



# FORMATION OF SPINEL IN MELT OF THE $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{CaF}_2$ SYSTEM AGGLOMERATED WELDING FLUX AND ITS EFFECT ON VISCOSITY OF SLAG

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X-ray examinations of structure of agglomerated flux of the  $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{CaF}_2$  system in solid and molten states evidence that in a temperature range above 1200 °C the  $\text{Al}_2\text{MgO}_4$  hard spinel phase with a melting temperature of 2105 °C forms in the slag melt. It determines physical-chemical properties of the melt and, in particular, the smooth character of viscosity changes in a temperature range of 1180–1540 °C. By manipulating proportions and concentrations of spinel-forming components  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$ , it is possible to achieve the optimal values of the temperature dependence of viscosity of the slag melt and, on this base, develop welding fluxes with predictable technological properties.

**Keywords:** *welding, agglomerated flux, structure of slag melts, viscosity, diffraction examinations, spinel*

Conventional-strength steels have been gradually replaced lately by increased- and high-strength steels. To weld such steels it is necessary to use a number of appropriate metallurgical processes and consumables.

Welding of conventional-strength steels is performed by using the  $\text{MnO}-\text{SiO}_2-\text{CaF}_2$  slag system fluxes characterised by good welding-technological properties. The latter are achieved due to the fact that structure of the melts of these fluxes is determined by a silicate skeleton of a differing polymerisation degree, which, in turn, determines physical-chemical properties of slag in the molten state at temperatures of existence of the weld pool. To provide formation of the defect-free welds in submerged-arc welding the slag pool should damp oscillations of the metal pool. Therefore, slags must be characterised by a smooth increase in viscosity with decrease in temperature, i.e. they must be «long» [1]. However, despite good technological properties, the manganese-silicate fluxes have limited possibilities in terms of affecting the values of mechanical properties of the weld metal, and impact toughness in particular. This is explained by the fact that welding by using these fluxes involves the processes of formation of silicate non-metallic inclusions and reduction of silicon in the weld metal, which are undesirable for increased-strength steels. To achieve required mechanical

properties in welding of high-strength steels, normally the use is made of high-basicity fluxes with an increased content of calcium oxide and fluoride. However, they fail to provide stability of the welding process and quality formation of the welds in multi-arc welding of pipes at a speed of more than 100 m/h, as they are «short», unlike the manganese-silicate fluxes.

Agglomerated fluxes are finding growing application in welding of high- and increased-strength steels. This is attributable to their wider metallurgical possibilities of affecting the weld pool metal. In general, the problems of submerged-arc welding of low-alloy high-strength steels by using agglomerated fluxes are considered in detail in studies by I.K. Pokhodnya [2], D. Olson [3], T. Eagar [4], etc. At the same time, there are almost no studies dedicated to the fundamental research of structure, physical-chemical properties of the slag melts in connection with technological properties of the welding fluxes.

There are several theories describing structure of the welding slag melts. But all of them apply to the equilibrium processes of metallurgy [5–8] characterised by complete remelting of slag components and formation of the liquid slag phase. Unlike the metallurgical processes, the welding processes are rapid. They feature substantial temperature gradients in different zones of the weld pool and, hence, are far from being equilibrium. Moreover, in melting during the welding process the majority of the agglomerated fluxes used now



are not a homogeneous liquid, like the fused fluxes, but a heterogeneous mixture of different phases, some of which are crystalline. At present, there are no slag theories describing the liquid-crystalline structure of a slag, which does not allow theoretical estimation of the effect of the crystalline component of the slag on the processes occurring in the weld pool.

Coarse crystallites present in the matrix of a liquid part of the slag must have a considerable effect on viscosity and, hence, welding-technological properties of the flux. Therefore, one of the purposes of this study was to qualitatively reveal the effect of the crystalline inclusions on viscosity of the slag.

For a number of years we have been developing agglomerated welding fluxes based on the  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-CaF}_2$  slag system. The results obtained prove the possibility of developing a new generation of welding fluxes based on the above system. Study [9] describes investigations of structure of a welding flux of the given system with a low MgO content (10 wt.%), and study [10] – investigations of the processes of melting and solidification of fluxes of the above slag system. As established in study [11], increase in the content of magnesium oxide in fluxes of the  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-CaF}_2$  system leads to decrease in thermodynamic activity of  $\text{SiO}_2$  in the slag melt. This fact is very important in terms of metallurgy of welding of high-strength steels, as it makes it possible to reasonably suppress the undesirable processes of silicon reduction and formation of silicate non-metallic inclusions in the weld metal.

