Prognostic models for electroslag remelting process and slag engineering

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Keywords: prognostic models, electroslag remelting (ESR); dynamic model of the ESR, subsystem, physicochemical modelling, gas-slag-metal interaction, slag properties, ion radii, integral parameter, cationic sublattice, electric conductivity, melting temperature, melting range.

ABSTRACT

Classical electroslag remelting of consumable electrodes is a drop-by-drop melt feeding through a slag layer into a renewing molten metal bath, slowly solidifying into a homogeneous, dense, defect-free ingot in a copper water-cooled mould. The new look at the additive nature of the ESR process in a protective atmosphere allowed us to formulate the principles of a comprehensive thermodynamic-based model that can predict dynamic changes in slag and metal composition at certain ingot remelting. The model considers drastically different slag-to-metal mass ratios at the beginning and end of remelting and predicts gas, slag and metal composition in a chain of thermodynamic subsystems. Despite consisting of calcium fluoride and stable oxides, the ESR slag can oxidize main and active elements from steel and alloys (primarily aluminium, titanium, and silicon) due to chemical reactions between slag and metal. ESR is not an electrochemical process in its nature. However, slags are ionic melts and deviation in their composition causes a change in their properties, affecting both operation mode and ingot quality.

Another important understanding derived from the modern metallurgy technological route is that the ability to refine metal from impurities is not a priority for the ESR because consumable electrode has already passed all stages of refining and deep degassing at ladle treatment that changes ESR slags engineering principles. The critical importance became slag's ability to generate process heat and keep the melting composition in the metal bath unchanged (except for non-metallic inclusions assimilation). Slag engineering for ESR required a compromise between chemical inertness to a metal composition and desired physical properties deriving from technological reasons. The direct Chemical Bonds Concept in a multicomponent oxide system was used to build predictive models of electric conductivity and the melting temperature of fluoride-oxide slag based on their chemical composition. Both models help to design a customized composition of effective slags for steel and alloy groups or individual grades, and they are significant steps in the development of a comprehensive model of electroslag remelting.

INTRODUCTION

In the technological chain of high-quality steel product manufacturing, electroslag remelting (ESR) takes one of the last but not least places. It refines the melt from impurities and inclusion and refines the ingot structure, increasing yield. That is exactly due to the homogeneity of the chemical composition and the dense dendritic structure over the cross-section and height of the ingot ESR metal, which is in demand for the most critical applications in modern industry (Medovar, B. and Boyko, G., 2013; Hoyle, G., 1983).

The low rate of metal supply through the slag layer, which simultaneously performs the functions of an electric heater and thermal buffer for the process and refining media, guarantees a relatively small depth of the liquid metal bath. The progressively replaced composition of the liquid metal bath provides significantly less segregation of elements than in a conventional same-diameter ingot. The second important feature of the ESR ingot is its dense dendritic structure, no shrinkage, and smooth side surface, which ensures a high product yield. As a result, the low rate of ESR ingot formation in copper water-cooled mould (tens to hundreds of times lower than traditional ingots and continuously cast billets) is a prerequisite of well-recognized worldwide "ESR quality".

The electrical conductivity of the slag bath determines the performance and efficiency of the melting process, while the slag melting temperature and interval determine metal overheat, liquid metal bath depth, and ingot surface formation pattern, which in turn are efficiency factors for metal refining and homogeneity of ESR ingot. Thus, ESR slag is an indispensable component of the process, and its composition and properties are crucial for metal quality, process efficiency and cost. Knowledge of slag's chemical and physical properties and their impact on the remelting process is key to achieving high quality and efficiency. This article aims to provide a clear understanding of the changes that occur in the physicochemical system during the remelting of consumable electrodes in a protective gas atmosphere using a single slag charged at the start of the process. It emphasizes the significant differences in slag-metal interaction conditions between ESR ingot formation's start and endpoints. The article asserts that slag is a critical component for ensuring consistency and stability in the ESR process and demonstrates the efficacy of an atomistic approach in predicting its crucial physical properties.

CONCEPT OF GAS-SLAG-METAL SYSTEM CHARACTERIZATION AT ESR REMELTING IN INERT GAS

Electroslag remelting is an arc-less process powered by the heat generated by the passage of electric current through the electric conductive slag bath (Fig.1, 5a). When slag temperature exceeds the melting point of a metal, the consumable electrode begins to melt (3). Metal drops (5) go down from the electrode tip through a slag layer (5a) and accumulate in the metal bath (6), which gradually solidifies, forming an ingot (7). The reacting system at the ESR in each instant moment consists of a film on the edge of the consumable electrode, a liquid slag bath with falling metal drops inside, and a liquid metal pool whose bottom end solidifies, forming an ingot (Medovar, B.I. and Boyko, G.A. 2013, Stovpchenko, G., et al., 2020a).

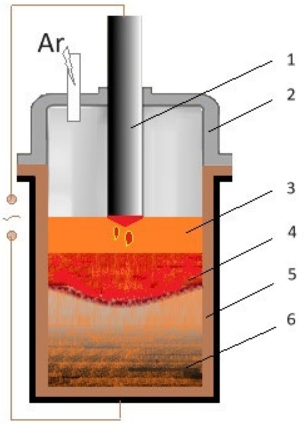

FIG 1- ESR in argon protective atmosphere: 1 – consumable electrode; 2 – protective gas hood; 3 — slag bath; 4 – liquid metal pool; 5 – mould; 6 – solid ingot.

High temperatures of the melts and the developed surface of slag-metal interactions bring reactions closer to equilibrium (Mills, K., 2021; Hou, D. et al., 2021; Duan, S. et al., 2019). Nevertheless, specific features of gas-slag-metal system interactions at electroslag remelting must be outlined to clearly understand characteristic conditions that are a basis for further technological improvement.

