



Physicochemical Modelling of ESR Ingot Composition Changes

Fyzikálně-chemické modelování změn složení elektro-struskově přetavených ingotů

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Abstract

Electroslag remelting (ESR) is an essential technological step for producing the highest-quality steel and alloys. Today, ESR is seen as a tool to enhance ingot structure, homogeneity, and yield, rather than just refining metal from sulphur and non-metallic inclusions, since the electrode has already passed through refining and deep degassing during primary melting and ladle treatment. Nevertheless, fluoride-oxide slag is a crucial part of the process, and its interaction with metal occurs throughout the whole remelting duration. Though ESR slag contains stable oxides mainly, it can still oxidize key elements in steel and alloys, especially oxygen-active elements (aluminium, titanium, and silicon). Our perspective on the additive nature of the ESR process in a protective atmosphere led to a better understanding of the drastic growth of slag-to-metal mass ratios during remelting, giving the ability to make a prognosis of changes in slag and metal composition. Dividing the entire process into subsystems enables forecasting the composition at a specific point in the process, at a relevant height of the ESR ingot. The results of thermodynamic modelling are valuable for improving ESR technology and selecting the most suitable slag composition from the existing palette or customizing the slag for a specific alloy.

Keywords: electroslag remelting, thermodynamic modelling, dynamics, gas-slag-metal interaction

Abstrakt

Elektrostruskové přetavování (ESR) představuje klíčový technologický krok při výrobě ocelí a slitin nejvyšší kvality. V současnosti je ESR vnímáno spíše jako nástroj ke zlepšení struktury, homogenity a výtěžnosti ingotů než pouze jako proces rafinace kovu od síry a nekovových vměstků, jelikož elektroda již prošla rafinací a hloubkovým odplyněním během primárního tavení a pánvového zpracování. Fluoridovo-oxidová struska je ním méně klíčovou součástí procesu a její interakce s kovem probíhá po celou dobu přetavování. Ačkoli struska ESR obsahuje převážně stabilní oxidy, může stále docházet k oxidaci klíčových prvků v oceli a slitinách, zejména prvků s vysokou afinitou ke kyslíku (hliník, titan a křemík). Pohled na aditivní povahu procesu ESR v ochranné atmosféře vedl k lepšímu pochopení výrazného nárůstu poměru hmotnosti strusky ke kovu během přetavování, což umožňuje predikci změn ve složení strusky i kovu. Rozdělení celého procesu na subsystemy umožňuje předpovídat složení v konkrétním bodě procesu, odpovídajícím určité výšce ESR ingotu. Výsledky termodynamického modelování představují cenný nástroj pro zlepšení technologie ESR a pro výběr nejvhodnějšího složení strusky z dostupné palety, případně pro její optimalizaci pro konkrétní slitinu.

Klíčová slova: elektrostruskové přetavování, termodynamické modelování, dynamika, interakce plyn-struska-kov

1. Introduction

Electroslag remelting (**Fig. 1**) is an arc-less, drop-mode melting process of a consumable electrode that is immersed in a layer of electrically conductive slag with sufficiently high resistance (much greater than that of other circuit components - the electrode, molten slag, liquid metal pool, solidified ingot, bottom plate, high current loop and transformer).

