Structure formation in materials based on Fe-C-Si and Fe-C-Al systems (cast irons) prepared from dispersed mechanical engineering waste

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Abstract. The paper presents an alternative technological process for producing compact forms of graphite inclusions in the materials based on the Fe-C-Si and Fe-C-Al (cast iron) systems. It differs from traditional methods of obtaining compact forms of graphite inclusions, which consist in modifying the molten iron or annealing white iron: the proposed technological process is based on a synergistic complex of foundry-metallurgical factors affecting the cast iron in the stages of its melt preparation and crystallization in a mold.

1 Introduction
Production activities of large machine-building enterprises are associated with the formation in sufficiently large quantities and a diverse range of waste, including dispersed types, which are a big problem in involving them in the process both because of their dispersion, and the presence of non-metallic inclusions and metallic elements. The release of 1 ton of suitable blanks is accompanied by the emission of up to 30 kg of dust. To assess the scale of formation of iron-containing dispersed wastes of machine-building production, it suffices to give examples of the operation of electric arc furnaces in which melting dust is captured in an amount of 10...20 kg/t in the production of cast iron, as well as forging and thermal workshops, in which scale is formed in an amount of 20...50 kg / ton of products.

When other divisions of the machine-building complex work, dispersed iron-containing wastes are also formed: sludge from electrochemical and electroerosive treatment, electroplating, from wastewater treatment, shot blasting, spraying, grinding, grinding operations, exposure and other types of metal cutting. All this is taken to dumps, in which over 500 thousand tons of iron-containing sludge are buried. At the same time, society suffers significant environmental damage, and machine-building enterprises are forced to bear the burden of costs associated with the organization of burials and the payment of fines. However, the elemental composition of dispersed waste gives reason to consider them as a promising raw material in the form of substitutes for polymetallic ores and limestone. In industries related to the production of primary metal, technological solutions for the disposal of these wastes are known. First of all, this refers to the aglodomen production and alternative options for the production of primary metal: “Midrex”, “Corex”, “Romelt” [1...4]. However, the discussed processes are intended for the smelting of primary metals in the conditions of a metallurgical plant and are unacceptable for machine-building enterprises producing structural casting materials. Moreover, as the
unfolding discussion shows [5...7], there is no complete clarity in terms of manufacturability, cost effectiveness and environmental friendliness of alternative processes for obtaining a primary metal, as well as utilization of dispersed production wastes in them.

Therefore, there is an urgent question about the maximum possible degree of waste disposal of the production of the machine-building complex inside it, the solution of which will make it possible to reduce the cost of manufactured products and improve the ecological situation in industrialized regions.

An effective solution to these problems can be found in the technological processes of procurement (foundry) engineering production.

2 Technological process for the production of materials based on Fe-C-Si and Fe-C-Al systems from iron-containing technogenic waste from mechanical engineering

The initial charge components for the implementation of this process are iron-containing dispersed waste engineering (ICWME), in which iron and other components are present both in the oxidized and in the reduced state. This utilization scheme ultimately provides for the production of materials based on Fe-C-Si and Fe-C-Al systems by synthesis from elements present in iron-containing machine-building waste. At the first stage of the technological process, a moistened mixture consisting of ICWME is obtained in the ratio of components, which makes it possible to obtain a melt with characteristics in terms of composition and properties required by the technological process. A solution of sodium chloride (NaCl) and iron trichloride (FeCl₃) together with etching waste from copper plates form the basis for the formation of the mixture. The last waste is saturated with copper ions, the presence of which in materials based on the Fe-C-Si and / or Fe-C-Al systems only improves its properties [8...10]. Pellets are made from the obtained composite molding material, which are dried in order to acquire sufficient strength necessary for transportation to the smelting unit.

Further granular composition is sent to a specialized melting unit. In this unit, the following physicochemical transformations proceed successively: heating the pellets to temperatures of 1000...1300 K, metallizing the oxides, melting the granules with the appearance of the liquid slag phase and the metal phase and their overheating. As a result of physicochemical transformations, a melt of materials is synthesized based on the systems Fe-C-Si and / or Fe-C-Al. The proposed technology makes it possible to produce both cast irons and steel [11,12], in view of the fact that the synthesis of a cast alloy is carried out from elements that are restored in the smelting unit both in the liquid and solid phases. Metallization in the solid phase is carried out in a countercurrent granular composition and reducing gas. During the solid-phase metallization metals such as iron, molybdenum, copper, nickel are restored.

