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On Peculiarities of the Influence of Chemical Composition on Formation of Structure and Properties of Alloyed Cast Irons in the As-Cast State

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We conducted a study of the structure, phase composition and wear resistance of iron-carbon alloys used and planned to be used in manufacture of hot deformation tools. As established, chromium-manganese cast iron with chromium content of 12.5...13.5% and manganese content of 15.0...16.0% is advisable to be used as a material, in particular, for piercing mandrels. As shown, reduction of expensive alloying elements (Cr, Ni) contained in chromium-manganese cast iron in comparison with traditional alloys such as $300X32H3\Phi JI$ and 'nikorin' is performed due to the higher contents of Mn. It was found that the increase in wear resistance of chromium-manganese cast iron is due to the high microhardness of the matrix, austenite-carbide eutectic based on carbide type Me₇C₃ and, apparently, it is conditioned by deformation-phase transformations that can occur during abrasion wear.

Key words: high-chromium cast iron, chromium-manganese alloy, chromium-nickel alloy, structure, phase composition, microhardness, wear resistance.

Проведено дослідження структури, фазового складу та зносостійкости залізовуглецевих стопів, що використовуються та плануються до використання у виготовленні інструментів гарячої деформації. Встановлено, що хромомарганцевий чавун із вмістом хрому 12,5...13,5% і марганцю 15,0...16,0% доцільно використовувати як матеріял, зокрема, для прошивних оправок. Показано, що зменшення дорогих леґуючих елементів

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(Cr, Ni), які містяться в хромомарганцевих чавунах у порівнянні з традиційними стопами типу 300Х32Н3ФЛ і «нікорін», здійснюється за рахунок більшого вмісту Mn. Встановлено, що підвищення зносостійкости хромомарганцевих чавунів зумовлене високою мікротвердістю матриці аустенітно-карбідної евтектики на основі карбіду типу Me_7C_3 і, очевидно, зумовлене деформаційно-фазовими перетвореннями, які можуть відбуватися під час абразивного зносу.

Ключові слова: високохромистий чавун, хромомарганцевий стоп, хромоніклевий стоп, структура, фазовий склад, мікротвердість, зносостійкість.

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1. INTRODUCTION

Currently, one of the main items of foreign exchange earnings of the state is the export of cast sections and rolled metal. Requirements for the quality of rolled products are growing every year, and competition with China is becoming increasingly significant due to purchase and modernization of metallurgical equipment. The problem of improving quality of rolled products with the possibility of simultaneous reduction of their cost price is becoming increasingly urgent. Thus, reduction of production process cost and increase of the overall quality of rolled products is an important direction of research. Rolling mills, rulers and mandrels of rolling mill frameworks belong to the main tool of hot deformation; operational characteristics of these tools affect productivity and quality of metal products. The cost of rolls, rulers and piercing mandrels is an integral part of the cost of finished hardware. At the same time, the urgency of issues related to improving operational stability of the rolling tools (and first of all, heir durability) is constantly growing.

Experience of national and foreign metallurgical practice, as well as available separate researches indicate that mill rolls made of alloy cast iron and alloy steels are used for hot deformation of ferrous and nonferrous metals. At that, the share of mill rolls made of cast iron makes up to $\cong 65\%$ of the total production volume of the mentioned metal products [1–4]. Depending on the operating conditions and the production method piercing mandrels are made of alloyed carbon steels, highchromium cast irons of 300X32H3 Φ JI type or chromium–nickel alloys of 'nikorin' type [1–4]. However, despite the high cost of production and availability of various methods of processing of high-chromium and chromium–nickel alloys, tools of hot deforming are characterized by low operational stability of only some dozens of hours. Thus, increasing the service life of quick-wear machine parts operating at high temperatures and loads is one of the priority tasks to be solved in the metallurgical and machine-building industries. Usually, increase in the service life of piercing mandrels is conditioned by improvements of the technological process, in particular due to effective combinations of chemical composition, structure parameters and ways to strengthen them.

Currently it is established that chromium-manganese cast irons with 12...18% of chromium and 5...16% of manganese, can be used as a promising material for production of rolling tools. Analysis of domestic and foreign scientific publications has shown that correlation of chemical composition, formed type of matrix, mechanical properties and wear resistance indices of alloys used for the production of hot deformation tools is insufficiently studied, so this area requires respective researches to be carried out [5-10].