**Experimental conditions and analysis of experimental data.** X-ray examinations of structure of molten and solid slags were carried out at the Physical Chemistry Chair of the Taras Shevchenko National University by using the upgraded X-ray diffractometer for examinations of melts. Monochromatisation of  $\text{MoK}_\alpha$ -radiation was performed by using a pair of balanced differential filters Zr–Y. Earlier, the diffractometer was used to advantage for examination of fused fluxes in glassy and solid states [12]. After upgrading, this diffractometer allows the diffraction examinations of specimens to be performed both in the liquid and solid states in a temperature range of 100–1700 °C. After granulation and drying of a flux, it was ground into a powder and subjected to X-ray analysis ( $\text{CuK}_\alpha$ -radiation, diffractometer DRON-3M). Also, investigations were carried out with a solid specimen of the slag after holding at 1500 °C on the sides of the crucible bottom and surface.

The E.O. Paton Electric Welding Institute studied the temperature dependence of viscosity of the investigated flux and a number of model fluxes of the same slag system in order to determine the effect of the solid phase in a liquid slag melt on physical-chemical properties. Viscosity of slags was measured by using the rotational viscometer in the Tamman furnace in a purified argon flow.

Scanning electron microscope JSM-7700F with the X-ray spectral microanalyser was used for obtaining images of the initial and remelted fluxes, and for local chemical analysis of microinclusions.

The powdered specimen of the flux on a graphite substrate and the solidified specimen of the slag produced from it by remelting in the molybdenum crucible at a temperature of 1500 °C in the high-purity helium atmosphere were subjected to electron optical examinations. The slag specimen was examined on the side of both bottom and surface of the molybdenum crucible. To prevent the effect of charging of the specimen by the electron beam, a 3 nm thick layer of pure platinum was sprayed on the specimen surface.

Filming of the flux specimen was carried out at temperatures of 600, 800, 1000, 1200, 1300, 1400 and 1500 °C in a high-temperature vacuum chamber in the high-purity helium atmosphere.

Chemical composition of the specimens was controlled by the X-ray fluorescent analysis method.

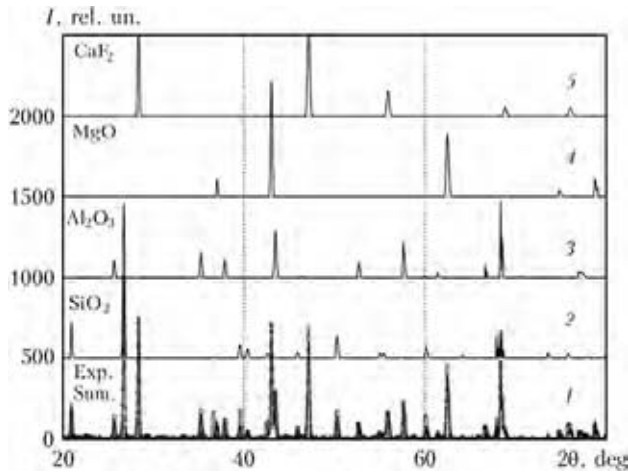
Structural software Powdercell and Mercury, data bases Match and Retrieve, which are disseminated free of charge through the Internet, were used to interpret the X-ray analysis data. The software developed in-house was used in calculations for investigation of the slag melt [12].

**Investigations at room temperature.** The calculated contents of the main components of the flux, i.e. MgO,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{CaF}_2$ , are given in Table 1. Liquid glass Na–K was added to the refined mechanical mixture in the granulator. After granulation, the flux was held for 24 h at a temperature of 20 °C, and then was baked for 1 h at 500 °C. The actual chemical composition of the flux, according to the X-ray fluorescent analysis data, is also given in Table 1.

Results of electron microscopic examinations of the powdered agglomerated flux indicate that

**Table 1.** Composition of welding flux, wt.%

Type of analysis	MgO	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{CaF}_2$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{Fe}_2\text{O}_3$
Calculated	30	25	20	25	–	–	–
Actual	25.8	18.7	28.4	22.2	1.58	0.8	1.88

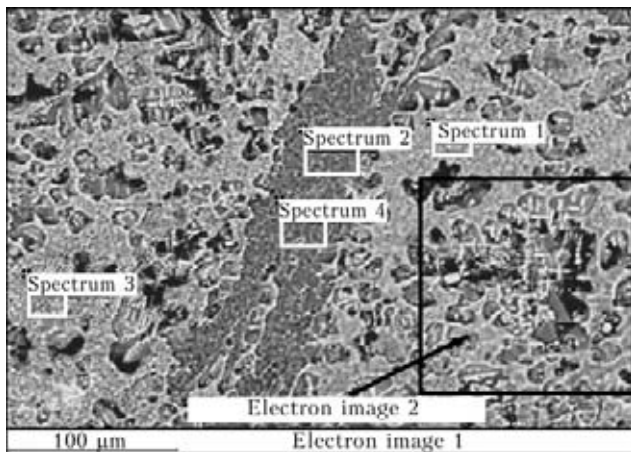


**Figure 1.** Diffraction patterns of agglomerated flux ground into a powder (points) and summation curve after upgrading of profile based on elementary cells of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO and CaF<sub>2</sub> according to Powdercell (solid line) (1), α-quartz (2), corundum (3), periclase (4), and fluorite (5)

particles of initial components MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and CaF<sub>2</sub> hardly undergo any changes as a result of granulation and subsequent baking at a temperature of 500 °C.

