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Physico-chemical justification and experimental verification of a waste-free method of oxidative dephosphorization of a high-phosphorus manganese alloy

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Фізико-хімічне обґрунтування та експериментальна перевірка безвідходного способу окисної дефосфорації високофосфористого марганцевого сплаву

Мета дослідження: фізико-хімічне обґрунтування умов процесу та розробка раціонального алгоритмуодностадійногобезвідходного способу окисного дефосфорування високофосфористого марганцевого сплаву. Методи: термодинамічний аналіз основних реакцій при окислювальному рафінуванні марганцевих сплавів з високим вмістом фосфору. Експериментальна перевірка основних стадій рафінування. Результати: Розглянуто фізико-хімічну сутність процесу рафінування високофосфористого марганцевого сплаву, який полягає у створенні умов для окиснення в сплаві марганцю, вуглецю та кремнію. Термодинамічний прогноз перебігу реакцій за заданих умов окисного рафінування супутнього металу підтверджує можливість отримання трьох продуктів: малофосфористого марганцевого шлаку, залізного розплаву та фосфоровмісного шлаку з вмістом оксиду фосфору 18-20 %. (фосфорне добриво). Наукова новизна: За результатами високотемпературного математичного моделювання встановлено, що найбільш раціональне споживання кисню, яке забезпечує досягнення поставлених завдань, становить ~ 13 $м^3$. В якості окислювача доцільно використовувати кисень, що надувається повітрям, який вводять у ванну конвертера за допомогою надувного сопла зверху. При цьому загальна витрата повітря на 100 кг сплаву повинна бути близько 50 $м^3$. Практична цінність: У роботі на основі термодинамічного прогнозу поведінки елементів супутнього сплаву в окисних умовах, оцінки термічної сторони процесу та подальшої експериментальної перевірки отримано результати, які підтверджують можливість створення безвідходної технологічної схеми рафінування високофосфористого сплаву. У цьому випадку рафінування сплаву доцільно проводити в умовах, наближених до умов сучасного виробництва малофосфористих марганцевих шлаків, при якому температура супутнього сплаву становить 1320...1350°С.

***Ключові слова:** електрометалургійне дефосфорування марганцевого концентрату, малофосфорний марганцевий шлак, високофосфорна марганцева лігатура, кисень, повітря, кисневий конвертер, продування.*

The purpose of the study: physicochemical justification of the process conditions and development of a rational algorithm for a single-stage waste-free method of oxidative dephosphorization of a high-phosphorus manganese alloy. Methods: thermodynamic analysis of the main reactions during oxidative refining of manganese alloys with a high phosphorus content. Experimental verification of the main stages of refining. Results: The physicochemical essence of the refining process of a high-phosphorus manganese alloy, which consists in creating conditions for oxidation in the alloy of manganese, carbon and silicon, is considered. The thermodynamic forecast of the course of reactions under the given conditions of oxidative refining of the associated metal confirms the possibility of obtaining three products: low-phosphorus manganese slag, ferric melt and phosphorus-containing slag with a phosphorus oxide content of 18-20% (phosphorus fertilizer). Scientific novelty: Based on the results of high-temperature mathematical modeling, it was established that the most rational oxygen consumption, which ensures the achievement of the tasks, is ~ 13 m^3. As an oxidant, it is advisable to use oxygen blown by air, which is introduced into the converter bath using an inflatable nozzle from above. In this case, the total air consumption per 100 kg of alloy should be about 50 m^3. Practical value: In the work, based on the thermodynamic forecast of the behavior of the elements of the accompanying alloy in oxidizing conditions, assessment of the thermal side of the process and further experimental verification, results were obtained that confirm the possibility of creating a waste-free technological scheme for refining a high-phosphorus alloy. In this case, it is advisable to carry out the refining of the alloy in conditions close to the conditions of modern production of low-phosphorus manganese slag, in which the temperature of the accompanying alloy is 1320...1350°C.