Gas atmosphere contacts with slag only. Gaseous products of slag-metal reactions and evaporations from slag are removed in the furnace atmosphere (which is inert and slowly renewed). The gas atmosphere over the slag bath has no direct contact with liquid metal and does not participate in the mentioned interactions, but in the case when it contains oxygen, the electrode surface can be oxidized. Using an oxygen-free atmosphere (mostly argon or nitrogen, depending on steel grade) solves this problem by preventing the growth of oxygen activity in a slag and oxygen transfer to the metal caused by variable valence oxides (primarily iron oxides) involving atmospheric oxygen. For this reason, the closed hood that covers a whole electrode to keep the protective gas atmosphere became a benchmark in today's ESR plants. Incrementally solidifying in the bottom of a liquid metal pool, the ingot leaves the reaction zone (after interacting with slag). On the contrary, molten slag continues to participate in refining processes and assimilates slag-metal interaction products and non-metallic inclusions from the consumable electrode.

The most common ESR practice must envisage charging the entire slag mass at the start of the remelting process, and no additions of premelted slag (or slag components) are used. Thus, it is crucial to understand that the slag-to-metal ratio changes throughout the entire remelting process, as all the products of the interactions between the slag and metal and most of the nonmetal inclusions from consumable electrodes are accumulated in the slag bath.

From the formal logic, it is understandable that a permanent change and drastic difference in the slag-metal mass ratio (Fig.2) causes radically different conditions for slag-metal interaction during electroslag remelting.

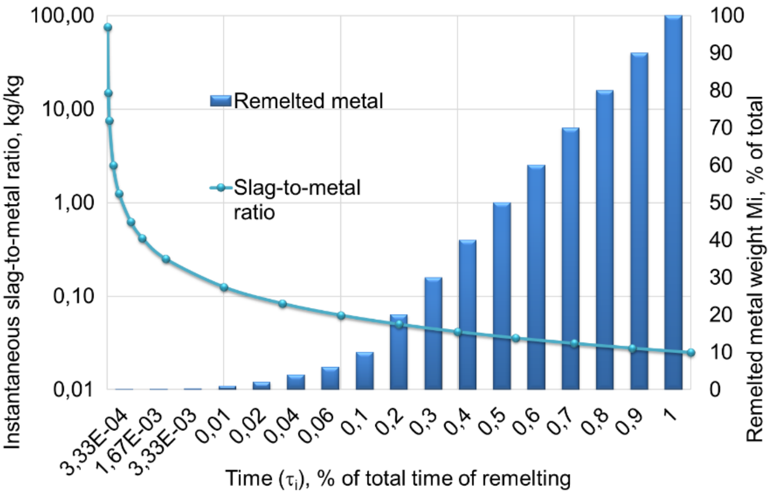

FIG 2—Graphical representation of slag-metal interaction mass conditions at ESR ingot formation (in an inert atmosphere) when a whole slag consumption makes 25 kg/ton of metal charged at the start.

The diagram summarises and demonstrates the characteristics of the physical and chemical processes that occur during electroslag remelting. The slag-to-metal ratio changes are shown for specific slag consumption of 25 kg/t of metal. However, the trend uncovered is general, regardless of its given value. Specific slag consumption usually makes 20-40 kg per ton, and exactly the last figure is usually used for thermodynamic calculations of the ESR, shoving just a very average result. However, due to the enormous slag-to-metal ratio in the first minutes of the remelting, the oxygen-bearing slag oxidates a metal the most at the beginning of the process. This effect cannot be neglected because the oxidative effect of slag remains tangible for quite a long time and can be a reason for ingot inhomogeneity along its height.

The physical properties of a slag itself are not less significant, and they must be tested for their relevance to the requirements for an efficient ESR process It is also important to find deeper dependencies between experimentally found values and chemical composition using atomistic approaches, which allows the prediction of molten slag physical properties and makes the choice of slags more deterministic. Directed Chemical Bonds Concept that was created by Prof. E. Prikhodko and continues to be developed by his followers at the Z. I. Nekrasov Institute of Ferrous Metallurgy of the NASU (Prikhodko, E., 1995, 2013; Stepanenko, D., 2023, Stovpchenko, G. et al., 2022) was chosen for these purposes.

METHODOLOGY OF RESEARCH

The first stage (Fig. 3) of the evaluation procedure of slag-metal interaction is to construct the proposed "quasi-dynamic" description (Fig.2) of the ESP process - a dynamic model of ESR in an inert atmosphere - in the form of a line of subsystems. This line of subsystems (masses of gas, slag and metal phases) for the predictive model of physicochemical interaction at ESR while consumable electrode remelting should be compiled using industrial data at certain ingot formation: typical slag consumption and rate of remelting. The input data is the mass of metal (mi) that is remelted to a certain point of time (τ_i), considering experimental data about the melting rate, the whole mass of slag and the volume of argon in the close chamber of the ESR plant. The proper time intervals (*i*), depending on the chosen purpose and number of calculations, should be determined, and for each conventional time, a subsystem of the whole masses of slag, gas and instantaneous mass of molten metal should be composed. For all subsystems, the remelted metal mass is only a variable (m_i); the primary mass of components of slag and gas phases are the same.

For each physicochemical subsystem, the masses and compositions of gas, slag, and metal phases at the chosen time of electroslag remelting should be calculated and used as initial data in software for equilibrium composition calculations. In the second modelling stage, thermodynamic calculations of the equilibrium state of the "gas-slag-metal" system using CALPHAD Methodology (Lukas, H. et al., 2008; Sundman, B., 2016) implemented in HSC Chemistry, Pandat, ThermoCalc and similar possibility software can be used for this purpose. In the presented examples, thermodynamic calculations for the "gas-slag-metal" system were made using HSC Chemistry software (HSC Chemistry 10, 2023).

