Tribology in Industry

The Influence of Titanium as a Desferoidizing Element on the Stability of Production of Magnesium Cast Irons with Compacted Graphite

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A B S T R A C T

The thermodynamic calculations and the obtained dependence of the Gibbs energy of the reactions of formation of titanium oxide, titanium sulfide, titanium nitride and titanium carbide in the melt of magnesium cast iron on their concentrations and melt temperature have been presented in the article. It has been shown that titanium, regardless of the concentration in melt, will primarily perform a deoxidizing effect, interacting with the oxygen. The lower negative values of the Gibbs energies are characterized by the reactions of the interaction of titanium with sulfur, at a concentration of the latter 0.01%, which indicates a decrease in the probability of such reaction occurrence. From a thermodynamic point of view, the reactions of titanium nitride and carbide formation are less probable. The values of the Gibbs energy of the interaction reaction of titanium depend to a large extent on the melt temperature. It has been found that for a more complete realization of the desulfurizing properties of titanium, it is advisable to enter the composition of cast iron during melting and overheating, when the melt temperature reaches maximum values. The optimal conditions for obtaining magnesium cast irons with compacted graphite has been determined. It has been found that the addition of titanium to magnesium cast iron, as a desferoidizing element containing 0.035% S, has a positive effect on stabilizing the formation of compacted graphite.

1. INTRODUCTION

Cast iron with a compacted grafite cast iron (CGI) is an effective material for the manufacture of machine parts that are subject to high static, shock and cyclic loads and work in conditions of heat change [1].

This type of cast iron in modern automotive industry is used for the manufacture of heads of cylinder blocks, exhaust manifolds, brake discs, crankshafts and camshafts, cylinder blocks, gears, turbocharger housings [2], loaded parts of machines and mechanisms [3-5]. Improving the

design and material of the brake discs can increase braking efficiency. The use of CGI has eliminated these problems [6].

Over the last decade, foundries have received technological tools for the production of CGI with a given degree of spheroidization of graphite inclusions. New technologies are based on the application and control of magnesium melt modification processes using computer technology. The combination of treatment of liquid cast iron with magnesium and despheroidizers, mainly titanium, the action of which is associated with blocking the formation of inclusions of spheroidal graphite (SG) and expanding the area of formation of inclusions of compacted graphite (CG) is a simpler technology for obtaining CGI.

2. ANALYSIS OF LITERATURE DATA AND PROBLEM STATEMENT

The multifaceted combination of different physicochemical processes that occur during the graphitization of magnesium cast iron still does not allow researchers to reach a single point of view on the mechanism of formation of CG inclusions. Disclosure of CG formation mechanism processes will promote opening of wide possibilities of management of structure and properties of magnesium cast iron that will allow developing effective technological processes for receiving cast products of various function.

The addition of desferroidizing elements in cast iron changes the thermodynamic conditions of crystallization and formation of compacted graphite. The most common for this purpose are additives Ti, Al and Zn, the action of which is not associated with the degeneracy of compact forms of graphite. The addition of any desferoidizing element in cast iron changes the thermodynamic conditions of crystallization and CG formation [7,8].

The use of titanium is more suitable for cast iron production, the addition of which into the melt can be provided by both ferrotitanium additives and naturally doped titanium-containing cast irons. The usage of titanium for steel processing is widespread, where its action is associated with the formation of dispersed inclusions of carbides, nitrides and sulfides [7,8]. At the same time, the ability of titanium to bind sulfur in chemical compounds, reducing its harmful effects in undesulfurized melts for the production of high-strength cast iron, remains virtually unexplored.

Heat transfer conditions from surfaces on the crystallization fronts on which exothermic reactions occur plays a significant role in the formation of graphite in the crystallization of cast iron: crystallization of austenite and release of graphite from liquid or solid carbon solution in iron with heat release [9].

In study [10] it has been found that thermal fatigue of the brake discs of railway vehicles reduces the service life of cast iron. The service life of parts can be extended by the regulatory composition and metallurgical structures. The mechanical properties of cast iron are easy to control by changing the content of Ni, Co and Mo. However, there is no change in the shape of graphite from lamellar to compacted. The use of Ni, Co and Mo also significantly increases the cost and impairs the casting properties of cast iron. The cast iron material with CG has a higher resistance to thermal cracking than the material with lamellar graphite. However, the author did not take into account that during the operation of brake discs in the conditions of emergency braking there is a cyclic heating of the material surface to temperatures close to pre-eutectoid transformation, and therefore in non-alloy cast irons the ferrite will decay. This will lead to additional stresses and defects, which will contribute to the development of cracks. To increase the stability of the material during braking, it is advisable that the metal base has a predominantly ferritic structure, and ferrite - increased hardness. This can be realized in CGI, which is obtained using titanium as a deglobularizer, the compounds of which are released in the form of fine inclusions of high hardness.

The use of 0.13% Ti, when casting thin-walled parts, has a much stronger effect on the hardening of cast iron [11]. It has been found that titanium additives reduce the content of spheroidal graphite in the cross section of the step sample with a thickness of 5 mm. Titanium causes curing of Ti carbides in cast iron. SEM studies revealed TiC crystals in the microstructure of cast iron. The addition of titanium leads to the curing of titanium carbides in the form of faceted crystals, which are evenly

distributed in the iron matrix. Metallographic analysis showed that their maximum size is <4 mkm, and their share is much lower than 1%. But, these authors did not study the effect of titanium inclusions on the sulfur content, but limited themselves to carbon - perhaps there was the formation of carbosulfides.

