Forming of the structure of binder film in waterglass mixtures depending on the setting method

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High residual strength of material of moulds and moulding cores after high-temperature effect by ferrous metals alloys is considered as one of the main disadvantages which restrict wide use of sand mixtures on waterglass binder in casting and foundry production. It is known that mechanical properties of sand mixtures on waterglass binder depend directly on the conditions of silicate binder film forming on the surface of refractory filling agent. Investigations aimed on examination of sodium silicate film structure forming depending on heat and chemical setting of mixtures as well as on the type of refractory filling agent were carried out at the first stage. The obtained data of this investigation showed that presence of numerous laminations, cracks in the area of seals and crystals of sodium carbonates (which are stress concentrators) in the film structure of sodium silicate aqueous solution provides the main effect on mechanical properties of sand mixtures on waterglass binder. Forming of these defects, in its turn, requires the conditions which promote running of carbonization process of sodium silicate aqueous solution. The second stage of this research included study of the effect of destruction of carbon-containing additive on integrity violation of a binder film. As a result, the suggestions about influence of crystals of sodium carbonates in sodium silicate film structure on lowering of residual strength of a waterglass mixture were confirmed.
Key words: waterglass mixture, sodium silicate film aqueous structure, crystals of sodium carbonates, carbon-containing additive, binder.
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Introduction

Modern casting and foundry production introduces permanently the most strict technological, economical and ecological requirements to manufactured products owing to high competition at the global market of metal products. Waterglass is one of the most prospective binding materials for manufacture of moulds and moulding cores for production of shaped castings from iron carbon alloys, what is connected with its ecological acceptability, low cost, accessibility and high adhesion properties of substrates with different chemical composition, nature and morphology. Additionally, waterglass mixtures allow to decrease operating cycle of manufacture of moulds and moulding cores by 8-10 times, to increase labour productivity more than by 30 % and to improve quality of manufactured products and sanitary-hygienic conditions in production facilities etc. [1-4]. However, solving of the problem of difficult knocking-out ability of waterglass moulds and moulding cores of iron and steel castings is rather actual problem of foundry production; it will allow to increase productivity of technological processes, to expand application range for waterglass binder relating to the features of castings production. Residual strength is one of the parameters that characterize knocking-out ability of castings from moulds, as well as moulding cores from castings. Respectively, the higher is the value of residual strength, the higher is possibility of difficult knocking-out ability of moulds (moulding cores). It is known that this parameter depends on several factors that have influence on forming a sodium silicate film on the surface of refractory filling agent. Among these factors the following can be mentioned: relationship between basic mixture components [5-7], thermal physical parameters of the system "mould (moulding core) – casting" [1, 2], influence of technological additives which provide softening of the mixture [8-11], methods of mixture preliminary preparation [12-14] etc. At the same time the setting method is very important; it also provides a mould (moulding core) with initial conditions for forming of the binder film structure and properties of waterglass mixture during interaction with melts [15-17]. Examination of film morphology in sodium silicate aqueous solution for different setting methods allows to add the existing theoretical regulations about softening mechanisms of sand mixtures with waterglass binder and to develop the efficient methods for improvement of knocking-off ability of moulds and moulding cores in the conditions of production of castings from ferrous alloys.

The aim of this research is examination of sodium silicate film structure and mechanical properties of sand mixtures on waterglass binder depending on the setting method and kind of refractory filling agent, for development of the method for improvement of knocking-off ability of moulds and moulding cores.

Materials and methods

To examine influence of the setting methods for sand mixtures on waterglass binder with different refractory filling agents, which differ by thermal accumulating capacity as well as by angularity coefficient, average grain size and homogeneity, on forming of the sodium silicate film structure, several materials were used. The following materials can be mentioned in this row: quartzite sand of the grade $1K_2O_3$03 (GOST 2138–91); chromite sand of grade AFS 45-55 (TU 07.29.19-003-86598018-2019); sodium waterglass with silicate module 2.8 and density 1490 kg/m^3 (GOST 13078-81). Mixtures with these materials were manufactured in laboratorial mixing runners of 018M2 model. Refractory filling agent was charged in laboratorial runners and mixed during two minutes, afterwards required amount of waterglass was added. Mixing was carried out during 8 minutes until achieving mixture humidity value 4 %. Compositions of mixtures for preparation of experimental cylindrical samples according to the GOST 23409/6-78 are presented in the **Table 1**.