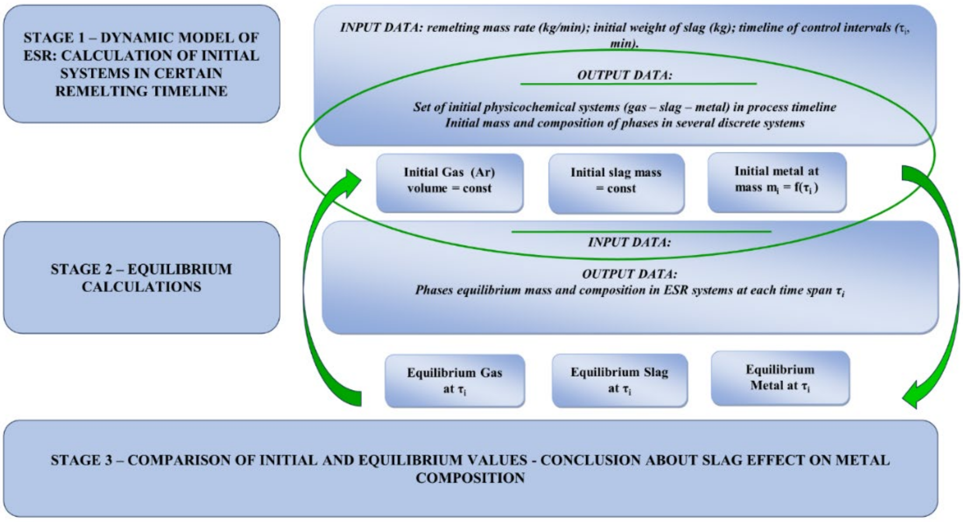

FIG. 3—The procedure of physicochemical modelling of the gas-slag-metal interaction in the inert atmosphere at the ESR process course.

In the third stage, primary mass data of subsystems and equilibrium calculations are compared to recognize changes in phases' masses and composition. The overall analysis of received results allows for the finding of prospective slag compositions from a chemical point of view.

Changes in metal composition were calculated according to the proposed dynamic physicochemical model of ESR for comparative slag $34CaF_2/30Al_2O_3/27CaO/0.5SiO_2/2.5MgO/6TiO_2$ and Inconel 718 (Table 1) at 1873 K.

TABLE 1 - The chemical composition of the Inconel 718 used in the calculation

Elements content, %wt.								
Ni	**Cr**	**Fe**	**Nb**	**Mo**	**Ti**	**Al**	**C**	**B**
53.7	18.2	18.2	5.4	3	1	0.5	0.03	0.004

The total system for dynamic ESR model demonstration comprised 300 kg of slag, 6,47 kg of argon atmosphere and a part of the total ingot mass (19,000 kg) of 1000 mm in diameter, corresponding to a certain time interval. This instantaneous metal mass and slag-to-metal ratio in a certain conditional time of remelting were found from the melting rate (14.2 kg/min), which was taken from the ESR practice of producing similar ingots. The main advantage of the proposed dynamic model is that it allows for predicting probable changes in ingot composition along its height caused by interaction conditions changes in gas-slag-metal. The main limitation is that it is very time-consuming (for 10 times points and 2 slags, it would require creating and calculating 20 subsystems), making it impractical for cases when process dynamic is the same or ingot inhomogeneity is not a problem.

For example, a comparison of the effects of different slags on a metal composition could be done by traditional single-system thermodynamic estimation, slightly modifying it. Our approach involves using a higher slag-to-metal ratio typical for the stationary stage of the ESR. The suggested reacting system includes the entire slag mass and the mass of a liquid metal pool in a volume equal to a half-sphere with a depth equal to a certain ingot radius. Such a system gives more pronounced changes in phase composition than using a specific consumption value. The estimation presented here was made for an ingot 1000 mm in diameter. Such a single reacting system consisted of 2200 kg of liquid metal, 300 kg of a slag bath, and 6.47 kg of argon. In the following calculations, the slag-to-metal ratio makes 0.14 (instead of a 0,016 value for the specific consumption at the above-described 19000 kg ESR ingot). The single-system comparison was made for slags (## 1-2, 1-3, 2-5, and 4-3) with the wider melting range whose compositions are given in Table 2.

TABLE 2. Composition and experimentally determined properties of slags system CaF_2 – Al_2O_3 – TiO_2 –MgO

Slag #	**Components content, % wt**				**Melting temperature / melting range, K**	**Electrical conductivity at 1873 K**
	CaF_2	**Al_2O_3**	**TiO_2**	**MgO**		
1-1	10	60	21	9	No data	625
1-2	20	54	18	8	1623 / 330	375
1-3	30	47	16	7	1653 / 190	279
2-1	70	0	30	0	No data	1064
2-2	63	10	27	0	1513 / 90	967
2-3	56	20	24	0	1543 / 80	760
2-4	49	30	21	0	1603 /80	449
2-5	42	40	18	0	1693 / 130	322
3-3	56	24	20	0	1533 / 60	541
4-1	50	22	18	10	1603 / 70	523
4-2	45	19	16	20	1473 /100	967
4-3	40	17	13	30	1583 / 110	625

Slags' physical properties should also be relevant to the ESR process. The molten slags' electrical conductivity and melting temperature range were measured experimentally (Table 2). The electrical conductivity of slags was measured using a bridge-type three-electrode measuring cell (Kolisnyk, V. et al.,1980) with KCL solution as the reference media. The melting interval was determined visually using an optical microscope to monitor slag particle behaviour on a heated molybdenum plate in argon. A tungsten rhenium thermocouple WRE5/20 was used to control the temperature.

