



Research article

Assessment of the effect of small additions of some rare earth elements on the structure and mechanical properties of castings from hypereutectic chromium white irons

Aleksander Panichkin¹, Alma Uskenbayeva^{1*}, Aidar Kenzhegulov^{1*}, Axaule Mamaeva¹, Akerke Imbarova¹, Balzhan Kshibekova¹, Zhassulan Alibekov¹, Didik Nurhadiyanto² and Isti Yunita²

¹ The Institute of Metallurgy and Ore Beneficiation JSC is a part of “Satbayev University” NJSC, 050013 Almaty, Kazakhstan

² Universitas Negeri Yogyakarta, 55281 Yogyakarta, Indonesia

* **Correspondence:** Email: a.uskenbayeva@satbayev.university, a.kenzhegulov@satbayev.university; Tel: +87474241152, 8 7072000062.

Abstract: Article considers the influence of additions of rare earth elements such as Sm, La, Ce, Nd, and Y on the structure and properties of hypereutectic high-chromium white cast iron of grade G-X300CrMo27-2. To obtain an increased content of carbides in the studied cast iron samples, the carbon content was 3.75–3.9 and 4.1–4.2 wt%. The amount of rare earth elements additives added to the melt is 0.2% by weight. Data were obtained on the effect of overheating and cooling rate in the crystallization interval on the effect of rare earth additives, the structure and properties of white cast iron castings are given. According to the results of the microprobe analysis, it was shown that, under the chosen crystallization conditions, Sm, La, and Ce can form solid solutions with primary and eutectic carbides $(\text{FeCr})_7\text{C}_3$. La and Ce form solid solutions with austenite. Nd and Y do not dissolve in iron chromium phases. All listed rare earth elements form phosphides and oxyphosphides. Experimental data are presented on the effect of rare earth elements on the size of primary $(\text{FeCr})_7\text{C}_3$ carbides and a hypothesis is proposed on the effect of rare earth elements on the crystallization process of hypereutectic chromium white cast irons. Experimental data are presented on the effect of REE additives on the microhardness of phases, hardness, strength, and resistance to abrasive wear of cast iron castings. It was found that the introduction of these additives into hypereutectic chromium white cast iron does not contribute to the modification of the structure and leads to an increase in the

size of primary crystals, as well as a decrease in their mechanical properties. However, the addition of Y increases the abrasive wear resistance, but reduces the strength of castings made from such white cast iron.

Keywords: hypereutectic white chromium cast iron; rare earth elements; structure modification; mechanical properties; abrasion resistance; carbide

1. Introduction

White chromium cast iron is widely used for the manufacture of components that operate under abrasive and shock-abrasive wear conditions, including in corrosive environments. Parts of mills, crushers, slurry pumps etc. are made of these materials [1–5]. The abrasion resistance of white cast iron determines the operation life of the equipment until parts are replaced. This is of great importance in the processing of mineral raw materials since the depletion of mineral reserves occurring in the world leads to the involvement in the processing of poorer hard-to-enrich raw materials and technogenic mineral formations. To extract valuable components from such raw materials, more intensive grinding is required [6–9]. This leads to a sharp increase in the wear of crushing and grinding equipment. To reduce production costs, it is necessary to increase the overhaul period. This can be achieved by using more wear-resistant materials, but this is not always possible and economically feasible. Another, more efficient way is to improve the performance of widely used white chromium cast irons.

The high wear resistance of chromium white cast iron is due to the content of a large amount of carbide in its structure. The most wear-resistant white cast irons are those containing M_7C_3 carbides [10,11]. It is believed that an increased content of carbide in the composition of chromium wear-resistant white cast iron increases its wear resistance [10–13]. This explains the reason for the increasing attention of researchers towards chromium white cast iron with a hypereutectic composition. Primary needle-like M_7C_3 crystals are marked in white cast iron during crystallization. Meanwhile, the crystallization interval of the alloys expands with increasing carbon content resulting in the isolation of large carbide crystals. The crystal size of primary carbide increases significantly with decreasing crystallization rate. In addition, hypereutectic alloys become susceptible to hot crack formation because of this structure. This results in a significant reduction in the impact toughness of the casting and even its spontaneous destruction due to internal stresses. The problem is exacerbated in the case of large-size castings and often leads to manufacturing defects.

For a wider application of hypereutectic chromium iron with increased carbon content, it is necessary to develop effective methods for crystallization alloys that allow for reduction in the size of the primary crystals. It should improve the mechanical properties of the castings and reduce the possibility of hot cracks formation. One effective way to reduce the size of precipitated crystals of various alloys [10–24] is the introduction into the melt of a substance that dissolves and interacts with the components of the melt with a change in its structure, in other words, to carry out modification or microalloying.

The effect of various additives on modification, can be traced back to publications in the case of hypereutectic chromium white cast irons [25–38] where it was described that inoculation could increase the rate of crystallization and solidification of the alloy, improve distribution and reduce

crystallization temperature interval. Thus, the crystallization time is shortened, and the dissolved substance can act properly on the melt [25]. It is known [26–31] that titanium and niobium additives in certain amounts separately can function as primary carbide nucleating agents, and can affect the morphology of M_7C_3 primary carbides in hypereutectic white cast iron, so that it becomes smoother. At the same time, it was explained that 2%, of rare-earth elements (REE) and Bi (Fe-Ti-REE-Bi) additives can increase impact toughness and wear resistance [30]. It should be noted that this modification has the best effect on low-carbon white cast iron. Rare earth elements act mainly as deoxidizing and desulfurizing additives when they are introduced into cast iron melts [30]. It was described in [35] that cerium additives (0.5 wt%) forming Ce_2S_3 can become heterogeneous centers of M_7C_3 carbides, which has a positive effect on impact strength and slightly increases hardness [35].

The joint effect of the addition of W, Mn, and Mo on the microstructure and properties of high-chromium hypereutectic white cast iron improves wear resistance and impact toughness by increasing the amount of carbide [32–34]. In [36–39], the addition of aluminum (0.3 wt%) also contributes to an increase in the dispersion of primary carbides. It was shown in [40] that the introduction of complex modifiers in the form of $(Ca, Sr)CO_3$, ferroboreon FB23 (FeB), silicocalcium SK-20 (Si-Ca) and boron-titanium-aluminum ligature BFT-1, together with thermal treatment (TT), can improve casting properties and increase heat resistance and shock-abrasive wear resistance of white cast iron. The resulting refining and reduction in the rate of shrinkage of castings in the initial period, according to the authors, helps to reduce internal stresses during the solidification and cooling of castings and, as a result, reduces the number of cold and hot cracks in them. The authors of this article believe that the mechanism of the influence of boron when it is introduced into the melt is that it is adsorbed on the surface of growing crystallites, hindering their growth, and thereby causing an increase in supercooling. This contributes to an increase in the dispersion of the structural components of the alloys under study.

In [41–43], it is shown that the following are inoculants: Ca, Ti, Zr, Ce; inhibitors: B, La, Ce, Y, Nd, Cd; invertors: Mg, Ca, Ti, Y, Zr, Ce, Ba. The possibility of influencing the shape of primary eutectic carbides by obtaining equiaxed crystals is shown.

Also promising is the impact of electric current pulses on the crystallizing melt [44], which leads to a change in the morphology of primary carbides in hypereutectic high-chromium white cast iron.

At the same time, it should be noted that no significant effect on the characteristics of such cast irons from the introduction of various additives has been identified. Basically, none of these studies have definitive proposals or specific recommendations for their application. Studies are presented that claim the benefits of modification. For example, the introduction of certain elements leads to an increase in impact strength and a decrease in the size of primary carbide crystals. Meanwhile, it is difficult to compare the results obtained in different works because the portion of the modifier additive introduced and the crystallization conditions are different between different authors and the melt cooling rate in the crystallization interval was not fixed. In addition, the temperature and melt holding time after addition of additives may have an effect due to the high activity of these elements with respect to oxygen. In this regard, further studies of the effect of these metal additives on the structure and properties of castings obtained under different cooling conditions are necessary to develop an effective method for modifying chromium cast iron. In particular, it is necessary to evaluate the effect of small additions of the most common rare earth elements on the structure and mechanical properties of castings from hypereutectic chromium white cast irons, which are obtained

under various cooling conditions, and to expand the understanding of the mechanism of action of these elements on the crystallization process.

