Effect of a Carbonaceous Additive on the Structure of an Aqueous Sodium Silicate Film on the Surface of a Refractory Chromite Filler

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Abstract. The results of studying the effect of a carbonaceous additive on the structure formation of aqueous sodium silicate film on the surface of a refractory chromite filler was shown. Ultradispersed pyrolytic carbon (pyrocarbon) was used as a carbonaceous additive. The structure of liquid glass films on the surface of a refractory filler was investigated after curing at temperatures of 180–400-600-900 °C, which are comparable to the temperature of convective drying of liquid glass molds and cores, as well as molds heating temperature during pouring with liquid metal. The structure of liquid glass films on a refractory filler was investigated using a Versa 3D two-beam scanning electron microscope, which made it possible to show the effect of pyrocarbon on the structure of a silicate binder film in each temperature range.

1. Introduction

Currently, liquid glass is one of the common binders in the producing of molding and core sands for foundry, due to a number of its positive qualities, such as non-toxicity, relatively low cost, high binding capacity, etc. [1–3]. The study of the curing processes of liquid glass mixtures is reflected by many researchers, and the study of liquid glass films formation on the surface of a refractory filler is of particular interest. The quality of the silicate binder film's structure and its adhesion to the refractory filler directly affect the strength characteristics of molding and core sands. But when working with liquid glass, it is also necessary to take into account the residual strength, which affects the difficulty of knocking out cores and castings from the mold. The works devoted to solving the problems of poor knocking-out ability propose and consider various methods such as modifying sodium silicate solution and liquid glass mixture [4–7], adding organic hardeners, optimizing compositions and using softening additives that affect residual strength [8–11].

Of the above methods, the introduction of organic, inorganic and complex additives into the mixture is most universal. The softening process with the introduction of these additives is realized due to the release of CO and CO₂ under high-temperature exposure. At the same time, with gas exit the internal stresses inside the mold are created and accompanied with binder's film integrity violation [12–14].

It is known that in the 70s the question of the aqueous sodium silicate film structure formation starts to attract attention [15]. Research methods and technologies of that time did not allow maintain fully detailed structural studies. The physical and mechanical properties are largely

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influenced by the quality of the liquid glass film, therefore, studies that allow investigate the effect of curing methods on films properties will lead to possibility of giving recommendations for control properties of liquid glass molds and cores.

In this work, the chromite sand was used as a filler, which is widely used in the manufacture of steel castings using core and facing mixtures, and also provides a cheaper alternative to special fillers such as zircon, while reducing or eliminating casting defects associated with using quartz sand [16]. Ultradispersed pyrolytic carbon (pyrocarbon) was used as a carbonaceous additive, which is carbon films formed by crystallization from gas phase at high pressure and temperature (1400–1600 °C) [17–19].

The purpose of this work is to study the effect of a carbonaceous additive on the structure formation of aqueous sodium silicate film on the surface of a refractory chromite filler.

2. Materials and methods

To determine the behavior of pyrocarbon at elevated temperatures, thermogravimetric (TGA) and differential thermal (DTA) analyzes were carried out simultaneously using a Q-1500D derivatograph manufactured by MOM, Hungary. A sample with pyrocarbon was loaded in the device and heated up to a temperature of 950 °C at 10 °C/min rate.

To study the effect of a carbonaceous additive on the structure of aqueous sodium silicate film, mixtures were prepared from chromite sand (TU 0741-001-23081308) as a filler and liquid glass (GOST 13078-81) as a binder. For comparative analysis, the mixture 1 did not contain a carbonaceous additive. Pyrocarbon was added to the mixture 2 in an amount of 2%. The samples were treated in a furnace at temperatures of 180–400–600–900 °C, which is comparable to the temperature of convective drying of liquid glass molds and cores, as well as molds heating temperature during pouring with liquid metal. The mixtures compositions for samples are presented in Table 1.

| Mixtures № | Chromite sand AFS 45-55 | Pyrocarbon | Liquid glass |
|------------|--------------------------|------------|-------------|
| 1          | 94                       | –          | 6           |
| 2          | 92                       | 2          | 6           |

After heat treatment of the samples, the structure of liquid glass films on a refractory filler was investigated using a Versa 3D two-beam scanning electron microscope, which made it possible to show the effect of pyrocarbon on the structure of a silicate binder film in each temperature range.

