1. Introduction

Silicon in a significant amount (up to 2.6 %) is present in the technical grade of gray cast irons, and it has a significant effect on the formation of the structure and the complex of physical and mechanical properties of the castings. The influence of silicon is manifested in an increase in the ferrite and graphite constituents in gray cast irons as well as in a significant change in the shape, size, and distribution of graphite inclusions [1]. Thus, silicon is the main regulator of the structure of cast irons while remaining a relatively cheap and affordable element. However, until nowadays, the role of silicon in the theory of graphite formation in cast iron remains unclear. In particular, the process of interaction of silicon with carbon monoxide has practically not been considered by specialists in graphitized cast irons. Therefore, the disclosure of the chemistry of this process will allow a new interpretation of the emergence and formation of graphite inclusions, and it will make a new contribution to the theory of graphite formation in gray cast iron. This will make it possible to manage more reasonably the structure and properties of cast iron castings as well as to develop optimal technological processes for their production.

2. Literature review and problem statement

A generally accepted theory is that introduction of silicon and its dissolution in liquid iron contribute to the formation of graphite. This is associated with an increase in the thermodynamic activity of carbon in silicon-enriched microvolumes of cast iron [1].

However, the presence of such microvolumes enriched in silicon is often not confirmed by micro-X-ray spectral analysis of cast iron. In addition, dissolution of silicon in liquid cast iron is accompanied by a high speed and uniform distribution throughout the volume [2].

Later, this theory was supplemented by the assumption that impurities that are present in ferrosilicon (aluminum, calcium, zirconium, etc.) enhance the graphitizing ability of silicon. In this case, not only supersaturated silicon microvolumes of liquid iron but also chemical compounds serving as embryos of graphite are formed [3].

Comparative tests of the effectiveness of the action of four different modifiers (FeSi75, Zircinoc, Foundry Grade, and Inogen) are carried out in [4]; they have shown that the presence of aluminum, calcium or zirconium in ferrosilicon contributes to the enhancement of graphitization, the improvement of the distribution of graphite inclusions, and the development of mechanical properties. It is noted that the effectiveness of the modifiers depends significantly on the time of exposure of the cast iron melt after processing before pouring it into the mold. After 8 minutes, the property level may decline. The reasons for such changes have not been determined. Therefore, it is proposed [4] to continue research on the effectiveness of various graphitizing modifiers for gray cast iron.

In another paper [5], it is noted that the use of silicon carbide, which does not contain impurities of aluminum, calcium, and other elements, causes an improved graphitizing effect in comparison with ferrosilicon.
As for the so-called “embryos” of graphite, there is also no unified opinion. There are hypotheses about the homogeneous and heterogeneous formation of graphite crystallization centers.

Proponents of the homogeneous formation prove that the centers of crystallization of graphite in cast iron are actually microinclusions of graphite, which come from the charge or modifiers. It is suggested that such microinclusions of graphite either do not completely dissolve in the melt or appear as a result of reactions in liquid iron [6].

In hypotheses about the heterogeneous nucleation of graphite inclusions in cast iron, various nonmetallic inclusions are most often mentioned as serving as substrates on which graphite is formed. In most cases, such non-metallic inclusions are various oxides and sulfides. For example, these are complex manganese sulfides [7, 8] or oxides of aluminum, silicon, magnesium, and other elements present in cast iron [9].

Moreover, the formation of inclusions of graphite with such additions can have a very complex mechanism. Thus, it was found [7] that oxygen and aluminum are present in the cores of nonmetallic inclusions of an irregular (polyhedral) or round (spherical) shape like (Mn, X) S (where X=Fe, Al, O, Ca, Si, Sr, Ti, etc.). Such inclusions are often covered with a thin layer of silicates, which are the main centers for the formation of lamellar graphite in experimentally smelted cast irons.

A three-stage model of graphite nucleation in gray cast irons is proposed in [10]. At the first stage, small inclusions of oxides (less than 2 µm) are formed, then larger (less than 5 µm) complex (Mn, X)S compounds are deposited. At the final stage, third graphite is deposited on the sides of the sulfides (Mn, X)S, which have a low crystallographic incompatibility with graphite. To maintain this sequence of graphite nucleation, three groups of elements are important.

