Methods of graphitized steels obtaining

E A Guseva\textsuperscript{1}, M V Konstantinova\textsuperscript{1}, S K Kargapol'tsev\textsuperscript{2}, V E Gozbenko\textsuperscript{2,3}, A V Sivtsov\textsuperscript{4}, A I Karлина\textsuperscript{1} and M G Shtayger\textsuperscript{5}

\textsuperscript{1}Irkutsk National Research Technical University, 83 Lermontova Street, Irkutsk, 664074, Russia
\textsuperscript{2}Irkutsk State Transport University, 15 Chernyshevskogo Street, Irkutsk, 664074, Russia
\textsuperscript{3}Angarsk State Technical University, 60 Chaykovskogo Street, Angarsk, 665835, Russia
\textsuperscript{4}Institute of metallurgy, Ural branch of the Russian Academy of Sciences, 101 Amudsena Street, Ekaterinburg, 620016, Russia
\textsuperscript{5}MC Mechel Steel, 1 Krasnoarmeyskaya Street, 125167, Moscow, Russia

E-mail: karlinat@mail.ru

Abstract. The article presents the analysis of various methods for the production of steel with inclusions of graphite. The article demonstrates the effect on the process of graphitization of alloying elements, various types of heat treatment, crystallization by a pulse-continuous method.

1. Introduction
In the operation of some parts there is a need for a combination of the properties of steel and gray cast iron. This is feasible when using graphitized steels.

If free carbon is released on the surface of steel products (which is characteristic of the cast iron structure), then the graphite contained in the cast iron act as a lubricant. Free carbon (graphite) causes an increased porosity of the castings. Due to this, the surface layers of the product can be impregnated with oil. Accordingly, such products will have good anti-friction properties [1].

Graphitization of steels under conditions close to equilibrium occurs in hypereutectoid alloys. In hypoeutectoid alloys, graphitization is possible only under certain conditions, for example, when modifying additives are used. Magnesium, calcium, cerium, lanthanum, stibium, bismuth and other elements can be used in this capacity.

2. Results and Discussion
Graphitization of high carbon steels alloyed with silicon occurs as a result of annealing at 950 °C. Silicon has a graphitizing effect [2, 3]. The graphite content is 0.7% after this type of heat treatment. As a result of the second stage of annealing at 760 °C the content of graphite increases to 0.9%. Due to the long duration of the process, such steel has not been applied in practice due to the high cost price [4].

Graphitization of low carbon and medium carbon steels is carried out by cementation followed by graphitizing annealing [5, 6]. Moreover, during cementation, hydrogen-charged iron is added to the solid carburizer [5]. Under normal cementation regimes, even with high silicon contents (up to 3%), no graphite formation occurs [1].
In the works [2, 7] it is proposed to obtain graphite inclusions on medium carbon steel directly during cementation. 55C2 steel was cemented. Before cementation, it was quenched and then placed in a standard solid carburizer. As a result of that kind of processing, graphite inclusions were obtained. It is shown that it is preliminary quenching that affected the formation and growth of graphite inclusions. As a result of marquenching, microcracks are formed at the points of contact of martensite needles. They are the ones that are filled with carbon coming from the carburizer.

In the works [8, 9], it is proposed to obtain graphite inclusions on the surface of medium carbon steels (steel 40) in the process of carbonitriding, which is carried out in a two-stage mode. As a result of the first low-temperature stage (550-600 °C), the surface is saturated with nitrogen, and carbonitride compounds are formed. In the process of the second high-temperature stage (820-950 °C) nitrogen is removed from the surface, which leads to the formation of pores and cracks, which are filled with carbon during the cementation process. To carry out this process, a nitro-cementing paste of a specific composition was proposed.

In the work [10], U10 steel was subjected to thermal cycling at temperatures close to A1 (in this case lamellar pearlite becomes granular), then heat cycling was carried out near the Curie point of cementite. This was done 35 times. As a result, small round inclusions of free carbon were found. It was concluded that steels with granular pearlite structure is prone to graphitization.

