Improvement of Mechanical Properties of Cast Ceramic Cores Based on Ethyl Silicate

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Abstract

The aim of the paper is experimental verification of the influence of the composition of the ceramic mixture on the mechanical properties of cast ethyl silicate cores. Cast ceramic cores have a great potential in the production of complex castings, especially in the field of hydropower. However, the disadvantage of the cast ceramic cores is their low strength during cores removing from the core box and handling with them. The research is focused mainly on the possibilities of increasing the handling strength of the cores during removal from the core box and after their ignition. The paper investigates different ways of increasing the strength of cast ceramic cores by adjusting the composition of the ceramic mixture. Further, the research verifies the possibility of increasing the strength of ceramic cores by adding synthetic fibers to the ceramic mixture. The paper also contains the results of measuring the strength of the cores after impregnation with a solution of phosphorous binder and subsequent annealing.

Keywords: Ethyl silicate, Shaw proces, Cast cores, Ceramics, Fibre reinforcement, Mechanical properties

1. Introduction

In foundry technology, the cores are used to create cavities inside the castings, for example by pre-cast holes, lubrication or cooling channels in engine blocks etc. The so-called inset cores are most often used to create external shapes of castings that otherwise would not be formed. In the case of complex castings, the foundry mold can essentially be a jigsaw puzzle composed of cores and inset cores. Currently, most cores are produced using foundry sand mixtures bonded with organic or inorganic binder systems, which offer sufficient core strength and, in the case of organic binder systems, excellent core disintegration after casting. The disadvantage of these binders is the higher reactivity of the binders with some types of cast materials. For these reasons, ceramic cores are used for precision castings, where the emphasis is on high surface quality and dimensional accuracy of the castings. Simple shapes can be pressed from dry mixtures. With complex cores, it is difficult and often impossible to achieve the required compaction

by pressing, so it is advisable to use cast cores. Another option is using the injection of ceramic materials into the core box. For the production of cores by injection, so-called pellets (a pre-prepared mixture of ceramics with an organic binder) are used. The pellets are liquefied in the injection device and the ceramic mixture thus prepared is placed into the mold cavity. Subsequently, the core is removed from the mold and placed in a furnace, where the binder is removed and the ceramic is annealed. During this process, the core shrinks by about 20%, so it is necessary to take this shrinkage into account when designing the mold [1-3].

The Shaw Process for the production of cast ceramic cores was developed in early 1940s. The principle of solidification of cast ceramic cores (Shaw) is usually based on the sol – gel state change of silicon dioxide colloidal solution. These solutions are electrostatically stabilized in an acidic or alkaline conditions to prevent sedimentation or coagulation. Sol – gel state change occurs when a catalyst is added to the system to disrupt electrostatic forces that prevent particle coagulation. The maximum and minimum stability of silica colloidal solutions is shown in Figure 1 [1-3].
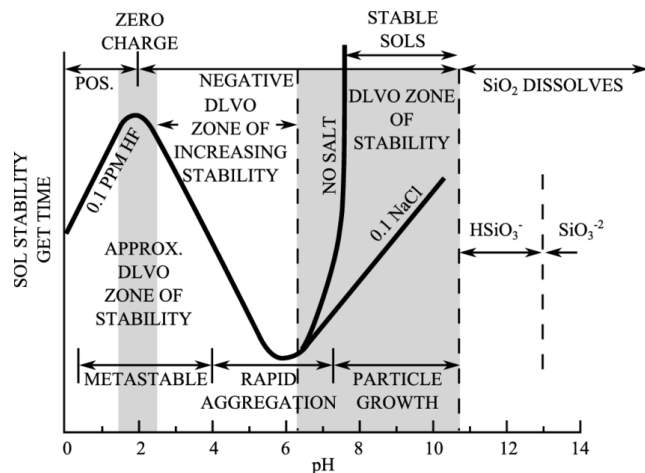
Fig. 1. Stability of coloidal system [4]

The biggest advantage of this technology is the production of complex ceramic molds or cores which would be difficult to manufacture by other method, Shaw process allows the use of cores for conventional core production, therefore its cost is its another advantage. The great advantage of cast ceramic cores is the high surface quality and dimensional accuracy, therefore this technology has found application mainly in the castings of water machines such as turbine impellers. Here, high precision and surface quality of the castings are required, as any unevenness on the castings' functional surface significantly reduces the efficiency of these water devices [1, 4-5].

