

Досліджено процес десульфурації чавуну магнієм, відновленим за рахунок теплоти екзотермічних реакцій. Проведеними дослідженнями термодинаміки відновлення оксиду магнію за різними схемами встановлено, що відновлення оксиду магнію принципово можливе вуглецем, кремнієм, марганцем, залізом та алюмінієм. Розраховані температури початку відновлення MgO залізом, марганцем, кремнієм, алюмінієм та вуглецем, які відповідно становлять 2956, 2546, 2313, 1585 та 1875 °C. При цьому визначено, що найбільш раціональним методом відновлення оксиду магнію є процес, який базується на зв'язуванні продуктів відновлення у сполуку $CaAl_2O_4$.

Виходячи з встановлених раціональних умов відновлення оксиду магнію, розраховано склад екзотермічної суміші для десульфурації чавуну, %: MgO – 15,0; FeO – 56,0; CaO – 7,0 та Al – 22,0. Експериментальними дослідженнями підтверджено найбільш вдале технічне рішення щодо введення розрахованої екзотермічної суміші у розплав з метою десульфурації, яке передбачає використання пристрою для введення активних реагентів у розплав, що оснащений камерою, яка руйнується під дією теплоти рідкого чавуну. Його використання дозволяє досягти середнього ступеню десульфурації на рівні 65–70 %. В промислових умовах проведено експериментальну десульфурацію хромистого чавуну, розробленою екзотермічною сумішшю. Відповідно до проведених досліджень, отримано ступінь десульфурації чавуну у ковчій на рівні 38 %; за матеріалом відливок – на рівні 45,7 %. Таким чином, є підстави стверджувати про ресурсо- та енергозощадження при застосуванні запропонованої технології позапічної десульфурації чавуну відновленим магнієм.

Ключові слова: позапічна обробка чавуну, десульфурація, оксид магнію, алюмотермія, комплексні оксиди, екзотермічна суміш

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DEVELOPMENT OF THEORETICAL FOUNDATIONS FOR THE HOT METAL DESULFURIZATION WITH MAGNESIUM REDUCED BY THE HEAT FROM EXOTHERMAL TRANSFORMATIONS

L. Molchanov

PhD, Associate Professor*

E-mail: kaf.stal@metal.nmetau.edu.ua

Y. Synehin

PhD, Associate Professor*

E-mail: sinegin.ev@gmail.com

S. Zhuravlova

PhD, Associate Professor*

E-mail: kaf.stal@metal.nmetau.edu.ua

K. Niziaiev

Doctor of Technical Sciences, Professor*

E-mail: metsteel.dmeti@gmail.com

*Department of Steel Metallurgy

National Metallurgical Academy of Ukraine

Gagarina ave., 4, Dnipro, Ukraine, 49600

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1. Introduction

Under current geopolitical conditions, enterprises in the mining and metallurgical sectors operate in a highly competitive environment, which is even much more complicated due to the deficit of resources and raw materials. Particularly acute is the issue to provide industry with quality raw materials. The amount of raw resources that meet the requirements of modern technological processes is very limited because they are almost exhausted. Therefore, at present, given the advancements in science and technology, technological processes tend to become more complicated through the use of poor-quality raw materials.

The basic raw material used for the production of steels is hot metal, whose quality is defined by the content of harmful impurities, specifically sulfur and phosphorus. The utilization of low-quality hot metals in technological processes of steel production (that significantly exceed acting regulations

for sulfur content) leads to complications and increases the cost of final products. A particularly negative impact on the processes of steel production is exerted by sulfur [1, 2]. This is predetermined by the physical-chemical patterns in its removal from melt. Therefore, in world practice, the processes of desulfurization are brought out of a steel-making unit to form a separate stage [3, 4].

There is a significant number of various technologies for the out-of-furnace hot metal desulfurization. According to data from the global experience [5, 6], the best among them is the desulfurization by powdered magnesium. However, using metallic magnesium in the technological process has a series of difficulties related to the conditions for transportation and storage, the complexity of technological equipment, and the high cost of the reagent.

Under such conditions, there remain the relevant issues on devising technologies for the out-of-furnace hot metal desulfurization, which would be distinguished by the simplicity

when implemented in industrial settings and could be based on low cost and low deficient materials.

2. Literature review and problem statement

Papers [7, 8] report findings from studying a hot metal desulfurization process by introducing powdered lime and a simultaneous use of powders based on lime, calcium and magnesium carbide. The authors demonstrated a model of the mono-ejection of $\text{CaO-CaC}_2\text{-Mg}$ reagents, which was determined based on the molar fractions and rate constants of individual powders. However, there were unsolved issues related to the formation of two-calcium silicate 2CaO-SiO_2 during the process of sulfur removal by a given mixture, which prevents further use of CaO for desulfurization. In addition, the effect of lime content in the mixture on the dynamics of desulfurization was not fully addressed. A variant to solve relevant tasks could be the use of magnesium and powdered mixtures based on it. This very approach was considered in studies [9, 10], whose authors investigated the mechanism of hot metal desulfurization by using the Mg and Mg-CaO . However, the authors of [10] found that most magnesium particles react too quickly, thereby producing the MgO oxides at the melt surface, which creates objective difficulties related to the uneven evolution of sulfide MgS and the impossibility for the reaction to occur in metal's bulk. One way to resolve this issue is the introduction of some lime, which forms more favorable kinetic conditions for effective sulfur removal. However, it was found that the ratio of the added CaO and Mg has a strong influence on the kinetic conditions of desulfurization. This ratio needs further investigation.

