

**Proidak Yu.S., Gorobets A.P., Zhadanos O.V., Kamkina L.V., Yaroshenko Ya.O.**  
**Physical and chemical audits and comparative analyses**  
**of scrap remelting technology indicators for high-alloyed steel**  
**with special purposes using the duplex-slag process**  
**and the resource-saving mono-slag process**

**Пройдак Ю.С., Горобець А.П., Жаданос, О.В., Камкіна Л.В., Ярошенко Я.О.**  
**Фізико-хімічні аудити та порівняльні аналізи показників**  
**технології переплавки брухту високолегованої сталі спеціального**  
**призначення з використанням дуплекс-шлакового**  
**та ресурсозберігаючого моношлакового процесів**

**Abstract. The goal.** The research purpose is a physicochemical audit and comparative analysis of the indicators of the technologies for remelting scrap of high-alloy special-purpose steels using a two-slag process and a resource-efficient single-slag process to create an innovative technology for the electric steelmaking process. **Methodology.** The research used miscellaneous methods and modern equipment for studying the physical chemistry of metallurgical processes, including optical metallography methods on the "Neophot-24" installation, to assess the microstructure of the metal and the mineralogical composition of the slags. Experimental and industrial smelting was carried out to determine the balance of alloying elements by certified chemical and spectral analysis of the metal and slag. **Results and scientific novelty.** To ensure the rational composition of the slag of reduced basicity during melting, a mixture with the following composition was synthesized from oxides classified as "chemically pure": 50%CaO-35%SiO<sub>2</sub>-5%Al<sub>2</sub>O<sub>3</sub>-5%MgO-5%FeO. This allows for the reduction of the loss of alloying elements and increases the efficiency of remelting. According to the results of the analysis conducted by the requirements of DSTU 8966:2019 regarding the contamination of the metal with non-metallic inclusions and their crystalline and chemical composition, it was found that the vast majority of inclusions are represented by silicates with a size of 7-10 μm. These indicators depend on the size and conditions of crystallization of the ingot. Changes in the content of alloying elements due to the remelting process were analyzed. It was confirmed that the losses of expensive alloying elements (Cr, Mo, W, V) depend not only on their chemical affinity for oxygen but also on the formation of compounds of the type CaO\*MeO in the slag, where MeO oxide has an acidic nature of interaction. New knowledge has been obtained regarding the physical properties and phase composition of lime-iron slag of the CrO-FeO-SiO<sub>2</sub>-(Me)O system where Me-Mn, Cr, V, Mo. The obtained scientific results significantly complement the research of domestic and foreign scientists due to the novelty of the approach and practical orientation to the needs of specific industries. **Practical value.** The developed technological solutions for predicting the optimal composition of the metal dump for metal scraps of alloyed special-purpose steels will increase the technical and economic performance of steelmaking in electric furnaces and promote the reuse of valuable materials. This is important in the context of the constant increase in the cost of raw materials and efforts aimed at reducing the impact on the environment, as well as on the sustainable development of Ukraine (solving environmental problems, reducing greenhouse gas emissions, reducing the consumption of ferroalloys, etc.).

**Keywords.** high-alloy steel, scrap, single-slag process, remelting, model slags of the CaO-FeO-SiO<sub>2</sub>-MeO system.

**Анотація. Мета.** Метою дослідження є фізико-хімічний аудит та порівняльний аналіз показників технології переплавки брухту високолегованих сталей спеціального призначення із застосуванням двошлакового процесу та ресурсоефективного одношлакового процесу для створення інноваційної технології електрометалургійного процесу. **Методологія.** У дослідженні використано різноманітні методи та сучасне обладнання для вивчення фізико-хімії металургійних процесів, включаючи методи оптичної металографії на установці "Neophot-24" для оцінки мікроструктури металу та мінералогічного складу шлаків. Проведено експериментальні та промислові плавки для визначення балансу легуючих елементів шляхом сертифікованого хімічного та спектрального аналізу металу та шлаку. **Результати та наукова новизна.** Для забезпечення раціонального складу шлаку зниженої основності під час плавки синтезовано суміш із наступним складом з оксидів, класифікованих як "хімічно чисті": 50%CaO-35%SiO<sub>2</sub>-5%Al<sub>2</sub>O<sub>3</sub>-5%MgO-5%FeO. Це дозволяє зменшити втрати легуючих елементів та підвищити ефективність переплавки. За результатами проведеного аналізу за вимогами ДСТУ 8966:2019 щодо забруднення металу неметалевими включеннями та їх кристалічного та хімічного складу встановлено, що переважна більшість включень представлена силікатами розміром 7-10 мкм. Ці