***Keywords:** electrometallurgical dephosphorization of manganese concentrate, low-phosphorus manganese slag, high-phosphorus manganese ligature, oxygen, air, oxygen converter, blowing.*

Introduction

Manganese ferroalloys are widely used in the smelting of steel and alloys, mainly in the form of ferromanganese and ferrosilicomanganese. When ferromanganese is smelted in ore reduction furnaces, ferromanganese brands and phosphorous slag are obtained. The main component of the charge in the smelting of manganese alloys is low-phosphorus slag, which is obtained from manganese concentrates in ore reduction furnaces by selective reduction of elements. From a thermodynamic point of view, phosphorus has a lower affinity for oxygen than manganese. This feature is used for the carbon reduction of phosphoric anhydride coke, iron oxides, all higher manganese oxides, as well as 5-10% manganese oxide to metallic manganese with the production of low phosphorus

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manganese slag and a small amount of metallic phase based on manganese, iron, silicon, phosphorus and carbon. At the same time, almost all manganese oxide and silica turn into slag. The established features of dephosphorization of manganese-based alloys can be used to justify a rational technological scheme and establish an effective algorithm for refining the accompanying high-phosphorus manganese alloy from phosphorus.

Such an alloy with a high phosphorus content is a waste of the existing method of producing low phosphorus manganese slag. The alloy has the following chemical composition, %: Mn - 64.6; Si - 0.75; C - 5.8; P - 1.37; Fe is the rest. The output of the accompanying alloy when smelting 1 ton of slag is about 96 kg. At the same time, up to 50 kg of manganese is lost for every ton of phosphorous slag, which leads to the accumulation of manganese waste with a high phosphorus content, which has limited use. the possibility of its use in justifying the conditions of oxidative refining, taking into account the different chemical affinity of the alloy elements (Mn, P, Si, C, Fe) to oxygen. At the same time, the final goal can be not only the production of commercial ferromanganese and slag with a high phosphorus content [1], but also the creation of a waste-free technology with the production of two products of different functional purposes - slag and metal.

Analysis of the features of the physical and chemical interaction of the elements of the accompanying manganese alloy in the conditions of oxidative refining.

The thermodynamic forecast of the course of the process of refining manganese alloy from phosphorus and other impurities, as well as the results of experimental verification, indicate the impossibility of increasing the efficiency of the process, in our opinion, without creating special conditions for its intensification. An increase in process indicators can be achieved by carrying out oxidative refining of the alloy by blowing it with a gaseous oxidizer. At the same time, the negative effect, which will manifest itself in a significant increase in the temperature of metal and slag, must be transformed into the advantages of the process, for example, by using melting coolants (gaseous, solid or liquid), the amount and composition of which will not decrease, but when certain refining conditions are created, will increase metallurgical value of refining products.

The choice of parameters of oxidative refining of the alloy, which will determine the features, mechanism and course of dephosphorization, depends not only on the initial composition of the alloy and slag-forming agents, but also on the new properties that the system acquires under the influence of external factors. The parameters of these effects on the studied process can be changed depending on the technological problems solved during the process in order to regulate the speed and direction of the main reactions of alloy refining.

Rational parameters of the refining process require the creation of a model of physical and chemical interactions between the reacting components based on a thermodynamic forecast of the course of the main reactions, an assessment of the thermal side of the process taking into account the known and established features of the kinetics of the processes under the given conditions of smelting. For the conditions of oxidative refining of a manganese alloy as one of the factors that determines its physical and chemical properties and the course of oxidation of alloy impurities, it is advisable to use the chemical affinity of the elements of the melt to oxygen. Since manganese is characterized by a chemical affinity for oxygen greater than that of iron [2, 3], it is practically impossible to effectively remove phosphorus in slag without significant losses of manganese through oxidative refining.

Phosphorus, which is contained in manganese ore concentrates) in the form of anion PO_4^{3-}, is adsorbed by manganese hydroxides and oxides, and is also represented by calcium phosphates [4-7]. In the process of smelting manganese ferroalloys, phosphorus is almost completely reduced not only by carbon, but also by silicon and manganese and turns into manganese ferroalloys [8-11].

The following manganese phosphides exist in the Mn–P system [12, 13]:

Manganese phosphide	Mn_3P	Mn_2P	Mn_3P_2	MnP
Phosphorus content in phosphide, %wt.	15,82	21,99	27,32	36,06

Table 1 Changes in the thermodynamic parameters of the main reactions during the oxidative refining of a manganese alloy with a high phosphorus content