Determination of tensile strength of the samples taken from investigating mixtures during compression in set state was conducted according to the GOST 23409.7-78 on the universal tension testing machine «PM-500» (maximal load 500 kN, measuring error ±1 %). Ten samples were fabricated for each mixture composition. Friability was determined according to the GOST 23409.9–78 on the sensor «hS-1». Standard cylindrical samples were prepared according to the GOST 23409.6–78, then they were preliminary weighed on laboratorial scales of second accuracy class and afterwards located on rotating rolls. Testing duration was one minute. Then the samples were extracted from the sensor and their friability was calculated. Three samples were fabricated for each mixture composition.

Morphological features of fracture surface of standard cylindrical samples after determination of tensile strength during compression were examined via scanning electron microscopy (SEM) on the sensor Versa 3D, FEI (Czech Republic) with magnification 130-20,000 times. The samples from mixtures with low electric conductivity (see Table 1, compositions 1, 3 and 5) were examined in low vacuum conditions for compensation of accumulation of excessive charge [18]; these examination conditions provided aqueous steam pressure in a microscope chamber 60-80 Pa, accelerating voltage 10 kV and beam current 20-50 pA. The samples from mixtures with high electric conductivity (see Table 1, compositions 2,4 and 6) were examined in high vacuum conditions ($3\cdot10^{-3}$ – $4\cdot10^{-4}$ Pa) using detector of back-scattered electrons with accelerating voltage 20 kV and beam current 4 nA. Processing of the obtained data was carried out with use of specialized software «xT microscope».

Results and discussion

Microstructure of sodium silicate film on the surface of quartzite (**Fig. 1***a*) and chromite (Fig. 1*b*) refractory filling agents after setting by convective drying at the temperature 180 °C is presented below.

When setting the samples via the method of convective drying, sodium silicate film of the mixtures manufactured on the base of quartzite filling agent, has globular structure. Forming of this film structure is explained by the process of evaporation (boiling) of adsorption and crystallizing water at the temperatures above 80 °C and above 110 °C respectively [19]. Violation of integrity of sodium silicate film on the surface of chromite refractory filling agent during the similar setting method occurs fragmentarily. Structure of filling agent film practically has no breaks. It is connected with more high thermal accumulating capacity for chromite filling agent, which has thermal accumulation coefficient higher by 46 % in comparison with quartzite sand [3].

Microstructure of sodium silicate film on the surface of quartzite (**Fig. 2***a*) and chromite (Fig. 2*b*) refractory filling agents after blowing by carbon dioxide in the core box under pressure 0.17 MPa during 45 seconds is presented below.

Silicate film of the mixture, which was subjected to setting by carbon dioxide, is characterized by more structure integrity owing to absence of temperature effect (which leads to evaporation of free water) and as a result of struc-

Table 1. **Composition of researching mixtures and their setting methods**

Index of mixtures	Mixture composition, % (mass.)				Setting method
	Sand		Sodium waterglass	H-butyl acetate (GOST 22300-76), over 100 %	
	Quartzite $1K_2O_3$03	Chromite AFS 45-55			
1	94	-	6	-	Convective drying in a drying oven at the temperature 180 °C during 40 min
2	-	94	6	-	
3	94	-	6	-	Blowing by carbon dioxide (CO_2-process) during 45 sec in a core box under pressure 0.17 MPa
4	-	94	6	-	
5	94	-	6	1	Setting by organic ester
6	-	94	6	1	

