Strength Properties Control of Mixtures Based on Soluble Glass with Ethereos Solidifiers

Olga Ponomarenko[1], Tatyana Berlizeva[1](✉), Igor Grimzin[2], Nataliia Yevtushenko[1], and Tatiana Lysenko[3]

[1] National Technical University "Kharkiv Polytechnic Institute", 2, Kyrpychova St., Kharkiv 61002, Ukraine
berlizeva.tatyana@gmail.com
[2] Research and Production Center "European Engineering Technologies", 101, Big Panasovskaya St., Kharkiv 61017, Ukraine
[3] Odessa National Polytechnic University (ONPU), 1, Shevchenko Ave., Odessa 65044, Ukraine

Abstract. The paper presents the mechanism of solidifying mixtures on a soluble glass base with complex ethereos solidifiers, such as ethylene glycol acetates, triacetate with furfuryl alcohol and furfuryl oxypropyl cyclocarbonates. The castings comparative manufacturing technology based on cold-solidifying mixtures on soluble glass with these solidifiers is given. To experimentally determine and establish the regularities of increasing of the compressive strength of the mixture using ether hardeners and technological additives: ethylene glycol monoacetate (EGMA), ethylene glycol diacetate (EGDA), ethyl silicate (ES-40), ethylene glycol (EG), tetraethoxysilane (TEOS), triacetate with furfuryl alcohol (TAC with FA) and furfuryl oxypropyl cyclocarbonates are established. The basic physical and mechanical properties of mixtures with these additives, such as compressive strength, survivability, friability, gas permeability, and knocking-out ability were determined by standard methods according to the state standards (GOST). The most effective ethereos solidifiers, which allow obtaining high-quality mixtures on soluble glass with the highest strength properties, were determined.

Keywords: Cold-solidifying mixture · Soluble glass · Ethylene glycol acetates · Furfuryl oxypropyl cyclocarbonates · Triacetate with furfuryl alcohol

1 Introduction

There is a large number of methods for the manufacture of casts and cores using numerous mixtures in modern foundry production. One of the most common is cold-solidifying mixtures (CSM). Depending on the nature of the binder, cold-solidifying mixtures can be divided into mixtures with organic (lignosulphonate, resins, etc.) and inorganic (soluble glass, phosphates, etc.) binders [1, 2].

One of the commonly used methods is the process of manufacturing cores and casts on soluble glass (SG), and the technology for their production is used at many enterprises. This is because soluble glass is an affordable, inexpensive and non-toxic

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binder. The use of SG as a binder for the manufacture of casting and core mixtures allows us to obtain more durable casts, reduce the metal consumption of castings by producing thinner products and improve the quality of castings.

Depending on the nature of solidifying, these mixtures can be divided into mixtures with a solidifier introduced together with a binder during their preparation, and mixtures solidified by blowing with a gaseous solidifier during or after filling equipment by them and their solidification [1–3].

2 Literature Review

The main disadvantage when using soluble glass cold-solidifying mixtures solidified by CO_2, SO_2 or by heat drying is the formation of fusible silicates at temperatures above 700 °C, which lead to sintering of the mixtures and an increase in their residual strength and deterioration of knocking-out ability [4].

The knocking-out ability of soluble glass mixtures depends on the content of soluble glass and its module. With an increase in the content of soluble glass and a decrease in its module (due to an increase in the liquid phase upon heating), knocking-out ability deteriorates. The knocking-out ability of liquid-glass mixtures is affected not only by the temperature of cast heating but also by the casting shrinkage. Since the steel shrinkage became greater than that of cast iron, the knocking-out ability of cores in steel castings is 1.5–1.6 times worse than that of cast iron [5].

Reducing the amount of soluble glass in the casting mixture is the simplest and most cost-effective way. However, in most cases, such a technological implementation leads to deterioration in the properties of the casting mixture itself.

One of the ways to improve the knocking-out ability of cast and core mixtures is the process of using compound ethers in conjunction with SG [6].

Therefore, the development and introduction into production of new complex additives for CSM on SG regulating the strength properties of mixtures is an urgent task of foundry production.