Paper [11] studied the use of slags based on alumina (Al_2O_3) and marble waste instead of lime. When using marble waste, the reaction of desulfurization progresses favorably due to the increase in liquid phase, but the disadvantage is the enhanced content of MgO , which is introduced along with the waste and negatively intervenes in the process of desulfurization, which makes it inappropriate to use marble wastes as desulfurizers.

The technologies of hot metal desulfurization by powdered magnesium by means of injection to the streams of a carrier gas take the leading role from the point of view of the high degree of desulfurization, which considerably simplifies further processing of hot metal [12, 13]. A mathematical model for an argon bubble, which contains vapors of magnesium in hot metal, is shown in paper [12] in order to interpret the process of desulfurization by introducing granulated magnesium. The model was used to investigate a change in the rate, pressure, size, and content of magnesium vapors in a bubble of gas and the rate of desulfurization, deoxidation and dissolution of magnesium. However, employing metallic magnesium in the technological process significantly increases the cost and energy- and resource-intensity of metallurgical articles due to the high cost of the reagent and additional costs for storage, as evidenced by data from work [14]. In addition, there is a series of issues related to the transportation and storage of magnesium in industrial workshops.

The above allows us to argue that it is expedient to conduct a research that would address the development of basic theoretical principles, structural and technological provisions for the desulfurization of hot metal by magnesium, which is reduced in the melt's volume.

Analysis of data from the scientific literature has revealed known current studies into the use of a finite element analysis for the simulation of physical-chemical processes in the melt of steel and hot metal [15, 16]; those papers, however, mostly explored the processes of crystallization and the formation of chemical heterogeneity in the final melts. This relates to the fact that existing commercially-available finite-element programs are not yet fully able to simulate the course of purely chemical processes. Therefore, it is inappropriate to use the finite element modeling in the work aimed at investigating the process of desulfurization.

3. The aim and objectives of the study

The aim of this study is to devise the theoretical foundations for hot metal desulfurization by magnesium reduced from oxide directly in the melt's volume. This would make it possible to develop basic technological parameters of this process in order to process hot metal under industrial conditions.

To accomplish the aim, the following tasks have been set:

- to establish by a thermodynamic analysis the most rational protocols for magnesium reduction from oxide and the conditions for their implementation;
- to define the rational composition of an exothermic mixture for the implementation of magnesium reduction from oxide in the melt's volume;
- to determine the most technologically expedient technique for hot metal desulfurization in accordance with the proposed technical solution;
- to determine the effectiveness of the processes of hot metal desulfurization by magnesium reduced from oxide in the melt's volume.

4. Procedure for conducting a study into the hot metal desulfurization by magnesium reduced from oxide directly in the melt's volume

Given the complexity of the set goal, it is necessary to undertake a comprehensive research, both theoretical and practical. Within the framework of a theoretical study we conducted the following: a thermodynamic analysis of the magnesium oxide reduction processes by different reagents; establishing patterns in the aluminothermic reduction of magnesium oxides and the optimal composition of an exothermic charge for hot metal desulfurization in the systems Al-MgO-FeO and Al-MgO-FeO-CaO . Thermodynamic study implied determining the influence of temperature and the chemical composition of starting reagents and reaction products on patterns in the reduction course, which was estimated by comparing the Gibbs energy magnitude for the respective equations of chemical transformations. At the same time, the main task was to establish a rational scheme for reducing magnesium oxides, which would ensure the greatest degree of reduction and the lowest temperature of reduction onset.

We calculated the composition of an exothermic mixture for magnesium reduction in the melt's volume based on thermality. Thermality is an indicator that characterizes the calorific value of one mass unit of materials entering the interaction. The total thermality of an exothermic mixture can be calculated from the following expression:

$$q = \frac{\Delta H_{298}^0}{\sum_{i=1}^n M_i}, \quad (1)$$

where M_i is the sum of molecular (atomic) masses of starting substances, taken in stoichiometric ratios, g/mol; ΔH_{298}^0 is the standard enthalpy of a chemical reaction, J/mol. Enthalpy of the chemical reaction of oxide reduction can be determined in accordance with the Hess's law from equation:

$$H_{298}^0 = \sum (\Delta H_{298}^0)_f - \sum (\Delta H_{298}^0)_i, \text{ J/mol}, \quad (2)$$

where $\sum (\Delta H_{298}^0)_f$ is the sum of enthalpies of final reaction products, J/mol; $\sum (\Delta H_{298}^0)_i$ is the sum of enthalpies of starting reaction substances, J/mol.

Experimental study implied determining the most effective composition of an exothermic mixture for liquid hot metal desulfurization, carrying out a comprehensive analysis of technological protocols for introducing active refining reagents to melt aimed at conducting desulfurization. To perform the study, we used hot metal of the following chemical composition, %: C – 4.38; Mn – 0.55; Si – 0.87; S – 0.032 and P – 0.148.

Establishing, under laboratory conditions, the most effective, in terms of desulfurization, composition of an exothermic mixture. It was carried out by treating liquid hot metal and determining the degree of melt desulfurization all other conditions being equal.

We determined the most effective technique for introducing an exothermic mixture to the melt by using a specialized experimental installation whose diagram is shown in Fig. 1.

Hard iron, in the amount of 600 g, was mechanically crushed to a fraction of 10–20 mm and loaded to a graphite crucible ($H=120$ mm, $\varnothing=50$ mm), which was placed inside the working space of a Tamman furnace. The furnace was heated to a temperature of 1,350 °C, upon reaching which we set a stationary heating mode (the heat produced by the graphite heater is used only to compensate for emissions in the environment) and held the crucible with the melt for 15–20 minutes.