The dependency between experimentally determined values and chemical composition was searched using the model of the ordered structure of oxide melts. The basics of E. V. Prikhodko's physicochemical model (Prikhodko, E.V. , 1995 a,b; Prikhodko, E.V.,2013) is the description of the act of elementary interaction of each pair of elements with unpolarised atomic radii Rui, Ruj at a distance d between them in a multicomponent system by calculating a set of partial parameters (1) – (4):

$$\begin{cases} R_{u_i} + R_{u_j} = d \\ lgR_{u_i} = lg\dot{R}_{u_i} - Z_{ij} \cdot tg\alpha_i \\ lgR_{u_j} = lg\dot{R}_{u_j} - Z_{ij} \cdot tg\alpha_A \end{cases} \qquad (1),$$

where *Zij* is calculated using the formula:

$$Z_{ij} = \frac{lg\frac{\dot{R}_{u_i} \cdot tg\alpha_i}{\dot{R}_{u_j} \cdot tg\alpha_j}}{(tg\alpha_i + tg\alpha_j)} + \frac{\Delta e_{ij}}{2} \qquad (2).$$

The slags' chemical composition effect on their properties was assessed by the index of the cationic sublattice ΔZm non-equilibrium state, which is expressed by the equation:

$$\Delta Zm = \left(Z_{K(K-A)} - Z_{K(K-K)}\right) - \left(\frac{\frac{R_{u_A}}{R_{u_K}} - 0.53}{15{,}43(tg\alpha_K)^{1{,}5075}} + 0{,}51\right) \qquad (3),$$

where *RuK, RuA* are the ionic radii of cations and anions; *ZK(K-A)* and *ZK(K-K)* are the average statistical charges of atoms in the cation-anion and cation-cation bonds, respectively, and *tgαK* is a weighted average parameter characterizing the change in the radii of cations when their charge changes:

$$tg\alpha K = \sum_{i=1}^{n} tg\alpha_i \qquad (4).$$

This semi-empirical approach considers slag a chemically united system whose melt properties depend on structure. Based on this concept, an oxide-fluoride melt composition can be transformed into integral criteria. Derived criteria are used to predict certain slag properties.

RESEARCH RESULTS

Outcomes of slag-metal interaction prediction in the course of electroslag remelting

Figure 4 presents the equilibrium content of elements in the metal phase that are most oxidized by sags' oxides and the slag-to-metal ratio corresponding to a certain conventional time of remelting in seven certain subsystems (shown as points on built curves).

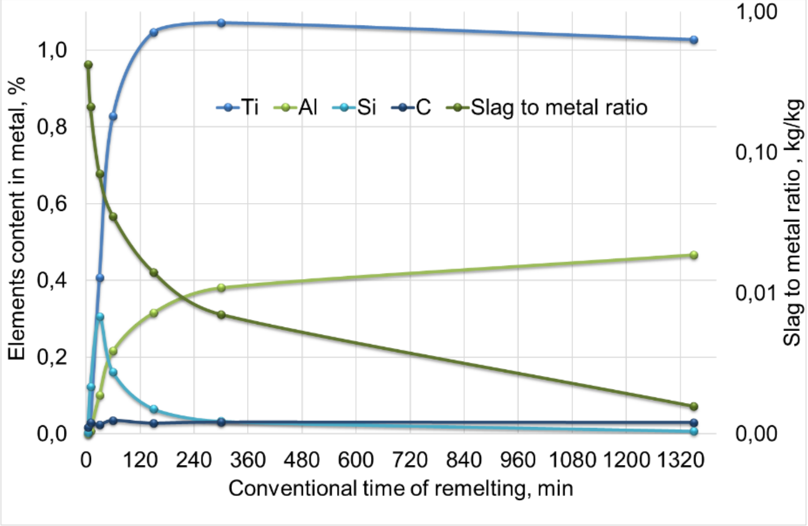

FIG 4—Equilibrium content of active to oxygen elements in metal phase and slag to metal ratio at Inconel 718 remelting with slag $34CaF_2$-$30Al_2O_3$-$27CaO$-$0.5SiO_2$-$2.5MgO$-$6TiO_2$.

The slag-metal mass ratio at the fifth minute of remelting is nearly 42 kg/kg and drops throughout the process to 0.016 kg/kg at the completion of the melt. It is well visible that the system is most reactive when the slag-to-metal ratio is very high at the beginning of the remelting. Due to that, slag's oxidation action sufficiently affects the content of elements, which react with oxygen at this period. The content in the metal of active elements whose presence is critical for alloy properties (Ti, Al) at the process beginning (first 30-60 minutes) is close to zero. The sufficient changes in the content of both titanium and aluminium occur for around the first two hours, while the mass losses of the metal phase and gains of the slag phase mainly occur (Figure 5).

After that period, when metal phase amounts start to be bigger (and the slag-to-metal ratio - smaller) than some critical values, the relative losses of equilibrium metal phase mass go down. This critical time can be supposed to be the time when the oxidative ability of slag is exhausted. Nevertheless, it does not mean that exchange reactions between slag and metal phases are stopped. It is visible (Figure 4) that titanium content grows during up to four hours. Despite a slight permanent reduction of its content during the lasting time, it is still higher than the initial value.

