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Physicochemical Principles of Spinel Formation during Electrode Arc Welding and Cladding Under Flux

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The peculiarities of the process of forming complex compounds, namely, spinels, in flux-cored arc welding for the slag TiO_2–MnO–SiO_2–MgO–CaO–FeO–Al_2O_3 system are studied. An experimental investigation of the mechanism of spinel formation in conditions of electrode arc welding and cladding under flux is carried out. Based on the analysis of microimages of the slag surface obtained using scanning electron microscopy, the mechanism of spinel formation, namely, the growth of microcomplex compounds into macrospinels, is presented. The main stages and mechanism of formation of the complex compounds, namely, spinels, are described. As shown, the structure of spinels is determined by the temperature conditions of the crystallization of the slag melt. The study reveals that one of the determining factors of high-temperature separation of the slag crust during multilayer cladding with overlap of the previous layer is the formation of spinels at the interphase boundary between the slag and the metal. Based on modern ideas about the structure of slag melts, a mechanism for the formation of complex compounds at the interphase boundary between slag and metal is proposed. The main factor determining the process of high-temperature separation of the slag coating for the TiO_2–MnO–SiO_2–MgO–CaO–FeO–Al_2O_3 system is the formation of complex compounds based on spinel-forming elements and slag oxides at the interphase boundary between the slag and the metal.

Key words: flux-cored arc welding and cladding, agglomerated fluxes, slag crust, interphase boundary between slag and metal, slag oxidative potential, spinels, separation of the slag coating.

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Досліджено особливості процесу утворення комплексних з'єднань — шпінелей під час електродугового зварювання під флюсом для шлакової системи TiO_2–MnO–SiO_2–MgO–CaO–FeO–Al_2O_3. Проведено експериментальне дослідження механізму утворення комплексних з'єднань — шпінелей в умовах електродугового зварювання та натоплення під флюсом. На основі аналізи мікрозображень поверхні шлаку, яких одержано за допомогою растрової електронної мікроскопії, представлено механізм утворення шпінелей — переростання мікрокомплексних сполук у макрошпінелі. Наведено основні етапи та механізм утворення комплексних з'єднань — шпінелей. З'ясовано, що структура шпінелей визначається температурними умовами кристалізації шлакового розтопу. В роботі показано, що одним з визначальних чинників високотемпературної віддільности шлакової корки за багатошарового натоплення із перекриттям попереднього шару є утворення шпінелей на міжфазній межі шлак–метал. На основі сучасних уявлень про будову шлакових розтопів запропоновано механізм утворення комплексних з'єднань на міжфазній межі шлак–метал. Основним чинником, що визначає процес високотемпературного відділення шлакового покриття для системи TiO_2–MnO–SiO_2–MgO–CaO–FeO–Al_2O_3, є утворення на міжфазній межі шлак–метал комплексних з'єднань на основі шпінелетвірних елементів та оксидів шлаку.

Ключові слова: зварювання та натоплення під флюсом, аґломеровані флюси, шлакова корка, міжфазна межа шлак–метал, окисний потенціял шлаку, шпінелі, відокремлення шлакового покриття.

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1. INTRODUCTION

In modern industrial production, there is an increasing use of repair welding of worn surfaces made of carbon and low-alloy steels in many industries. The technological conditions for welding such materials involve heating to 500–600°C, which usually leads to problems with separating the slag coating after welding. Existing materials for arc welding and flux-cored welding cannot provide guaranteed separation of the slag coating at temperatures above 250–300°C. This is particularly relevant for multilayer welding with overlapping of the previous layer, which can lead to a disruption of the technological process due to the flow of processes at the slag–metal interphase boundary determined by the physicochemical properties of the slag and the chemical composition of the weld metal.

Improving the technological characteristic of flux, such as high-temperature separation of the slag crust, would generally lead to significant economic benefits by ensuring the continuity of multilayer welding/repair of parts that require heating to 500–600°C. This would eliminate the technological operation of forced separation of the slag crust, reducing costs for eliminating defects from slag inclusions and reducing the overall production time.