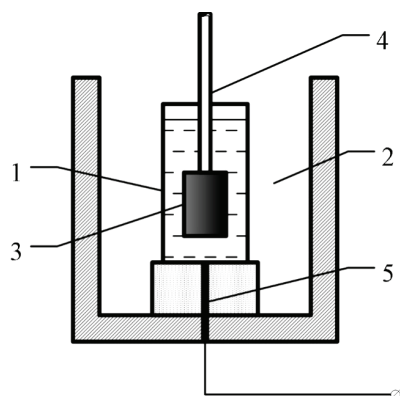


Fig. 1. A diagram of experimental installation used to assess the effectiveness of introducing an exothermic mixture to melt: 1 – graphite crucible with liquid hot metal; 2 – working space of Tamman furnace; 3 – device for introducing exothermic mixture to melt; 4 – bracket; 5 – thermocouple BP-20/BP-5

In the course of our research, the exothermic mixture was loaded for its introduction to device 3, which by means of

bracket 4 was immersed into the volume of liquid hot metal in crucible 1, at half its depth. Completion of treatment was determined visually based on a decrease in the intensity of liquid hot metal boiling. Upon finishing the treatment, crucible was held in the Tamman furnace workspace over 10–15 minutes. Further cooling was conducted in the open air via free heat exchange with the environment. After final cooling, the samples were investigated by X-ray spectral analysis for sulfur content.

According to existing technology, we determined sulfur content at five points: the obtained samples were sawn along the vertical axis – we determined sulfur content at the level of the lower part of the crucible, 25, 50, 75, and 100 % of height from the bottom of the crucible. To compare the effectiveness of different technologies for the introduction of an exothermic mixture to melt, we applied such a parameter as the degree of desulfurization. It can be calculated from the following formula:

$$\delta S = \frac{S_i - S_f}{S_i} \cdot 100, \quad (3)$$

where S_i and S_f are the initial and final sulfur content in melt, %.

In the process of our research, the efficiency of introducing an exothermic mixture to the melt surface was determined, using bell-shaped devices and those that are destroyed by the heat of a metal melt.

To establish reliability of experimental data, we treated liquid hot metal with the devised exothermal mixture at industrial scale. The base selected for our research, under industrial conditions, was a foundry shop equipped with two arc electric furnaces DSP-3A and DSP-3M. In accordance with a standard technology liquid melt from the furnace was sent to a foundry ladle with capacity 2–5 tons.

5. Results from studying the desulfurization of hot metal by magnesium reduced from oxide directly in the melt's volume

5.1. Determining a rational protocol for magnesium reduction from oxide

Magnesium belongs to the group of alkaline earth metals, which are thermodynamically unstable under standard conditions (pressure 1 atm. and temperature 298 K). Given this, under conditions of an Earth atmosphere it exists in the form of chemical compounds (oxides or salts). According to the set task of our study, magnesium is to be obtained by direct reduction from oxide in the melt, therefore, it is necessary to assess efficiency of the process of its reduction by different reducers. The following substances are proposed as the reducing agents: aluminum, silicon, carbon, manganese, and iron. To run a thermodynamic analysis, we shall consider the oxidation reactions of magnesium, aluminum, silicon, carbon, manganese, and iron. A change in the values of Gibbs energy for them taking into consideration the phase transformations are given in Table 1.

Dependence of the Gibbs energy value for reactions of oxidation of elements on temperature is shown in Fig. 2. In accordance with data shown in it the overlapping curves testify to the possibility, in principle, to reduce the oxides of magnesium by aluminum, silicon, manganese, iron, and carbon. Based on the graphical dependence, it is possible to establish that the start temperature for reducing a magnesium oxide by aluminum, silicon, manganese, iron, and carbon, is 1,585, 2,313, 2,546, 2,956 and 1,875 °C, respectively.

Table 1

Standard Gibbs energy equation for the reactions to form magnesium, aluminum, silicon, carbon, manganese, and iron oxides, considering phase transformations

| No. of entry | Reaction | ΔG_T° , J/mol·O ₂ | ΔT , K |
|--------------|--|---|----------------|
| 1 | $2\langle\text{Mg}\rangle + \{\text{O}_2\} = 2\langle\text{MgO}\rangle$ | $-1206766 - 24.66 \cdot T \cdot \lg T + 283.82 \cdot T$ | 298–923 |
| 2 | $2(\text{Mg}) + \{\text{O}_2\} = 2\langle\text{MgO}\rangle$ | $-1215126 - 2,006 \cdot T \cdot \lg T + 225.3 \cdot T$ | 923–1380 |
| 3 | $2\{\text{Mg}\} + \{\text{O}_2\} = 2\langle\text{MgO}\rangle$ | $-1518176 - 61.61 \cdot T \cdot \lg T + 632.85 \cdot T$ | 1380–2500 |
| 4 | $\langle\text{Si}\rangle + \{\text{O}_2\} = \langle\text{SiO}_2\rangle$ | $-901208 + 173.47 \cdot T$ | 298–1700 |
| 5 | $(\text{Si}) + \{\text{O}_2\} = \langle\text{SiO}_2\rangle$ | $-951786 + 203.57 \cdot T$ | 1700–2000 |
| 6 | $4/3\langle\text{Al}\rangle + \{\text{O}_2\} = 2/3\langle\text{Al}_2\text{O}_3\rangle$ | $-1116924 - 11.09 \cdot T \cdot \lg T + 244.22 \cdot T$ | 298–923 |
| 7 | $4/3(\text{Al}) + \{\text{O}_2\} = 2/3\langle\text{Al}_2\text{O}_3\rangle$ | $-1130718 - 10.45 \cdot T \cdot \lg T + 256.99 \cdot T$ | 923–1800 |
| 8 | $2\langle\text{Fe}\rangle + \{\text{O}_2\} = 2\langle\text{FeO}\rangle$ | $-529272 + 130.58 \cdot T$ | 298–1642 |
| 9 | $2(\text{Fe}) + \{\text{O}_2\} = 2\langle\text{FeO}\rangle$ | $-464983 + 90.54 \cdot T$ | 1808–2000 |
| 10 | $2\langle\text{Mn}\rangle + \{\text{O}_2\} = 2\langle\text{MnO}\rangle$ | $-768702 + 145.46 \cdot T$ | 298–1500 |
| 11 | $2(\text{Mn}) + \{\text{O}_2\} = 2\langle\text{MnO}\rangle$ | $-797544 + 164.69 \cdot T$ | 1500–2050 |
| 12 | $2\langle\text{C}\rangle + \{\text{O}_2\} = 2\langle\text{CO}\rangle$ | $-223600 - 175 \cdot T$ | 298–2000 |