No.	Reaction	Thermodynamic parameters at 1500°C		
		ΔH, kJ	ΔS, J/K	ΔG, kJ
1	$2Mn_3P + 5{,}5O_2(g) = 6MnO + P_2O_5$	-3367.019	-748.907	-2039.094
2	$2MnP + 3{,}5O_2(g) = 2MnO + P_2O_5$	-1957.288	-511.493	-1050.334
3	$2Mn_2P + 4{,}5O_2(g) = 4MnO + P_2O_5$	-2585.445	-650.295	-1432.374
4	$5Mn + P_2O_5 = 5MnO + 2P$	-595.446	-36.214	-531.234
5	$2Fe + O_2(g) = 2FeO$	-476.438	-99.367	-300.246
6	$Si + FeO = Fe + SiO_2$	-470.537	-98.685	-295.554
7	7 MnO + C = Mn + CO(g)	288.379	172.248	-17.042
8	$Mn_2P = 2Mn + P$	209.509	45.040	-5.476
9	$Mn_3P = 3Mn + P$	274.350	101.357	-6.727
10	MnP = Mn + P	170.308	43.343	-6.234

As shown in [13], there is a stronger interaction between Mn and P atoms than between Fe and P atoms.

Thermochemical calculations of the main reactions that can be carried out under the conditions of oxidative refining of a manganese alloy with an increased phosphorus content were performed using the FactSage package, which consists of a number of information, database, calculation and manipulation modules that allow access and manipulation of pure substances and databases solutions [14].

According to the data presented in the table 1, manganese phosphides have high strength and their dissociation is possible at a fairly high temperature: reaction (8) - ~ 4500°C; (9) - ~ 2500°C; (10) - ~ 3800°C. Analysis of thermodynamic conditions shows that the essence and mechanism of physicochemical transformations during oxidative refining of highly phosphorous manganese can be as follows. The high thermodynamic strength of Mn_2P, Mn_3P and MnP phosphides presupposes primarily reactions (1)-(3) with the formation of MnO and P_2O_5. Simultaneously with these reactions, the reaction of manganese oxidation of the alloy develops during interaction with P_2O_5 and the formation of slag based on manganese oxides and phosphorus, which dissolves in iron, creating a metallic phase. In this case, the physicochemical model of oxidative refining of a manganese alloy with a high phosphorus content will be determined by the factors of thermodynamics and real kinetics. The simultaneous implementation of reactions not forbidden by thermodynamics with a speed determined by the chemical affinity of the elements to oxygen and their mutual influence is taken into account. In addition, the exothermic nature of oxidation-reduction reactions (except for the reaction of carbon oxidation with iron oxide), the arrival of thermal energy from which leads to a significant increase in the temperature of slag and metal, which requires the creation of a cooling effect by adding melt coolers. The high chemical activity of manganese to oxygen creates conditions for intensive oxidation of manganese, and "protects" phosphorus and iron from oxidation with the formation of a metallic phase. The formation of the slag phase on the basis of manganese oxide and cooling materials, the quantitative ratio of which ensures in the process of oxidative refining the necessary melting temperature of the slag phase, its fluidity and, accordingly, the achievement of high refining speeds.

Thus, the main provisions that can be used in justifying the scheme and establishing rational parameters of oxidative refining of the alloy were adopted: higher chemical affinity of manganese to oxygen compared to phosphorus; exothermic nature of the oxidation reactions of manganese, silicon, iron and carbon with oxygen; the need to cool the melt during the oxidative refining of the alloy [15]; exclusion from the composition of lime smelting coolers [16]; approximation of the average temperature of the process to the initial temperature of the highly phosphorous alloy of current production [17].

In order to create a rational method of dephosphorylation of manganese alloys that is efficient in terms of costs and results, an analogy was drawn between the physical and chemical features of the redistribution of melts based on iron and manganese. Under the conditions of steel melting in the oxygen converter, the excess amount of elements of the iron-carbon melt is oxidized by blowing oxygen and iron oxides (except for sulfur, the transition of which is carried out by an exchange-type reaction). At the same time, a mandatory condition for effective desulfurization is the creation of the main slag. The oxygen-converter process is also characterized by the gas mode of its implementation, as a result of which steel and an inevitable by-product are obtained - slag, in which harmful impurities, including phosphorus, are assimilated.

The production of manganese alloys is carried out under reducing conditions by endothermic reactions of carbon-thermal reduction of manganese, silicon and iron oxides using external sources of thermal energy. When working with manganese raw materials, several technologies are implemented to obtain at least two types of materials and, accordingly, two types of waste [18]. These features are determined by the fact that the phosphorus of well-known manganese phosphides, which have a fairly high strength, is largely transferred from the ore raw material to the alloy, and when the necessary conditions are created, it can be assimilated by the slag or remain in the alloy [11]. From a physicchemical point of view, the implementation of dephosphorization of a highly phosphorous manganese alloy with the production of an additional amount of commercial ferromanganese by a method similar to the dephosphorization of steel (ferrite method) using basic slag is practically impossible, since manganese has a greater affinity for oxygen than iron [2].