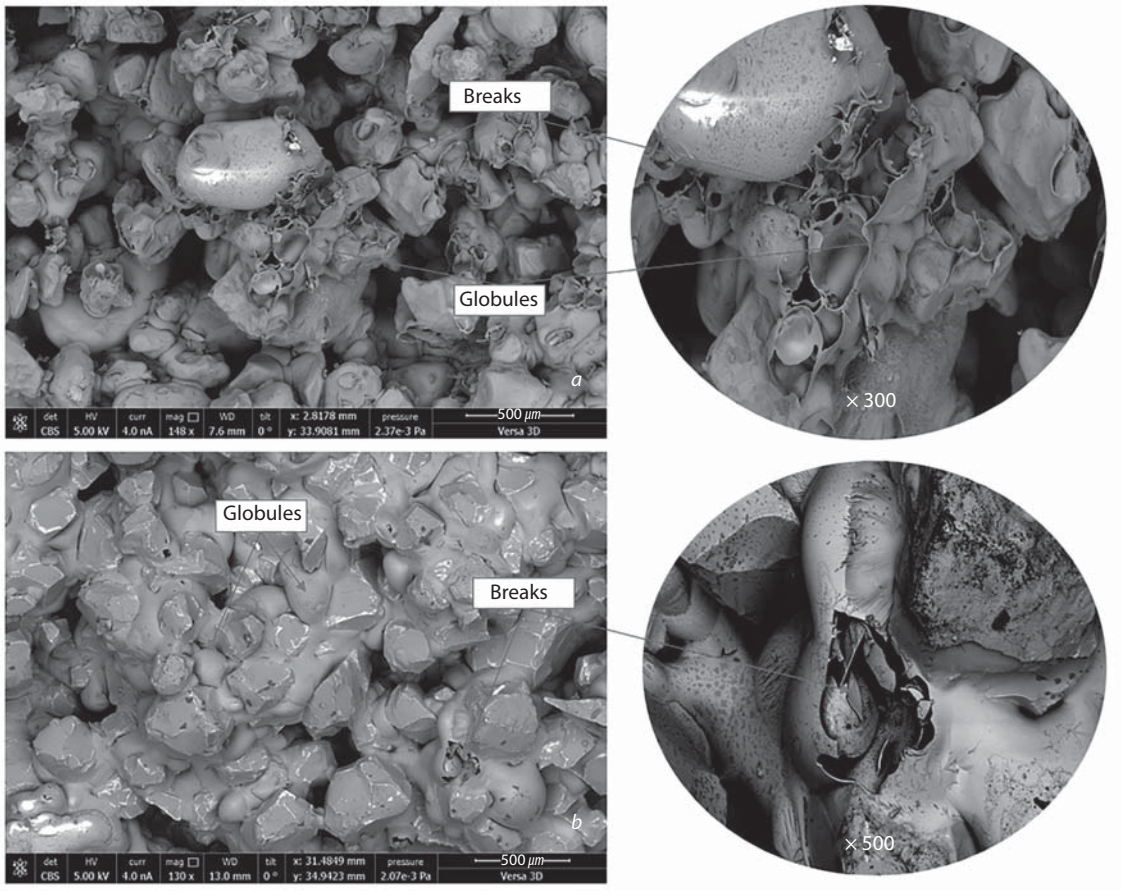

Fig. 1. Microstructure of sodium silicate film for the mixtures on the base of quartzite (*a*) and chromite (*b*) filling agents after convective drying

ture globularization of sodium silicate films after convective drying. Cracks on joint seals of sodium silicate films between quartzite sand grains and local film lamination from a filling agent is explained by binder shrinkage in the moment of forming of gel-silicon acid. The following violations of film integrity were revealed during examination of film structure in sodium silicate mixtures with chromite filling agent: cracks in the area of seals; local binder film lamination from the surface of chromite filling agent; presence of acicular crystals (their forming is connected with conduction of carbonization process during mixture blowing by carbon dioxide [20]. Crystals of sodium carbonates are stress concentrators in a binder film and lead to film breaks and its lamination from refractory filling agent (together with shrinkage). Carbonization process during blowing of waterglass mixtures on the base of chromite filling agent with angular grain form occurs more intensively than for mixtures on the base of quartzite sand semi-circular grain form. These filling agents with different grain form are characterized with the following parameters respectively: angularity coefficient 1.36 and 1.16 units; average grain size 0.3 and 0.315 mm; homogeneity coefficient 75 and 66 %. Chromite filling agent has more free "packing", while quartzite sand has more high gas permeability – 430 units compared with 255 units for chromite sand.