Note: $\langle \rangle$ – solid state of matter; $()$ – liquid state of matter; $\{ \}$ – gaseous state of matter

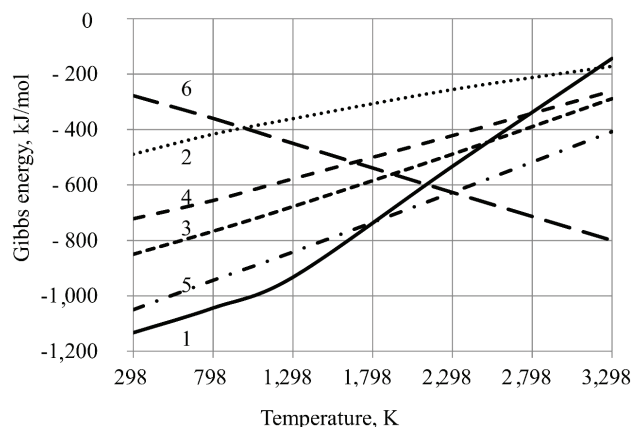
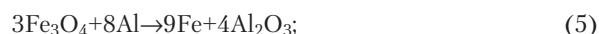


Fig. 2. ΔG – T diagrams of oxide formation:
1 – magnesium; 2 – iron; 3 – silicon; 4 – manganese;
5 – aluminum; 6 – carbon

It was established that in order to use iron and manganese as a reducer, the temperature of reduction onset increases by 643.6 and 233.5 °C, respectively, compared with the use of silicon. That is, the reduction of magnesium oxide by iron and manganese would be accompanied by much greater consumption of heat than when using aluminum, silicon, and carbon, which is impractical under industrial conditions.

Within the framework of the current study, it was proposed in order to compensate for the heat deficit in the process of magnesium oxide reduction to use heat from the parallel exothermic reactions of aluminothermal reduction of metal oxides. The most appropriate source of heat during the reduction of magnesium oxide from oxide directly in the volume of an iron carbon melt is the aluminothermal processes of reducing the oxides of vanadium, molybdenum (IV), tungsten, and iron, due to the significant heat release. Since tungsten, molybdenum, and vanadium belong to a group of alloying elements, which are distinguished by high cost, their utilization in our case is impractical. To implement the process of magnesium oxide reduction directly in the volume of a metal melt, the most probable heat source is the

reactions of aluminothermal reduction of iron oxides, which proceed according to the following reactions:



Taking into consideration that the most common in the industry are the oxides of iron (II) and (III), subsequent calculations were performed directly for the cases of their simultaneous and separate reduction. Since the maximum temperature in the front of the process specified above is 2,500 °C, then, under these conditions, it is possible to reduce magnesium oxide by silicon, carbon, and aluminum. We shall consider each process in more detail.

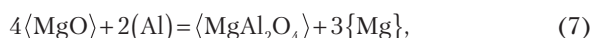
The use of carbon as a magnesium oxide reducer is almost impossible in industrial settings. Since the reduction of magnesium oxides is planned to be carried out under a layer of a liquid metal melt (under elevated pressure and limited volume), using carbon as a reducing agent is unlikely. This is due to the high probability of oxidation of vapors of metals reduced by carbon monoxide in the process of decreasing their temperature when interacting with the iron carbon melt. Separation of products final from the reaction is almost impossible under such conditions of reduction.

Given that the temperature for starting the magnesium reduction is much higher compared with the temperature for starting the process that forms gaseous silicon monoxide, there is a very high thermodynamic probability for this process to occur in the presence of silicon and its oxide. Considering this, there is a probability to reduce the efficiency of magnesium oxide reduction, as well as the high likelihood of oxidation of vapors from the reduced metal by silicon monoxide at decreasing temperature, due to their interaction with the iron carbon melt. Therefore, in order to implement the silicothermal magnesium oxide reduction under a layer of a liquid metal, it is necessary to ensure the separation of gaseous silicon monoxide and magnesium fumes. The set task is accomplished by lowering the onset temperature of

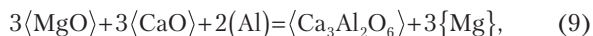
magnesium oxide reduction reaction and by increasing the temperature for starting the reaction of silicon monoxide formation. Industrial implementation of silicothermal reduction of alkaline earth metal oxides should be carried out under low pressure (vacuum). Since there is an excess pressure under the layer of a liquid metal, it is practically impossible to implement the process of silicothermal reduction of magnesium oxide in accordance with an industrial technology. The use of silicon as a magnesium oxide reducer requires significant complication of the technology and the introduction of additional materials for binding silicon monoxide.

