

MINISTRY OF SCIENCE AND HIGHER EDUCATION  
RUSSIAN FEDERATION  
FEDERAL STATE AUTONOMOUS  
EDUCATIONAL INSTITUTION OF HIGHER EDUCATION  
"KAZAN (VOLGA) FEDERAL UNIVERSITY"

UDC 621.75: 669.71

As a manuscript

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«SCIENTIFIC BASES OF INNOVATIVE SOLUTIONS FOR THE PRODUCTION OF  
MATERIALS OF THE SYSTEM Fe-C-Si and Fe-C-Al WITH RECYCLING  
TECHNOGENIC WASTE OF ENGINEERING»

Specialty: 05.16.09 - Materials Science (in mechanical engineering)

Autoabstract

thesis for the degree

Doctors of Technical Sciences

Naberezhnye Chelny - 2018

The work was done in the departments of “Materials, technology and quality” and “Mechanical Engineering” at the Naberezhnye Chelny Institute (branch) of the federal state autonomous educational institution of higher education “Kazan (Volga Region) Federal University”.

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Protection will be held: "\_28\_" \_\_\_\_12\_\_\_\_2018 at 13.30 at the meeting of the dissertation council D 212.081.31 at "Kazan (Volga Region) Federal University": 423800, RT, Naberezhnye Chelny, pr. Mira, 13A, ULK-5 , aud.309.

The dissertation can be found in the Kazan (Volga Region) Federal University library.

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**The urgency of the problem.** The modern development of technology is inextricably linked with the research and development of new materials, which, along with high strength, also

have the necessary special properties - heat resistance, wear resistance, thermomechanical fatigue, etc.

Among the successful solutions in the production of materials in the 20th century should be called the development and implementation of high-strength cast iron (HF) in mechanical engineering based on the Fe-C-Si system. Recently in the country and abroad extends the scope of HF based on the system Fe-C-Al. This is explained by the fact that these alloys, which include Al, possess a number of valuable physical and operational properties. However, the search for more effective compositions based on the materials of the system Fe-C-Si and Fe-C-Al with a compact form of graphite continues to the present. Of particular note is the importance of numerous theoretical and experimental works of famous scientists: N.N. Alexandrova, N.I. Beha, Yu.G. Bobro, I.N. Bogacheva, A.M. Bochvar, V.A. Vasilyeva, K.N. Vdovina, K.I. Vashchenko, N.G. Girshovich, B.B. Gulyaeva, S.V. Davydov, A.A. Zhukova, M.A. Ioffe, G.A. Kosnikova, V.M. Kolokoltseva, N.N. Rubtsova, A.A. Ryzhikov and many other researchers, who solved numerous problems of determining the laws of the formation of globular graphite, the use of various modifiers and technological processes for obtaining HF and the production of blanks, which was the fundamental basis for expanding the scope of HF.

Analysis of the literature suggests that the available scientific and technical information and practice of extensive use of materials based on the system Fe-C-Si and Fe-C-Al in the production of the most critical parts of mechanical engineering working under intensive loads, elevated temperatures in contact with aggressive media, in the conditions of abrasive wear, etc. based on the use of quality raw materials. However, at present, the stability of obtaining compact forms of graphite inclusions has decreased due to the wide range of raw materials and the various methods of modifying processing of melts.

Currently, the production of engineering and metallurgical products is accompanied by the formation of a large number of dispersed industrial waste of a wide range. These wastes for the most part are not used in production, are dumped, causing harm to the environment.

The development of new compositions of materials based on the Fe-C-Si and Fe-C-Al system and the physicochemical processes of their formation with a given structure and properties, combined with the implementation of innovative recycling technologies for dispersed technogenic waste from mechanical engineering is a pressing problem with technological, economic and environmental points of view.

The work was done with the support of the Ministry of Education and Science of the Russian Federation, within the framework of the State Task No. 9.3236.2017 / 4.6, the State Contract under the 220th Resolution No. 14.z50.31.0023.

The purpose of the study is to develop the theoretical and technological foundations of innovative solutions for obtaining high-quality materials based on the Fe-C-Si and Fe-C-Al system with elements for recycling dispersed industrial wastes.

To achieve this goal, the following main tasks **were accomplished:**

- explore the features of structure formation in materials based on the system Fe-C-Al;
- explore the process of graphitization of materials based on the system Fe-C-Si and Fe-C-Al during centrifugation;
- to investigate the influence of technological parameters on the processes of formation of the structure and properties of materials based on the system Fe-C-Si and Fe-C-Al prepared from dispersed technogenic waste from mechanical engineering;

- to develop technologies for the preparation of melt materials based on the Fe-C-Si and Fe-C-Al system from dispersed iron-containing technogenic waste of mechanical engineering, equipment and technical solutions for its implementation;

- to develop and justify the composition and physico-chemical processes of formation of materials based on the system Fe-C-Si and Fe-C-Al for products in mechanical engineering.

**The object of the study** is the physicochemical processes of the formation of high-quality materials based on the Fe-C-Si and Fe-C-Al system with elements of recycling of man-made waste.

