

THE DEVELOPMENT OF NEW CASTING ALLOYS INTENDED FOR OPERATION UNDER EXTREME CONDITIONS AND SOME TECHNIQUES OF MAKING CASTINGS FROM THEM

Mikhail Yamshinskij

*Department of foundry of ferrous and nonferrous metals
National Technical University of Ukraine "KPI"
37 Peremohy ave., Kyiv, Ukraine, 03056
yamshinskiy@ukr.net*

Grigoriy Fedorov

*Department of foundry of ferrous and nonferrous metals
National Technical University of Ukraine "KPI"
37 Peremohy ave., Kyiv, Ukraine, 03056
foundry@iff.kpi.ua*

Anatoliy Verkhovliuk

*Department of foundry of ferrous and nonferrous metals
National Technical University of Ukraine "KPI"
37 Peremohy ave., Kyiv, Ukraine, 03056
vam@ptima.kiev.ua*

Abstract

The article studies new heat-resistant and wear resistant materials for operation under extreme conditions, especially in the power industry. The methods that improve the quality of a metal in metal castings through the influence of alloying elements on its structure and properties have been considered. These methods are very effective for reducing the tendency of a metal to form a coarse-grained structure. The paper describes optimal techniques for melting special alloys in induction and electric furnaces. A set of rules for the selection of a melting temperature before pouring a metal into the casting forms depending on the dimensions, wall thickness, geometry of castings have been determined. The behavior of new alloys under the conditions of high temperatures, aggressive environments has been studied.

It has been established that heat-resistant Cr-Al steels exhibit high heat resistance and wear resistance properties; they 6–8 times surpass Cr-Ni steels in oxidation resistance. The proposed Cr-Mn cast iron processed in an integrated manner with REM (rare earth metals) and Ti is superior to a basic cast iron in conditions of a heavy wear. Numerous industrial trials confirm the usefulness of recommended new casting materials for use under extreme conditions.

Keywords: heat-resistant steel, Cr-Al steel, heat resistance, aggressive environment, wear-resistant cast iron, ash-handling pump, ash pump.

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1. Introduction

High (up to 1350 °C) and low (to –190 °C) temperatures, aggressive environments, intensive abrasive, impact-abrasive and hydro-abrasive wears and other factors are considered as extreme conditions for the operation of metal goods.

Fe-based heat-resistant alloys like Cr, Cr-Ni and Cr-Al steels are classified as the materials operating in the conditions of high temperatures and aggressive environments [1, 2]. They are used for production of moulded parts for combustion appliances of boiler units at thermal power plants, equipment for metallurgical, chemical and high temperature technologies machine-building companies.

The analysis of operating conditions of such details has defined that heat-resistant alloys, recently being used for their manufacture, have significant drawbacks: their structure includes expensive and scarce elements (nickel, cobalt, molybdenum and others). They are low-tech as a casting material (containing small percentage of carbon – up to 0.1 %) and have limited perfor-

mance characteristics (e. g., the maximum operating temperature does not exceed 1100 °C). Thus, new alloys must have high melting temperatures and thermal stability (oxidation resistance, heat resistance and growth resistance), satisfactory casting properties, be inexpensive and available.

Development of new alloys requires deep knowledge of their likely behavior at high temperatures and in aggressive environments. This makes it possible to select a group of elements capable to maximize service features of alloys with saving satisfactory casting and high mechanical properties.

The alloying of Fe-based steels essentially changes their structure and properties due to the reduction of thermal conductivity of metal, changes in the crystallization processes and, in many cases, the deterioration of casting properties. The role of alloying elements in heat-resistant alloys consists primarily of changing a scale's composition and structure, the kinetics of metal oxidation in various aggressive environments.

Such elements as carbon, chromium, silicon, aluminum, titanium and others are the main part of heat-resistant steels. Let's consider the impact some of them have on main technological properties of these alloys.

2. Experimental procedures

The alloys were melted in an induction crucible furnace IST-0.06 with a basic lining using the refining method of the estimated amount of a charge [5].