3 Research Methodology

The research is aimed at developing effective compositions of soluble glass cast and core mixtures with complex additives that allow you to control the strength of the casts and cores at the stage of their preparation, while maintaining the basic properties of the mixtures, such as survivability, gas production, gas permeability, friability and contribute to softening the mixture after pouring with metal and their cooling.

During the experiments, the mixture was prepared as follows: per 100 mass% of sand, we took 4 mass% of soluble glass with a module of 2,36 and a density of 1,47 g/cm^3. As a filler of the casting mixtures, quartz sand of the grade $2K_1O_102$ GOST 2138-91 was used [7, 8].

The paper has researched such properties as compressive strength, survivability, friability, gas permeability, knocking-out ability.

Casting materials must have properties that meet certain cast or core mixtures; conditions for knocking-out casts and removing requirements: manufacturing techniques for casts and cores; conditions for the interaction of the cast with liquid metal during casting, solidification, and cooling of the casting; core preparation technologies [9–11].

The mechanical properties determine the strength characteristics of the mold during its manufacture, as well as when pouring it with alloy and solidifying the casting.

Testing the compressive strength of the mixtures was carried out in accordance with GOST 23409.7–78 (strength in the “wet” state) and GOST 23402.9–78 (strength in the “dry” state). For this purpose, a set was used to determine the tensile strength of cast and core mixtures of modules 04116У with a device for compressing dry samples up to 15 MPa manufactured by UkrNIILitmash by special order of National Technical University “Kharkiv Polytechnic Institute”.

Technological properties characterize the conditions for obtaining high-quality casts and cores, as well as the conditions for the manufacture of castings with the lowest labor input and high surface quality (without cracks and blockages).

The starting materials should provide the technological properties of the mixtures on soluble glass binders, such as survivability, friability and knocking-out ability.

Survivability of self-hardening mixtures is the main parameter limiting the production cycle of cores and foundry casts. The survivability index of cold-solidifying mixtures usually was the length of time (in minutes), after which the value of its strength decreased by 30% of the maximum one.

Friability of cast and core mixtures in accordance with GOST 23409.9–78 was determined on standard cylinder specimens with a diameter and height of 50 mm. Samples were tested in the dry state. The evaluation of the friability of the mixture was made according to the amount of weight loss by a standard sample placed in a rotating wire roller, while the friability rate was expressed as a percentage.

The knocking-out ability of a mixture means the removing complexity degree of cores from castings and castings from molds. One of the simplest and most affordable methods for quantification of the knocking-out ability used in this paper was to determine the residual strength of heated and cooled reference materials. The essence of the method is as follows: the manufactured standard cylindrical samples are matured for 24 h, after which they are placed in a muffle furnace and kept at a temperature of 800 °C for 1 h. Then they are cooled and tested for strength. The difference in the readings of the strength characteristics of the samples, which were kept for 24 h and the samples subjected to heat treatment, indirectly characterizes the knocking-out ability parameter of castings.

The hydraulic properties of the mixtures mainly determine the gas formation conditions and the gaseous products removal from the mold cavity when casting with alloy, thermophysical properties – the conditions of thermal processes during solidification of the casting in the mold.

Gas permeability is a property of various porous materials, which is characterized by the ability to pass gases through itself and is one of the most important properties of casting and core mixtures. Insufficient gas permeability of the mixtures complicates the removal of gaseous products from the mold cavity during the pouring period. The gas permeability of casting and core mixtures was determined by blowing air through a standard sample made from a tested casting or core mixture GOST 23409.12–78.

4 Results

Three series of experiments were carried out to study the effectiveness of mixtures on soluble glass with ether additives.

The first series of experiments were carried out to establish the physicomechanical properties of mixtures based on ethylene glycol acetates (EGA). Ethylene glycol monoacetate (EGMA) and ethylene glycol diacetates (EGDA) were used as the basis for ether solidifiers [6].

Ethylene glycol (EG), tetraethoxysilane (TEOS), ethyl silicate (ES-40) were added to EGMA and EGDA in an amount of up to 10%. TEOS and ES-40 are silicon-organic compounds. They can also play the role of SG solidifying agents when using minimal doses of amine type catalysts that accelerate the hydrolysis of siloxanes in an alkaline medium with the release of silicic acid.