X-ray phase analysis (Figure 1) showed that after granulation and drying the specimen contained only the initial components, such as α-quartz, trigonal Al<sub>2</sub>O<sub>3</sub>, and cubic MgO and CaF<sub>2</sub>. No primary products of solidification of the components based on the liquid glass were detected.

Figures 2–5 show microstructures and data of microanalysis of the bottom and surface of the specimen after remelting in the molybdenum crucible. Microstructures on the crucible surface and

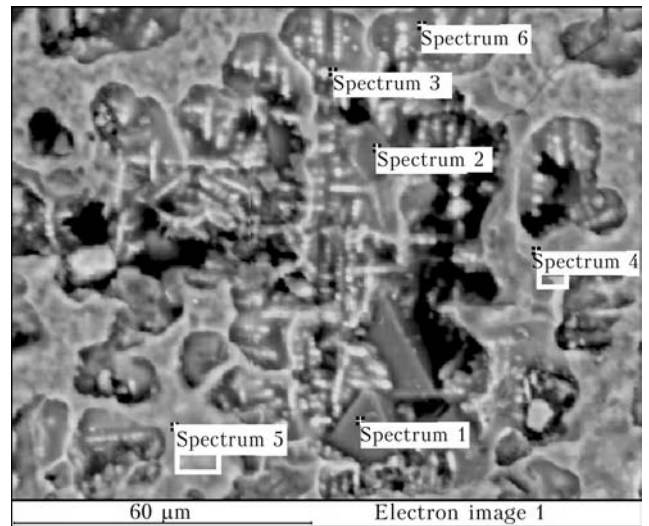


Spectrum	O	F	Mg	Al	Si	Ca
1	55.4	13.2	7.5	3.9	10.1	10.0
2	54.4	6.2	25.5	0.9	11.6	1.4
3	55.3	13.0	7.4	4.3	10.3	9.7
4	54.3	6.6	25.0	1.4	11.2	1.5

**Figure 2.** Microstructure of remelted flux (crucible bottom, image 1), and results of X-ray spectral analysis (at.%). Spectra 2 and 4 can be identified as Mg<sub>2</sub>SiO<sub>4</sub>

bottom sides differ to some extent. The crystalline phases formed on the bottom side are finer (Figure 2, spectrum 3). It can be clearly seen that the continuous matrix of one of the phases (the lightest one) contains inclusions of other, finer phases. It is practically impossible to identify this phase as one compound. Most probably, this phase was formed as a result of melting of low-melting point components of the flux and dissolution of some solid components in the melt. If we discard impurities the content of which is less than 2 at.% and ignore a too high concentration of fluorine, the darker phase at the centre (Figure 2, spectra 2 and 4) can be identified as Mg<sub>2</sub>SiO<sub>4</sub>. The magnified part of image 1 (in black frame) is illustrated as electron image 2 in Figure 3, where spinel Al<sub>2</sub>MgO<sub>4</sub> in crystallites looking like octahedron, and CaF<sub>2</sub> in the form similar to spherulites can be clearly seen (spectra 3 and 6). On the bottom side, X-ray spectral analysis fixed no regions with sodium oxide inclusions.

Examinations conducted on the remelted flux surface side evidence a more complicated character of interactions between the components, compared to the bottom side. Inclusions heavily saturated with impurities (Figure 4, spectrum 5)



Spectrum	O	F	Mg	Al	Si	Ca
1	65.5	1.1	12.8	20.2	0.3	0.2
2	58.3	3.9	14.0	22.2	0.9	0.8
3	44.3	32.8	4.0	2.1	5.4	11.3
4	59.6	14.6	7.2	3.0	8.6	7.0
5	56.7	12.5	6.8	3.8	10.9	9.3
6	44.1	33.3	3.5	2.0	5.0	12.1