In the case of flux-cored welding/cladding, the interaction of the slag–metal phases at the interphase boundary of the tail part of the welding bath in the area where the formation of complex compounds (spinels) is possible, has been poorly studied. Accordingly, processes that result from the interaction of slag–metal and are determined by the mutual transition of individual elements at the interphase boundaries of the reaction zone of welding during automatic flux-cored welding, have been insufficiently studied. This is due to the complexity of conducting research accompanied by very high temperature gradients and sufficiently high crystallization rates. Traditional chemical analysis allows determining the composition of only the initial raw materials, but not the final product of the welding process. However, even such data are very scarce in the literature. Furthermore, there is a lack of data, which would characterize fully the relationship between the composition of the molten flux, the base metal of the weld, and the formation of spinels, which, in turn, worsen the high-temperature detachment of the slag crust.

To ensure guaranteed separation of the slag crust, all interrelated parameters that determine the process of slag crust separation must be taken into account: the physicochemical properties of the flux, welding and cladding regimes, chemical composition of welding materials and base metal. The separation of the slag crust depends on the physicochemical properties of the slag, such as the melting temperature of the slag, interfacial tension, and the temperature of slag crystallization. In turn, physicochemical properties are determined by oxidation processes at the slag–metal interface.

Control of oxidation processes is carried out by changing the ratio of flux components, which together with welding and cladding regimes affects the formation of the weld joint. In this work, the main attention is paid to the process of spinel formation, which is one of the main factors that affect the ease of slag crust detachment.

The ratio of welding material components can significantly affect the processes that occur at the slag–metal interface and, as a result, the concentration of certain alloying elements in different areas of the weld leads to a greater or lesser degree of local slag–metal adhesion, depending on the affinity of the elements to oxygen.

The guaranteed separation of slag crust is ensured by controlling parameters such as the difference in thermal expansion coefficients of the metal and slag and the probability of spinel formation.

One solution to this situation could be to study the algorithm of processes that occur at the slag–metal interphase boundary in the low-temperature part of the welding/melting reaction zone based on modern concepts of the ionic and molecular structure of slag melts to predict the formation of complex compounds—spinels.

The presence and composition of complex compounds (spinels) are determined by the reactions that occur at the interphase boundary, as well as the concentration and temperature conditions of the interacting metal and slag phases. The first factor is the temperature conditions for the formation of complex compounds, which are determined by the interaction of the solidified weld metal and the liquid slag. The temperature range is limited by the metal crystallization temperature (1500–1400°C) and the slag-crust solidification temperature. During slag solidification, the following processes occur: the transformation of the liquid slag solution into a solid solution, the release of complex compounds from the liquid and solid solutions, and chemical interaction at the slag–metal interphase boundary.

When the solid solution forms, it can have a glassy or amorphous structure. The process of converting liquid slag into a solid solution is accompanied by the release of certain complexes of complex oxides. Such compounds may be chemically neutral to the solution or interact with it. In the first case, no chemical reactions occur at the slag–metal boundary, in the second case, the slag may grow on the metal surface as a result of the chemical interaction of the slags' complex compounds with the surface of the weld metal [1].

The adhesion of the slag crust to the metal surface is carried out through a thin layer formed at the boundary between the slag–metal system (Fig. 1) and depends on its chemical composition. The more metal oxides form complex compounds with slag oxides on the boundary in a thin layer, the worse the separation becomes.