The fluidity of the alloys was determined using a Kerry's spiral special cup, allowing to stabilize metal pressure and temperature in each experiment [6].

Linear shrinkage was studied on a special appliance, which allows linear changes of a sample with the dimensions 200×25×20 mm to be turned into a proportional change in voltage during a shrink process using a potentiometric linear encoder. A signal from a sensor was recorded on a chart record of a XY recorder N-703 with a functional dependence $\varepsilon=f(t, ^\circ\text{C})$.

The resistance of alloys to crack development was determined using a circular process sample with a diameter 160 mm, wall thickness 7 mm and 100 mm in height. The cross section of the thermal unit was 30×19 mm throughout the height of the sample. To slow the shrinkage down, cores made from liquid glass mixture were utilized. The criterion of crack resistance is the crack area, which is formed on the inner surface of the thicker area of the sample. The area of the crack was determined based on the print on a scale – coordinate paper [7].

Mechanical properties of the alloys were studied using standard techniques. Heat resistance of steel was investigated with a tube – type furnace, which allows to heat samples 20 mm long and 10 mm in diameter up to 1400 °C in various gas atmospheres and soak for a long time [8].

The study of wear resistance of the cast iron was carried out on a special appliance, which models real operation conditions of details in a hydro-abrasive environment (a mixture of quartz pit sand and water) by means of rotating samples 65×25×10 mm in size.

To study the structure, hardness and microhardness of structural components samples cut from moulded prismatic pieces 100×30×20 mm in size were used. The cross section of these samples corresponds to the average cross section of the walls of details of ash pumps.

3. Results

3.1. The effect of Cr and Al on casting properties of heat-resistant alloys

Technological properties of heat-resistant steels are determined by content of main elements – Cr and Al [9]. The effects of Cr in the concentration range from 13 to 37 % and Al to 7.1 % were studied. The results of changes of main casting characteristics of Cr steels in accordance with the content of these elements are shown in **Fig. 1**.

It was established that the increase in the concentration of Cr in steel improves practical fluidity due to the decrease in temperature of liquidus and reduced crystallization interval in accordance with the phase diagram of Fe-Cr.

The increase of Al content in high-chromium steels up to 1.5–2.0 % keeps their practical fluidity on a high level. Further increase in Al content reduces fluidity of steels as a result of intensive foam formation in a metal.

Thus, to maintain the high fluidity of Cr steels the content of Al should not exceed 2 % (Fig. 1, *a*).

Cr and Al are referred to elements that help in formation of an alloyed ferrite, which has a lower shrinkage ratio when compared to an alloyed austenite [10]. Therefore, the increase in concentration level of Cr and Al in steels reduces the linear shrinkage (Fig. 1, *b*) and improves crack resistance of alloys.

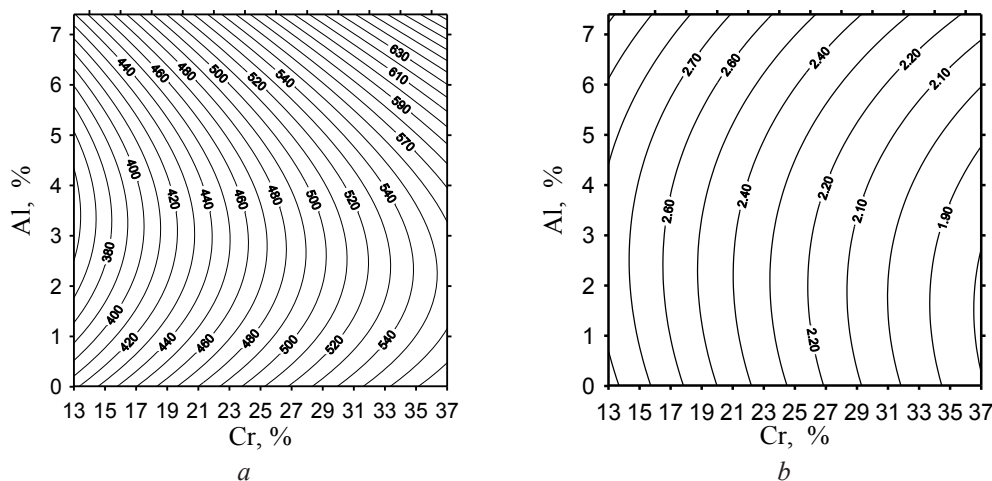


Fig. 1. Casting properties of heat resistant steels depending on the Cr and Al content:
a – practical fluidity; *b* – a linear shrinkage

The reduction of steels' thermal conductivity, after the rise of Cr and Al content, increases the defects of a shrinkage type and a concentrated shrinkage cavity [9, 10].