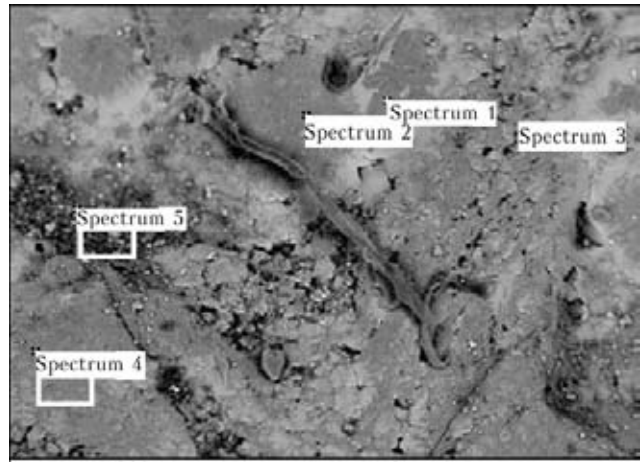
**Figure 3.** Microstructure of remelted flux (crucible bottom, image 2, see Figure 2), and results of X-ray spectral analysis (at.%). Spectra 1 and 2 can be identified as Al<sub>2</sub>MgO<sub>4</sub>, and spectra 3 and 6 – as CaF<sub>2</sub>



can be detected on the surface. It should be noted that sodium is concentrated particularly on this type of the inclusions. Spectrum 2 can be interpreted as  $(MgCa)_2SiO_4$ , probably with the aluminium cation impurities, the concentration of fluorine being ignored. Spectrum 3 is closest to  $CaF_2$ , but with an excess of oxygen. Spectra 1 and 4 in Figure 4 seem to form on a base of the partially solidified low-melting point phase, like spectra 1 and 3 in Figure 2. However, they differ in composition both from each other and from similar images on the bottom side.

Of notice is the fact that fluorine in considerable amounts is present almost in all reflections, while oxygen exceeds stoichiometric compositions of the identified phases (see Figures 2–5). Spinel crystallites contain the least amounts of impurities, although the Al/Mg ratio is about 1.58 on the bottom side and 1.50 on the surface side (in stoichiometric spinel the Al/Mg ratio is equal to 2). Almost all the specimens contain no sodium. Most probably, it is concentrated in sites of accumulation of impurity oxides (Figure 4, spectrum 5), or along the crystalline grain boundaries. It should be noted that spectra of the close phases on the bottom side differ from those on the surface side (Figure 5).

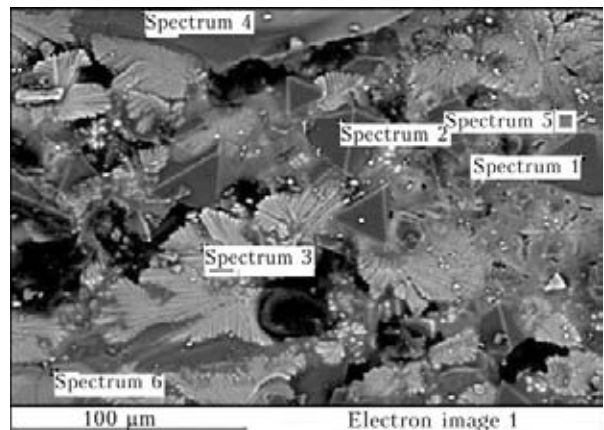
The X-ray pattern of the surface side of a specimen remelted at a temperature of 1500 °C is shown in Figure 6. The main phases on the crucible surface side are cubic spinel (space group  $Fd-3m$  (227),  $a = 0.8100$  nm), cubic  $CaF_2$  (space group  $F4/m-32/m$  (225),  $a = 0.546$  nm) and  $Mg_2SiO_4$ . It is reported that the  $Mg_2SiO_4$  phase can exist in several modifications. The cubic modification of this phase (of the spinel type) with parameter  $a = 0.806-0.811$  nm is very close to the classic spinel. Diffraction reflections of the spinel form of  $Mg_2SiO_4$  almost fully coincide with the spinel reflections, providing that they have identical lattice parameters. It is noteworthy that reflection (440) both for spinel and for  $Mg_2SiO_4$  is localised in a region of 65.25° to 2θ. However, this reflection is not the most intensive one for these two phases. X-ray phase analysis (see Figure 6) confirms the presence of an orthorhombic phase ( $Pbnm$ ) of  $Mg_2SiO_4$  with  $a = 0.4822$ ,  $b = 1.1108$  and  $c = 0.6382$  nm. Also, there is a phase close to the spinel one for  $Al_2O_3$ . However, the lattice parameter of this spinel is much lower compared to the magnesium aluminate one ( $a = 0.7932$  nm). It is likely that at the beginning, as the temperature is increased, the corundum-like lattice of  $Al_2O_3$  transforms into the cubic form close to the spinel one, diffusion of MgO into such a lattice considerably grows,