Orthosilicic acid ethyl ester $(C_2H_5O)_4Si$, also called tetraethoxysilane, is the product of the reaction of ethyl alcohol with silicon tetrachloride. This reaction can be written as follows:

$$SiCl_4 + 4C_2H_5OH \rightarrow (C_2H_5O)_4Si + 4HCl \tag{1}$$

Ethylsilicate and tetraethoxysilane solutions are colloidal solutions – a sol that transforms into a silica gel that binds sand grains.

EG, TEOS and ES-40 additives were introduced in different quantities. The amount of EG ranged from 5 to 10 mass% of the amount of solidifier EGMA, and TEOS and ES-40 - from 1 to 3 mass% of the amount of hardener EGMA and EGDA.

The mixture was prepared as follows: 0.4–0.6 mass% of ether solidifiers with additives was added per 100 mass% of silica sand, then they were mixed for 3 min and then 4 mass% of sodium soluble glass was administrated and stirred for another 2 min.

The paper investigates 19 compositions of mixtures with soluble glass based on ether solidifiers with additives. The samples compressive strength data analysis showed that the highest compressive strengths are achieved in CSM on soluble glass with solidifiers of the following compositions: 1) EGDA – 91 mass% with EG – 9 mass% and 2) EGMA – 98 mass% with TEOS – 2 mass%.

The compressive strength of mixtures with solidifiers of the first composition is the following: after 1 h – 0,8 MPa, after 3 h 1,2 MPa; for the second composition – after 1 h – 1,0 MPa, after 3 h – 1,4 MPa [12, 13].

When using the studied ether solidifiers with additives, the residual strength decreases by 1,4 … 1.,6 times and amounts to 3 … 5 MPa. For the test samples, friability after 24 h was $\leq 0.15\%$, gas permeability was more than 120 units. The research results showed that the survivability of mixtures using soluble solidifiers varied widely and ranged from 8 to 50 min.

The use of compound ethers can reduce the consumption of soluble glass, improve the quality of mixtures, as well as reduce the residual strength of the molds and cores and reduce the defect of castings.

The authors' papers [14, 15] studied the physical and mechanical properties of mixtures and established the effectiveness of introducing into a mixture of soluble glass with triacetin additives.

For the second series of experiments, an additive was proposed in which, besides triacetin (TAC), a certain amount of furfuryl alcohol (FA) was introduced.

The mixture was prepared as follows: 0,4 mass% of a liquid additive of triacetin with furfuryl alcohol (TAC with FA) was added per 100 mass% of silica sand in a ratio of 1:1, then was stirred for 3 min, and then 4 mass% of sodium soluble glass was introduced and was stirred for another 2 min.

The solidifying of a mixture containing TAC with FA occurs according to the reactions in Fig. 1.

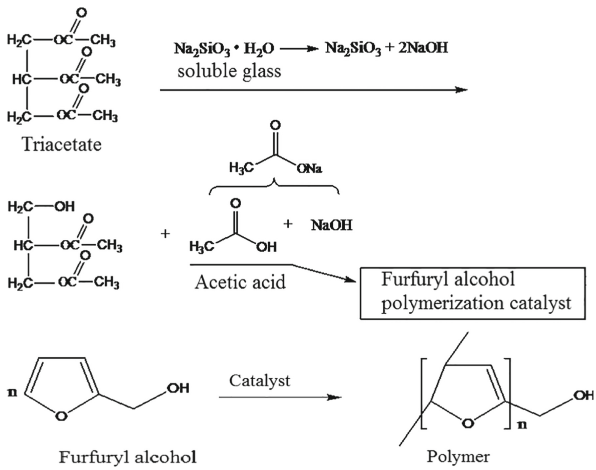


Fig. 1. The solidifying reaction of a mixture containing TAC with FA.

The solidifying of the composition begins with the hydrolysis of soluble glass with the subsequent acetic acid release and the formation of silicic acid and its condensation into a gel.