The aim of this research was to study the distribution of rare earth elements using the of Sm, Nd, La, Ce and Y in hypereutectic white chromium cast iron grade G-X300CrMo27-1 with an increased carbon content to clarify their effect on the structure and mechanical properties of cast irons during crystallization at different rates of cooling.

2. Materials and methods

Three series of experiments were carried out. Rare earth elements were added to the cast iron melt in an amount of 0.2 wt%. In the first series, a modifying additive of a rare earth element in an amount of 0.2 wt% was introduced at a temperature 5–10 degrees above the liquidus line. In the second series, the addition of a rare earth element in an amount of 0.2 wt% was introduced at a temperature 50–60 degrees above the liquidus line. Such conditions for the introduction of micro additives were necessary to assess the influence of the overheating degree on the effect of modification since it is known that under such conditions the introduction of modifiers into alloys can significantly affect the effect of modification [40,43]. The cooling rate in the crystallization interval was 0.083–0.1 deg/s. Such cooling rates maximally reproduce the crystallization conditions when large-sized thick-walled castings are produced under production conditions without the use of cooling in sand-mix foundry mold designs. In the third series of experiments, a 0.2 wt% REE additive was introduced at 30–60 °C above the liquidus line and the alloy was cooled in the crystallization interval at a rate of 4.67–5 deg/s. This cooling rate reproduces the crystallization conditions of thin-walled castings.

Tests were carried out with the pre-melting hypereutectic alloy G-X300CrMo27-1 containing 4.1–4.2 wt% carbon in the first and second series of experiments (Table 1). The alloy was preformed and cast at high speed to minimize chemical composition variations caused by the poor solubility of ferrochromium and other alloying elements. The homogeneous ingot thus obtained, after checking the chemical composition, was cut into pieces and these parts were used for subsequent experiments to study the effect of modifying additives on slowly crystallized ingots. The preliminary alloy is melted in a vacuum induction furnace at 1450–1500 °C and cast into a 30 mm steel mold. The following load materials are used: Grade C steel, ferrochrome FeCr60C70LSLP, ferromanganese FMn78(A), graphite powder, Mo and Ni chips. The charge is placed on the bottom of the inductor which is coated with Insetag-86XT. Melting was performed in a vacuum ($1-4 \times 10^{-2}$ mm.Hg.) to complete melting of the charge components and further holding the melt for 30 min at 1450–1500 °C. The melt was poured into a split steel mold with a 30 mm cylindrical opening. Casting composition was determined by Axios X-ray fluorescent wave dispersive combination spectrometer and sulfur and carbon content was determined by Bruker G4 ICARUS TF analyzer. The alloy crystallization interval was determined with a NETZSCH STA 449 F3 Jupiter synchronous thermal analyzer (Table 1). The obtained ingots are divided into equal parts.

Further modification experiments were performed in the Nabertherm RHTV 120-600/C40 high temperature tube furnace. The alloy (190–200 g) is melted in corundum crucibles with 30 mm, as a result, cylindrical ingots with a length of $\varnothing 35$ mm were obtained. Heating was carried out at a rate of 0, 16 deg/s to 1500 °C with constant purging of the furnace with argon, then the temperature was maintained at 1500 °C for 60 min to dissolve carbide. The melt was cooled to the modifier introduction temperature (Table 1) and kept for 30 min. A weight of the modifier (in the amount of 0.2 wt%) attached to the end of the wire of the AISI 304 alloy was introduced under the melt mirror and stirred the alloy with the wire. Then, the furnace was switched off in 5 min if 0.2 wt% REE was introduced which provided a cooling rate of 0.083–0.1 deg/s. The furnace chamber was purged with argon in the cooling process up to 600 °C. A white cast iron ingot was obtained without modification under identical conditions in order to compare the structure and properties. The obtained samples were cut along the vertical axis, and sheets were prepared for studies of the structure, hardness, microhardness, and microprobe analysis. Plates were cut from the second half of the castings for abrasion testing. The temperature was monitored using a Type B thermocouple located in close proximity to the specimen. The experiments were repeated at least twice.

Tests were performed with the hypereutectic alloy G-X300CrMo27-1 containing 3.75–3.9 wt% carbon in the third series of experiments (Table 1). The alloy was melted in a vacuum induction furnace. After the melt was held at 1450–1480 °C to dissolve the components of the charge, a modifying additive in an amount of 0.2 wt% was introduced under the surface of the melt by a manipulator. The melt was poured into a graphite mold in two minutes, and an ingot 24 mm and 300 mm long was obtained. Cooling rate in the range of 4.67–5 deg/s was provided in this case. The ingot was tested for three-point bending. Microstructure research was performed 15 mm from the bottom of the ingot on cross sections. Samples for abrasion tests were cut at a distance 15 to 50 mm from the bottom of the ingot. The experiments were repeated at least twice.

Table 1. The composition of chromium cast iron samples and their crystallization range.

	Chemical composition, wt%										Interval of crystallization, °C	Cooling rate, deg/min	REE introduction temperature, °C
	Fe	Cr	C	Mo	Ni	Mn	Si	P	S	Ti			
G-X300CrMo27-1	rest	23–28	3–3.5	1–2	≤1.2	0.5–1.5	0.2–1	≤0.1	≤0.06	-	-	-	-
1 series of experiments	rest	23	4.1–4.2	0.5–1	0.2–0.3	0.7–0.8	0.8	0.02	0.04	0.13	1203–1432	5–6 for 0.2% REE	1440
2 series of experiments	rest	23	4.1–4.2	0.5–1	0.2–0.3	0.7–0.8	0.8	0.02	0.04	0.13	1203–1432	5–6 for 0.2% REE	1480–1490
3 series of experiments	rest	24	3.75–3.9	0.5–1	0.2–0.3	0.7–0.8	0.8	0.02	0.04	0.13	1203–1415	280–300	1445–1475

Sm, Nd and La were introduced into the melt as pure elements (96–98 wt% of the main component). Y was introduced as an alloy of 6%Y, 13%Cr, and the rest iron. Ce was introduced in the form of ferroalloy Mc50F6 (Ce-62%; La-30.8%; Nd-0.1%; Fe-0.6%; Pr-0.3%; Mg-0.8%). The calculation of the required sample weight was based on the content of Ce and Y in the case of ferroalloys.

The study of the distribution of modifying additives was performed for the samples without prior etching of the structure on a Jeol JXA-8230 microprobe analyzer. For metallographic analysis, the structure of the alloys was found using the reagent 100 mL HCl + 7 mL H₂SO₄ + 30 g CuSO₄, by rubbing with a cotton swab, and was studied with a Leica DM IRM optical inverted microscope. The average area and size of primary carbides were counted using Image J software. The structure analysis was performed in the bottom, middle, and top of the ingot for samples of experiment series 1 and 2. Vickers scale hardness measurements were performed with a HBV-30A hardness tester. Microhardness of separate phases was measured using PMT-3 device at a load on an indenter of 50 g. Three-point bending tests of iron ingots were performed with a Shimadzu AGx 100 kN electromechanical testing machine. The scheme is shown in Figure 1.

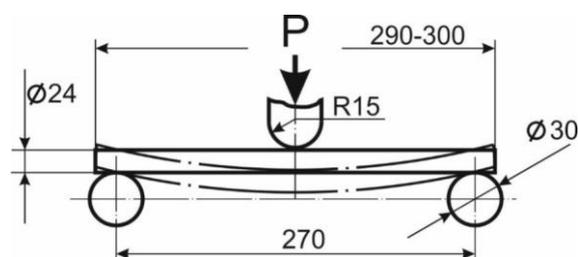


Figure 1. Scheme of the bend test setup.

