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EFFECT OF HEAT TREATMENT ON THE STRENGTH OF
ALUMINUM-BOROSILICATE GLASS FIBRE(U) DEFENCE RESEARCH
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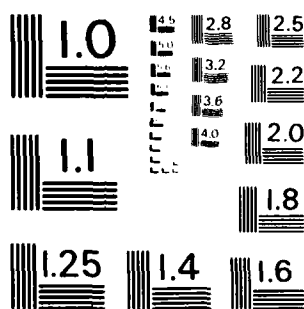
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Effect of heat treatment on the strength of aluminium-
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The effect of heat treatment of aluminium-borosilicate glass fibre on its strength (in the range of temperatures between 50 and 500°C) was investigated. With the aid of methods for the study of the surface (low-temperature adsorption, mercury porosimetry) it was found that the direct cause of the sharp decrease σ in the interval $t = 200-300^\circ\text{C}$ appears to be the formation of relatively coarse defects, i.e. cracks.

On the basis of mass spectrometric measurements, and also NMR spectra investigation of B^{11} nuclei, it was assumed that the formation of defects on the surface is associated with the chemisorption of atmospheric oxygen on coordinatively unsaturated centres of the surface.

The sharp drop in the strength of silicate fibres during heat treatment in the temperature range 300 to 600°C has received attention from many workers since, on the one hand, the solution of this problem has an important practical significance because many industrial articles from composite materials are operated at high temperatures and, on the other hand, the nature of the physical mechanism of weakening is closely associated with the problem of the structure of glass.

Numerous studies have been published in which researchers investigated the strength of sheet glass⁽¹⁾, and also of quartz⁽²⁾ or glass fibres⁽³⁾ of various compositions treated in the range of temperatures between 100 and 800°C (see also review studies⁽⁴⁾). However, despite the large number of studies devoted to this problem, there is no universally accepted theory of the mechanism of processes which occur during heat treatment. In the present study, we describe certain experiments directed towards clarifying this problem.

Experimental methods. The subject of the investigation was industrial aluminium-borosilicate glass fibre with a mean diameter of 6.5μ and average strength of $\sigma \approx 250 \text{ kg/mm}^2$. The heat treatment of specimens was carried out in a muffle furnace which made it possible to maintain the temperature of up to 700°C with an accuracy of $\pm 10^\circ$. The duration of the holding time at the given temperature was 1 hour.

The tensile strength σ of initial and of heat-treated specimens was determined using standard methods under atmospheric conditions. The length of the investigated specimen was in all cases identical and amounted to 10 mm. The rate of the loading was always constant and equal to 0.5 g/sec . Besides the average strength, we also measured the modulus of elasticity E . Results of the measurements of mechanical properties are shown in Fig. 1, a.

The diameter of the fibres was determined with the aid of MBI-6 microscope and the eyepiece of MOV-1-15 micrometer at a magnification of 600. This method secures an accuracy of measurement of $\approx 3\%$. More accurate results are obtained by the interpretation of diffraction patterns of scattered light for individual glass fibres⁽⁵⁾. In these measurements, as a radiation source, we used an LG-35 laser. Results calculated from data according to the light scattering had an accuracy of $\pm 0.06 \mu$, i.e. $\approx 1\%$. The magnitude of average diameters in the initial fibres obtained by both methods practically coincided. The determination of the diameter of the heat-treated glass fibre was carried out only on the basis of light scattering.

The value of the specific surface of the fibre S_0 was determined with the aid of low-temperature adsorption of nitrogen according to the BET method⁽¹⁾. For the calculation of S_0 we used for the surface areas of the nitrogen molecule the values $13.6 \text{ \AA}^2$ and $14.8 \text{ \AA}^2$ for hydroxylated

1) For the investigation of the adsorption, we used a beam scales with sensitivity of $1.8 \cdot 10^{-6} \text{ g}$.

(up to 300°C) and dehydroxylated (between 300 and 600°C) specimens respectively⁽⁶⁾. Results of measurements of the specific surface are shown in Fig. 2. In the same Fig. is shown, by a dotted line, the value of the geometrical surface of the initial fibre S_0 calculated from the mean value of the diameter.

For the investigation of defects on the surface of glass fibre mercury porometry was used. The possibility of using this method for checking the structure of the glass fibre surface was explained in our study⁽⁷⁾. The results of measurements are shown in Figs. 2 and 3.