The first group of elements is represented by strong deoxidizers (for example, Al and Zr), which are necessary for the formation of a large number of very small microinclusions.

The second group of elements includes manganese and sulfur for the formation of MnS sulfides. The third group consists of elements such as inoculators, acting in the first and second stage and improving the formation of graphite on the inclusions (Mn, X)S. In industrial cast iron, the compounds (Mn, X)S are more complex and have a higher graphitizing ability. This is due to the reduced ratio of Mn/S and a large number of microinclusions (the first stage of graphitization) in the presence of impurity elements – inoculators.

It should be noted that there are practically no convincing objections to the published numerous theories of nucleation of graphite inclusions in cast iron. However, the chemistry of the process itself is not considered. The process of deoxidation – the flow of chemical reactions in the metallic melt (interaction of a deoxidizer element with oxygen of carbon monoxide) – is practically absent in all studies.

Taking into account the aforementioned data, it is necessary to emphasize that silicon, being in a metal solution, interacts quite well with carbon monoxide, forming a surface-active monoxide (suboxide) of silicon and graphite in the reaction:

\[ \text{Si} + \text{CO} \rightarrow \text{SiO} + \text{C}. \]  

The formation of silicon monoxide is observed in cast irons modified with silicon [11] as well as in silicon-bearing steel grades [12]. Many steel grades, including foundries (E3, 25ChGSA, 30ChGSA, etc.), contain vitreous silicate globules. They are solid solutions of SiO–SiO₂ of non-stoichiometric composition, which is well revealed by the optical constant – the refractive index by the petrographic method of analysis [12]. Probably, the formed surface-active silicon monoxide will have a significant effect on the morphology of graphite in cast iron. However, such data are very limited in technical and scientific literature, so they require additional research.

### 3. The aim and objectives of the study

The aim of this study was to research the chemistry of the process of silicon interaction with carbon monoxide and the formation of silicon monoxide in cast iron as well as to determine its role in the occurrence and shape change of the graphite phase.

To achieve this aim, it was necessary to solve the following tasks:

- to study silicon monoxide as a product of the chemical reaction formed when silicon is introduced into liquid iron, using petrographic, X-ray spectral and other methods of analysis;
- to establish the role of silicon monoxide in the formation of graphite inclusions of different morphologies.

### 4. Materials and methods for studying the effect of silicon on the morphology of graphite

The influence of silicon on graphitization in gray cast irons was studied with the help of metallographic microengine spectral and petrographic methods. The tests were carried out on hypereutectic gray cast irons (EN-GJL-100, EN-GJL-150 EN 1561:1997), which were obtained in laboratory and industrial conditions from a traditional charge, using pig iron.

To adjust the chemical composition of cast iron, steel scrap (item 3) and ferrosilicon (FeSi45) were used. Cast iron was smelted in induction furnaces with acidic lining.

To control the chemical composition and structure of the metal, standard samples were cast.

The metallographic analysis was carried out with the help of the microscopes MIM-8M (USSR) and Zeiss Axiosvert 200 MAT (Germany) as well as the high-temperature microscope ALA-TOO IMASH 20-75 (USSR).

The micro-X-ray spectral analysis was carried out using the electronic scanning microscope SUPRA 40 WDS (Karl Zeiss, Germany).

Petrographic studies were performed in reflected light on an MBI-6 (USSR) microscope and in transmitted light on a crystal-optical microscope MIN-8 (USSR) using standard sets of immersion liquids [12].

Additional tests were made on silicon-containing inclusions in steels: electrotechnical (E3), economically doped (25ChGSA), etc. The results that were obtained with the MI-1309 mass spectrometer (USSR) [12] were used in the present study.