CGI, as shown in [12], better resists the formation of macroscopic cracks in brake discs made of gray cast iron, from thermal fatigue and thermomechanical loads during braking. This can be explained by the greater cutting effect of the inclusions of lamellar graphite on the metal base to reduce which [13], two improved cast irons with modification of graphite morphology have been proposed.

The aim of the research [14] is the assessment of the fatigue capacity of HF 50-7 cast iron, which is used for railway brake discs. The properties of stresses and fatigue strength of the low cycle for all temperatures. Stress strain curves, cyclic hardening / softening curves, cyclic stress and strain curves, stress hysteresis loops, and fatigue duration curves have been obtained for all temperatures. The Young's modulus remained temperature-resistant, while the stress resistance and ultimate tensile strength decreased with increasing temperature. The authors did not give a comparative characteristic of the thermal conductivity of cast iron with spheroidal graphite, which is one of the reasons for the decrease in tribological properties.

Studies conducted in [15] have been shown that at any test load, the wear of the CGI discs is higher than for all tested gray cast irons, except for a load of 4 MPa, at which MF250 had the greatest wear. It has been found that gray cast irons had similar wear for lower load levels (2.0 or 0.7 MPa), taking into account standard deviations. The wear of gray cast iron decreases with decreasing applied load. This does not apply to CGI, where wear does not change monotonically with decreasing pressure. Since CGI represents the highest mechanical strength among the studied materials, it can have the highest wear resistance. However, this value has not been found. The large amount of ferrite in the metal matrix of CGI and the lower ability to heat transfer of this material may be the main reasons for this action.

Particles of solid titanium carbide improve wear resistance [6,16], which with a diameter of 2 to 6 μm are dispersed in a relatively soft metal matrix. A Ti level below 0.015% precipitates less than 40 solids / mm2, resulting in high wear values, but in the case of above 0.025%, precipitates more than 60 solids / mm2, contributing to low wear. The content of 0.02% Ti serves as a guide for cast irons used in brake rotors and drums. The friction force and temperature are exactly the same for the three gray cast irons mentioned. A high level of friction force and temperature was observed during the testing of cast iron discs with CGI. These results confirm the hypothesis of greater braking efficiency of brake rotors made of CGI at a given load.

The average coefficient of friction is exactly the same for gray cast irons GI250 and GIHC. During the test of CGI disks [17], when using loads of 32,21N, 16,50N, 4,06N, the level of friction forces and the coefficient of friction characteristic of gray cast irons have been observed. The friction forces obtained for CGI at loads of 32,21N, 16,50N, 4,06N are similar to the loads of 40,85 N, 21,23 N and 7,01 N, which are typical for tests of gray cast irons. These results confirm the hypothesis of greater braking efficiency of brake rotors made of CGI for these load levels. It should be noted that in the considered cast irons there was no titanium.

It has been found in [18] that aluminum and titanium in CIVG affect the formation of a porosity defect in castings. The aluminum content in the range from 0.02 to 0.1% is critical. CGI and high-strength cast iron with a high content of Al has a greater tendency to form shrinkage cavities, oxide films and pores. The increase in pore frequency is also determined when the Ti content is higher than 0.1%. The authors did not take into account that titanium forms carbosulfides but not nitrides, as indicated in this paper.

The study [19] shows a decrease in the coefficient of friction with increasing titanium content in the disk material (Brembo, 1997), but it is not clear to which type of cast iron it belongs. To provide better resistance to thermal fatigue used gray cast iron, cast iron with nickel, chromium and molybdenum used by General Motors. However, the disadvantage of these alloys is the high cost.

The formation of a functional copper-containing surface layer on the couplings of automotive engine parts using tribotechnology of alignment [20] causes a reduction in their wear during operation. The formed coating creates an antifriction elastic layer that reduces deformation in the material of the parts. A comparative analysis of the results using the coercimetric method confirms that the proposed leveling tribotechnology reduces the stress state and allows improving the wear resistance and technical condition of diesel cylinders.

It has been established [21] that in researching the characteristics of viscous friction there is no analytical description of the process of damped oscillations at viscous stability and recommendations for the practical calculation of the characteristics of friction. The obtained results are aimed at finding design and technological solutions to reduce energy losses due to friction.

The most effective method of increasing the wear resistance of machine parts and equipment is to implement the effect of self-organization. The wear resistance of the material, the radius of curvature of the surfaces and the coefficient of change of the shape of the parts have been determined [22]. The process of self-organization has been studied throughout the experiment. The technology of hardening (laser welding of mix (PS-14-60 + 6% B4C)) which is more effective than traditional volume heat treatment is offered.

