is to be related to the rupture of the continuousness of melt when introducing elements, active to dissolved oxygen. This process is accompanied by formation of gaseous oxides of lower valency or the opposite – solid oxides, the molar volume of which is less than the sum of the molar volumes of an oxide-forming element and oxygen, or even of the oxide-forming element itself (the phenomenon of "defect of volume").

A lot of attention is currently paid to the study of the internal structure of graphite of nodular shape. The paper [10] confirmed by using light and raster electronic microscopes that the inclusion of graphite has a poly-crystalline structure and it consists of pyramid-shaped crystals. This version is in line with the prevailing views on the structure of the inclusion of graphite of nodular form in ductile cast iron and is supported by most specialists on graphitized cast irons.

However, the paper [11] established by using X-ray diffraction analysis that the inclusions of graphite in cast iron do not constitute poly-crystals but they rather have turbostratic structure. In such a structure, there is no strict order of layers characteristic to the crystal structure of graphite. Therefore, the mechanisms of formation of graphite based on crystallographic considerations cannot be accepted as final.

To improve the knowledge about the structure of the inclusions of graphite and the mechanism of their formation in cast irons, other modern methods of analysis are also applied: colour microscopy [12], electron microscopy [13], nano-tomography [14] and other methods.

Of particular interest when studying the structure and formation of inclusions of nodular-shaped graphite in cast irons is associated with the influence of the gaseous phase (oxygen, hydrogen, nitrogen, etc.), of the products of reaction of these elements with carbon or elements – spheroidizers (magnesium, calcium, etc.) and the formation of nonstoichiometric compounds.

One of the universal research methods of these processes is a petrographic method that allows studying of graphite inclusions not only in reflected, but in transmitted light. However, scientific literature does not pay significant attention to this research method in the analysis of inclusions of graphite in cast iron. Data on petrographic analysis of graphite inclusions are practically non-existent. That is why in this work, in addition to the metallographic and X-ray methods of study of inclusions of graphite, petrographic method is also attached, which has more possibilities.

3. The purpose and objectives of the study

Our studies aimed to confirm and complement the “bubble” theory of formation of graphite nodular-shaped inclusions in ductile irons at inoculation by magnesium.

To achieve the set goal, the following tasks were solved:
– to explore the morphology of nodular graphite in ductile irons by using metallographic, petrographic and X-ray methods;
– to establish the mechanism and stages of formation of nodular shaped graphite in ductile irons inoculated by magnesium.

4. Materials and methods of research of nodular shaped graphite in cast irons

4.1. Technology of obtaining specimens of ductile iron for the study of graphite inclusions

Ductile iron was smelted in an induction furnace with a capacity of 30 kg. To obtain a nodular shaped graphite, we put 0.5–0.7 % nickel – magnesium ligature (15 % Mg) and 0.8–1.0 % ferrosilicon with barium (FS65Ba1) on the bottom of the bucket. Chemical composition of cast iron matched the mark DI 500-2 (Ukraine International Standard GOST 3925-99). We received cylindrical oil slugs with outside diameter 65 mm and length 175 mm on the centrifugal machine. We also cast standard samples according to GOST 3925-99 (Ukraine International Standard) to sand molds for the control of the chemical composition and structure of cast iron.
We cut out the specimens for the study from the castings obtained by various methods, in a cast state and after graphitizing annealing.

4. 2. Methods and equipment used for metallographic, petrographic and X-ray analyses

The section metallographic specimens were prepared by using a generally accepted method. Metallographic analysis was conducted by using the microscope MIM-7 and "Zeiss. Epityp-2".

Petrographic studies were performed in reflected light on the microscope MBI-6 at 90–1900 magnifications. Extraction of nodular shaped graphite from the surface of the section metallographic specimen was carried out by using preparatory needle under the stereoscopic microscope MBS-2. Optical properties of selected inclusions were determined by using standard sets of immersion liquids on the crystal-optical microscope MIN-8 at 100–1000 magnifications according to the methodology proposed in the paper [15]. We defined shape, sizes and other properties of graphite inclusions in the transmitted light.

X-ray microanalysis was conducted by using electronic raster microscopes SUPRA 40 WDS (Karl Zeiss) and JSM-6360 with adapters INCA 350 Oxford Instrumentals and JED 2300, respectively.

5. Results of the study of nodular shaped graphite inclusions in ductile irons

The conducted research in reflected light on the universal microscope MBI-6 helped to uncover and establish the following. The vast number of nodular shaped graphite inclusions in cast irons bear heredity of the crystal hexagonal lattice of graphite – their sphere in the section of a metallographic specimen is contoured by six faces and it consists of six parts of conical shape, the peaks of which converge in the centre of inclusion.

The microstructure of all parts is both heterogeneous and polycrystalline. There is a supply channel of a gas bubble in some inclusions (Fig. 1, a). The inclusions that have not completed the process of sphere formation are of a great interest. A hexagonal form of graphite, whose cavity is made of a condensed gas phase, is observed in the centre of such inclusions. The phase consists of calcium, aluminium, silicon and other suboxides, which overlap the CO diffusion into a gas bubble (Fig. 1, b). As far as the gas bubble is concerned, its cavity is better manifested in the transmitted light in immersion preparations (Fig. 1, c).