Spectrum	O	F	Na	Mg	Al	Si	Ca
1	59.5	10.3	–	11.8	6.2	8.1	4.09
2	55.1	7.7	–	17.2	4.4	10.6	4.92
3	44.3	32.8	–	4.0	2.1	5.4	11.30
4	56.5	14.8	–	15.5	2.6	7.2	3.36
5	58.6	17.9	1.3	7.0	2.5	3.8	7.90

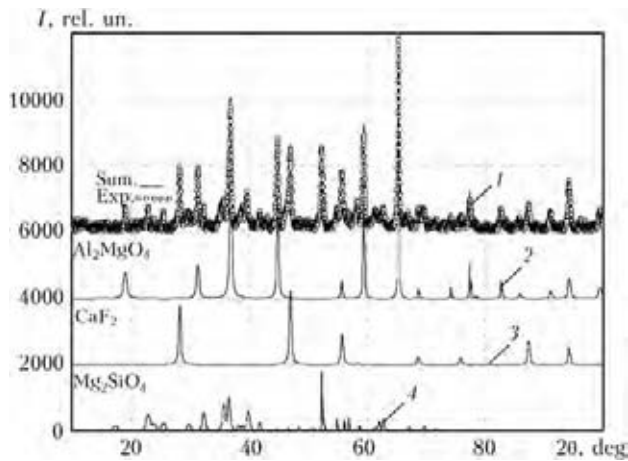
**Figure 4.** Microstructure of products of solidification of the low-melting point phase of remelted flux (crucible surface), and results of X-ray spectral analysis (at.%)

and the normal spinel phase forms. The relative intensity of this reflection for phases of the spinel type does not exceed 70 % (or much lower) of 100 % reflection (311) in a region of 36.85°. In our case the most intensive reflection is (440).



Spectrum	O	F	Mg	Al	Si	Ca
1	66.8	–	13.2	19.8	0.1	0.1
2	73.5	–	10.7	15.6	0.1	0.1
3	24.1	51.7	1.5	1.5	3.7	17.5
4	65.6	1.3	21.7	0	11.0	0.3
5	67.3	–	13.0	19.5	0.1	0.1
6	67.5	–	12.9	19.4	0.1	0.1

**Figure 5.** Microstructure of products of solidification of the main part of remelted flux (crucible surface), and results of X-ray spectral analysis (at.%). Spectra 1, 2, 5 and 6 can be identified as  $Al_2MgO_4$ , and spectrum 4 – as  $Mg_2SiO_4$



**Figure 6.** Diffraction patterns of the flux remelted at 1500 °C on the surface side: 1 – experiment and summation curve of spinel  $\text{Al}_2\text{MgO}_4$ , calcium fluoride and  $\text{Mg}_2\text{SiO}_4$ ; 2–4 – upgraded profiles, according to PCW, of spinel  $\text{Al}_2\text{MgO}_4$  (2),  $\text{CaF}_2$  (3) and  $\text{Mg}_2\text{SiO}_4$  (4)

It seems that this possibility exists when at first one of the phases forms, and when the other phase starts growing epitaxially on one of its faces, or, which is more probable, when in formation of the liquid phase together with the crystalline spinel its crystallites become oriented in a certain direction relative to the melt surface. It should be added that the  $\text{Al}_2\text{MgO}_4$  spinel crystallites in the form of black octahedrons are unambiguously interpreted by electron microscopy analysis (see Figures 3 and 5), and the phase close to spinel  $\text{Mg}_2\text{SiO}_4$  is not solidified in the form of octahedrons. X-ray spectral analysis confirms the presence of  $\text{Mg}_2\text{SiO}_4$ , probably in the  $(\text{CaMg})_2\text{SiO}_4$  form (see Figures 2 and 4).

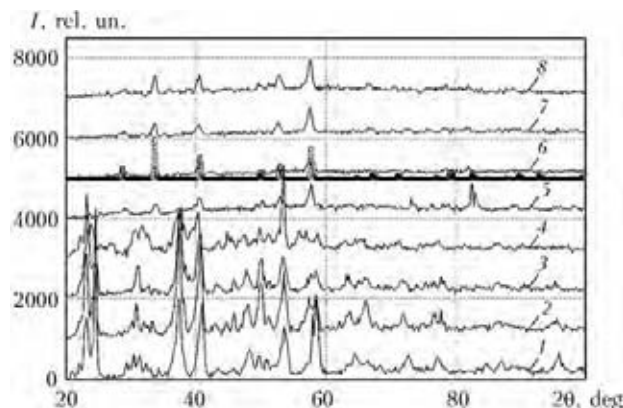
Spinel is not the main phase on the bottom side. Moreover, it was difficult to detect spinel on the bottom side because of its low concentration. Figure 2 shows probably the only spinel phase found at the bottom, and in Figure 3 it is shown on an increased scale. Spectra 1 and 3 (see

Figure 2) are characterised by a marked presence of all the elements, and they are hard to interpret unambiguously. It is likely that this is the phase that formed from the melt and had no time to solidify by preserving a partially amorphous state. No phases with a close composition were fixed in the diffraction patterns. Therefore, the spinel octahedrons (see Figure 3, spectra 1 and 2),  $\text{Mg}_2\text{SiO}_4$  (see Figure 2, spectra 2 and 4),  $\text{CaF}_2$  in the formations looking like spherulites and the liquid-type phase were unambiguously interpreted on the bottom side.