The structural features of massive castings in the process of crystallization and operation at the temperatures of magnetic transformation of carbide phases (magnetostriction phenomenon) have been revealed [23]. The conducted research introduces a new understanding of the phase composition of cast iron with high chromium content, the variability of the phase composition during the magnetic transformation of carbide phases and the decomposition of retained austenite. The estimation of phase variability and their interrelation during casting and heat treatment has been given. A new approach to the formation of a structure in a multiphase alloy by the optical-mathematical method of describing metallographic images has been proposed [24].

New methods for the study of various structures formed in chromium-containing carbon alloys [25], which allow to predict changes in the local heterogeneity of structural components through various processing operations using computer optical-mathematical evaluation has been improved. Computer analysis of images of metallographic structure evaluates the heterogeneity of cast iron with high chromium content due to the distribution of the degree of dispersion. The modeling of local inhomogeneity of structural components includes new parameters for estimating and applying invariant transformations of the M-triple to simulate changes in local homogeneity in structural components by changing certain energy parameters. Nevertheless, the results require a more detailed analysis, the role of such a factor as the degree of density of the dislocation structure.

It has been shown that the characteristic friction bands are formed with the appearance of the graphite network of the substrate [26,27]. To increase the durability of the piston rings in operation, it is recommended to deposit ion-plasma nanocoatings with additional quality control and to ensure the reduction of residual stresses.

The research of behavioural destruction of cast iron samples with spheroidal graphite (SGI) and CGI in ordere to determine the strength parameters has been carried out in study [28]. It has been found that SGI have greater resistance to destruction than CGI. At the same time, CGI showed higher decohesion at the graphite-matrix boundary, which leads to a decrease in ductility. The difference between the pearlite phases of the matrices of the two materials is revealed, which causes different hardness and can be predicted using the methods of artificial intelligence [29]. In these cast irons there is titanium with a different content (0.034...0.074).

It has been noted [30] that the CGI microstructure has excellent mechanical properties at high temperatures. Studies of microstructure and hardness have been performed on samples of different CGI thicknesses. It has been shown that the duration of pouring affects both the cooling rate and the Mg/S content. It has been found that increasing the cross-sectional thickness reduces the cooling rate, which promotes the formation of CGI with a pearlitic rather than martensitic

matrix, and also reduces the amount of spheroidal graphite. The hardness decreased with increasing cross-sectional thickness and increasing the duration of pouring.

The studied CGI has been obtained by low treatment with a magnesium alloy. The obtained CGI is classified according to ASTM A842-85 [31]. The results of tensile tests showed a significant difference in the samples without the addition of titanium and with the addition of titanium. It has been noted that the titanium content in the range from 0.06% to 0.20% provides the formation of compact graphite and can be used in the production of CGI, by adding certain components [32].

3. THE AIM AND OBJECTIVES OF THE STUDY

The aim of the study is to establish patterns of stable production of magnesium cast iron with CG using titanium additives as desferoidizing element.

To achieve this goal, the following tasks have been set:

- to perform thermodynamic calculation of titanium action in the melt of magnesium cast iron;

- to carry out researches on improvement and optimization of technology of reception of CGI on melts with the titanium maintenance received in the IST-0.06 induction furnace with acid lining.

4. RESEARCH MATERIALS AND METHODS OF THE RECEIVED MAGNESIUM CAST IRONS WITH VERMICULAR GRAPHITE

The study has used melts of the following chemical composition: C 3.5…3.6%, Si 1.8…2.2%, Mn 0.5…0.6%, up to 0.1% P. Experiments to develop a technology for producing CGI on refined melts obtained in a laboratory resistance furnace with a graphite crucible have been performed. Melts containing less than 0.01% sulfur have been obtained by remelting the charge, consisting of cast iron scrap of high-strength magnesium cast iron, high-quality carbon steel, electrode warfare and ferroalloys.

Calculations of titanium action in the melt of magnesium cast irons have been performed by estimating the changes in enthalpy, entropy and Gibbs energy of the components of cast iron depending on their concentration. Thermodynamic calculations of reactions have been performed according to the following formulas.

Changing the enthalpy of reactions:

$$\Delta H_T^o = \Delta H_{298}^o + (T-298)\left[\Delta a + 0.5\Delta \text{\textit{в}} \cdot 10^{-3}(T+298) + \frac{\Delta c \cdot 10^5}{298 \cdot T}\right] \quad (1)$$

$$\Delta H_T^o = \Delta H_{T_{i-1}}^o \pm \Delta H_{\text{пр},T_{i-1}} + (T-T_{i-1})\left[\Delta a_i + 0.5\Delta \text{\textit{в}}_i \cdot 10^{-3}(T+T_{i-1}) + \frac{\Delta c_i \cdot 10^5}{T \cdot T_{i-1}}\right] \quad (2)$$

Changing the entropy of reactions:

$$\Delta S_T^o = \Delta S_{298}^o + \Delta a \ln(T/298) +$$

$$+(T-298)\left[\Delta b \cdot 10^{-3} + \Delta c \cdot 10^5(T+298)/2 \cdot 298^2 \cdot T^2\right] \quad (3)$$

$$\Delta S_T^o = \Delta S_{T_{i-1}}^o \pm \Delta H_{\text{пр},T_{i-1}}/T_{i-1} +$$

$$+\Delta a_i \ln\left(T/T_i\right) + (T-T_{i-1})\left[\Delta b \cdot 10^{-3} +\right.$$

$$\left. + \Delta c_i \cdot 10^5(T_{i-1}+T)/2T_{i-1}^2 \cdot T^2\right] \quad (4)$$