A major disadvantage of the Shaw Process is the low handling strength of the cores. Larger and heavier cores often collapse under their own weight during handling, so steel reinforcements were introduced into these cores. However, the use of reinforcements often result in cracking of the cores during annealing, which is caused by the different thermal expansion of the steel reinforcements and the ceramic mixture.

In the case of increasing the handling strength of the cores and the overall optimization of this technology, the Shaw method could become a competitor or an alternative to injected ceramic cores.

2. Experimental procedure

2.1. Description of the experiment

The aim of the experiment is to verify the effect of the ceramic mixture composition on the strength of cast ethyl silicate cores. The work is based on the basic recipe for the production of cast ceramic cores by the Shaw method, whose composition was modified in order to increase the mechanical properties of cast cores. The experiment verifies the following modifications of the recipe: the effect of adding synthetic fibers to the mixture and the effect of adding phosphates to the mixture. For all monitored mixtures, standard test specimens were cast into the core box, on which the mechanical properties of the treated mixtures were tested.

2.2. Standard recipe

The ceramic suspension for cast ceramic cores consists of a refractory material corundum + molochite flour (particles smaller than 0.02 see Table 1), a binder fluid (binder) and an accelerator (gelling agent).

Table 1.
Sieve analysis

sieve	residue		sum
[mm]	g	%	%
1,600	1,56	3,20	3,20
0,800	5,46	10,90	14,10
0,630	2,56	5,10	19,20
0,400	5,06	10,10	29,30
0,315	3,31	6,60	35,90
0,200	5,47	10,90	46,80
0,160	1,52	3,00	49,80
0,071	3,77	7,50	57,30
0,056	1,27	2,50	59,80
0,020	0,07	0,10	59,90
0,000	0	0,00	59,90
0,010	20,15	40,10	100,00
total	50,20	100	

Binding fluid preparation procedure:
The binding liquid is mixed from ethyl silicate, ethyl alcohol and diluted hydrochloric acid in the following volume ratio:
10 parts of ethyl silicate (40 % SiO_2)
18 parts of ethyl alcohol
3.1 parts of HCl (31%) diluted in water 1:12

200 ml of ethyl silicate, 360 ml of ethyl alcohol and 62 ml of HCl (31%) diluted 1:12 were successively prepared in volumetric flasks. Ethyl silicate was then poured into a laboratory mixer (vertical revolving arm mixer) and the mixing speed was set to the lowest setting (66 rpm). Ethyl alcohol was gradually added to the ethyl silicate with stirring. After pouring the ethyl alcohol, the acid was added slowly, and the temperature of the liquid was measured with a laboratory thermometer. The acid must not be added to the solution quickly as an exothermic reaction occurs and the solution must not reach more than 50 °C. Total mixing time was 10 minutes. The prepared binding liquid was poured into a sealable plastic container and let in a container to rest (at least 4 hours). The binding liquid was used the day after its preparation.

The composition of the binding fluid was not changed in the experiment.

Accelerator preparation
1 kg of ammonium acetate was used to prepare the accelerator, which was thoroughly mixed with 4 l of water.
Ammonium acetate is a white hygroscopic crystalline substance soluble in water. It is used as an acidity regulator, in this case as a gelling agent.

Gelation test

- 100 ml of Binding liquid
- 15 ml of Accelerator

The solution gels within 3.5 minutes, if not, the amount can be increased up to 20 ml. If gelation does not occur even then, the binding liquid is inadequate and a new one must be mixed.

100 ml of binding liquid was poured into a measuring vessel. 15 ml of accelerator was added to the vessel while the stopwatch was turned on and the solution was mixed. A gradual increase in liquid viscosity was observed during mixing. The moment the liquid began to stick to the stirrer and tear, the stopwatch was stopped.

