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INVESTIGATION OF THE THERMOSTABILITY OF GLASS-CERAMICS OF A LITHIUM ALUMOSILICATE COMPOSITION

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This paper presents the results of investigations of the thermostability of the glass-ceramics obtained by ceramic technology with the use of the method of casting blanks from high-density aqueous suspensions of lithium alumosilicate glass with their subsequent sintering and crystallization under combined conditions of treatment. It is shown that the basic factors influencing the thermostability of materials are the values of the elastic modulus, CTLE, and porosity. Experiments and calculations indicate that the glass-ceramics exceeds the known radiotechnical-purpose pyroceramics in thermostability and can be used in articles designed to operate under hard conditions.

An important characteristic of materials meant for the manufacture of structures of flying vehicles is their thermostability. For simplicity and convenience, the widely used thermoshock resistance test is reduced to a sharp cooling of samples heated to a given temperature in a water bath with running water.

However, the methods for investigating the thermostability presented in State Standard 11103-85 and State Standard 473.5-81 are formal in their approach because of the requirements for the sample (polishing), which in most cases do not correspond to the real conditions for manufacturing products, and the criterion for estimating the thermostability, the appearance of cracks in the specimen or other signs of destruction, represents a purely subjective factor unsuitable for estimating the serviceability of constructions. What is more, the real operating conditions of different products, for example, aerial fairings of flying vehicles, provide the reverse situation, namely, a sharp heating of the construction and its fairly smooth cooling.

In our opinion, in [1] the most reliable results on the investigation of the pyroceramic AS-418 thermostability are presented. In carrying out tests, the authors measured the degradation of the strength of specimens, which, upon heating to a given temperature on one of the surfaces, were subjected to a local droplet thermal shock. The authors believe that such a thermal shock and the subsequent measurement of the flexural strength, with the damage site of the specimen positioned, in testing, in the zone of the maximum tensile stresses, most fully reflect the operating conditions of the structures of flying vehicles. The test data for specimens from nonreinforced pyroceramic AS-418 of a lithium alumosilicate composition, according to [1], are given in Fig. 1.

However, because of the extreme importance of this parameter, it makes sense to consider the behavior of the material under different conditions of thermal loading. To this end, we have investigated the behavior of lithium alumosilicate glass-ceramic under various conditions — the method of throwing specimens heated to the final temperature into running water; sharp heating and quick cooling of specimens; one-sided sharp heating and quick cooling of the heated surface; exposure of the material to the flame of an oxygen-acetylene torch.

The glass-ceramic specimens for the investigations were obtained by the method of molding blanks from high-density water slips of lithium alumosilicate glass with their subsequent sintering and crystallization

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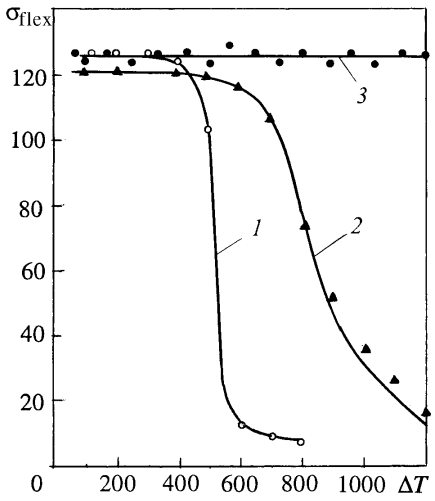