It should be understood that the set of properties of alloyed cast iron is formed immediately after heat treatment, and the development of new modes requires reliable information about the hereditary relationship of the original cast structure with the final structural state. This is important because it is known that the main purpose of heat treatment is to form a homogeneous structure of cast alloys that are not subject to traditional hot plastic deforming.

Given the above, the peculiarities of structure formation processes, formation of phase composition and properties of iron-carbon alloys (nickel-chromium, high-chromium and chromium-manganese cast irons in the initial cast state and hereditary relationship with the final structure of finished metal products is a topical direction of researches in the sphere of finding rational ways for further increase of operational stability of hot deformation tools.

2. MATERIAL AND METHODS OF RESEARCH

The chromium-nickel alloy 'nikorin', high-chromium cast iron of $300X32H3\Phi$ JI type and research casts of chromium-manganese alloys obtained in laboratory conditions were investigated in the work. Chemical composition of the alloys taken for carrying out researches is given in Table 1.

The structure of the alloys in the initial (as-cast) state was determined after etching of microslices in 10% alcoholic solution of nitric acid. The structure was evaluated according to ΓOCT 3443-87 and $\square CTY$ 8851:2019 with a help of an optical microscope (Neophot-31) and an electronic focused beam microscope (JSM-35).

Identification of phases in the researched alloys was performed according to the method of x-ray crystal analysis using diffractometers $\square POH-2$, $\square POH-3M$ with the use of CuK_{α} - and CoK_{α} -radiation. To determine lattice parameter of unconverted austenite the profiles of refraction peaks $(111)_{\gamma}$, $(002)_{\gamma}$, $(113)_{\gamma}$ were used according by three mutually perpendicular sides of the specimens. At that, each side was rec-

Content of ele-	300Х32Н3ФЛ	'Nikorin' chromium-	Research casts of chromium– manganese cast irons		
ments, % weight	cast iron	nickel alloy	Alloy No. 1	Alloy No. 2	Alloy No. 3
С	3.0 - 3.2	1.2 - 1.4	2.2 - 2.4	2.5 – 2.8	2.9 - 3.2
Cr	29.5 - 34.5	36 - 38	12.0 - 13.0	15.5 - 16.5	12.5 - 13.5
Ni	3.0 - 3.2	57 - 59	0.8 - 0.9	0.9 - 1.0	1.0 - 1.2
Al	—	1.3 - 1.9	_	_	_
Ti	_	0.6 - 0.7	_	_	_
V	0.2 - 0.3	-	0.2 - 0.3	0.2 - 0.3	0.2 - 0.3
Mn	0.3 - 0.6	0.2 - 0.3	5.2 - 6.2	10.0 - 11.0	15.0 - 16.0
\mathbf{Si}	${\leq}1.2$	0.6 - 0.8	0.9 - 1.0	0.8 - 0.9	0.8 - 0.9
Cu	≤ 0.4	_	0.10 - 0.20	0.08 - 0.09	0.1 - 0.2
S	≤ 0.045	_	≤ 0.009	≤ 0.009	≤ 0.003
Р	≤ 0.045	_	$\leq\!\!0.013$	≤ 0.027	≤ 0.025
Fe	58.0 - 60.0	0.7 - 1.3	77 - 78	67.5 - 68.5	65.0 - 66.0

TABLE 1. Chemical composition of alloys taken for carrying out researches.

orded five times at a rate of $(1/8)^{\circ}/\text{min}$).

The lattice parameter was calculated according to the position of the mass centre of the above-mentioned diffractometric maxima. The results obtained were subjected to statistical processing according to the standard methods. The amount of residual austenite was determined based on the ratio of integral intensities of the lines (011) (and (111) (according to the formula (1)[11]:

$$V_{\gamma}(\%) = [(I_{HKL\gamma}/P_{HKL\gamma})/(I_{HKL\alpha}/P_{HKL\alpha} + I_{HKL\gamma}/P_{HKL\gamma})], \qquad (1)$$

where V_{γ} —volume ratio of austenite; $I_{HKL\gamma}$ is the integral intensity of the line $(111)_{\gamma}$; $I_{HKL\alpha}$ is the integral intensity of the line $(011)_{\alpha}$; $P_{HKL\gamma}$ is multiplicity factor for the line $(111)_{\gamma}$; $P_{HKL\alpha}$ is multiplicity factor for the line $(011)_{\alpha}$.