**The subject of research** is materials based on the system Fe-C-Si and Fe-C-Al for mechanical engineering blanks.

**Research methods.** The solution of the tasks is based on the methods of statistical analysis of research results and information on the manufacturability of materials based on the system Fe-C-Si and Fe-C-Al at the stages of manufacturing blanks; traditional, improved and specially developed new methods for controlling the properties of materials based on the Fe-C-Si and Fe-C-Al systems, such as metallographic, dilatometric, X-ray diffraction and chemical-spectral analysis, electron microscopic, fractographic, thermal, standard tests on manufacturability and mechanical properties.

**Scientific novelty:**

1. A nomographic method has been developed for determining a given structure and properties of materials based on the Fe-C-Al system, based on joint consideration of thermodynamic and kinetic diagrams, which allows predicting the alloy composition, parameters and conditions for melt processing to form a given structure and material properties of the blanks.

2. A mathematical model of physicochemical, hydrodynamic transformations occurring with melt elements of materials based on the Fe-C-Si and Fe-C-Al system during centrifugation has been developed. According to this model, melt centrifuging of materials based on the Fe-C-Si and Fe-C-Al system creates conditions for the spheroidization of crystallizing graphite without modifying effects due to the synergistic combination of dynamic and cooling effects.

3. The scientific foundations of the physicochemical processes of forming materials based on the Fe-C-Si and Fe-C-Al system 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 system Fe-C-Si and Fe-C-Al, excluding any heredity, including negative ones;

- formation of materials based on the Fe-C-Si and Fe-C-Al system from the melt of the drop-like state in the highly superheated slag phase, creating conditions for deep refining of the metal and its overheating into the supercritical state ( $T > 1853$  K), forming carbide-forming fluctuations;

- electric current melt processing of materials based on the system Fe-C-Si and Fe-C-Al;

- quenching of materials based on the Fe – C – Si and Fe – C – Al system from the liquid state, ensuring its metastable crystallization, with subsequent isothermal holding at  $T = 1223 \dots 1273$  K for a duration of  $\sim 2$  hours without claims to the content of surface active elements.

4. Developed and scientifically substantiated the process of structure formation of materials based on the Fe-C-Si and Fe-C-Al system with the production of compact graphite,

based on the realization of the exothermic effect during the formation of the liquid phase from dispersed technogenic waste of engineering production without the energy consumption of third-party sources with regulated cooling, stabilizing the decomposition of carbide phases in isothermal conditions.

5. The functionality of working capacity for a cast bimetallic press tooling from materials based on the Fe-C-Al system for the support layer has been developed and scientifically substantiated. It is established that the resistance of thermomechanical fatigue (TMU) and wear depend on the loading parameters of the object, taking into account the initial properties and structure of the material.

**The practical significance and implementation of the work.** The studies have found practical application in the development and implementation of technological processes for the manufacture of materials based on the Fe-C-Si and Fe-C-Al systems for products in mechanical engineering. The technology has been developed and a pilot-industrial version of the melting unit has been created for the preparation of melt materials based on the Fe-C-Si and Fe-C-Al system from dispersed iron-containing technogenic waste from engineering production. The technological process includes obtaining a composite material in the form of granules from dispersed wastes of different composition and synthesizing the melt in a melting unit. Due to the refined effect of the slag phase, the combination of the protective reducing atmosphere and the effect of the electric field on the metal phase, a melt of materials based on the Fe-C-Si and Fe-C-Al system of the required structure is obtained.

A technology is proposed for producing materials based on the Fe-C-Si and Fe-C-Al system with a compact form of graphite inclusions without the use of modifiers (protected by RF patent No. 2487950), consisting in accelerated cooling of the melt in metallic form to a temperature of ~ 1200 K and subsequent isothermal extract of the crystallized preform at a temperature of 1200 ... 1250 K. The size of graphite inclusions does not exceed 60 microns, which are evenly distributed over the cross section of the preform.

An experimental installation was made to control the content of components of the melt being prepared, based on obtaining the atomic emission spectrum of the products of the melt loss using a high-voltage flare discharge, which allows continuous monitoring of the metal composition and thereby reduce the waste of components and shorten the melting time (protected by RF patent No. 2375687).

On the basis of research on the influence of the intensity of cooling forms on the temperature fields and the rate of directional solidification of blanks, materials and technology for producing a bimetallic press tooling were developed using a Fe-C-Al system (protected by RF patent No. 2507026) as a supporting layer and ferritic carbide steel (protected by the patent of the Russian Federation No. 2487958) as a working layer.

The chemical compositions of complex-doped materials based on the Fe-C-Si and Fe-C-Al system designed for products in mechanical engineering (protected by the RF patent №2487187) have been developed using mathematical planning methods.

The materials developed on the basis of the Fe-C-Si and Fe-C-Al system have undergone pilot testing and are used in a number of industrial organizations of Naberezhnye Chelny and Izhevsk, which is confirmed by the relevant implementation acts presented in the annex to the thesis.

The results of the work were introduced into the educational process at the "Department of Materials, Technologies and Quality" of the Naberezhnye Chelny Institute (branch) KFU in

the disciplines of "Materials Science", "Methods for the study of materials and technology", "Materials Science and Technologies of Modern and Advanced Materials", "Composite materials with a metal matrix".

**On defense are taken out:**

1. Patterns of structure formation and methods for calculating the components and properties of materials of the system Fe-C-Al.

2. Mathematical model of the distribution of components of the mixture during centrifugation.

3. Technology, design features of the melting equipment and parameters for the preparation of the melt of the materials of the system Fe-C-Si and Fe-C-Al from dispersed waste of engineering production.