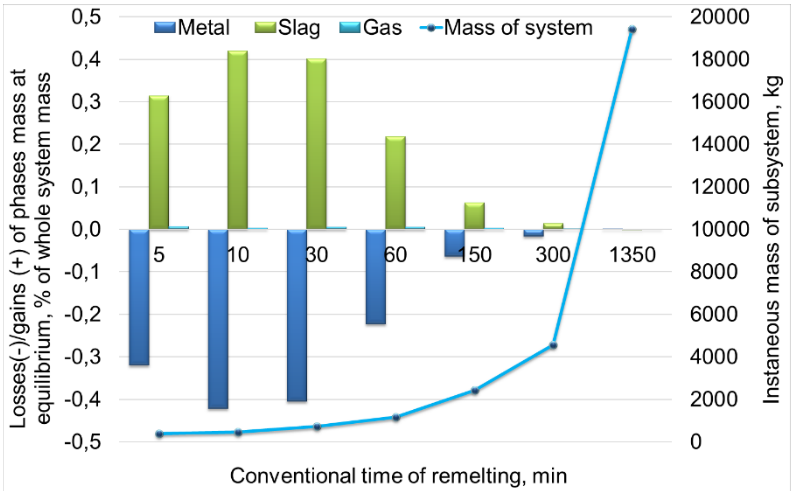

FIG 5—Phases losses/gains in the reactive subsystems at a course of ESR in argon atmosphere (line is plotted by additional vertical axis).

Aluminium content grows to the end of the remelting but doesn't reach the initial content due to silicon reduction from the slag, which goes most actively in the first minutes. At the start of the process, the silicon content goes to maximum and reduces during more than two hours of remelting, and it is still in metal until the end of the melt. Carbon in metal shifts by 0.01-0.02 % from the initial value in the period of metal losses. Thus, the calculations under the developed dynamic model of the gas-slag-metal interaction during the ESR process under a protective atmosphere show that even in an inert gas atmosphere, changes in oxygen-active elements content in the metal phase take place, which cause inhomogeneity of their content along ingot height.

When the dynamic of the ESR process is the same (same ingot, melting rate) or precise evaluation is not important, the assessment of interactions in the gas-slag-metal system can be done using a single system approach - the results of such a way for comparing four ESR slag actions (Figure 6).

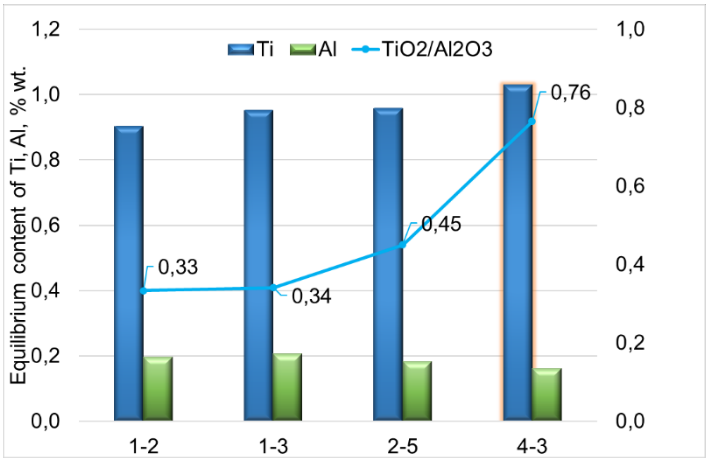

FIG 6—Al and Ti equilibrium content in the metal phase interacted with slags having different TiO_2/Al_2O_3 ratios in their compositions (Table 2).

Inconel 718 has an extensive solidification range (1483–1617 K), so slags with the widest melting range (1-2, 1-3, 2-5 and 4-3) were compared. For slag with the highest TiO_2/Al_2O_3 ratio, the titanium content in the metal is slightly higher than the initial one (1 wt.%), possibly due to the reduction of titanium from the slag. This version is also supported by the greatest loss in aluminium content in metal compared to other slags used. However, the cause may also be a metal loss, as was found for the comparative slag $34CaF_2$-$30Al_2O_3$-27CaO-$0.5SiO_2$-2.5MgO-$6TiO_2$.The titanium content close to the original was calculated using 1-3 and 2-5 slags. Aluminium losses in the metal are minimal for slags 1-2 and 1-3. Slag 1-3 is the most inert from the point of view of preserving both elements.

Outcomes of slag's physical properties modelling using Directed Chemical Bonds Concept

The atomistic approach was used to interpret slag's measured properties from the Directed Chemical Bonds Concept (DCBC) standpoint to build predictive models for slag engineering considering the physical properties of ESR slag melts. Table 3 lists the unpolarised radii of atoms ($\dot{R}_{u_i}$) and the gradient of changes in the radii of atoms from their charge ($t\dot{g}\alpha_i$) that belongs to elements in the studied slag system CaF_2 – Al_2O_3 – TiO_2 – MgO (Table 2).

TABLE 3 – Radii of elements ($\dot{R}_{u_i}$) and gradients of their change from their charge (tgαi) to interaction

Element	$\dot{R}_{u_i}$, (10^{-1}nm)	$t\dot{g}\alpha_i$
Ca	2.02	0.151
Ti	1.45	0.085
Al	1.468	0.156
Mg	1.6	0.196
O	0.73	0.136
F	0.96	0.142

Tab. 4 presents the interatomic interaction parameters calculated for experimental slag compositions of the CaF2—Al2O3—TiO2—MgO system.