During steel smelting, dephosphorization takes place with the participation of the slag phase containing (FeO) as an oxidant, according to the corresponding reaction:

$$2[P]+5(FeO)+4(CaO)=(4CaO\cdot P_2O_5)+5[Fe] \quad (1)$$

Under the conditions of ferromanganese production, such an oxidizing agent can be (MnO) according to the reaction:

$$2[P]+5(MnO)+4(CaO)=(4CaO\cdot P_2O_5)+5[Mn], \quad (2)$$

Calculations showed that this reaction in the direct direction does not occur, since manganese has a greater affinity for oxygen than phosphorus. Manganese acts as a reducing agent of phosphoric anhydride, even if phosphoric anhydride is bound to calcium oxide:

$$(4CaO\cdot P_2O_5)+5[Mn]=2[P]+5(MnO)+4(CaO) \quad (3)$$

However, in the conditions of refining an alloy with a high phosphorus content, the reaction of oxidation of phosphorus by iron oxide, which occurs intensively during steel smelting, will not lead to a significant decrease in the phosphorus content in the alloy, since during the refining of ferromanganese simultaneously with this reaction, the reduction of phosphoric anhydride by the manganese of the alloy will more likely occur by reaction (3). As a result of the simultaneous flow of reactions (1) and (3), iron oxide will oxidize manganese with its transition into the slag phase. Thus, in the conditions of ferromanganese smelting, oxidative refining of ferromanganese from phosphorus is practically impossible thermodynamically. The main idea that determines the final results of refining in its development is to create conditions for the predominant oxidation of manganese, oxidation of a certain part of carbon and silicon with the formation of a low-phosphorus slag based on manganese and metal oxides based on iron and phosphorus.

In order to justify the rational physical and chemical conditions for the oxidative refining of the accompanying manganese alloy, thermodynamic calculations of the forecast of the behaviour of the elements in the conditions of the oxidative refining of the alloy were carried out. In the future, based on the results of the thermodynamic forecast and the established kinetic laws of the process, it is necessary to substantiate the optimal conditions and propose a technological scheme of refining, which will ensure the implementation of a waste-free method of oxidative refining of the alloy.

When calculating the values of changes in Gibbs energy for the reactions that take place during the oxidative refining of the accompanying manganese alloy, in order to approximate real conditions, the values of changes in ΔG of dissolution in iron C, Si, Mn, and P were taken into account according to the expressions given in [19]. The results of calculations of changes in the Gibbs energy of the studied reactions as a function of temperature confirm the possibility of creating the necessary conditions, which in the process of oxidative refining of the accompanying manganese alloy with a high content of phosphorus, will ensure a significant minimization of the oxidation of phosphorus in the alloy and its transition to the slag phase. In this case, silicon, manganese, iron and carbon of the metal alloy will "protect" phosphorus from oxidation.

One of the most important parameters of the oxidative refining of a by-metal is the temperature of the process. Taking into account the fact that the temperature of the accompanying metal according to the current low-phosphorus slag smelting technology is about 1350°C, the interval of 1400...1600°C was previously adopted as the most rational temperature interval for the release of refining products, with the possibility of approaching the temperature at the outlet to the temperature of the original accompanying metal. The adopted temperature interval is justified by the fact that when using only air blast as an oxidizer, without additional cooling of the melt, the final temperature can reach 2000°C, which requires the use of solid coolers of the melt. Another, no less important parameter of the oxidative refining of the accompanying metal is the amount and type of oxidizing agent. To ensure the maximum degree of oxidation of manganese and minimum phosphorus, it is advisable to use a combination of two types of oxidizing agents - gaseous and solid. Air is chosen as the main oxidizing agent necessary for the intensification of the process. Its use in the refining of the accompanying metal is justified by the possibility of obtaining two positive effects of synergy: oxidation of elements (Mn, Si and C) with air oxygen and cooling of the melt with air nitrogen. In the case of a significant increase in the temperature of metal and slag at the outlet, its reduction can be achieved by adding materials that are effective coolers, for example, rolling slag. According to data [20], the cooling effect of scale is about 4 times higher than that of scrap metal.

