

CAST IRONS

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CAST FUNCTIONALLY GRADED MATERIALS BASED ON CHROMIUM WHITE IRONS FOR FABRICATING GRINDING BODIES

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The possibility of the use of directed crystallization for obtaining a graded structure in grinding balls from chromium white irons is assessed. The chemical composition of the iron is determined. The structure and the microhardness of the balls are studied after a heat treatment. Tests of the grinding balls are performed. Directed crystallization in metallic molds is used to provide a graded structure from the surface to the center of the balls. Preliminary modification with manganese also affects the formation of the structure. The structure of the surface layer in the radial direction is represented by austenitic dendrites and a quasi-eutectic based on $(\text{Cr, Fe})_7\text{C}_3$ carbides and meets the principle of composite hardening making the balls highly abrasion-resistant. The core of the grinding balls consists of a dispersed spherulitic eutectic and base leading carbides of type M_7C_3 , which raises the resistance of the balls to impact loads during service.

Key words: grinding bodies, ball, functionally graded materials, microstructure, white cast iron, eutectic, carbides, hardness.

INTRODUCTION

Important requirements for grinding bodies are high wear resistance and impact strength [1, 2]. These operating properties are largely determined by the hardness. However, a high hardness does not always provide a high endurance and preservation of appropriate operating conditions during the service life of grinding bodies. Hard grinding bodies experiencing impact loads during operation break, or their surface undergoes gradual spalling intensifying the abrasive wear.

The wear resistance can be raised by creating a specific metallic matrix in the surface layer, which meets the Charpy principle (rule) [3]. This principle, which has been applied initially to antifriction alloys, consists in creating a structure represented by isolated hard inclusions fixed in a ductile ma-

trix in a material that undergoes friction in service [4]. The wear-resistant alloys operating under conditions of abrasive wear should obey a principle of composite hardening (a variant of the Charpy rule) [5, 6]. Like the Charpy rule, the principle of composite hardening stipulates the presence of ductile and hard structural components in the material. In this case, the wear resistance is intensified by the bulk reinforcement provided by eutectic colonies. Alloyed cast irons containing austenite-carbide eutectics of type A – MC (VC and TiC in particular) or A – M_7C_3 ($(\text{Cr, Fe})_7\text{C}_3$) meet this principle better than other materials. White cast irons with Fe_3C – A ledeburite do not obey the rule in question because their matrix is represented by cementite, and the isolate fine inclusions are represented by austenite. Therefore, in contrast to ledeburite, an important condition for the eutectics meeting the principle of composite hardening is an inverse location of the structural components, i.e., their matrix should consist of ductile austenite and the reinforcing phase should be represented by carbides of types MC and M_7C_3 . The eutectic formed in this case is termed an inverted-type one. Under the conditions of intense heat removal typical for casting into metallic molds and directed crystallization by

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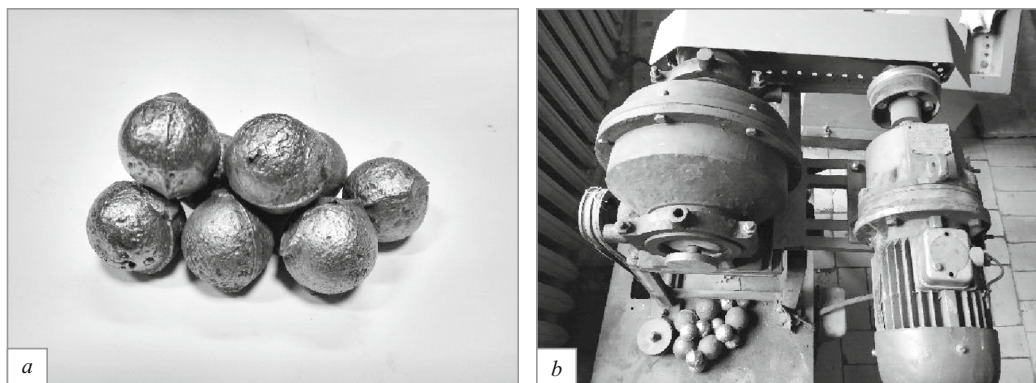


Fig. 1. Grinding balls with diameter 30 mm (a) and laboratory ball crusher for their testing (b).

the in situ method, the cast iron is a composite based on eutectic colonies [7].