Preparation of ceramic suspension

To prepare the ceramic suspension for 10 test specimens, 2 kg of refractory material, 320 ml of binder fluid and 48 ml of accelerator were required.

A mixture of refractory material was poured into a laboratory mixer. While being stirred, the binder liquid was gradually poured into the mixture, and the mixture was diluted with ethyl alcohol to the desired consistency (80 ml). Finally, an accelerator was added, which was quickly mixed (5 – 10 s) and the resulting mixture was poured into the core box. When diluting the mixture with alcohol, the amount of accelerator solution added subsequently should be taken into account so that the mixture does not become too thin. After the mixture solidified (15 minutes), the test specimens were removed from the core. The compressive strength (handling strength) of 5 samples was then measured on a calibrated measuring instrument (Form Service LRU - D). The remaining 5 samples were ignited and after burning the volatile substances and cooling, the compressive strength of the samples was measured (handling strength after burnoff).

Test specimens, parameters monitored on test specimens

The test specimen is a standard cylindrical test specimen (Ø50 mm, height 50 mm - volume 100 cm^3) for testing the strength of the molding compound. Compressive strength measurements and shear strength measurements [kPa] were used to evaluate the. strength of the samples.

Handling strength – strength after removal test specimen from the core box

Handling strength after burnoff - strength after removing the specimen from the core box and burning off the ethy lalcohol and after its cooling

Strength after annealing – strength after annealing and cooling of the specimen

2.3. Addition of phosphates to the ceramic mixture

Phosphates are able to form polymeric compounds with suitable oxides, in some cases from 200 °C (Al_2O_3), then the strength of the mixture begins to increase. Theoretically, in the right condition, these compounds should be able to increase manipulative strength of cores or prevent mold or core from collapsing during annealing.

Phosphate bond

Phosphate bond is anorganic-chemical bond composed of two components, acidic and alkaline. The acidic component consists of phosphoric acid H_3PO_4 and acidic phosphates. The alkaline component consists of oxides such as alumina (optionally others oxides). The phosphate bond is determined by the phosphoric acid's ability to form polymeric compounds, so-called polyphosphates. The scheme is shown in Figure. 2 [6-8].
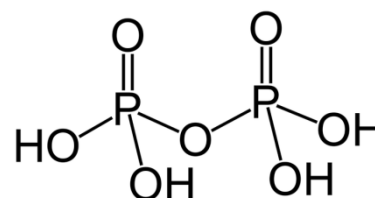

Fig. 2. Structural formula of $H_4P_2O_7$ [6]

By the ratio of phosphoric acid used, oxide and catalyst phosphates or hydrogen phosphates are produced. The reactions happen during different temperatures with different intensity depending on the type of the oxide used. In case of SiO_2, TiO_2, Al_2O_3, ZrO_2 and MnO_2, it is necessary to heat the mixture to 100 – 400 °C. According to the process of reaction with H_3PO_4, it is possible to divide the oxides into three groups:

- Acidic oxides, which do not react with phosphoric acid.
- Alkaline oxides, which react with phosphoric acid violently, due to the violent reaction porous and fragile structure forms.
- Slightly alkaline to amphoteric oxides [8].

Addition of phosphorous binder FFB 705

Binding fluid: 320 ml of standard binding fluid
Accelerator: 48 ml of ammonium acetate
Refractory material: 2 kg mixture of corundum with a fine proportion of molochite flour.
Added substance: phosphorous binder FFB 705 (5% of binding fluid volume)

It was decided to try to add FFB 705 binder, which is based on aluminate phosphates, directly to the mixture. Unfortunately, this binder does not dissolve in ethyl alcohol and did not gel when the binder was added to the mixture and therefore the test specimens did not solidify. However, after igniting the mixture and burning the alcohol, a significant increase in strength was observed and therefore this binder was used in the following experiment.