Microstructure of sodium silicate film for mixtures on the base of quartzite (**Fig. 3***a*) and chromite (Fig. 3*b*) filling agents after setting by organic ester is presented below.

Excepting small number of cracks in the points of contact of filling agent grains (in seals), which are forming during binder shrinkage of a filling agent in the process of forming of gel-silicon acid, the sodium silicate film structure is rather monolithic. Thereby, friability of such mixture will be low, while tensile strength for compression after setting will be high.

Taking into account that mechanical properties of sand mixtures on waterglass binder, after their setting by ester, depend on holding time in the air [4], friability and tensile strength for compression were determined after holding of samples in the air during 0.5-24 hours in the conditions of relative humidity(52 ± 1) % (according to the data from hygrometer). The values of tensile strength for compression and friability of samples were chosen as strength parameters of the mixture, that was subjected to setting by ester, after their 24 hour holding in the air for comparative analysis of mechanical properties of the examined mixtures after setting by convective drying, carbon dioxide and organic ester.

The results of determination of mechanical properties (tensile strength for compression σ_{comp}, MPa; friability X, %)

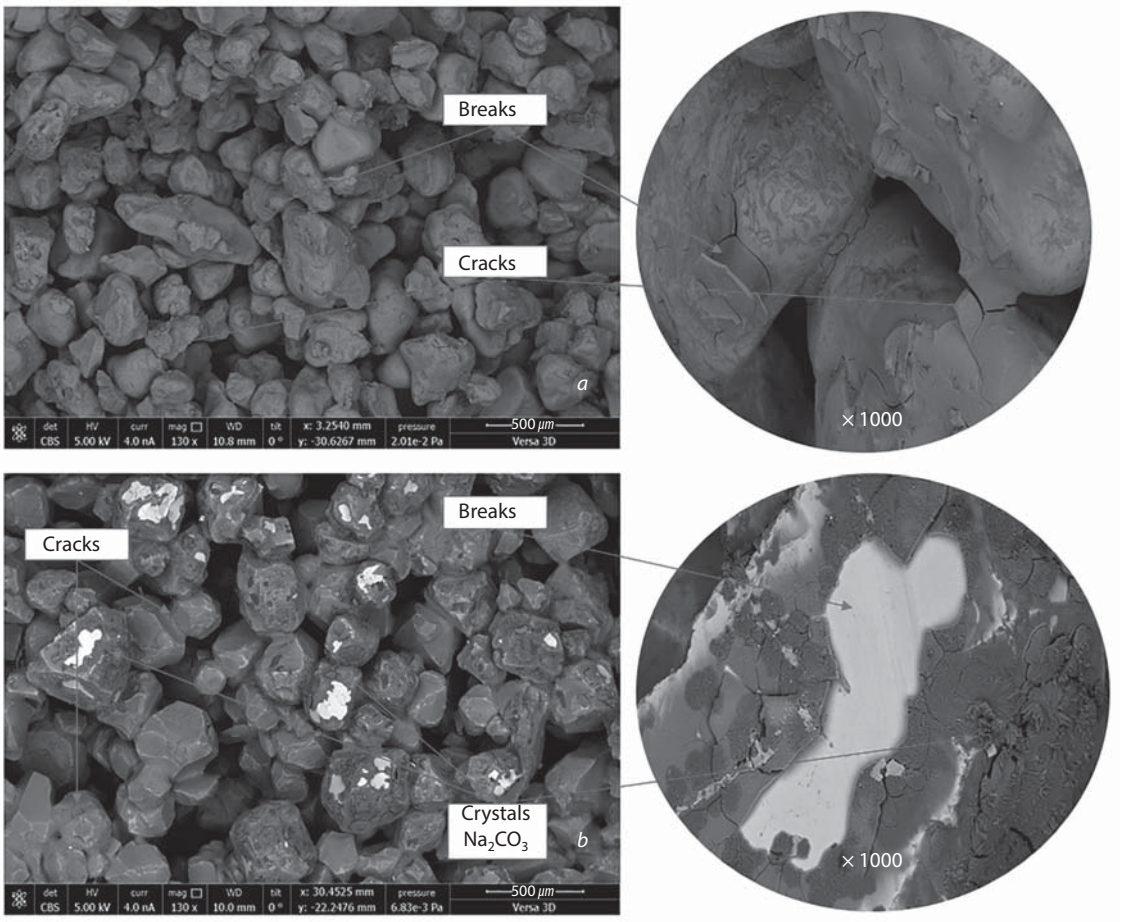

Fig. 2. Microstructure of sodium silicate film for the mixtures on the base of quartzite (*a*) and chromite (*b*) filling agents after blowing by carbon dioxide

of investigating mixtures depending on setting method and kind of refractory filling agent are presented on the **Fig. 4**.