The X-ray pattern of the remelted flux on the bottom side is hard to interpret. Almost every peak has strong asymmetry on the side of small scattering angles, this evidencing a poor phase formation on the bottom side. For example, the phases close in structure, i.e. the spinel form of aluminium dioxide,  $\text{Mg}_2\text{SiO}_4$ , and high- and low-temperature spinels, which have the same structural type of lattice parameters  $a$ , i.e.  $Fd\bar{3}m$ , but can range from 7.90 to 8.20 nm, persist on the bottom side. In general, the phases appearing on the bottom side are poorly formed and hard to distinguish. X-ray analysis confirms the presence of spinel  $\text{Al}_2\text{MgO}_4$ ,  $\text{Mg}_2\text{SiO}_4$  and  $\text{CaF}_2$ .

**High-temperature X-ray solid-state examinations.** To trace the sequence of solid-state reactions, the ceramic flux ground into a powder was placed into a molybdenum crucible, which was mounted on a work table inside a high-temperature vacuum chamber of the diffractometer for examinations of melts [12], and subjected to high-temperature X-ray phase analysis. As shown by the analysis, structural changes in a specimen occur over the entire temperature range (Figure 7). Up to 1200 °C, they take place in the solid phase. At low temperatures, the structural changes are slow and occur mainly inside the phases. For example, the most intensive peak corresponding to the 100 % intensity of hexagonal  $\alpha$ -quartz dramatically decreases already at 600 °C. At the same time, there appear the peaks corresponding to other modifications of silica.

Solid-state interactions between the phases begin at higher temperatures. It should be taken into account that the main components in the agglomerated flux are contained in the matrix of a binding material (Na–K liquid glass annealing product). Formation of vacancies in the matrix during evaporation of water will lead to the fact that the inter-phase interaction will take place due to diffusion of atoms of the flux components into the matrix at a rather high rate. Probably, nuclei of the new phases, which can partially dissolve at the initial stage of melting of some



**Figure 7.** Diffraction patterns of the flux (MoK $\alpha$ -radiation) at room temperature (1), 600 (2), 800 (3), 1000 (4), 1200 (5), 1300 (6), 1400 (7) and 1500 (8) °C. Diffraction pattern of pure spinel (points) is superimposed on diffraction pattern at 1300 °C. Diffusion background is fully removed



flux components in the molten phase, or, on the contrary, can accumulate due to intensified interaction with the molten phase, will start forming in the matrix on a base of the liquid glass remainders. Below 1200 °C, the melts preserve the main components, although, as can be seen from Figure 7, intensive decrease in their peaks and, hence, destruction of the initial structures take place. At 1200 °C, the diffraction patterns show practically no reflections corresponding to the initial flux components. The flux melts. However, a new crystalline phase, i.e. spinel  $\text{Al}_2\text{MgO}_4$ , forms against the background of the molten component.

The diffraction pattern of pure spinel is superimposed on the diffraction pattern of a specimen at a temperature of 1300 °C (see Figure 7). Then the spinel reflections in a temperature range of 1200–1500 °C coincide in location with the specimen reflections. The relative intensity of the reflections is in some disagreement with the tabular data. This can be the case if the crystallites of spinel in the melt are oriented with a certain plane relative to the melt surface, rather than being chaotically located. As the melt surface is saturated with spinel to a much greater degree, and the bottom — to a lesser degree, it can be assumed that the spinel is lighter than the liquid phase and, as such, it floats to the surface.

