INFLUENCE OF REFRACTORY DISPERSED PHASES ON PHYSICAL-CHEMICAL PROPERTIES OF SLAG METLS OF MgO–Al$_2$O$_3$–SiO$_2$–CaF$_2$ SYSTEM

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The article is devoted to the study of basic mechanisms of control of structure and physical-chemical properties of slag oxide-fluoride melts to develop fluxes with predicted chemical, metallurgical and technological parameters for welding high-strength low-alloyed steels. The addition of MgO into the slag melts of the MgO–Al$_2$O$_3$–SiO$_2$–CaF$_2$ system provides an abnormal decrease in the thermodynamic activity of silicon oxide in them due to the formation of a refractory dispersed phase MgO·Al$_2$O$_3$ in the melt. On the basis of methods of national standard and gravimetric one the procedures for determination of quantitative content of MgO·Al$_2$O$_3$ in liquid and solid slags of the MgO–Al$_2$O$_3$–SiO$_2$–CaF$_2$ system were proposed. Its optimum content in a slag melt was determined, in which the combination of optimal chemical, metallurgical and technological properties of flux during electric arc welding is provided. 12 Ref., 1 Table, 5 Figures.

K e y w o r d s : *fluxes for electric arc welding, slag melts, refractory dispersed particles, toughness, electric conductivity, thermodynamic activity*

The existing conceptions about the behaviour of welding slag melts, which are based on the ion theory of electrolytic dissociation of atoms, are somewhat obsolete. The structure of real welding slags is much more complicated than that of perfect and ideal ionic solutions. In metallurgical and welding slags predominantly a polar bond exists. When describing the structure of such slag melts, the leading role is assigned to the opinions defined by the ability of oxides-complexing agents to polymerize in the melt, forming a framework, as well as by the ability of cations (for example, Na$^+$, Ca^{2+}) to break this framework, releasing, as a result, the atoms of free non-bridging oxygen [1–3]. In the recent years, the ion theory has been criticized in the metallurgical literature due to the lack of adequate approaches in describing the polymerization processes of SiO$_2$ and other oxides. In the metallurgical literature, a number of new theories [4, 5] were proposed, which describe the formation of polymer heteromolecular complexes in the melt (nanomicelles, associates, clusters, etc.). K. Mills notes [2] that in the recent years our knowledge about the structure of slag melts has significantly improved with the development of new techniques such as X-ray and neuron diffraction, Raman spectroscopy and nuclear magnetic resonance. In particular, it was established, that metallurgical slag melts are not a homogeneous liquid, as it was considered earlier, but heterogeneous, i.e. those, containing solid and liquid phases [6, 7].

The carried out analysis of gradient-temperature conditions of a weld pool existence in submerged electric arc welding [8] and the study of state diagrams of the oxide-fluoride systems [9, 10] showed that slag melts are heterogeneous during welding. This was confirmed by the method of high-temperature X-ray diffraction during investigations of the slag system MgO–Al$_2$O$_3$–SiO$_2$–CaF$_2$ in the solid and molten state [11]. It was established that when the concentration of MgO is higher than 20 % and Al$_2$O$_3$ is higher than 25 % at the temperatures above 800 °C, due to the increase in the diffusion of aluminium and magnesium ions, the compound MgO·Al$_2$O$_3$ is formed at a melting point of 2135 °C. Such a compound is the only solid crystalline phase in the studied melts at the temperatures up to 1500 °C. By the method of scanning electron microscopy with a local chemical analysis of phases, it was determined that MgO·Al$_2$O$_3$ is observed in the form of octahedra with the sizes of 10–35 μm after melting of fluxes and in slag crusts in the process of welding.

The aim of this work was to determine the quantitative content of refractory dispersed phases MgO·Al$_2$O$_3$ in the welding slags of the system MgO–Al$_2$O$_3$–SiO$_2$–CaF$_2$, their influence on physical-chemical properties of slag melts, chemical and metallurgi-

Composition of model agglomerated fluxes of the system $MgO–Al_2O_3–SiO_2–CaF_2$, content of $MgOAl_2O_3$ in them and results of chemical analysis of the 5th layer of surfacing under these fluxes by the wire Sv-07G1NMA

Object	Content of components, %				Content of $MgO·Al_2O_3$, %		Content of elements in the weld metal and wire, %				
	MgO	SiO_2	Al_2O_3	CaF_2	Method of national standard	Gravi-metric method	C	Si	Mn	Ni	Mo
Wire Sv-07G1NMA	–	–	–	–	–	–	0.087	0.371	1.44	0.61	0.62
Flux 7	–	40	25	25	0	0	0.040	0.561	0.69	0.46	0.48
9	20	20	35	25	22	21	0.046	0.525	0.81	0.48	0.49
4	30	20	25	25	20	19	0.049	0.484	0.81	0.46	0.48
15	40	10	25	25	28	27	0.05	0.315	1.03	0.47	0.51

cal and technological parameters of fluxes in electric arc welding.