Wear resistance was determined according to the scheme shown in Figure 2 according to GOST 23.208-79, which is a close analog of the test according to ASTM G65. Garnet sand was used in the tests, its particle size and shape are shown in Figure 3.

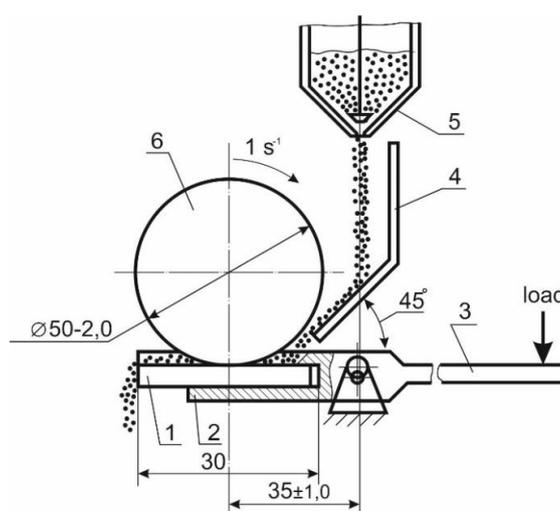


Figure 2. Scheme of the wear test facility: 1—sample; 2—sample holder; 3—lever; 4—groove; 5—dosing device; 6—rubber roller.

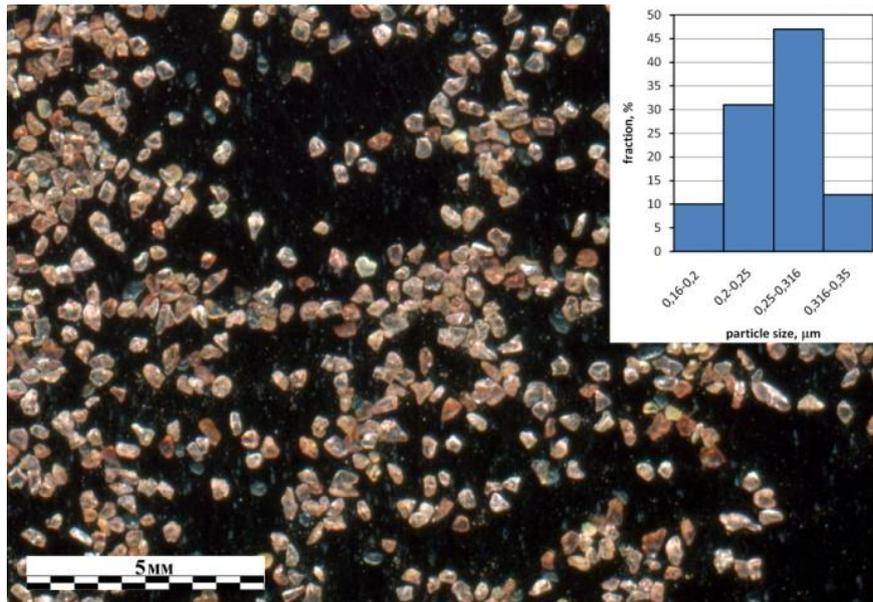


Figure 3. Image with histogram of garnet sand.

An annealed 2C45 steel plate with a hardness of 196 HV was used as a reference specimen in the wear tests. A sample $30 \times 50 \times 5$ mm in size was placed in a holder and its surface was pressed to the roller with a force of 44.1 ± 0.25 N with a lever. After that, the sand supply was started and the rotation of the rubber disk was turned on. The wear was carried out at an ambient temperature of 22–25 °C, with a rubber roller rotation frequency of 1 s^{-1} , and the number of revolutions was 1800. Accordingly, the wear path was 282.6 m, and the test duration was 1800 s, after which the tests were automatically interrupted. After testing, the wear area was examined at a magnification of up to 5 times. In the case of detection of pores and cracks in the place of wear, the sample was rejected. The samples that passed the control were weighed before and after testing on an analytical balance with an accuracy of four decimal places. Wear tests were carried out at least 3 times. Based on the results of weighing the samples before and after the tests, the arithmetic mean of the weight loss of the reference sample and the arithmetic mean of the weight loss of the test material samples were determined. The relative wear resistance of the material under study was calculated by Eq 1.

$$K_t = \frac{\bar{g}_r * \rho_t * N_t}{\bar{g}_t * \rho_r * N_r} \quad (1)$$

where \bar{g}_r —arithmetic mean value of mass loss of reference samples;

\bar{g}_t —arithmetic mean value of weight loss of the studied samples;

ρ_r, ρ_t —density of the reference and test materials, g/cm^3 ;

N_r, N_t —the number of revolutions of the roller when testing the reference and test materials.

3. Results

3.1. Microprobe analysis of the phase composition of white chromium cast iron castings

The results of microprobe analysis indicate that the distribution of rare earth elements in the phases of white chromium cast iron differs for each element. So, at a low crystallization rate (series of experiments 1 and 2), Sm forms solid solutions with primary and eutectic $(\text{FeCr})_7\text{C}_3$ carbides and is insoluble in austenite solid solution FeCrC (Figure 4). La and Ce form solid solutions with austenite and are insoluble in primary and eutectic carbides (Figure 5). Nd and Y did not form solid solutions with the white cast iron phase and stood out as high concentration inclusions (Figures 6 and 7). At the same time, all the listed REEs form compounds with phosphorus and oxygen with other alloying elements. Sm forms compounds with the highest concentration of P reaching 14 wt% and also binds a small amount of oxygen. Ce, La and Nd compounds with phosphorus contain molybdenum, oxygen and carbon. Yttrium, combined with iron and chromium, incorporates a small amount of phosphorus (2.78 wt%). This distribution mechanism of these REEs was identical for the first and second series of experiments.

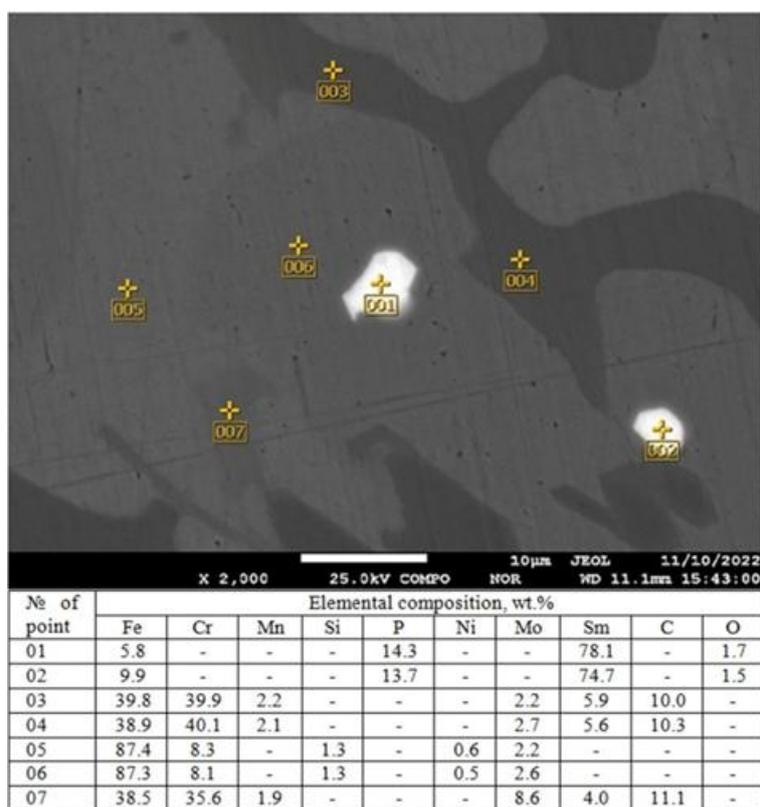


Figure 4. Distribution of samarium in white cast iron phases crystallized at a cooling rate of 0.083–0.1 deg/s.