The main impurity in synthesized materials based on Fe-C-Si and / or Fe-C-Al systems is carbon, which has a reduction potential with respect to iron oxides and a carbon potential relative to reduced iron. Carbon saturation of the metal melt to a predetermined level is carried out as a result of cementing metallization.

The pellet composition, which underwent physicochemical heat treatment in a countercurrent reactor, enters the liquid bath of the melting unit as a result of the screw rotation. In the bath of the melting unit, under the action of the heat of an electric arc of direct current, the granular composition melts. Flag and metal phase are formed. In the process of liquid-phase metallization, such elements as silicon, manganese, tungsten, vanadium, aluminum, and magnesium are restored. In the melting unit, the anode is a non-consumable top electrode, and the cathode is a liquid metal bath with a bottom electrode connected to a DC source. Such a connection to a DC source implies an effective liquid-phase metallization in a melting furnace using electrolysis processes. The above proposed mode of melting of the granular composition creates conditions for obtaining high-quality alloy due to the refining effect of slag, possessing a high basicity and temperature, the presence of a reducing atmosphere that has a protective character in all phases of the smelter, as well as the effect of an electric current passing through the liquid metal melt [13].

3 The influence of technological features of the preparation of melt from dispersed waste engineering to the process of structure formation in materials based on systems Fe-C-Si and / or Fe-C-Al
The developed specialized melting unit, along with the fact that it allows to process ICWME, has another positive feature, which consists in obtaining high-quality materials based on Fe-C-Si and / or Fe-C-Al systems. This is achieved by the fact that dispersed wastes used as charge materials contain a lower content of sulfur and phosphorus (less than 0.02%). This circumstance allows the smelting of materials based on Fe-C-Si and / or Fe-C-Al systems without the use of highly basic slags and their processing of a liquid alloy. As a result of direct electric current passing through the liquid slag and metal, a change occurs in the structure of the metal matrix and graphite inclusions [13]. Such a liquid material based on Fe–C–Si and / or Fe–C–Al systems is prone to compact graphitization according to a synergistic model of this process [14,15], as well as experimental data [16,17].

One of the important factors contributing to compact graphitization of materials based on Fe-C-Si and / or Fe-C-Al systems is melt overheating. The higher the heat of the melt, the higher its susceptibility to metastable crystallization. In this case, there are conditions for the occurrence of carbide deviations (fluctuations) in which the carbon activity determines a sufficiently large thermodynamic potential of graphitization. The value of the thermodynamic potential of graphitization is determined by the interaction of a number of factors and conditions, such as the temperature of overheating of the melt; the degree of melt refining from surface active substances; the presence of elements that form quasichemical ordering in the melt with iron and carbon.

The creation and activation of the thermodynamic potential of compact graphitization is possible by two mechanisms. The first mechanism of compact graphitization involves overheating of the melt to a supercritical state, in which the potential of compact graphitization is created on the basis of the formation of ordered macro-zones with pseudocarbide stoichiometry. The destruction of these zones, leading to the formation of point graphite - a building material for the formation of compact graphite inclusions, is carried out using graphitizing modifiers, either slow cooling or optimal supercooling and crystallization of highly superheated and deeply refined melts. In the second case, the potential of compact graphitization is created by entering the melt in the subcritical state, but at a temperature higher than the ionization temperature, a modifier (magnesium, yttrium, cerium containing additives) capable of forming metastable carbides in the melt with graphite clusters and iron. Thus, the thermodynamic mechanism of compact graphitization assigns an important role to the state of the melt of materials based on Fe-C-Si and / or Fe-C-Al systems, which has a strong influence on the structure formation in the workpiece.