4. Methods of monitoring the content of components in the melt of the materials of the system Fe-C-Si and Fe-C-Al according to the composition of the exhaust gases and methods of testing materials of the system Fe-C-Si and Fe-C-Al.

5. Compositions and manufacturing technology of products in mechanical engineering from materials of the system Fe-C-Si and Fe-C-Al.

**He reliability and validity** of the decisions taken in the dissertation is confirmed by:

- a comprehensive study of the structure, properties and other characteristics of materials of the system Fe-C-Si and Fe-C-Al using standard and specially developed methods of control and testing;

- the correctness of the choice of initial assumptions and limitations in the design and experimental studies and substantiation of the parameters of melting, casting and control;

- consistency of theoretical and experimental data, confirmed by the results of long-term production experience;

- checking the adequacy, reliability and reproducibility of mathematical models by the statistical criteria of Cochren, Student and Fisher;

- repeatability of results in a variety of studies using licensed equipment.

**Approbation of work.** The main results of the dissertation were discussed at international, All-Russian, inter-university conferences and seminars: Penza (1987), Barnaul (1988), Naberezhnye Chelny (1988, 1995, 1996, 1998, 2010), Zaporozhye (1988), Odessa (1988), Gorky (1988, 1989), Karaganda (1989), g St. Petersburg (1996), Tolyatti (1996), Kharkov (2008), Samara (2008), Moscow (2009), Donetsk (2010), Kazan (2013), Naberezhnye Chelny (2017).

The dissertation materials were repeatedly reported and discussed at the extended meetings of the Materials, Technologies and Quality Department of the Naberezhnye Chelny Institute (branch) of the KFU (Naberezhnye Chelny), at the extended meetings of the Metallography, Thermal and Plastic Processing of Metals Department of the Nizhny Novgorod State Technical University. Alekseeva (Nizhny Novgorod), at the expanded meetings of the department "Foundry production and materials science" of Magnitogorsk State Technical University (Magnitogorsk), the department "Welding, foundry production and materials science" "Penza State University" (Penza), on extended meetings of the department "Technology of Metals and Metallurgy" "Izhevsk State Technical University named after M.T. Kalashnikov" (Izhevsk).

**Publications.** On the topic of the thesis, 63 works were published, including 2 monographs, 35 scientific articles, of which 20 in peer-reviewed journals recommended by HAC, 5 patents for invention.

Personal contribution of the author. The dissertation presents the results obtained by the author independently, as well as together with the employees of KAMAZ OJSC, the KFU NPH, who carried out scientific research under the supervision of the author of the thesis. With the direct participation and under his leadership conducted pilot tests and implementation of the results in production. In published articles and monographs, the contribution of the author consisted in the direct writing and editing of materials, ranging from the formulation of research tasks to the analysis and analysis of the results obtained. Personally conducted patent research, drafted applications for inventions and carried out subsequent work until the patent was obtained.

The author is grateful to the staff of the Naberezhnye Chelny Institute (branch) of the of Kazan Federal University, the staff of the departments of the Faculty of Materials Science and High-Temperature Technologies of the NSTU. R.E. Alekseeva for assisting in the work on his thesis.

**The structure and scope of the thesis.** The thesis consists of an introduction, five chapters, main conclusions, a list of references and applications. The main part of the thesis is presented on 366 pages of typewritten text, contains 87 figures, 66 tables, a bibliography of 349 titles and applications.

#### THE CONTENT OF THE WORK

**The introduction substantiates** the relevance of the chosen topic, the goals and objectives of the research, formulates the scientific novelty and practical significance of the work.

**The first chapter** is devoted to the analysis of the materials used in the world practice of the system Fe-C-Si and Fe-C-Al: compositions, properties, production technologies, problems and prospects.

A review of publications and previously completed studies on the topics considered is given, unresolved tasks are highlighted, the purpose and objectives of the study are defined.

The study of the influence of chemical elements (C, Si, Al, Mn, P, S, Cr, etc.) on the structure formation, mechanical properties and processes of graphitization in the materials of the Fe-C-Si system and Fe-C-Al is devoted to the work of eminent scientists N. N.Aleksandrova, Yu.G.Bobro, N.G.Girshovich, A.A.Zhukova, N.I. Klochneva and others. Their research allowed to establish patterns of formation of a structural state in alloys depending on chemical composition, technology of smelting, modifying doping conditions of crystallization and subsequent heat treatment.

The materials of the Fe-C-Al system are promising materials for the manufacture of products operating under conditions of elevated mechanical and non-stationary thermal loads, high temperatures, corrosive media, and intense wear, but the volume of their introduction into production is insufficient. Currently, the literature does not have a fairly simple and reliable method for calculating the structure of materials of the Fe-C-Al system with compact graphite, which takes into account both kinetic and thermodynamic factors, and operating conditions. Currently, there is no process for stable production of a given form of graphite in the materials of the Fe-C-Al system.

Modern ideas about the structure of the liquid phase of the system Fe – C – Si and Fe – C – Al are formed by various theories and hypotheses. The patterns of structure formation in the Fe-C-Si and Fe-C-Al materials are determined by energy, crystal-chemical and diffusion (kinetic) factors, which depend on the chemical composition of the materials of the Fe-C-Si system and Fe-C-Al, as well as temperature melt processing timing. In view of the above, undoubted theoretical and practical interest is the further study of patterns of structure formation in alloys in order to develop scientifically grounded technological processes for the production of materials of the Fe-C-Si and Fe-C-Al system with improved properties for the manufacture of products for various purposes.