Immersing the cores in phosphoric acid and phosphorous binder FFB 705

Binding fluid: 320 ml standard binding fluid
Accelerator: 48 ml ammonium acetate
Refractory material: 2 kg mixture of corundum with a fine proportion of molochite flour

The ceramic mixture was prepared in the laboratory mixer in the same way as in the subchapter 2.2. After the mixture solidified, the test specimens were removed and ignited. The test specimens prepared in this way were subsequently immersed for 30 s in a

solution of phosphoric acid diluted 1:5 with water (6 bodies) and in a binder solution of FFB 705 diluted 1:1 with water (6 bodies). Two annealing modes were selected for the given samples: at 400 ° C and at 600 ° C, on which the mechanical properties were tested. At these temperatures, there should be a significant increase in strength, see Figure 3.
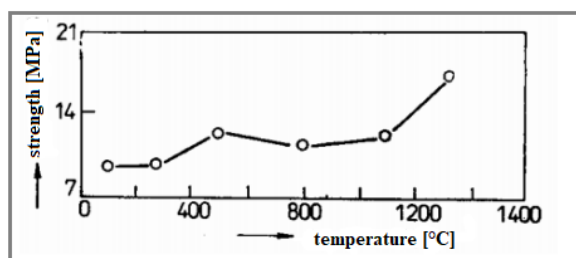

Fig. 3. Dependence of the corundum mass strength connected by a phosphate bond on temperature [8]

The annealing process was as follows. First, the samples were heated to about 150 °C for 20 minutes to remove any residual water. The final annealing temperature was set to 400 °C resp. 600 °C with a duration of 3 hours.

The shear strength of the annealed samples was subsequently measured because the compressive strengths exceeded the scale range of the measuring instrument used (2 MPa).

2.4. Use of synthetic fibers instead of steel reinforcement

During the production of larger and more complex cores by the Shaw method, they were deformed by their own weight, when the cores were removed from the core box. To prevent this, steel reinforcements were used to strengthen the core during handling. The problem with the use of steel reinforcements occurred during the drying and annealing of cores, when the cores cracked due to the different thermal expansion of the steel reinforcements and the ceramic mixture. Therefore, steel reinforcements are not the optimal solution. Natural or synthetic fibers can be added to the solution of ceramic mixture, what is currently used in the production of shells in the Investment casting method [9].

In the study [10], a combination of glass fibers and aluminosilicate fibers were used, which were added to the ceramic suspension. In both cases, higher strengths were measured than in the fiber-free suspension. The highest value 4.15 MPa, was reached after annealing at 950 °C. It has also been found that the addition of fibers increases the permeability of the shell.

Other synthetic fibers used in practice are polyamide, nylon or, in the case of alcohol-based suspensions, PVA fibers. Nylon fibers and basalt fibers were used for this experiment.

Use of nylon fibers

Binding liquid: 320 ml of standard binding liquid
Accelerator: 48 ml of ammonium acetate
Refractory material: 2 kg mixture of corundum with a fine proportion of molochite flour

Added substance: nylon fibers (length 2 mm, diameter 13 μm)

The procedure for preparing the samples differs from previous experiments only by adding the fibers to the mixer before adding the binder liquid, in order to spread the fibers in the mixture as best as possible. The WEXPERM nylon fibers used for the secondary suspension in the production of ceramic shells were used in the experiment. Four sets of samples were prepared, which differed in the content of added fibers. With increasing fiber content in the mixture, it was necessary to dilute the mixture more with alcohol to the desired fluidity. With a fiber content of 1 wt. % in the mixture, it was necessary to add twice as much alcohol to the mixture as to a standard mixture without fibers.

Use of basalt fibers

Binding liquid: 320 ml standard binding liquid
Accelerator: 48 ml ammonium acetate
Refractory material: 2 kg mixture of corundum with a fine proportion of molochite flour
Added substance: basalt fibers (length 6 mm, diameter 20 μm)

Basalt fibers are used in technical work as a substitute for steel reinforcement in concrete mixtures. Their purpose is to increase the strength of the concrete and prevent the concrete from crumbling under stress.

Sample preparation was the same as for the addition of nylon fibers. Three sets of samples were prepared, which differed in the content of added fibers. Again it was observed that with increasing fiber content in the mixture, it was necessary to dilute the mixture more with alcohol to the desired fluidity.