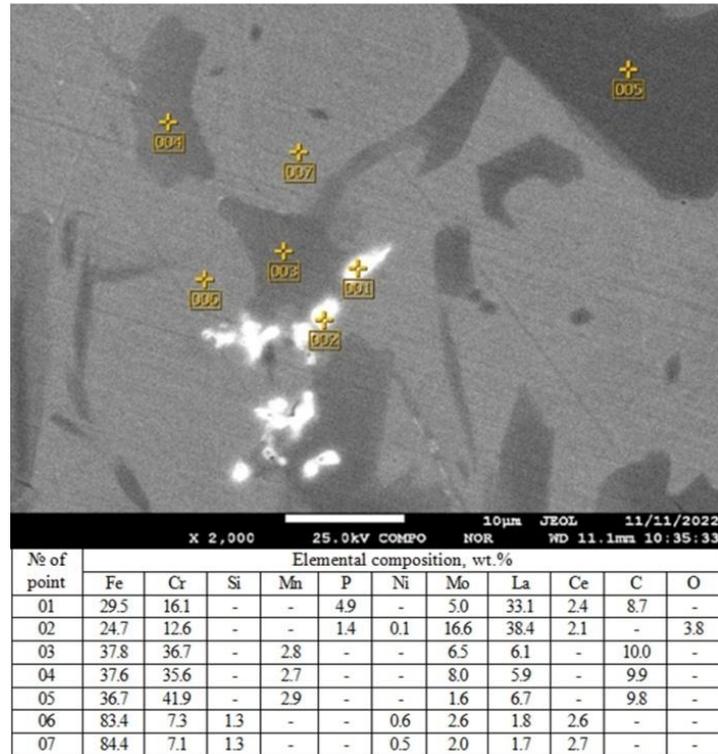


Figure 5. Distribution of lanthanum and cerium in iron phases crystallized at a cooling rate of 0.083–0.1 deg/s.

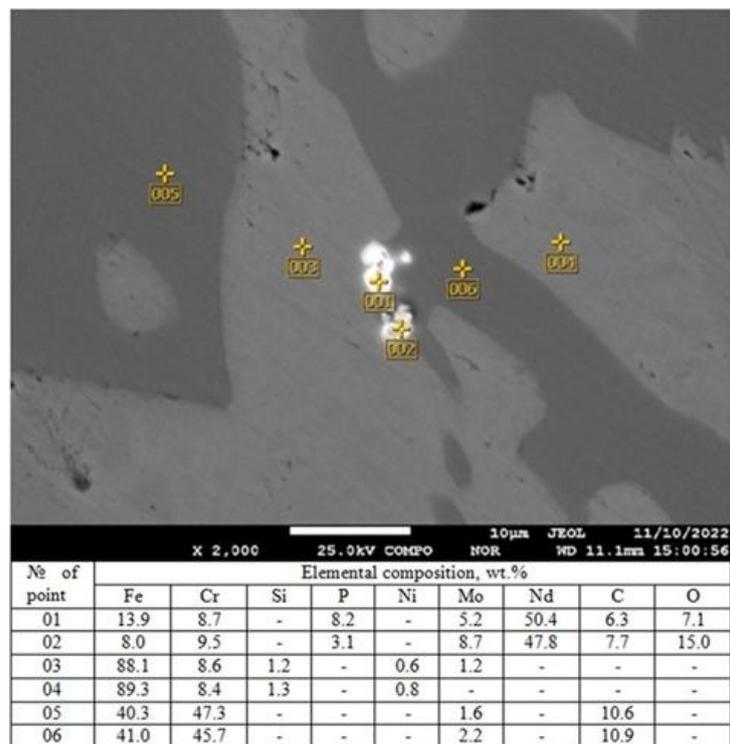


Figure 6. Distribution of neodymium in the iron phases crystallized at a cooling rate of 0.083–0.1 deg/s.

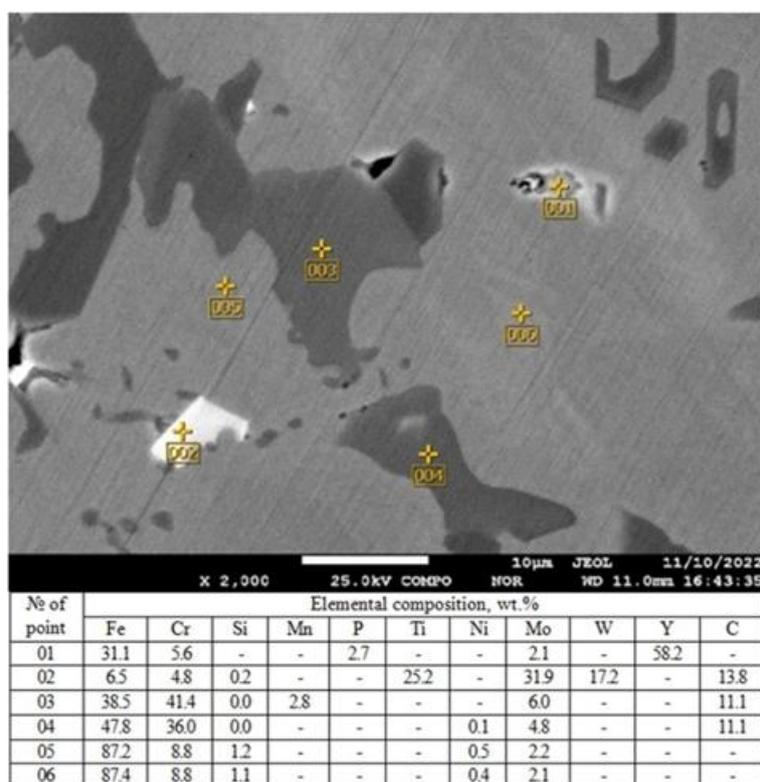


Figure 7. Distribution of yttrium in white cast iron phases crystallized at a cooling rate of 0.083–0.1 deg/s.

The REEs distribution did not change significantly during the formation phase of the white cast iron structure under crystallization conditions with a high cooling rate (the third series of experiments). Sm is dissolved in eutectic and primary $(\text{FeCr})_7\text{C}_3$ carbides and is insoluble in austenite and at a lower crystallization level (Figure 8). However, Sm compounds with P and O contain more C and Fe. In this case, the compound is isolated either in the form of equiaxed crystals or in the form of thin films that format the austenite grains boundaries. Under such crystallization conditions, Ce and La dissolve to eutectic $(\text{FeCr})_7\text{C}_3$ carbides in small quantities in addition to forming a solid solution with the austenite (Figure 9). La and Ce compounds with P were isolated as dispersed and hypereutectics inclusions. Nd, as well as at a low degree of crystallization, is insoluble in the ferrous phase and is released only in the form of independent compounds containing Fe, Cr, P and C which are formed in the form of small inclusions of an equiaxed shape (Figure 10). Y is insoluble in austenite and $(\text{FeCr})_7\text{C}_3$ carbide and concentrates in the phase with a high Mo content and forms independent compounds with Fe and Cr (Figure 11). These compounds are concentrated locally at the boundary of eutectic carbides and austenite.

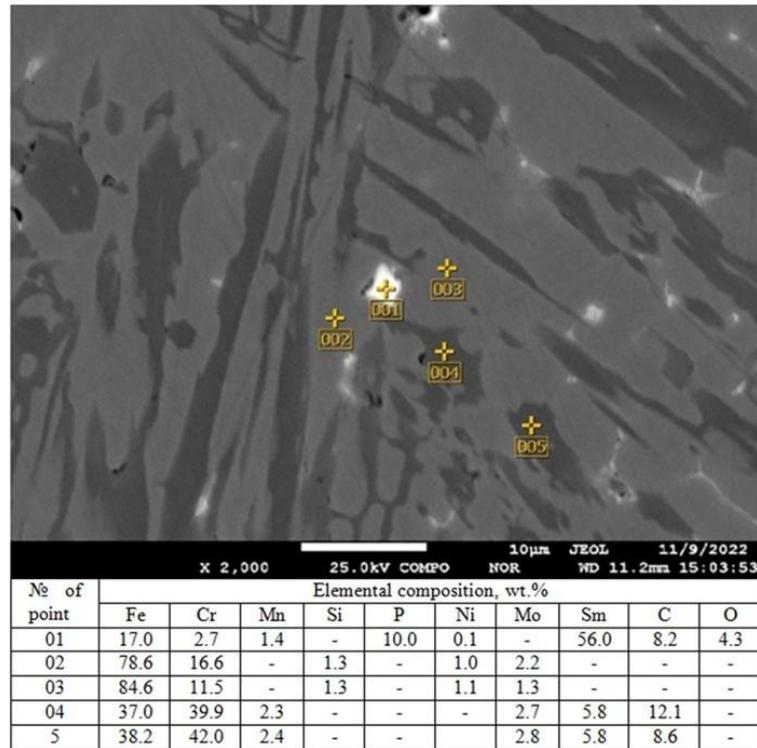


Figure 8. Distribution of samarium in the iron phases crystallized at a cooling rate of 4.67–5 deg/s.