This is related to the fact that reactions at the slag–metal interface

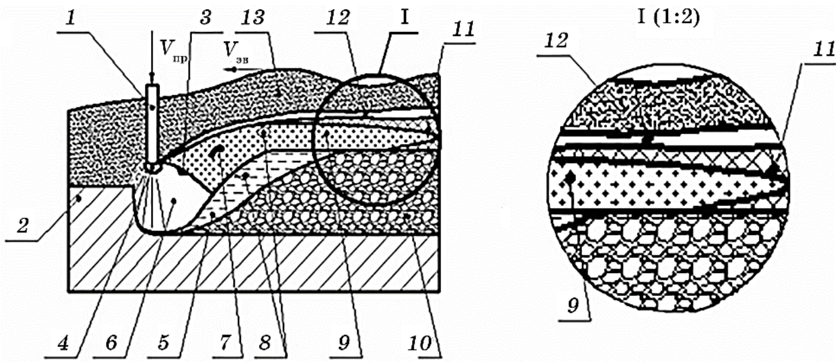


Fig. 1. Diagram of flux-cored arc welding and cladding, where *1*—welding wire, *2*—base metal, *3*—droplets on the surface of the slag dome, *4*—droplet, *5*—liquid metal of the weld pool, *6*—gas phase, *7*—metal droplets in the slag, *8*—gas bubbles, *9*—liquid slag, *10*—weld (*9*–*10*—interphase boundary slag–metal in the tail part of the reaction zone of welding), *11*—slag crust, *12*—semi-molten grains of flux, *13*—flux.

occur in the back part of the welding reaction zone, where the flux is transformed into liquid slag, which covers the surface of the metal and can remain liquid for some time after the metal has already solidified. Accordingly, this affects the formation of the transition layer between the metal and slag, which increases the probability of spinel formation.

The presence of slag residues after separation of the slag crust is related to the physicochemical interaction between the slag and metal, which forms an intermediate slag layer with a crystalline lattice that promotes the growth of slag on the surface of the melted metal. The concentration of certain alloying elements in specific areas of the weld leads to a greater or lesser degree of local adhesion of the slag to the metal, depending on the affinity of the elements to oxygen. According to existing ideas, the distribution of adhesion forces between the slag coating and metal has an uneven character.

Regulating the process of separating the slag crust during welding and cladding can be based on predicting the physicochemical properties of slag melts, including reactions at the slag–metal interface. The nature and characteristics of these reactions are determined by the time of existence of the metal and slag melts, their concentration conditions, and the activity of components. Therefore, the possibility of controlling the process of separating the slag crust from the surface of the weld metal under flux by predicting changes in the physicochemical properties of the slag melt, including its temperature range of crystallization and controlled changes in the activity of participants in reactions at the slag–metal interface, is most likely achievable.

The chemically active structural elements of a slag melt are spinels. From a chemical point of view, spinels (from ‘German Spinell’) are a group of minerals of the class of complex oxides that have a general formula of AB_2O_4 or $A(A, B)O_4$, where A—Mg, Zn, Mn, Fe, Co, Ni and B—Al, Fe, Cr, Mn, Ti, V [1]. Spinel is a system of solid solutions with a well-developed isomorphism of cations A and B. Their formation process is associated with crystal growth. Chemical compounds formed on the basis of oxygen at the slag–metal interphase boundary, depending on the concentration conditions of the presence of cations A or B and oxygen anions, can lead to the formation of different types of spinels. Spinels crystallize in the form of octahedral and tetrahedral compounds. Based on existing ideas in chemistry, the elementary structure of spinels has 32 oxygen anions, which form a dense cubic packing with 64 tetrahedral vacancies (8 cations occupied) and 32 octahedral vacancies (16 cations occupied) [2]. Dense packing of oxygen in spinels is also noted in the theory of nanoscale components of a slag melt and complex compounds of elementary particles [2]. This explains the high chemical and thermal stability characteristic of all types of spinels. Spinels are characterized by high-temperature formation conditions of 1920–1400°C, which correlate with the temperature interval of the formation of the crystalline phase of spinels [3, 4]. The main difference in the mechanism of spinel formation during welding and surfacing is the presence of a metallic component at the interphase boundary. This leads to the fact that conducting a direct analogy with the processes considered in the theory of spinel formation as chemical mineralogical compounds is impossible. In the conditions of welding, in addition to the concentration conditions, which significantly differ at the slag–metal boundary, the difference in the thermophysical properties of the slag and metal has a significant impact on the process of spinel formation. The result of this is the presence of a process of bonding a slag crust with the metal of the weld, and as a result, the influence of the peculiarities of spinel formation on the separation of slag, which is confirmed by experimental data on the separation of slag coating during surfacing, as well as the chemical composition of complex compounds that arise on the surface of the weld metal [3, 4].