3. 2. Mechanical properties of heat-resistant steels depending on the content of Cr and Al

The increase of Cr and Al concentration in the investigated steels is accompanied by a reduction of their density, because both Cr and Al have less density as compared to Fe (7160 and 2710 kg/m³ against 7862 kg/m³ accordingly).

Investigated steels have a coarse – grained structure, which can't be changed by any mode of heat treatment. As a result, their strength properties at normal temperatures are much lower than in same steels with a fine – grained structure.

The increase of Cr concentration in the investigated range promotes grain growth from 87 to 120 microns, and from 69 to 87 microns with the increase of Al content up to 3 %. This change of the grain's size reduces both strength (Fig. 2, *a*) and ductility (Fig. 2, *b*) of heat-resistant steels.

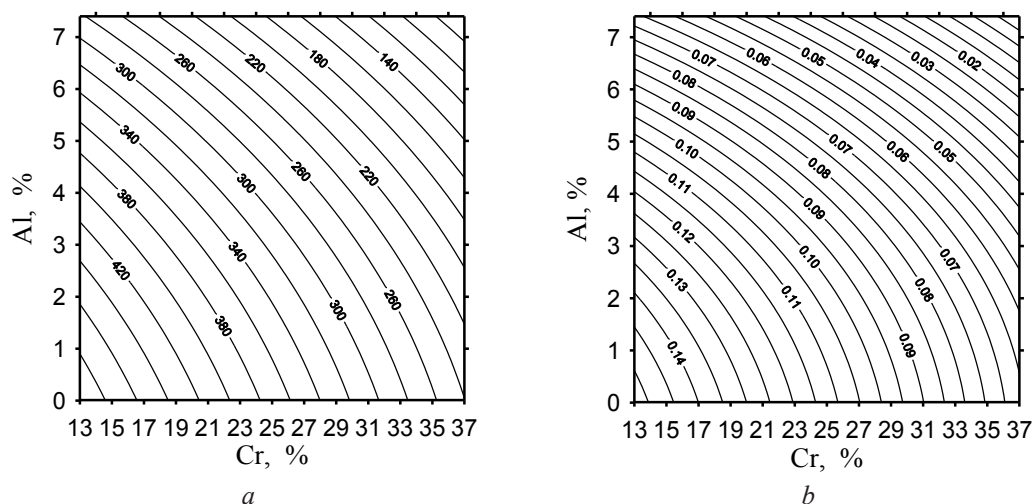


Fig. 2. The change of mechanical properties of heat resistant steels depending on the Cr and Al content: *a* – ultimate tensile strength; *b* – impact strength

The studies have found that Al content in the heat resistant steels should be determined by the minimum, which maintains their high heat resistance, and the maximum, when casting and mechanical properties are getting worse.

Thus, considering casting properties optimum content in heat-resistant steels of Cr should be 28–32 % and Al 1.5–2.0 %.