The following critical threshold temperature effects were established by experiments [18... 20]: 1723...1753 K (first threshold), 1833...1853 K (second threshold). There are grounds [21] to consider the third threshold as 1883...1893 K, the fourth - 1973...1983 K. The appearance of different thresholds is caused by the presence of different factors with the initiating influence of some one. All factors influencing the effect of overheating of the melt of materials based on the systems Fe-C-Si and / or Fe-C-Al are classified by mechanisms of action at the macro-micro and submicroscopic levels. At the macro level, the effect of the following factors is noted: the disappearance of free germinal centers of graphite and, as a result, an increase in the propensity of materials based on Fe-C-Si and / or Fe-C-Al systems to metastable crystallization; refining the melt from non-metallic inclusions (silicates, sulfides, phosphides, oxides of refractory metals, nitrides, etc.); elimination of the "negative" heredity of the charge. Factors acting on the micro level include: restructuring of materials based on Fe-C-Si and / or Fe-C-Al systems with increasing temperature; polymorphic transformations in some elements of the melt (primarily iron, silicon, etc.); redistribution of chemical bonds; transition of the melt from the colloidal suspension state to the true solution state. The factors acting on the submicroscopic level are associated with donor – acceptor transitions in the melt elements; increasing the chemical activity of the elements of the melt; the occurrence of concentration deviations (fluctuations); their development into homogeneous nucleation, spinodal melt stratification.

The use of the listed mechanisms operating at different levels led to the development of technological measures for the intra-furnace melt processing: high overheating, isothermal holding at high temperatures of overheating, slag and thermo-slag electric arc treatment. The effectiveness of these technological measures of infrahep treatment is so high that it results in a compact form of graphite in materials based on the Fe-C-Si and / or Fe-C-Al systems without the use of traditional
spheroidizing modification [21,22]. High-temperature and thermo-time processing of materials based on Fe-C-Si and / or Fe-C-Al systems contributes to its compact graphitization [23...27].

Analysis of the existing and obtained results in the issue of manufacturing high-quality materials based on Fe-C-Si and / or Fe-C-Al systems using the intra-furnace processing of the alloy and the theoretical rationale given above can be sufficiently attributed to the conditions of formation of materials for on the basis of Fe-C-Si and / or Fe-C-Al systems in a developed specialized melting unit. The formation of liquid materials based on the systems Fe – C – Si and / or Fe – C – Al is carried out in a highly superheated slag phase from elements that are in an oxidized state as a result of their metallization. In this case, difficulties with the negative influence of the heredity of charge materials disappear. The creation of a liquid metal phase is carried out by passing charge granules through a liquid slag phase. Passing through the liquid slag phase a droplet-shaped metal is subjected to deep refining due to the developed surface. Deep refining of metal is also enhanced by the electrocapillary effect under the action of direct current. At the same time non-metallic components are transferred to the slag, and the metal is deposited on the bottom. Overheating of the liquid phases in the melting bath is such that it overlaps the first and second thresholds. The effect of slag treatment is enhanced by the action of an electric arc, especially when used as provided in the proposed DC unit [21].

Thus, in the smelting unit under discussion, conditions are created for the manifestation of a synergistic effect of temperature, thermal, slag, electric arc and electric current treatments affecting the melt inclination of materials based on Fe-C-Si and / or Fe-C-Al systems to the formation of compact forms of graphite during crystallization with a high level of supercooling.

4 Metallographic examinations

The study analyzed the microstructure and shape of graphite inclusions of materials based on Fe-C-Si and / or Fe-C-Al systems synthesized by direct route from ICWME in a specialized electrothermal melting unit. Natural objects in the form of blanks of the piston group of the KAMAZ automobile, poured into sandy-clay forms [28, 29] served as samples. The structure of the rings is checked on the cross section, for which the section opposite the castle part of the ring was cut. The structure of the metal matrix, as well as the form of graphite inclusions, was evaluated according to State Standard 3443-87 "Castings from cast iron with various forms of graphite". The structure analysis was carried out on a Neofot 32 microscope. The chemical composition of materials based on the Fe-C-Al system of piston rings was characterized by the following elemental contents,% (wt.): C - 3.6 ... 4.0; Al - 2.4 ... 3.0; Mn - 0.5 ... 0.8; Cr - ≤0.3; Cu - ≤0.3; S - <0.02; P - <0.03. The chemical composition of materials based on the Fe – C – Si system of piston rings was characterized by the following elemental contents,% (wt.): C — 3.5 ... 4.0; Si - 3.2 ... 3.6; Mn - 0.4 ... 0.7; Mo - 0.014 ... 0.04; Cu - 0.75 ... 1.0; S - <0.02; P - <0.15.

Figure 1 shows the typical structures of materials based on the Fe-C-Si system, obtained in a specialized ICWME melting unit at various superheating temperatures without the use of modifiers.