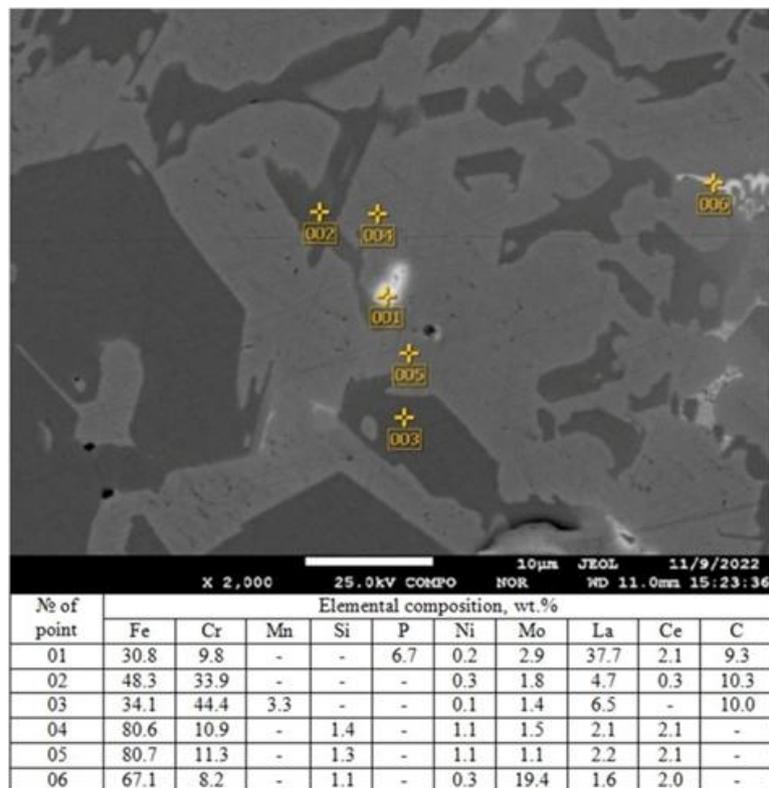


Figure 9. Distribution of lanthanum and cerium in white cast iron phases crystallized at a cooling rate of 4.67–5 deg/s.

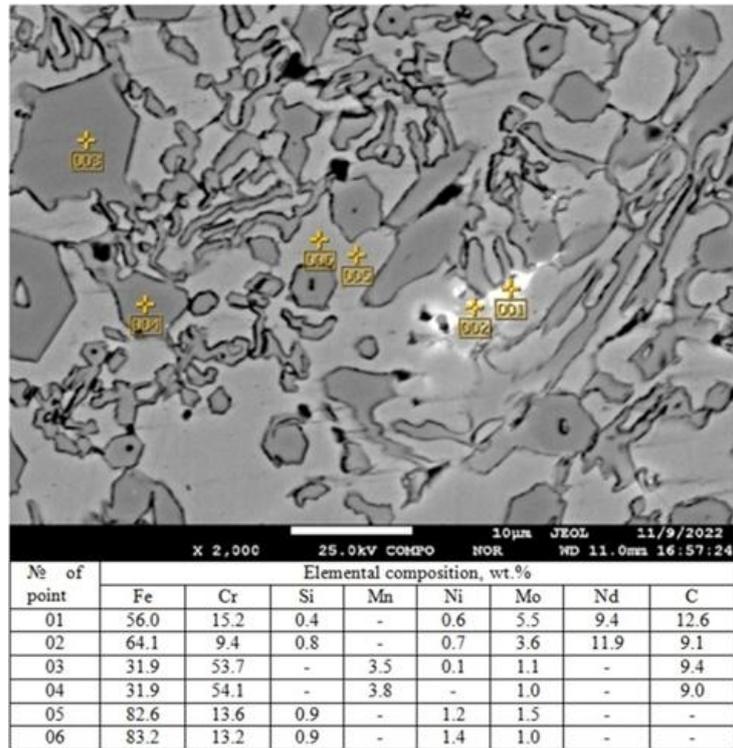


Figure 10. Distribution of neodymium in the iron phases crystallized at a cooling rate of 4.67–5 deg/s.

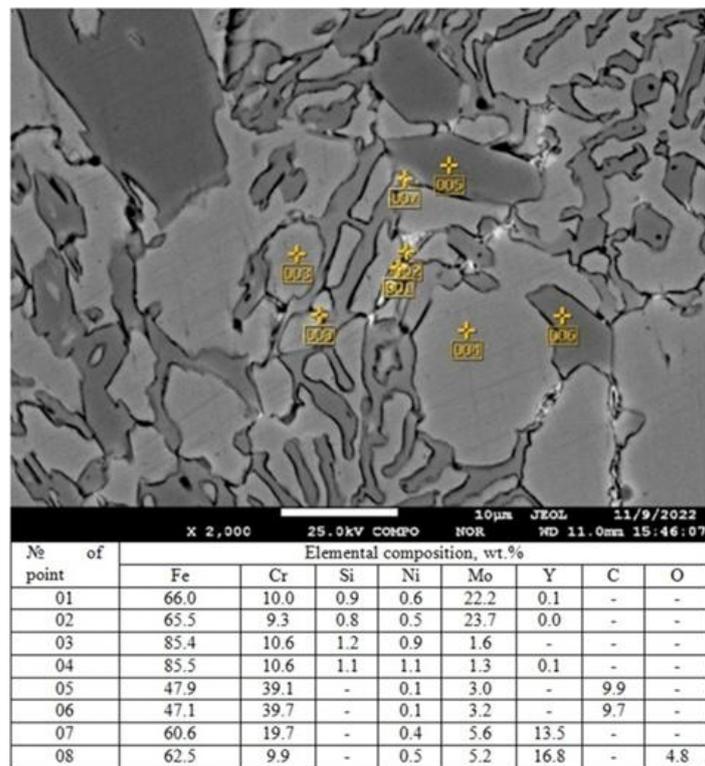


Figure 11. Distribution of yttrium in white cast iron phases crystallized at a cooling rate of 4.67–5 deg/s.

3.2. Analysis of the microstructure of white chromium cast iron castings

Comparison of the microstructure of the castings obtained at different crystallization rates showed that the REE additive had no significant effect on the crystal morphology of primary $(\text{FeCr})_7\text{C}_3$ carbide and eutectic. Primary crystalline carbide $(\text{FeCr})_7\text{C}_3$ is needle-shaped in reference samples and white cast irons with REE additives, some needles having elongated cavities of variable cross-section. This cavity is filled with eutectic alloy. During slow crystallization, several primary carbides are isolated in the form of needles having a dendritic structure in cross-section. The eutectic has skeleton carbide structure. The alloy matrix consists of austenite at high cooling rates. Austenite decomposes to pearlite and martensite fringes and form at the boundary with $(\text{FeCr})_7\text{C}_3$ carbide precipitates at low cooling rates.