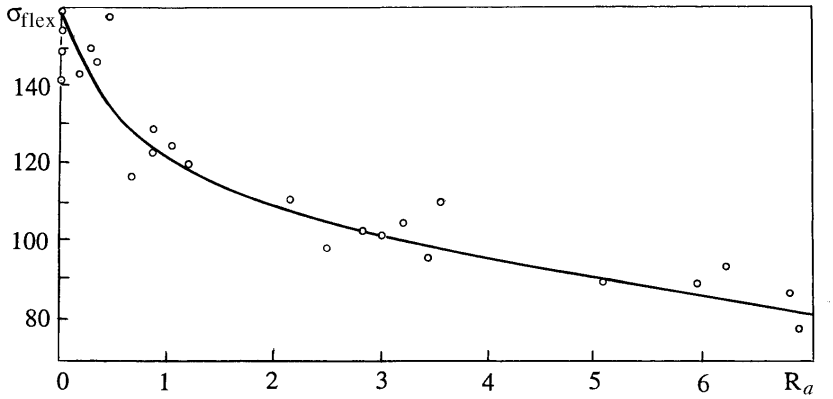


Fig. 1. The dependence of the flexural strength of pyroceramic AS-418 and glass-ceramic on the temperature difference at a thermoshock: 1) pyroceramic AS-418 (one-time droplet shock onto the heated surface of the specimen); 2) throwing of glass-ceramic specimens into water; 3) cooling of glass-ceramic specimens in air. σ_{flex}, MPa; ΔT, ^{o}C.

Fig. 2. The dependence of the flexural strength of lithium alumosilicate glass-ceramics on the surface roughness of the 7 × 7 × 60 mm test specimens. σ_{flex}, MPa; R_a, μ.

in a combined regime of thermal treatment. For the investigations, specimens of required sizes were made from large-size blanks by mechanical treatment.

In the first case, we subjected 30 × 30 × 4 mm specimens of OTM-357 glass–ceramic to a thermal shock according to the scheme 20^{o}C–T^{o}C–water with subsequent thorough inspection of their surface.

It should be noted that on the surface of the specimens with a polished surface traces of damage in the form of microcracks were detected at a 20^{o}C–1000^{o}C–water thermoshock. On the surface of the specimens with a roughness of R_a = 0.7 μm (standard polishing of specimens by a diamond tool) microcracks are detected at a 20^{o}C–850^{o}C–water thermoshock and the same specimens subjected to etching in a 6% solution of HF under similar test conditions reveal no defects. These experiments permit the conclusion that the results of thermostability tests largely depend on the state of the surface of the specimens being tested. Indeed, Fig. 2 shows that with increasing degree of imperfection of the surface of specimens their strength decreases. From this it follows that the sharp recesses left in the body of the material after mechanical treatment of specimens with a tool are able to considerably decrease their thermostability. Polishing of specimens removes the top ridges of the rough surface, but the microdefects are not completely removed.

Etching of specimens in HF solution does not decrease the surface roughness after mechanical treatment but makes it possible to blunt the sharp edges of defects in the depth of the material, thus reducing the influence of microdefects. This is also evidenced by the data of [1], where it was possible to increase the strength and thermostability of a specimen from pyroceramic AS-418 by etching its surface.

Analyzing the results on the thermostability of glass-ceramic OTM-357 based on the method of subjective evaluation of the quality of specimens (whether microcracks appeared or not), we arrived at the conclusion that a quantitative, objective evaluation of the thermoshock resistance of a material by determining the degradation of its flexural strength is needed. To this end, 7 × 7 × 60 mm glass-ceramic specimens with a surface roughness of R_a = 0.7 μm were subjected to a thermoshock according to the scheme 20^{o}C–T^{o}C–water in the range of maximum temperatures between 150 and 1200^{o}C with subsequent determination of their