As can be seen (Fig. 1, c), a rounded shape of the bubble is contoured by six facets (heredity of graphite crystal lattice) and is equipped with a supply channel. The formed bubble shell is very thin (1.5–2.0 µm), quite fragile, it is easily flaked in the manufacture of the micro section metallographic specimen, transparent, of light-grey colour with a slight greenish tint. The shell is amorphous, optically isotropic, it possesses high and variable refraction index N=1.750–1.770, which points to a complex and variable composition of the solid solution of the bubble. The walls of a supply channel thicken from the bubble to the base of the hexagonal graphite, reaching 3–4 microns and larger, they are of vividly displayed greyish–greenish colour, translucent, isotropic. The index of refraction N=1.770 and higher, which is also indicative of the formation of a solid solution of a complex and variable composition.

It should be noted that the periclase – MgO has a cubic crystalline structure, transparent, colourless, isotropic, with a refraction index N=1.737, corresponding to the stoichiometric composition. It is easily defined in the transmitted light.

Fig. 2 presents the variety of nodular shaped graphite inclusions, which were observed in the studied cast iron.

Presented graphite inclusions offer a great variety of the structures of central and peripheral zones, the presence of pores and breaks, the presence of foreign phases and compounds.

The results of micro-X-ray analysis of graphite inclusions are shown in Fig. 3. Table 1 shows the results of a local point analysis of graphite inclusions, according to Fig. 4.
6. Discussion of the results of the study of nodular shaped graphite inclusions in ductile iron

Thus, the obtained data and well-known properties of magnesium, as one of the strongest deoxidizers and most common spheroidizers, allow presenting the following mechanism of formation of nodular shaped graphite, due to the intensive interaction of magnesium with carbon monoxide by reaction

$$2\text{Mg}_{\text{liq}} + \text{CO}_{\text{gas}} \rightarrow \text{Mg}_2\text{O}_{\text{solid}} + \text{C}_{\text{solid}}.$$  (2)

This reaction occurs with the “explosion” and simultaneous formation of a gas bubble, a supply channel, the base of which is a hexagonal graphite with a cavity in its central part. The bubble shell and the supply channel consist of metastable magnesium suboxide. The authors [15] found the presence of Mg$_2$O in the rough defects of the “separation” of steel C0.45Mn17Al3. In addition, the existence of Mg$_2$O suboxide was cited in other papers [16].

All three components are inextricably linked and present a uniform system, by which the diffusion of carbon monoxide and other gases (SiO, AlO, Si$_2$O, Al$_2$O, Ca$_2$O etc.) occurs, dissolved in liquid cast iron. Fig. 1 a, b shows the nodular shaped graphite, combined with the supply channel, and the base is the mouth of the supply channel. In other words, in the process of interaction of magnesium with carbon monoxide, a unified system formed, thanks to which the gas phase diffusion occurs with the formation of the so-called nodular graphite.

It should be noted that due to the scarcity of oxygen in cast iron, due to its high content of silicon, manganese and other elements with a high affinity to oxygen, compounds with low valency form.

These properties are common to all metals, especially transitional. Thus, the metals of the first three groups of the periodic system form the compounds with normal valency only under normal conditions, and at high temperatures – with low valency [17]. This was reflected in the metal after the electroslag remelting, in which there is also a lack of oxygen observed and the formation of compounds with lowered valency occurs – Ca$_2$O, Si$_2$O, Al$_2$O [18, 19].

Carbon monoxide, diffusing into a bubble cavity, disproportionates – splits into graphite and gas by reaction

$$2\text{CO}_{\text{gas}} \rightarrow \text{C}_{\text{solid}} + \text{CO}_{\text{gas}}.$$  (3)

The graphite, formed in such a way, has a tabular form (aggregates of thin pieces, rectangular or hexagonal plates) and many small particles of different shapes. The thinnest plates of graphite are light grey and transparent, anisotropic, with refraction index N=1.98 and higher. The aggregates of such plates are opaque, isotropic, grey in colour with matte surface. Some plates and the aggregates of the graphite plates are, interestingly, magnetic, or weakly magnetic. In the section of the metallographic specimen, distribution of these aggregates is observed in six segments, ranging from the periphery (large tabular crystals deposit) to the centre – small particles of graphite. Then, in accordance with the degree of carbon monoxide inlet, tabular crystals are laid tightly around the entire perimeter of a gas bubble, thus forming a nodular shaped graphite and filling it fully or partially.

Full filling up of a gas bubble is carried out with the free carbon monoxide access – when the supply channel is open.
(Fig. 2, a), and partial – when the supply channel is blocked by the condensate of a gas phase, dissolved in liquid cast iron (Fig. 2, b).

The increasing amount of graphite in the volume of the bubble gradually replaces the gas phase (CO₂ and other gases) that leads to the rupture of the bubble shell and, consequently, to the formation of meandering or zigzag contour of a nodular shaped graphite inclusion. Often the ruptures run deeper – on the borders of this or that segment, tearing them apart fully or partially (Fig. 2, c, d).