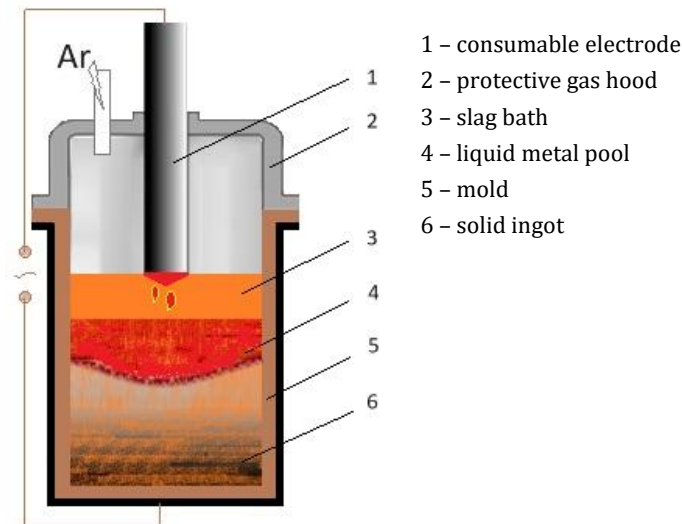


Fig. 1 Simplified diagram of the ESR in argon protective atmosphere

Obr. 1 Zjednodušené schéma ESR v ochranné atmosféře argonu

The passage of electric current through the slag generates heat, which powers the melting process. Drops fall through a refining slag layer, forming a molten metal bath, solidifying within a copper water-cooled mould into a dense, low-defect ingot. Slag properties are crucial for both generating heat (ESR process thermal efficacy), maintaining the metal bath's composition maximally close to the initial composition of the consumable electrode (except for absorbing non-metallic inclusions), solidification conditions (temperature regimes), and smooth ingot surface formation.

The slow rate of metal supply from the consumable electrode through the slag layer, which acts as both an electric heater and thermal buffer, leads to a shallow liquid metal pool. Permanently renewal of liquid metal pool by drops coming from consumable electrode helps sufficiently reduce segregation, the slow melting rate and high-gradient solidification in the copper water-cooled mould provide a minimal (in comparison to cast forging ingots or continuously cast billets of the same diameter) volume of the simultaneously solidifying liquid metal bath and mushy zone. This is a reason for worldwide recognition of "ESR quality of ingot" featuring a dense dendritic structure, no shrinkage, and a smooth side surface, ensuring high product yield. Thus, effective ESR technology necessitates a slag engineering that balances chemical inertness and optimal physical properties (melting temperature interval, electrical conductivity, viscosity, etc.).

This article aims to explain the changes in the physicochemical conditions that occur during the remelting of consumable electrodes in a protective gas atmosphere using a single slag introduced at the beginning of the process because of the drastic reduction of slag-to-metal ratio.



2. Physicochemical Features of the Electroslag Remelting Process

From a physicochemical point of view, the electroslag remelting process has several characteristic features in comparison to batch-type melting processes of traditional steelmaking (in electric arc and basic oxygen furnaces (EAF and BOF) and ladle treatment (ladle furnace and vacuum degassing) as well as to usual forging ingot or continuous casting.

The primary distinction is that ESR is a melting, refining, and casting process simultaneously. Two opposite processes in their nature and favourable conditions—melting and solidification—occur at the same time in a copper water-cooled mold. The positive for melting/refining is that no metal contamination by refractories, and a well-developed surface of interaction between slag and metal. Unfavourable conditions for melting—resistive-type heating and intensive cooling—cause ESR's low energy efficiency. The positive is that metal comes slowly, and the liquid metal pool is permanently renewed. Intensive heat inflows from the melting zone compromise the solidification rate and cause uneven temperature distribution on the vertical axis. However, heat outflows to intensively cooled mold surface is the source of high temperature gradient at solidification, providing a dense dendrite structure of the EAR ingot. The most heat is generated at the contact surface between the resistive slag bath and the consumable electrode side surface and tip, forming a liquid metal film that drips due to gravity; temperature gradually decrease from hot area of a slag bath (variation along vertical axis in slag bath can reach 200 K to a metal pool surface and further away to its bottom end, where the ESR ingot forms under the cooling action of the copper water-cooled mould.

There are three contact surfaces between slag and metal (liquid film on the tip of the consumable electrode, metal drops sinking through the slag bath, and the contact surface between the liquid slag bath and liquid metal pool). The formation and movement of metal droplets constantly refresh all interfaces. Different estimations of their geometrical and residence time parameters and relative shares in the refining exist, but all authors agree that the total metal-slag interaction surface is highly developed. The high temperatures of the melts (1900-2100K) and the extensive surface of slag-metal interactions bring the reactions closer to equilibrium that allows the use of thermodynamics.