Microhardness determined according to $\Gamma OCT 9450-76$ using $\Pi MT-3$ instrument. Hardness of alloys was determined according to $\square CTY$ ISO 6508-1:2013 (Rockwell method) using TK 14-250, and TP 5006 devices.

Abrasion wear tests were performed at an increased temperature (950°C) using 2070 CMT-1 installation according to ΓOCT 30480-97, based on 'shaft-plane' scheme [12]. Specimens in form of a parallelepiped ($10 \times 10 \times 27$ mm) were used for performing tests. Steel 45 was used as the counterface (counterbody). At elevated test temperatures the

specimens were mounted to a special frame, 500 N was created and they were heated by means of abrasion at a sliding rate of 2 m/s during one minute. Within a period of one minute temperature at the contact zone reached 950°C, (the temperature was measured using a high-precision pyrometer GM2200.

Wear resistance tests of the researched alloys were carried out as follows. The process of wear in time consists of two unequal stages: wearing in and stationary condition. Formulas for the rate of wear $i_t = \frac{dI}{dt}$ and wear I(t) as a function on time t are as follows:

$$i_t(t) = (i_0 - \langle i_t \rangle) \exp(-t/T) + \langle i_t \rangle,$$
 (2)

$$I(t) = (i_0 - \langle i_t \rangle) T[l - \exp(-t/T)] + \langle i_t \rangle t, \qquad (3)$$

where i_0 and $\langle i_t \rangle$ are initial and average stationary value of the rate of wear; *T* is time of wearing in relaxation; *I*(*t*) is wear.

By means of substituting in formulas (2) and (3) time t for friction path l we obtain formula describing wear intensity I(l) along the abrasion path.

Accuracy of the estimates is determined by the resolution of instruments and dispersion of the wear process.

The difference between six-minute wear and one minute wear is divided by the abrasion path and the value of average wear intensity (i) is obtained. During the test friction force is measured and the coefficient of wear resistance (n) is calculated.

In order to determine wear intensity, the specimen should be measured before and after the test and by means of dividing the wear by the friction path wear intensity in dimensionless units is obtained.

Wear rate is determined in the same way by means of measuring the specimen before and after the tests, and applying the ratio of wear to the test time.

The coefficient of wear resistance is defined as the inverse logarithm of wear intensity.

3. RESEARCH RESULTS

During the researches the comparative analysis of the structure, phase composition and wear resistance of iron-carbon alloys ($300X32H3\Phi$ JI cast iron and 'nikorin' alloy) used and planned to be used in manufacture of piercing mandrels of rolling mill frameworks.

Figure 1 shows the structure of mandrels made of high-chromium cast iron 300X32H3ΦЛ and 'nikorin' alloy.

According to the graphic materials a rather inhomogeneous structure is formed along the cross section of the $300X32H3\Phi$ Л cast iron casting.



Fig. 1. Structure of high-chromium and chromium–nickel alloys in the as-cast state. a, b—surface and axial zone of casting respectively (300X32H3 Φ JI cast iron); c, d—surface and axial zone of casting respectively 'nikorin' alloy).

The structure of the mandrel from its surface to the centre of the casting gradually changes, excess carbides are enlarged and their number is increased. In the axial zone of the ingot there are large excess carbides in the form of needles, hexagons and austenite-carbide eutectic colonies (A + C). Small amount of excess coarse-needle carbides and their uneven location in the surface layer indicates accelerated cooling of the mandrel during crystallization and cooling in the mould. The austenite-carbide eutectic formed in the surface layer is finely differentiated with a small interlamellar spacing of highly branched eutectic phases. In the central part of the casting, the degree of differentiation of the austenite-carbide eutectic decreases, *i.e.*, a more coarsely differentiated eutectic is formed. As a result of accelerated cooling, decomposition of supercooled austenite does not have time to begin, and the process of isolation of secondary excess carbides from the solid solution and their growth is inhibited.

Analysis of the structure of the 'nikorin' alloy showed that according to the cross section of the casting a practically uniform structure is formed, in contrast to the $300X32H3\Phi$ JI cast iron. Two types of carbides Me₇C₃ (Cr₇C₃) and TiC were detected in the structure of 'nikorin' alloy. TiC carbides are distributed unevenly both in the volume of Me₇C₃ (Cr₇C₃) carbides and in the austenite matrix. Titanium fibbers have a correct cubic shape.

The structure of researched melts of chromium-manganese cast

irons with different contents of chromium and manganese is shown in Fig. 2.