To provide a high abrasive wear resistance of grinding balls, they are often produced from chromium white cast irons [8, 9]. In accordance with the performance specifications, the carbide phase in the grinding bodies should be distributed uniformly in the matrix and have of a maximum content of $(\text{Cr, Fe})_7\text{C}_3$ carbides³ with preferred orientation of crystallographic axis c perpendicular to the worn surface [10]. The metallic matrix should meet the following requirements: confine the carbides with a maximum strength, provide minimum deformations, and contain relatively thin layers of austenite between the Cr_7C_3 carbides to minimize the selective wear of the matrix with the abrasive. It is assumed that the optimum structure for the matrix is a martensitic one with retained metastable austenite susceptible to strain hardening to meet the Bogachev–Mints principle [11].

Creation of a bilayer structure with a hard surface and a ductile middle, which plays the role of a consolidating center and absorbs the impact energy, provides effective impact resistance in service of grinding bodies [12]. These properties, which vary over the thickness of the ball, are possessed by functionally graded materials a distinguishing feature of which is gradual variation of the structure from layer to layer [13]. The concept of creation of such materials can be implemented by various methods from advanced additive technologies [14–18] to traditional casting processes [19, 20]. Specifically, this approach is used in the production of forming rolls from indefinite cast irons, in which the functional layer is formed from a white cast iron and the core consists of a graphitized cast iron [21, 22].

Consumers may face the problem of a low operational stability of grinding bodies, which is determined by relatively low parameters of the wear and impact resistances. These properties can be raised by developing a method for controlling the processes of structure formation.

The aim of the present work was to create a method for manufacturing grinding balls with a graded structure from cast condition by directed crystallization and subsequent heat treatment providing an optimum combination of operating properties, i.e., a high abrasive wear resistance on the surface due to formation of a structure meeting the principle of composite hardening and a strong and tough matrix capable to resist impact loads during service in ball crushers.

METHODS OF STUDY

We melted the iron in an IChT-0.06 induction furnace with acid lining. The blend materials were pig iron P-2 and scrap steel St3. The alloying agent was ferrochrome FKh001A preliminarily crushed and loaded to the bottom of the furnace before the melting. The out-of-furnace treatment was performed by the autoclave method by introducing magnesium into the ladle with capacity 25 kg. The chemical composition of the alloys was controlled using a SPECTROMAXx spectrometer. The average chemical composition calculated from the results of three measurements is presented in Table 1. An experimental batch of grinding balls with diameter 30 mm was obtained by chill casting (Fig. 1a). We determined the content of the chemical elements in the surface zone and in the core of the balls.

The heat treatment of the balls consisted of quenching from $980 \pm 10^\circ\text{C}$ with air cooling and tempering at $230 - 250^\circ\text{C}$.

The metallographic studies of the grinding balls were made using a computer-aided unit created on the base of a Leica DM IRM inverted metallographic microscope. The specimens were etched in a 4% alcoholic solution of picric acid.

The microhardness of the individual carbide phases of the metallic matrix was determined using a Shimadzu HMV-2 microhardness tester. The hardness of the specimens was measured using a Nemesis-9003 universal hardness tester.

³ Analysis of the Fe–C–Cr phase diagram shows that the maximum content of $(\text{Cr, Fe})_7\text{C}_3$ -type carbides in eutectic cast irons is about 30–35% [10].