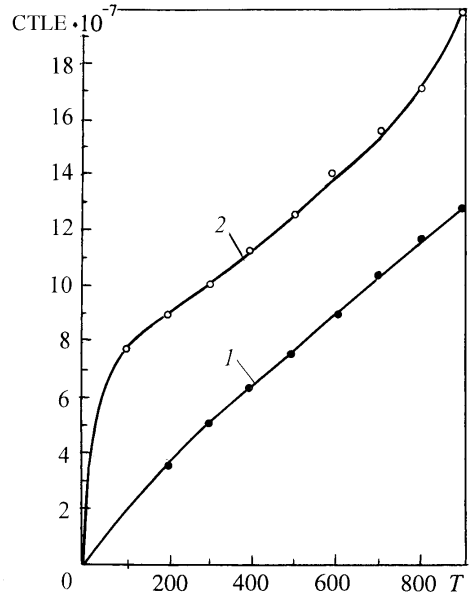


Fig. 3. The temperature dependence of the mean values of the CTLE of glass-ceramic (1) and pyroceramic AS-418 (2). *T*, °C; CTLE, deg^{-1}.

flexural strength. In so doing, the specimens were instantly placed in a furnace heated to the final temperature, held at the final temperature for 15 min, and then thrown into running water. And although the test conditions in this case were much harder than the test conditions for the pyroceramic AS-418 specimens in [1], it is deemed fairly interesting to compare these results (Fig. 1). The glass-ceramic stability determined under the harder conditions appeared to considerably exceed the thermostability of pyroceramic AS-418. The tendency for a decrease in the flexural strength of the glass-ceramic begins to show up at a thermoshock from 750°C; however, the drop in strength is not catastrophic, as is the case with pyroceramic AS-418. And even after a thermoshock from 1200°C the glass-ceramic still has a residual strength up to 1.5 MPa.

These results were not surprising because at comparable values of the flexural strength of pyroceramic AS-418 and glass–ceramic OTM-357 the latter has lower values of the thermal linear expansion coefficient (Fig. 3) and elastic modulus. What is more, the glass-ceramic contains in its bulk up to 1–2% of closed pores, which do not lead to an increase in the moisture absorption of the material, but are a barrier to the propagation of cracks. A complex of these indices provides a higher thermoshock resistance of the glass-ceramic.

In the following experiment on 7 × 7 × 60 mm specimens of glass-ceramic OTM-537 (R_a = 0.7 μm), we determined the resistance of the material to sharp heating with air cooling. To this end, the specimens were instantly (within no more than 1 sec) placed in a furnace heated to a given temperature, held in it for 60 sec in one case and for 15 min in another, and then they were instantly removed from the furnace and cooled in air.

It has been found that sharp heating and cooling in a still air medium of glass-ceramic OTM-357 specimens do not lead to a degradation of their strength properties in testing in the 100–120°C temperature range (see Fig. 1).

Of particular interest are the investigations on the resistance of glass-ceramics to rate heating and cooling, since no analogous tests have been reported in the literature, although such experiments are the closest to the operating conditions of the aerial fairings of flying vehicles and can reflect the possibilities of the material to a greater extent.

The experimental technique included the manufacture of a batch of 7 × 7 × 60 mm glass-ceramic specimens (R_a = 0.7 μm), determination of the initial flexural strength of this batch of specimens, setting of

TABLE 1. Relative Changes in the Flexural Strength ($\Delta\sigma_{flex}$) of Glass–Ceramic after Rate Heating and Cooling (%)

Material	σ_{flex}	Conditions of one-sided rate heating and cooling				
		$T_m = 850^oC$; $V_h = 100^oC/sec$; $\tau_{t.m} = 80$ sec; $V_{cool} = 8^oC/sec$; $(850–580)^oC$	$T_m = 1170^oC$; $V_h = 150^oC/sec$; $\tau_{t.m} = 15$ sec; $V_{cool} = 2^oC/sec$; $(1170–700)^oC$	$T_m = 1300^oC$; $V_h = 160^oC/sec$; $\tau_{t.m} = 15$ sec; $V_{cool} = 40^oC/sec$; $(1300–650)^oC$	$T_m = 1300^oC$; $V_h = 150^oC/sec$; $\tau_{t.m} = 5$ sec; $V_{cool} = 150^oC/sec$; $(1300–650)^oC$	$T_m = 1300^oC$; $V_h = 150^oC/sec$; $\tau_{t.m} = 15$ sec; $V_{cool} = 320^oC/sec$; $(1300–650)^oC$
Glass-ceramic OTM-357	103	+ 5.8	+ 14.6	+ 15.5	+ 14.6	+ 6.8

