PROPERTIES OF FUSED SILICA CERAMICS

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The need for increasing the working temperatures and thermal loads in contemporary technical equipment requires the use of materials with excellent thermal stability and high melting temperatures.

Fused silica occupies a special place among these materials; it has a high thermal-shock resistance and a low coefficient of thermal expansion. However, the use of fused silica is limited since when complicated articles are prepared from it difficulties arise because of its high viscosity. These difficulties can be largely overcome if we use the ceramic technology for obtaining the articles [1-10]. The use of this technology enables us to obtain products with a porosity of from practically zero to 30%, and in this manner to regulate their properties. In connection with this, the need arises to investigate the properties of ceramics made from fused silica in relation to porosity and temperature.

The present authors carried out experimental investigations of the relationship between thermal conductivity, specific heat, elasticity modulus, strength and thermal expansion, and porosity and temperature. The starting material used to prepare the specimens was waste transparent fused silica obtained by melting rock crystal with a content of 99.9% SiO_2. The original material was ground in a silica-lined ball mill with fused silica grinding media.

The specimens were prepared by slip casting in plaster molds and fired at temperatures of from 1000 to 1350°C with a soak of from 0.5 to 10 h.

The thermal conductivity and specific heat of the specimens were determined by the quasistationary heat-cycle method with limiting second order conditions (constant with time and with respect to the surface of the heat current). The method enabled us to determine the thermal conductivity and specific heat of the specimens during a single experiment. We then calculated the coefficient of temperature conductivity from the values obtained for these properties and the density of the material.

We prepared specimens in the form of plates measuring $70 \times 70 \times 12$ mm to determine the thermophysical properties.

The measurement error did not exceed 8%. The spread in the experimental data is shown in Figs. 1, 3-10. The equipment was checked before the test was done, and we determined the thermal conductivity of

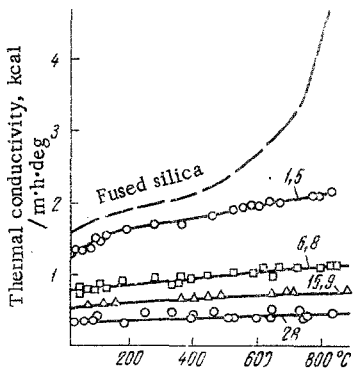

Fig. 1. Relationship between thermal conductivity and temperature. Nos. on the curves indicate porosity of specimens, %.

TABLE 1. Values of the Constants, A, B, and λ_0 for Materials of Different Porosity

Porosity, %	A	$B \cdot 10^3$	λ_0,* kcal /m·h·deg
1,5	0,993	0,690	0,78
6,8	0,833	0,715	0,56
15,9	0,840	0,800	0,38
28,0	0,900	0,500	0,26

*Except for porosity 1.5%, λ_0 corresponds to the thermal conductivity at 0°C.

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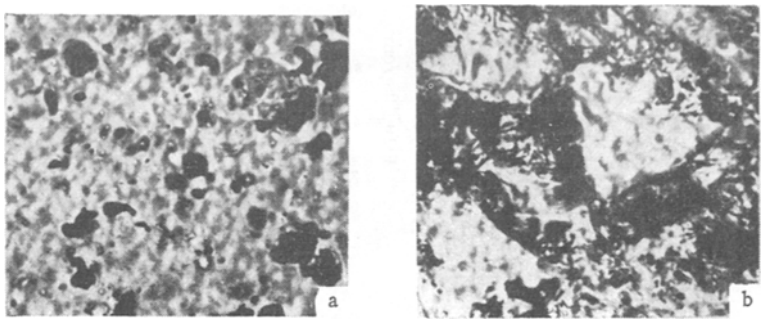

Fig. 2. Microstructure of material with a porosity of 1.5% (a) and 15.9% (b), × 600, reflected light.

transparent plates made from fused quartz, recommended as the standard for the range of thermal conductivity coefficient values, λ, from 1 to 5 kcal/(m·h·deg).