For the investigation of conversions which occur during heat-treatment of the glass fibre, we used NMR for B^{11} nuclei which, as is well-known, made it possible⁽⁸⁾ to trace the changes in the number of BO_4 and BO_3 groupings in boron-containing glasses. The method for measuring and processing experimental data was described earlier in our studies^(9,10). The results of measurements are shown in Fig. 4,a.

Evaluation of the results

Data shown in Fig. 1,a pertaining to mechanical properties of aluminium-borosilicate glass fibre indicate that specimens subjected to heat-treatment for one hour undergo practically no change in strength at temperatures up to 200°C. The heat-treatment at more elevated temperatures leads to a sharp decrease in strength. The modulus of elasticity E of the investigated specimen remained practically unchanged in the investigated range of temperatures. Similar relationships were obtained by several authors for different types of glasses and fibres (see e.g. studies^(2,3)).

The observed changes in properties were explained as being due to various causes: a) Structural reorganisation inside the fibres; b) Surface crystallisation; v) Non-identical heat expansion coefficients of the surface layer and of the bulk of the glass; g) Effect of foreign inclusions on the surface⁽²⁾; d) Dehydration and brittleness of the surface layer⁽¹⁾.

In spite of differences in the treatment of these experimental results, most research workers come to the conclusion that the sharp decrease in the strength of glass fibre during heat-treatment was caused by the development of surface defects (microcracks). By experiments involving treatment of a fibre weakened by the heat effect in solutions of hydrofluoric acid, it was shown that its strength can be significantly increased and brought to a level which is characteristic of glass in magnitude (according to G.M. Martenev's classification⁽¹¹⁾).

In Fig. 1, b we show data on the strength of fibres subjected to heating at 500°C (1 hr.) and subsequently treated with a mordant in solutions of hydrofluoric acid of varying concentrations. The results show that short-term (1 min.) immersion of heat-treated glass fibre in 0.02 N HF solution in fact permits a significant increase in its strength. This shows that the decrease in strength during heat treatment, in line with assumptions in the above-mentioned studies, is associated with processes on its surface. Therefore, the analysis of the results of the investigation of the surface shown in Fig. 2 is of special interest.

The magnitude of the specific surface of the glass fibre S_0 does not change greatly in the range of temperatures between 200 and 500°C (Fig. 2, a). A certain increase in the surface at temperatures between 200 and 300°C is probably associated with the release of the microroughness from condensed and adsorbed admixtures. Attention was focussed on the difference in the magnitudes S_0 obtained from adsorption measurements and S_d calculated from measurements of the diameter. This difference is apparently explained by the presence on the surface of the glass fibre of a system of microdefects (cracks, microroughness). The magnitudes of diameter obtained from light scattering data also indicate that they are not dependent on the temperature of the treatment of the specimen.

Thus, it can be stated that, during the heat-treatment in the investigated range of temperatures, the magnitude of the specific surface does not change significantly. This conclusion is in agreement

with the finding of study⁽¹²⁾ in which, using a gas-chromatographic method, the effect of heat-treatment was investigated (under identical temperature conditions) on the magnitude of the surface of powders from boron-containing glasses. The authors found that the magnitudes of the specific surface determined by the heat-desorption method of argon did not change as a result of the heat-treatment of the specimen.

In Fig. 2,a, are shown the results of measurements of the volume of defects, microcracks, on the surface of glass fibre as a function of the temperature of the specimen, obtained by the mercury porometry method. These data show that the volume of defects v_p changes significantly in the range of temperatures of up to 200°C but increases greatly at higher temperatures (between 200 and 500°C). The decrease in the volume of defects observed at $t = 600^\circ\text{C}$ is obviously associated with the commencement of the process of sintering.

Therefore, after heat-treatment, data of mercury porometry directly indicate that the indirect cause of the sharp decrease in strength at temperatures above 200°C is the development of a system of defects, cracks, on the surface. In Fig. 2,b is shown the dependence of the strength of the fibre on the magnitude of the volume of defects. It is found that, beginning with a certain critical value $v_p \approx 2 \cdot 10^{-3} \text{ cm}^3$, the value of $\tilde{\sigma}$ decreases sharply. However, the dependence $\tilde{\sigma} = f(v_p)$ does not yet permit the determination of precisely which defects are responsible for the decrease in strength.