When furfuryl alcohol is added to the mixture, a three-dimensional polymer is formed. After pouring with metal, the polymer network formed by alcohol partially destructs, reducing the residual strength of the mixture.

The mixture was prepared in a similar way for experiments. First, a special TAC additive with FA was introduced and the mixture was stirred for 3 min, then soluble glass was added and mixed for another 2 min.

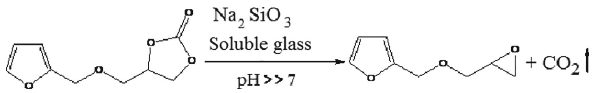
Indicators of compressive strength after 1 h – 1,08 … 1,3 MPa; after 3 h – 1,40 … 1,85 MPa; after 24 h – 2,57 … 3,34 MPa. Survivability indices – 9 … 30 min., friability – 0,1 … 0,5%, residual strength – 1,04 … 3,42 MPa [11].

As a result of studies of the strength characteristics of CSM, a special additive based on triacetate with furfuryl alcohol (TAC with FA), which allows increasing the compressive strength after 1 h compared to EGMA and EGDA. The residual strength of the mixture after pouring with metal and cooling was reduced by 4 … 6 times compared with the CO_2 process.

The third series of experiments investigated the physical and mechanical properties of casting mixtures based on soluble glass with the addition of furfuryl oxypropyl cyclocarbonates (FOPCC). It aims to study the effect of additives on the knocking-out ability of mixtures.

A new universal additive obtained in NTU "KhPI" – furfuryl oxypropyl cyclocarbonates (FOPCC) based on raw materials of plant origin (Ukrainian Patent UA No. 95138) was proposed for the third series of experiments. The universal additive FOPCC is an environmentally friendly material since when pouring metal into the cast as a result of thermochemical destruction, FOPCC decomposes and releases CO_2 and water vapor into the environment in the volume of the formed composition.

The scheme of the process of solidifying mixtures on soluble glass with FOPCC can be represented by the scheme in Fig. 2.



$$Na_2O{\cdot}2SiO_2 + CO_2 = Na_2CO_3 + 2SiO_2 + Q$$

$$mSiO_2 + nH_2O = mSiO_2{\cdot}nH_2O$$

$$mSiO_2{\cdot}nH_2O = mSiO_2{\cdot}pH_2O + (n-p)H_2O$$

Fig. 2. The scheme of the process of solidifying mixtures on soluble glass with FOPCC.

The composition solidifies (quartz sand + FOPCC + soluble glass) during the interaction of the FOPCC universal additive with soluble glass. Any cyclocarbonates (propylene cyclocarbonate, FOPCC, etc.) in an alkaline medium (pH >> 7) are unstable and decompose with the release of CO_2, which reacts with soluble glass to form polysilicates in the volume of the formed composition. Such systems can be attributed to nanostructured composite materials because the interaction processes between FOPCC and SG take place on the surface of quartz sand in monomolecular layers.

FOPCC organic additive has a dual function: it stabilizes the dispersion of filler particles (silica sand), since FOPCC molecules envelop the particles, creating additional solvation shells, on the one hand, and low surface tension weakens capillary forces in the pores and this determines the degree of compression during maturation (drying), on the other hand.

The most important characteristic of a silica system, when used as a binder, is the gellation time – the time for the sol-gel transition takes place. The main stage in the process of gel formation is the collision of two silica particles with a fairly low charge on the surface. During the interaction of such particles between them, siloxane bonds are formed that irreversibly hold the particles together.

The highest gelation rate is approximately pH = 5. The moment of decomposition of FOPCC with the release of CO_2, is precisely connected with a sharp decrease in the pH of soluble glass and the system is converted from the sol structure to the gel structure, and the presence of an organic residue in the system in the form of furfuryl glycidyl ether accelerates the growth of the gelation rate.

The softening of the moldable mixture is associated with the thermal destruction process of furfuryl glycidyl ether according to the scheme in Fig. 3.