Structural analysis showed that addition of 0.2 wt% REE to molten iron led to an increase in the size of primary carbides in castings obtained at low cooling rates (Figures 12 and 13). Additives such as La, MC50F6 (Ce+La) and Nd at 5–60 °C above the liquidus line increase the size of primary $(\text{FeCr})_7\text{C}_3$ carbides significantly (20–80%). The effect increases with decreasing crystallization rate. At the same time, the addition of 0.05 wt% Sm and Y did not significantly reduce the crystal size. When the REE additive is added close to the liquidus line (5–10 degrees higher), the most significant increase in primary crystal size (more than 100%) is due to Nd. In addition, the sizes of primary carbides in the castings received by the addition of Sm, MC50F6 (Ce+La) and Y increased by 40–50%.

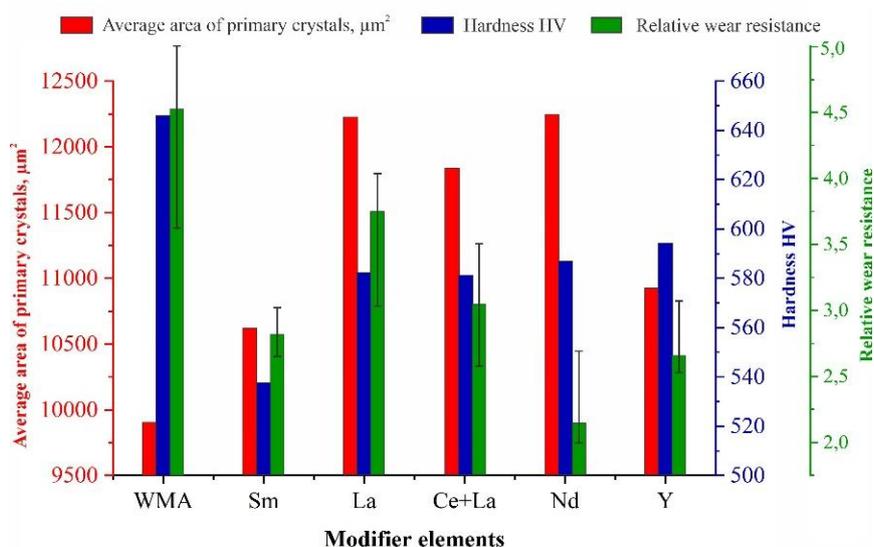


Figure 12. Effect of 0.2 wt% REE additions on primary crystal size and mechanical properties of white cast iron castings (series of experiments 2).

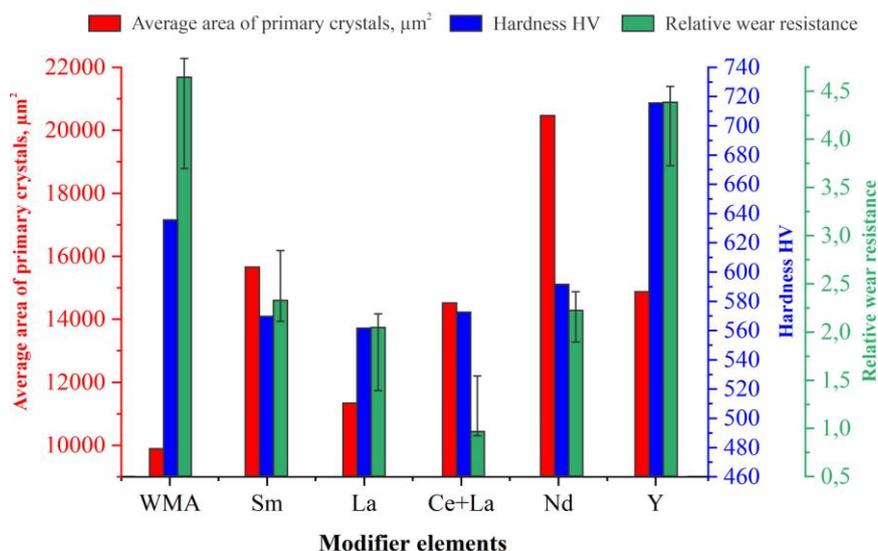


Figure 13. Effect of 0.2 wt% REE additions on primary crystal size and mechanical properties of white cast iron castings (series of experiments 1).

The degree of effect of REE additives on primary $(\text{FeCr})_7\text{C}_3$ carbides size in white cast iron changes under crystallization conditions at a high cooling rate. Thus, the crystal size was reduced by 70% in white cast iron samples with the addition of Nd, and reduced by 45% with the addition of MC50F6 (Ce+La) (Figure 14). The additions of Sm, La and Y under these crystallization conditions increased the primary crystal size by 100, 33 and 43%, respectively.

3.3. The results of changing the mechanical properties of castings from white chromium cast irons

The castings obtained under conditions of low crystallization rate (0.083–0.1 deg/s), after the introduction of REE additives were characterized by lower hardness than the reference samples (Figures 12 and 13). Castings with Y additions are an exception. The hardness is close to and in some cases exceeds the hardness of the reference sample. The smallest decrease in hardness is caused by the addition of Nd. Increasing the cooling rate of the alloy up to 4.67–5 deg/s. results in a change in the effect of REE additive on the hardness of the castings. The hardness of the castings with the addition of Sm, La, MC50F6 (Ce+La), Nd and Y exceeded the hardness of the reference sample by 6.4, 4.5, 9.7, 5.6 and 3.1%, respectively. The REE additive reduced the strength of white cast iron in the bending test (Figure 14). The strength is most significantly reduced by the addition of Nd.

Testing of castings obtained at low cooling rates showed that they had 5–8 times lower relative wear resistance in comparison with castings obtained at cooling rates of 4.67–5 deg/s. (Figures 12 and 14). The addition of 0.2 wt% Sm, La and MC50F6 (Ce+La) to the white cast irons at all cooling rates caused a decrease in relative wear resistance. Nd reduces the relative wear resistance in the castings obtained at low crystallization rates and does not significantly increase it after cooling the castings at high rates. The Y additive most significantly increases the relative wear resistance of white cast iron, both at low and high cooling rates.

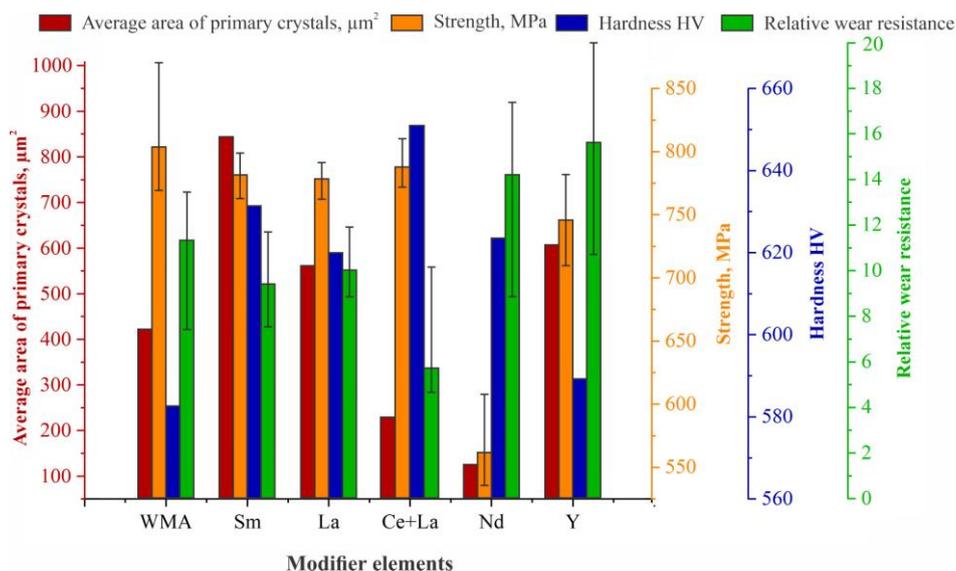


Figure 14. Impact of 0.2 wt% REE additives on the primary carbides size and mechanical properties of iron castings (series of experiments 3).