Investigation of the structure of liquid and solid slags by the method of high-temperature X-ray diffraction. The methods for determination of the content of compound $MgO·Al_2O_3$ in solid and molten slags by the methods of gravimetric analysis and national standard, respectively, were developed. The gravimetric method is based on the ability of the spinel not to dissolve in most strong acids. The principle of the national standard method is in the fact that a diffractogram is obtained, in which the studied substance is present and a substance, used as a national standard. In our case, monoclinic tungsten oxide WO_3 was chosen. According to the ratio of heights of the peaks of the national standard substance and the studied substance, the content of the latter was determined. The experimental calibration diagrams for WO_3 and $MgO·Al_2O_3$ are in a good correlation with the results of simulation conducted with the application of PowderCell program. The results of $MgO·Al_2O_3$ content in the model agglomerated fluxes of the system $MgO–Al_2O_3–SiO_2–CaF_2$, determined by the gravimetric method, are in a good correlation with the data of the national standard method (Table).
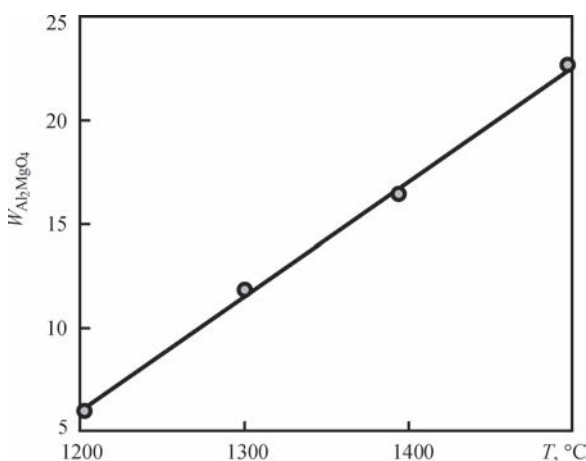

Figure 1. Dependence of mass fraction of $W_{MgAl_2O_4}$ in the flux of the system $MgO–Al_2O_3–SiO_2–CaF_2$ on the temperature

It was established, that the content of $MgO·Al_2O_3$ in the model of agglomerated fluxes during heating up to 1500 °C and in the slag crusts during welding is approximately the same. The influence of temperature-concentration factors, which determine the processes of formation of $MgO·Al_2O_3$ in the melts of the system $MgO–Al_2O_3–SiO_2–CaF_2$, was investigated. When introducing CaF_2 into the slag system $MgO–Al_2O_3–SiO_2$, the temperature of the initial formation of $MgO·Al_2O_3$ decreases from 1300 °C to 1100–1150 °C. The temperature dependence of the content $MgO·Al_2O_3$ in the range of 1200–1500 °C has a linear character (Figure 1). On the basis of the obtained results, the recommendations for the formation of refractory dispersed phases in slag melts in the industrial manufacture of agglomerated and fused fluxes were worked out. Thus, a high-temperature calcination of the charge can be performed not for separate components, as it takes place today, but for mixtures. Perspective is the adding of substances containing fluorine: fluorite or fluorspar into the mixture of magnesite and alumina. In addition, fused fluxes for welding and related processes or fused semi-products with a controlled content of dispersed phases in a melt can be melted in gas-flame or electric arc furnaces due to changes in the conditions of the charge loading into the furnace, temperature melting modes, etc.

Investigations of the activity of SiO_2 and O^{-2} ions by the method of electromotive force. In the work [12] we proposed a method for the in-process determination of the SiO_2 activity in oxide and oxide-fluoride slag melts and designed an original electrolytic sensor for measuring the EMF, which is stable in oxide-fluoride slag melts at the temperatures up to 1500 °C.