Note: $(850–580)^oC$ — the range of temperatures with a given rate of cooling; + — increase in the index with respect to the initial value

the specimens in a housing from a TZMK-type insulating material, placement in the housing of a control specimen with a thermocouple, application to the outer surface of the test specimens of a light-absorbing coat from a Cr_2O_3 suspension, and arrangement of the specimens in the center of the heating area of a battery of quartz lamps. Then one-sided heating and cooling of the specimens was carried out by the given program and their flexural strength was determined. In so doing, the surface of the specimens subjected to the thermal loading was located in the area of tensile stresses. By the relative change in the strength of the specimens before and after testing one can judge the changes taking place in the material and its use in particular objects.

The test data on the resistance of glass-ceramic OTM-357 to one-sided rate heating and cooling are given in Table 1.

The general trend is the absence of a decrease in the flexural strength of the glass-ceramic compared to the initial values at thermal loading of the specimens with rates of elevation up to 150^o/sec and of cooling up to 320^oC/sec, which were attained either by maintaining the given rates of heating and cooling by the test bed heaters or by increasing the rate of cooling at the cost of air blasting of the heated specimens.

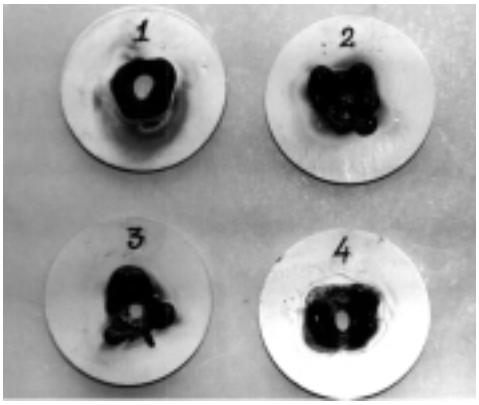
As a result of these investigations, it has been established that the realized rates of heating and cooling do not lead to a degradation of the strength properties of the glass-ceramic, but two trends are apparent. First, in all the cases of testing, an increase in the flexural strength values of the specimens with respect to the initial values is noted, which we associate with the hardening effect; second, an increase in the rate of cooling from 40 to 320^oC/sec lowers the level of porosity, but this range of cooling rates is not yet critical for the glass-ceramic (Table 1).

The results obtained are fundamentally important, since they convincingly indicate that a short-term exposure of the glass-ceramic to rather high temperatures (up to 1300^oC) is not critical for it either. What is more, the glass-ceramic reveals no signs of destruction (microcracks, chipping, etc.) even in the cases of burning through holes by an oxyacetylene torch (Figs. 4 and 5). We did not manage to note in these tests the rates of heating and cooling of the specimens as well as the actual temperature in the area of the action of the torch flame on the specimens, but the very fact that the specimens and the fairing fragment remained intact is indicative of the high potentialities of the material.

Analogous tests of crystallized specimens obtained from a glass blank of the same chemical composition lead to the appearance of through-thickness cracks in them (Fig. 4).

Having at our disposal the results on the physicotechnical properties of glass-ceramic and the literature information on the properties of other materials, we can carry out a comparative evaluation of their thermoshock resistance.

In calculating the thermostability of materials, we proceeded from the conditions that the stresses on the plate surface caused by the continued temperature drop are independent of the plate thickness and the thermostability can be calculated by the formula [2]



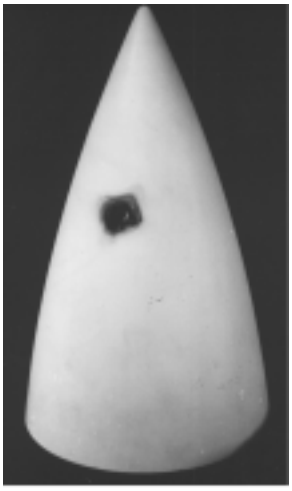


Fig. 4. Specimens from pyroceramic (1–3) and crystallized initial monolithic lithium alumosilicate glass (4) with holes burned by an acetylene torch (specimen 4 has concentric through-thickness cracks).