Using aluminum as a reducer has a series of advantages, the main of which is a significant reduction in the starting temperature of reduction in comparison with other reducing agents, as well as the condensed state of aluminum oxides. At temperatures below 3,000 K for the Al–O system, all oxide compounds exist in a condensed state. The process of aluminothermal reduction leads to the formation of aluminum oxide, which intensively enters the interaction with oxides of alkaline earth metals, thereby forming complex oxide compounds. All this prevents aluminothermal reduction of oxides. Thus, in order to overcome existing situation, it is necessary to bind aluminum oxide in the complex oxide compounds and remove from the alkaline earth metal reduction zone. In order to find stable complex oxide compounds, the following oxide systems were analyzed: $\text{CaO}-\text{Al}_2\text{O}_3$ and $\text{MgO}-\text{Al}_2\text{O}_3$. They revealed the following compounds: $\text{Ca}_3\text{Al}_2\text{O}_6$, $\text{Ca}_5\text{Al}_6\text{O}_{14}$, $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, CaAl_2O_4 , CaAl_4O_7 , $\text{CaAl}_{12}\text{O}_{19}$ and MgAl_2O_4 . The thermodynamic characteristics of these complex oxide compounds were used for calculations. Taking into consideration the stability of complex oxide compounds and the conditions of reaction progress (the volume of liquid hot metal is a neutral-reducing environment), subsequent analysis involved compounds designated by CaAl_2O_4 , $\text{Ca}_3\text{Al}_2\text{O}_6$ and MgAl_2O_4 .

Consider in more detail the chemical reactions of aluminothermal reduction of magnesium oxides, which take the following form:



Adding calcium oxide may enable the aluminothermal reduction of magnesium according to the following reactions:



To compare the likelihood of reactions (7) to (10), a $G-T$ diagram was built (Fig. 3). Formation of complex oxides in the process of aluminothermal reduction of magnesium oxide contributes to reducing the temperature for starting a reduction process.

Based on our research, it was found that aluminothermia is the most appropriate method to reduce magnesium oxides directly in the volume of the liquid metal melt. The best technology to improve the conditions for its progress is the technology that implies binding the reaction products (aluminum oxide) into complex oxide compounds.

Our thermodynamic analysis of the progress of chemical reactions for magnesium oxide reduction has shown

that it is preferable to conduct the process in accordance with the protocol implying the formation of complex oxide compounds, and to use aluminum as a reducer. However, in this case, the mass of the starting charge increases, which could lead to a significant increase in heat consumption on its heating.

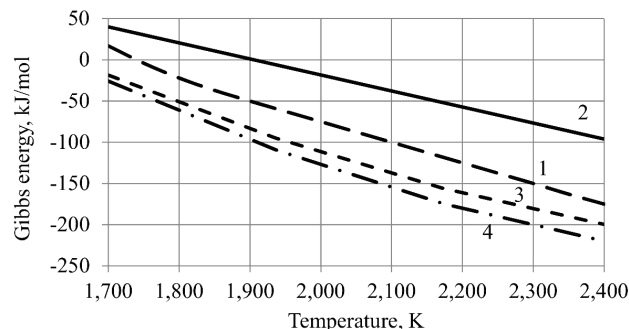


Fig. 3. $G-T$ diagram for reactions of aluminothermal reduction of magnesium oxides: 1 – reaction (7); 2 – reaction (8); 3 – reaction (9); 4 – reaction (10)

5. 2. Determining the rational composition of an exothermic mixture

To determine the ratio of magnesium to calcium oxides in the composition of the exothermic mixture, we applied equations (7), (9) and (10). The heat sources considered were the reactions of aluminothermal reduction of iron oxides (II). Calculation of the exothermic mixture components' ratio was conducted taking into consideration a «Zhemchuzhnyy rule», whereby thermality of the devised composition of the mixture did not exceed 2,500 kJ/kg. Results from calculating various compositions of the exothermic mixture for reduction of magnesium from oxide directly in the volume of a metal melt, at the expense of the heat from parallel chemical reactions, are given in Table 2.

Table 2

The composition and thermality of the starting mixture to reduce magnesium from oxide directly in the volume of a metal melt at the expense of the heat from compatible chemical reactions

| No. of entry | No. of reaction | Composition of exothermic mixture, % | | | | Thermality, J/g |
|--------------|-----------------|--------------------------------------|-------|-------|-------|-----------------|
| | | FeO | MgO | Al | CaO | |
| 1 | 7 | 63.00 | 15.00 | 22.00 | – | 2,500 |
| 2 | 9 | 51.00 | 13.00 | 18.00 | 18.00 | 2,500 |
| 3 | 10 | 56.00 | 15.00 | 22.00 | 7.00 | 2,500 |

5. 3. Determining the most technologically expedient technique for hot metal desulfurization

At the first stage of experimental introduction of the exothermic mixture to the melt we used devices equipped with bell-shaped evaporating chambers. First, we introduced the exothermic mixture to the melt using a special device with a cylindrical evaporating chamber, equipped with eight holes. The designed device was made from steel 36CrNiMo₄ (DIN EN 10297-1). It had the following structural features: a cylinder-shaped evaporating chamber with a diameter of 25 mm and a height of 30 mm; eight holes of 4 mm diameter

were made in the chamber for the removal to the melt of an active reagent. Distance from the end of the free edge of the evaporating chamber to the axis of the hole in the lower row was 6 mm; between the axes of the holes in the upper and lower rows – 10 mm. We used the device, equipped with a cylindrical evaporating chamber with eight round holes with a diameter of 4 mm, to introduce the exothermic mixture to the melt in the following way: we placed, inside the evaporating chamber, the specified amount of the exothermic mixture in a paper bag and compacted it; by using a special experimental installation the evaporating chamber was taken to the melt. The use of a given device was due to a significant splash formation, which in turn resulted in a decrease in the degree of melt desulfurization in general. The mean degree of desulfurization was 49.2 ± 5.7 %.