It was concluded, that a decrease in the activity of SiO_2 (Figure 2, *a*) in the melts of the system $MgO–Al_2O_3–SiO_2–CaF_2$ from 0.06 to 0.012 wt.% occurs due to the formation of refractory dispersed phases of $MgO·Al_2O_3$ in the melt. During the development of modern agglomerated fluxes, it is important to study the influence of metals, being in the composition of
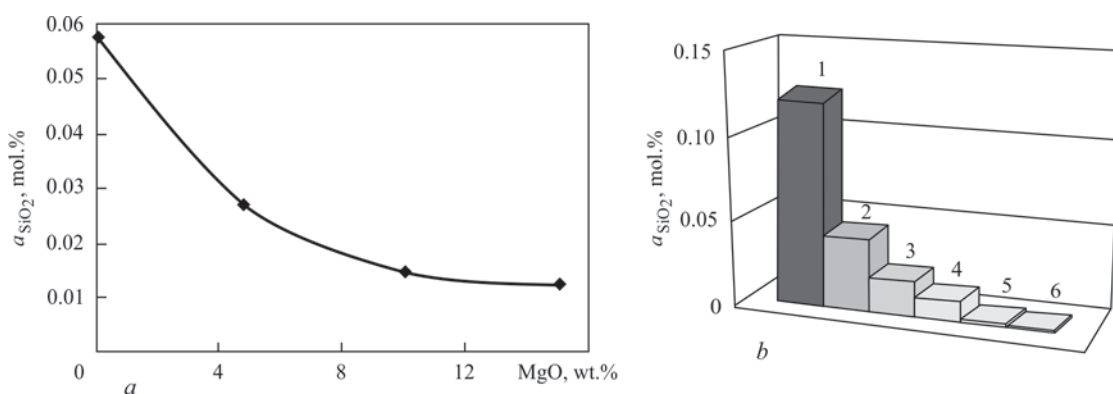
Figure 2. Dependence of thermodynamic activity of SiO_2 in a slag melt of the system $MgO–Al_2O_3–SiO_2–CaF_2$ at 1400 °C on the content of MgO (*a*) and the influence of the following metals on it in the amount of 1 % (*b*): *1* — flux without admixtures; *2* — Fe–Mn; *3* — Mn; *4* — Fe–Si; *5* — Fe–Ti; *6* — Si–Ca

the alloying base of the flux, on the oxidizing effect of molten fluxes on a weld pool metal. A thermodynamic analysis of the probability of running chemical reactions of interaction of silicon oxide with different metals was carried out and their influence in the amount of 1 % on the thermodynamic activity of SiO_2 in the melts of the system $MgO–Al_2O_3–SiO_2–CaF_2$ was experimentally investigated. The most effective (reduction by 2–3 orders) is the adding of silicocalcium and ferrotitanium into the composition of fluxes (Figure 2, *b*).

The influence of the activity of oxygen ions and the activity of silicon oxide on the transition of oxygen and alloying elements into the deposited metal at applying the model agglomerated fluxes of the system $MgO–Al_2O_3–SiO_2–CaF_2$ with different contents of $MgO·Al_2O_3$ (Table), formed in the fluxes during their heating, was studied. The dependence between the content of $MgO·Al_2O_3$ in the flux, the thermodynamic activity of oxygen ions in the slag melt (Figures 3, 4) and the oxygen content in the weld metal was established. The best deoxidizing ability belongs to the flux with the highest content of $MgO·Al_2O_3$ among investigated fluxes, which is at the level of 28 %. In
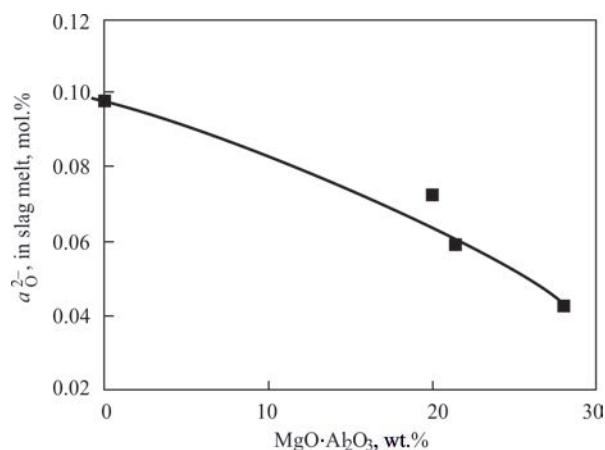
the field of compositions containing $MgO·Al_2O_3$ of 19–22 wt.% in the melt, the approximate parameters for the activity of oxygen ions and silicon oxide in the melt were obtained. At the same time, a partial increase in the content of Al_2O_3 in the flux due to the corresponding reduction in the content of MgO is not accompanied by an increase in the activity of oxygen ions, by the losses of Mn and a significant increase in the recovery of Si in the deposited metal (Table) at significantly better properties of the flux formation. With an increase in the activity of oxygen ions in the slag melt to higher than 0.06 mol.%, an increase in the oxygen content in the deposited metal is observed (Figure 4).