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показники залежать від розміру та умов кристалізації зливка. Проаналізовано зміни вмісту легуючих елементів внаслідок процесу переплавки. Підтверджено, що втрати дорогих легуючих елементів (Cr, Mo, W, V) залежать не тільки від їхньої хімічної спорідненості з киснем, а й від утворення сполук типу  $\text{CaO} \cdot \text{MeO}$  у шлаку, де оксид  $\text{MeO}$  має кислу природу взаємодії. Отримано нові знання щодо фізичних властивостей та фазового складу вапняно-залізного шлаку системи  $\text{CrO-FeO-SiO}_2\text{(Me)O}$ , де Me-Mn, Cr, V, Mo. Отримані наукові результати значно доповнюють дослідження вітчизняних та зарубіжних вчених завдяки новизні підходу та практичній спрямованості на потреби конкретних галузей. **Практична цінність.** Розроблені технологічні рішення для прогнозування оптимального складу металевої шихти для металобрухту легованих сталей спеціального призначення дозволять підвищити техніко-економічні показники виробництва сталі в електрорепечках та сприятимуть повторному використанню цінних матеріалів. Це важливо в контексті постійного зростання вартості сировини та зусиль, спрямованих на зменшення впливу на навколишнє середовище, а також на сталий розвиток України (вирішення екологічних проблем, зменшення викидів парникових газів, зменшення споживання феросплавів тощо).

**Ключові слова:** високолегована сталь, брухт, моношлаковий процес, переплавка, модельні шлаки системи  $\text{CaO-FeO-SiO}_2\text{-MeO}$ .

**Introduction.** The global trend in the development of steelmaking metallurgy focuses on steel production in basic oxygen converters and electric arc furnaces. From a metal recycling perspective, the electric steelmaking process has a clear advantage, as it is designed for remelting 100% scrap, whereas, in basic oxygen furnace (BOF) production, this figure is only 30%. An important techno-economic indicator for both steelmaking processes is the increase in unit productivity, so oxygen is used to introduce thermal energy through the oxidation of elements [1].

The strategy of electric steelmaking in Ukraine's ferrous metallurgy enterprises and machine-building foundry complexes is based on the remelting of common and alloyed steel scraps using a wide range of ferroalloys [2]. In both the classical two-slag refining process and modern melting technologies with alternative energy sources, oxygen is essential for oxidation and refining operations. However, this leads to the almost complete oxidation of highly reactive elements in the charge, such as silicon, vanadium, chromium, and molybdenum. During the melting of the metal charge in an electric arc furnace, significant losses occur of silicon (95%), vanadium (100%), manganese (50%), and chromium (50%). The ferroalloys containing these elements belong to the category of import-dependent metallurgical products with extremely high costs: Ferrovandium: \$9.1–9.7 per kg, Ferrochrome: \$0.9–1.2 per kg, Ferromolybdenum: \$6.9–7.1 per kg [3].

The presented data highlights the necessity for developing technological solutions for the remelting of special-purpose steels alloyed with high-cost elements. The solution to this issue will significantly reduce the consumption of imported ferroalloys and improve both the technical and economic efficiency of alloy steel electric melting. At the same time, it will enable the maximum possible reduction of material and energy costs in metal production, ultimately lowering production costs and increasing profitability.