Figure 1 shows the relationship between thermal conductivity and the specimens of fused silica ceramics and temperature for different porosity values. For comparison we also show the relationship for λ for transparent fused quartz from collated literature data [11]. In the range from 100 to 800°C the relationship between thermal conductivity and temperature is described with an accuracy of up to 2% by the following equation

$$\lambda = A\lambda_0 (1 + BT). \quad (1)$$

The constants, A, B, and λ_0 are listed in Table 1.

The general rule is a linear increase in thermal conductivity with rise in temperature. This agrees with theoretical data on the temperature relationship for the thermal conductivity of amorphous materials and the background (lattice) conductivity.

The share of the conductivity of the air located in the pores of the refractory, and the transfer of heat due to heat exchange by radiation through the pores, is negligibly small compared with the background conductivity of the base material. In other words, the intensity of the increase in thermal conductivity with temperature rise should increase with increase in porosity.

The typical microstructure of the material with a porosity of 1.5 and 15.9% is shown in Fig. 2, a and b. The microstructure contains practically no anisotropy of form, magnitude, or number of pores. The pores

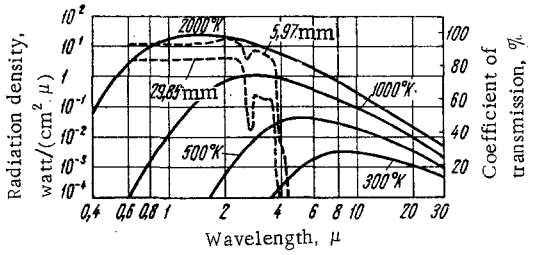

Fig. 3

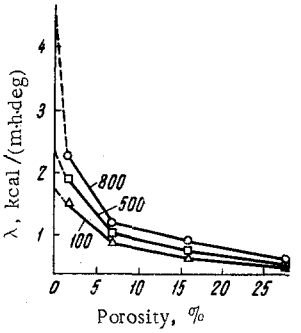

Fig. 4

Fig. 3. Density of absolute black body radiation (——) and spectral transmission of transparent fused quartz (- - - -) for specimens of different thicknesses.

Fig. 4. Relationship between coefficient of thermal conductivity λ, and porosity. Figures on the curve indicate temperature, °C.

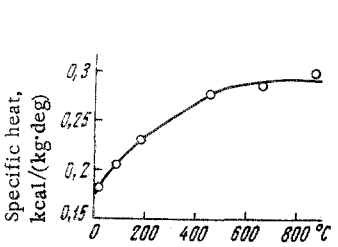

Fig. 5

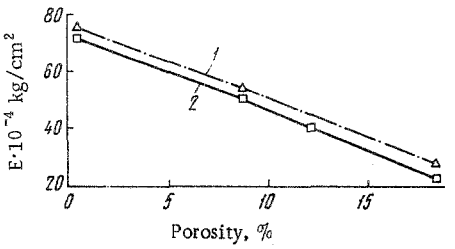

Fig. 6

Fig. 5. True specific heat of fused silica ceramics.

Fig. 6. Temperature conductivity of fused silica ceramics. Nos. on the curve indicate porosity, %.

of the materials with a porosity of 1.5% approximate in shape to spherical cavities with average statistical sizes of 3 μ; in the ceramic with a porosity of 15.9% they form a continuous network between the individual particles of the base material.

From 40 to 130°C the relationship between thermal conductivity and temperature is nonlinear. The deviation from the linear relationship is greatest for the material having a porosity of 1.5%, and is weak for specimens with a higher porosity.

To compare the temperature relationships for the coefficients of thermal conductivity of fused quartz ceramics with a porosity of 1.5% and transparent fused quartz it is possible to distinguish two temperature ranges, that is, from 30 to 400°C, and above 400°C. Up to 400°C both curves are the same. With an increase in temperature we note a rapidly mounting divergence because of the more intensive increase in thermal conductivity of the transparent fused quartz. At 400°C the λ value for the dense ceramic is 80% of the λ value for the transparent fused quartz, and at 800°C it is only 47%.

This divergence cannot be explained by any essential difference in the structure of the glass (its crystallization), since it is undetectable by x-ray or electron microscopic investigations of the specimens.