High-strength cast iron, characterized by a combination of high technological, physico-mechanical and operational characteristics, is widely used to replace steel casting, forgings, stampings, ductile and gray cast iron, ensuring reliability and durability in various modes of operation. Production efficiency and product quality is continuously associated with the problem of full use of the possibilities that were laid down in the materials of the Fe-C-Si and Fe-C-Al system and their manufacturing technology. In this regard, it is important to study the influence of the composition and technological methods with their complex impact on the structure, structure and properties of products.

The increase in the mechanical properties of high-strength cast iron is achieved using special types of heat treatment. However, the issues of obtaining materials for the Fe-C-Si and Fe-C-Al systems have not yet been fully studied, and the potential capabilities of these materials are not fully disclosed.

In industry, there is also an acute question about the maximum possible degree of utilization of waste produced by the machine-building complex, the solution of which will make it possible to reduce the price of manufactured products and improve the ecological situation. First of all, this refers to iron-containing dispersed waste of thermal and electroplating production.

The problem of utilization of industrial waste is relevant and for its solution a new approach is needed to create both the technology of melt preparation and the creation of a specialized melting unit.

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The problem of utilization of industrial waste is relevant and for its solution a new approach is needed to create both the technology of melt preparation and the creation of a specialized melting unit.

Analysis of the operation of press equipment (molds, molds, dies for solid-liquid stamping, etc.) shows that their work is characterized by high parameters of cyclic temperature-force loading of the tool and is accompanied by active interaction of tool materials with surface-active agents. Research has established some specific reasons for the low performance of stamps for solid-liquid stamping, mainly due to the physicochemical activity, the nature of the materials used, and others. complex scientific and technical problem. Its multiplicity with the current state of the issue makes it difficult to formulate even the basic requirements for the materials used, the design, the technology of manufacturing and operation of dies. The task can be

significantly simplified in the transition to a substantive analysis of the influence of specially grouped factors on the performance of the shaping tool, the main of which is thermal and external force action.

Analyzing the literature, we can conclude that the development of high-strength cast iron compositions from the Fe-C-Si and Fe-C-Al materials for specific products is a complex scientific and technical problem. In this regard, the development of scientifically based recommendations on the use of high-strength cast iron and the improvement of their manufacturing technology for a wide range of products is one of the main tasks of the work.

**The second chapter** is devoted to the theoretical and methodological substantiation of the structure, composition and production technology of materials of the Fe-C-Al system in mechanical engineering.

Theoretical methods for calculating the structure and properties of materials in the Fe-C-Al system are considered.

It is known that the structure of the materials of the Fe – C – Si and Fe – C – Al system in the cast state is determined by two factors: the thermodynamic activity of the components in the melt and crystallizing phases, and the cooling rate of the casting that controls diffusion processes in the solidifying preform.

Having the ability to analytically calculate the graphitization curve of materials of the system Fe-C-Si and Fe-C-Al taking into account thermodynamic factors, it is possible to predict the structure of cast alloys with a certain accuracy and control it by complex doping.

The construction of the kinetic part of the diagram is based on the known equations of the theory of the formation of the workpiece. The calculation is based on the determination of the rate of solidification of the slab and the duration of solidification. Knowing the mass and wall thickness of the workpiece, it is possible to calculate the linear rate of solidification for forms with different values of heat-accumulating capacity at different fill temperatures.

A mathematical model for the distribution of components of the mixture during centrifugation is proposed. The process of substance transport in a centrifuge is described by the equation of O. Lamma. In the particular case of the distribution of the components of the mixture in a crucible of parabolic shape, one can determine the radii and heights of the components.

The third chapter discusses the technological features of the preparation of the melt for products from ferrous metals using dispersed waste from mechanical engineering, as well as an analysis of the influence of these features on the structure formation in the melts. For this purpose, a schematic diagram of the technological process of recycling of dispersed iron-containing waste from the machine-building complex was developed and an experimental-industrial version of the smelting unit was manufactured.

The starting materials for the preparation of the melt were dispersed production wastes containing Fe and other elements, both in the oxidized state and in the reduced state. This recycling scheme ultimately provides for for workpieces by synthesizing it from the necessary elements present in dispersed waste.

The initial stage of the process of recycling dispersed waste is the formation of composite granules in such a way that their qualitative and quantitative composition causes the preparation at the final stage of liquid smelting products with specified characteristics. Next, the composite material enters the melting unit, consisting of a countercurrent reactor and a melting bath, in which the following physical and chemical transformations occur: heating the material to



temperatures of about 1073 ... 1273 K, metallization of oxidized elements, melting to form two liquid phases (slag and metal) and their overheating.

The specific feature of the casting alloy synthesis according to the proposed technology is that it is produced at the expense of the elements of two aggregative states of the composite material restored in the smelting plant: solid and liquid. Solid-phase cementing metallization is carried out in countercurrent composite material and reducing gas. At this stage, elements such as Fe, Ni, Mo, Cu, C are transferred to the metallic state. Liquid-phase metallization of elements such as Si, Mn, W, V, Al, Mg and superheating of the liquid smelting products occurs in the melting bath of the installation.

