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**TRANSFORMATION OF THE IRON
IN THE STEEL OF THERMOCHEMICAL PROCESSING
OF THE SURFACE OF THE BLUE CYLIN**

Abstract. The production of pig iron and steel is based on a two stage technology - cast iron smelting and oxidizing melting of steel. The first stage results in carbonization of the metal; the second, on the contrary, its decarbonization.

Decarbonization of cast iron from the melt under this scheme results in significant losses of valuable metals, degradation in metal quality and technical-and-economic efficiency of the process. The author offers to carry out an alternative way i.e. to decarbonize a solidphase cast iron by thermochemical treating its working surface using metal oxide powders as a case and carbon dissolved in cast iron as a reducing agent. Heating of the given system up to the set temperature and time-exposure resulted in direct recovery of metal by dissolved carbon, ecarburization of the outer surface and embedding of recovered metal into it. We established that depending on the temperature of heating and holding time there was possible to convert/to embed cast iron into layers of steel coating up to a specified depth.

Key words: metals, iron, iron, steel, ore, coal, carbon, recovery, melting, crystallization, decarburization, structure.

The production of pig iron and steel, as the fundamental basis of the industry, is under intensive development reaching today enormous proportions [1-3]. The elements of traditional technology - blast furnace smelting of cast iron and steel smelting in oxygen converters account for about 80% of world production of iron and steel [4, 5]. However, this two stage technology including such processes as preparation and processing of iron ore and metallurgical has some specific shortcomings threats basically associated with the accumulation of solid waste dumps and gas emissions into atmosphere [6]. Therefore, some industrially developed countries begin using new steel production technologies like metallization of iron ore products in electric smelting units [7-10]. But traditional «Domna-Converter» methods still used in production of pig iron and steel can't be changed overnight. But scientific research aimed to create new metallization technologies gives good results, both theoretical and practical. As in nature iron ore resources are found in the form of oxide compounds, their preparation and processing considers the organization metal recovery works at a global scale. The latter in practice requires the production and use of reagents, their choice being of critical importance [11]. Nature has given mankind not only oxide iron ore, but also a huge mass of coal and hydrocarbon fuel as sources for production of reagents like hot reducing gases (HRG) used for recovery processes in blast and shaft furnaces. However, the reduction potential of CO, H₂ is limited. They are able to provide a complete recovery of iron from iron ore but unable to recover to a metallic state such valuable impurities hidden in the charge, as manganese, chromium and vanadium. That is why during the reduction of complex IORM in the blast furnace, these impurity metals are completely recovered by solid coke carbon and pass into cast iron, which represents by itself a naturally alloyed intermediate metal product. Its transformation into a structural product i.e. steel is associated with its decarbonation during oxidative remelt in the oxygen converter. But the paradox of this two-stage

technology is that oxidative smelt oxidizes not only carbon and all valuable metals passed into cast iron during smelt reduction.

The problem of retaining these valuable metals at converting pig iron into steel is topical practically speaking but still unsolved. The problem can be solved by the carbon dissolved in cast iron. This particular aspect is reviewed in this article.

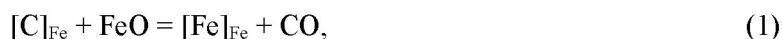
Solid carbon is as they say a nature phenomenon. It has a high electronic potential which make it a highly effective reagent. It is well known not only for being a highly effective recovery agent, but also as a regulator of metal alloy structure, in particular, of «iron-carbon» alloy. Relating to iron metallurgy, Carbon as a very effective reductive agent plays a key role direct reduction of iron, i.e. it first provides for the production of metallic iron from oxide iron ore raw material, and secondly, when dissolving in it turns the resulting metallic iron into a structural material of various purpose. Another peculiarity of solid carbon is that its atomic radius is half the size of the atomic radius of iron, which guaranties a high penetration of carbon into crystal lattice of iron. Iron also has a different crystal lattice, in this connection, it is divided into α -iron crystal lattice with a body-centered cubic (bcc) and γ -iron crystal lattice with a face-centered cubic (fcc). In the crystal lattice of γ -iron, the interatomic distance is much larger than in α -iron. Therefore, in carbon solubility at penetration into the crystal lattice of a particular iron is different. In α -iron, carbon solubility is limited from 0.025% at 727°C to 0.1% at 1499°C and forms a phase called ferrite. In γ -iron, the solubility of carbon increases; its maximum concentration reaches up to 2.14% and forms a phase of the iron-carbon alloy called austenite [12, 13]. Carbon not only dissolves, but also forms a chemical compound with iron cementite Fe_3C under the principle of donor-acceptor mechanism [14]. Since iron also has a significant electronic potential, but smaller than that of carbon, the bond strength of cementite is low and at certain heating conditions it can dissociate and form a dissolved carbon. Thus, the interaction of iron with carbon is associated with the formation of the following phases of iron-carbon alloys: ferrite (concentration up to 0.1% C); austenite (concentration up to 2.14% C) and cementite (maximum concentration to 6.67% C), with cementite being dissolved in the phases of ferrite and austenite. The process of cementite dissolution in austenite at 1153°C is associated with eutectoid change and phase formation - ledeburite with an average carbon concentration of up to 4.3%. In practice, this is iron, in which the more of the carbon is in the form of interstitial solution and the smaller - in the form of a weak or thin chemical compound Fe_3C . Taking into account that cementite is able to dissolve in ferritic-austenite phases and that we can use carbon in solid-phase reactions, we shall be using a simple term for it calling it a «dissolved carbon».