The introduction of REE additives increases the microhardness of all phases included in iron castings (Figure 15) obtained at a cooling rate of 0.083–0.1 deg/s. Change of hardness of primary and eutectic $(\text{FeCr})_7\text{C}_3$ carbides is not significant and is 6–12%. Addition of La reduced the hardness of eutectic $(\text{FeCr})_7\text{C}_3$ carbides by 8%. Microhardness of austenite and martensite in castings after the introduction of REE increased by 18–72%. It was most significantly affected by the introduction of La and the least by Y. Microhardness of pearlite increased by 4–28%, the most essential effect had additions Sm and MC50F6 (Ce+La).

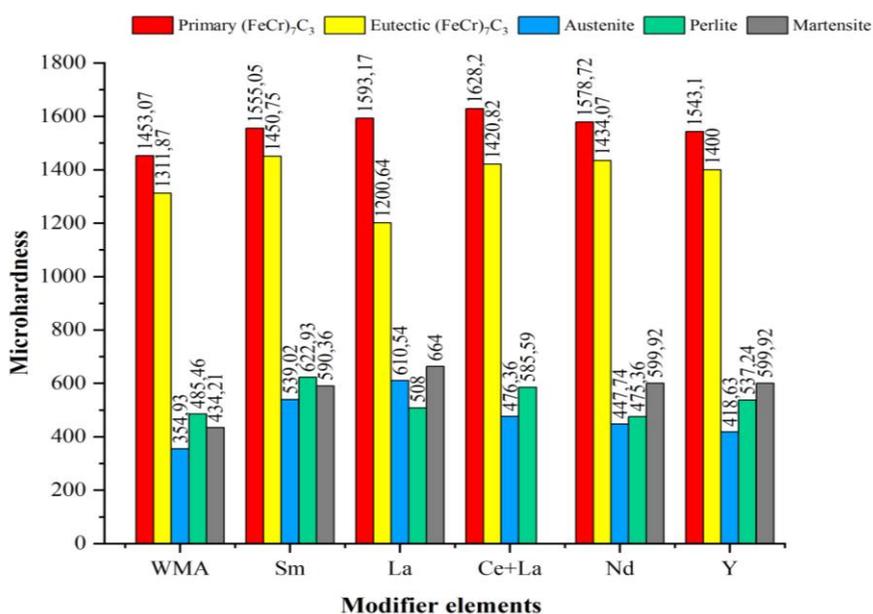


Figure 15. Effect of REE additives on the microhardness of phases in white cast iron castings obtained at a cooling rate of 0.083–1 deg/s.

4. Discussion

The established distribution of rare-earth metals in the structure of white cast irons demonstrates that no additional crystallization centers are formed during their introduction into the melt. Formed phosphides and oxyphosphides of REE in most cases considered are allocated in the form of large enough inclusions. They are located on the grain boundary and have no isomorphic connection with the primary and eutectic $(\text{FeCr})_7\text{C}_3$ carbides and austenite. The exception is Sm which forms both compact inclusions with phosphorus and thin extended precipitations formed in austenite. Accordingly, such compounds are not crystallization centers and cannot affect the size of $(\text{FeCr})_7\text{C}_3$ carbides.

Of the considered REE, only Sm forms solid solutions with primary and eutectic $(\text{FeCr})_7\text{C}_3$ carbides, at different rates of crystallization. Its concentration in these phases reaches 5.8 wt%. La and Ce form solid solutions with eutectic $(\text{FeCr})_7\text{C}_3$ carbides only in case of their formation under conditions of high crystallization rate. La concentration therein reaches 4.7 wt% and Ce-2.4 wt%. Only Ce and La dissolve in austenite in castings crystallized at various rates. Solubility of other elements in the iron phases is possible but their concentration is outside the measurement limits of the microprobe analyzer used in the studies. Accordingly, Sm, La, and Ce should have the greatest effect on the mechanical properties of the iron phases due to the formation of solid solutions with them. When La is added, it is confirmed by the highest hardness of austenite and martensite according to the results of measurements. However, the dissolution of Sm does not have the expected significant effect on the hardness of $(\text{FeCr})_7\text{C}_3$ carbides. Insignificant increase in the microhardness of all phases included in the white cast iron after the introduction of REE additives also shows their solubility in them.

The addition of 0.2 wt% REE in the melt of white cast iron G-X300CrMo27-1 causes a significant increase in the size of primary $(\text{FeCr})_7\text{C}_3$ carbides in the castings obtained at low and high crystallization rates. This mechanism can be explained by a decrease in the number of crystallization centers in iron melts that contain REE. It is confirmed by the fact that the essential increase effect in the size of $(\text{FeCr})_7\text{C}_3$ carbides is observed even at introduction of 0.05 wt% of some REE. This effect does not always depend on crystallization rate and is not connected with solubility of REE in primary carbides. It is known that oxides of aluminum and silicon are present in melts of chromium white cast irons and are in a suspended state in the form of very dispersed films and particles in them [36]. Such oxides are not reduced by carbon dissolved in the melt. They can be centers of crystallization of primary carbides. It is also known that REE are effective deoxidizers and they are used for deoxidation of steels [37]. In this regard, the most likely explanation for the decrease in crystallization centers is the reduction of refractory oxides suspended in the volume of iron melts due to the formation of oxyphosphides REE. It led to the fact that the first carbides nucleated below the liquidus line grew, and new carbide precipitates formed in insignificant numbers.

To assess the possibility of reduction of oxides SiO_2 , Al_2O_3 and Cr_2O_3 in contact with Ce, La and Y, thermodynamic calculations were carried out and the possibility of Eqs 2–10 was estimated. For this, the software package HSC Chemistry 8 (ver. 8.1.4) was used. Gibbs energy calculations were carried out for the temperature range 1000–1500 °C (Figure 16). As follows from the data obtained, the occurrence of reactions 3–10 is thermodynamically possible. Consequently, REE additions to melts of chromium wear-resistant white cast irons can lead to a reduction in oxide

particles in the melt volume and, consequently, to a reduction in the centers of crystallization of primary carbides.



The increase in the microhardness of the phases entering the white cast iron after the introduction of REE should have increased its hardness and abrasion resistance. However, the effect turned out to be the opposite. Castings with the addition of REE (with the exception of Y), obtained at a low cooling rate, have lower hardness and significantly lower abrasion resistance than the comparison samples. It can be explained by the fact that, due to dissolution of even insignificant amounts of REE in carbides internal stresses arise in them, facilitating their destruction under the effect of high loads. It is confirmed by the fact that 50 g microcracks appeared in primary $(\text{FeCr})_7\text{C}_3$ carbides at measurement of microhardness at a load on the diamond indenter. The study of the surface structure of samples after abrasive wear tests showed that the primary $(\text{FeCr})_7\text{C}_3$ carbides are the main phase that breaks under the action of abrasive particles (Figure 17).

The increase in the hardness of castings with REE, during their crystallization at a speed of 4.67–5 deg/s. is explained by the formation of supersaturated solid solutions of REE in carbides and austenite, and in the case of white cast irons with MC50F6 (Ce+La) and Nd additives by the formation of more dispersed primary $(\text{FeCr})_7\text{C}_3$ carbides. The observed decrease in strength may be due to the occurrence of internal stresses and defects in the form of microcracks. Despite the increase in hardness, only castings with Nd and Y additions had a higher abrasion resistance, while the addition of Sm, MC50F6 (Ce+La), and especially La significantly reduced the wear resistance of white cast irons. It also shows that the higher solubility of these elements in austenite and carbides worsens their mechanical properties.

In view of the fact that the main requirement for products made of chromium white irons is high wear resistance, this characteristic should be put in the first place when the effectiveness of modification of the structure and properties of irons is assessed [45–47]. The conducted studies on the example of white cast iron of the hypereutectic composition of G-X300CrMo27-1 grade with increased carbon content have shown that it is extremely important to achieve a decrease in the size of primary $(\text{FeCr})_7\text{C}_3$ carbides and not to impair their properties and the properties of other phases in order to increase the wear resistance.