Analysis of the results obtained during mechanical tests of investigating materials and microstructural examinations of sodium silicate films after different setting methods allowed to reveal the factors which influence on mechanical properties of sand mixtures with waterglass binder. So, the most low tensile strength for compression and the most high friability of the mixtures with quartzite and chromite refractory filling agents after blowing by carbon dioxide were connected with the process of decarbonization of sodium silicate aqueous solution in comparison with the values after convective drying and setting by organic ester. Above-mentioned carbonization process is accompanied by forming of sodium carbonate crystals and shrinkage of silicate binder gel, what leads to crack forming on "seals" (see Fig. 2). The mixtures which were subjected to setting by organic ester, on the contrary are characterized by high strength and low friability, because only shrinkage processes during binder dehydration have effect on mixture softening for this setting method. As a result, small number of cracks is forming in a sodium silicate film (see Fig. 3). Despite large number of breaks in sodium silicate film globules after setting via convective drying (see Fig. 1), the values of tensile strength for compression are comparable with the values of mechanical properties of mixtures after their setting by organic ester. It is connected with distribution of sodium silicate film breaks directly on the surface of sand and its integrity in the areas of "seals". Difference between mechanical properties of waterglass mixtures on the base of quartzite and ferrite filling agents is explained by their different thermal accumulating capacity, which influences on intensity of free water removal during convective drying and gas permeability having the effect on carbonization process of silicate film.

This research allowed to suggest that it is necessary to create conditions promoting running of carbonization process of sodium silicate aqueous solution in the wide temperature range for lowering residual strength of a waterglass mixture and improvement of knock-off ability of moulds and moulding cores. It can be achieved, for example, due to introduction of carbon-containing additives in composition of the mixture with waterglass binder; their destruction is accompanied by extraction of carbon dioxide. It will lead, in its turn, to forming of crystals of sodium carbonates on the binder film structure according to the following reaction:

$$Na_2O(Si_2O_5)n + CO_2 + 2nH_2O \rightarrow nH_4SiO_4\downarrow + Na_2CO_3$$

To confirm the stated suggestion, the investigation on the effect of destruction of carbon-containing additive