TABLE 1. Chemical Composition of the Cast Iron and Distribution of Elements over Ball Sections

Object of study	Content of elements, wt.%							
	C	Cr	Si	Mn	Ni	Mg	P	S
White cast iron	3.15	20.60	0.41	0.38	0.150	0.02	0.020	0.020
Ball surface	3.00	20.59	0.40	0.37	0.150	0.02	0.015	0.019
Ball center	3.24	20.68	0.42	0.40	0.145	0.02	0.023	0.021

Full scale tests of the grinding balls were performed in a laboratory ball crusher by grinding various ferroalloys (Fig. 1b).

RESULTS AND DISCUSSION

Table 1 presents the results of the assessment of the average (after three measurements) chemical composition of the cast iron in the center and on the surface of the balls. It can be seen that the carbon and phosphorus contents on the surface and in the center of the balls differ, which implies development of segregation processes during the solidification. For example, the carbon content on the surface is 3.0%, whereas in the center it is 3.26%.

Chromium cast irons obey a dependence [23], which makes it possible to determine the content of carbides K from the known concentrations of carbon (% C) and chromium (% Cr), i.e.,

$$K = 11.3 \times (\% C) + 0.5 \times (\% Cr) - 13.4. \quad (1)$$

It follows from formula (1) that the content of carbides depends substantially on the carbon content. Computations show that the content of carbides on the surface and in the center of the balls is 30.7 and 33.5%, respectively. Increase of the carbon concentration in the center of the ball is accompanied by growth of the content of $(Cr, Fe)_7C_3$ carbides, which will be shown to affect both the properties and the morphology of the structure.

A typical microstructure of cast iron at a distance of about 5 mm from the surface of a ball is presented in Fig. 2. It is represented by austenitic dendrites and an austenite-carbide eutectic, which matches a hypoeutectic pattern. The structure is fine and the dendrites have well-manifested anisotropy. By the data of the structure analysis (Fig. 2a), the first to crystallize from the melt are the austenitic dendrites. Since they do not undergo a retarding action of other phases during the crystallization, their structure is developed the most. Individual dendrites in the plane of the metallographic section have quite large linear sizes (go virtually through the