The massive use of cast iron as a structural metal product is known to be limited by its fragility. Therefore, a global technology is aimed at reducing carbon concentration in cast iron up to the level of carbon concentration in steel [15].

As said above, decarbonization of cast iron from its melt under traditional technology is associated with significant loss of valuable metals, production costs and environmental problems.

Considering the said shortcomings we believe search for ways of selective weakening carbon concentration in cast iron to be a promising aspect.

The thing is that the high electronic potential and mobility of dissolved carbon enable to organize a mass exchange process not only in the melt, but also in a solidphase cast iron. The mechanism of behavior of solid-phase reactions with dissolved carbon participation in the mass-exchange process is more preferential than with a free carbon [16-20]. Carbon dissolved in cast iron under a certain temperature can interact on the contact surface with powdered metal oxides.



where $[\text{C}]_{\text{Fe}}$ - carbon dissolved in iron; $[\text{Fe}]_{\text{Fe}}$ - iron recovered by dissolved carbon and imbedded into cast iron structure.

After the reactions (1) - (2), the dissolved carbon transforms into a gas phase, while a reduced metal is imbedded into the crystal lattice of the matrix with a positive thermal effect. Thus, there is occurring not only a process of cast iron decarbonization but also the imbedding of reduced metal into the outer zone of cast iron.

The physical-chemical properties of the cast iron itself have a favorable effect on the organization of the said process. First, its melting point is much lower than that of steel. Secondly, it has a higher liquid mobility than steel that enables to produce cast metal product of a required shape. Third, it retains valuable alloying metals in its composition.

Taking into account the said features of cast iron and the high activity of dissolved carbon as a reducing reagent, one can organize solid-phase reactions of (1) - (2) type and solve a new task of converting cast iron surface layers from the ledeburite high-carbon phase into ferritic-austenite low-and medium-carbon phase. The solution of this task has scientific and practical values.

Experimental research. Experimental studies on process organization consisted of successive stages:

1. Cast iron smelting from oxide iron-ore concentrate.
2. Pouring cast iron into square shape ceramic cells.



Figure 1 – Lab equipment and apparatus:

- 1.1 - bunkers for charge components; 1.2 – Electric-vibrating cutting machine;
1.3 – batch blending system; 1.4 - charge granulator; 1.5 - oven «SUOL-044 12-M2» for metallization;
1.6 - smelt furnace «RHTC 80 - 230/15 Controller B410»

3. Preparation of cast-iron plates 5.0-8.0 mm.thick.
4. Surface treatment of cast iron plates.
5. Preparation of disperse oxide iron powders.
6. Carrying out a solidphase mass exchange process between the surface of cast iron plates and iron oxide powders. Lab equipment and instrumentation for experimental tests see in figure 1.

For iron smelting, we used iron ore concentrates produced by local MPPs developing Sokolovskoe (SSGPO) and Abayil deposits; charcoal, as a reducing reagent and chemical compositions shown in table 1.