#### Literature Analysis and Problem Statement.

Taking into account that a significant amount of high- and medium-alloy steel scrap is generated worldwide each year (exceeding 10 million tons, according to [4]), finding efficient solutions for its rational utilization is of great scientific interest on a global scale. Among the studies of the secondary utilization of high-alloy scrap, the next notable scientific works should be

highlighted. In [4], a scheme for induction melting and electrical slag remelting is proposed for scrap processing. Based on this scheme, a pilot experiment and thermodynamic analysis were conducted to investigate the influence of temperature, oxygen content, and element composition on the recovery percentage of alloying elements. In [5], attention is given to metal scrap processing, which is contaminated with oils emitting volatile organic compounds (VOCs) of the benzene series during heating and poses risks to both physical and mental health. The study characterizes VOC emissions and examines the pyrolysis behavior and de-oiling process of contaminated scrap to assess environmental risks. A method for separating the melting process is proposed to enable the economical and environmentally friendly recovery of valuable metals from de-oiled waste. Additionally, the thermodynamics of the  $\text{Al}_2\text{O}_3\text{-SiO}_2$  and  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  systems were calculated to optimize slag formation. Study [6] evaluated the environmental and economic benefits of alternative recycling schemes for end-of-life vehicles. These schemes aim to optimize the utilization of alloying elements found in steel scrap recovered from decommissioned vehicles, enabling more efficient resource use. Article [7] describes a new process for simultaneous preheating and removal of galvanized coatings from scrap surfaces before the melting phase to prevent the formation of harmful dust and hazardous air emissions. The zinc coating is removed in the gas phase through the combustion of chloride-containing syngas and is collected in a specialized recovery system. Two possible innovative process pathways are outlined, incorporating pre-treatment of plastic waste, gasification/pyrolysis of shredded plastic, preheating of steel scrap, and zinc recovery processes. In [8], the authors constructed molecular dynamics models for binary systems  $\text{CaO-FeO}$ ,  $\text{MgO-SiO}_2$ ,  $\text{FeO-SiO}_2$ ,  $\text{CaO-SiO}_2$ , and the ternary system  $\text{CaO-FeO-SiO}_2$  at a temperature of 1873 K using Born–Mayer potential functions. These potentials included effective dipole-dipole interactions for pairs such as Ca–Fe, Mg–Si, Fe–Si, and Ca–Si. The parameters for the dipole-dipole interaction were determined by adjusting the calculated Gibbs free energies of formation for the binary systems  $\text{CaO-FeO}$ ,  $\text{FeO-SiO}_2$ ,  $\text{MgO-SiO}_2$ , and  $\text{CaO-SiO}_2$  to match experimental data. The thermodynamic properties of  $\text{CaO-FeO-SiO}_2$  solutions were studied by converting

several iron ions to calcium ions. This approach allowed the calculation of the changes in Gibbs free energy and the ratio of activity coefficients  $\gamma_{CaO}/\gamma_{FeO}$  in the ternary system. The significant scientific interest in modeling the chemical composition of slag during the remelting of high-alloy steel scrap is presented in the study [9], which focuses on predicting the chemical composition of refining slag using an artificial neural network.

Thus, a physicochemical audit and comparative analysis of the indicators of the remelting technologies for high-alloy special-purpose steels - using both the two-slag process and the resource-efficient one-slag process - will provide relevant recommendations and complement existing research.

**Purpose and Objectives of the Research.** The research purpose is to conduct a physicochemical audit and comparative analysis of the indicators of high-alloy special-purpose steel scrap remelting technologies using the two-slag process and the resource-efficient one-slag process to develop an innovative technology for the electric steelmaking process.

**Research Description.** In the classical technology of remelting high-alloy steel scrap in electric arc furnaces, a metal semi-product with a controlled phosphorus content is initially melted under a heavily oxidized slag. Once the oxidation process is complete this slag is removed, and a new slag is created, followed by desulfurization, deoxidation, and alloying with ferroalloys.