Thus, when using rolling slag in the process of oxidative refining of the accompanying metal, two more positive effects can be realized: cooling of the melt and additional oxidation of alloy impurities. The total cooling effect for the option of implementing the process at 1500°C is determined by the difference between the heat input from the oxidation reactions of silicon (~ 17,000 kJ/kg silicon), manganese (~ 3,000 kJ/kg manganese), iron (~ 4,250 kJ/kg iron) and heating costs melting coolers to a given temperature (slag, SiO2, MgO, etc.), dissociation of iron oxides that are part of the slag: Q_{Fe2O3} = 5.134kJ/kg and Q_{FeO} = 3.744kJ/kg, the implementation of the endothermic reaction of carbon alloy oxidation by iron oxide to CO (~ 9500 kJ/kg of carbon). According to calculations, the specific heat consumption when using slag is about 4200 kJ/kg of slag. Heat losses in the converter-type unit are estimated to be 3.5% of the total heat energy input. Heat losses with exhaust gases, which are formed during oxidative refining of manganese alloy with air blast (N_2 and CO), were also taken into account.

In order to establish the possible influence of oxygen consumption (O_2 of air blowing and oxygen of iron oxides (FeO + Fe_2O_3) and process temperature on indicators of oxidative refining of manganese alloy (compositions of metal and slag), data were obtained that establish a relationship between oxygen consumption and compositions of slag and metal phases for the conditions of oxidative refining of the alloy at different temperatures of 1400...1900°C. The given values of changes in the Gibbs energy of the investigated reactions as a function of temperature confirm the possibility of creating the necessary conditions that, in the process of oxidative refining of the accompanying manganese alloy with a high phosphorus content, will ensure a significant minimization of the phosphorus oxidation of the alloy and its transition into the slag phase. In this case, phosphorus will be "protected" by silicon, manganese, iron and carbon of the metal alloy.

The analysis of the obtained dependences of the compositions of the metal and slag phases on the oxygen consumption and the temperature of the process allows us to assume that when using ~ 13m^3 of oxygen for the entire refining process of highly phosphorous metal, the achievement of the set tasks is ensured - obtaining manganese low phosphorous slag and a metal phase based on iron and phosphorus. When only air blowing is used as an oxidizer, the air consumption, which will ensure that 13 m^3 of oxygen enters the bath, is about 61.9 m^3 (oxygen - 13 m^3 and nitrogen - 48.9 m^3). A decrease in the oxygen consumption below $13m^3$ per 100 kg of alloy leads to a decrease in the content in the slag phase (MnO), an increase in the air consumption above $13m^3$ in the investigated temperature range (1400...1900°C) - to a decrease in the content in the slag (MnO) due to an increase in it content (FeO). The intensity of formation (FeO) will increase with a decrease in the content of carbon, silicon and manganese in the metal. At the same time, a decrease in temperature by 100°C leads to a decrease in the completeness of the transition of manganese to slag by ~ 0.8%. Increasing the temperature of the process by 100°C increases the phosphorus content in the slag by 0.7% while increasing the FeO content in it by ~ 0.9%.

Based on the analysis of the obtained data, no significant effect of temperature on the composition of the slag and metal phase at a constant oxygen consumption was found. the ambient temperature of the release of slag and metal melts is determined by the melting temperature of low-phosphorus manganese slag, which is about 1400°C, which is significantly higher than the melting temperature of the remains of the iron-based metal phase, which contains 4-6% phosphorus.

Experimental evaluation of the refining efficiency of the accompanying manganese alloy under oxidizing conditions.

Experimental melting was carried out on a high-temperature model of a 30 kg converter-type unit with a magnesite lining. As an object of refining, the accompanying manganese metal obtained during the production of low-phosphorous manganese slag in the amount of 30 kg with the following composition in % by weight was used: Mn -50.00; Fe – 42.00; C – 3.50; Si – 0.20; P – 4.30.

As a gaseous oxidizer, air was used, which was introduced from the compressor into the liquid alloy through the upper blowing two-nozzle lance, which was cooled by running water. The specific air consumption per nozzle was 0.55 m^3/min. The inner diameters of the nozzles of the blowing nozzle were equal to 3.8 mm. The temperature of the accompanying metal, which was melted in the induction furnace, was 1320°C. The lining of the melting unit was heated up to ~ 1200°C before the experimental companion metal was released into it. The location of the lance above the level of the still metal was 76 mm (20 calibres). The blowing time is 13 minutes. The total time of the process of oxidative refining of the accompanying manganese metal with three times the addition of flux (3·0.5 min.) was ~ 14.5 min. Flux additives were made using briquettes based on them (diameter - 3.2 cm; thickness - 3.5 cm). The temperature of the metal melt was measured using a BP5/20 thermocouple immersed in the melt: the first measurement - after the release of the accompanying metal into the laboratory unit, the following - before the introduction of the flux, the last temperature measurement was carried out 0.5 minutes after the end of purging.