Table 1 – Chemical composition of charge components

Batch component name	Chemical composition, %											
	Fe	FeO	MnO	V ₂ O ₃	SiO ₂	Al ₂ O ₃	CaO	MgO	TiO ₂	S	P	C
Concentrate SSGPO	62,3	18,2	0,18	0,022	4,18	1,12	1,24	0,92	0,24	0,19	0,009	–
Concentrate from the Abayil iron ore deposit	66,56	8,54	2,63	–	5,82	1,24	0,72	–	–	0,02	0,05	–
Charcoal	–	–	–	–	1,56	0,82	–	–	–	0,03	–	94,0

Based on the chemical composition of stated iron ore concentrates, we calculated stoichiometric consumption of charcoal per unit mass of the concentrates, with taking into account a complete reduction of iron and impurity metals and carbonization of metal melt up to 4.2-4.5% C, i.e. pig-iron production. Ore-coal mixtures were prepared by adding a set quantity of charcoal to 1 kg of the concentrate. After additional grinding fractures to size less than 1.0 mm on a pellet granulator we produced ore-coal pellets in 150-200 gr and 8.0-16.0 mm in size. The pellets melting pots were placed into the reaction zone of a tube furnace «SUOL-044 12-M2» for metallization. The batch was heated at a rate of 10°C/min. to 1000-1050°C, keeping this temperature for 25-30 min until the end of complete reduction of iron and partially of impurity metals - manganese, vanadium. After removing a metalized product from furnace it was cooled with no access to air. After cooling the metalized pellets were loaded into refractory pots of a specified shape and put again into a smelt furnace, see figure 2.

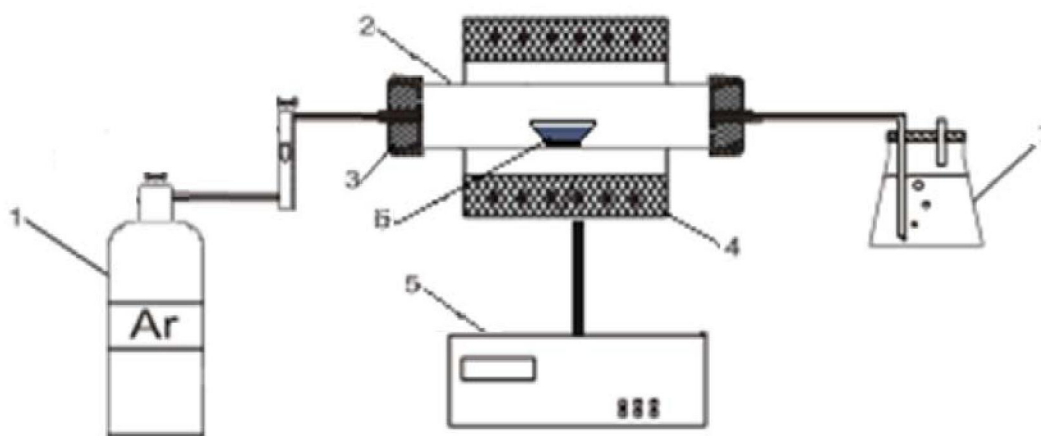


Figure 2 – Scheme installing a hermetic cell and pot in smelt furnace:
 1 – argon cylinder; 2 - waterproof cell; 3- inlet/outlet union; 4 - working zone of smelt furnace;
 5 – thermometer; 6 – boat with metal products; 7 – water bottle

The working space of the cell was kept under the atmosphere of neutral gas, argon, in order to avoid secondary oxidation of metalized granules. The temperature of the system was being raised at a rate of 15°C/min up to 1450-1500°C, the temperature needed for the start of melting metalized granules and production of cast iron melt. The pot location diagram see in figure 2. Since ore bearing pellets were containing a set quantity of solid carbon embedded into its composition for recovery of impurity metals, at the temperature stated above, manganese and vanadium were reduced to cast iron. The cast iron melt was cumulating in the lower part of a rectangular shape crucible/pot. Then the cell with crucible were pulled

out of the furnace. After cooling, hardened layers of slag and cast iron were knocked out of the crucible. Then the cast iron in the form of a rectangular plate was weighed on electronic scales. On processing the surface of cast iron, we produced plate-shaped ingots 5.0-8.0 mm thick, 20 mm wide and 35.0-40.0 mm long. Chemical composition of cast iron plates see in table 2.

Table 2 – Chemical composition of cast iron prototypes

By the number of experiments	Chemical composition, %					
	C	Mn	Si	V	S	P
Experience number 1	4,15	0,17	0,53	0,020	0,035	0,010
Experience number 2	4,20	0,16	0,56	0,021	0,038	0,015
Experience number 3	4,40	2,12	0,67	–	0,025	0,040

The surface of cast-iron plates melted and processed after this method was subject to thermochemical treatment with organization of solid-phase reactions between dissolved carbon and metal oxide powder.