An analysis of the spectral transmission of fused silica ceramics and transparent fused quartz in the infrared region of the spectrum enabled us to establish that in the wavelength region of from 0.5 to 4.5 μ the fused silica ceramics have zero transparency, while the transparent fused quartz transmits up to 90% of the incident radiation with different specimen thicknesses.

Figure 3 for comparison shows the spectra for absolute black body radiation at different temperatures [12] and the spectral transmission of fused quartz [13]. It is seen that part of the radiation energy in the

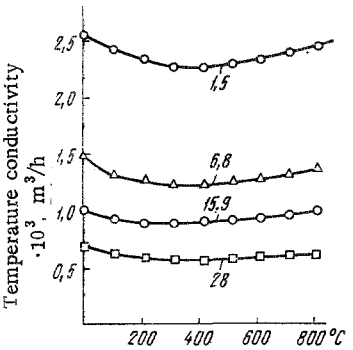

Fig. 7

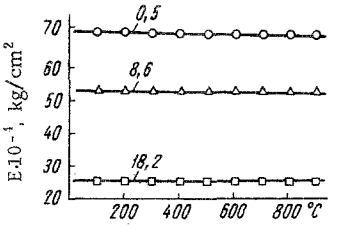

Fig. 8

Fig. 7. Relationship between dynamic (1) and static (2) moduli of elasticity and porosity.

Fig. 8. Relationship between dynamic modulus of elasticity and temperature. Figures on curves indicate porosity of specimens.

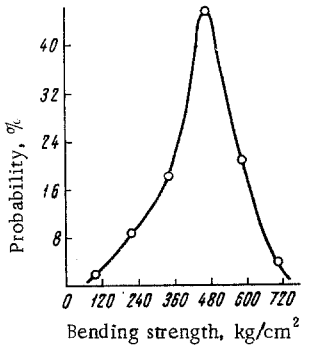

Fig. 9

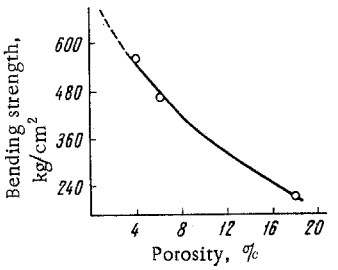

Fig. 10

Fig. 9. Probability distribution for bending strength of fused silica ceramics with a porosity of 6%.

Fig. 10. Relationship between bending strength and porosity of specimens.

wavelength range 0.5-4.5 μ freely penetrates through the transparent fused quartz, without creating a temperature fall over the thickness of the specimen. The proportion of this radiation rises with increase in temperature, since an increasing share of the energy of the heating element is radiated in the wavelength region of 0.5-4.5 μ.

The presence of straight-through radiation can explain the intensive increase in thermal conductivity of fused silica with rise in temperature compared with the thermal conductivity of fused silica ceramics. At low temperatures part of the energy radiated in the wavelength range 0.5-4.5 μ is low, so the curves showing the relationship between λ for the two materials are similar and correspond to the theoretically obtained relationships for amorphous material. At high temperatures the discrepancy is due to the increase in the proportion of straight-through radiation.

Figure 4 shows the relationship between λ for fused quartz ceramics and the porosity at 100, 500, and 800°C. With an increase in the porosity the coefficient of thermal conductivity diminishes. The character of the reduction with a porosity above 1.5% is the same for all three curves: in the porosity range from 0 (transparent fused quartz) to 1.5% we note a sharp divergence.

The intensity of the fall in thermal conductivity in this range depends on the temperature. At 100 and 500°C the thermal conductivity diminishes by 15 and 21% respectively, and at 800°C by 53%. This sudden reduction in thermal conductivity at 800°C cannot be explained by the reduction in density. A change in the density of ceramic materials of 1.5% normally gives rise to a change in thermal conductivity of less than 10%. It is probable in this case that the sharp reduction can be explained by the disappearance of the transparency of the material in the infrared region.