In some literature sources [16,20,30,35,48], one can trace how the effect of REE on low-alloyed chromium white cast irons of hypoeutectic and eutectic compositions was evaluated. In these studies,

most authors believe that the mechanism of the influence of rare-earth metal additions on the crystallization process of such white cast irons is due to the fact that, during the formation of the austenite phase, REE is released at the crystallization front, which leads to supercooling and the formation of polycrystals, which prevents the growth of eutectic carbides M_3C and changes their morphology. In this case, the improvement of the properties of castings made of white cast iron with REE additives is justified.

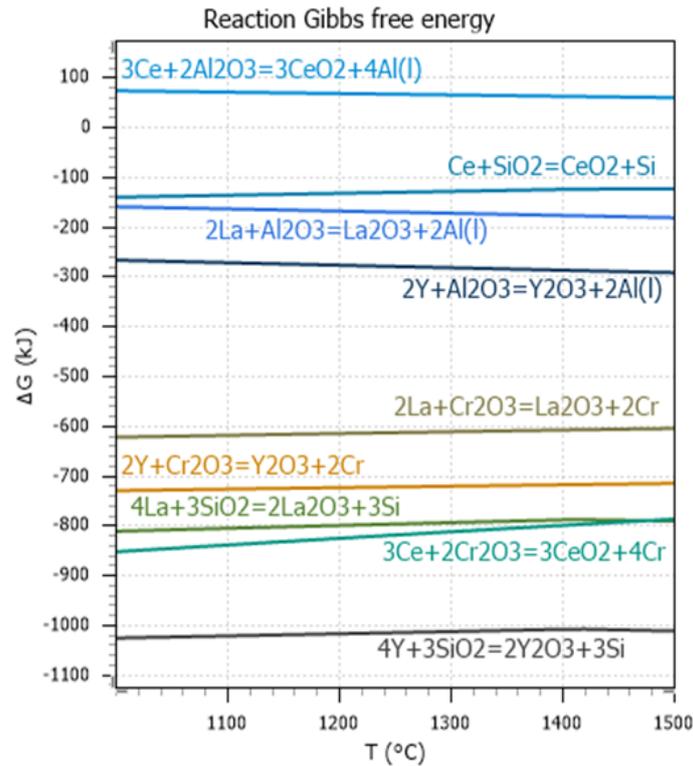


Figure 16. Change in the Gibbs energy of reactions 2–10.

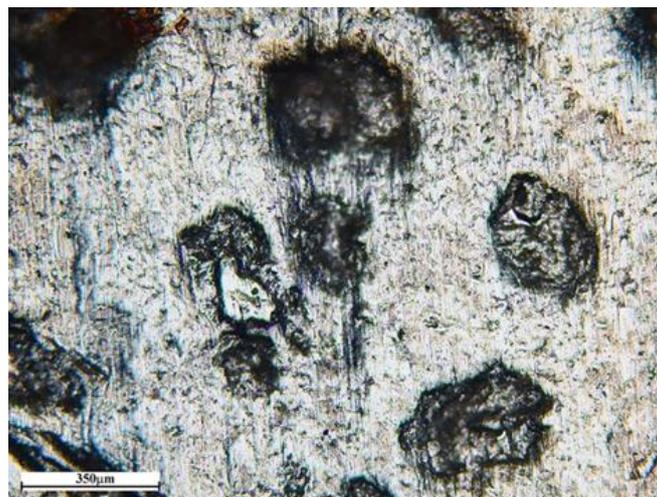


Figure 17. Destruction of primary $(\text{FeCr})_7\text{C}_3$ carbides when exposed to abrasive particles on the surface of white cast iron with 0.2 wt% Sm additive.

At the same time, the influence of REE additives on the structure and properties of hypereutectic high-alloy chromium white cast irons has been studied very little. For example, Zhi et al. [48] believe that the addition of cerium to hypereutectic chromium iron causes the primary crystals to be refined from impurities, resulting in the formation of Ce_2S_3 , which is a heterogeneous substrate of M_7C_3 carbides. The authors of recently published works on the effect of Ce [49] and Y [50] additives on the mechanical properties of white chromium cast irons, based on thermodynamic analysis, concluded that $Fe_3Cr_3CeC_3$ and $Fe_3Cr_3YC_3$ carbides are formed. According to the authors of these articles, the mechanism of the effect of these additives on the properties of carbides lies in the redistribution of electrons and the formation of more stable chemical bonds in the carbide $(FeCr)_7C_3$ due to the Ce and Y atoms.

Thus, the actual mechanism of the effect of REE additives on the crystallization process of hypereutectic chromium white cast irons remains to be studied, for which it is extremely important to accumulate the results of experimental studies. Since REE are active elements, it can be assumed that, depending on the content of impurities in the melt, the conditions for melting white cast iron and the method of introducing such an additive, as well as the rate of crystallization, the effect on the structure and properties of castings will vary significantly.

5. Conclusions

This article presents for the first time the results of a study of the effect of Sm, Nd, La, Ce, and Y additives in an amount of 0.2 wt% on the structure and mechanical properties of ingots from hypereutectic white chromium white cast iron grade G-X300CrMo27-1 with an overestimated carbon content and provides data on REE distribution in its structure.

- (1) It has been experimentally established that the addition of rare earth elements Sm, Ce, La, Nd, and Y in an amount of 0.2% does not significantly affect the morphology of primary and eutectic $(FeCr)_7C_3$ carbides in high-chromium white cast iron grade G-X300CrMo27-1. At the same time, additives cause an increase in the size of primary crystals in castings obtained with a low cooling rate (0.083–1 deg/s) and a decrease in their hardness in comparison with castings without such additives. Additives Sm, La and MC50F6 (Ce+La) at low and high cooling rates reduce the resistance to abrasive wear. The exception is castings with Y addition, which are characterized by increased hardness and wear resistance, at both low and high cooling rates. Nd reduces wear resistance in castings produced at low crystallization rates and increases it slightly after cooling at a high rate. The microhardness of all phases that make up white cast iron castings increased with the introduction of rare earth elements in all series of the experiment.
- (2) A high cooling rate reduces the size of primary crystals in castings with Nd addition by 70%, and with MC50F6 (Ce+La) addition by 45%. However, Sm additions by 100%, La additions by 33%, and with Y additions by 43%, on the contrary, increase the size of primary crystals under such crystallization conditions. At an increased cooling rate of the alloy, the hardness of castings with additions of Sm, La, MC50F6 (Ce+La), Nd, and Y is higher than the hardness of the reference sample by 6.4, 4.5, 9.7, 5.6, and 3.1%. However, these additives reduced the strength of white cast iron in bending tests. The addition of Nd reduced the strength most significantly.
- (3) It is shown that, at the indicated cooling rates, Sm, La, and Ce additives form solid solutions with primary and eutectic $(FeCr)_7C_3$ carbides. Additives La and Ce form solid solutions with

austenite. Nd and Y do not dissolve in the chromium iron phases; they precipitate as inclusions at a high concentration.

- (4) It was revealed that the listed rare earth elements form compounds with phosphorus and oxygen, which include other alloying elements. It is likely that the introduction of these additives led to the reduction of refractory oxides suspended in the volume of white cast iron melts and the formation of oxyphosphides, which is confirmed by the results of thermodynamic calculations. This allowed crystals nucleated below the liquidus line to grow, while new crystals were formed in small quantities, which accordingly led to a decrease in crystallization centers.

Thus, the introduction of separately small Sm, Ce, La and Nd additives in the melt of hypereutectic chromium white cast irons during their melting is not an effective method to modify the structure of their castings and negatively affects their characteristics and, especially, the abrasion resistance. A non-significant positive effect on the wear resistance of castings made of such castings has Y additives, while they reduce the strength of the alloy. The effect of REE on the structure of castings decreases with an increase in the introduction temperature of additives from 5–10 to 50–60 °C above the liquidus line. Increase of the cooling rate in the crystallization interval of melts of chromium white cast irons significantly increases the abrasion resistance of their castings.

Use of AI tools declaration

The authors declare they have not used Artificial Intelligence (AI) tools in the creation of this article.

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Conflicts of interest

The authors declare that there is no conflict of interest regarding the publication of this manuscript.

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