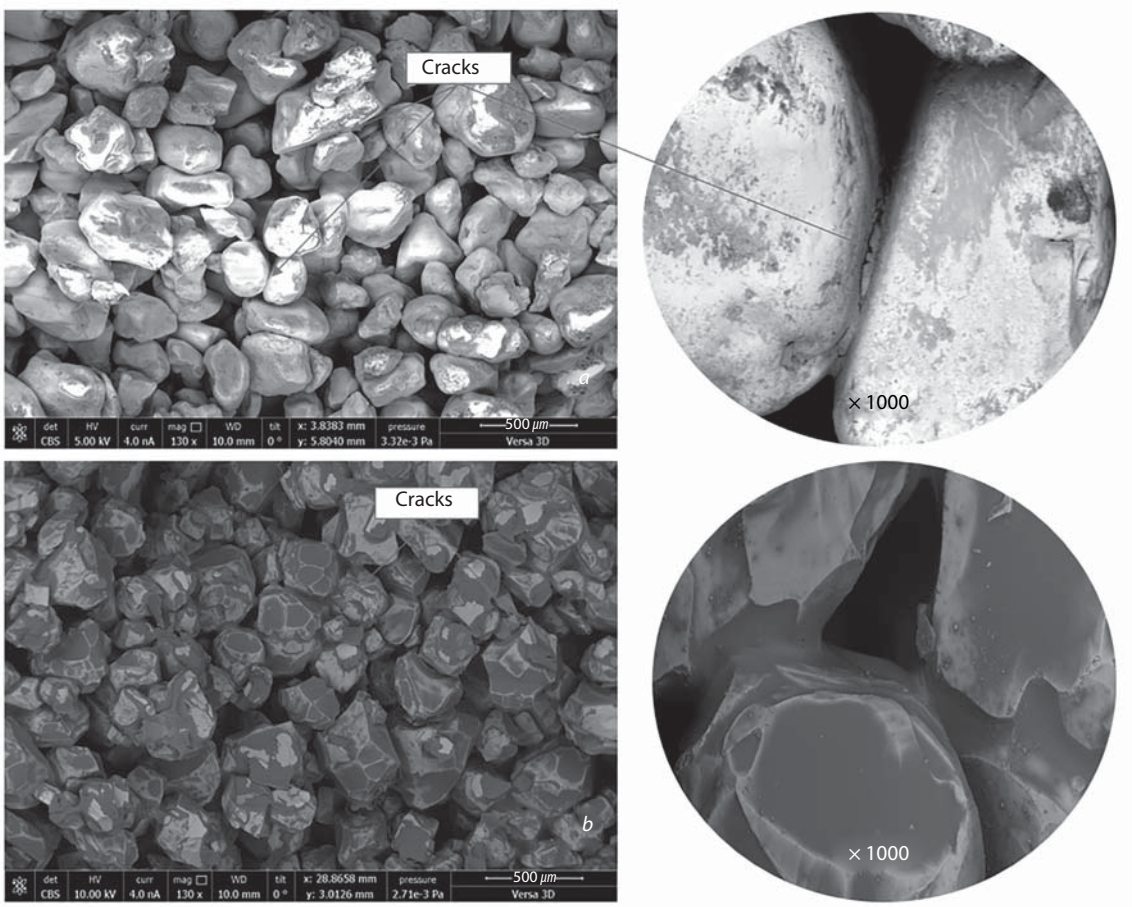

Fig. 3. Microstructure of sodium silicate film for the mixtures on the base of quartzite (*a*) and chromite (*b*) filling agents after setting by butyl acetate

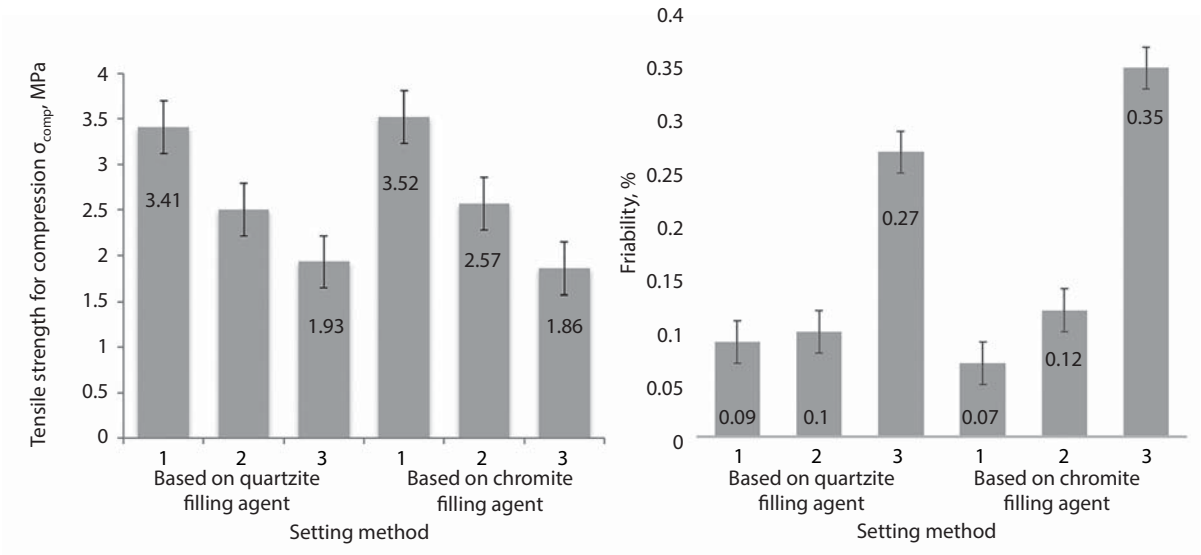

Fig. 4. Mechanical testing of investigating mixtures after different setting methods: 1 – setting by ester; 2 – convective drying; 3 – blowing by carbon dioxide