An increase in the porosity of from 1.5 to 6.8% reduces the thermal conductivity by 44, 47, and 47% at 100, 500, and 800°C respectively. Further increase in the porosity to 28% produces a reduction in thermal conductivity of 55, 56, and 56% at 100, 500, and 800°C. The analytical relationship between the coefficient of thermal conductivity λ and porosity P in the range 1.5-28% with an accuracy of up to 8% is described by the following equation

$$\lambda = D\,(1 - 1.02P^{-0.05}), \tag{2}$$

where D is a constant which depends on the temperature and equals 6.87, 8.7, and 10.4 for 100, 500 and 800°C respectively.

The porosity value in equation (2) is subsequently used in absolute values. In the porosity range 6.8-28% the results of the experiments are more accurately described by the exponent. Thus, at 500°C with an accuracy of up to 2% they are described by the equation

$$\lambda = 1.11 \exp(-3.87P). \tag{3}$$

The relationship between the true specific heat of fused silica ceramics and temperature is shown in Fig. 5.

The character of the temperature relationship with specific heat agrees well with the theoretical relationship [14] for materials in which the basic heat used for heating is expended on the increase in the energy of the complexes of interbonded atoms and ions, and where the number of free electrons is low.

With an increase in temperature of from 30 to 500°C the specific heat increases intensely, and after 500°C gradually approximates to a constant.

The relationships between the temperature conductivity a and the porosity and the temperature were calculated from

$$a = \frac{3.6\lambda}{\rho_0 c_p} \text{ m}^2/\text{h} \tag{4}$$

where ρ_0 is the density of fused quartz, kg/m^3.

The results obtained are shown in Fig. 6. The temperature conductivity hardly depends on the temperature. At first the temperature conductivity diminishes with rise in temperature, reaching a minimum at 400°C, and then rising. The minimum value is only 10% lower than the maximum. For the material having a porosity of 1.5%, the temperature conductivity at 100°C equals 2.48×10^{-3} m^2/h, and at 800°C it is 2.52×10^{-3} m^2/h.

The modulus of elasticity of the fused silica ceramics at room temperature was determined by the static method, and at high temperatures by the dynamic method. Plates measuring $120 \times 20 \times 3$ mm were used as the specimens.

Figure 7 shows the change in elasticity modulus at room temperature as a function of porosity. With an accuracy of up to 5% the relationship can be described by the following equation

$$E = E_0 (1 - 4P), \tag{5}$$

where E and E_0 are the modulus values with a porosity of P and zero.

For the static elasticity modulus E_0 proved to be equal to 7.1×10^5 kg/cm^2, which agrees well with the value for the elasticity modulus of fused silica (7.0×10^5 kg/cm^2) obtained on the same equipment and given in the literature [15]. The experimental value for the dynamic elasticity modulus is 5% higher than the static (see Fig. 7). Its relationship with porosity is also described by equation (5), where $E_0 = 7.5 \times 10^5$ kg/cm^2

An analysis of the results shows that an increase in porosity of 1% produces a reduction in the modulus of elasticity of 4% for specimens having a porosity of 1.5-28%. The resulting linear relationship for the modulus of elasticity of fused silica ceramics and porosity agrees well with data given for oxide ceramic materials [16], but disagrees with that cited in [7] in which the authors obtained a degree relationship for the elasticity modulus of ceramics made from fused silica, and porosity. However, the small number of experimental points and their great spread throws doubt on the validity of the degree relationship.

The modulus of elasticity hardly changes with increase in temperature (Fig. 8). Up to 800°C the elasticity modulus does not depend on temperature, although theoretically we should observe a reduction in it. The discrepancy can be explained by the fact that the reduction in the elasticity modulus is located within experimental error (up to 5%).

The coefficient of thermal expansion of ceramics does not depend on porosity, and corresponds to the same value for fused silica. With an increase in temperature the average coefficient of thermal expansion diminishes. For a temperature range of from 30 to 800°C it equals 5.3×10^{-7} deg^{-1}.