Change in Gibbs energy of reactions:

$$\Delta G_T^o = \Delta H_T^o - T\Delta S_T^o \quad (5)$$

where ΔH_{298}^o and ΔH_T^o – changes in the enthalpy of reactions at 298K and T, К; Δa_i, $\Delta \text{\textit{в}}_i$, Δc_i – changes in temperature dependences ΔC_p on i temperature section; ΔS_{298}^o and ΔS_T^o – changes in the entropy of reactions at 298K and T, К; $\Delta H_{T_{i-1}}^o$ and $\Delta S_{T_{i-1}}^o$ – changes in enthalpy and entropy of reactions at the beginning i section; ΔG_{298}^o and ΔG_T^o – changes in the Gibbs energy of reactions at 298 K and T, К; $\Delta H_{\text{trans},T_{i-1}}$ – enthalpy change of phase transformation.

According to the method of calculating the changes in enthalpy, entropy, Gibbs energy of the reactions of formation of titanium oxide, titanium sulfide, titanium nitride and titanium carbide in the melt of magnesium cast iron and based on the original data of Table 1 the calculations of thermodynamic characteristics of these reactions have been carried out.

Table 1. Thermodynamic data for calculating the thermodynamic characteristics of the reactions of formation of titanium oxide, titanium sulfide, titanium nitride and titanium carbide.

Reagent	$\Delta H^{o}_{form.}$ 298, $\frac{kJ}{mol}$	$S^{o}_{form.}$ 298, $\frac{J}{mol}$	$\Delta G^{o}_{form.}$ 298, $\frac{kJ}{mol}$	$T_{trans.}$, К	$\Delta H_{trans.}$, $\frac{kJ}{mol}$	Coefficients of the equation $C_p = a + b \cdot 10^{-3}T + c \cdot 10^{5}T^{-2}$ J / mol ·К		
						a	b	c
Ti$_\alpha$	0	30.70	0	1155	3.97	21.98	10.55	0
Ti$_\beta$	-	-	0	2800	19.96	31.40	0	0
Ti liq.	-	-	0	3500	422.87	32.65	0	0
C gas.	-716.67	157.99	671.29	0	0	20.86	0	1.0
O gas.	-247.63	161.23	0	0	0	20.86	0	0
O$_2$ gas.	0	205.04	0	0	0	31.46	3.39	-3.37
S gas.	-278.8	167.75	238.31	0	0	0	0	0
S$_2$ gas.	-128.37	228.03	79.42	0	0	36.11	1.09	-3.51
N gas.	-473.47	153.44	0	0	0	20.82	0	0
N$_2$ gas.	0	191.5	0	0	0	27.88	4.27	0
TiO$_2$sol.	-944.12	52.28	-889.49	2128	66.96	75.23	1.17	-18.21
TiC sol.	-190.64	24.30	-205.70	0	0	49.56	3.35	-15.0
TiN sol.	-336.87	30.33	-635.4	0	0	49.90	3.94	-12.40
TiS$_2$ sol.	-334.94	78.42	-134.4	420	0	33.83	114.77	0

Thermodynamic calculations took into account the concentrations in the melt of magnesium cast iron: titanium - 0.1%...0.5%; oxygen - 0.01%; sulfur - 0.01%; nitrogen - 0.01%; carbon - 4.0% [33,34].

The experiments to improve and optimize the technology of obtaining CIVG have been performed on melts obtained in an induction furnace IST-0.06 with acid lining.
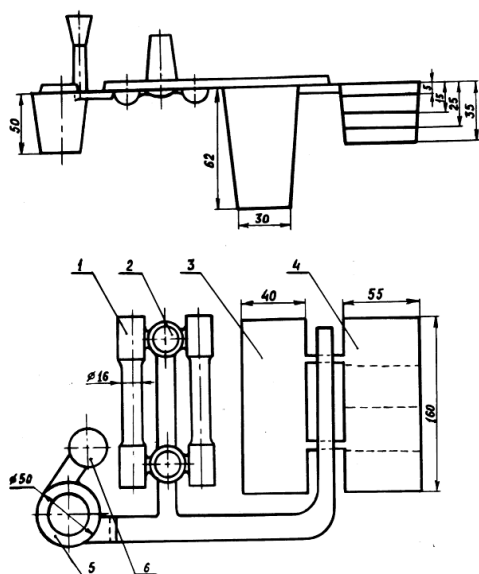
Fig. 1. The design of the experimental casting: 1 - bursting sample; 2 - addition; 3 - blank for the manufacture of bursting samples; 4 -stepped test; 5 - reaction chamber; 6 -stilt.

The study has been performed by the usage of the method of modification inside the mold. The experimental casting was poured. It consists of a step test for metallographic research (section

thickness 5, 15, 25, 35 mm), blanks for determining and testing the mechanical properties of high-strength cast iron and two rupture samples with a diameter of 16 mm, used for accelerated control of mechanical properties. The foundry system of the experimental casting (Fig. 1) includes a reaction chamber in the form of a truncated cone.