**Discussion of results.** The insignificant additions the content of which is not in excess of 1 wt.% being ignored, to interpret the results obtained it is necessary to use a complex constitutional diagram of  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{MgO}-\text{SiO}_2-\text{CaF}_2$ . But this oxide-fluoride diagram is not available in the scientific literature. The closest, well-studied constitutional diagram for the four-component system is  $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  [13]. As discovered in investigation of the agglomerated flux of the calculated  $\text{MgO}$  (10 wt.%)- $\text{Al}_2\text{O}_3$  (25 wt.%)- $\text{SiO}_2$  (40 wt.%)- $\text{CaF}_2$  (25 wt.%) composition,  $\text{CaF}_2$  at least partially transforms into an oxide [9, 14]. It was established for this flux that the main phase has the form of anorthite, i.e.  $\text{CaAl}_2\text{Si}_2\text{O}_8$ , where calcium has the oxide form. Probably,  $\text{MgF}_2$  forms in small amounts. Spinel  $\text{Al}_2\text{MgO}_4$  does not form in this case. The spinel fields appear in the  $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  diagram already in a section of 15 wt.%  $\text{Al}_2\text{O}_3$ . In the  $\text{MgO}-\text{Al}_2\text{O}_3$  binary constitutional diagram the spinel is almost stoichiometric at low temperatures, and features a wide range of homogeneity at high temperatures. Earlier the spinel was not distinguished from the cubic modification of  $\text{Al}_2\text{O}_3$ . Solid solutions based on spinel  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$  are found

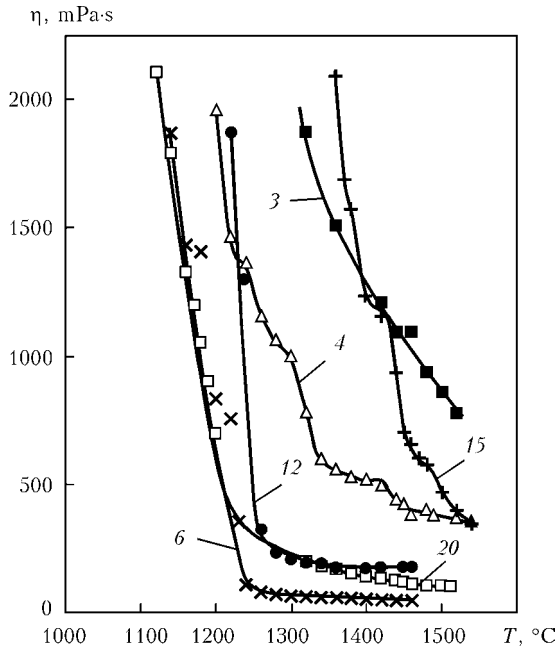
in the entire concentration range of the constitutional diagram at a temperature of up to 2000 °C. Investigations of the solid solutions of  $\text{Al}_2\text{O}_3$  in the spinel show that they have cation vacancies, which are readily filled up from external sources. Reaction of formation of the spinel in the solid phase from aluminium oxide begins approximately at 750 °C [15]. According to [13], the initial stage of formation of the spinel occurs by the surface diffusion of alumina into  $\text{MgO}$ , which is followed by the volume diffusion of atoms (ions) of magnesium and aluminium through the oxygen sub-lattice to transform the hexagonal arrangement of this sub-lattice in corundum into the cubic one (probably, the corundum itself first forms the cubic lattice of the spinel type). A high melting temperature of spinel and physical-chemical properties of the slag melts it determines arouse considerable interest in the spinel when developing a new generation of welding fluxes. The spinel phase persists after remelting of the flux during the welding process and its transformation into a slag crust.

Therefore, the presence of spinel is an experimental fact, and it is necessary to reveal all advantages and drawbacks of the presence of a solid spinel phase in the melt, as well as its effect on the welding process. It is possible to distinguish four moments which can be affected by formation of the crystalline spinel, although, in general, there may be much more of such moments.

1. If the thermal expansion coefficients of spinel and liquid phase solidification products differ greatly at the temperatures of detachment of the slag crust from the weld metal (250–500 °C), this will induce microstresses in the matrix of the former liquid phase, thus creating preconditions for good detachability of the slag crust from the surface of the metal welded.

2. The presence of the crystalline phase in the liquid slag melt at a temperature of about 1100–2000 °C will have a considerable effect on viscosity of the melt. Increase in the content of the crystalline spinel in the molten slag may lead to increase in viscosity and make the molten slag «longer», this being a positive factor in terms of the technological properties of the flux, which was already noted at the beginning of the article.

3. The general decrease in the content of electricity carriers in the slag during formation of the spinel phase due to decrease in the quantity and mobility of elementary particles (ions and electrons) may lead to a substantial decrease in electrical conductivity. This also is a positive factor, as it will allow mitigating the effect of



**Figure 8.** Temperature dependence of viscosity of model slags of the MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–CaF<sub>2</sub> system (numbers of curves correspond to numbers of fluxes in Table 2)

shunting of the current through the slag and improving stability of the process in case of multi-arc welding.

4. The presence of the solid phase in the slag melt will reduce thermodynamic activity of some components of the flux and, hence, affect its metallurgical properties, as was confirmed by the investigations [11].