An analysis was made of the conditions for the metallization of the base of iron alloys — silicon. The organization of the technological process in a pilot plant allows metallization of iron with the greatest possible degree of utilization of the chemical energy of carbon due to the two stages of this process. The conditions of the smelting bath of the installation cause the thermodynamic conditions for the transition of silicon from the slag phase to the metallic phase. The degree of implementation of this process is determined by a number of technological parameters: the composition of the granular composition, affecting the basicity of the slag phase; the amount of granular composition relative to the melted material of the system Fe-C-Si and Fe-C-Al; liquid phase temperature; the speed of the melting process; the number and dispersion of graphite electrodes, which determine the size of the carbon-melt interface. The factors noted above are levers in controlling the amount of silicon in the Fe-C-Si and Fe-C-Al system materials.

The developed specialized melting unit, along with the fact that it allows to recycle dispersed iron-containing waste of the machine-building complex, has another positive feature, which consists in obtaining high-quality materials of the Fe-C-Si and Fe-C-Al system. The latter is based on the fact that the smelted metal due to the presence in the unit in all its phases of the reducing potential and the purity of the granular compositions relative to surfactants (S, P) contains them in small quantities (no more than 0.02%). It is characteristic that the production of deeply refined materials of the Fe-C-Si and Fe-C-Al system does not require metallurgical operations involving the guidance of highly basic slags and their processing of molten metal. In addition, during the smelting process, an electric current flows through the liquid metal phase. This circumstance has a positive effect on the formation of the structure of the metal matrix and graphite inclusions.

Materials of the system Fe-C-Si and Fe-C-Al, smelted in a specialized melting unit, have a tendency to compact graphitization, since the melting conditions correspond to those necessary to satisfy the thermodynamic criterion of the above-mentioned graphitization in the form of chemical potential C in carbide type orderings . In the smelting unit under discussion, the conditions are created for the manifestation of the synergistic effect of temperature, thermal, slag, electric arc and electric current treatments affecting the tendency of the Fe-C-Si and Fe-C-Al materials to melt to form compact forms of graphite during crystallization under conditions that provide sufficient degree of supercooling. The materials of the system Fe-C-Si and Fe-C-Al are formed in the highly superheated slag phase from elements obtained by their metallization from the oxidized state. Therefore, there is no problem of the influence of the "bad" heredity of the furnace charge. The process of formation of the liquid metal phase occurs in the "rain" method, that is, from the granules falling into the slag phase. Moreover, due to the developed surface between the drop-like state of the materials of the system Fe-C-Si and Fe-C-Al and the

slag phase, conditions are created for deep refining of the metal. The latter circumstance is also enhanced by the action of the electrocapillary effect, which occurs due to the passage of direct electric current through the liquid phases of the melting bath of a specialized electrothermal unit and leads to a qualitative distribution of granular compositions between the liquid phases (metal and slag) due to the assimilation of non-metallic components into the slag and metal deposition into the bottom phase. The overheating of the liquid phases in the melting bath is such that it covers all the threshold temperature effects of the molten metal, due to the processes occurring at the micro and submicroscopic levels. The effect of slag treatment is enhanced by the action of an electric arc, especially when used as provided for in our proposed self-contained smelting unit of direct electric current.

Studies of the microstructure of the materials of the Fe-C-Si and Fe-C-Al system, synthesized directly from dispersed iron-containing waste in a specialized electrothermal melting unit without the use of modifying treatment, showed that vermicular curvature is the dominant ( $\approx 60\%$ ) form of graphite inclusions. This graphite is represented in the structure as uniformly distributed and isolated inclusions. In the structure, there is also observed the spherical and lamellar form of graphite inclusions, whose share is 15 and 25%, respectively. Moreover, the nature of the lamellar form of graphite inclusions has changed significantly. Remaining in the form of straight and swirling, the size of inclusions ( $< 15$  microns) with interdendritic distribution in the form of colonies and points has sharply decreased. Spherical graphite has a regular shape with a diameter of uniformly distributed inclusions of 15 ... 30 microns. In addition, there are in the structure and clusters of small inclusions. Changes in the pearlite metal base were also observed in the direction of increasing its dispersion, characterized by the values of the distance between the plates of cementite 0.7 ... 1  $\mu\text{m}$ . In accordance with this, the hardness of the materials of the Fe – C – Si and Fe – C – Al system increased to 215 HB.

The results of a comparative analysis of the properties of blanks from melts prepared by direct synthesis based on dispersed wastes of mechanical engineering and the traditional technology adopted in PJSC KAMAZ are presented.

An analysis was made of billet oil-removable and compression piston rings, valve seats and die inserts for getting forgings - the fork of the KAMA3 car (steel 3H5MFNSL). The blanks made according to the traditional technology are at least identical in the whole range of properties as compared with the blanks made according to the technology of direct synthesis, and in some cases some properties are higher.

**Chapter 4** is devoted to methods of studying the structure and properties of materials of the system Fe-C-Si and Fe-C-Al, intended for products in mechanical engineering.

A method of continuous control of chemical elements in the process of alloy smelting using a spectrum analyzer of exhaust gas flows is proposed. For the implementation of spectral analysis of exhaust gases, a spectrum analyzer of an experimental industrial sample with two-parameter control was developed, sufficient to control the melting using a spectroanalytical signal received from one representative of the carried out components.

The spectrum analyzer used the method of synthesizing gas streams of a given composition, introduced into controlled streams to quantify their chemical composition. Synthesis is carried out by evaporation of the corresponding standard samples certified by chemical composition.