3. Results

Addition of phosphates to the ceramic mixture

After the addition of the phosphorus binder FFB 705, the mixture did not gel (solidify) and the samples were unusable for measurement. This method of adding phosphates to the mixture is therefore unsuitable and is unusable for ethyl silicate cast ceramic core technology.

Immersing the cores in phosphoric acid and phosphorous binder FFB 705

The measured values (Figure 4) show that by immersing the cores and their annealing there is a significant increase in strength compared to the standard annealed (1000 °C) mixture without being immersed. The best results were achieved by immersing the cores in FFB 705 already at the annealing temperature of 400 °C, lower strengths were achieved at the temperature of 600 °C. In contrast, the strength of samples immersed in phosphoric acid increases with increasing annealing temperature.
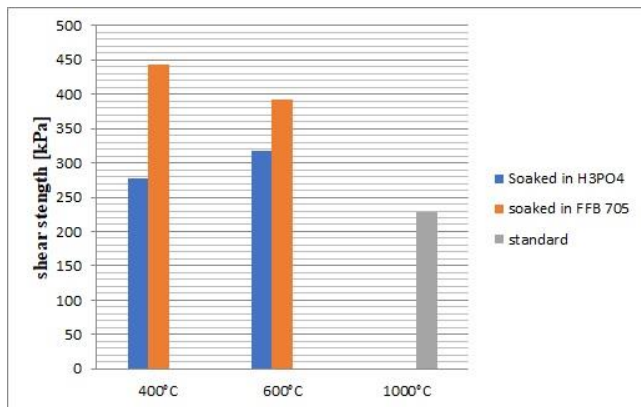
Fig. 4. The shear strength of soaked cores

Use of synthetic fibers instead of steel reinforcement

Use of nylon fibers

The measured results are shown in the Figure 5. The highest values of compressive handling strength are reached by a mixture with a fiber content of 0.05 wt%. Increasing the fiber content above 0.05 wt% reduces the strength, and at a fiber content of 1 wt%, the strength is even lower than samples without the addition of fibers. All samples after annealing at 1000 °C exceeded 2 MPa, the maximum measurable value of the measuring instrument, except for samples with a content of 1 wt% (1390 kPa). Therefore, the measurement of shear strength was chosen. Increasing the fiber content in the mixture above 0.5 wt% does not make sense in terms of increasing the strength characteristics. According to the measured results, the optimal amount of added fibers appears to be 0.05 wt%. Core breakage was not observed when nylon fibers were used. With the use of nylon cores is the strength of the cores lower after annealing, which is probably caused by the notch effect of the cavities created after burnt fibers.
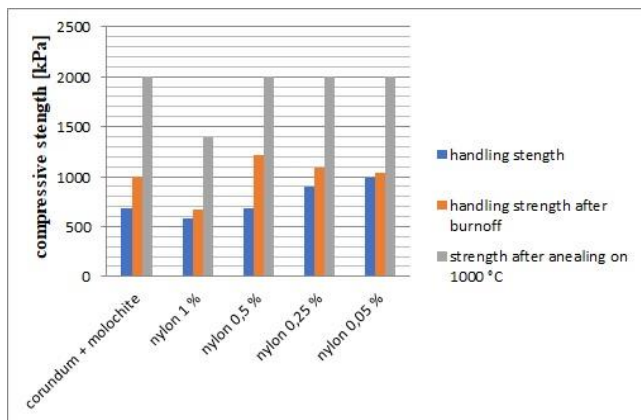

Fig. 5. The dependence of the compressive strength on the nylon fiber content of the mixture

Use of basalt fibers

When comparing the measured values (Figure 6) of handling compressive strengths, no positive effect of basalt fiber content on the handling strength of the cores was observed.