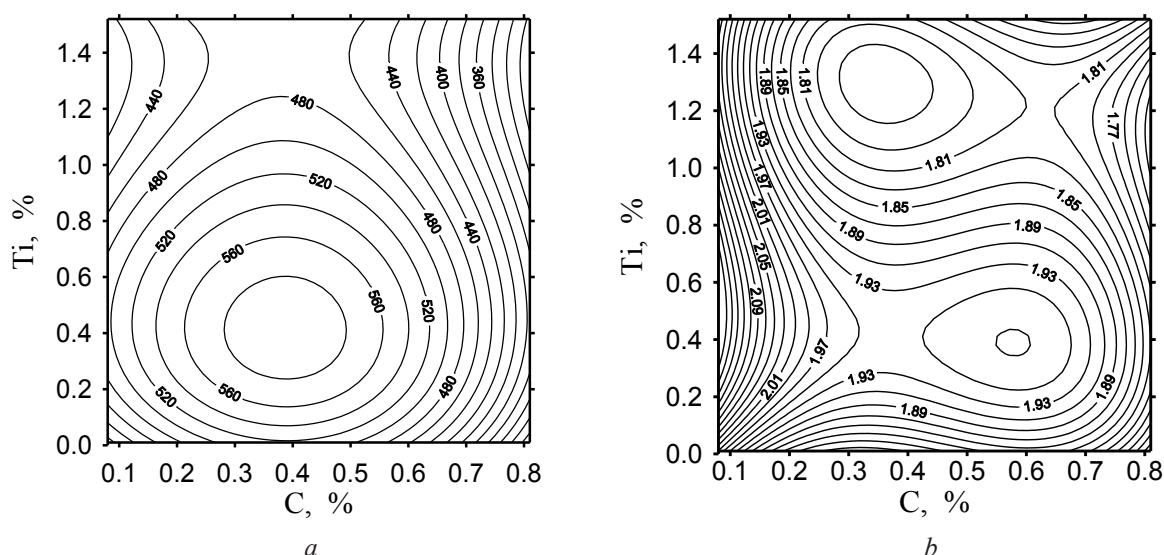
3.3. The influence of carbon and titanium on casting properties of Cr-Al steels

The improvement of properties of heat-resistant steels can be achieved by further processing them with titanium, vanadium, niobium and other elements. The cheapest and the most effective is titanium [11, 12].

The effect of C with concentrations ranging from 0.08 to 0.81 % and Ti up to 1.45 % on casting and mechanical properties has been studied.

The determination of the optimum ratio of Ti and C in Cr-Al steels with regard to their impact on casting, mechanical and special properties are of theoretical and practical interest.

It has been found that the increase of C improves practical fluidity of all investigated steels. Addition of Ti up to 0.35 % also increases the fluidity of steels (Fig. 3, a).



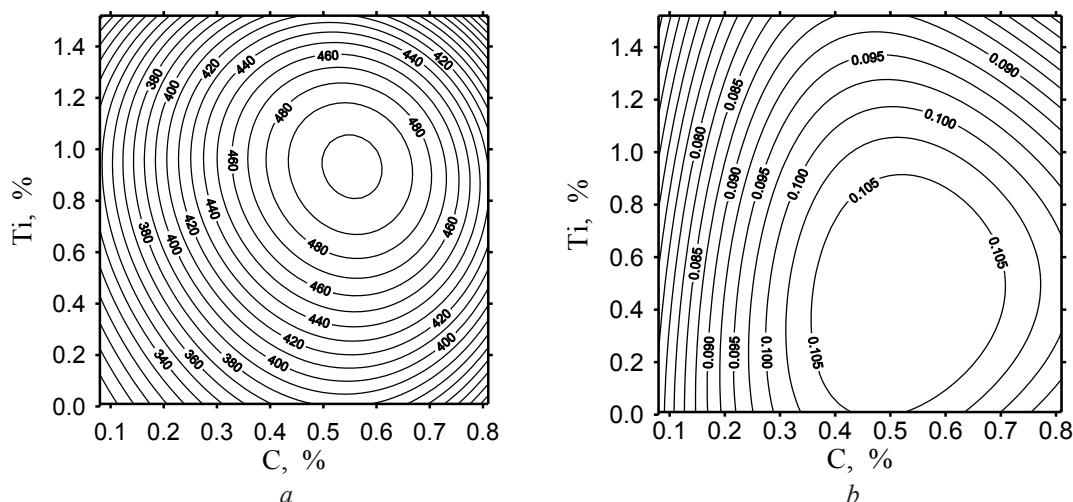


Fig. 4. The change of mechanical properties of Cr-Al steels depending on the C and Ti content:
a – ultimate tensile strength; b – impact strength