The introduction of additives on the surface of the liquid bath was carried out with the cessation of air blowing of the metal bath for 0.5 min. The first portion was placed on the surface of the metal bath after blowing for 2 minutes; the second - after blowing for 4 minutes; the third - after blowing for another 4 minutes. After the addition of the last portion of additives, purging was carried out for 3 minutes, which is necessary to maintain the slag in a liquid state, to implement the final period of oxidation of manganese with air oxygen, to raise the temperature of the slag and metal residues to the outlet temperature (~1550...1600°C) and to average the metal and slag phase by chemical composition and temperature. At the end of the process, slag and metal samples were taken and their chemical composition was determined.

Table 2. Results of experimental high-temperature modeling of oxidative refining of highly phosphorous metal

No.	Type of product of oxidative refining								T,°C on release
	Low-phosphorus manganese slag, %wt.				Metal phase (ferrophosphorus), %wt.				
	MnO	FeO	SiO_2	P_2O_5	Fe	Mn	P	Si	
1	69.30	1.58	31.80	0.01	86.60	6.99	6.38	0.002	1530
2	73.8	1.25	29.7	0.02	85.40	6.57	6.30	0.003	1410
3			8.5	18.5	remainder	2.7	0.002		1540

The temperature of the metal before the introduction of the first portion of the fluxes onto the surface of the melt was ~ 1425°C; before introducing the second portion of the melt onto the surface ~ 1495°C; the third ~ 1550°C. The temperature at the end of the oxidation refining process before the release of slag and metal was about 1595°C. As a result of the implementation of the method of refining 30 kg of accompanying metal (waste from the production of low phosphorous slag) in laboratory conditions using a high-temperature model of the converter type, low phosphorous slag in the amount of 25.6 kg (melt No. 1) and a metal close in composition to ferrophosphorus in the amount 17.4 kg. The obtained ferrophosphorus in a liquid state was transferred to the converter, limestone was loaded and melt blowing was carried out. As a result, a commercial metal containing 2-3% Mn was obtained, the rest - iron and slag with a P_2O_5 content of 18-20%, the rest CaO SiO_2. Such slag can also be used as a phosphate fertilizer.

The obtained results indicate the expediency of using in industrial conditions of refining a highly phosphorous manganese alloy in oxidizing conditions using air blowing.

The choice of the most rational algorithm for the mode of blowing and slag formation is determined by the peculiarities of the real kinetics of oxidation reactions, mainly by the change in the intensity of the carbon oxidation reaction of the metal melt. With a significant increase in the intensity of carbon oxidation, which corresponds to an increase in temperature to ~1450°C and leads to a significant increase in gaseous products formed in the volume of the metal melt, it is advisable to reduce the specific air consumption during this period. After the introduction of flux additives and scum for cooling the metal bath, with a significant decrease in the carbon content in the metal (~ to 0.2 ÷ 0.3%), the specific air flow can be increased to the optimal level.

In work based on thermodynamic forecast the behavior of the elements of the accompanying alloy under oxidizing conditions, evaluation of the thermal side of the process and further experimental verification, the results were obtained, which confirm the possibility of creating a waste-free technological scheme for refining a highly phosphorous alloy (Fig. 1).