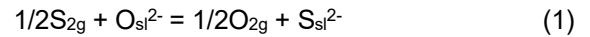
To form slags with a specified composition, before loading the furnace, 10–15 kg/t of lime or 18–23 kg/t of limestone is added. The slags formed during melting ( $B = 1.5–1.7$ ) are deoxidized and removed. The slag from the melting period is deoxidized using mixtures that consist of 30–40% fresh burnt lime, 5–15% fluorspar, 10–25% electrode scrap, and 15–25% ferrosilicon. After removing the melting-period slag, a new slag is created by adding 20–40 kg/t of lime, 3–10 kg/t of fluorspar, and 2.5–3 kg/t of ferrosilicon to the metal bath. Once the low-viscosity slag is fully formed, the metal is heated to 1500–1540°C and alloyed with ferromanganese. In situations where the carbon content in the metal is between 1.15–1.20%, medium-carbon or low-carbon ferromanganese is used for alloying.

Before tapping the steel from the furnace, the slags from the reduction period are deoxidized with granular aluminum or a deoxidizing mixture. The final deoxidation of the steel is carried out with aluminum in the ladle.

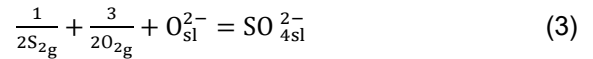
An analysis of changes in the chemical composition of the metal and slag during the melting process shows that the main losses of alloying elements occur during the melting of the charge. Almost 90% of the lost alloying elements transfer into the slag, while 10% transition into the gas phase. The practice of double slag removal, applied at several plants, leads to the loss of a significant portion of alloying elements with the waste slags.

The main idea of the simultaneous process is to use oxidizing slag for phosphorus removal (dephosphorization) and subsequently restore it for desulfurization and other physicochemical operations.

Depending on the degree of oxidation, sulfur in slags can exist in either sulfide (1) or sulfate (2) forms [10]:



$$K_1 = \frac{\alpha_{S_2} \cdot p_{O_2}^{1/2}}{\alpha_{O_2} \cdot p_{S_2}^{1/2}} \quad (2)$$



$$K_2 = \frac{\alpha_{SO_4}^{2-}}{\alpha_{O_2} \cdot p_{S_2}^{1/2} \cdot p_{O_2}^{3/2}} \quad (4)$$

For a given temperature and slag composition, the equilibrium sulfur concentration is determined solely by the ratio  $(p_{O_2}/p_{S_2})^{1/2}$ , rather than the absolute values of the partial pressures of oxygen and sulfur. At the same time, the partial pressure of oxygen ordains the form in which sulfur is present in the slag melt:

at  $p_{O_2} \leq 10^{-5}$  atm., sulfur exists in the slag as sulfide ions (MeS);

при  $p_{O_2} \leq 10^{-3}$  atm., sulfur is present as sulfate ions (MeSO<sub>4</sub>).

The parameter "sulfide capacity" -  $C_S$  is used to evaluate the properties of desulfurizing slag systems:

$$K_1 \cdot \frac{\alpha_O}{\gamma_O} = C_S = (S) \cdot \left(\frac{p_{O_2}}{p_{S_2}}\right)^{\frac{1}{2}} \quad (5)$$

The characteristics of the sulfide capacity of slags in the ternary CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system [11], as shown in Figure 1, indicate that the maximum value of the  $C_S$  parameter is found in the CaO-Al<sub>2</sub>O<sub>3</sub> composition, making it the most suitable slag base for desulfurization. At the same time, according to data presented in E.T. Turkdogan's monograph [10], in the CaO-SiO<sub>2</sub> slag system, the solubility of CaS at temperatures of 1500–1550°C increases from 2.5% to 5% as the basicity ratio CaO/SiO<sub>2</sub> decreases from 1.5 to 0.5.

Clearly, for optimizing slag composition, the basicity factor of the slag is essential, as is the activity of its components. In CaO-CaF<sub>2</sub> systems, which act as the fundamental slag-forming system in domestic electrosmelting practices, as well as in slags within the CaF<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system, the calculated activity values of the system's components (Fig. 2) are of practical significance.