Structural analysis of the researched chromium-manganese alloys showed that crystallization begins with the release of primary austenite dendrites and ends with the formation of eutectic colonies A + $+ Me_7C_3$. Me_7C_3 carbides in longitudinal and cross sections and finely differentiated austenite-carbide eutectic based on Me_7C_3 carbide are observed in the structure.

Figure 3 shows diffraction patterns of 300X32H3ΦJI cast iron and 'nikorin' alloy.

According to x-ray diffraction analysis, $300X32H3\Phi JI$ cast iron revealed excess Me₇C₃ carbides [13] and it was found that the matrix consists of 52% austenite and 48% ferrite. Presence of ferrite is apparently due to the lack of stability of austenite, which decomposes with formation of ferrite and carbides during cooling. Ferrite is an undesirable component in the structure of cast iron and it can lead to decrease of wear resistance and heat resistance of cast iron alongside with macrodefects. The chromium–nickel alloy (see Fig. 3, *b*) includes excessive eutectic carbides Me₇C₃ (Cr₇C₃), high-nickel austenite, as evidenced by intensity of line (111), titanium carbides TiC, intermetallic compounds Ni₃Al and σ -phase (FeCr), which reduces stability of alloys during operation under tensile stress. This is due to the fact that the σ -phase has a high hardness, however, is very fragile [14–17].

 Me_7C_3 - Cr_7C_3 carbides [18–2], cementite, austenite, and ferrite were



Fig. 2. Structure of the researched chromium-manganese alloys in the as-cast state: a-alloy No. 1; b-alloy No. 2; c-alloy No. 3.



Fig. 3. Diffractograms of $300X32H3\Phi JI$ high-chromium cast iron (*a*) and 'ni-korin' chromium-nickel alloy (*b*).

found in chromium-manganese alloys (Fig. 4). Quantitative data of the x-ray diffraction analysis of the researched alloys are given in Table 2.

Analysis of the Table data gives an opportunity to assert that the structure of 300X32H3 Φ JI cast iron includes the α -phase; the degree of imperfection ($\beta_{0.5}$) of its lattice is 0.43, the parameter of α -phase lattice (a_{α}) is equal to 2.88. Alongside with this the cast iron matrix includes 52% residual austenite and ferrite. α -phase was not detected in 'nikorin' alloy, its matrix consists of almost 100% of high-nickel austenite.

Chromium-manganese alloys equilibrium α -phase, the degree of lattice imperfection is 0.57...0.59, and the α -phase lattice parameter is 2.87...2.88. Amount of austenite in the matrix of researched alloys is increased from 87% to 94% with increasing content of carbon and alloying elements (Cr and Mn).

Hardness of $300X32H3\Phi JI$ cast iron in the as-cast state is the highest (49 *HRC*), while hardness of 'nikorin' alloy is 47 *HRC*. Hardness of chromium-manganese alloys No. 2 and No. 3 makes up 42 *HRC*, and hardness of alloy No 1 appeared to be much lower—35 HRC.



Fig. 4. Diffractograms of researched chromium-manganese cast irons in the as-cast state: a-alloy No. 1; b-alloy No. 2; c-alloy No. 3.

Table 3 shows results of measuring microhardness of the matrix and Me_7C_3 carbides of the researched alloys.

In the $300X32H3\Phi JI$, microhardness of the matrix appears slightly higher than in the chromium-nickel alloy. At the same time, micro-

Researched alloys	a_{lpha} at (011) $_{lpha}$	$a_{\gamma} \operatorname{at}$ (022) $_{\gamma}$	Degree of imperfection of α -phase ($\beta_{0.5}$)	% γ in the matrix	HRC
300Х32Н3ФЛ	2.88	3.48	0.43	52	49
'Nikorin'	_	3.58	-	≥100	47
Alloy No. 1	2.87	3.60	0.59	87	35
Alloy No. 2	2.88	3.62	0.59	92	42
Alloy No. 3	2.87	3.62	0.57	94	42

TABLE 2. Data of x-ray diffraction analysis of researched alloys.

hardness of Me_7C_3 carbides in 300X32H3 Φ JI cast iron and 'nikorin' alloy is equal.

Matrix microhardness and microhardness of eutectic carbides in alloys No. 1, No. 2, and No. 3 are increased with increasing amounts of carbon, chromium and manganese.

This difference in properties is obviously due to liquation (distribution of alloying elements between phases and structural components), which is formed during crystallization of researched alloys, which is also typical for manufacture of alloyed carbon steels [23, 24].