The most important factor in terms of ensuring the required technological properties of the welding flux is a temperature dependence of its viscosity. Several model agglomerated welding fluxes of the investigated system were made for further investigations of viscosity. The calculated compositions of the fluxes are given in Table 2, and the viscosity measurement results are shown in Figure 8. It was found that the intensity of reflection of the crystalline spinel decreases from specimen to specimen in the following order: 3 → 15 → 4 → 12, this being in correlation with decrease in sum of the spinel components, i.e. MgO + Al<sub>2</sub>O<sub>3</sub> (see the last column in Table 2). In our opinion, the sum of the spinel components in the first approximation can serve for quantitative evaluation of the spinel until the other criterion is found, which can correlate with the content of the crystalline spinel in a specimen. In specimens 6 and 20, no spinel was detected because of the absence of Al<sub>2</sub>O<sub>3</sub>, and its content in specimen 12 is too low because of a low content of Al<sub>2</sub>O<sub>3</sub>.

It was established that fluxes (6, 12 and 20) with the content of magnesium and silicon equal to 35–40 % and aluminium oxide equal to 10 %

**Table 2.** Calculated compositions of model welding fluxes, wt.%

Flux number	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaF <sub>2</sub>	MgO + Al <sub>2</sub> O <sub>3</sub>
3	40	30	15	15	70
4	30	25	20	25	55
6	40	0	35	25	–
12	40	10	40	10	50
15	40	25	10	25	65
20	35	0	40	25	–

are characterised by a jump-like change in viscosity in a temperature range of 1150–1250 °C. These are the so-called «short» fluxes. Fluxes 3 and 15 with 40 wt.% of magnesium oxide and 25–30 wt.% of aluminium oxide are characterised by a high viscosity over the entire range of the studied temperatures. The absence of the flat part on the viscosity curve is indicative of an incomplete melting of these slags and presence of a large number of solid particles in the melt, which could be observed in the course of the experiment. Most probably, this phase is Al<sub>2</sub>MgO<sub>4</sub>. Flux 4 investigated here has a somewhat lower calculated content of magnesium oxide (30 wt.%), and the content of aluminium oxide in it is 25 wt.% (see Tables 1 and 2). This flux is characterised by a rather smooth change in viscosity over the entire temperature range (see Figure 8; flux 4 in Table 2). In this case the curve comprises some «steps», which can be explained by solidification of extra portions of the Al<sub>2</sub>MgO<sub>4</sub> solid phase from the melt. As to the character of the temperature dependence of viscosity, flux 4 is close to manganese-silicate flux AN-60. Welding-technological tests of the fluxes indicated in Table 2 showed that flux 4 has the best properties. Therefore, it is the presence of the solid phase in the slag melt, in our opinion, that determines the character of the temperature dependence of viscosity. It is likely that by manipulating with the proportions and concentrations of spinel components Al<sub>2</sub>O<sub>3</sub> and MgO it is possible to achieve the required viscosity values and character of the temperature dependence, and, on this base, develop fluxes with the controllable viscosity and predictable technological properties. We believe that fluxes, in the melts of which the crystalline spinel forms, will combine good technological and metallurgical properties.

## CONCLUSIONS

1. X-ray examinations of structure of the MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–CaF<sub>2</sub> system agglomerated flux in the initial, molten and solid states, after holding at 1500 °C, were carried out. Images of the initial



and remelted flux were obtained by using scanning electron microscope JSM-7700F fitted with the X-ray spectral microanalyser, and local chemical compositions of the microinclusions were determined. Viscosity of the slags was measured by using the rotational viscometer in a purified argon flow inside the Tamman furnace.

2. The examinations conducted evidence a complex character of interactions taking place in the agglomerated flux before formation of the molten slag phase. The main structural changes in heating the flux to 1200 °C occur due to the solid-phase interactions in a product formed by a cake of the liquid glass with the adjacent main components of the flux.

3. Formation of the liquid phase begins in a temperature range of about 1200 °C due to melting of the cake of the liquid glass with the main components and complex unstable compounds. The solid  $\text{Al}_2\text{MgO}_4$  spinel phase having a melting temperature of 2105 °C forms in this case in the melt. Full melting of the flux of the investigated composition does not take place in a temperature range of up to 1500 °C. This phase persists in the slag crust after remelting of the flux during the welding process. The presence of the solid  $\text{Al}_2\text{MgO}_4$  phase in the slag melt of the  $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{CaF}_2$  system determines its physical-chemical properties, in particular the smooth character of viscosity changes in a temperature range of 1180–1540 °C.

4. It is an established fact that by manipulating the proportions and concentrations of spinel-forming components  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  it is possible to achieve the optimal values of the temperature dependence of viscosity of the slag melt and, on this base, develop welding fluxes with controllable technological properties.

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