To improve the interaction of the melt with the modifier, its tangential supply to the reaction chamber has been used. This provides for the entire period of filling the form of dissolution of an equal amount of modifier with a high degree of assimilation.

The dissolution factor is the main parameter that determines the dissolution kinetics of the nodulizing alloy in the melt during intraform modification:

$$DF = V/S,\qquad(6)$$

where V – the speed of pouring metal into the mold, kg/s; S – the horizontal cross-sectional area of the reaction chamber, cm^2.

This indicator determines the amount of nodulizing alloy absorbed by the melt during modification, and is regulated by changing the rate of pouring the melt into the shape and size of the reaction chamber. The construction of the model equipment of the experimental casting allowed the use of variable reaction chambers with a diameter of D1 in the range of 30...60 mm and thus change the dissolution factor (DF) in the range of 0.01...0.07 kg / s cm^2.

Table 2. Conditions for obtaining, structure and chemical composition of cast iron treated in the ladle with the addition of 0.1% FeSi30REM30 modifier followed by (MICF) mixture of modifiers 90% FeSiMg6 and 10% FeSi30REM30.

No melt	Ti,%	S,%	DF, kg/cm²s	Mg$_{res}$, %	Microstructure and hardness of cast iron					
					Section thickness 5 mm			Section thickness 35 mm		
					VG,%	HB	The amout of grphite inclussions, mm^{-2}	VG,%	HB	Perlite content,%
1	0.1	0.035	0.03	0.029	25	217	375	65	207	35
2	0.1	0.035	0.04	0.019	85	207	310	90	197	30
3	0.1	0.010	0.04	0.022	30	227	290	45	227	35
4	0.3	0.035	0.03	0.029	35	241	410	75	235	20
5	0.3	0.035	0.04	0.021	85	235	390	95	223	10
6	0.5	0.035	0.03	0.029	45	269	495	85	262	15
7	0.5	0.035	0.04	0.021	90	262	420	75	255	10
8	0.5	0.010	0.04	0.022	30	293	365	55	287	20
9	0.1	0.035	0.03	0.029	40	207	280	75	207	30
10	0.3	0.035	0.03	0.030	50	235	235	80	227	20
11	0.5	0.035	0.03	0.030	65	262	262	90	255	15

The modifiers have been used in experiments on the production of cast iron with vermicular graphite as globularizing additives FeSiMg7 (Technical specification TS 14-5-134-2005 [34]) i FeSi30REM30 (TS 14-5-136-81 [35]). Before modifying the nodulizing alloy has been crushed and sieved, using a melt treatment fraction of 1.5… 2.5 mm. The effect of titanium content in cast iron on the expansion of the region of vermicular graphite formation in MICF mixture of modifiers FeSiMg6 and FeSi30REM30, and to reduce the harmful effects of sulfur, was determined on cast iron containing 0.010 and 0.035% S and pre-treated in a ladle of 0.1% FeSi30REM30 modifier (Table 2). Titanium in the amount of 0.1…0.5% has been added into the melt during melting in the form of crushed ferrotitanium FeTi35 (National Standard or State Standard System GOST 4761 – 91) brand.

The study of the distribution of the main components and impurities of cast iron C, Si, Mn, Mg, Cr, Ti, S, and P has been performed using the methods of micro-X-ray spectral analysis on an X-ray microanalyzer MS-46 company "Cameca" at U = 18-20 kV [36]. The distribution of elements contained in cast iron in increased quantities (Si, Mn, C) or characterized by a tendency to segregation (Ti, P, Cr), has been studied by topography along a line passing through the selected object.

At low concentrations of the analyzed elements in the studied phases, the measurement of the intensity of the characteristic radiation in the micro-X-ray spectral analysis has been performed by pointwise method simultaneously on four elements, in comparison with the radiation intensity of these elements from the standards with a known chemical composition. When estimating the level of MgK$_{\alpha 1}$ radiation intensity from graphite inclusions, only readings at points with MgK$_{\alpha 1}$ radiation intensity less than 3.0 imp/s have been taken into account. This eliminated the measurement errors associated with the partial output of the electron beam of the probe on the metal matrix. The evaluation of the analyzed elements concentration of in the phases of cast iron has been performed by comparing the intensities of radiation from chemically pure metals (Table 3).

Table 3. The background intensity of the analyzed elements on the standards of chemically pure substances.

Standard	Radiation intensity, imp/s	
	TiK_{α_1}	MgK_{α_1}
Carbon	4.83	1.40
Iron	7.83	4.67

The fine structure of the phases and structural components of cast irons has been studied by shaded lacquer prints using a transmission universal electron microscope UEMV-100K at magnifications of 3500-10000 times. To identify the phases formed in the cast iron, the electron microscope UEMV-100K at a voltage of 100 kV performed a microdiffraction study using two-stage carbon replicas with extracted phases. An aluminum film, which was obtained by condensation in vacuum has been used as a reference for the calculation of electrograms used aluminum film, which was obtained by condensation in vacuum.