Fig. 5. A fragment of a glass-ceramic fairing with a hole burned by an acetylene torch.

TABLE 2. The Calculated Thermostability Values of Different Materials Used for Making Aerial Fairings

Properties	Branch of material						
	Pirokeram-9606	Pirokeram-9608	Pyroceramic-AS-370	Pyroceramic-AS-418	High-alumina ceramic (Al_2O_3)	Quartz ceramic with a porosity of 8–10%	Class-ceramic OTM-357
Flexural strength, MPa	182.0	114.0	179.0	12.0	315.0	45.0	11.0
Coefficient of thermal linear expansion, $1/^oC$	$57\cdot10^{-7}$	$20\cdot10^{-7}$	$48\cdot10^{-7}$	$28.5\cdot10^{-7}$	$73\cdot10^{-7}$	$6\cdot10^{-7}$	$13\cdot10^{-7}$
Elastic modulus, MPa	$121\cdot10^3$	$87.5\cdot10^3$	$132\cdot10^3$	$85\cdot10^3$	$280\cdot10^3$	$45\cdot10^3$	$53\cdot10^3$
Poisson coefficient	0.25	0.25	0.34	0.29	0.32	0.25	0.29
Maximum temperature drop, ^oC	400	980	370	700	210	2500	2260

$$\Delta T = \frac{2\sigma(1-\mu)}{E\alpha},$$

where ΔT is the temperature drop the material can withstand without destruction; σ is the ultimate flexural strength.

The results of the calculation of the thermostability values of a number of materials are shown in Table 2, whose analysis shows that the basic parameters determining the thermostability of a particular material are the coefficient of thermal linear expansion, the elastic modulus, and the porosity. Thus, the quartz ceramic has the highest thermostability among the materials given in Table 2, although its strength properties are much lower, but its coefficient of thermal linear expansion and elastic modulus thereby are much lower than in the other materials, and the material has a porosity within 8–10%. Quartz glass is the basis for manufacturing quartz ceramics and, according to the estimates of a number of authors [3, 4], has a thermostability of 800–1000^{o}C. The reason for such sharp differences in the thermoshock resistance between these materials is the higher value of the elastic modulus of quartz glass and the presence of a monolithic structure.

The calculation performed shows that in terms of thermostability the glass-ceramic is second only to the quartz ceramic and the absolute values of thermostability are extremely high.

The results of the calculation are convincingly supported by experiments. In this case, similar to quartz ceramics, the high thermostability of glass-ceramics is due to the favorable combination of the CTLE and elastic modulus values and the presence of closed pores in the material.

Thus, the obtained results of the investigations of the changes in the properties of glass ceramics under the conditions of different kinds of thermal loading are suggestive of the wide range of possibilities of its use in structures subjected to analogous actions.

NOTATION

ΔT, temperature drop, ^{o}C; a, coefficient of thermal linear expansion (CTLE), deg^{-1}; R_a, surface roughness, μ; σ_{flex}, ultimate flexural strength, MPa; T_m, maximum temperature of the specimen surface, ^{o}C; V_h, rate of temperature elevation (heating), ^{o}C/sec; $\tau_{t.m}$, time of holding at the maximum temperature of the specimen surface; V_{cool}, rate of cooling of the specimen surface, ^{o}C/sec; $\Delta\sigma_{flex}$, relative change in the flexural strength of specimens after a thermoshock, %; μ, Poisson coefficient; E, elastic modulus.

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