Table 1

Technological properties of Cr-Al steels

№	Properties	Parameters
1	Fluidity at 1580 °C, mm	460–630
2	Linear shrinkage at the temperature of metal before pouring into the mold 1580 °C, %	1.75–2.30
3	Linear shrinkage at the temperature of metal before pouring into the mold 1700 °C, %	1.30–1.65
4	Cracks' squire on a technological sample with the diameter 160 mm and height 100 mm before pouring a metal into the mold at the temperature of 1580 °C, cm ²	0.75–1.50
5	Full volume shrinkage at 1580 °C, %	11.6–13.5
6	Ultimate tensile strength, MPa	360–450
7	Impact strength, KC, MJ/m ²	0.09–0.11
8	Hardness, HB	180–230

3. 5. The investigation of special properties of Cr-Al steels

Oxidation resistance of steels was determined in an atmosphere of overheated air to 1300 °C, air +25 % of water vapor, air +45 % of CO₂, air +45 % of water vapor. The results of the study are presented in the **Table 2**.

Table 2

Oxidation resistance of Cr-Al steel in relation to its Al content and experimentation environment
(Test conditions: temperature – 1300 °C, time 100 h)

№	Environment	Oxidation resistance, mg/cm ²					
		The aluminium content, %					
		0.02	0.92	1.96	2.84	5.05	6.76
1		9.85	6.10	4.00	3.50	3.20	3.18
2	air +25 % H ₂ O	12.80	8.20	5.35	4.10	3.65	3.58
3	air +45 % CO ₂	16.10	9.75	6.15	4.85	3.95	3.90
4	air +45 % H ₂ O	17.95	11.05	7.85	5.90	4.45	4.20

Comparison of oxidation resistance of heat resistant steels of different classes is shown in **Table 3**.

Table 3

Oxidation resistance of heat-resistant steels of different classes in the atmosphere of overheated air

№	Grade of steel	Oxidation resistance (mass loss), gr/m ² h	
		1250 °C	1300 °C
1	DIN. GX16CrNi25-21	3.9–4.2	4.5–4.8
2	DIN. X15CrNiSi25-20	2.7–3.1	3.0–3.5
3	X30Cr30Al2Ti	0.4–0.5	0.6–0.7
4	X15Cr26Al2NiTiCu	0.4–0.5	0.7–0.8

Consequently, heat-resistant Cr-Al steels possess high oxidation resistance, temperature resistance and durability. They are 6–8 times less sensitive to oxidation than Cr-Ni steels at operation temperatures 1250 °C and 1,5–2,0 times more heat resistant, 2,0–3,0 times more durable.

Ferrite Cr-Al steels are characterized by the highest electrical resistance, so they can be used to produce heaters for heat-treatment furnaces, moulded resistors, and other products [13].

New nickel-free heat resistant steels can be used in manufacturing moulded parts in the power industry, ferrous metallurgy, chemical and other industries [14–16].

The examples of moulded parts of different sizes, geometry, mass, which were produced with different casting techniques are shown below (**Fig. 5**). Tips and nozzles are produced in an expendable sand-clay form. The use of parts made from these steels (burners tops, nozzles, gas nozzles and others) at thermal power plants allows 4–6 times to extend their service life, cut cost, reduce maintenance costs, fuel consumption for electricity production and completely eliminate alloys, containing nickel, cobalt, molybdenum, from heat-resistant structures [17, 18].

The power industry is one of the main consumers of wear-resistant alloys. Generic items from these alloys are shown in the **Fig. 6**. Details of solid fuel preparation systems and systems of ash and slag removal from boilers are being in service here under the conditions of intensive abrasive or hydro-abrasive wear [19].