For the solution of this problem, it is essential to examine the histograms (porograms). Curves of the dispersion of the volume of defects according to sizes (with a reminder that the characteristic size a in the given case appears to be the effective width of the crack⁽⁷⁾) show that, during heat-treatment, not all groups of pores change uniformly. This is shown in Fig. 3 where, on the axis of ordinates, is plotted the increase in the volume of defects Δv_i in the determined

interval of dimensions a , pertaining to the corresponding magnitude $(\Delta v_i)_0$ for the initial fibre and, along the axis of abscissae, the temperature of heat-treatment. The overall range of dimensions a was conditionally divided into three groups: micropores (between 25 and 100 Å), intermediate (100-400 Å) and macropores (400-3500 Å). An analysis of the results showed that $\Delta v_{100-400}/(\Delta v_{100-400})_0$ is practically independent of the temperature (not shown in Fig. 3)

The volume of micro and macrodefects depends on the temperature of the treatment. The volume of micropores decreases somewhat with an increase in temperature (curve 1 in Fig. 3) if the volume of macropores increases several times with an increase in the temperature of heat-treatment. A particularly sharp increase is observed at temperatures between 200 and 400°C, where $\Delta v_{400-3500} \approx 100 (\Delta v_{400-3500})_0$ of the initial specimen.

It is pointed out that the usual surface of the glass fibre can in the process remain unchanged, since the fundamental contribution to S_0 is made by micropores, the volume of which decreases slightly with an increase in temperature. On the other hand, the sharp increase in the volume of macropores (the contribution of which to S_0 is insignificant) with an increase in temperature to all appearances somewhat compensates for the decrease in surface because of the "skinning over" of micropores in such a way as to make S_0 unchanged within the limits of the accuracy of measurements. Thus, an analysis of the results of mercury porosimetry shows that the increase in volume of defects during heat-treatment at $t > 200^\circ\text{C}$ primarily occurs because of the appearance of relatively coarse cracks which, in fact, leads to the decrease in the strength of the glass fibre.

With the aid of NMR spectra on B^{11} nuclei, we showed in studies^(9,10) that, during the heat-treatment of aluminium-borosilicate fibre in the temperature range, which is of interest to us, a change occurs in the coordination number of boron caused by the donor-acceptor

interaction of atmospheric oxygen with the surface of the glass fibre at temperatures of between 200 and 500°C. Reflecting this process, the dependence of the number of BO_4 (N_4) groups to the number of BO_3 (N_3) groups on the temperature of the heat-treatment is shown in Fig. 4,a; in Fig. 4,b is given the dependence of the amount of oxygen C absorbed by the fibre on the temperature.

On replacing air by inert gas (argon) in the ampoule used for heat-treatment of the fibre, the value N_4/N_3 decreased significantly in the range of temperatures between 200 and 500°C (curves 2 in Fig. 4,a). Conclusions derived in studies^(10,11) permit us to assume that the reduction in strength observed in the experiment and the increase in the volume of defects are associated with the interaction of the surface of the glass fibre with atmospheric oxygen. To clarify this relation, we carried out a series of experiments in vacuo (at a pressure of 0.1 mm mercury column) and in an atmosphere of argon¹.

The average strength of specimens heat-treated in argon and in vacuo (curves 2 and 3 in Fig. 1) was found to be much higher than for those heat-treated in air (curve 1 in Fig. 1). An investigation of the surface with the aid of mercury porometry showed that, for fibres heat-treated in argon, the usual volume of defects depends slightly on temperature (Fig.2,b), whilst the relative volume of microdefects decreases more strongly and $\Delta v(400-3500)/\Delta v(400-3500)_0$ increases with temperature to a much lower extent than for specimens heat-treated in air (see curves 2,4 and 1,3 in Fig. 3). Data for specimens heat-treated in vacuo occupy an intermediate position (curve 5 in Fig. 3).

Thus, results of the investigation of the fibre surface treated in argon and in vacuo are fully correlated with data for the strength, confirming the earlier expressed assumption about the effect of atmospheric oxygen (in which it is usual to carry out the heat treatment) on the

1. For the test, we used argon brand "pure", without any particular purification. Mass-spectroscopic analysis showed, however, that the gas we used contained detectable admixtures of nitrogen and oxygen (0.5 and 0.4% respectively).

strength of glass fibre. Results we obtained (Figs. 1a, 2b and 3) confirm that even small amounts of oxygen (admixture in Ar, insufficiently high vacuum) can lead to a visible reduction in strength during the heat-treatment of glass fibre (at $t > 200^{\circ}\text{C}$).