Results of comparative Abrasion wear tests at temperature 950° C and loading of 500 N of the researched alloys in the as-cast state are given in Table 4.

The obtained results give an opportunity to assert that chromiummanganese cast irons (alloys Nos. 1–3) in the as-cast state show the highest wear resistance (minimum wear intensity and a high coefficient of wear resistance) during abrasion wear under elevated temperature and load.

The phase and structural transformations that occur during abrasion wear are obviously due to the redistribution of alloying elements between the phases and structural components of the researched alloys.

Researched alloys	Matrix microhardness, MPa	Me ₇ C ₃ carbides microhardness, MPa		
300Х32Н3ФЛ	3285	18920		
'Nikorin'	2769	18921		
Alloy No. 1	4137	7920		
Alloy No. 2	4228	8934		
Alloy No. 3	4663	9195		

TABLE 3. Microhardness measurement results.

Researched alloys	Load, N	Velocity, m/s	Wear intensity <i>i</i>	Coefficient of wear resistance n
300Х32Н3ФЛ			$1.19 \cdot 10^{-7}$	6.92
'Nikorin'			$9.3 \cdot 10^{-7}$	6.03
Alloy No. 1			$1.10 \cdot 10^{-7}$	6.95
Alloy No. 2	500	2	$7.52 \cdot 10^{-8}$	7.12
Alloy No. 3			$5.7 \cdot 10^{-8}$	7.24

TABLE 4. Tests for wear resistance of researched alloys in the as-cast state.

Thus, the increase in wear resistance of chromium-manganese cast irons (alloy No. 3) is due to the high microhardness of the matrix, austenite-carbide eutectic based on Me_7C_3 carbide and is determined by the degree of alloying and the shape parameter of the eutectic carbide [25, 26], as well as during abrasion wear. In particular, the latter statement requires additional comprehensive researches.

4. CONCLUSIONS

1. We researched peculiarities of structure formation, phase composition and properties of high-chromium ($300X32H3\Phi JI$), chromiumnickel ('nikorin') and chromium-manganese cast irons in the as-cast state (cast irons used and planned to be used in the manufacture of hot deformation rolling mills).

2. It is established that cross section of $300X32H3\Phi$ JI cast iron forms a significant structural in homogeneity in contrast to 'nikorin' alloy (its structure is more homogeneous). It is shown that the structure of 300X32H3ФЛ cast iron in the as-cast state includes excessive Me₇C₃ carbides and its matrix consists of austenite (52%) and ferrite (48%). The structure of 'nikorin' alloy contains chromium carbides-Me₇C₃ (Cr_7C_3), titanium carbides—TiC, intermetallic compounds—Ni₃Al, σ phase (FeCr), and its matrix consists of 100% high-nickel austenite. Me₇C₃ carbides are observed in the structure of chromium-manganese cast irons in both longitudinal section and cross-section, and finely differentiated austenite-carbide eutectic based on Me_7C_3 carbide. Me_7C_3 - Cr_7C_3 carbides, cementite, austenite and ferrite were detected by x-ray diffraction method. Amount of austenite in the matrix of chromium-manganese cast irons increases from 87% to 94% with increasing content of carbon and alloying elements. Alongside with increased amount of austenite, microhardness of the researched chromium-manganese cast irons also grows. Change in properties of chromium-manganese alloys may be due to liquation, which is formed during the crystallization and cooling of the alloyed cast iron.

3. It is established that as a result of abrasion wear at a temperature of 950°C and loads of 500 N chromium-manganese cast irons have the highest wear resistance (wear intensity $1.1 \cdot 10^{-7} \dots 5.7 \cdot 10^{-8}$ and a high coefficient of wear resistance 6.95...7.24) in comparison with 300X32H3 Φ JI and 'nikorin' alloy. The greatest wear resistance among the researched alloys is typical for chromium-manganese cast iron with chromium contents of 13% and manganese contents of 15...16% (alloy No. 3).

4. Further research should be focused on studying deformation-phase transformations that can occur during abrasion wear and determining effective modes of final heat treatment of hot deformation tools, which will give an opportunity to reasonably use chromium-manganese alloys with reduced chromium and nickel content due to their substitution with manganese.

5. The results of research allow us to draw a preliminary conclusion that the use of chromium-manganese cast iron alongside with effective modes of final heat treatment will increase the operational stability of hot deformation tools (piercing mandrels) while reducing production costs.

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