Splash formation was caused by a very intense transition of magnesium vapors to the melt. Such a state was due to the significant total area of the holes in the evaporating chamber, which is why, to overcome this problem, in the next experiment it was proposed to reduce the number of holes in the evaporating chamber to three. Structurally, the proposed device differs from the preceding one only in that its evaporating chamber is equipped with three holes with a diameter of 4 mm each, which are located on a spiral helical line with a speed of 10 mm, and the angle between the axes of the holes is 120° . The technology of introducing an exothermic mixture to the volume of liquid hot metal was similar to the previous case. The significant disadvantages of the device considered include incomplete transition of magnesium vapors to the melt from the evaporating chamber. Thus, in the treatment according to this technology, a certain part of magnesium vapors remains in the volume of the evaporating chamber and does not interact with the liquid hot metal. When one removes the device from the volume of the liquid hot metal, there is a contact between magnesium vapors and the oxidizing environment of air causing their oxidation. During the experiments, that led to the occurrence of a flash at the moment when the device was removed. The average degree of desulfurization when applying the device for the introduction of an exothermic mixture to the melt, equipped with a cylindrical evaporating chamber with three holes, amounted to 51.3 ± 7.2 %.

To improve the technology of introducing an exothermic mixture to liquid hot metal, it was proposed to change the shape of holes in the evaporating chamber to the slit-type. This makes it possible to increase the contact surface between the fumes from an active reagent and melt by reducing the size of bubbles. Structurally, the proposed devices differ from the preceding ones by the shape of holes openings in the evaporating chamber. Thus, in a first case, twelve longitudinal holes (2 mm wide each) are used, located in parallel to the vertical axis of the device, and, in a second case, sixteen slit-sectional holes (2 mm wide and a with a sector angle of 140° each) located perpendicularly to the vertical axis of the device. The technology of introducing an exothermic mixture to the volume of liquid hot metal was similar to the previous case. The use of devices designed as specified above could significantly reduce the pyro-effect during treatment, but it does not make it possible to achieve the full utilization of an active reagent. A feature of using the device for the introduction of an exothermic mixture to the melt with a cylindrical evaporating chamber and slit-like holes located perpendicular to the vertical axis of the device was that we observed, in the

hole location zone, a significant local destruction that led to an increase in the rate of magnesium transition to the melt, which is accompanied by more intense bath boiling, splash formation and a pyro-effect. The mean degree of desulfurization when applying devices with a cylindrical evaporating chamber, equipped with slit-like holes located in parallel to the vertical axis of the device, amounted to 64.5 ± 5.0 %, and for the case of a similar device with slit holes located perpendicularly to the vertical axis of the device – 64.8 ± 7.6 %.

The next stage of our study was to test the effectiveness of using, for the introduction of an exothermic mixture to the melt, those devices that are destroyed by the heat from a liquid metal melt. Initially, we applied the device for the introduction of active reagents to the melt, which is destroyed under the influence of the melt heat. The device's shape was close to a parallelepiped. In general, the designed device consists of a bracket and a chamber to add reagents, which are connected by a detachable pin. Structurally, the bracket is made from heat-resistant steel 36CrNiMo₄ (DIN EN 10297-1), the chamber to introduce reagents – from black tin, 0.2 mm thick. Under the action of heat from liquid hot metal, the chamber for introducing the exothermic mixture is destroyed, which leads to its direct contact with the liquid hot metal, which triggers magnesium reduction reactions. Reduced magnesium evaporates and participates in melt refining. Applying the designed device makes it possible to achieve the mean level of desulfurization of 65.2 ± 4.1 %, it has, however, a series of disadvantages among which the most significant is a considerable complexity of the device production process.

Generalized results from experimental determination of effectiveness of the devised technological operations for introducing an exothermic mixture to melt are given in Table 3.

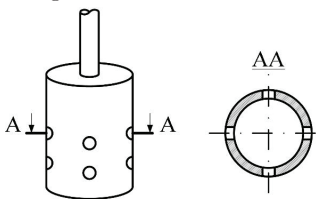
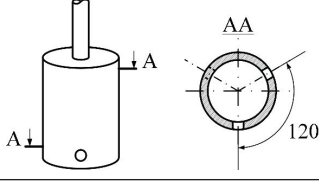
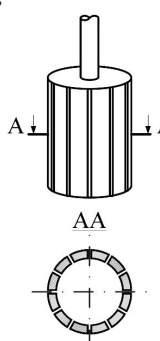
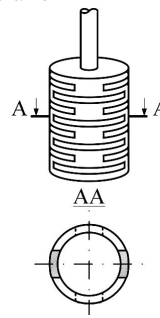
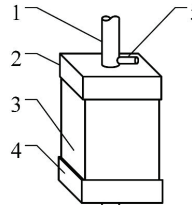
Our study has determined that the most technological method for introducing an exothermic mixture to the melt is the use of devices that are destroyed by the heat from a liquid melt; that makes it possible to achieve the highest technological results.