### 5. Results of the study of silicon monoxide in steels and gray cast irons

Fig. 1 shows globular inclusions detected in electrical steel E3. Inclusions differ in size, color (from colorless to
bluish-green and brownish-red), and transparency. Accordingly, they have different refractive indices \( N \) as well as different amounts of silicon in inclusions (Fig. 2) and silicon suboxides dissolved in them (Fig. 3).

![Figure 1. Globular inclusions, isolated from steel E3. Light passing \( \times 400 \)](image)

![Figure 2. Spectra of characteristic radiation of globular inclusions, isolated from steels 25ChGSA and E3: a — colorless; b — bluish-green; c and d — brownish-red; \( N \) is the index of refraction](image)

![Figure 3. A mass spectrogram of globular inclusions, isolated from steel E3 (Fig. 1): a — brownish-red; b — with a decay structure](image)

by heating them to 1,000–1,250 °C on a high-temperature microscope. At a temperature of 900 °C, which is typical, colorless globules with low indices of \( N = 1.460–1.480 \) increased in volume; at a temperature of 1,000 °C, craters appeared on the surface of bluish-green globules, from which gaseous (vaporous) silicon monoxide was intensively released.

A further increase in temperature led to cracking or complete rupture of silicate globules (Fig. 4, a—c). The more SiO was contained in the solid solution of SiO — SiO₂, the more rapidly the globules were destroyed.

![Figure 4. Globular inclusions of silicon monoxide \( \times 1000 \): a — before heating; b — after heating to 1,000–1,050 °C; c — at 1,100–1,250 °C](image)

A similar behavior of surface-active silicon monoxide should be assumed to occur in the liquid melt of gray cast iron, which was confirmed by the tests.

Thus, at a high temperature of 1,380–1360 °C, silicon interacts quite actively with carbon monoxide, accompanied by outbursts or even explosions. As a result of this interaction, a vaporized oxide of SiO and primary graphite crystals are formed. By color and reflectivity, they are very close and, therefore, poorly discernible on the section in reflected light. In transmitted light, silicon oxide is easily identified by the characteristic brownish-red color and a high refractive index \( N_\varphi \approx 2.15 \) and \( N_\rho \approx 2.06 \).

6. Discussion of the results of studying the influence of silicon on graphite formation in gray cast iron

Plates of graphite, formed as a result of the reaction of silicon with carbon monoxide, are distributed in the form of well-branched rosettes (Fig. 5). The latter consist of 5–6 petals and, as a rule, grow from one center, which is the place of silicon interaction with carbon monoxide. Plates are formed by the basic hexagonal planes of graphite. Such plates are aggregates of the finest petals, overlapping one another, which is well revealed in transmitted light when they are rubbed.

![Figure 5. A highly branched rosette form of graphite](image)
With decreasing temperature, the formation of the total amount of graphite is markedly increased. Along with 5–6 petal rosettes, there appear 3–4 petal ones as well as individual rectilinear plates (Fig. 6).

Further lowering of the temperature and, in general, changes in the physicochemical properties of the melt reduce the active interaction of silicon with carbon monoxide. The reaction rate slows down and proceeds less actively. This leads to the formation of rosettes of a smaller size and a less branched shape, as well as to the formation of small colonies of such rosette inserts. In addition to the rosette shape, a ramiform type of graphite appears (Fig. 7); it is formed due not only to the surface-active (gaseous) silicon monoxide but also to mobility – the motion of the melt (individual plates are bent in one direction or another).

The ramiform type of graphite, as a rule, is associated with straight-lamellar graphite. The number of rectilinear plates considerably increases, but their dimensions, including of ramiform graphite, decrease.

In some areas, inclusions of “degenerate” plate-like graphite of a vermicular form of branching were observed. The emergence of this form of graphite was due not only to the interaction of silicon with carbon monoxide but also due to the interaction in this case of silicon monoxide with graphite. As the temperature of the metallic melt decreases, the surface activity of SiO declines, too; its mobility decreases, and, at the site of its formation, it dissolves both in the melt and in graphite, changing its morphology to vermicular. In other words, the changed physicochemical conditions of the melt and the rate of reaction of the interaction of SiO with graphite have proved to be favorable for the formation of imperfect vermicular graphite.