Calcium fluoride accelerates the dissolution of lime and increases the fluidity of slags by reducing their viscosity. This enhancement subsequently improves the rate of steel desulfurization. Thus, the effect of CaF<sub>2</sub> is reflected in the kinetics of the desulfurization process. Some retrospective studies have shown that the presence of CaF<sub>2</sub> in basic slags can significantly increase their basicity, thereby improving steel desulfurization accordingly.

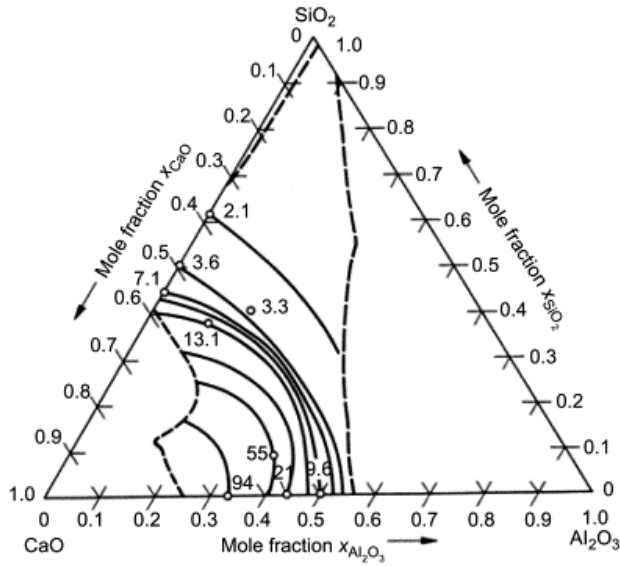


Figure 1. The sulfide capacity  $C_s \cdot 10^6$  of slags in the ternary CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system at the temperature 1650°C [12]

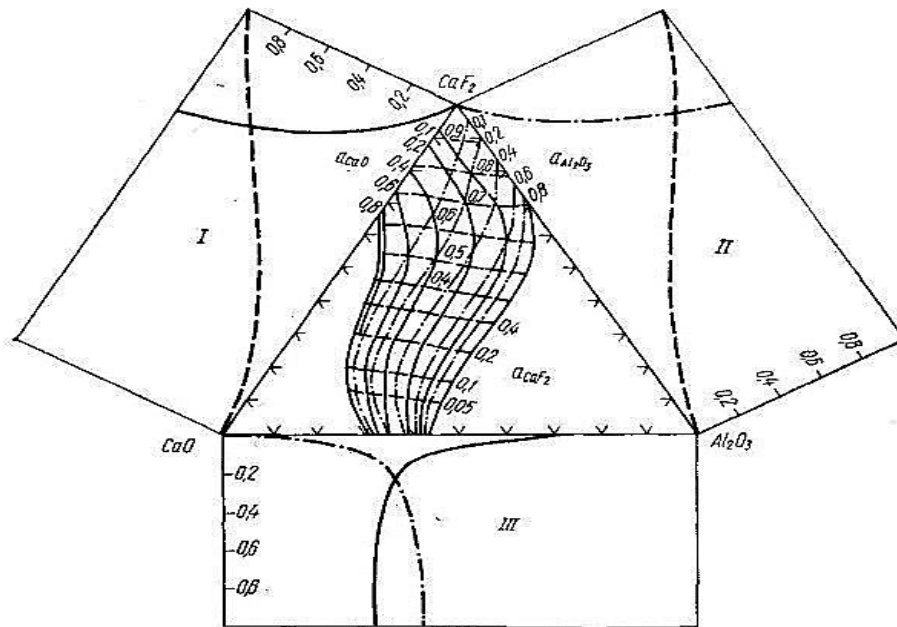


Figure 1. The activities of CO (solid lines), CaF<sub>2</sub> (dashed lines), and Al<sub>2</sub>O<sub>3</sub> (dash-dotted lines), determined at 1500°C in various systems, are as follows: I – CaF<sub>2</sub>-CaO; II – CaF<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>; III – CaO-Al<sub>2</sub>O<sub>3</sub> [12]