5. RESULTS

The results of thermodynamic calculations of the Gibbs energy dependence of titanium oxide formation reactions, titanium sulfide, titanium nitride and titanium carbide in the magnesium cast iron melt on their concentrations and melt temperature are presented in Fig. 2.
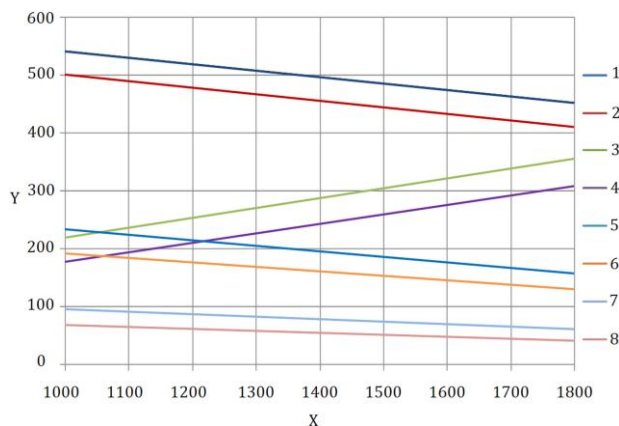
Fig. 2. The Gibbs energy dependence of titanium oxide formation reactions, with oxygen, sulfur, nitrogen and carbon in the melt of magnesium cast iron on their concentrations and temperature of the melt: Y – Gibbs energy -ΔG, kJ/mol; X – temperature of the melt T, К; 1,2 – TiO_2; 3,4 – TiS_2; 5,6 – TiN; 7,8 – TiC; 1,3,5,7 [Ti] =0,5%; 2,4,6,8 [Ti] = 0,1%; 1,2 [O] =0,01%; 3,4 [S] = 0,01 %; 5,6 [N] =0,01%; 7,8 [C] =4,0%.

According to these results, a structural diagram has been obtained, which connects the structure formation in the studied cast irons with the content of Ti and Mg_{res} (Fig. 3).
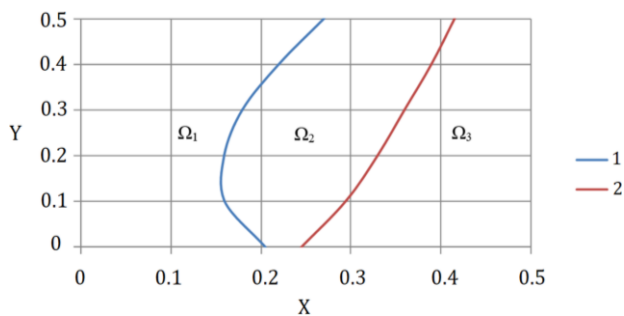

Fig. 3. Dependence of the shape of graphite inclusions in the cross section of the casting with a thickness of 35 mm in cast iron, treated in a ladle of 0.1% master alloy FeSi30REM30 from the residual content of magnesium and titanium: Y – titanium content Ti, %; X – residual magnesium content Mg_{res}, %; 1 – 90% compacted graphite; 2 – 60% compacted graphite. Areas of graphite forms: Ω_1 – lamellar graphite; Ω_2 – compacted graphite; Ω_3 – spheroidal graphite.

In the metal matrix of titanium-containing modified cast irons there is a significant number (up to 10000 mm^{-2}) of inclusions up to 1.5 μm in size, the color of which varies from light gray to pale yellow (Fig. 4-6).

According to the results of melting No. 8 (Table 3), the microstructure of titanium-containing cast iron in the cross section with a thickness of 35 mm has been obtained (Fig. 4).
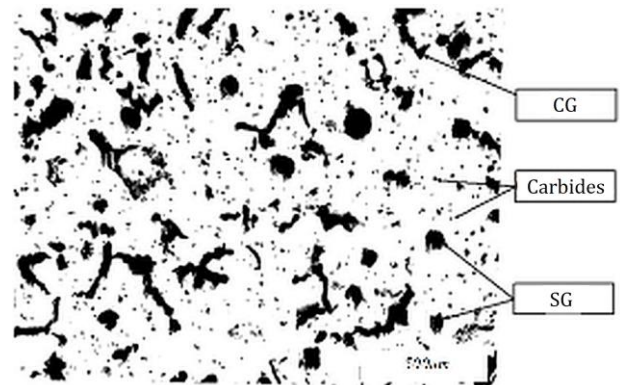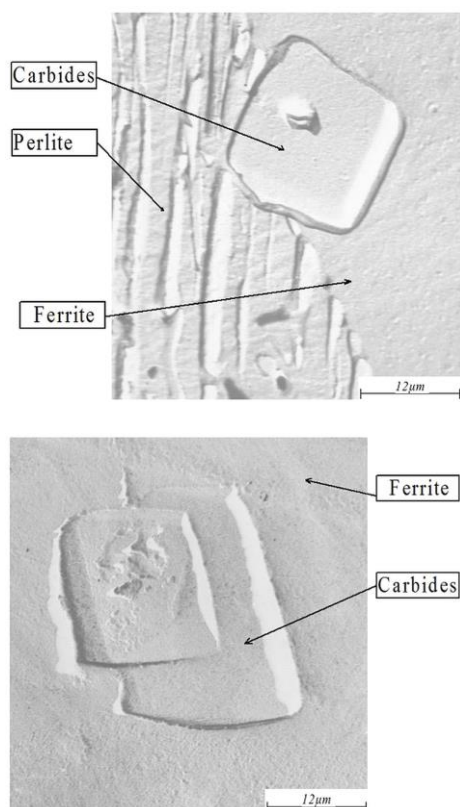