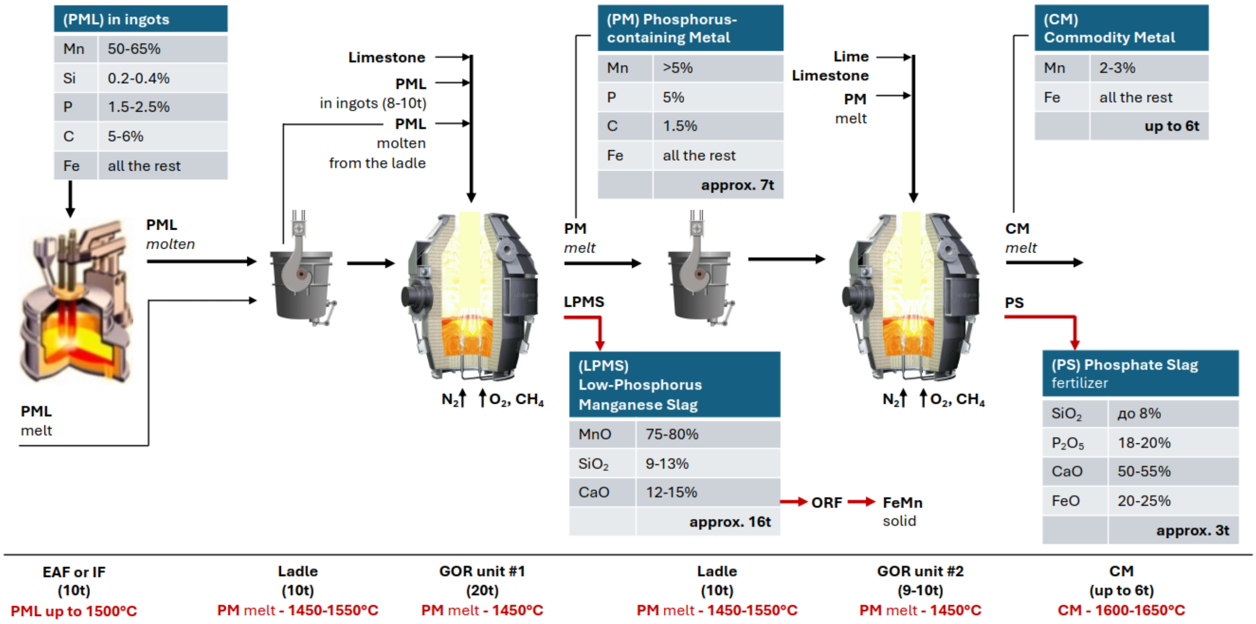

Fig.1. The technological flow chart for processing of phosphorus-containing manganese ligature (PLM)

The classical scheme of ferromanganese alloys production under the conditions of recycling high-phosphorus manganese ores of the Nikopol deposit has been significantly changed. Under the leadership of Academician Gasik M.I. specialists of the former Dnepropetrovsk Metallurgical Institute and Nikopol Ferroalloy Plant proposed and adopted the technology of smelting first low-phosphorus manganese slag from the concentrate of high-phosphorus manganese ore, and then, using this slag, proposed to smelt high-quality ferromanganese. Low-phosphorus manganese slag contains 38-39% Mn (50-51% MnO), 32-34% SiO2 and 0.02% P and serves as a quality material for smelting manganese alloys in ore-recovery furnace.

Iron, phosphorus and partially manganese reduced during processing form a metallic melt with high content of manganese and phosphorus. The composition of the melt, which was determined at the plant as a ligature, is manganese - 55-65%, carbon - 5-6%, silicon - 0.2%, phosphorus - 1.5-2.5% and the rest - iron. Up to 50 tons of such ligature are smelted per day. The produced melt is a valuable material in terms of manganese content, but high concentrations of phosphorus make its use impossible. Tens of thousands of tons of ligature in ingots are stored and await processing using efficient technology.

Therefore, processing of phosphorus manganese ligature, a valuable by-product of low-phosphorus manganese slag smelting, is an urgent and demanded task.

The performed laboratory research and calculations allowed to propose a step-by-step separation by selective oxidation of the main components of phosphoric manganese ligature - manganese, carbon, phosphorus and iron. On 1t and 5t converters of gas-oxygen refining of the National Metallurgical Academy of Ukraine and the plant “Promarmatura” in Mirgorod the semi-industrial and industrial testing of the components of the proposed method of processing of phosphorus manganese ligature (PML) was carried out. In particular, the possibility of oxidative blowing of PML melt and obtaining low-phosphorus manganese slag, as well as blowing of phosphorus-containing melt to phosphate slag.

For Nikopol Ferroalloy Plant a technological sequence of FML processing was developed, the scheme of which is proposed in Fig. 1.

Three steelmaking units are used for processing: 10t electric arc furnace (EAF) (or induction furnace of the same capacity), gas-oxygen refining converters 20t - #1 and 10t - #2 (Fig. 2). Gas-oxygen refining converters (GOR) provide oxidative blowing of melts and intensive mixing during melting. The National Metallurgical Academy of Ukraine has accumulated extensive experience in oxidative blowing in the GOR converter.