3. Results and discussion

Analysis of the derivatogram (Figure 1) showed that heating up to 400 °C does not cause any significant changes in pyrocarbon, which is confirmed by the DTA and DTG data.

The weight loss of the sample in this temperature range is no more than 5% via the burnout of impurities in pyrocarbon. At temperatures above 400 °C, a sample’s weight loss with a small endothermic effect is observed due to the oxidation of the carbonaceous additive with the release of CO and CO₂. At the same time weight loss continuous throughout the experiment, which is confirmed by the direction of the TGA curve.

Figure 2 shows the structure of liquid glass films sample, in which no carbon additive was introduced. At sample temperature of 180 °C (Figure 2 a), the places of contact of the filler grains (cuffs) are swollen due to the evaporation of water (from liquid glass), but no film defects such as tears were found, the surface is solid in comparison with similar samples using quartz sand [20]. This is due to the high heat-storage ability of chromite (2380 compared to 1628 W·c⁰/²/(m²·K) for quartz sand), which leads to formation of moisture condensation zone at greater depth than in quartz sand mixtures. At the same time,
on samples cured at 400 and 600 °C (Figure 2. b, c), defects formed by water evaporation are observed, the structure of the film is disturbed, which is clearly visible both on the chromite grains and on the cuffs.

Figure 1. Differential thermal curves of pyrocarbon.

Figure 2. Structure of liquid glass films on refractory chromite filler grains without pyrocarbon addition at heating temperature of: a – 180 °C (×500); b – 400 °C (×250), c – 600 °C (×500), d – 900 °C (×250).
At sample temperature of 900 °C (Figure 2 d), the structure of the film has no cracks and chips, which is associated with the ability of liquid glass to melt, passing into a liquid state at temperatures above 793 °C [3].

Figure 3 shows the structure of liquid glass films sample in which carbonaceous additive was introduced.

![Figure 3. Structure of liquid glass films on refractory chromite filler grains with pyrocarbon addition at heating temperature of: a – 180 °C (×1000); b – 400 °C (×1000), c – 600 °C (×500), d – 900 °C (×1000).](image)

Defects associated with the removal of water from the composition of liquid glass, as well as the release of CO and CO₂ and impurities of the carbonaceous additive, are observed on the binder's film in the samples in which pyrocarbon was introduced.

At 180 °C (Figure 3 a) the film is smoother, with visible cracks formed during shrinkage of the binder. There are also traces of gas escaping in the form of small circular holes. The films structure of samples after heat treatment at temperatures of 400 and 600 °C (Figure 3 b, c), contains defects associated with the removal of water (globular structure of the film), and more film tears formed by release of CO and CO₂ due to pyrocarbon oxidation in this temperature range, which is confirmed by the endothermic effect on differential thermal curves (Figure 1). At temperature of 600 and 900 °C (Figure 3 c, d), via carbonization process during the release of CO₂ a formation of crystals is occurred on the aqueous sodium silicate film, which provokes tearing of the film and its delamination from the refractory filler.

4. Conclusion
It has been experimentally established that the addition of ultradispersed pyrocarbon affects the structure formation of the aqueous sodium silicate film on the refractory filler grains.

A film of aqueous sodium silicate on sample that did not contain pyrocarbon has defects associated with the removal of water (component of liquid glass) at temperatures of 400 and 600 °C. At temperature of 180 and 900 °C, the structure of the film is continuous with no tears, which is associated with the heat-storage ability of chromite and the ability of the binder to melt at temperatures above 793 °C.
On the liquid glass films of the sample in which the carbon additive was introduced, observed defects are associated with the removal of water, the release of CO and CO$_2$ during heating of the samples, as well as the formation of carbonization crystals, which provokes tearing of the film and its delamination from the refractory filler.

The study of the effect of various additives on the structure formation of aqueous sodium silicate film on the surface of refractory fillers will allow in the future to predict the process of structure formation of liquid glass mixtures.

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