It should be noted that along with the formation of nodular shaped graphite inclusions and, consequently, the filling up of its volume with graphite, the supply channel is also filled, on which hexagonal graphite plates grow (Fig. 1, b).

Layering of thin base layers of graphite on each other leads to the thickening of the walls of the “overgrowing” of the supply channel, thus narrowing its cavity. The carbon monoxide, coming in through a narrow supply channel in the remaining volume of the bubble, possesses other properties already – it does not disproportionate. It is located in the so-called “tempered” condition; it has a film form, amorphous or cryptocrystalline microstructure and has a strong metallic gliter. It is distributed fanlike from the supply channel to the periphery of the hexagonal conical parts, covering the entire surface of the earlier formed primary crystals of graphite (Fig. 2, a, b).

This finalizes the process of complete formation of nodular graphite inclusions. In the case of closure of the supply channel by a condensate of suboxides of other elements (such as calcium, aluminium, silicon, etc.), dissolved in liquid cast iron, further formation of nodular graphite is interrupted (Fig. 2, b).

The role of impurities – suboxides, dissolved in liquid cast iron – should be emphasized here.

The above-mentioned silicon, aluminium, calcium, magnesium suboxides, characteristically, have the same properties as carbon monoxide. Unstable SiO and AlO, similar to CO, diffuse into the volume of the gas bubble and disproportionate on the metal and the oxide of higher valency, in this case forming typical structures of the decay. Sometimes such structures are observed in the vicinity of the supply channel on the surface of graphite, already formed. More stable Al₂O₃, Si₂O₃, CaO suboxides are present, similar to Mg₂O, in a metastable state. The suboxides interact and dissolve well in their oxides to form solid solutions of a complex and variable nonstoichiometric composition. They, as well as secondary graphite, diffuse into the volume of the gas bubble, do not disproportionate, and are in “tempered” state. They condense near the supply channel and, often in large amounts, disrupt the process of formation of nodular shaped graphite. In addition, suboxides shut the supply channel, thereby blocking access of carbon monoxide to the volume of the gas bubble (Fig. 2, b).

According to the qualitative X-ray microanalysis, the presence of magnesium was recorded along the diameter of nodular graphite inclusion (Fig. 3).

In this case, as can be seen (Fig. 3, d), recurring peaks of magnesium indicate the heterogeneity of magnesium suboxides, i.e. of the bubble and that corresponds well with the above-mentioned optical properties.

Quantitative X-ray microanalysis in separate points confirms the heterogeneity of the resulting supply system (Fig. 4 and Table 1).

Weight contents of magnesium, oxygen and iron, listed in Table 1 go together well and attest to the formation of complex nonstoichiometric composition of magnesium and iron suboxides. Based on the optical properties of the supply system and X-ray microanalysis, one can draw the following conclusion: in the moment of interaction of magnesium with carbon monoxide, a metastable gas phase of magnesium and iron suboxides, of a complex composition, is formed.

It should be noted that the steam – iron suboxide phase interacts well with carbon monoxide, resulting in some graphite plates acquiring magnetic properties. In other words, iron suboxide, interacting with CO, participates not only in the process of building a supply system, but also in the formation of nodular shaped graphite.

Further research on the graphite inclusions is advisable to carry out by attracting mass-spectrometric analysis which enables to determine isotopic and molecular composition of gas phase and hard compounds in graphite inclusions. Such a method of research is promising, as it allows taking into account certain limitations inherent in this study. Among them, obviously, the impossibility to determine the exact composition of magnesium, iron suboxides and other elements should be noted. Attaining such factual data will certainly enhance the understanding of the formation of graphite nodular inclusions and will help increase the production of castings made of ductile iron.

7. Conclusions

1. Three morphological varieties of graphite were identified, formed in different periods of changes in physical-chemical conditions of liquid cast iron: in the moment of interaction of magnesium with carbon monoxide – clear-cut hexagonal; during the period of disproportionation of carbon monoxide in the volume of the gas bubble – aggregates of crystals of various shapes; during the “tempering” of carbon monoxide – film (cryptocrystalline).

2. A new mechanism of the formation of nodular shaped graphite was proposed, which is driven by the intensive interaction of magnesium with carbon monoxide and simultaneous formation of a gas bubble, supply channel, consisting of metastable magnesium suboxide, and graphite, representing the base – the mouth for the supply channel. A single supply system is created, along which the diffusion of carbon monoxide and other gases, dissolved in the liquid cast iron, occurs. It was found that a full filling-up of the total volume of a gas bubble by graphite is carried out in three stages: the first two stages – by primary graphite, which deposits on the inner shell of the bubble, starting from the periphery to the centre, then it forms a nodular shape of graphite and the third and final – by secondary graphite.

It is shown that the presence of impurities disrupts the process of formation of nodular shaped graphite and, in this case, the volume of the gas bubble is filled in two stages, mainly by crystals of primary graphite.

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