2. EXPERIMENTAL PROCEDURE

The purpose of this work was to investigate experimentally the mechanism of complex compound formation (spinels) under conditions of flux-cored arc welding and cladding.

Special agglomerated fluxes (SAF) SAF-2 and SAF-3 of a TiO_2–MnO–SiO_2–MgO–CaO–FeO–Al_2O_3 slag system with a low content of CaO, FeO, and K_2O were produced for the research. The selection of this slag system was determined by the inclusion of elements that should affect the process of spinel formation. The presence of CaO, FeO, and K_2O oxides as a result of impurities in the raw materials used

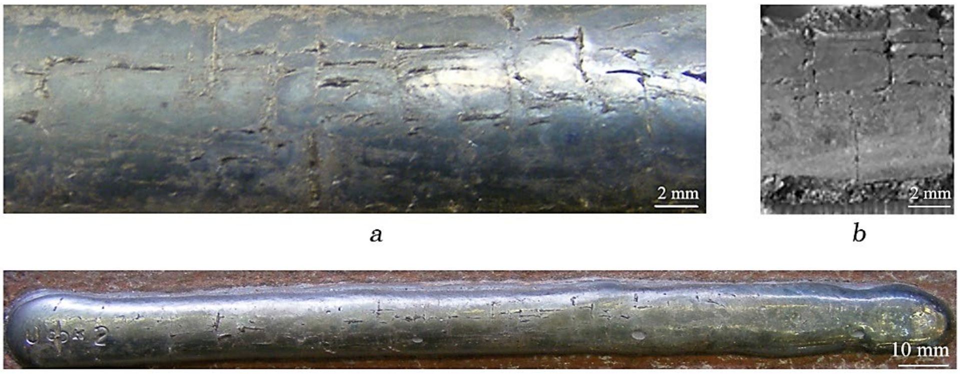


Fig. 2. Shows an image of the weld (*c*), a magnified fragment of the weld surface (*a*), and a slag crust (*b*) under the flux SAF-2 slag system TiO_2–MnO–SiO_2–MgO–CaO–FeO–Al_2O_3.

in flux production technology, and the presence of SiO_2 oxide was due to the need to ensure the fluxes-forming ability. To change the fluxes-oxidation potential, the MgO to TiO_2 ratio was varied in the flux composition. For SAF-2 flux, it was of 0.45, for SAF-3, it was of 1.0. The content of other components was kept unchanged whenever possible.

Under experimental fluxes SAF-2 and SAF-3, samples of the Sv-08G1NMA wire with a diameter of 3 mm were welded. The welding parameters were constant direct current, $I = 420–450$ A, $V = 34–36$ m/s, $U = 32–36$ V [5, 6]. After welding, non-metallic macroinclusions (macrospinels) on the weld metal surface, slag crust, and microinclusions on the slag surface were investigated. The study of macroobjects was carried out using digital photography. The slag microstructure was studied using scanning electron microscopy at magnifications of 250–1570 times.

It was found that macroinclusions are present on the surface of welded joints, the shape of which depends on the MgO to TiO_2 ratio. For the SAF-2 flux, the shape of macroinclusions is longitudinal, and for the SAF-3 flux, it is point-like (Fig. 2, *a*–*c*). The sizes of longitudinal macroinclusions are as follow: thickness of ≅ 0.1–0.3 mm, length of ≅ 2–7 mm; for point-like ones: diameter of ≅ 0.05–0.012 mm. The location of macroinclusions: for the SAF-2 flux, the main part is located in the centre of the joint in the welding direction and perpendicular to the axis of the joint (Fig. 2, *a*, *c*).