TABLE 4 – The parameters of interatomic interaction in the studied slags' melts

Slag #	d	Δe	tgα	∆Zm	Zka	Zkk	Zaa	Zak
1-1	3.2513	-2.7444	0.1502	0.0108	-0.23031	-1.32999	-3.57101	-2.5141
1-2	3.2274	-2.5349	0.1506	0.0062	-0.12664	-1.22344	-3.45441	-2.40823
1-3	3.2209	-2.3552	0.1505	0.0031	-0.04222	-1.13722	-3.3533	-2.3131
2-1	3.8161	-2.7419	0.1315	0.0269	-0.42814	-1.56892	-3.45975	-2.31482
2-2	3.6791	-2.6378	0.1351	0.0194	-0.33979	-1.46586	-3.42745	-2.2989
2-3	3.5347	-2.5097	0.1383	0.0125	-0.24118	-1.35587	-3.38104	-2.26926
2-4	3.3836	-2.3573	0.1413	0.0062	-0.13198	-1.2385	-3.32003	-2.22589
2-5	3.2256	-2.1782	0.1439	0.0007	-0.01087	-1.1124	-3.24295	-2.16775
3-3	3.4051	-2.2597	0.1412	0.0051	-0.08413	-1.18915	-3.26822	-2.17643
4-1	3.5018	-2.5083	0.15	0.0108	-0.14606	-1.2391	-3.41106	-2.3627
4-2	3.5744	-2.6832	0.1577	0.0111	-0.17787	-1.25373	-3.52106	-2.50572
4-3	3.6024	-2.7749	0.1649	0.0058	-0.16662	-1.2217	-3.59282	-2.60856

These parameters characterize the chemical and structural state of the slag systems: *d* (10^{-1} nm) is the average interatomic distance of interacting ions in the melt; *Δe* represents the number of electrons localized in the direction of their connection, e; *tgα* means the weighted average value of the gradients of changes in ion radii with changing its charge; *ρ* expresses the ratio of the number of cations to the number of anions; ∆*Zm*, as was mentioned above, is the indicator of non-equilibrium state of cationic sublattice.

The analysis showed that the parameter of the non-equilibrium state of cationic sublattice ΔZ_m demonstrates a close relationship with the chemical composition of the slags under study (Fig. 7). The physicochemical essence of the parameter ΔZm characterizes the stability of the cationic sublattice: the stability condition is that ΔZm tends to zero.

Combined with the established relationship ΔZm – Al_2O_3, the minimal value of integrated criteria is reached at Al_2O_3 content, approaching its maximum values from the investigated range (Fig.7 a) and at CaF_2 content is close to the minimal level and TiO_2 13-18% (for the system under study).

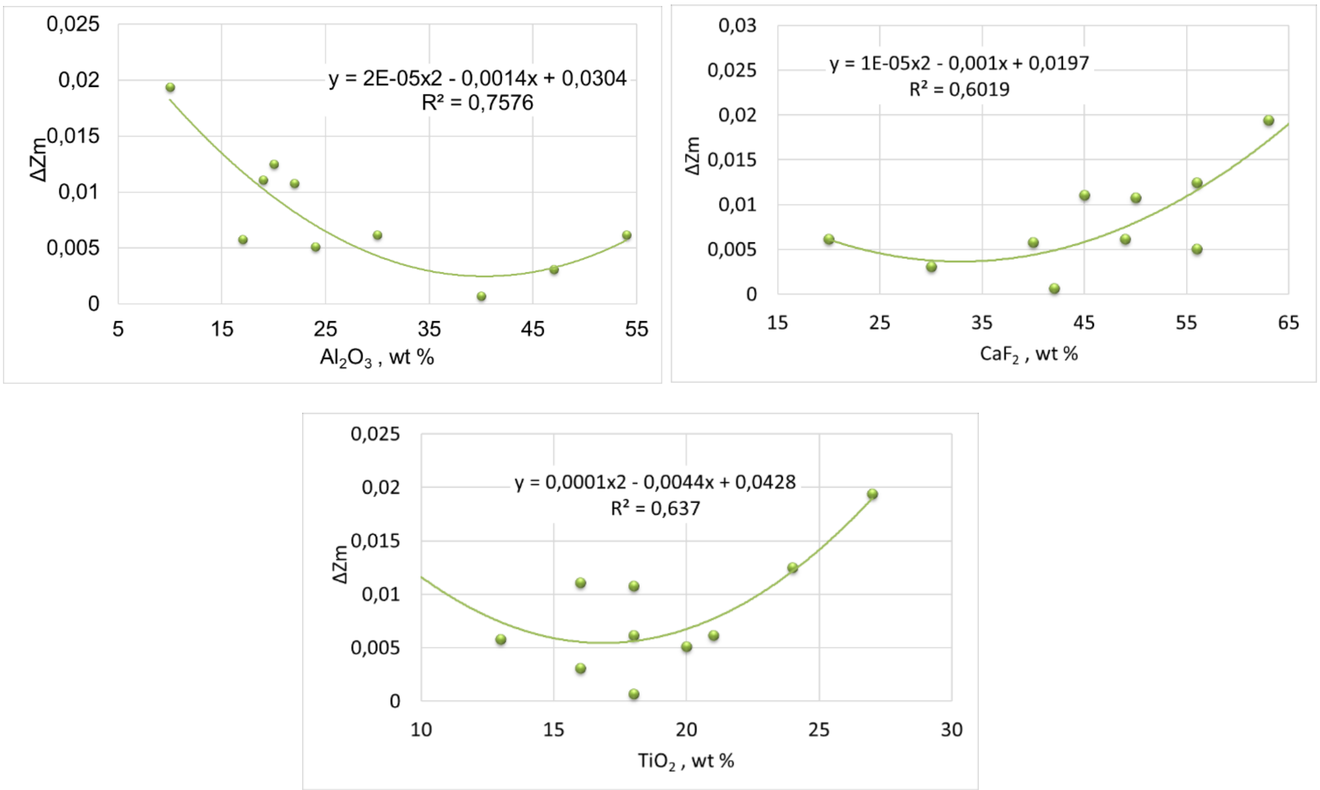

FIG 7—Relationship between the content of Al_2O_3 (a), CaF_2 (b) and TiO_2 (c) with the non-equilibrium index of the cationic sublattice ΔZ_m.