The proposed method for determining the physicochemical parameters of a metallurgical process in real time of its course, based on spectroanalytical data, allows you to:

- to adjust the composition of the alloy in the process of its preparation prior to blending of the required components;

- to control the temperature of the liquid metal in electric arc furnaces with graphite electrodes, both during the smelting and idle period of the furnace.

A method for testing the special characteristics of materials for a cast press tooling is proposed.

When developing a methodology for testing materials for thermomechanical fatigue, the following tasks were solved:

- determination of the main causes of fatigue failure dies;

- calculated and experimental determination of the parameters of loading dies (stress state, temperature-force loading mode and other influences).

The method for estimating the resistance of thermomechanical fatigue and wear is based on establishing the dependence of the functional performance  $P_x$  press equipment and the loading parameters of the object, taking into account the initial properties and structure of the material:

The experiment was carried out in relation to the assessment of the reliability of materials for injection molding molds for aluminum alloys on a specially designed installation. High-strength cast iron was tested for thermomechanical fatigue and solubility in the AL-2 melt.

The size of the cracks of thermomechanical fatigue was determined by fracture fractography (in case of destruction of a sample) and metallographically on the lateral surface of the samples on thin sections made by cutting the samples along the longitudinal axis. The solubility was estimated from the change in sample size by height ( $\Delta h$ , mm).

The ranking results showed that the kinetics of the development of cracks of thermomechanical fatigue is mainly determined by the level of critical stresses. Obviously, when the intensity of loading press equipment below the critical level of stress in the local volume, fatigue cracks do not occur and wear is determined by other types of damage (dissolution, erosion, etc.).

Methods are proposed for determining the properties of materials of the Fe-C-Si and Fe-C-Al system.

Tests for wear resistance of the materials of the system Fe-C-Si and Fe-C-Al were carried out on a specially designed installation. We investigated 16 groups of different samples.

Determination of heat resistance was carried out by the method of eddy currents, on a specially designed installation. The amount of thermal cycles before the output signal increased by  $e$ -time ( $\approx 2.7$ ) was taken as the heat resistance value.

The basis of the method of comparative evaluation of heat resistance adopted weight method (to increase the mass of the sample), regulated by GOST 6130-71.

Experimental determination of carbon activity was carried out by the method of electromotive forces (EMF) in a specially designed installation. The determination of activity by this method is based on the creation of a concentration galvanic cell. EMF must be determined by compensation. According to the results of the experiment, it is clear that the change in the value of the interaction parameters during the transition from infinitely dilute solutions (steel) to saturated solutions (cast iron) practically remains constant.

X-ray diffraction studies of the samples were carried out on diffractometers DRON-4-7 with the use of monochromatic  $\text{CoK}\alpha$ , - radiation. Registration of diffraction patterns produced by the method of "point by point" in automatic mode using a computer.

The study of the structure and properties of high-strength cast iron after centrifuging the melt. The study was performed on blanks in the form of a truncated paraboloid. With the selected centrifuging modes, the duration was 2400 s; rotation speed 200 rpm; melt temperature 1873 K. The results of the study of the microstructure of materials of the Fe-C-Si system after centrifugation indicate the complex nature of the processes occurring along the height of the ingot. The established characteristic features of structure formation are due to the laws of mass transfer and crystallization of the materials of the Fe – C – Si system during centrifugation. The simulation results of these processes are in good agreement with studies of the microstructure and chemical composition across the width of the ingot after centrifugation. The obtained results of the study of the microstructure and chemical composition of the materials of the Fe-C-Si system during centrifugation under various conditions of melting and crystallization of the ingots make it possible to supplement the existing ideas about the causes and mechanisms of structure formation in the materials of the system Fe-C-Si.

In particular, it was found that when the melt is heated and the impurities are redistributed during centrifugation, a mechanism of formation of compact ordered zones with a pseudocarbide metastable stoichiometry is possible. The formation of compact graphite from them in this case is possible due to the mode of supercooling of the melt. Thus, we can conclude that the thermodynamic potential of compact graphitization can be artificially created not only by introducing modifiers, but also by redistributing impurities.

The fifth chapter in the thesis is devoted to the development of the compositions of the materials of the system Fe-C-Si and Fe-C-Al, to the substantiation of technical and technological solutions in their production for products of the intended purpose. Such as bimetallic forge stamps of hot deformation, heavily loaded engine parts, sleeves of mud pumps, crucibles of distributing furnaces, press tools for casting, thermal and cleaning equipment.

The composition and technology of production of austenitic-bainite materials of the Fe-C-Si system with spherical graphite (ABChG) are proposed.

The main object of study was high-strength nodular cast iron. The change in the structure of the materials of the Fe – C – Si system was ensured by changing the chemical composition and the rate of cooling of the samples in the form.

The joint influence of Ni, Cu, B and V on the structure and properties of cast irons, as well as various combinations of its constituent elements, was investigated. Boron and vanadium do not have a significant effect on the mechanical properties of high-strength nodular cast iron in an isothermally hardened state, which confirms the correctness of the decision to be used in further research as the main alloying elements Ni and Cu.