For the SAF-3 flux, macroinclusions have a localized character and are present in certain areas of the welded joint. The macroinclusions are distributed chaotically along the length of the weld joint, practically along its entire length (Fig. 3, *a*, *c*).

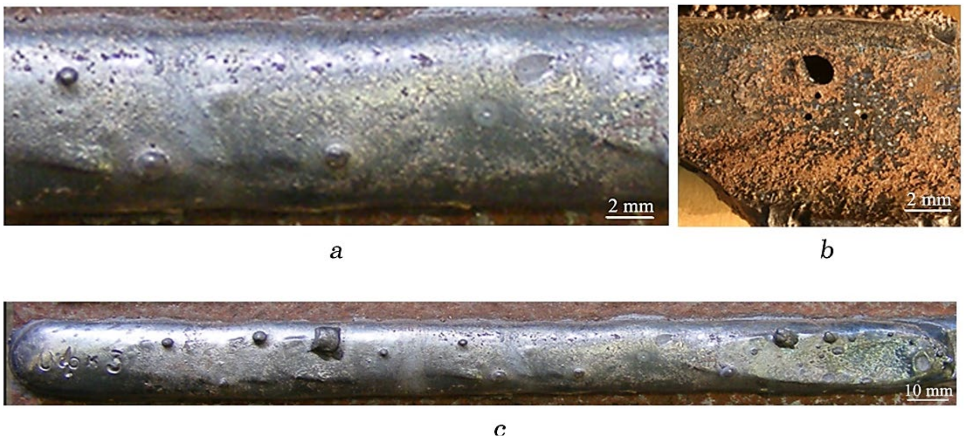


Fig. 3. Image of the weld (*c*), enlarged fragment of the weld surface (*a*), and slag crust (*b*) under the SAF-2 flux of the TiO_2–MnO–SiO_2–MgO–CaO–FeO–Al_2O_3 slag system.

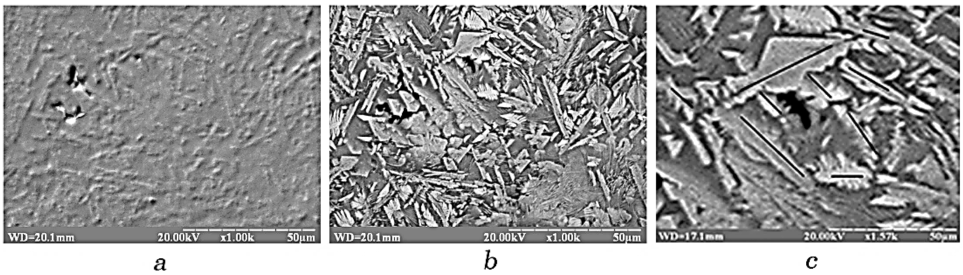
Photographs of the slag (Figs. 2, *b* and 3, *b*) show that the macroinclusions on the weld joints and their reflections on the slag crust coincide in location, size, and are quite voluminous.

Taking into account that macroinclusions have a volumetric shape and their traces are present on both the metal and the slag (Fig. 2 and 3), and that the chemical interaction between the metal and the slag can only occur when there are common compounds, it can be assumed that the obtained macroinclusions have a spinel-like character, which is confirmed by their chemical composition. The next stage of the study was to determine the structural components of the surface of the slag crust using scanning electron microscopy (SEM). To do this, samples of the slag crust were cut out with a size of 5×5 mm. The surface of the slag that borders the metal of the weld was examined.

Based on the analysis of the SEM data of the slag surface coating, it was found that for SAF-2 flux, the crystals that form when the slag cools down are on a common base and are evenly distributed (Fig. 4, *a*, *b*). The crystals have the form of irregular polygons with a length of 2–25 microns and a width of 1–5 microns and are separated by a base, on which they are located. Larger microconnectors of a round shape with irregular edges measuring 15–30 microns are also observed, which represent polygons that have grown together. Visual analysis of the microimage of the slag crust surface shows that the crystals are oriented in perpendicular directions (Fig. 4, *d*), which means that the arrangement of micro- and macrospinels (Fig. 2, *a*) coincides. This allows us to assume that micropolygons grow into macroinclusions.