In the course of earlier studies, a series of variants for the composition of an exothermic mixture for reducing magnesium directly in the volume of a liquid metal melt have been developed (Table 2), which have close thermality and differ by the content of calcium oxide. Since it is practically unknown which of the mixtures is best for the process of desulfurization of liquid hot metal, we experimentally determined the best composition for an exothermic mixture for reducing magnesium oxide directly in the volume of a metal melt. This experiment involved a device to introduce active reagents to the melt whose design is specified in Table 3 under No. 5. The methodology of the research was similar to the case where we determined the rational structure of the device for the introduction of active reagents to the melt.

The results of our studies have made it possible to establish that the best technological performance was obtained when using a mixture No. 3 (Table 2). Thus, its application enabled achieving the mean degree of melt desulfurization at the level of 70.2 ± 3.9 % versus 67.2 ± 3.1 % and 65.9 ± 2.9 %, respectively, when using mixtures No. 1 and 2. Thus, it is most appropriate, under industrial conditions, in order to reduce magnesium oxide directly in the melt's volume to use the exothermic mixture, which is calculated taking into consideration the formation of CaAl₂O₄.

Table 3

Results of treating liquid hot metal with an exothermic mixture using the designed devices*

| No. of entry | Variant of treatment and design of device for introducing exothermic mixture | n , pcs. | M_i , g | M_m , g | Sulfur content in hot metal, % | | ΔS , % |
|--------------|--|------------|-----------|-----------|--------------------------------|---------------|----------------|
| | | | | | S_i | S_f | |
| 1 | Introduction of exothermic mixture to melt using device equipped with a cylindrical evaporating chamber with 8 round holes of 4 mm in diameter  | 3 | 600 | 12 | 0.032 | 0.0163±0.0009 | 49.2±2.17 |
| 2 | Introduction of exothermic mixture to melt using device equipped with a cylindrical evaporating chamber with 3 round holes of 4 mm in diameter  | 3 | 600 | 12 | 0.032 | 0.0156±0.0013 | 51.3±4.2 |
| 3 | Introduction of exothermic mixture to melt using device equipped with a cylindrical evaporating chamber with slit-like holes located in parallel to the device's vertical axis  | 3 | 600 | 12 | 0.032 | 0.0114±0.0009 | 64.5±2.9 |
| 4 | Introduction of exothermic mixture to melt using device equipped with a cylindrical evaporating chamber with slit-like holes located perpendicularly to the device's vertical axis  | 3 | 600 | 12 | 0.032 | 0.0109±0.0011 | 64.8±4.4 |
| 5 | Introduction of active reagents to melt by using device that is destroyed by heat from a liquid melt: 1 – bracket; 2 – upper stub; 3 – limiter; 4 – bottom stub; 5 – retainer studs  | 3 | 600 | 12 | 0.032 | 0.0111±0.0007 | 65.2±2.4 |

Note: * – numerator shows means, denominator – ranges of values; n – number of experiments; M_i and M_m – mass of hot metal and exothermic mixture; S_i and S_f – sulfur content in hot metal before treatment and at the end; ΔS – degree of desulfurization

5. 4. Evaluating effectiveness of the proposed technology

When conducting an industrial study, hot metal was melted in the arc steel-making furnace DSP-3M. The weight of smelting was 4 t. Its production was carried out consistently in two ladles, with a capacity of 2 tons each. Treatment involved the exothermic mixture whose composition was calculated taking into consideration the formation of the complex compound CaAl_2O_4 . In the course of our study, it was proposed to use, instead of magnesium oxide, the magnesite powder PPE-88, instead of calcium oxide – metallurgical lime, grade IC-1, instead of iron oxides – rolled scale, instead of aluminum – waste from machining aluminum alloys that contains metallic aluminum in the amount not less than 85 %. In this case, the composition of the exothermic mixture used for the desulfurization of hot metal under industrial conditions was as follows: rolled scale – 62 %; magnesite powder PES-88 – 13 %; metallurgical lime, grade IC-1, 6 %; waste from machining aluminum alloys – 19 %. To make the exothermic mixture, we used the components of fractional composition <5 mm, which, in the specified proportion, were averaged and packed in plastic bags, weighing 10 kg each.

Foundry ladles were heated to a temperature of 880–900 °C before melt release using a gas burner, after which they were installed in the pit followed by smelting release. When a first ladle in the series was being filled, the sample of metal was taken. A control metal sample was taken in the middle of pouring the melt from a ladle to castings. Given that the enterprise uses foundry ladles with a capacity of 2 tons (its filling time was about 2.5 min.), the introduction of the exothermic mixture was carried out in a powdered form in the amount of 10 kg/t of hot metal (a total of 20 kg/ladle).

The progress of liquid hot metal treatment with the exothermal mixture was monitored visually and recorded by means of photo and video equipment. Photographs of the treatment process are shown in Fig. 4. In accordance with it, the exothermic mixture, contained in a ladle, begins to interact with the melt, before release of smelting, at the first stages of the introduction. When a ladle is filled to 25 % of the height there emerges a significant surface area of contact between the exothermal mixture and melt, which leads to an intense progress of reduction processes, accompanied by a certain pyro-effect (Fig. 4, *b*). When a ladle is filled to 50 % of the height, in accordance with the devised protocol, a second batch of the exothermic mixture was introduced. At the same time, there was a certain pyro-effect in the form of sparks, which originated from the volume of the ladle and a bright flash, which is the evidence of the intensive progress of aluminothermic reduction processes of metal oxides (Fig. 4, *c*).