For isothermal quenching of the materials of the Fe-C-Si system, instead of salt baths, it is proposed to use installations with a “fpseudo-boiling”. The data obtained allow us to conclude that the use of the installation of a “pseudo-boiling” layer for isothermal hardening of high-strength cast irons, with appropriate processing of modes, allows to obtain the mechanical properties of high-strength cast irons not lower than with the use of salt baths. For isothermal hardening of the materials of the Fe-C-Si system, instead of salt baths, it is proposed to use installations with a “fpseudo-boiling”. The data obtained allow us to conclude that the use of the installation of a “pseudo-boiling” layer for isothermal hardening of high-strength cast irons, with appropriate processing of modes, allows to obtain the mechanical properties of high-strength cast irons not lower than with the use of salt baths.

The use of high-strength cast iron of high heat resistance for the manufacture of the support layer of bimetallic hot-deformed dies has been investigated. Increased durability and reliability of hot-forming dies, experiencing complex-cyclical temperature-force loading, is achieved through the use of cast bimetallic products. High-heat-resistant and heat-resistant alloys of the following grades are used as the surface layer: 5HZV4F2MB, 4H3V2FM2SL and 2H16N19TZV2Yu2MBRF. The use of high-strength cast irons as a support layer is expedient from both an economic and technological point of view. Due to the lower melting point of the materials of the Fe-C-Al system, when the base layer is poured, there is an additional internal cooling of the surface alloyed steel layer. This contributes to a decrease in grain size, a decrease in the diffusion of alloying elements, and thereby an increase in the characteristics of heat resistance and thermomechanical fatigue of the surface layer of the dies.

The feasibility of using high-strength cast iron for the manufacture of the support layer is also due to its higher thermal conductivity, which allows the operation of dies to improve heat dissipation from the heated working surface of the tool to the mass or cooler installed in the die's supporting part. The noted factor significantly reduces the temperature gradient and the level of stresses in the contact zone of the stamp and, as a result, causes an increase in its efficiency.

For the manufacture of the support layer of bimetallic dies in the present work, high-strength cast irons with enhanced strength, ductility, impact toughness and heat resistance are developed. The developed materials include, in addition to C, Si, and Mn, elements such as Cr, Ni, Ti, Mg, Ce, Ca, Al, and Cu in combination, which provide high mechanical and special properties.

The results of industrial tests showed an increase in durability of cast bimetallic dies in comparison with serial forged dies made of 4H5MFS steel by 6.4 and 5.2 times for the above described options, respectively. In this case, the rejection of bimetallic dies due to damage to the support layer was not observed.

The high-strength titanium material of the Fe-C-Si system of high heat resistance and thermomechanical fatigue for solid-liquid stamping of parts from non-ferrous alloys, molds and die-casting molds is investigated injection molding.

Based on the analysis of the results of the study of thermomechanical fatigue in the work for the manufacture of dies for solid-liquid stamping, the most rational composition of high-strength titanium material of the Fe-C-Si system was proposed, % weight: C - 3.5... 4.0; Ti is 3.2 ... 3.4; Si - 2.4 ... 2.6; Ni — 0.4; S <0.04; P <0.05. The mechanical characteristics of the developed material of the Fe-C-Si system correspond to the following values:  $\sigma_B = 350... 400$  MPa;  $\sigma_T = 280 ... 320$  MPa;  $\delta = 0.5\%$  and HRC = 30 ... 50. The microstructure of the materials of the Fe-C-Si system consists of compact graphite, around which there is a bull-eye type ferrite, large ferrite grains, dispersed titanium carbides and small pearlite sections (<15%). The embedded alloy has high heat resistance and resistance to thermomechanical fatigue. From the developed material of the Fe-C-Si system, solid-molded dies were made, which showed an increase in durability when stamping brass (compared to forged dies from 4H5MFS steel) by 30%. When stamping bronze, cast stamps from materials of the Fe-C-Si system showed a slightly lower resistance (about 0.9) from serial forged products.

The proposed measures to increase the operational life of the materials of the system Fe-C-Si and Fe-C-Al for crucibles casting furnaces

Crucibles made from austenite-bainite material of the system Fe-C-Si and Fe-C-Al with a spherical shape of graphite showed the highest operational life.

Studied the structure and properties of wear-resistant material of the Fe-C-Al system used for valve tappets of internal combustion engines (ICE).

Proposed refined chemical composition of wear-resistant material of the system Fe-C-Al, mass. %: 3.1 ... 3.4 C; 9.8 ... 19.7 Al; 0.5 ... 0.65Mn; 0.4 ... 0.75 Ni; 0.4 ... 0.6% Mo; 1.0 ... 1.7Cu; 0.3 ... 0.6 Si; 0.2 ... 0.6 V; 0.01 ... 0.10 Ca; 0.05 ... 0.20 B; 0.03 ... 0.10Ba;  $P \leq 0,2$ ; 0.8..0.15 S, the rest is Fe. The technology of production and the composition of materials of the system and Fe-C-Al for centrifugal casting responsible castings are proposed.

The composition of the material of the Fe-C-Al system and its manufacturing technology without the use of expensive alloying elements and spheroidizing additives have been developed and introduced. The proposed composition of the materials of the Fe-C-Al system is 2.4 ... 3.2% C; 0.17 ... 1.04% Si; 1.1 ... 2.6% Al; 0.71 ... 1.16% Mn; 0.2 ... 0.4% Cr; 0.011 ... 0.025% B; 0.35 ... 0.66% Cu; 0.09 ... 0.13% Ni; S and  $P \leq 0.1\%$ . The combination of technological solutions during smelting and subsequent effects on the melt in the process of modifying, crystallizing and cooling the alloy containing boron made it possible to obtain uniformity in hardness and structure of the blanks during centrifugal and continuous casting, increase the threshold of workability by cutting the blanks, and bring the structure basis to 96 % content of perlite and completely eliminate white cast iron.