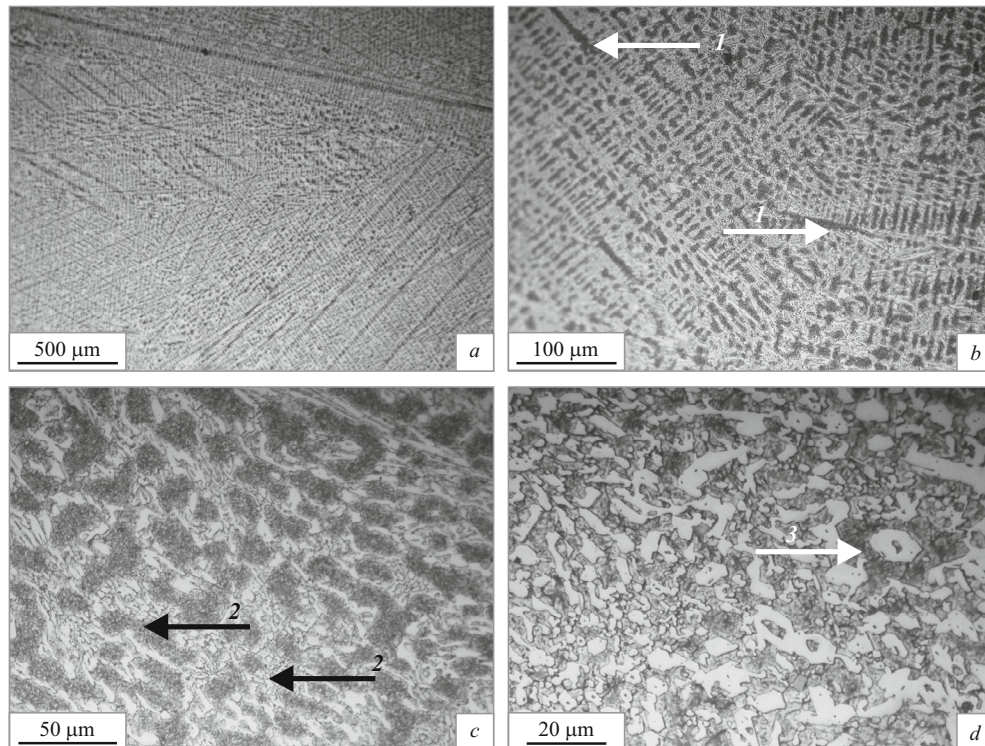


Fig. 2. Post-heat-treatment microstructure of cast iron at a distance of 5 mm from the surface of the ball: 1) iron dendrite; 2) $M_7C_3 - A$; 3) M_7C_3 ; a) $\times 50$; b) $\times 200$; c) $\times 500$; d) $\times 1000$.

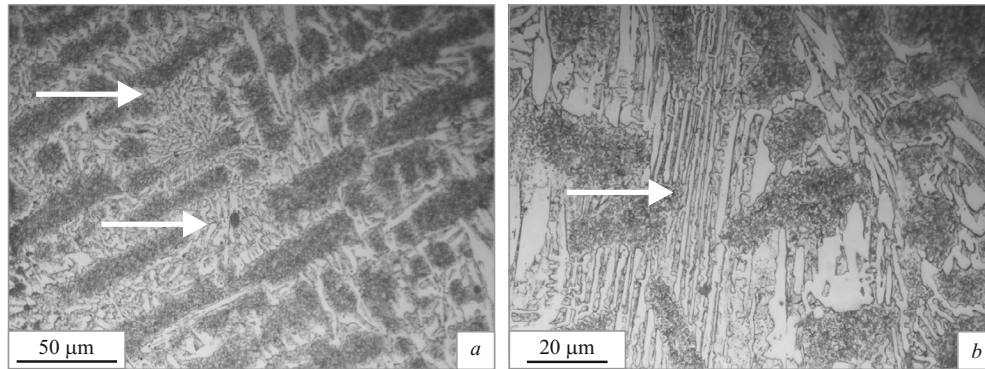


Fig. 3. Post-heat-treatment microstructure of a colony of A – M_7C_3 quasi-eutectic (marked with the arrows) in a ball: a) cross section, $\times 500$; b) longitudinal section, $\times 1000$.

whole of the field of vision). The major axes of the dendritic crystals grow over the normal to the surface of the working cavity of the chill mold. The orientation of the austenitic dendrites is a consequence of their growth in the direction opposite to that of the heat removal.

Figure 2b exhibits obvious second-order arms, the distance between which does not exceed $10\ \mu\text{m}$, which indicates a high rate of their solidification. The ball has a relatively small size, and the respectively high cooling rate due to the intense heat removal into the metallic mold promotes formation a primary dendritic structure.

An A – M_7C_3 austenite-carbide eutectic is located in the arm spacing (Fig. 2c). The susceptibility of chromium-alloyed white cast irons to formation of quasi-eutectic structures under the conditions of nonequilibrium crystallization has been reported in [24]. In our case, the conditions for development of nonequilibrium crystallization in formation of quasi-eutectic structures are created due to the intense removal of heat into the metallic mold. Austenite is the leading phase forming the matrix of the A – M_7C_3 quasi-eutectic. This mechanism of formation of the quasi-eutectic is confirmed by the fact that the austenite crystals belonging to the quasi-eutectic are formed sooner on the austenitic dendrites already present in the solidifying ball, which is more favorable from the standpoint of the thermodynamics where the energy is concerned. By the data of the analysis of the morphological structure of the mechanical mixture, the inclusions of the carbide phase are of type M_7C_3 . This is confirmed by Fig. 2d, where we observe a hexagonal base of the Cr_7C_3 leading carbide crystal surrounded with an austenitic shell. With allowance for the leading role of austenite in the formation of the A – M_7C_3 quasi-eutectic and for the “island” arrangement of the M_7C_3 carbide, we may infer that the surface zone of the balls is an inverted-type eutectic matching the Zhukov–Silman principle of composite hardening. The additional composite hardening of the surface layer of the balls is a result of formation of austenitic dendrites oriented orthogonally to the surface of the grinding ball, which

provides a high level of wear resistance in the surface zone of the cast iron articles.