Determination of influence of the $MgO·Al_2O_3$ content in liquid fluxes on their physical and chemical properties and welding-technological characteristics. It was determined that in the range of compositions MgO — 20–25 %; Al_2O_3 — 25–35 %; SiO_2 — 15–20 %; CaF_2 — 15–25 %, a combination of optimal chemical, metallurgical and technological properties of a flux during electric arc welding is provided due to the formation of refractory dispersed phases $MgO·Al_2O_3$ in a slag melt in the range of 19–22 %. It was established that their formation in the melt expands the temperature range of solidification
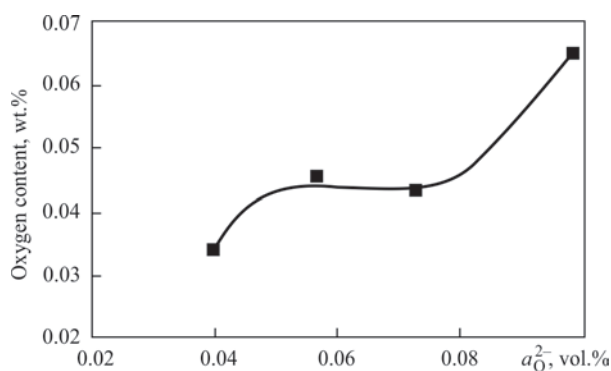

Figure 3. Dependence of the activity of oxygen ions in slag melts of the system $MgO–Al_2O_3–SiO_2–CaF_2$ on the content of the compound $MgO·Al_2O_3$ in them

Figure 4. Dependence of the oxygen content in the deposited metal on the activity of oxygen ions in the melt of the system $MgO–Al_2O_3–SiO_2–CaF_2$
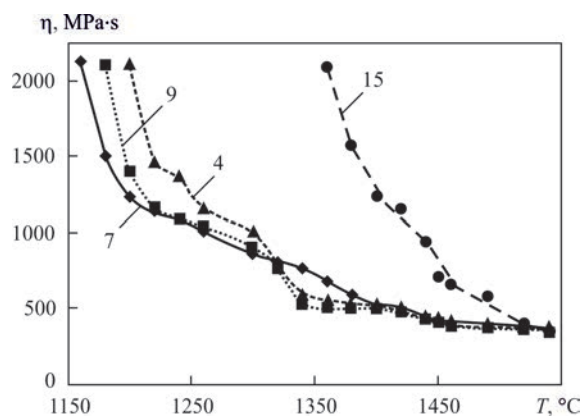
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Figure 5. Temperature dependence of toughness of model agglomerated fluxes of the system MgO–Al$_2$O$_3$–SiO$_2$–CaF$_2$ (compositions of fluxes 4, 7, 9, 15 are given in Table)

of fluxes up to 1180–1510 °C. It is shown that for the temperature dependences of toughness (η) (Figure 5) of these fluxes a gradual increase in the toughness in the process of cooling is characteristic, caused by a multistage formation in the melt of solid dispersed phases. At the same time, the conditions for removal of gases from the welding zone are improved. In the above-mentioned range of compositions, the optimal values of electrical conductivity were also achieved at the level of 0.11–0.16 (Ohm·cm)$^{-1}$, which is important for preventing the shunting of arcs in multiarc welding. With an increase in the content of MgO·Al$_2$O$_3$ to 28 %, the melt toughness increases. It results in deterioration of weld shape and the formation of undercuts during welding.

Conclusions

1. The influence of temperature-concentration factors on the processes of MgO·Al$_2$O$_3$ formation in the melts of the system MgO–Al$_2$O$_3$–SiO$_2$–CaF$_2$ was determined. The recommendations for the formation of refractory dispersed phases in slag melts in the technological processes of manufacture of agglomerated and fused fluxes were worked out.

2. On the basis of methods of the national standard and gravimetric method, the procedures for determining the quantitative content of MgO·Al$_2$O$_3$ in liquid and solid slags of the system MgO–Al$_2$O$_3$–SiO$_2$–CaF$_2$ were proposed.

3. Reduction in thermodynamic activity of SiO$_2$ in the melts of the system MgO–Al$_2$O$_3$–SiO$_2$–CaF$_2$ from

0.06 to 0.012 mol.% when adding MgO into the flux in the amount of up to 15% is caused by the formation of refractory dispersed phases of MgO·Al$_2$O$_3$ in the slag melt. The influence of metals adding into the slag melts on the thermodynamic activity of silicon oxide was determined.

4. It was established, that the formation of MgO·Al$_2$O$_3$ in the melt expands the temperature range of fluxes solidification up to 1180–1510 °C. For polytherms of toughness of these slags, a gradual increase in the toughness in the cooling process is characteristic, caused by the multi-stage formation of solid dispersed phases in the melt.

5. It was determined, that at the composition of a refractory dispersed phase of MgO·Al$_2$O$_3$ in a slag melt in the amount of 19–22 %, the combination of optimal chemical, metallurgical and technological properties of a flux during arc welding is provided

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