Core breakage was not observed when basalt fibers were used. When using basalt fibers, the strength of the cores after annealing increased and the fibers form a composite.
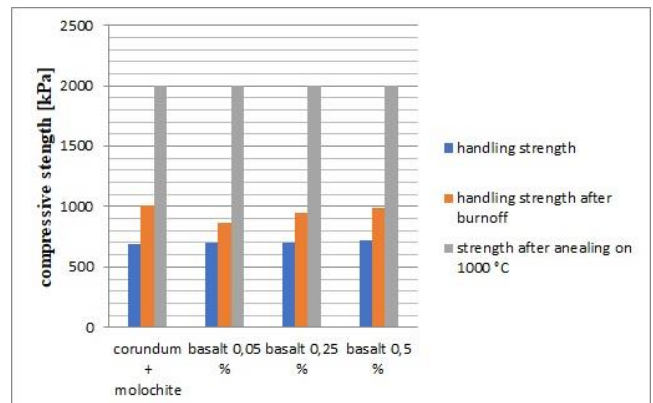

Fig. 6. The dependence of the compressive strength on the basalt fiber content of the mixture

Shear strength

The bar graph (Figure 7) shows the shear strength values of the samples that exceeded the compressive strength measurement capabilities. Cores imersing in phosphoric acid solution had the highest shear strength after annealing at 600°C. The graph shows that the highest values were reached by the components samples after immersing in a solution of FFB 705 binder and annealed at 400 °C. Furthermore, a decrease in strength is observed with increasing content of nylon fibers. In the case of basalt fibers, on the other hand, the strengths increases with increasing fiber content.
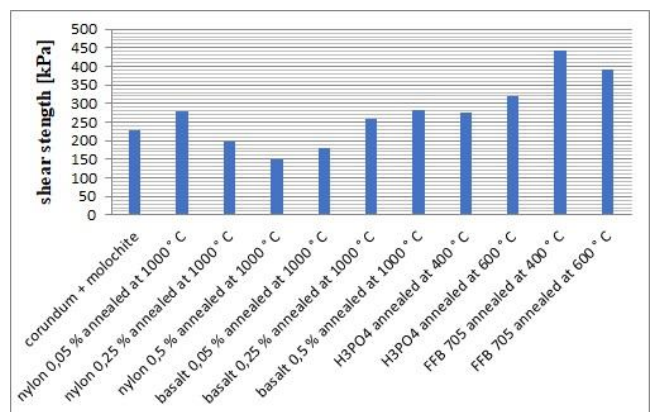

Fig. 7. The dependence of the shear strength on the added components in the mixture

4. Conclusions

FFB 705 binder cannot be added to the ceramic mixture because gelation does not occur after its addition.

A further increase in strength was made by immersing the cores in phosphoric acid and binder FFB 705 and subsequent annealing. A slight decrease in shear strength after annealing at 600°C was observed for the cores soaked in the phosphoric binder solution compared to the cores annealed at 400°C. The decrease in the strength of phosphoric binders at a temperature of 600 °C is also reported in the literature, see Figure 3. As stated in the literature, see figure 3, during the annealing of cores soaked in phosphoric acid or a phosphoric binder solution, it would probably be possible to achieve higher strengths at higher temperatures than those used in the experiment. However, higher annealing temperatures would mean significantly higher energy requirements of the process. As shown by the experiment, see Figure 7, even during the annealing of cores soaked in phosphoric acid or phosphoric binder, a significant increase in strength occurs already at a temperature of 400 °C compared to non-soaked annealed cores.

The highest shear strength was achieved by dipping the cores into a solution of FFB 705 binder and their annealing at 400 °C.

The best results of handling strength after the addition of the fibers were obtained by using a refractory mixture of corundum with molochite flour and adding 0.05 wt% of nylon fibers to the ceramic mixture. A larger amount of ethyl alcohol had to be added to mixtures with a higher fiber content in order to achieve the required fluidity of the mixture.

Core breakage was not observed when nylon and basalt fibers were used. Only when nylon cores are used, the strength of the cores after annealing is lower, which is probably caused by the notch effect of the cavities created after the burnt fibers. On the contrary, when using basalt fibers, the strength of the cores increased after annealing and the fibers form a composite.

Too high fiber content in the ceramic mixture has a negative effect on the on the fluidity of the ceramic mixture and the filling of the core box cavity and handling strength.

Acknowledgement

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