The decomposition of cementite with the formation of graphite during thermal cycling for steel 20 was established in [11].

During operation of steam pipelines made of steel 20, natural thermal cycling occurs, since the steam pipeline is turned on and off with a certain sequence. Operation results in the occurrence of graphite inclusions of a rounded shape, located mainly on the border of ferritic grain, on which tertiary cementite was located in the initial state, or in the volume of ferritic grain near non-metallic inclusions. The volume fraction of graphite inclusions is 1.4 % (by volume) [12].

Sometimes the process of graphitization occurs during the operation of installations, for example, steam power installations. In such cases, the formation of graphite leads to emergency situations. Molybdenum steels are more often subject to this process. It is believed that the coarse-grained steels became less susceptible to the process of graphitization than the fine-grained ones. Therefore, carrying out normalization contributes to the formation of graphite, as compared to annealing. The spheroidization of cementite, which is in the composition of pearlite, most often contributes to the formation of graphite. The regions, which are cooled unevenly during the heat treatment, are also subjected to the process of graphitization. The heat-affected zone in the welds in high-pressure steam pipelines is a zone of large formation of graphite inclusions, i.e. this is the risk zone [13].

Studies were carried out on steel modified with ferrosilicon [14]. It has been established that rounded graphite is located in the microstructure of casting, and the amount and variety of forms of graphite inclusions also increase with increasing the thickness of casting.

In the work [15] it was shown that thin-walled castings in steels are more graphitized than thick-walled ones. At the same time, it is known that, for cast irons, the degree of graphitization increases with the increase in the casting thickness [16]. The shape and size of graphite inclusions in cast irons depends on the crystallization conditions, the modifiers introduced, and the annealing modes of the castings. Thus, promising modifiers proposed in a number of works [17-20] made from production waste of silicon and ferrosilicon allow obtaining vermicular graphite instead of lamellar one.

Carbon and silicon are graphitizers in steel. The influence of the amount of silicon and the cooling rate of the castings were considered in the works [21, 22], the results of which agree well with each other. The additives of ferromanganese and ferrosilicon were injected in dry sandy-argillaceous forms directly before pouring the liquid metal into the bucket. It was established that the addition of ferrosilicon led to the emergence of free graphite in the structure, i.e., ferrosilicon is a modifier for the formation of graphite in steels. In the process of modification, silicon-enriched microvolumes are formed in the liquid metal. They are the centers of graphitization. With the increase in the amount of silicon and the content of carbon, the formation of graphite becomes larger and its forms change. The shapes of graphite vary from scattered small to evenly distributed flocculent and spherical. The metal
base also changes. The effect of the casting thickness on the formation and growth of graphite inclusions was also investigated. It was found that with increasing wall thickness of the casting, the size of graphite inclusions and their number increased. As a result of the performed operations, the mechanical properties of graphitized steel also changed. In the paper [10] it was shown that, when steel is poured, it is already possible to obtain microstructures, including graphite of various shapes, by applying the modification in the bucket.

Graphitized steels are materials with low technological ductility. With traditional methods of producing that kind of steels, technologies of slow cooling are used directly in the casting molds. The emerging microstructure has a coarse pattern. The released graphite inclusions are not uniformly distributed in the casting body. To obtain a structure that includes fine globular graphite, either long-term annealing or thermomechanical treatment is used. These operations are quite lengthy.

The research work [23] considers methods of pulse-continuous crystallization of castings. That kind of methods makes it possible to obtain spherical graphite in the structure of cast steel, which is evenly distributed.

The work [24] shows the effect of chemical composition on the mechanical properties of graphitized steel, in particular, on tensile strength, fatigue strength, relative elongation, and the effect of carbon and silicon, as well as copper on graphitization of steels. The dependences of the effect of carbon, silicon and copper on the values of both cyclic and static strength are revealed. High mechanical properties are provided by steel containing 0.8-1 % of carbon; 2.2-2.4 % of silicon; 3.0-3.2 % of copper; 0.6-0.7 % of manganese; 0.15-0.18 % of chromium; 0.2-0.25 % of aluminum; 0.02 % of sulfur and 0.03 % of phosphorus.