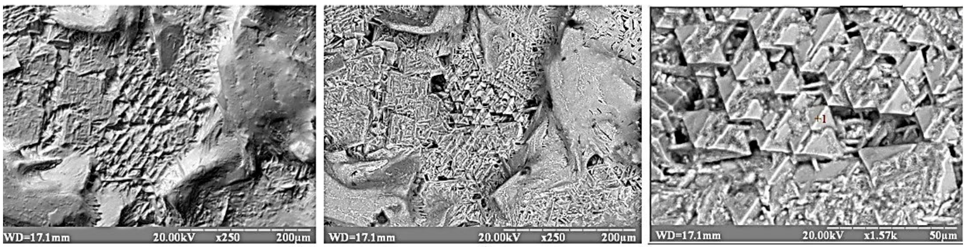
Based on SEM analysis, a visual and chemical analysis of the slag showed that microconnections of the following composition are locally located on the surface of the slag crust: SiO_2 (5–10%), TiO_2 (40–70%), MnO (20–40%), MgO (0.4–0.9%), FeO (1–3%), CaO (2–3%). Known features of the structure of complex compounds, such as spinels, and data obtained on the chemical composition of microconnections, allow us to assert that the microinclusions on the surface of the slag are spinels.

The analysis of microimages of the slag obtained under SAF-3 flux



a *b* *c*

Fig. 4. Microphotographs of the slag surface at different depths of focus (*a*, *b*) and the orientation of the crystals on the surface of the slag coating (*c*).



a *b* *c*

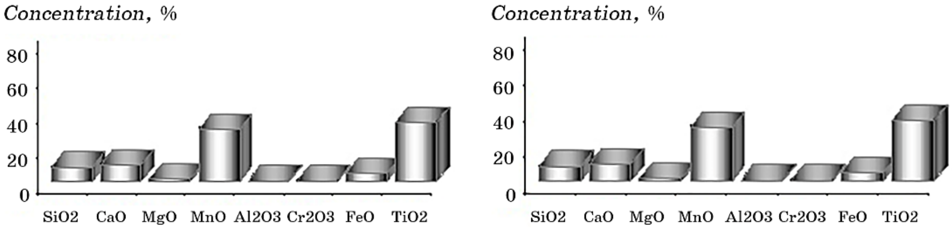
Fig. 5. Micrograph of the surface of the slag at different focusing depths (*a*, *b*) and orientation of pyramidal-shaped crystals on the surface of the slag coating (*c*).

showed significant heterogeneity of the coating (Fig. 5, *a*, *b*). Crystals that form during slag cooling are grouped in certain areas and are characterized by significant unevenness in height (Fig. 5, *a*, *b*). Visually, areas consisting of pyramid-shaped crystals (Fig. 5, *c*) of the same orientation and size of 4.5–7.5 µm are observed. The chemical composition of the areas and their appearance during macro- and microvisual analysis show that macroconnections on the surface of the weld metal are the result of the overgrowth of pyramid-shaped microspinels into macrospinels, as is the case with the overgrowth of polygons for SAF-2 flux.

Data from visual analysis of micro- and macrospinels and their chemical composition (Fig. 6) allows us to conclude that macrospinels are an extension of microspinels, the shape of which depends on the ratio of MgO and TiO_2 oxides, *i.e.*, on the slags' oxidation potential.

It has been established that there are three main interrelated factors, which determine the separation process: chemical bonding metal, slag, and physical adhesion in the presence of a similar lattice, which can occur simultaneously but have different nature.