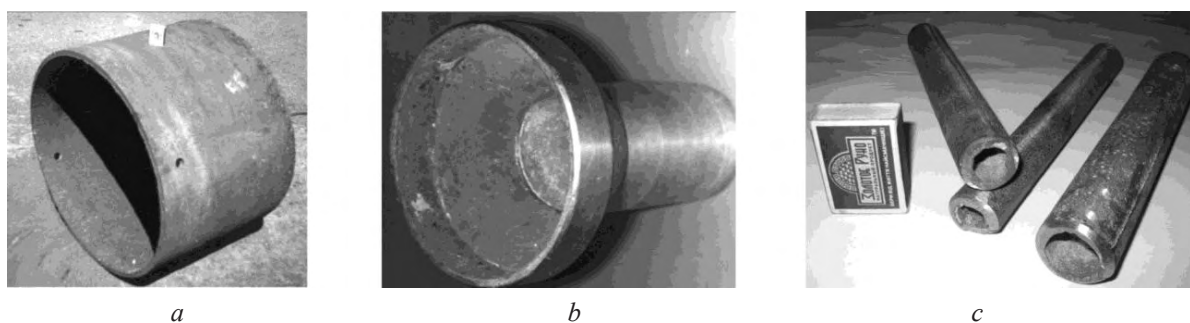


Fig. 5. Generic items for combustion appliances of thermal power stations (diameter 300, 600 and 930 mm; height – 600 mm; wall thickness – 15–20 mm): *a* – a nozzle №1; *b* – a nozzle №2; *c* – tips of gas nozzles (length 220 mm, diameter 26 and 35 mm, wall thickness 5 mm, mass 0.6 and 0.9 kg)

The period of operation of the pump is usually limited by wear of an impeller or a body, which is made mainly of wear-resistant white cast iron 280H28N2 brand. The pump breaks down

and can not create necessary pressure when through holes are formed in an impeller wheel or in a body. At the same time, wear of the impeller wheel or body doesn't exceed 5–10 %.



Fig. 6. Fast wearing parts of ash pumping systems of ash pumps at thermal power stations:
a – a body, *b* – a disk, *c* – a wheel

The improvement of the structure of the alloy, its technological and operational properties becomes possible due to additional micro-alloying and modification. Modification by several elements simultaneously (i. e., complex modification) is especially effective [20, 21].

The influence of complex modification on the structure and properties of wear-resistant Cr-Mn cast iron with a certain chemical composition, %: C – 2,8–3,1; Cr – 19–21; Mn – 4,2–4,4; Si – 0,6–0,9; S ≤ 0,05; P ≤ 0,05, previously developed by the authors, have been studied in this work [22]. After experimental samples from the standard, basic cast iron had been poured, Ti in the form of ferrotitanium FTi35 was loaded into a crucible of the furnace. REM in the form of a rich alloy containing 48.5 % of Ce were also loaded in the crucible of the furnace just before tapping the metal from the furnace.

The introduction of Ti together with an element, which has a high affinity to sulfur and other harmful impurities, has scientific and practical interest. Such promising elements are REM [24].

Chemical composition of the investigated cast irons is shown in **Table 4**.

Table 4
Chemical content of investigated cast irons

Cast iron index	Elements content, %						P maximum	S
	C	Cr	Mn	Si	Ti	REM*		
9.1	2.91	18.9	4.38	0.64	–	–	0.05	0.05
9.2	2.88	18.5	4.30	0.65	0.20	0.10	0.05	0.05
9.3	3.00	19.8	4.24	0.74	0.15	0.20	0.05	0.05
9.4	2.90	19.2	4.32	0.72	0.13	0.50	0.05	0.05

Note: * estimated amount

This work was carried out for details working in hydro-abrasive environments. It was found that simultaneous addition of Ti and REM in the cast iron has significant influence on the structure and mechanical properties of the basic Cr-Mn cast iron. An alloy treated with 0.15 % of Ti and 0.2 % of REM has maximum durability and microhardness of austenite grains. The microhardness of the chromium carbides varied at the level 11–14 GPa and didn't depend on Ti or REM content. The hardness of the surface of original and modified samples shifted slightly and reached to 48–50 HRC. This is explained by the fact that main structural changes and according-

ly changes of the service properties of the alloy occur during the solidification process inside of the sample rather than on its surface.