In the works [25, 26], on the basis of Fe-C-Cu state diagrams, the influence of copper on the formation of lamellar or spherical graphite, i.e. on the process of graphitization, was considered and analysed. The article shows the effect of the microstructure on the mechanical properties, in particular, on the tribotechnical ones. It describes the conditions for the formation of phases that contain copper. The problem of the optimal combination of copper content with additive elements and carbon present in the alloy is analyzed. The solubility of copper in the main phases and structural components is also determined.

It is of interest to estimate the possibility of graphitization of the surface layers of steel subjected to plasma cementation. In the works [27-29] it proved to be possible to saturate the steel surface with carbon to concentrations corresponding to the composition of cast irons, while its structure corresponded to that of white cast irons.

Plasma surface treatment refers to methods of surface hardening using highly concentrated energy sources with a specific power of more than \(10^8 \text{ W/m}^2\). For this purpose, the plasmatron Multiplaz 3500 was used. The surface was saturated with carbon atoms as a result of bombardment by carbon ions formed in the cathode region of a glow discharge.

As a plasma-forming substance, several formulations containing alcohol, benzene, water and their mixtures were proposed, and the optimum composition of the plasma-forming mixture was established. The carbon source was a graphite coating applied previously to the samples, which consisted of graphite powder, liquid glass, cutting compounds and water.

As a result of the plasma cementation process, the formation of atomic carbon in a large amount takes place, and at a temperature difference it easily penetrates (diffuses) into the surface layers of the metal.

With the simultaneous impact of graphite coating deposited on the metal surface, and the action of the plasma arc, a state may arise in which a thin layer of melting occurs on the surface (micro-melting mode). A large amount of cementite emerges, and the concentration of carbon in the layer is much higher than the concentration obtained by saturation in the solid phase. During micromelting, the maximum depth is 107-190 μm, carbon is unevenly distributed over the cementation depth, which leads to the formation of various types of microstructure. When macro-melting, the cementation depth increases significantly. It can reach 3 mm and more, with carbon being more evenly distributed throughout the volume of the melted metal.
The cemented layer consists of two zones (Figure 1). The first zone is characterized by a significant supersaturation of carbon, its structure corresponds to that of white cast iron. In the second zone, the carbon concentration is gradually approaching the initial concentration.

![Figure 1. Cemented layer with melting mode; (a) ×200, (b) ×500.](image)

The series of experiments on the treatment of the models of steel after the plasma cementation were carried out, the purpose of which was to obtain the graphite inclusions in the surface layer.

The subsequent heat treatment was the annealing of models. The task was to evaluate both the possibility in principle of obtaining the graphite starts and to establish the most rational regimes of the annealing of the cemented models.

A study of the models, annealed after the regime of macro-melting, with different regimes of annealing shows that graphitization it is not observed visually. The measurement of microhardness showed the absence of graphite inclusions as well.

With an increase in the duration of exposure, natural grain growth occurs.

3. Conclusion
The authors believe that the attempt to carry out graphitization in thin layers is bound to failure, since the subsequent high-temperature annealing (900 –1000 °C) results in the active outflow of carbon into the deeper layers due to the high rate of its diffusion.

Perhaps, another way may be very promising: already at the plasma processing stage, to apply the coatings that would allow obtaining a diffusion layer, the composition and structure of which would provide attractive properties.