The theory of the structure of slag melt based on theories of nanomicelles and complex molecules formed on the basis of oxygen is more advanced and can be applied to explain and predict processes in slag



a *b*

Fig. 6. Concentration of oxides in spinels during surfacing with flux SAF-2 (*a*) and SAF-3 (*b*) according to the chemical analysis based on SEM.

melt and at the interphase boundary, provided that the existing crystalline forms of octahedral and tetrahedral compounds formed during slag and metal crystallization are taken into account.

The mechanism of spinel formation has been elucidated, which consists of the following stages: the occurrence of chemical reactions to form microspinels in the form of complex compounds at the interphase boundary of liquid slag and metal in the temperature range of 1450–1350°C; the appearance of a crystalline phase at the boundary of interacting phases; the transition of microspinels to macrospinels at 1350–1100°C with adhesion of the metal surface seam to the slag coating. As a result of the mechanism of spinel formation during arc welding and flux-cored arc welding, complex compounds (spinels) are formed at the slag–metal interfacial boundary during the formation of slag coatings and in the presence of spinel-forming elements in microvolumes as a result of chemical reactions. The dense packing of oxygen in spinels, which corresponds to the structure of nanomicelles that are components of oxide slag melts, leads to the merging of microspinels, which can grow into macroformations. The oxidation potential of the slag, which is determined by the flux composition, has the main influence on these processes in the presence of spinel-forming elements.

Based on the obtained research results, final testing is currently underway for an innovative welding flux that allows for self-separation of the slag crust, which manifests immediately after the welding process. The slag crust self-detaches from the seam with the 'self-jumping' effect, which simplifies the work of welders and eliminates the labour-intensive operation of manual cleaning/separation of the slag crust from the seam, reducing the likelihood of slag inclusions during multipass/multilayer welding/cladding.

3. CONCLUSIONS

From the list of related parameters that determine the process of high-temperature separation of slag crust, the physicochemical process of spinel formation at the interphase boundary between liquid slag and solid metal of the seam was investigated.

As a result of the research, the mechanism of spinel formation during flux-cored arc welding and cladding of low- and medium-alloy steels was demonstrated.

The main structurally dependent connections that affect the conditions of interaction at the slag–metal interphase boundary were identified.

It was established that in the presence of spinel-forming elements at the slag–metal boundary, the formation of crystallization centres occurs, which are characterized by spinels that subsequently grow into macrospinels.

Based on modern concepts of the structure of slag melts, a mechanism for the formation of complex compounds at the slag–metal interphase boundary with the growth of microcomplex compounds into macrospinels is proposed. The external appearance of the slag crust structure, obtained using SEM, indicates that for the SAF-2 flux, spinels have a larger size (up to 25 microns) than for the SAF-3 flux (up to 10 microns). This leads to the growth of microspinels into macrospinels for the SAF-3 flux. The shape and structure of these aggregates are determined by the oxidizing potential of the slag.

REFERENCES

1. L. A. Zhdanov, V. L. Kovalenko, N. M. Strelenko, and E. P. Chvertko, *Soldagem & Inspeção*, No. 18: 314 (2013) (in Brazil).
2. N. M. Strelenko, L. A. Zhdanov, and K. O. Zvorykin, *Tekhnologicheskie Sistemy*, **47**, No. 3: 77 (2009) (in Ukrainian).
3. N. M. Strelenko, L. A. Zhdanov, and K. O. Zvorykin, *Tekhnologicheskie Sistemy*, **51**, No. 2: 83 (2010) (in Ukrainian).
4. L. A. Zhdanov and N. M. Strelenko, *Bulletin of Kyiv Polytechnic Institute. Series Mechanical Engineering*, **61**, No. 2: 123 (2011) (in Ukrainian).
5. L. A. Zhdanov, V. L. Kovalenko, V. T. Kotyk, and K. O. Zvorykyn, *Tekhnologicheskie Sistemy*, **28**, No. 2: 65 (2005) (in Ukrainian).
6. V. L. Kovalenko, R. V. Mastenko, N. M. Strelenko, and C. O. Zvorykin, *Tekhnologicheskie Sistemy*, **80**, No. 3: 56 (2017) (in Ukrainian).