Several other features of the electroslag remelting of a consumable electrode are essential to understanding the core of ESR ingot formation, which were put as the base in the physicochemical modelling of changes in gas-slag-metal system composition during ingot Electroslag Remelting. The liquid metal has no direct contact with an atmosphere, as the slag bath separates them. Gaseous phase emissions from slag-metal reactions and evaporative processes from the slag are expelled into the furnace atmosphere, which undergoes gradual replenishment. The gaseous environment above the slag bath does not engage directly with the molten metal, but the electrode surface oxidizes in the presence of oxygen.

An oxygen-free atmosphere—mainly argon or nitrogen (depending on the steel grade)—effectively mitigates this issue by blocking oxygen activity in the slag and its transmission to the metal. For this reason, modern ESR facilities typically employ a closed hood that encloses the entire electrode to sustain a protective gaseous atmosphere. The solid metal of a consumable electrode doesn't participate in the slag-metal interaction before it melts. Liquid metal pool incrementally solidifies at its bottom, and an ingot exits the reaction zone after interacting with the slag, and the forming products of reactions of metal components interacting with slag are permanently removed. In contrast, molten slag continues refining processes, assimilating slag-metal interaction products and non-metallic inclusions from the electrode.

Often, ESR involves charging the entire slag mass at the start of the remelting process, without adding premelted slag or its components. The solidified ingot metal composition changes along its height because slag-to-metal ratio permanently reduces from very high values at the beginning of the remelting to a so-called “slag consumption” value (20-50 kg per ton). In this case, the slag bath composition changes due to the accumulation of reaction products between slag and metal and losses on evaporation in the gas phase. From this perspective, the technology involving the continuous addition of slag for its refreshment and compensation losses for slag skin formation partially mitigates changes in slag composition. Nevertheless, even at fresh slag additions, the slag-to-metal ratio drastically varies throughout the electroslag remelting process. Unsurprisingly, a lasting change and substantial shift in the slag-metal mass ratio (**Fig. 2**) lead to vastly different conditions for slag-metal interaction during electroslag remelting.

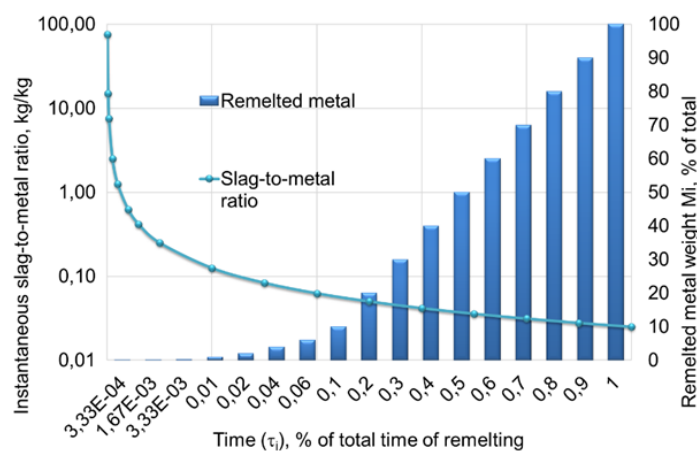


Fig. 2 Timeline of slag-to-metal ratio at appropriate mass of remelted metal at ESR ingot remelting when a whole slag consumption makes 25 kg/ton of metal

Obr. 2 Změna poměru struka-kov v čase při odpovídající hmotnosti přetaveného kovu pomocí ESR, kdy celková spotřeba strusky činí 25 kg/t kovu

The diagram provides a summary and demonstration of the characteristics inherent in the physical and chemical processes that transpire during electroslag remelting. The variations in the slag-to-metal ratio are illustrated for a designated slag consumption of 25 kg/t of metal. This uncovered trend is general, regardless of the specific value of slag consumption. Specific slag consumption typically ranges from 20 to 40 kg per ton, with the higher **Fig. 2** often used for thermodynamic calculations of the ESR, providing just a very average result. However, due to the considerable slag-to-metal ratio in the initial minutes of remelting, the oxygen-bearing slag oxidizes the metal most significantly at the start of the process. This effect cannot be overlooked as the oxidative influence of slag remains significant for quite a long time and can cause ingot inhomogeneity along its height.