(wastes of contact purification of residual oils according to TU 38.30112-83) on violation of binder film integrity and lowering of residual strength of waterglass mixture after calcination was conducted at the temperature characterizing through heating of moulds and moulding cores in the conditions of castings fabrication from ferrous and non-ferrous metals. Wastes of contact purification of residual oils (WCPRO) present calcium bentonite impregnated by petroleum oils, they are related to the group of complex carbon-containing additives, because they con-

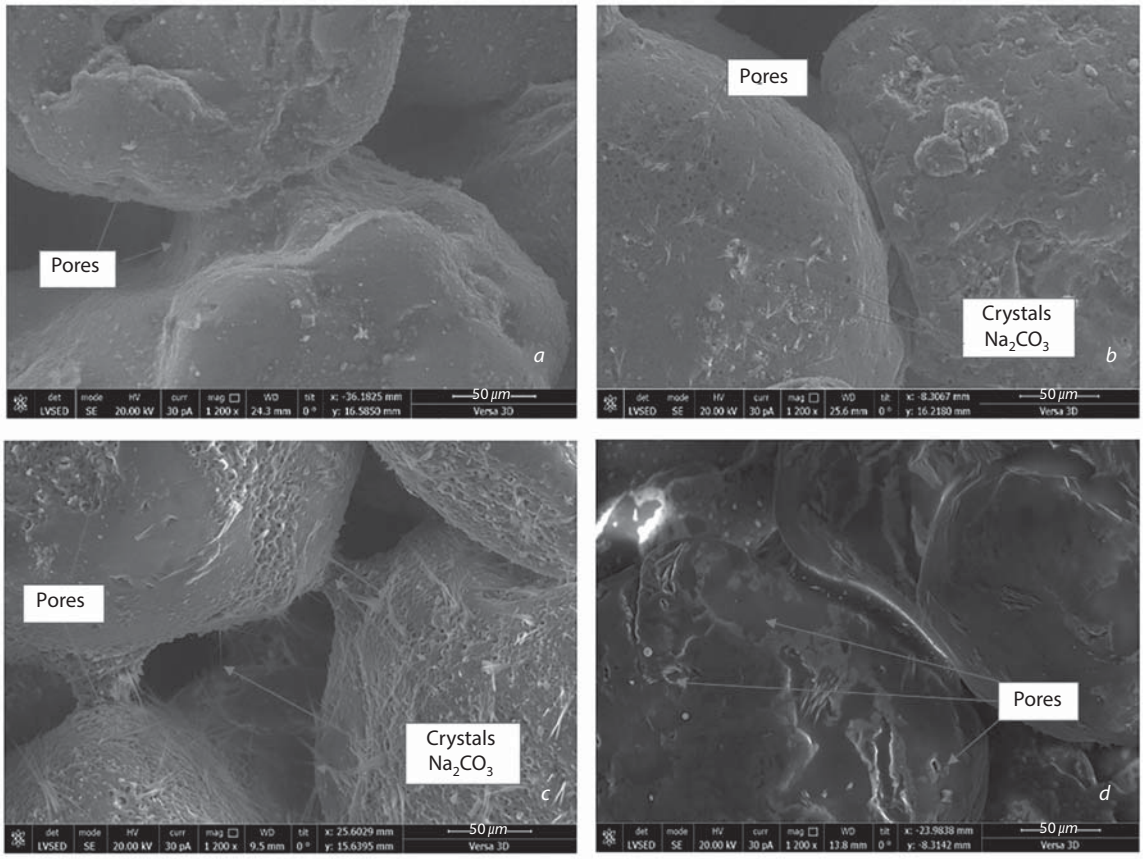

Fig. 5. Microstructure of sodium silicate films in the mixtures with WCPRO addition after calcination at the temperatures:
***a* – 180 °C (1200 power); *b* – 400 °C (1200 power), *c* – 600 °C (1200 power), *d* – 800 °C (1200 power)**