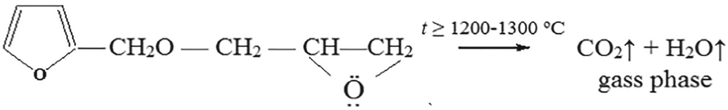
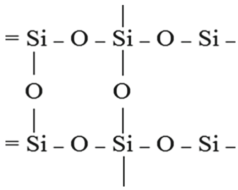


Fig. 3. Scheme of the process of softening the molding sand with FOPCC.

FOPCC is an environmentally friendly material since when metal is poured into a cast as a result of thermochemical destruction, it decomposes and releases CO_2 and water vapor into the environment in the volume of the formed composition.

Thus, the role of CO_2, which is released from the FOPCC in the process of forming casts or cores, is to bind (neutralize) a "very alkaline" SG solution and upon reaching pH = 5 a gel is formed with the structure of the polysilicate.

The introduction of FOPCC into the composition has a double function - it leads to the formation of SiO_2 nanoparticles, which act as crystallization and nucleation centers, and the released CO_2 (inside) brings the pH value to the optimal rates of soluble glass sol transition into a gel with a polysilicate structure and tetrahedral bonds.



As a result of the experiments, the main properties of the properties of CSM on soluble glass using FOPCC were determined: compressive strength, survivability, gas production, gas permeability, friability, and knocking-out ability, which affect the quality of castings in sand molds. The compressive strength indices for the technological sample, on average, are: after 1 h – 1.8–2.0 MPa; after 3 h – 2.5–3.0 MPa; after 24 h – 3.5–4.0 MPa. The survivability of the mixture is within 10–20 min. Friability of mixtures is in the range of 0.10–0.24%, gas permeability >400 units, residual strength – 0.74–2.06 MPa.

The compressive strength of mixtures on soluble glass with various ethereos solidifiers based on all experiments is presented in the form of dependencies in Fig. 4.

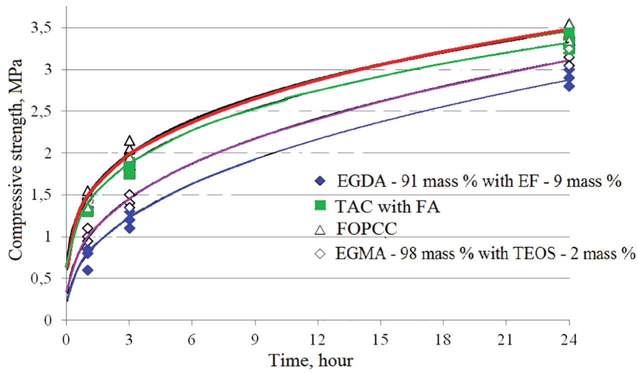


Fig. 4. The compressive strength of mixtures on soluble glass with various ethereos solidifiers.

The presented dependencies in a general form can be described by an exponential function $y = ax^n$ and presented in the form of mathematical dependences having the form of a parabola of the nth (n^{th}) order, for $n < 1$.

Table 1 shows the mathematical dependencies of the increase in the strength of the mixture in time and the reliability of the approximation R^2, *y* is the compressive strength of the mixture, MPa, *x* is time, hours.

Table 1. Mathematical dependencies of increasing the strength of a mixture based on SG with EGA.

Composition of solidifiers based on ethereos solidifiers	Mathematical dependences of the strength of the mixture	Approximation confidence value R^2
EGDA – 91 mass% with EG – 9 mass%	$y = 0{,}786 \times ^{0{,}407}$	$R^2 = 0{,}998$
EGMA – 98 mass% with TEOS – 2 mass%	$y = 0{,}974 \times ^{0{,}364}$	$R^2 = 0{,}996$
TAC with FA	$y = 1{,}387 \times ^{0{,}275}$	$R^2 = 0{,}999$
FOPCC	$y = 1{,}408 \times ^{0{,}267}$	$R^2 = 0{,}995$

The mathematical dependencies of the compressive strength of the mixture correlate well with the approximation confidence value.

During the experiments, special attention was paid to the knocking-out ability of mixtures of residual strength, because the knocking-out process is the most difficult operation in terms of sanitary and hygienic conditions from the entire casting production cycle, which is accompanied by a large dust, gas, heat and high noise level.

