Sol-gel technology for the production of high-strength refractory materials based on binders

S N Pogorelov, G S Semenyak, A O Kolmogorova
Institute of Architecture and Construction, South Ural State University, 76, Lenin Avenue, Chelyabinsk 454080, Russia

E-mail: pogorelovsn@susu.ru

Abstract. The technology of production of die tooling based on high-alumina cement, used for the manufacture of aluminum alloys, transforming into a plastic state at high temperatures, is considered. This technology is based on the sol-gel method, characterized in that the formation of a crystalline high-strength structure for die tools based on high-alumina cement occurs cyclically with stage exposure at certain temperatures. First, a sol is formed - a free dispersed system, then a gel structure - a bound dispersed system. The final structure is crystalline, high strength with a compressive strength of up to 180-190 MPa. A distinctive feature is the possibility of destruction of the form after the manufacture of products. This is necessary because the manufactured products have a developed geometric shape and the product can not be obtained from the mold by ordinary removing the formwork.

1. Introduction
A sol-gel transition is the process of transformation of a sol into a gel, which occurs with an increase in the concentration of particles of the dispersed phase in the sol or under the influence of other external influences (cooling, pH, ionic strength of the solution) [1-3]. It is known that the sol-gel process is widely considered in chemical technology. The process of transition of the binder-liquid system (gelation) refers both to the chemical process and to the technology of cement compositions [4, 5].

The sol-gel method is a method for producing materials, including nanomaterials, including obtaining a sol with its subsequent transfer to a gel, i.e., to a colloidal system consisting of a liquid dispersion medium enclosed in a spatial network formed by connected particles of a dispersed phase [6-11].

The common name "sol-gel process" unites a large group of methods for obtaining (synthesis) of materials from solutions, an essential element of which is the formation of gel at one of the stages of the process. The most famous variant of the sol-gel process is based on the processes of controlled hydrolysis of compounds, usually metal alkoxides or the corresponding chlorides, in an aqueous or organic medium.

2. Relevance
High aluminate cements have an increased set of strength in the early stages. An increase in temperature promotes the rapid formation of numerous fine crystalline and gel-like reaction products, which accelerates the formation of a mechanical skeleton [12,13].
One of the main applications of aluminate cements is the production of heat-resistant concrete does not require high grades, so heat-resistant concrete is mainly used for the manufacture of lining bricks and blocks. Sol-gel technology allows the use of these cements to produce high-grade concrete, which, in particular, can be used for the manufacture of forming elements in stamping. The theoretical strength of cement stone reaches 1370 MPa [13], and when using special methods of molding and processing, results in 700 MPa are practically achieved, which speaks in favor of the use of binders for the manufacture of die tooling.

Aluminate cements behave ambiguously at low temperatures (up to 500 °C), often reducing strength [14]. Sol-gel technology contributes to an increase in the strength of products not only at the curing stage under normal conditions, but also during heat treatment. There are known works on the use of sol-gel technology for ceramics at low temperatures [15-18].

The manufacture of ceramics using the sol-gel technology has significant advantages over traditional technologies and, first of all, due to lowering the temperature of heat treatment during the formation of the material structure [19,20].

3. Theoretical part
This article presents the results of the development of a technological process for the production of high-strength refractory ceramics using sol-gel technology, suitable in its technical properties for the manufacture of forming elements of complex shape and configuration in a press tool for isothermal pressing of aluminum alloy billets.

The raw material for the manufacture of ceramics is high-alumina cement HACs-75 (70) class A, obtained at the Novosineglazovsky plant of silicate brick by grinding clinker of the Kluchevsky ferroalloy plant. The quality of this cement is characterized by the following indicators: grade strength - 50 MPa; refractoriness - 1710 °C; chemical composition of clinker, wt. %: Al2O3 - 77.4; CaO - 18.7; MgO - 1.6; Cr2O3 - 0.4; SiO2 0.4; Fe2O3 0.2; carbon not more than 0.15.

High alumina cement, having a complex composition, is very sensitive to heat treatment. Preliminary studies of temperature deformations showed that the following should be considered as the most critical temperatures: 100, 200, 250, 350, 400, 450, 500, 600 °C (Figure 1).