When a ladle was filled to 75 % of the height, the surface of the liquid hot metal displayed a significant pyro-effect and the formation of white smoke, which is an indirect evidence of the progress of oxidation processes of reduced magnesium to oxide (Fig. 4, *d*). When the ladle was full, the pyro-effect at the surface of the melt disappeared, as the entire introduced exothermic mixture had reacted (Fig. 4, *e*). According to a standard technology, after filling the ladle, a special flux

was added to the surface of hot metal in order to thicken the slag (this reduces the probability of slag entering the body of the casting). After filling the ladle, it was aged for 4 minutes, followed by pouring the hot metal to sand-clay molds. The chemical composition was controlled at the following links within the technological cycle: at the stage of smelting release to a ladle, during pouring of a half ladle and directly in molds. Results of chemical composition control are given in Table 4.



Fig. 4. Photographs of the process of treating liquid hot metal with the devised exothermic mixture: *a* – melting release onset; *b* – filling 25 % of ladle height; *c* – filling 50 % of ladle height; *d* – filling 75 % of ladle height; *e* – end of filling a first ladle; *f* – introduction of sand to the surface of the melt for slag thickening

Table 4

Results of hot metal chemical composition control*

| No. of entry | Sample | Component content, % | | | | | |
|--------------|----------------|----------------------|-----------|-----------|-------------|---------------|-----------|
| | | C | Si | Mn | P | S | Cr |
| 1 | from a furnace | 3.31 | 1.40 | 0.94 | 0.161 | 0.1400 | 2.84 |
| 2 | from a ladle | 3.18 | 1.40 | 0.81 | 0.161 | 0.0868 | 2.35 |
| 3 | from castings | 3.14 | 1.77 | 0.93 | 0.141 | 0.0760 | 2.84 |
| | | 3.26–3.15 | 1.38–1.82 | 0.80–0.95 | 0.140–0.163 | 0.0900–0.0721 | 2.85–2.31 |

Note: * – numerator shows the mean value; denominator – range of values

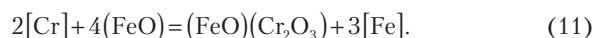
According to data given in Table 4, the devised technology for desulfurization of liquid hot metal with an exothermic mixture, which contains magnesium oxide, showed the degree of melt desulfurization in a ladle at the level of 38.0 %, and the mean degree of hot metal desulfurization based on the material of castings – at the level of 45.7 %. At the same time, a decrease in the temperature of hot metal during the release from a furnace treated with the mixture amounted to

14 °C against 20±4.7 °C without treatment. We measured temperature in the furnace before release, and immediately after filling the ladle, by the immersion thermocouple PR-30/6 with a relative error of ±3 °C.

6. Discussion of results of studying the out-of-furnace hot metal desulfurization by magnesium

The liquation of hot metal elements in ladles and castings (Table 4) is caused by, first of all, the insufficient time of hot metal aging before pouring. Thus, in our experimental study, the aging of hot metal in a ladle lasted about 4 minutes, which does not meet the aging time of at least 7 minutes required for ladles whose capacity is less than 10 t.

A certain decline in the degree of desulfurization as compared to planned is caused by the presence of chromium in the composition of hot metal. Its presence increases the viscosity of melt, which worsens the conditions for mixing an exothermic mixture with the melt, as well as the processes of magnesium mass transfer. In addition, it should be noted that the composition of the exothermic mixture includes iron oxides, which, in the interaction with chromium, lead to the formation of iron chromite according to the following equation:



Under such a course of events, a certain part of the iron oxides included in the composition of the exothermic mixture is spent to form complex compounds with chromium oxides, which results in the decreased efficiency of reduction processes in general and leads to deterioration of processes of refining melt with magnesium.

Based on our study in industrial setting, it was determined that it is possible, when using an exothermic mixture containing magnesium oxide for the desulfurization of chromium hot metal, to reach the degree of desulfurization at the level of 35–40 %; however, implementing the devised technology for refining hot metal requires additional processing of the melt treatment regimes in order to reduce the liquation of chemical elements in the melt's volume.

7. Conclusions

1. We have performed a thermodynamic analysis of magnesium oxide reduction processes according to various protocols with the use of different reducers. The advantages and disadvantages of each process have been determined. Based on our calculations, it was determined that it is in principle possible to reduce magnesium oxide with carbon, silicon, manganese, iron, and aluminum. However, when using iron and manganese as a reducer, the temperature of reduction start is increased by 644 and 234 °C, respectively, in comparison with the use of silicon. The data from our theoretical study allowed us to establish that in order to reduce magnesium oxides the most likely candidate to be a heat source is the processes of aluminothermal reduction of iron oxides, namely the oxides of iron (II) and (III).

2. We have calculated a series of exothermic mixtures for magnesium reduction from oxide directly in the volume of a metal melt at the expense of heat from parallel exothermic chemical reactions. Experimental desulfurization of chromium hot metal with the devised exothermic mixture was performed under industrial conditions. Based on our study, the obtained degree of hot metal desulfurization in a ladle is at the level of 38 %; based on the material of castings – at the level of 45.7 %.

3. The most successful technical solution has been defined for the introduction of an exothermic mixture to melt aimed at desulfurization, which implies the use of devices for introducing active reagents to melt, which is equipped with a chamber that is destroyed by the heat from liquid hot metal. Its application makes it possible to achieve the mean degree of desulfurization of 65–70 %.

4. It has been established by experimental treatment of liquid hot metal under laboratory conditions that the best results in terms of desulfurization are achieved when using an exothermic mixture of the following chemical composition, %: MgO – 15.0; FeO – 56.0; CaO – 7.0 and Al – 22.0. Its application makes it possible to reach the overall degree of hot metal desulfurization at the level of 65–70 %.

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