The established dependences between ΔZm parameter and composition of the slags' system under study and its properties (Fig. 7) make it possible to consider slags with minimal content (% wt) of CaF_2 – 30 (Fig. 7b) and TiO_2 - 13 (Fig. 7c) having not very high melting temperatures range and also satisfactory melting range according to Table 2.

As shown in Fig. 8, the parameter ΔZm has ……..an acceptable relationship with the considered physical properties of slags.

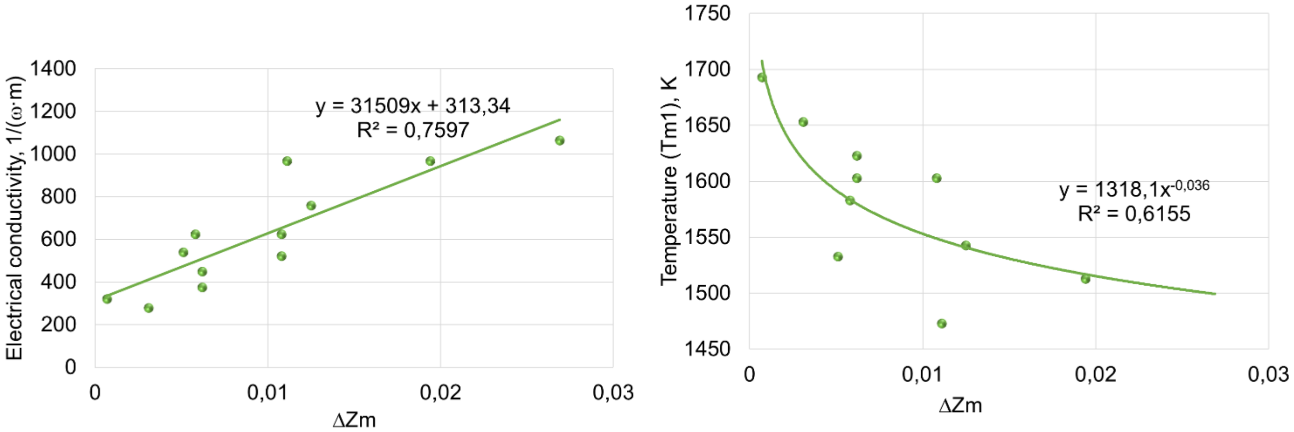

FIG 8—Relationship between the non-equilibrium parameter of the cationic sublattice ΔZm and the properties of experimental slags: a – electrical conductivity; b – liquidus temperature of slag melting.

The involvement of the DCBC ab initio approach allows building models of electrical conductivity and temperature of melting from the integral parameter of the non-equilibrium state of cationic sublattice, ΔZm. Found dependencies are grounds for using this integral criterion when predicting these and other important properties of oxide-fluoride and other metallurgical slags.

DISCUSSION

Possibilities and limitations of the dynamic model of electrosalg remelting process

The current level of development of numerical methods for thermodynamic systems simulation has opened up new opportunities for improving existing and developing new industrial processes. However, digitalization alone is insufficient since the simulation results must accurately reflect the real system. The accuracy of the system description and the reliability of thermodynamic programs play a decisive role in assessing complex processes, especially in the metallurgical industry, where sampling and analysis of samples are quite complex and expensive.

The provided view on ESR ingot composition formation while ESR differs from the traditional approach to the physicochemical calculation, which is usually used for ESR ingot composition estimation. Representation of this process as a line of subsystems allows for a step ahead in understanding the ESR ingot formation pattern and makes it possible to predict changes in slag-metal interaction during the process. The simpler single-system approach of thermodynamic calculations for the stable stage of electroslag remelting in argon is also relevant for comparing different slags under the same process conditions (same ingot, melting rate, and temperature) or as a preliminary estimation. Calculations carried out using both the dynamic physicochemical model ESR process with several subsystems, and a single-system approach show that even with neutral gas and oxide-fluoride slags, gas-slag-metal interaction causes changes in the content of active-to-oxygen elements such as titanium and aluminium, silicon etc. The intensity of chemical composition changes is biggest at the higher slag-to-metal ratio. The highest slag-to-metal ratio is at the beginning of the process and permanently reduces during the process to the value of specific slag consumption usually used for thermodynamics estimation of the ESR.

The chemical composition of the phases changes as a result of oxidation-reduction reactions. Besides, slag's ability to desulphurize metal and assimilate non-metallic inclusions gradually reduces during the ESR process. Moreover, a slag bath accumulates all products of chemical interactions between metal and slag, changing its chemical and, accordingly, physical properties, which are crucial for the stability of the process and the resulting quality of the ingot.

The slag is inert to metal when no or very minor oxidation occurs, and it is usually good for ingot quality and technology operation. For such slags (with low content of stable oxides or fluorides only), the thermodynamic calculations show no changes outside the permissible range in the chemical composition of phases. Otherwise, when changes are significant, the composition of a consumable electrode should be adjusted, or slag should be changed for a less reactive one, or, in quite rare cases, metal alloying through the slag should be envisaged, requiring additional calculations.

The proposed more precise description of the electroslag remelting process as a line of subsystems can be used to predict changes in ingot composition along its height. The most important advantage of the dynamic model is its possibility to predict and exclude factors affecting the metal composition along the ESR ingot height or to respond to them properly. Such analysis can be done in different contexts depending on the purpose of the research (e.g., changes in the content of active components in the system). Summarising, the predictive physicochemical model of ESR ingot formation in dynamic can be used to achieve several goals:

- adjust existing composition or search for new slags. For example, new slag composition could replace high CaF_2 composition at ESR of alloyed and high-alloyed steels in both stationary and short-collar moulds. The industrial tests conducted on the developed slag have shown the following benefits: oxide inclusion content was reduced by 0.5 points and power consumption - by 17%. The more environmentally friendly with more than 2 times less calcium fluoride composition at a lower cost of 23-25% was developed (Stovpchenko, G. et al., 2020b; Lisova, L. et al., 2020);
- maintaining the active components content (Ti, Al, etc.) at high-alloyed steels and alloys while

remelting (Stovpchenko et al., 2023) and a low level of oxygen in steel during ESR (Medovar, L. et al. 2018a; Stovpchenko, G. et al., 2018a);

- development of slags with specific properties, for example, self-disintegrating slag (Stovpchenko, G. et al., 2018b);
- development of slags for new steels and alloys (AHSS, superalloys, etc.) remelting (Stovpchenko, G. et al., 2014; Davidchenko, S. et al., 2017; Medovar, L. et al., 2023).