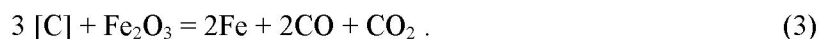


Figure 3 – Microstructure of the section of the original cast iron

Iron oxide was used as oxide powder. It was produced by etching the sheet metal surface at the “ArcelorMittal Temirtau” metallurgical plant. See its chemical composition:

$$\text{Fe}_{\text{о6и}} = 68,6\%; \quad \text{Fe}_2\text{O}_3 = 98,0\%; \quad \text{S} = 0,02\%; \quad \text{P} = 0,03\%.$$

The iron oxide was ground to 0.074 mm size; the surface of cast iron plate was polished, covered with a set quantity of powdered iron oxide and placed in a hermetic lab cell made of a quartz tube. The cell with the stuff inside was placed into the tubular electric heater "RHTC 80-230/15 Controller B410", that was preheated to 500°C. Further, the heating temperature was raised to 1100°C, that resulted in gas reaction released during a process of direct iron recovery with the carbon dissolved in cast iron.



The rate of solid phase reaction was limited by the diffusion regime. Therefore, the system was kept under the said temperature for 50, 60, 90 min. correspondingly according to the order of experiment procedures. After each time-exposure, the cell with the stuff inside was being taken from the oven and cooled to room temperature. The surface of the burnt and thermochemically treated cast iron plates was polished and prepared to make a microstructural analysis of the product. The microstructure of polished section of initial gray iron see in figure 3.

The microstructure of end faces of thermochemically treated cast iron plate, see in figure 4 a), b), c).

The figures clearly show the structure of the initial cast iron plate containing uniformly distributed graphite inclusions. The thermochemically treated cast iron plates figure 4 (a), (b), (c) show that after thermochemical treatment graphite inclusions seen on the edge of the cast iron plates have practically disappeared due to the reaction (3).

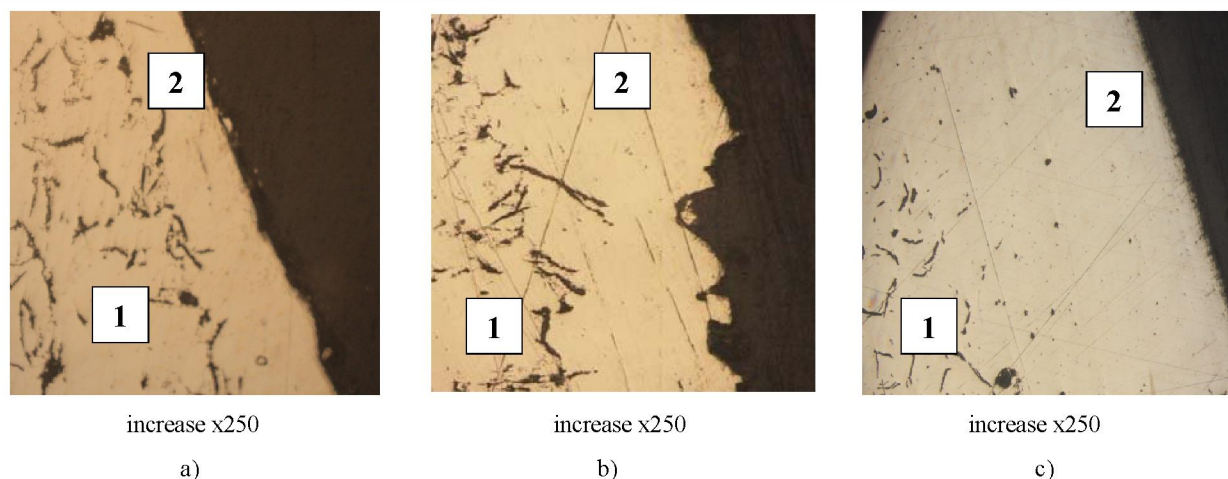


Figure 4 – Microstructure of the end face of thermochemically treated cast iron plate:
 1 - inner layer (cast iron); 2 - outer layer (steel):
 a) at $t = 1100\text{ }^{\circ}\text{C}$, $\tau = 50\text{ мин.}$; b) at $t = 1100\text{ }^{\circ}\text{C}$, $\tau = 60\text{ мин.}$; c) at $t = 1150\text{ }^{\circ}\text{C}$, $\tau = 90\text{ мин.}$

Boundaries between decarburized and non-decarbonized layers are clearly visible. figure 4 a), b), c) show that the thickness of a decarburized layer increases as the calcination temperature rises (figure 4 b, c) and the time exposure at one and the same temperature (figure 4 a, b). The chemical analysis of the selected samples of chips from two opposite plate layers showed that in the decarburized layer the carbon content decreased on average to 0.20-0.35%, while in the non-carbonized layer the carbon content was within 3.20-3, 50%, i.e. there also was taking place a small decrease of carbon concentration due to diffusion transfer of a dissolved carbon from its large concentration section towards the smaller one.