Fig. 4. Microstructure of cast iron containing titanium (melting No 8), in section 35 mm thick, x200.
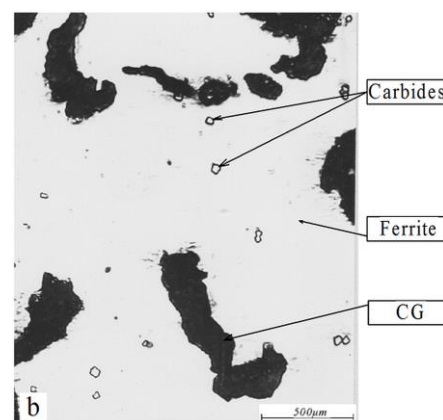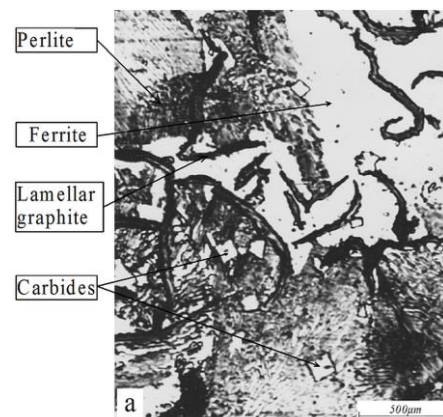
Fig. 5. Titanium-containing inclusions in the microstructure of cast iron with a content of 0.3% Ti (sample cross section 35 mm thick): (a) unmodified cast iron; (b) modified cast iron (melting No 8), x200.

Fig. 6. The structure of titanium-containing inclusions in magnesium cast irons with compacted graphite containing 0.3% Ti (x10000).

In the analysis of cast irons containing 0.035% S (melting No 1, 2, 4-7, 9-11, Table 3), in the composition of such inclusions in the micro-X-ray spectral analysis the presence of sulfur is registered.

Micro-X-ray spectral examination by the point method showed that regardless of the sulfur content in the modified cast iron in the areas of titanium-containing inclusions, the presence of magnesium is registered (Table 4).

The results of the analysis of microdiffraction patterns (Fig. 7b, Table 5) obtained from fine inclusions extracted in replicas from the surface of sections of modified cast irons.
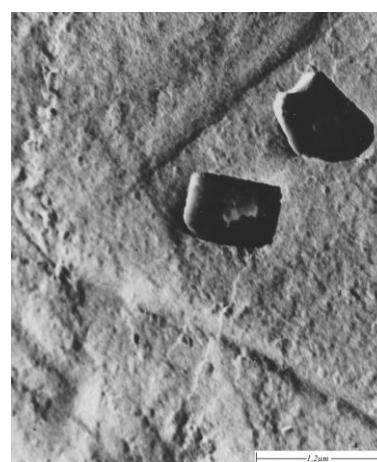
(a)

(b)

Fig. 7. Titanium-containing inclusions: a) extracted in the process of removing lacquer replicas from the surface of the section, in preparation for transmission electron microscopy (x100000); b) microdiffraction pattern obtained in the analysis of these inclusions.

Table 4. The average values of the radiation intensity of $MgK_{\alpha1}$ and $TiK_{\alpha1}$ from the structural components of cast iron with vermicular graphite.

No Melt	The analyzed element	Radiation intensity from structural components of cast irons, imp/s					
		Spheroidal graphite	CG	ferrite	perlite	phosphides	Fine inclusions
4 (Table 3)	Mg	1.571	1.473	4.766	5.253	4.720	23.948
	Ti	4.835	4.840	8.124	8.983	9.431	1537.693
5 (Table 3)	Mg	1.573	1.472	4.674	5.249	4.717	17.356
	Ti	4.830	4.837	8.126	8.897	9.411	1624.175
Output cast iron	Ti	-	-	8.123	8.967	9.428	1824.437

Table 5. Interplanar distances of the analyzed titanium-containing inclusions $Ti_4C_2S_2$.

Parameter	Crystallographic indices hkl						
	100	102	006	110	200	210	300
Estimated value,Di, A	2.97	2.58	1.79	1.69	1.47	1.11	0.96
Experimentally determined value Di, A	2.98	2.61	1.77	1.70	1.46	1.13	0.96

6. DISCUSSION

Thermodynamic calculations show that titanium, regardless of the concentration in liquid iron, primarily performs a deoxidizing effect, interacting with the oxygen present in the melt (Fig. 1). Slightly smaller negative values of Gibbs energies are characterized by the reactions of the interaction of titanium with sulfur, at a concentration of the latter 0.01. Decreasing of its concentration leads to an increase in the Gibbs energy of desulfurization reactions by 1.7 times. It indicates a decrease in the probability of such a reaction. At least, from a thermodynamic point of view, the reactions of formation of nitrides and carbides of titanium are possible. The values of the Gibbs energy of the interaction reaction dissolved in iron Ti and S, in contrast to other studied reactions, largely depend on the temperature of the melt, with a growing trend of negative values ΔG_T^o with increasing temperature. For a more complete implementation of the desulfurizing properties of titanium, it is advisable to add the cast iron during melting and overheating, when the melt temperature reaches maximum values [9,16].