The bending strength of ceramics was determined on specimens measuring $70 \times 9 \times 8$ mm. The specimens were loaded on a four-support system. The distance between the loading supports was 20 mm, and the thrust supports 50 mm. Tests were done at room temperature. Because of the large spread in the strength values we tested from 70 to 120 specimens of the same porosity. The results obtained for specimens of each porosity were treated statistically, and we constructed probability curves for the distribution of strength values. The probability curve constructed from the bending strengths of 110 specimens with a

porosity of 6 ± 1% is shown in Fig. 9. The distribution curve is assymetrical. The lower strength values compared with the more probable values refer to 60% of the total number of specimens, and the higher values 40%. The distribution curves with the best approximation are described by equations of the type

$$P(\sigma) = \frac{m}{K^m} \sigma^{-1} \exp\left[-\left(\frac{\sigma}{K}\right)^m\right], \quad (6)$$

where m and K are constants, and σ is the bending strength.

The relationship between the most probable bending strength and porosity is shown in Fig. 10. The most intense reduction in the bending strength is noted with an increase in porosity of up to 6%. The results obtained for specimens with a porosity of from 4 to 18% with an accuracy of up to 4% can be described by the exponent

$$\sigma = \sigma_0 \exp(-7.4P),$$

where σ and σ_0 are the most probable bending strengths, kg/cm^2, with a porosity of P and 0.

$\sigma_0 = 740$ kg/cm^2, which agrees with the bending strength value of fused quartz. The maximum bending strength reached 820 kg/cm^2.

The relationship shown in Fig. 10 was obtained for specimens characterized before firing by different original porosity values. This factor can seriously affect the magnitude of the strength values [17].

CONCLUSIONS

We investigated the relationship between thermal conductivity, specific heat, and temperature conductivity of fused silica ceramics with a true porosity of 1.5-28%, and temperature. Above 500°C we detected a sharp deviation in the thermal conductivity of fused silica ceramics from this factor recorded for fused silica. The deviation is explained by the presence of straight-through radiant heat currents during the tests of the fused silica.

We established a linear relationship between static and dynamic elasticity modulus and porosity, but could not detect a relationship for temperature.

We investigated the relationship between the most probable bending strength value and porosity. This relationship can be described by the exponent with an accuracy of up to 4%.

LITERATURE CITED

1. O. N. Botvinkin and A. I. Zaporozhskii, Fused Quartz [in Russian], Stroiizdat (1965).
2. P. P. Budnikov and Yu. E. Pivinskii, Uspekhi Khimii, 36, No. 3, 514 (1967).
3. N. I. Voronin and R. S. Churakova, Ogneupory, No. 1, 47 (1967).
4. I. E. Nishanova et al., in: Highly Refractory Materials [in Russian], Metallurgiya, (1966), p. 82.
5. R. Ya. Popil'skii and I. E. Nishanova, Trans. D. I. Mendeleev Moscow Institute of Chemical Technology, No. 50, 195 (1966).
6. J. D. Fleminy, Amer. Ceram. Soc. Bull., 40, 748 (1961).
7. R. E. Gannon et al., Amer. Ceram. Soc. Bull., 44, 460 (1965).
8. W. Schulle, Silikattechnik, 13, 282 (1962).
9. W. Schulle and J. Ulbricht, Silikattechnik, 13, 229 (1962).
10. J. D. Walton, Ceramic Age, 76, No. 2, 33 (1960); No. 3, 23 (1960).
11. B. N. Oleinik, Teplofizika Vysokikh Temperatur, 2, No. 1, 109 (1964).
12. G. L. Hanford, Infrared Radiation [Russian translation], Énergiya (1964), p. 23.
13. R. Borkhert and V. Yubits, Infrared Heating Techniques [Russian translation], Gosénergoizdat (1963), p. 76.
14. Ch. Kittel, Elementary Physics of Solids [in Russian], Izd-vo Nauka (1965), p. 59.
15. E. M. Voronkov et al., Optical Materials for Infrared Techniques [in Russian], Manual, Nauka (1965), p. 144.
16. B. A. Chandler and E. C. Duderstand, J. Nuclear Materials, 8, No. 3, 276 (1963).
17. F. T. Gorobets and Yu. E. Pivinskii, Ogneupory, No. 8, 45 (1968).