![Figure 1. HACs-based dilatometry of cement stone.](image)

In this case, temperature deformations up to 600 °C are cyclical in nature, and after its achievement a stable expansion is observed. A characteristic feature of the behavior of the material is that upon repeated determination of temperature strains on the same samples, a linear nature of expansion is observed, which is also characteristic of metal alloys. The final production of high-strength refractory
materials based on high-alumina cement requires solving the issue of the heat treatment mode. Particular attention should be paid to the nature of the deformation processes.

Technologically, this is solved by applying heat treatment, which consists in stepwise heating of the material every 100 °C with exposure at each stage for 0.5 ... 1.0 hours. The heat treatment of molded products at temperatures up to 100 °C and 100% humidity, contributes to the formation of a gel structure and the initial stages of crystallization of the material. Such heat treatment should be carried out on the disassembled samples after preliminary exposure in order to avoid the appearance of degradation arising due to the high elasticity of the pressed products.

4. Experimental part
The study of the molding conditions has shown the advantage of obtaining high mechanical properties of the stone with a small WCR, not only during vibration compaction, but also during pressing. The optimal values of the technological parameters should be considered WCR = 0.2 and the pressure during pressing 10.0 ... 12.5 MPa with preliminary vibration compaction under a load of 0.05 ... 0.10 MPa (Figures 2, 3).

The most optimal should be considered preliminary exposure at 100% humidity for 18 ... 24 hours. Isothermal exposure - 6 hours, cooling with the camera.

The final temperature of heat treatment should be considered 500 °C for the use of cement stone based on high alumina cement, as forming elements in the manufacture of preparations from aluminum alloys that transform into a plastic state at temperatures up to 570 °C and 650 °C for aluminum alloys that transform into a plastic state at temperatures over 650 °C.

![Figure 2. The effect of WCR on the strength of HAC cement stone in vibration compaction.](image)

![Figure 3. The effect of heat treatment on the strength (a) and density (b) of the cement stone obtained by pressing.](image)

The use of intensive vibration compaction under pressure up to 20 MPa preserves the nature of changes in the strength and density of cement stone, while the strength increases significantly (Figure 4).

Obtaining high-strength concrete indicates the benefits of heat treatment. Intensive vibration compaction allows achieving compressive strength of up to 200 MPa with stepwise heat treatment of up to 350 ... 400 °C, which indicates the possibility of using high-alumina cement to produce die tooling based on aluminum alloys.
Subject to these parameters, the compressive strength of cement stone obtained by sol-gel technology with stepwise heat treatment up to 350 ... 400 °C reaches 190 and 180 MPa, respectively.

An important technological process is the need to break the mold after manufacturing products. The fact is that the products of stock tooling have a very developed geometric shape, which is called a necessity. One of the ways to destroy the mold is to add components to the mix that can be destroyed after the tooling is manufactured.

One of these methods is the use of calcareous rocks, consisting mainly of CaCO3. Under the influence of high temperatures, CaCO3 passes into anhydrous lime CaO. After manufacturing the product, when the form is no longer needed, its composition, consisting of high-alumina cement and lime, is easily destroyed when placed in an aqueous environment. The destruction process is more efficient when the form is found in warm distilled water.

In addition to limestone, magnesian rocks that have MgO in their composition can be used. Magnesite rocks include MgCO3 magnesite itself, brusite, nema-lite - magnesium hydroxides Mg(OH)2 and others. It should be noted that the process of destruction with the use of magnesite rocks is particularly effective, which allows you to destroy the forming elements of large sizes.

Less effective dolomite CaCO3•MgCO3 and its variety of ludwigite. As a rule, dolomite can be used in the manufacture of small products, which also does not exclude its use in the manufacture of large-sized and very developed geometrically products.

5. Conclusions
The results presented in the article indicate the possibility of using high-alumina cement to obtain die tooling products, which allows manufacturing aluminum alloy products by plastic deformation at temperatures up to 650 °C. It is important to note that this also makes it possible to manufacture products of a developed shape, such as, after the manufacture of products, dies are quite easy to destroy using well-known methods.

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