Changes in a slag's physical properties, such as viscosity, electrical conductivity, and surface tension, are just as significant. They need to be tested to see if they meet the requirements for an efficient ESR process. It's also crucial to uncover deeper connections between experimentally measured values and chemical composition using atomistic approaches. This allows for predicting the physical properties of molten slag, making it easier to select the right slag. The Directed Chemical Bonds Concept, created by Prof. E. Prikhodko and further developed by his team at the Z. I. Nekrasov Institute of Ferrous Metallurgy of the NASU [10], demonstrates promising results for these purposes.

3. Methodology for Modelling Changes in ESR Ingot and Slag Compositions over Time

Analysing the additive nature of the ESR process in a protective atmosphere, the authors provided insights enables developing a procedure for slag-metal interaction modelling during the ESR (**Fig. 3**).

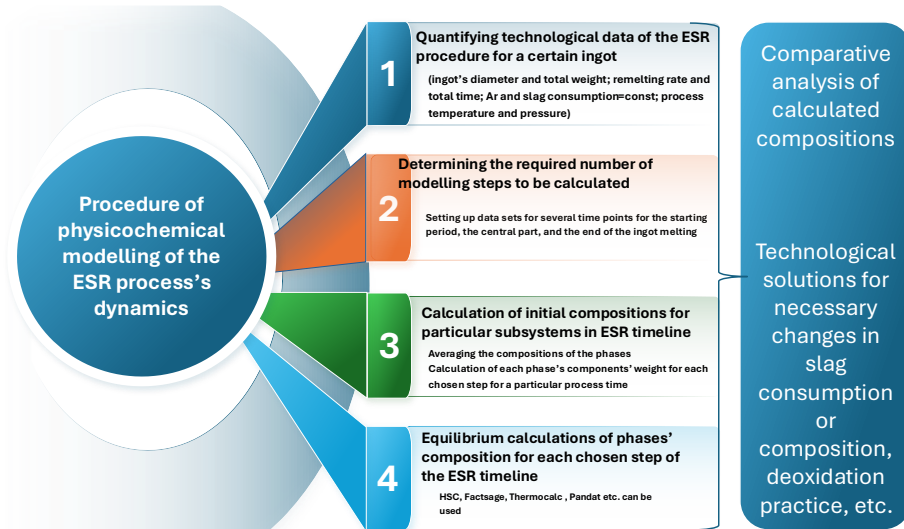


Fig. 3 Procedure of the gas-slag-metal interaction modelling during electroslag remelting

Obr. 3 Postup modelování interakce plyn–struska–kov při elektrostruskovém přetavování

At first, the technological data of certain ESR ingot manufacturing should be collected. For example, the dynamic ESR model demonstration system 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 particular time interval. The metal mass and slag-to-metal ratio during remelting were derived from a melting rate of 14.2 kg/min, obtained from ESR practices for similar ingots.

The second stage evaluates the number of modelling steps required to address this task. Based on the chosen purposes, appropriate time intervals (i) should be established. The most reasonable approach is to combine the calculated subsystems with an actual probe of the ingot. The beginning of remelting is interesting due to the highest slag-to-metal ratio. However, this ingot portion will be discarded, prompting calculations of higher ingot horizons.