The paper used the method of residual strength of heated and cooled standard samples to determine the quantitative assessment of knocking-out ability.

Figure 5 shows the residual strength of mixtures with various solidifiers.

Table 2 presents the characteristics of the mixtures based on additives studied in this work.

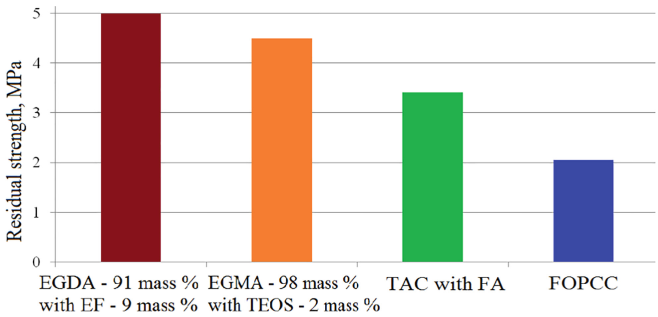


Fig. 5. The residual strength of mixtures on SG with various ethereos solidifiers.

Table 2. Physical, mechanical and technological properties of soluble glass mixtures with additives.

Parameter	Units of measurements	Additive		
		EGA	TAC with FA	FOPCC
The mass ratio in the mixture	Soluble glass/additive	4,0/(0,4…0,6)	4,0/(0,5…3,0)	4,0/(0,3…0,4)
Survivability	min	8…50	10…20	12…25
Friability	%	≤ 0,15	0,1…0,5	0,066…0,13
Gas production	cm^3/g	13…16	less than 10,5	4,9…7,4
Gas permeability	un.	more than 120	more than 120	450…500
Compressive strength	MPa			
1 h		0,45…1,1	1,08…1,3	1.27…1.45
3 h		0,95…1,4	1,40…1,85	1.73…2.05
24 h		1,90…2,5	2,57…3,34	2,14…3.43
Residual strength	MPa	3,0…5,0	1,05…3,42	0,74…2,06
Notional value		1,1	1,3…1.4	1,1

The analysis of comparative characteristics showed that at present the most promising is the use of TAC with FA special additive and FOPCC universal additive in mixtures with soluble glass.

5 Conclusions

1. The regularities of increasing the compressive strength of the mixture were experimentally determined and established using ether solidifiers and processing aids ethylene glycol monoacetate (EGMA), ethylene glycol diacetate (EGDA), ethyl silicate (ES-40), ethylene glycol (EG), tetraethoxysilane (TEOS).

2. A special additive for CSM on soluble glass based on triacetate with furfuryl alcohol (TAC with FA) has been proposed and tested, which allows increasing the compressive strength after 1 h compared to EGMA and EGDA. The residual strength of the mixture after pouring with metal and cooling was reduced by 4–6 times compared with the CO_2 process.
3. A new universal additive for CSM on SG based on furfuryl oxypropyl cyclocarbonates has been developed, which allows us to increase the strength of casts and cores at the stage of their preparation and helps to weaken the mixture after pouring with metal and cooling them. The universal additive FOPCC is an environmentally friendly material since when pouring metal into the mold as a result of thermal degradation, FOPCC decomposes and releases CO_2 and water vapor into the environment in the volume of the formed composition (Ukrainian Patent UA No. 95138).
4. The basic properties of CSM on SG using the universal additive FOPCC are determined: strength, survivability, gas production, gas permeability, friability, moisture, and residual strength, on which the quality of castings when casting in sand molds depends.
5. The use of soluble ethereal additives reduces the consumption of soluble glass to 2.5–4.0% and thereby by 1.5–2.0 times improves the knocking out ability of molds and core. Mixed additives of esters consisting of 2–3 items, a special additive TAC with FA and a universal additive FOPCC are effective.
6. The technological process of preparation of cold-hardening mixtures on liquid glass with the use of additives FOPCC was developed to obtain high-quality castings, which are introduced at the enterprises of Ukraine and in the educational process for the student's specialty "Equipment and technology of foundry production".

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