Melt treatment by MICF method, adding titanium to the composition of cast iron contributes to the expansion of the area of CG formation by changing the position of both the upper and lower limits. Increasing the content of Ti to 0.5% (Fig. 3) causes a shift of the upper limit from 0.026 to 0.042% Mg_{res}. With the addition of titanium in an amount of up to 0.2%, there is also a shift of the lower boundary of the region of CG formation in the direction of lower Mg_{res} content. This increase in the efficiency of the modifying action of magnesium in the presence of titanium may be connected with the partial binding of sulfur to titanium sulfides. A further increase in the titanium content, more than 0.2%, leads to a shift of the lower limit of the CG formation in the direction of a higher content of Mg_{res}, reducing the efficiency of magnesium with a less significant expansion of the area of CG formation.

The presence of titanium in the cast iron provides an effective graphitizing effect. And already at a content of 0.1% Ti in sections of the casting with a thickness of 5 mm stops the formation of edge bleaching. It is accompanied by an increase in the number of graphite inclusions. Titanium also has a significant ferritizing effect on the structure of the metal matrix, reducing the content of perlite in it to 10… 15%. The study of the distribution in the structure of the metal matrix of Si and Mn has shown that due to the addition of titanium there is a marked decrease in the direct liquation of manganese and the reverse liquation of silicon to the boundaries of eutectic grains. This increase in the homogeneity of constant components distribution is obviously the reason for the expansion of ferrite sites in the structure of CGI.

These inclusions (Fig. 4-6) are mainly located in ferritic areas. Some inclusions are in contact with graphite and perlite inclusions. In the process of removing lacquer replicas from the surface of the section in preparation for transmission electron microscopy, part of the small inclusions have been extracted. This indicates their weak connection with the surrounding metal matrix (Fig. 5).

Light gray inclusions of square and trapezoidal shapes have been observed in the original unmodified titanium-containing cast iron. These are characterized by similar optical properties with inclusions in modified cast irons (Fig. 5 a). However, their number is 15-20 times lower than in modifiedcast iron, and their sizes reach 3…5 microns. This indicates a significant influence of modifying elements on the process of formation of titanium-containing inclusions.

The analysis of the optical compositions of titanium compounds, showed that similar properties and structure have the inclusion of titanium sulfides. Linear micro-X-ray spectral analysis of refined cast irons with titanium (melts No 3 and 8, Table 3) showed that the composition of such inclusions contain titanium and carbon.

The presence of titanium in the cast iron helps to reduce the contamination of the upper part of the casting with modification products in the form of "black spots". Thus, the addition of titanium to cast iron containing 0.035% S, affect both the stabilization of CG formation and increase the purity of castings from floated modification products.

Micro X-ray Spectral study by the point method showed that the radiation intensity $MgK_{\alpha 1}$ from titanium-containing inclusions increases markedly with increasing Mg_{res} in cast iron (Table 4). At the same time, the intensity of radiation $MgK_{\alpha 1}$ on graphite inclusions remains

virtually unchanged. This indicates that the segregation of magnesium in titanium-containing inclusions contributes to buffer stabilization at a certain level of magnesium concentration in the melt and crystallizing phases, sufficient for CG formation.

The results of the analysis of microdiffraction patterns (Fig. 7b, Table 5) obtained from fine inclusions extracted in replicas from the surface of sections of modified cast irons, allow to identify them as a chemical compound with hexagonal syngony $Ti_4C_2S_2$.

The results of the research show that the magnesium CGI obtained by the developed technology has a low tendency to metastable crystallization in thin sections of the casting and is characterized by reinforced fine-grained titanium-containing inclusions ferrite metal matrix. This cast iron is characterized by high hardness. It is expected that this material will have increased thermophysical properties. In addition, its expedient usage can be brake disks of high-speed vehicles.

7. CONCLUSION

1. Thermodynamic calculations have been performed and the dependence of the Gibbs energy of the reactions of formation of titanium oxide, titanium sulfide, titanium nitride and titanium carbide in the magnesium cast iron melt on their concentrations and melt temperature has been obtained.

2. It has been found that the characted of the change in Gibbs energy ΔG_T^o <0 indicates the thermodynamic possibility of the course of spontaneous reactions. Titanium is interacting with the oxygen present in the melt. Lower negative values of Gibbs energies are characterized by the reactions of the interaction of titanium with sulfur. At a concentration of the latter 0.01%, indicates a decrease in the probability of such a reaction. From a thermodynamic point of view, the reactions of titanium nitride and carbide formation are less probable. The values of the Gibbs energy of the reaction of the dissolution of titanium and sulfur in iron, in contrast to other studied reactions, depend to the greatest extent on the melt temperature.

3. The use of additional treatment of magnesium cast iron with the main desferroidizing element titanium promotes the formation of centers of graphite formation and expands the area of CG formation. The addition of titanium to magnesium cast iron, as a desferoidizing element containing 0.035% S, has a positive effect on stabilizing CG formation and increase the purity of the casting from the floated modification products. The titanium content can be limited to 0.1%, which is sufficient for the formation of CG inclusions.

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