After averaging the compositions of the gas-slag-metal phases, the calculation of the weight of each phase's components for each chosen moment in a specific process should be performed, forming the line of proper subsystems. The input data is the mass of metal remelted at a specific time (i), considering the melting rate, total mass of slag, and argon volume in the ESR plant's closed chamber. For each designated time, develop a subsystem with the total masses of slag, gas, and the instantaneous mass of molten metal that will be used as initial data in software for equilibrium composition calculation. In all subsystems, the remelted metal mass is a variable (m_i), while the primary masses of slag and gas phases remain constant.

Thermodynamic calculations of the equilibrium state of the "gas-slag-metal" system, using CALPHAD methodology can be done using HSC Chemistry, Pandat, ThermoCalc, and similar software. In the presented examples, thermodynamic calculations for the "gas-slag-metal" system were performed using HSC Chemistry software [2].

The comparative analysis of primary mass data from subsystems and equilibrium calculations enables recognizing changes in the masses and compositions of phases. The primary advantage of the proposed approach to modelling probable changes in ingot composition along its height is that it enables the prediction of changes in gas-slag-metal interaction conditions.

The main limitation is its time-consuming nature, making it impractical when changes in ingot composition are not critical. Nevertheless, this approach assists in identifying suitable technological solutions for necessary changes in slag consumption or composition, deoxidation practices, and so on.

4. Outcomes of Slag-Metal Interaction Prediction in the Course of Electroslag Remelting

Changes in metal composition were calculated according to the proposed procedure of physicochemical modelling of the ESR for slag $34\text{CaF}_2/30\text{Al}_2\text{O}_3/27\text{CaO}/0.5\text{SiO}_2/2.5\text{MgO}/6\text{TiO}_2$ and superalloy Inconel 718 at 1873 K (Tab. 1).

Tab. 1 The chemical composition of the Inconel 718 used in the calculation

Tab. 1 Chemické složení slitiny Inconel 718 použitý v rámci výpočtu

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 equilibrium contents of the most oxidisable elements in the metal and the matching slag-to-metal ratio for a specific time for seven subsystems are shown as points on the curves of Fig. 4.

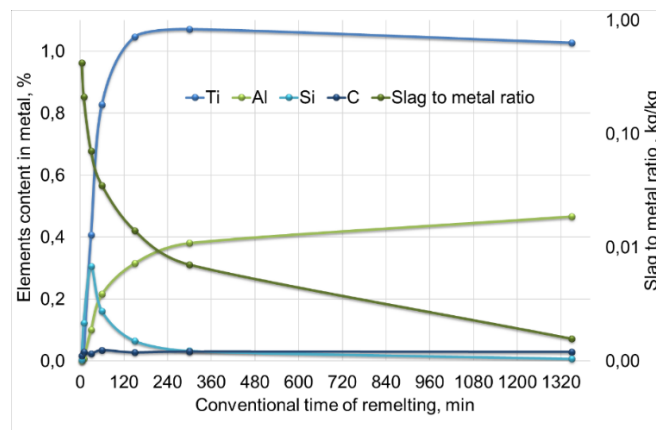


Fig. 4 Equilibrium content of active-to-oxygen elements in the metal phase and slag to metal ratio at Inconel 718 remelting with slag $34\text{CaF}_2-30\text{Al}_2\text{O}_3-27\text{CaO}-0.5\text{SiO}_2-2.5\text{MgO}-6\text{TiO}_2$

Obr. 4 Rovnovážný obsah prvků aktivních vůči kyslíku v kovové fázi a poměr strusky ke kovu při přetavování slitiny Inconel 718 se struskou $34\text{CaF}_2-30\text{Al}_2\text{O}_3-27\text{CaO}-0.5\text{SiO}_2-2.5\text{MgO}-6\text{TiO}_2$

The slag-metal mass ratio at the fifth minute of remelting is approximately 42 kg/kg and decreases to 0.016 kg/kg by the end of the melt. It is clearly visible that the system is most reactive when the slag-to-metal ratio is very high at the beginning of the remelting process. Consequently, the oxidation action of the slag significantly impacts the content of elements that react with oxygen at this period. The content of active elements critical for alloy properties (Ti, Al) in the initial stages of the process (first 60 minutes) is nearly zero. The weighty changes of the elements content occur within two hours, while the mass losses of metal and the gains in slag primarily occur (Fig. 5).