This way of thermochemical treatment of cast iron surface can be used in manufacturing cast iron products of a more complex shape and adding them required mechanical characteristics. The surface thermochemical treatment can be one and two-sided as well depending on working conditions of cast product surfaces. For example, a cast iron tube is a quite common construction. Thermochemical treatment of its outer surface leads to the increase of toughness and weldability while the inner surface of cast iron remains anticorrosive, by that increasing the efficiency of use of processed cast iron tubes in all spheres of industry.

Cast iron smelting and the production of cast manufactures from them is more affordable and low-cost, compared with the steel and steel structures manufacture. The results of experimental tests presented in this paper can be used at making metal products and structures with the use of cast iron and open great perspectives for the development of small and medium-sized businesses.

The conclusion. Our experiment results show that thermochemical treatment of the surface of a cast iron product in a solid-phase state, under the method designed, enables to transform its surface layer into a steel coating. The thickness of steel coating depends on heating temperature and time-exposure applied at processing the system. The increase in steel coating thickness makes the cast iron product more tough and ductile. The organization of a such technological process has good development perspectives and high performance indicators.

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ҚҰЙЫЛҒАН ШОЙЫННЫҢ БЕТКІ ҚАБАТЫН ТЕРМОХИМИЯЛЫҚ ӨНДЕУ АРҚЫЛЫ БОЛАТҚА АЙНАЛДЫРУ

Аннотация. Шойын мен болат өндірісі кешенді екі сатылы: шойынды редукциялап-балқытуға және болатты тотықтандырып балқыту процестеріне негізделген. Бірінші сатының нәтижесінде көміртекті металл алу, ал екінші сатысында керісінше металл көміртексізденеді.

Осы сұлба бойынша балқымадан шойынды көміртексіздендіру бағалы легірлеуші металдардың ауқымды жоғалуына және металдың сапасының, процестің техника-экономикалық тиімділігінің төмендеуіне байланысты. Шойынның жұмысшы бетінде қаптау қабатын құру мақсатында металл тотықтарының ұнтақтарын қаптама және шойында еріген көміртегін редукциялаушы реагент ретінде пайдалану арқылы қаттыфазалы термохимиялық көміртексіздендіріп өндеудің альтернативті процесі ұсынылды. Осы жүйені берілген температураға дейін және белгілі бір уақыт аралығында еріген көміртегімен металды тікелей редукциялап-балқыту нәтижесінде беттік қабаттың көміртексізденеді және құрылымына редукцияланған металл енеді.

Қыздыру температурасына және уақытқа тәуелді түрде шойында берілген тереңдікке дейін болат қабатының қалыптасуының мүмкіндігі анықталды.

Түйін сөздер: металдар, темір, шойын, болат, кен, көмір, көміртек, редукциялап-балқыту, балқыту, кристалдану, көміртексіздену, құрылым.

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ПРЕОБРАЗОВАНИЕ ЧУГУНА В СТАЛЬ ТЕРМОХИМИЧЕСКОЙ ОБРАБОТКИ ПОВЕРХНОСТИ ЛИТОГО ЧУГУНА

Аннотация. Производство чугуна и стали основано на двустадийном последовательном комплексе восстановительной плавки чугуна и окислительной плавки стали. Результатом первой стадии является получение науглероженного металла, а второй стадии – наоборот его обезуглероживание.

Обезуглероживание чугуна из расплава по такой схеме связано со значительными потерями ценных металлов и снижением качества металла и технико-экономической эффективности процесса. Предложен альтернативный процесс обезуглероживания чугуна в твердофазном состоянии термохимической обработкой его рабочей поверхности с использованием металлооксидных порошков в качестве покрытия и растворенного углерода в чугуне в качестве восстановителя. При нагреве такой системы до заданной температуры и времени выдержки получены результаты прямого восстановления металла растворенным углеродом, обезуглероживание поверхностного слоя и внедрение в него восстановленного металла. В зависимости от температуры нагрева и времени выдержки установлена возможность преобразования чугуна в слой стального покрытия на заданную глубину.

Ключевые слова: металлы, железо, чугун, сталь, руда, уголь, углерод, восстановление, плавка, кристаллизация, обезуглероживание, структура.

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