In general, the proposed physicochemical dynamic model of the ESR process in the new paradigm could be a good tool for predicting how a slag composition affects an ingot's homogeneity on its height and the yield of a suitable metal. Such prediction is crucial in manufacturing high-alloyed steels and alloys by electroslag remelting. Uncontrolled changes in slag composition while remelting can cause ingot scrappage. However, it is even more dangerous when minor changes occur unheeded and are ignored, posing a significant risk of responsible parts damage at exploitation.

Possibilities and limitations of the Directed Chemical Bonds Concept in the prediction of electrical conductivity and melting temperature of ESR slags

Based on DCBC principles, atomistic models were developed to predict the physical properties of Ti-bearing ESR slags. Although these models were built using a limited amount of experimental data, the results demonstrate that the parameter of the non-equilibrium state of cationic sublattice ΔZm can be used to predict the properties of molten slags.

ΔZm parameter's validity explains that the crystal lattice restructuring of solid oxides at high temperatures occurs with a disordered liquid slag melt formation. The non-equilibrium state of the cationic sublattice of slag (Fig 9) can be caused by structural differentiation depending on the geometric sizes ratio of neighbouring ions and the relative arrangement of cation-anion clusters formed in complex composition melts.

a) equilibrium state

b) non-equilibrium state

FIG 9—Scheme of the cationic sublattice displacement inside the anion sublattice.

In the centre of such clusters are cations (calcium, aluminium, titanium, magnesium) surrounded by oxygen anions (fluorine and or complex anions). In a homogeneous melt, electron density distribution between cations and anions can be relatively stable. When an element is ionized, its radius changes significantly (Tab. 3): cations decrease in size due to transferring part of their electronic field to the anions in their immediate environment. In this case, the multicomponent slag system tends to the most favourable energy state, which can be described using the integral parameters of interatomic interaction (the model parameter ΔZm tends to zero). The bonds between cations and anions in a liquid melt at a given chemical composition and temperature retain short-range order, which determines the structure and complex properties of the liquid melt.

Atomistic models constructed using the integral parameter of the non-equilibrium state of cationic sublattice, ΔZm, offer promising possibilities for evaluating the physical properties of slags. ΔZm and other integral criteria offer promising possibilities for properties evaluation for other slags' and metals' melts (Togobitskaya, D., 2023; Muravyova, I. et al., 2021; Stepanenko, D. et al.; 2017; Babachenko, A.I., 2020). Integral criteria are particularly effective when studying the multivariate compositions of melts, where more than one component is altered.

A proposed DCBC predictive model using ab initio principles helps develop a fundamental understanding of the phenomena occurring during slag melting and their interaction with metal melts in various metallurgical processes. It should be mentioned that slag engineering is now one of the trends because of the urgent necessity to be prepared for changes in the green transition of steelmaking, which is already ongoing. The issue is that an increased share of DRI in electric arc furnaces increases the forming slag's volume and changes its composition. To keep efficient steel production, it became very important to have the possibility to make theoretical predictions of different slag (and alloys as well) characteristics. The melting temperature and electric conductivity were considered in this article, and viscosity, sulphide capacity, surface tension, and others can be predicted for various multicomponent molten slags whose composition changes in a wide range. The proposed concept makes it possible to reduce experimental measurements and tests, which are time-consuming and resource-consuming. This methodology is particularly relevant in metallurgy and materials science, where a detailed understanding of the underlying principles of chemical composition's effect on properties is essential for developing new materials and technologies.

Future works include experimental proof of dynamic models using slag and metal sampling at heavy ESR ingot producing and improvement of accuracy of DCBC models for physical properties of slag prediction using a sufficiently larger amount of experimental data for Ti-bearing and other metallurgical slags.

CONCLUSIONS

Both the dynamic physicochemical model ESR process in neutral gas presented as a chain of subsystems and a single-system estimation revealed that despite using neutral gas and oxide-fluoride slags participate in gas-slag-metal interaction, causing changes in the content of active-to-oxygen elements such as titanium, aluminium, and silicon in a metal. The highest intensity of chemical composition changes occurs at the higher slag-to-metal ratio, which is at the start of the process and permanently reduces at its end to the value of a specific slag consumption.

The dynamic model is promising to study the composition changes along ingot height caused by the oxidative action of slag during the process, making it possible to predict ready ESR ingot's homogeneity and increase the yield of a suitable metal.

Directed Chemical Bonds Concept presenting a semi-empiric system providing effective concentration and convolution of the ab initio information on the type of bonds in multicomponent systems was employed to find integral criteria for predicting physicochemical and thermophysical properties of slags from their composition. The parameter ΔZm characterizing the non-equilibrium state of the cation sublattice in the oxide melt is the suitable predictor of electric conductivity and melting temperature of studied slags.

The developed physicochemical dynamic model of the ESR combined with an ab initio approach of the Directed Chemical Bonds Concept that can predict slag properties becomes a step towards a comprehensive model of the ESR ingot formation and tailored functional slags development for specific compositions of alloys whose homogeneity is crucial for quality.

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