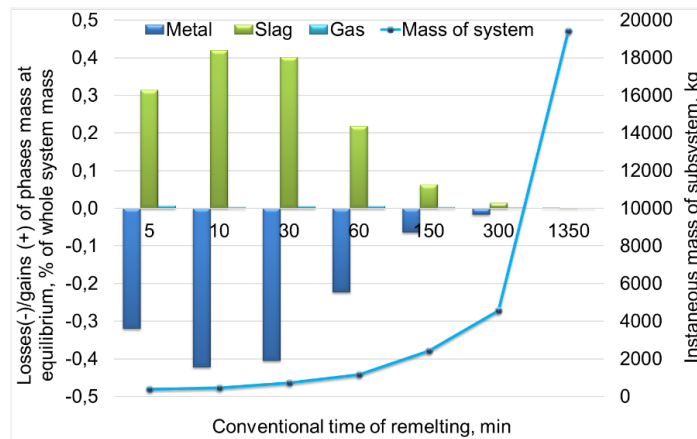


Fig. 5 Phase losses/gains in the reactive subsystems during the ESR in argon atmosphere

Obr. 5 Úbytky a přírůstky jednotlivých fází v reaktivních subsystémech během ESR v argonové atmosféře

The slag-metal mass ratio at the fifth minute of remelting is approximately 42 kg/kg and decreases to 0.016 kg/kg by the melt end. It is clearly visible that the system is most reactive when the slag-to-metal ratio is very high at the beginning of the remelting process. Consequently, the oxidation action of the slag significantly impacts the content of elements that react with oxygen at this period. The content of active elements critical for alloy properties (Ti, Al) in the initial stages of the process (first 60 minutes) is nearly zero. The weighty changes of the elements content occur within two hours, while the mass losses of metal and the gains in slag primarily occur (Fig. 5).

After that period, relative losses of equilibrium metal phase mass diminish as the metal phase begins to be bigger (and the slag-to-metal ratio decreases) beyond critical values. This moment marks the depletion of the slag's oxidative capacity. However, exchange reactions between slag and metal phases continue. As shown in Fig. 4, titanium content increases for up to four hours. Although it slightly decreases over time, it remains higher than the initial value.

The aluminium content rises until the end of the remelting process, but does not reach the initial level because of a reduction in silicon from the slag, which occurs most actively during the first few minutes. At the beginning of the process, the silicon content peaks and then decreases over more than two hours of remelting, remaining in the metal until the end of the melt. The carbon content in the metal shifts by 0.01-0.02% from the initial value during the period of metal losses. Therefore, calculations based on the developed dynamic model of gas-slag-metal interaction during the ESR process in a protective atmosphere indicate that even in an inert gas environment, changes in the content of oxygen-active elements in the metal phase occur, resulting in inhomogeneity of their distribution along the height of the ingot.

5. Exploring the Opportunities and Limitations of Electroslag Remelted Ingot Composition Modelling in Dynamics

Our view on how ESR ingot composition forms diverge from traditional physicochemical calculations commonly used to estimate ESR ingot composition. By modelling this process as a series of subsystems, we can gain a clearer understanding of the ESR ingot formation pattern and 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 useful for comparing different slags under the same process conditions (same ingot, melting rate, and temperature) or as a preliminary estimate. Calculations conducted using both the physicochemical modelling of the ESR process dynamics with various subsystems and a single-system approach indicate that even with neutral gas and oxide-fluoride slags, gas-slag-metal interaction leads to alterations in the content of active-to-oxygen elements such as titanium, aluminum, silicon, and others. The intensity of changes in chemical composition is highest at higher slag-to-metal ratios, occurring at the beginning of the process and continually decreases throughout the process to the level of specific slag consumption typically used for thermodynamic estimation of the ESR.