![Figure 1](image1.jpg)

**Figure 1 - Microstructure of materials based on the Fe-C-Si system, obtained in a specialized melting unit from ICWME with overheating up to 1773K (a) and 1873 K (b): a – x100; b - x100**
The formation of various types of graphite in materials based on Fe-C-Si and / or Fe-C-Al systems is the result of direct melt carbon extraction during eutectic crystallization and further supersaturation of austenite with carbon. To obtain compact forms of graphite, high overheating of materials based on Fe-C-Si and / or Fe-C-Al systems is required, which in this case goes from a colloidal suspension state to a true solution due to deep refining from non-metallic inclusions, as well as from oxygen, sulfur and phosphorus. Analysis of changes in the nature of the formation of graphite according to Figure 1 confirms this.

So materials based on Fe-C-Si and / or Fe-C-Al systems, melted with overheating up to 1773K, have a lamellar rectilinear and vorticated form of graphite with a length varying from 25 to 90 microns. The size of graphite inclusions is 45 ... 50 microns. The distribution of inclusions in the structure of materials based on Fe-C-Si and / or Fe-C-Al systems is mostly uniform with an interdendritic shade. The share of graphite inclusions is about 6... 7%.

Increased overheating of liquid materials based on Fe-C-Si and / or Fe-C-Al systems in the melting process (1873 K) leads to a change in the graphite structure. The main form of graphite inclusions (≈60%) is a vermicular, tortuous shape. This graphite is represented in the structure as uniformly distributed and isolated inclusions. In the structure of materials, there is also observed a compact and lamellar form of graphite inclusions, the volume of which is, respectively, ≈ 15 and 25%. The size of graphite inclusions was significantly reduced to <15 μm with an interdendritic distribution in the form of colonies and points. Compact graphite has a spherical shape with dimensions of inclusions 15 ... 30 microns. In addition, there are in the structure and clusters of small inclusions. Further overheating of the melt of materials based on Fe-C-Si and / or Fe-C-Al systems leads to an increase in the dispersion of the pearlite base of the metal matrix and a change in the distance between the cementite plates when the liquid material is overheated based on Fe-C-Si and / or Fe systems-C-Al up to 1773 K up to 1 micron and with overheating up to 1873 K up to 0.7 micron. At the same time, the hardness of materials based on Fe-C-Si and / or Fe-C-Al systems increased from 200 HB to 215 HB.

Figures 2...5 show the effect of superheat temperature, carbon and part thickness on the microstructure of materials based on the Fe-C-Al system containing 1.7% silicon.
In low carbon (2.7% C) materials based on the Fe – C – Al system, small amounts of interdendritic carbides are found in the thinnest sections (10 mm). Suppression of these carbides is possible by increasing the thickness to 50 mm (Figure 5).

For blanks with small thicknesses (10 mm), overheating is effective from the point of view of suppressing carbides in low-carbon materials based on the Fe-C-Al system. For medium thicknesses.
(25 mm) in materials based on the Fe-C-Al system containing 2.7% carbon, overheating results in the appearance of a large number of graphite globules distributed in the perlite-ferritic matrix. For large thicknesses (50 mm) in materials based on the Fe-C-Al system containing 3.7% carbon, overheating leads to the formation of significant quantities of crushed graphite.

The structure of the matrix and the morphology of graphite are very sensitive to the content of graphite. For a carbon content of 2.7%, globules of graphite of two different sizes are observed in the pearlite matrix. As the carbon content increases to 3.7%, the proportion of ferrite in the matrix increases significantly (Figure 3) and degenerate forms of graphite appear.

The interdendritic clusters of crushed graphite (“chunky”) can be observed in thick sections (50 mm), especially with an increased carbon content in materials based on the Fe-C-Al system.

5 Conclusions and perspectives

The scientific fundamentals of the physicochemical processes of forming materials based on Fe-C-Si and / or Fe-C-Al systems with compact graphite inclusions without modifying the melt synthesized using dispersed industrial wastes containing elements in an oxidized state have been developed. The factors synergistically causing compact graphitization are established:
- direct synthesis of materials based on the systems Fe-C-Si and / or Fe-C-Al, excluding any heredity, including negative ones;
- formation of materials based on Fe-C-Si and / or Fe-C-Al systems from a melt of a drop-like state in a highly superheated slag phase, creating conditions for deep refining of the metal and its overheating into a supercritical state (T> 1853 K), forming carbide-forming fluctuations;
- electric current melt processing of materials based on systems Fe-C-Si and / or Fe-C-Al.

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