The carbide phase observed in the structure of the eutectic colonies (Fig. 3) has the shape of rosettes or polyhedrons. Similar structures have been detected in chromium cast irons in [25].

The metallic matrix near the surface of the cast iron has a structure of tempered martensite with a relatively low content of retained austenite. During the heat treatment, the structure acquires M_7C_3 -type secondary carbides. The secondary carbide phase forms primarily on the primary carbides.

The chemical composition of the central part of the ball differs from that on the surface due to the development of segregation processes, in particular, with respect to carbon. In addition, the conditions of the heat removal change during the solidification of the central part of the ball due to the comparatively low thermal conductivity of the earlier solidified surface zone having a structure of white chromium cast iron. The changes in the composition and in the solidification conditions cause substantial changes in the mechanism of structure formation (Fig. 4).

Figure 4b presents the microstructure of the transition zone arising at the boundary of occurrence of different mechanisms of structure formation over cross section of a ball. The changes in the structure of the surface and of the central zones result in changes in their properties, which allows us to conclude that the structure over the cross section of the ball has a graded pattern.

The austenitic dendrites growing into the central zone of the ball are characterized by a great distance between the second-order arms. This means that the austenite crystals in the center of the ball grow at a lower rate than on its surface under the conditions of the less intense removal of heat (Fig. 4b). Analyzing the morphological features of the structure we can judge on the mechanism of its formation. The austenitic dendrites grow from the surface and squeeze the liquid enriched with carbon and impurities into the central zone of the ball. Closer to the core of the ball, the dendritic growth of the austenite crystals is decelerated, and their