The chemical composition of phases changes due to oxidation-reduction reactions. Additionally, slag's ability to desulphurise metal and assimilate non-metallic inclusions gradually decreases during the ESR process. A slag bath accumulates products of chemical interactions between metal and slag, altering its chemical and physical properties, which are vital for process stability and ingot quality. The slag is inert to metal when no or very minor oxidation occurs, and it is usually the goal for ingot quality and technological operations. 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. Any additions (deoxidizing or alloying materials) can be made only into a slag bath that reduces the precision of resulting changes in the liquid metal pool compositions due to difficulties in control and adjustment, as the final composition can be verified only in a solidified ingot. Thus, an ingot primarily inherits the composition of the consumable electrode. 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 relatively rare cases, metal alloying through the slag should be envisaged, requiring additional calculations.

One significant benefit of ESR dynamics modelling is its ability to predict and account for factors that influence the metal composition along the height of the ESR ingot or respond to them accordingly. This analysis can be applied in various contexts, depending on the research's purpose (e.g., shifts in the content of active components in the system).

Summarising, the predictive physicochemical model of ESR ingot formation in dynamics can be used to achieve several goals:

- tailoring existing compositions or searching for new slag for specific alloys. For example, a new slag composition could replace the high CaF_2 content in the ESR of alloyed and high-alloyed steels in both stationary and short-collar molds. 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 decreased by 17%. A more environmentally friendly option was developed, featuring less than half the calcium fluoride content at a lower cost of 23-25%. [3, 9];
- maintaining the active components content (Ti, Al, etc.) at high-alloyed steels and alloys while remelting [11] and a low level of oxygen in steel during ESR [4, 7];
- development of slags with specific properties, like self-disintegrating slag [8];
- development of slags for new steels and alloys (AHSS, superalloys, etc.) remelting [1, 5, 6].

Overall, the proposed physicochemical modelling for the ESR process in the new paradigm could serve as an effective tool for predicting how slag composition impacts the homogeneity of an ingot's height and the yield of a suitable metal.



Such predictions are crucial in the manufacturing of high-alloy steels and alloys through electroslag remelting. Uncontrolled changes in slag composition during remelting can lead to the scrapping of ESR ingots, which can weigh up to 250 tons. Moreover, the situation worsens when minor changes are overlooked, placing critical parts at risk of damage when the product is put into use.

6. Conclusion

A significant diminishing of the slag-to-metal mass ratios from the beginning to the end of an ingot formation is typical for electroslag remelting with a constant slag mass charged at the start of the process, and a gradually increasing remelted metal mass. Adding fresh slag during remelting can partially compensate for slag skin formation losses and keep the slag-to-metal mass ratio more stable, but the overall slag capacity for altering metal composition increases.

The proposed procedure of ESR ingot formation in dynamics shows promise for studying the changes in composition along the ingot's height caused by slag action during the process.

For the ESR process in an inert atmosphere, knowing the slag metal ratio at a particular moment of the electroslag remelting allows building the line of gas-metal-slag subsystems to calculate equilibrium compositions and predict changes in slag and ingot metal compositions. It was shown that fluoride-oxide ESR slags are not entirely neutral to metal and can oxidise steel and alloys (primarily active alloying elements like aluminium, titanium, and silicon) due to chemical reactions between slag and 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 to the value of a specific slag consumption at its end.

This makes it possible to predict the composition along the height of the ESR ingot and increases the yield of suitable metal. Predicting slag and metal composition changes at a particular moment has practical value and can be used for technology improvement. This also paves the way for creating tailored slags for specific alloy compositions, where homogeneity is essential for quality.

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