The authors of studies [13, 14] were likely the first in domestic literature to substantiate that the steel desulfurization coefficient  $\Sigma(\text{CaO} + \text{MgO})$  does not

increase but rather decreases when using oxide-fluoride slags with increased CaF<sub>2</sub> content. This conclusion follows from the data presented below:

CaF <sub>2</sub> content, %	The value of the steel desulfurization coefficient $L_s = \frac{(\%S)}{[\%S]}$	
	$\Sigma(\text{CaO} + \text{MgO}) < 65 \%$	$\Sigma(\text{CaO} + \text{MgO}) > 65 \%$
< 4,0	96 (17 melts)	67 (19 melts)
> 4,0	81 (6 melts)	53,3 (8 melts)

With the same slag fluidity, characterized by the sum of components  $\Sigma(\text{CaO} + \text{MgO})$ , an increase in CaF<sub>2</sub> content in the slag above 4% reduces the sulfur distribution coefficient by 15%. M.M. Chuyko and V.B.

Rutkovskiy [13, 14] explained the decrease in the desulfurizing ability of furnace oxide-fluoride slags by the increased activity of ferrous oxide, as follows from the expression:

$$L_S = (S)/[S] = K_S a_{(CaO)}/a_{(FeO)}, \quad (6)$$

where  $K_S$  - is the equilibrium constant of the metal desulfurization reaction;  $a_{(CaO)}$  - is the activity of the "free" concentration of calcium oxide, determined by the method of M.M. Chuyko.

The integral assessment of the metal's desulfurization reaction efficiency by slag systems is determined by achieving a balance between the metal and the slag, the oxygen activity in the metal, and the composition of the slag and metal, taking into account the relative weight of the slag.

$$[S]_{fin.} = \frac{\alpha_{[O]} \left( (S)_{sl.} + \frac{[S]_{start.}}{m} \right)}{f_S * C_S + \frac{\alpha_{[O]}}{m}} \quad (7)$$

where  $S_{start, fin.}$  – the sulfur content in the metal before and after desulfurization;  $\alpha_{[O]}$  – oxygen activity in the metal;  $f_S$  – the sulfur activity coefficient;  $C_S$  – the sulfide capacity of the slag;  $m$  – the relative weight of the slag (kg) per kg of steel.

Equation (7) defines the relationship between the activities of oxygen and sulfur and characterizes the desulfurization process as a mass transfer reaction in the "metal-slag" system.

5 laboratory melts were conducted to verify the feasibility of implementing a resource-efficient single-slag technology for remelting high-alloy steel scrap. The chemical composition of the initial metal samples is provided in Table 1.

Table 1. Chemical composition of the metal before remelting, wt. %

No sample	Application	C	Si	Mn	Cr	Ni	Mo	V	P ppm	S ppm
1	Demining roller	0,245	0,272	0,82	2,04	1,05	0,309	0,006	160	90
2	Stainless steel	0,152	0,56	1,30	18,61	9,99	0,10	0,04	220	170
3	Tank armor	0,331	1,49	0,417	1,06	2,31	0,27	0,006	110	56
4	Gun barrel A	0,371	0,316	0,26	1,00	3,12	0,47	0,12	46	37
5	Gun breech B	0,340	0,180	0,61	1,00	2,79	0,49	0,112	37	46

The melts were conducted in a 30 kW Tamman furnace with a graphite heater. Metal samples weighing 120-150 g were melted in alumina crucibles for 30 minutes at a temperature of 1600°C. To ensure a rational composition of the low-basicity slag for the melts, a mixture was synthesized from oxides classified as "chemically pure" with the following composition: 50% CaO, 35% SiO<sub>2</sub>, 5% Al<sub>2</sub>O<sub>3</sub>, 5% MgO, 5% FeO. This mixture was subsequently melted in alumina crucibles to homogenize the slag composition. The slag quantity was 10% of the sample mass.