Table 2. **The results of determination of residual strength of investigating mixture**

OKOOM 2%			
Temperature of mixtures calcination, °C	Average value of residual strength, σ_w, MPa	Dispersion	Confidence interval of the average value on significance condition $\alpha = 0.05$
180	2.42	0.0024	± 0.0355
400	1.32	0.0018	± 0.0307
600	0.62	0.0016	± 0.0290
800	1.62	0.0016	± 0.0288

tain both inorganic component (calcium bentonite clay, its destruction is accompanied by water removal, while water is necessary for supporting the process of sodium silicate carbonization) and organic part (its destruction is accompanied by extraction of carbon oxides). This additive in the amount 2 % (mass.) was introduced in composition of the sand mixture on waterglass binder (92 % of quartzite sand and 6 % (mass.) of sodium waterglass). Setting of this mixture was carried out via the method of convective drying.

Microstructure of sodium silicate films in the mixtures with WCPRO addition are presented on the **Fig. 5**.

Violation of sodium silicate film integrity in the form of porosity (see Fig. 5*a*) after calcination of the mixture at the temperature 180 °C is connected with removal of free water of waterglass, bentonite clay (included in WCPRO composition) and gas emission of hydrocarbons. Appearance of sodium carbonate crystals in sodium silicate film structure after calcination at the temperature 400 °C (see Fig. 5*b*) and essential enlargement of their sizes and amount after calcination (see Fig. 5*c*) is connected with increase of carbonization process intensity due to carbon dioxide forming during WCPRO thermal oxidizing destruction and decomposition of montmorillonite which is included in its composition. Increase of the film porosity (see Fig. 5*c*) after mixture calcination at the temperature 600 °C is explained by intensive gas emission of light, heavy aromatic, paraffin-naphthene hydrocarbons during WCPRO

thermal oxidizing destruction. The film structure became more monolithic after calcination at the temperature 800 °C due to binder smelting ability (see Fig. 5*d*). Presence of local porosity is explained by intensive gas emission during WCPRO thermal oxidizing destruction.

The results of determination of residual strength of investigating mixtures, which include carbon-containing additives, after calcination at the temperatures 180 °C, 400 °C, 600 °C and 800 °C are presented in the **Table 2**.

It can be seen from the Table 2 that local porosity in sodium silicate films of the investigating mixtures has not influence practically on lowering of residual strength after calcination of the samples at the temperature 180 °C. Lowering of residual strength of the mixtures containing WCPRO after calcination at the temperatures 400 °C and 600 °C is characterized by presence of porosity and acicular crystals in the sodium silicate film structure. Increase of residual strength after calcination at the temperature 800 °C is connected with binder ability to "cure" structure discontinuities after its melting at the temperatures 793-795 °C [1, 4, 5].

Thus, to get efficient decrease of residual strength of sand mixtures on waterglass binder and, respectively, for improvement of knocking-off ability of moulds and moulding cores from steel and iron castings, it is required to provide the conditions for supporting binder film integrity violation in the wide temperature range 180-800 °C and for militating sodium silicate healing after its melting at the temperatures 793-795 °C. It can be achieved by introduction of combined carbon-containing additives in composition of sand mixtures on waterglass binder; destruction of these additives leads to forming of numerous sodium carbonate crystals (as stress concentrators) and pores in the binder film structure.

Conclusions

1. It was established that blowing by carbon dioxide of the sand mixture on waterglass binder after setting has maximal influence on mechanical properties of such mixtures in comparison with the method of convective drying and setting be ester; as a result, acicular crystals of sodium carbonates are forming on the binder film structure owing to carbonization process of sodium silicate aqueous solution. Intensity of carbonization process depends in this case on shape, average size and homogeneity of grains of refractory filling agent.

2. It is shown that the following conditions are required for decrease of residual strength of sand mixture on waterglass binder and, respectively, for improvement of knocking-off of moulds and moulding cores from steel and iron castings: presence of numerous laminations, cracks in the seal areas and sodium carbonate crystals, which are stress concentrators. Forming of these crystals requires, in its turn, the conditions that promote running of continuous carbonization process of sodium silicate aqueous solution within the wide temperature range 180-800 °C.

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