References
[1] Guderman E E Special steels (Moscow: Metallurgiya Publ.) vol 1 p 736
[2] Letov S S, Letova O V, Pivovar N A 2015 Modern automotive materials and technologies (SAMIT) 120-123
[3] Kolmykov V I, Letov S S, Pereverzev V M 2003 Materials and strengthening technologies 124-127
[4] Kolmakov V I, Letov S S, Letova O V 2006 Modern instrumentation systems. information technologies and innovations 279-283
[5] Zhurakovsky V M, Sadchikov V Ya 1980 Metallography and heat treatment of metals 4 61-63
[6] Moshnyagnul V V, Vimitsky A G, Zemskov G V 1972 Metallography and heat treatment of metals 11 69-71.
[7] Letov S S 2003 Materials and strengthening technologies 140-141.
[8] Letova O V 2012 Surface graphitization of structural steels with two-stage carbonitriding, author's abstract of diss. of Ph.D., Kursk State University p 17
[9] Letova O V 2012 Surface graphitization of structural steels with two-stage carbonitriding: author's abstract of diss. of Ph.D., Kursk State University p 1146
[10] Gvozdev A E, Malyarov A V, Tikhonov I V, Sergeev N N, Kalinin A A, Starikov K N 2015 The deformation and destruction of materials and nano-materials 23-24.
[11] Tikhonov I V, Kuzovleva O V, Starikov N E, Gvozdov A E 2008 Rolled metal production 8 36-37
[12] Gvozdev A E, Malyarov A V, Tikhonova I V, Sergeev N N, Kalinin A A 2015 Deformation and destruction of materials and nanomaterials 238-239
[13] Begunov A I, Osipova T A 2010 Proceedings of Irkutsk State Technical University 1 257-259
[14] Bublikov V B, Kozak D S, Nesteruk S P, Zelenaya L A 2004 Casting processes 2 41-46
[15] Todorov R P, Nikolov M L 1976 The structure and properties of graphitized steel castings (Moscow: Metallurgiya Publ.)
[16] Vitusevich V T, Biletsky A K, Naumenko M I 2003 Casting processes 1 40-45.
[17] Karlina A I, Balanovsky A E, Kondrat’ev V V, Kolosov A D, Ivanchik N N 2018 Advances in Engineering Research conference proceedings 169-173
[18] Kondratiev V V, Karlina A I, Guseva E A, Konstantinova M V, Gorovoy V O 2018 IOP Conference Series: Materials Science and Engineering International Multi-Conference on Industrial Engineering and Modern Technologies 042064
[19] Kondratiev V V, Kolosov A D, Gorovoy V O, Nebogin S A, Elkin K S 2018 IOP Conference Series: Materials Science and Engineering 411 012036.
[20] Kondratiev V V, Nebogin S A, Kolosov A D, Gorovoy V O, Nemarov A A 2018 IOP Conference Series: Materials Science and Engineering 411 012037
[21] Savchenko V A, Volchok V P 2007 Casting and metallurgy 4 89-91
[22] Zhukov A A 1993 New about graphitized steel. Foundry, 1993. No. 3.
[23] Alexandrova N M 2006 The Materials Science Basics of New Technologies for Continuous Casting and Radiation-Heat Treatment of Hard-to-Deform Steel and Alloys, Author's abstract of diss. of Doctor of Engineering Sciences, Institute of Metal Science and Metal Physics FSUE "TsNIchermet" them. I.P. Bardeen " p 26
[24] Akimov I V 2015 Vestnik of Dnipropetrovsk National University of Railway Transport. Science and progress for transport 3(57) 129-133
[25] Sil’man G I, Kamynin V V, Tarasov A A Metallurgy and heat treatment of metals 7 15-20.
[26] Silman G I, Kamynin V V, Serpik L G, Goncharov V V 2008 Contribution of scientists and specialists to the national economy 36-43
[27] Balanovsky A E, Wu V G 2017 Letter about materials vol 7 2 pp 175-179
[28] Wu Van Gyui 2015 Bulletin of Science and Education of North-West Russia vol 1 205-211
[29] Gyui Wu Van 2018 Cementation of low carbon steels using plasma heating of graphite-containing coatings and process gas environments, author's abstract of diss. of Ph.D. of Engineering Science, Komsomolsk-on-Amur State University p 23.