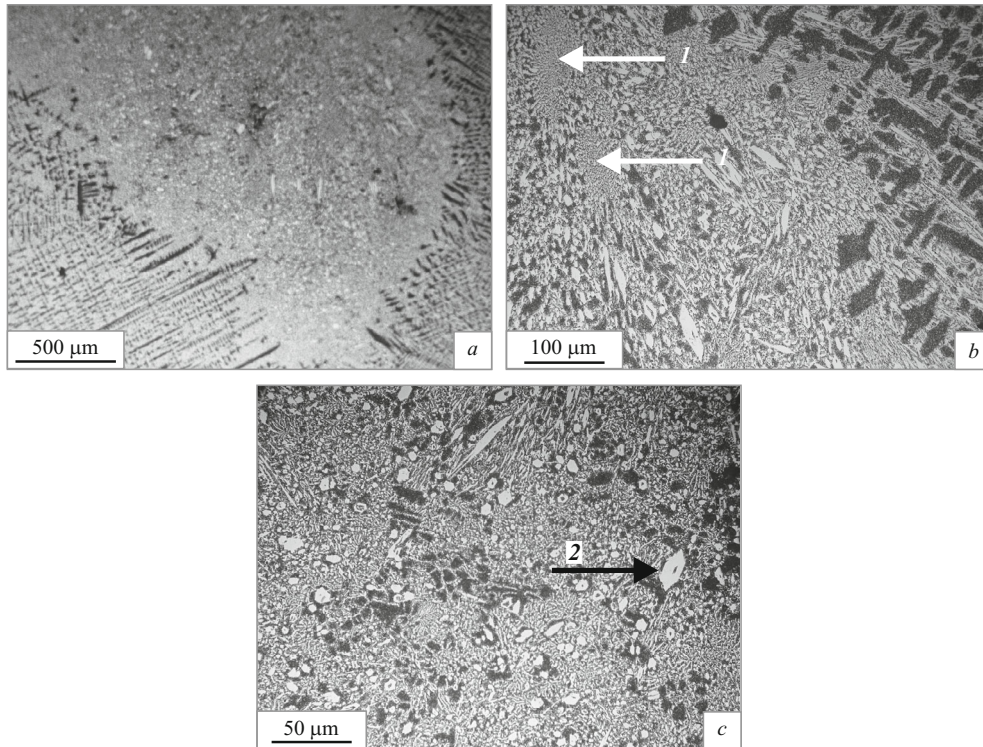


Fig. 4. Post-heat-treatment microstructure in the center of a ball (*a*, *c*) and at the boundary of structural zones (*b*): *a*) $\times 50$; *b*, *c*) $\times 200$; 1) $M_7C_3 - A$; 2) M_7C_3 .

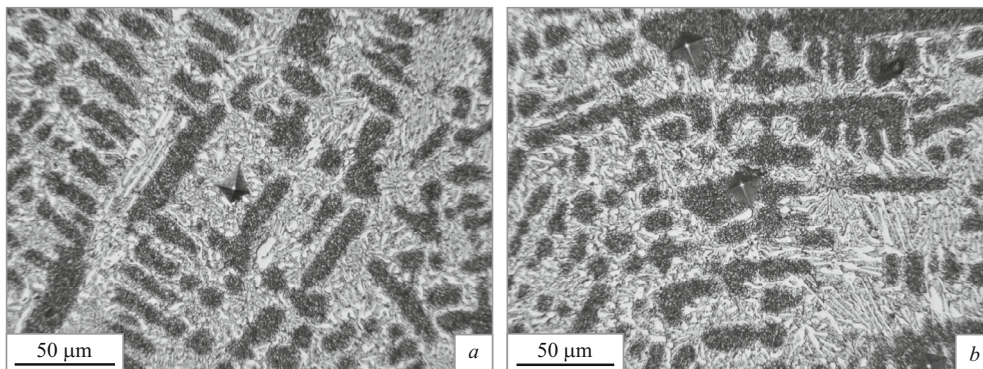


Fig. 5. Indents due to the measurement of microhardness of cast iron after heat treatment: *a*) carbide phase entering the $Fe_\gamma - Me_7C_3$ quasi-eutectic, $\times 500$; *b*) metallic matrix (tempered martensite), $\times 500$.

structure coarsens. The iron melt reaching a eutectic concentration in the central part of the ball starts to crystallize yielding base M_7C_3 carbides surrounded by an $M_7C_3 - A$ eutectic (Fig. 4*c*). Now the leading phase forming the matrix of the eutectic is an M_7C_3 -type carbide rather than the $A - M_7C_3$ quasi-eutectic of the surface layer formed on the austenite crystals. The crystallization conditions in the center of the ball are close to equilibrium ones due to the low cooling rate, which promotes appearance of fine-grained eutectic structures represented by a carbide-austenite eutectic spherulite in accordance with the classification of [26, 27].

The crystals of the M_7C_3 carbide that serve a base for formation of a eutectic in the chromium cast iron have a pencil shape. The hexagonal morphology of the base eutectic carbides is explainable by anisotropy of their growth in the crystallization process. Piercing the core, they reinforce the central zone of the ball. The comparatively large form of the crystals of the base carbide phase indicates development of diffusion process in the matrix melt preserved in the center of the casting until the end of the process of its solidification. This is an additional confirmation of the fact that the surface layer of the ball formed at the early stage of the solidification possesses a low thermal conductivity. The solid skeleton,

which is represented by austenitic dendrites and an austenite-carbide quasi-eutectic, blocks the removal of heat during the solidification and thus promotes development of processes of equilibrium crystallization in the fine dispersed eutectic carbide-austenite structure. The coarse inclusions of the primary carbide are susceptible to brittleness and subsequent spalling, which makes such a structure undesirable on the surface of grinding bodies. However, when located in the center, it provides a high strength together with the martensitic matrix and consolidates the peripheral anisotropic dendritic-quasi-eutectic layers thus rendering the grinding bodies quite impact resistant.