After remelting the high-alloy steel scrap samples, the prepared metal samples were analyzed using optical metallography on a "Neophot-24" setup, and slag samples were analyzed for X-ray phase analysis of the slag components. This allowed the determination of non-metallic inclusions and their crystal-chemical composition in the metal according to the requirements of DSTU 8966:2019. It was established that the main part of inclusions were silicates, ranging from 7-10 μm, depending on the size and crystallization conditions of the cast. Changes in the content of alloying elements due to the remelting process were analyzed. It was confirmed that the loss of expensive alloying elements (Cr, Mo, W, V) depends not only on their chemical affinity to oxygen but also on the formation of compounds like CaO\*MeO in the slag, where MeO is an oxide with acidic interaction properties.

The results made it possible to conduct an industrial melt for remelting steel 110Г13Л without oxidation at the operating enterprise of PJSC "Dniprovs'ky strilochny zavod". The metal charge consisted of 1000 kg of steel scrap and 9000 kg of steel 110Г13Л scrap. The following slag-forming materials were used: limestone 214 kg, fluorite 75 kg, and modifier 39 kg. At the end of the melting period, the slag had the following

composition: FeO - 2.34%, MnO - 25.38%, and its basicity was 1.1. Before the metal was released from the furnace, the slag's basicity was 2.5 with the following chemical composition: FeO - 1.62%, MnO - 10.44%. The metal loss amounted to 954 kg.

Thus, the conducted research enabled the determination of the phase components of the CaO-FeO-SiO<sub>2</sub>-MeO (Me – Cr, Mo, V, Mn) slag systems using physical metallography methods. The viscosity of the slags from the experimental melts was determined using vibration viscosimetry, allowing the prediction of mass transfer reactions in the metal-slag system. The study of the metal from the experimental melt of steel 110Г13Л, following the standards of research control, confirmed the complete compliance of the remelted metal's quality with the DSTU standard

## Conclusions

The conducted research allows the proposal of a new, resource-efficient, one-slag technology for remelting high-alloy special-purpose steel scrap. This technology can be implemented in metallurgical enterprises.

To ensure a rational slag composition with reduced basicity during the melting process, a mixture of oxides classified as "chemically pure" has been synthesized with the following composition: 50% CaO, 35% SiO<sub>2</sub>, 5% Al<sub>2</sub>O<sub>3</sub>, 5% MgO, and 5% FeO. This composition helps reduce the loss of alloying elements and improves the remelting efficiency.

Based on the analysis conducted according to the requirements of DSTU 8966:2019 regarding the contamination of metal by non-metallic inclusions and their crystalline and chemical composition, it was found that the majority of inclusions are represented by silicates, with sizes ranging from 7 to 10 μm. These

indicators depend on the size and crystallization conditions of the ingot. The changes in the content of alloying elements as a result of the remelting process were analyzed. It was confirmed that the losses of expensive alloying elements (Cr, Mo, W, V) depend not only on their chemical affinity to oxygen but also on the formation of compounds in the slag of the type  $\text{CaO} \cdot \text{MeO}$ , where MeO is an oxide with acidic interaction properties.

The newly obtained knowledge regarding the physical properties and phase composition of lime-iron slag in the system  $\text{CrO-FeO-SiO}_2\text{-(Me)O}$ , where Me are Mn, Cr, V, and Mo, significantly complements the research of both domestic and international scientists. This is due to the novelty of the approach and its practical orientation towards the needs of specific industries.

The developed technological solutions for predicting the optimal composition of the metal charge for high-alloy special-purpose steel scrap will improve the technical and economic indicators of steel production in electric furnaces and contribute to the reuse of valuable materials. This is crucial in the context of the constant rise in raw material costs and the ongoing efforts to reduce environmental impact, as well as to support Ukraine's sustainable development (addressing environmental issues, reducing greenhouse gas emissions, minimizing ferroalloy consumption, etc.).

Implementing the results obtained at Ukrainian metallurgical enterprises will allow for a reduction in electrical energy consumption within the industry, which in turn will enable this energy to be redirected to other sectors and the needs of the population.

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