Approaching the solidus temperature (a sharp decrease in the temperature and physicochemical conditions), the zone of primary graphite is replaced by a eutectic zone.

The presented data indicate that the formation of graphite – the building of its morphology – depends on the rate of reaction in the interaction of silicon with carbon monoxide, which is due to temperature changes and the physicochemical conditions of the melt.

Thus, at a high hypereutectic temperature, in the interval between the liquidus and the solidus, four morphological forms of graphite formation have been revealed: rosette, rectilinear-plate, ramiform, and vermicular. These forms are formed at various periods of temperature decrease, changes in the physical and chemical properties of the melt and, accordingly, changes in the activity of the reaction in the interaction of silicon with carbon monoxide. The varying conditions of the melt affect not only the formation of one or another form of graphite but also its size, quantity and distribution. Thus, on the basis of the foregoing, four zones of graphite formation can be distinguished:

- a zone of large 5–6 petal rosettes;
- a zone of smaller 3–4 petal rosettes;
- a zone of small rosettes that form colonies of individual straight plates in the form of twigs (a ramified form of graphite);
- a zone of ramiform graphite and straight plates (straight-lamellar);
- a zone of vermiciform, imperfect lamellar graphite.

It should be noted that the third zone is often characterized by the presence of particles and films of silicon monoxide, the products of its decomposition, as well as the products of the interaction of suboxides (vapor phases of iron, manganese, calcium, aluminum, etc.). Such products often condense on the surface of already formed graphite. The results of the micro-X-ray spectral analysis of plate inclusions of graphite are shown in Fig. 8.
These products have a complex non-stoichiometric composition and often contain impurities of sulfur, oxygen, and iron, which is confirmed by local micro-X-ray spectral analysis (Fig. 9 and Table 1).

![Graphite Inclusion](image)

**Table 1**

<table>
<thead>
<tr>
<th>Points of analysis</th>
<th>Content of elements, mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrum 1</td>
<td>carbon</td>
</tr>
<tr>
<td></td>
<td>90.78</td>
</tr>
<tr>
<td>Spectrum 2</td>
<td>87.35</td>
</tr>
</tbody>
</table>

In addition, the local analysis was carried out in various sections of graphite (at least 20 points). The registered contents are the following: oxygen (from 3.5 to 6.5 %), silicon (from 0.01 to 23 %), sulfur (from 0.01 to 2 %), and iron (from 1.5 to 5.5 %). The higher oxygen content indicates its suboxic nature, i.e., the presence of the marked elements represents a gaseous (vapor) phase dissolved in graphite.

It should be noted that in areas where sulfur is present, the absence of sulfide-forming elements (manganese and calcium) was often observed. This may indicate that sulfur interacts in this case with oxygen and carbon.

## 7. Conclusions

1. It has been found that the interaction of silicon with carbon monoxide in gray iron leads to the formation of silicon monoxide (the refractive indices are $N_p=2.15$ and $N_q=2.06$) and primary graphite crystals. The revealed elements are particles of silicon monoxide as the products of its decomposition and interaction with other vaporous phases of iron on the surface of graphite formed as well as in the composition of graphite inclusions. The local micro-X-ray spectral analysis of plate graphite inclusions (at least 20 points) recorded the contents of oxygen (3.5 to 6.9 %), silicon (0.01 to 0.23 %), sulfur (0.01 to 0.2 %), and iron (1.5 to 5.6 %). The higher oxygen content displays its suboxic nature, i.e., the presence of the marked elements represents a gaseous (vapor) phase dissolved in graphite.

2. The study has shown the role of silicon monoxide in the emergence and formation of graphite inclusions of various morphologies. Four zones of the formation of lamellar graphite (rosette, rectilinear-plate, ramiform, and vermicular) have been identified due to the rate of reaction and, accordingly, the temperature and physicochemical conditions of the melt. A mechanism is proposed for the formation of graphite in gray iron due to the release of surface-active silicon monoxide.

## References