In agreement with study⁽³⁾, two types of processes occur during the heat-treatment of the glass fibre. In the first, a transition of structural elements of the fibre into an equilibrium state takes place which is characteristic of bulk glass and is accompanied by an increase in density and by a reduction in the strength of the bond between structural groups of the glass because of variations in temperature. This process leads to a monotonic decrease in strength as a function of the duration of heat-treatment. In the second, during operation of the heat-treatment in an oxygen-containing medium (e.g. air) at temperatures above 200°C , the surface of the glass fibre chemically absorbs oxygen leading to a change in the surroundings of the coordinatively unsaturated atoms, i.e. boron, aluminium and also (according to certain communications⁽¹³⁾) silicon.

Data available in the literature indicate that additions of boron and aluminium introduced into silica glass and silica impart sharply expressed chemisorptive properties with respect to molecules able to enter into a coordination bond⁽¹⁴⁾. The presence of chemisorptive gas-acceptor molecules is bound to lead to a deformation of intramolecular bonds in the surface layer⁽¹⁵⁾ and, consequently, produces a stressed state of the surface. Since it seems that the seat of the location of oxygen appears to contain the most active portions, i.e. the surfaces of crack-defects, rupture of molecular bonds can be expected especially in these areas and, consequently, the development of the volume of defects.

Obviously, an opposite process of reducing surface stresses is also possible. For that, obviously, it is essential to remove the chemisorptive oxygen from the surface or replace it by hydroxyl groups.

As is well-known, treatment of the surface by solutions of hydrofluoric acid leads to the recovery of the strength. Data obtained in the present study show (Fig.1) that the effect of reinforcement is the greater the more diluted the HF solution (treatment in a 0.02 % HF increased σ up to 220 kg/mm² whilst, using a 0.5 % HF, we only succeeded in attaining 170 kg/mm²). Moreover, the treatment of a fibre heat-treated in air with distilled water also leads to a sharp increase of the strength up to a level $\sim$ 200 kg/mm². A similar effect was observed in study⁽¹⁸⁾ in which an increase was observed in σ of high-strength heat-treated sheet glass during its treatment by water. The authors explained this phenomenon by the "plasticising" action of water on the surface of glass.

The observations made in the present study show that the cause for the increase in the strength of heat-treated fibres after "etching" is obviously not so much because of the removal of the defective surface layer, as is generally assumed⁽¹¹⁾, but because of the chemical modification of the surface. In study⁽¹⁰⁾, it was shown that, during the treatment of glass fibre heat-treated in air at 500°C in a 0.2 % HF, the ratio of N_4/N_3 is visibly reduced which indicates the rupture of some of the coordinative bonds.

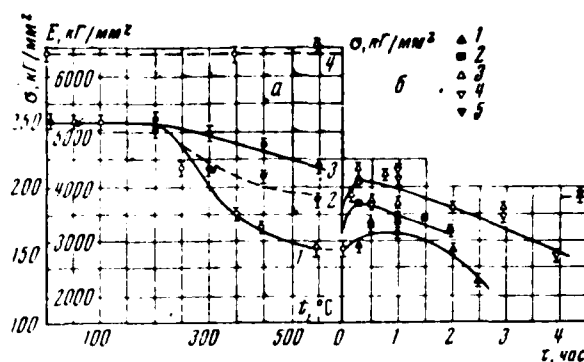
Therefore, the obtained results testify that the sharp decrease in strength during short heat-treatment of aluminium-borosilicate glass fibre is not the result of high temperatures, but is produced by the interaction of coordinatively unsaturated centres on the glass surface with the surrounding atmosphere (atmospheric oxygen). The mechanism suggested for the reduction in strength during heat-treatment of glass fibre is probably taking place not only in the case of aluminium-borosilicate glass fibre, but also in other silicate fibres. It is not impossible that, under conditions of sharp cooling during the drawing-out of a fibre, groupings of lower non-stoichiometric oxides of silicon (types of SiO chains) may form on its surface which, during repeated heating-up to temperatures of more than 300°C

in ordinary air, may decompose by changing to a stable state (SiO_2)⁽¹⁴⁾.