The results of the measurement of the microhardness of the carbide phase entering the quasi-eutectic, the eutectic, and the metallic matrix on the surface and in the center of a heat-treated ball are given in Fig. 5 and Table 2.

The measurements of the hardness gave the following results: surface hardness of the balls 58.5, 60, 60.5, 60, and 61.5 *HRC* (60.1 *HRC* on the average); hardness in the middle 62; 61, 63.5, 61.7 and 61.5 *HRC* (61.94 *HRC* on the average). The results of the measurements of the hardness reflect the general tendency determined for the variation of the microhardness of the main structural components of the cast iron. The proportion of the structural (the carbide content determined by formula (1)) and of the mechanical (the hardness) parameters allows us to calculate the gradient, i.e.,

$$G = K_{\text{surf}}/K_{\text{centr}} = HRC_{\text{surf}}/HRC_{\text{centr}} = 0.92 \div 0.97, \quad (2)$$

where K_{surf} , K_{centr} and HRC_{surf} , HRC_{centr} are the contents of carbides and the hardness of the surface and central zones of the grinding balls, respectively.

We also tested the balls in a laboratory ball crusher. An experimental batch of balls was used to grind different ferroalloys and fluxes (ferrosilicon, ferromanganese, ferrochrome, ferromolybdenum, electrode scrap, welding fluxes). After 120 h of operation of the crusher with the experimental balls none of them failed, and the total wear of the balls was 0.047 wt.%.

CONCLUSIONS

We have considered the possibility of raising the operating endurance of grinding balls by creating a graded structure over their cross section. To solve this task, we used the method of directed crystallization in combination with subsequent heat treatment to produce the balls. We studied an experimental batch of grinding balls with diameter 30 mm and graded structure over cross section. The surface zone of the balls was represented by an orthogonally oriented hypoeutectic structure (tempered martensite) and an austenite-carbide quasi-eutectic of type A – M_7C_3 . This type of structure belongs to inverted-type eutectics meeting the principle of composite hardening, which provides a high level of wear resistance in the surface zone of the cast iron. The center of the

TABLE 2. Post-Heat-Treatment Microhardness of the Carbide Phase and of the Metallic Matrix of the Balls

Phase	Zone	$L_1, \mu\text{m}$	$L_2, \mu\text{m}$	$HV, \text{kgf/mm}^2$
Carbide phase of quasi-eutectic and eutectic (Fig. 5a)	Ball surface	27.90	29.77	669
		28.15	31.41	627
		28.18	31.61	622
	Average value	28.08	30.93	639
	Ball center	26.83	31.29	659
		26.61	29.56	705
27.42		29.12	696	
Average value	26.95	29.99	687	
Metallic matrix (Fig. 5b)	Ball surface	30.28	33.14	553
		28.15	32.83	598
		29.28	32.53	592
	Average value	29.23	32.83	581
	Ball center	31.53	34.99	503
		30.14	34.26	536
31.95		32.81	530	
Average value	31.21	34.02	523	

Notations: L_1 and L_2 — diagonal lengths of the indent in two perpendicular directions.

ball acquires a fine dispersed eutectic structure represented by a carbide-austenite eutectic of type M_7C_3 -A. Together with the martensitic metallic matrix this structure provides a high strength of the article and consolidates the peripheral anisotropic hypoeutectic layers rendering the grinding bodies highly impact resistant during their service in a ball crusher.

Formation of a functionally graded structure, which is anisotropic and hypoeutectic in the surface layer and high-strength, eutectic and fine in the center, is a result of the change in the conditions of heat removal and carbon segregation affecting favorably the mechanical properties of the grinding balls. The difference in the hardness and microhardness values in the surface layer and in the center of the balls is a result of formation of a graded structure.

The tests of the experimental batch of grinding balls in a laboratory crusher in grinding of various ferroalloys and fluxes have proved a high level of their operating properties.

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