Fig. 2. Gas-oxygen refining converter (GOR)

PML ingots are melted in 10t EAF (or induction furnace). The melt is poured into a ladle and transferred to the GOR converter section, after which it is charged into 20t converter #1 through a neck at a temperature of about 1500°C. Oxygen blowing is carried out through bottom tuyere. During blowing 10t of PML ingots are loaded in several portions to cool the smelting and limestone is loaded to form slag. Blowing mode and cooling of the smelting is carried out in such a way that oxygen blowing provides oxidation of manganese and partially carbon, while phosphorus is retained in the iron melt. As a result of oxidation manganese forms low-phosphorus slag (LPMS) and its concentration in the melt decreases from 50-65% to 5%. When manganese concentration in the melt exceeds 5%, the latter blocks phosphorus oxidation and its transfer to slag. In this connection, oxygen blowing in the first GOR converter is finished after manganese concentration in the melt reaches about 5%. A large amount of low-phosphorus slag is formed, which is tapped from the converter to the slag bowl 3 times. Slag composition: MnO - 75-80%, CaO - 12-15%, SiO2 - 9-13%. Up to 17 tons of LPMS obtained (smelted) is used as a commercial product for smelting ferromanganese in the subsequent ore-reduction furnace. Another smelting product is phosphorus metal (PM), which contains up to 1.5% carbon, more than 5% manganese and about 5% phosphorus. The latter (about 7t) is poured into a ladle and transported to GOR converter #2.

Approximate consumption of materials and energy per 1 t of PML in the GOR unit No.1:

1. Electricity consumption – 300-350 kWh.
2. Oxygen consumption for oxidation of manganese – 130 m^3/t
3. Oxygen consumption for by-product decarburization of metal – 45 m^3/t
4. Natural gas consumption – 15-17 m^3/t
5. Nitrogen consumption – 15 m^3/t

The purpose of GOR converter #2 is to remove carbon and successfully dephosphorise. In this oxygen blowing process, converter #2 solves these tasks. During the blowdown, lime is loaded into the converter in portions and slag is removed at a P_2O_5 content of 18-20%. After that new slag is induced and further oxidation of phosphorus is carried out with further slag removal when it reaches 18-20% of phosphorus oxide. Obtained phosphate slag (PS) contains 18-20% P_2O_5, 50-55% CaO, up to 8% SiO_2 and 20-25% FeO. The amount of phosphate slag is up to 3 tons per smelting or about 160kg per ton of phosphate manganese ligature. Phosphate slag is a high-quality fertiliser for agriculture.

As a result of refining in the GKR #2 converter a melt with relatively low carbon content and manganese concentration up to 2-3% is obtained, which is in demand as a metal billet. The amount of metal is ~ 6t per melt or 300kg per ton of PML.

At the approximate duration of melting in GOR unit No.1 and GOR unit No.2 is about 2 hours.

There are ~ 10 melts per day.

Using 20 tons of GOR unit No.1 and up to 10 tons of GOR unit No.2 it is possible to process in a day ~ 200 tons of PML and approximately to receive:

low-phosphorus manganese slag (LPMS) – 160t (for manganese ferroalloys production)
phosphate slag – 30t (phosphate fertilizer)
commodity metal – 60t (ingots/billets for steel production)

Per month (20 working days):
commodity LPMS – 3 200t
phosphate slags – 600t
commodity metal – 1 200t

Conclusions. Based on the results of thermodynamic calculations, a rational algorithm for a waste-free method of oxidative dephosphorization of the accompanying highly phosphorous manganese alloy, which is formed during the electrometallurgical dephosphorization of manganese concentrate, was determined. The physico-chemical essence of the process of refining a highly phosphorous manganese alloy is considered, which consists in creating conditions for the oxidation of manganese, carbon and silicon in the alloy. The thermodynamic prediction of the course of reactions under the given conditions of oxidative refining of the accompanying metal confirms the possibility of obtaining three products: low phosphorous manganese slag, iron-based melt and phosphorus-containing slag with a content of phosphorus oxide of 18-20% (phosphorous fertilizer). It is promising and effective to use blowing of the melt with oxygen in an oxygen converter using a blowing nozzle from above with an oxygen consumption of 15...13 m^3. At the same time, the total air consumption per 100 kg of alloy should be about 50 m^3. On the basis of the thermodynamic forecast of the behavior of the elements of the accompanying alloy under oxidizing conditions, the assessment of the thermal side of the process and further experimental verification, the results were obtained that confirm the possibility of creating a waste-free technological scheme for the refining of a highly phosphorous alloy. At the same time, it is advisable to refine the alloy in conditions close to the conditions of current production of low-phosphorous manganese slag, in which the temperature of the accompanying alloy is 1320...1350°C.

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