#### **The main conclusions and results of the work:**

1. The method of calculating the activity of the components of the materials of the Fe-C-Al system has been improved, taking into account the degree of saturation of the  $Si_H$  melt with component i. It is established that the interaction parameter  $\epsilon_C^{Al}$  at the transition from infinite dilution to the saturated state varies from 5.524 to 2.352, obeying a hyperbolic dependence. The interaction parameter  $\epsilon_C^C$  in the transition from infinite condition to a saturated state varies from 9.65 to 10.53, and the activity of carbon  $a_C$  varies from 0.0078 to 0.644.

2. Calculated carbon potential  $\pi_{Ck}$  for various types of blanks from materials based on the Fe-C-Al system with spherical graphite: 0.9 ... 1.2 kJ/mol for corrosion-resistant; 0.6 ... 0.85 kJ/mol for heat-resistant; 1.1 ... 2.2 kJ/mol for wear-resistant; 1.5 ... 3.5 kJ/mol for blanks without chill; 1.2 ... 2.5 kJ/ mol for heat-resistant blanks. A quantitative relationship has been established between the graphite phase Crp/C and the linear solidification rate of the first graphite region of materials based on the Fe- C-Al system. With an solidification rate from 0.041 mm/s to 0.155 mm/s, the amount of Crp /C decreases from 0.98 to 0.

3. Developed nomogram to select the structure, composition and material properties based on Fe-C-Al spherical graphite based on the purpose of the workpiece and the mold material.

4. A mathematical model for the distribution of components based on the system Fe-C-Si melt during centrifugation was proposed. The distribution of components on the basis of the Fe - C - Si system in a parabolic crucible is determined by the height and distance from the axis of rotation.

5. It has been established that with selected centrifuging modes with a vertical axis of rotation (process time  $\tau = 2400$  s, rotation speed  $\omega = 200$  rpm, melt temperature  $T = 1873$  K) as the samples are cooled with the furnace, large clusters of lamellar are observed near the open surface graphite with particle sizes of  $\sim 50 \dots 200$  microns. The matrix is a lamellar perlite with inclusions of ferrite up to 30%. As the ingot surface approaches, the large-plate graphite (PG > 12) abruptly enters the zone of fine-grained twisted graphite (PGF2). In the middle part of the ingot height, the bulk of graphite has a globular shape with sizes of 15 ... 30 microns.

6. The technology has been developed and a pilot-industrial version of the melting unit has been created for the preparation of melt materials based on the Fe-C-Si and Fe-C-Al system from dispersed iron-containing machine-building production. The technological process includes obtaining a composite material in the form of granules from dispersed wastes of different composition and synthesizing the melt in a melting unit. Due to the refining effect of the slag phase, the combination of the protective reducing atmosphere and the effect of the electric field on the metal phase, a melt of materials based on the Fe-C-Si and Fe-C-Al system of the required composition is obtained.

7. A connection has been established between the technological parameters of melt preparation and the structure formation of the alloy in cast products. The compact form of graphite is achieved by overheating the melt, contributing to deep refining from non-metallic inclusions and surface-active components - O<sub>2</sub>, P and S, as well as strengthening the tendency of materials based on the Fe-C-Si and Fe-C-Al system to supercooling.

8. For the first time, a technology has been proposed for producing materials based on the Fe-C-Si and Fe-C-Al system with a compact form of graphite inclusions from dispersed iron-containing waste of engineering production without using modifiers, consisting in accelerated cooling of the melt in metallic form to a temperature of ~ 1200 K and subsequent isothermal exposure of the crystallized preform at a temperature of 1200 ... 1250 K. The size of the graphite inclusions does not exceed 60 μm, which are evenly distributed over the cross section of the preform. The quality of blanks produced from the melt prepared from dispersed iron-containing waste according to the developed technology is at the level of blanks made according to the basic variant.

9. A methodology was developed and an experimental installation was made to control the content of components of the prepared melt during the metallurgical process, based on obtaining the atomic emission spectrum of the products of the melt carbon by using a high-voltage flare discharge. The dependence of the intensity of the analytical signal of the emission of the spectral line of Na 589 nm contained in graphite electrodes of an arc furnace on the temperature in the furnace is established.

10. The composition and production technology of austenite-bainite materials based on Fe-C-Si with spherical graphite, which have high mechanical properties in a cast and isothermally hardened state, has been developed and substantiated. This is achieved due to the complex doping of the alloy Ni, Cu, B and V.

11. The methods of mathematical planning of experiments have developed and introduced the compositions of materials based on the Fe-C-Si and Fe-C-Al system:

- for the production of bimetallic cast press tooling as a support layer with high thermal conductivity and the level of mechanical properties;
- for cast dies of solid-liquid stamping of non-ferrous alloys with high resistance to thermomechanical fatigue;
- for corrosion resistant bushings;
- for crucible holding furnaces;
- for the manufacture of molds of silicate bricks, molds, cylinder group blanks, glass molds.

**The main results of the thesis are reflected in the works.**

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