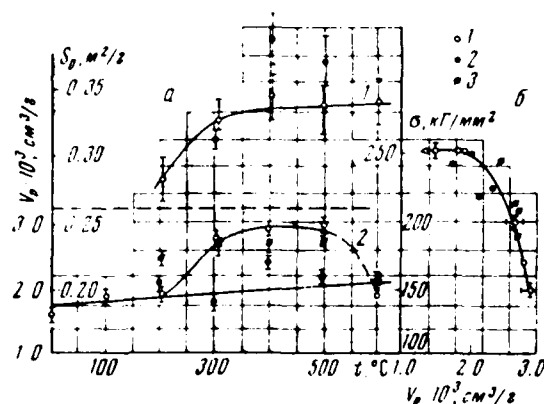
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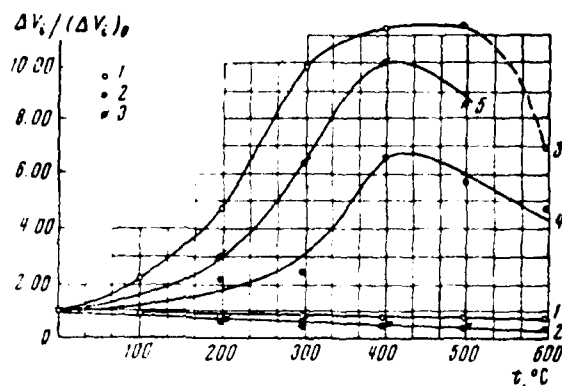
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1. Change in the strength properties of the glass fibre arising from the treatment
 - a, Dependence of tensile strength σ (1-3) and of modulus of elasticity E on the temperature of the heat-treatment t during a holding time of 1 h;
 - b, Dependence of the strength of the glass fibre heat-treated at $t = 500^{\circ}\text{C}$ on the duration of the treatment τ in solutions of hydrofluoric acid: 1- 0.5 % H_2F_2 ; 2- 0.2 %; 3- 0.02 %; 4- distilled H_2O ; 5- distilled H_2O ; $\tau = 24$ h

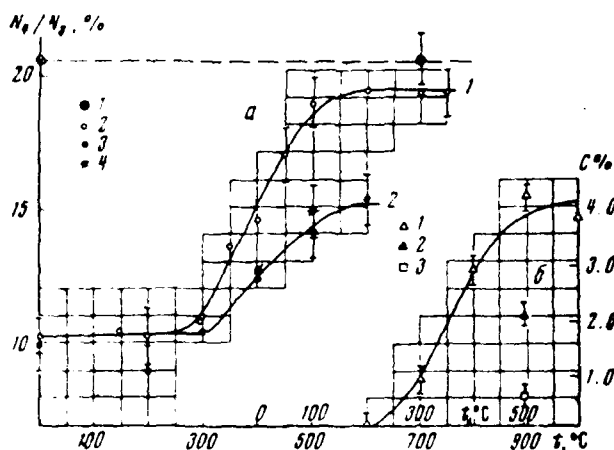


- 2.a. Dependence of the magnitude of the specific surface S_0 (1) and of the specific volume of defects (cracks) v_p (2) on the temperature of the heat treatment;
- b. Change in the strength of the glass fibre σ as a function of the specific volume of defects v_p :
 - 1-Medium of air; 2- Argon; 3 - Vacuum



3. Change in the relative volume of various groups of defects on the surface of the glass fibre $\Delta v_i / (\Delta v_i)_0$ as a function of the temperature of heat-treatment

Curves: 1,2 - for $a = 25 + 100 \text{ \AA}$, curves 3,5 - for $a = 400 + 3500 \text{ \AA}$,
1 - medium of air; 2 - Argon; 3 - Vacuum



- 4.a. Change in the number of groupings BO_4 (N_4/N_3) during heat-treatment of glass fibre:

1 - Glass (monolith); 2 - medium of air; 3 - Argon; 4 - Vacuum

- b. Absorption C of oxygen during heat-treatment: 1- ABS glass fibre;

2 - Powder of ABS glass; 3 - Powder of quartz glass

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Abstract The effect of heat treatment on the strength of aluminium-borosilicate glass fibre was investigated in the temperature range 50-500 deg C. Low temperature adsorption and mercury porometry methods were used to study the surface of the glass and it was found that the direct cause of the sharp decrease in strength in the interval 200 to 300 deg C was the formation of cracks in the surface. Mass spectrometric measurements coupled with nuclear magnetic resonance spectral investigation of boron (11) nuclei lead to the conclusion that the formation of these defects was associated with the chemisorption of atmospheric oxygen on co-ordinatively unsaturated centres at the surface.			

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