The structure of the original cast iron consists of branched primary dendrites of austenite and the eutectic $\gamma + (\text{Cr, Fe, Mn})_7\text{C}_3$ (**Fig. 7**). Simultaneous modification of the cast iron with Ti and REM significantly refines the structure of the original Cr-Mn cast iron. The width and especially the length of primary austenite dendrites is greatly reduced in the central part of samples.

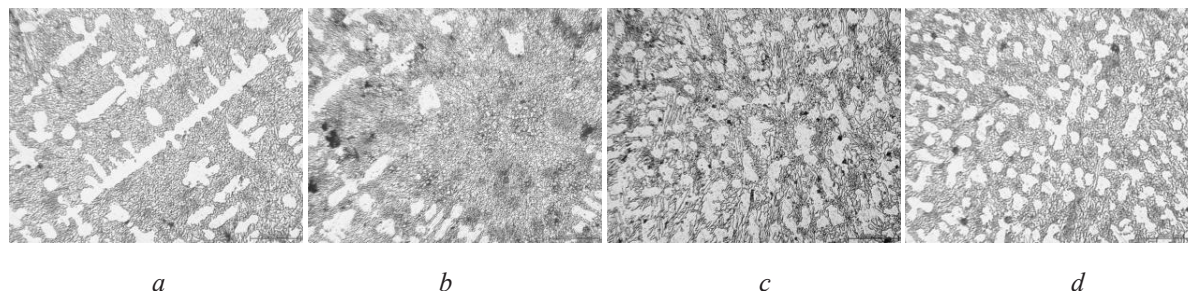


Fig. 7. The structure of Cr-Mn cast iron modified with Ti and REM ($\times 100$):
a – without Ti and REM; *b* – 0.2 % Ti and 0.1 % REM; *c* – 0.15 % Ti and 0.2 % REM;
d – 0.13 % Ti and 0.5 % REM

The addition of Ti in the cast iron facilitates the formation of carbides and carbonitrides, located mainly in the austenite and at the boundaries of the matrix-carbide phase. In chromium carbides they are practically absent. Taking into account the correspondence of crystalline grids' types, they are the centers of austenite crystallization and modify a liquid alloy on the type II. REM additives stimulate the modification of a liquid alloy on the type I. Ce and its compounds, formed before the crystallization of the alloy, are adsorbed like surface – active agents at the border of growing austenite dendrites, restricting their growth. REM effectively binds the sulfur and oxygen in Cr-Mn cast iron and is a part of sulphides and oxysulphides mainly of spherical shape. REM oxysulphides are uniformly spread in the structure, their number gets bigger as the total content of REM in the alloy increases. In addition, there are inclusions in which sulfides of REM are close to titanium carbonitrides. Taking into consideration the high affinity of Ti to sulfur, it can be assumed that these are oxycarbosulphides of complex chemical composition.

Structural studies of pickled samples at high magnification on the optical and scanning electron microscopes have established that within austenite dendrites modified by REM and Ti there are fine particles of size 1–4 μm (**Fig. 7, b**). The highest number of such inclusions are found in alloys containing REM 0.2 and 0.5 %.

The cast iron modified with 0.2 % of REM and 0.15 % of Ti has wear resistance 15 % higher than the original one. Pilot tests have confirmed the efficiency of such cast iron for use in manufacturing pieces of the hydraulic ash transport system machinery at thermal power plants [25, 26].

4. Conclusion

1. Cr-Al steel with the following chemical composition of %: C=0.25–0.35; Cr=28.0–32.0; Al=1.5–2.5; Mn=0.6–0.8; Si=0.5–1.0 has the best combination of casting, mechanical and special properties. P and S content should be not more than 0.025 % for each element.

2. New heat-resistant nickel-free Cr–Al steels may be used for the production of moulded parts of equipment for high temperatures technologies.

3. To produce moulded parts working under conditions of intensive wear, Cr-Mn cast iron additionally processed with titanium additives in amount of 0.15–0.2 % and REM in amount of 0.15–0.25 % (estimated) should be used.

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