STUDY OF THE RHEOLOGY OF SINTERED GLASS CERAMIC MATERIALS BY TORSION OF THIN-WALLED TUBES

D. V. Andreev[1] **and A. I. Zakharov**[1]

Translated from *Novye Ogneupory*, No. 1, pp. 36 – 44, January, 2012.

Original article submitted October 13, 2011.

The capabilities of a newly developed method of rheological study of roasted semifinished articles in simple shear and in shear combined with axial strain induced by additionally applied compressive or tensile stresses are demonstrated. The method is based on the principle of torsion of thin-walled tubes realized in a newly created device and makes it possible to determine the mutual influence of the components of the strain rate tensor of the material, where the strain may be a consequence of dilatancy, anisotropy, asymmetry of a mechanical reaction or other factors. The rheological properties of semifinished articles belonging to the group of porcelains which have been preliminarily roasted at 900°C, lithium-aluminosilicate glass ceramic, and sintered semiporcelain are studied.

Keywords: porcelain, glass ceramic, sitall, strain, rheology, viscosity, simple shear, torsion, dilatancy, liquid-phase sintering, shrinkage, roasting

INTRODUCTION

Efforts have been focused on reducing the roasting time and roasting temperature as a means of reducing energy consumption in the production of ceramic articles. Active fusing agents that form a liquid phase at low temperatures are basically used for this purpose, though the probability of strain of the article thereby grows and the precision of its dimensions falls. In addition to technological methods of reducing strain, which are always limited by the properties of the materials and the particular mode of production, there also exists the engineering capability for reduction of deformation by compensation of deformation with appropriate correction of the shape of the model or by increasing the rigidity of the construction of the article; prediction of deformation is needed to realize these capabilities.

In the traditional technology of staged manufacture of new models of products where there is unacceptable deformation in roasting, correction of the dimensions of the model together with repetition of all the stages is required. The time spent on correction and fabrication of the mold may be substantially reduced through the use of computer modeling. CAD and CAE programs are used in the creation of the computer models of constructions and materials; it is also necessary to know the characteristics of the roasted article.

In the course of roasting a semifinished ceramic article experiences the effect of multidirectional forces caused by stresses associated with sintering (shrinkage) and temperature expansion, phase transformations, and the effect of deadweight. The rheological behavior of the material in the course of roasting may be described by any one of the well-known models (governing relations) in light of the above factors. Any one of a number of different models may be used to describe the rheology of a material, from simple phenomenological models to complex theoretical models. The latter types of models are generally on the basis of a particular type of idealized mechanical models or, in the case of great universality, are distinguished by a set of structural parameters that are not amenable to determination with any required degree of precision. The use of phenomenological models is associated with difficulties in the realization of three-dimensional schemes for testing the samples and for this reason the most commonly employed models are semi-empirical. Tests of samples in special cases of the stress-deformed state are used to determine the phenomenological parameters of these models while iterational calibration, manual variation, etc. are used to determine the structural parameters. In [1] porcelain plates and sanitary pottery ware served as the subject of study and simulation; the dimensions of the articles at different stages of sintering were

[1] FGBOUVPO Mendeleev Chemical Engineering University of Russia, Moscow, Russia.

1083-4877/12/05301-0031

interpolated with the use of equations of diffusion sintering and grain growth and in light of temperature gradients, gravity component, and the effect of external friction in shrinkage.

The commonly employed techniques of flexural loading that are used in the study of mechanical properties may be conveniently employed for the classification of materials with respect to predisposition to strain. Due to the complex stress-deformed state which is realized in this case, however, these techniques have not found use in simulation of strain. High-temperature compression tests of cylindrical samples are now generally conducted to determine the rheological parameters of models. Truton or uniaxial viscosity and the viscous Poisson coefficient or shear and bulk viscosity are calculated from the measured longitudinal and transverse dimensions of a sample in the course of roasting in constant discontinuous or cyclic loading [2]. The latter two parameters are generally found in modern models [3], hence one of the drawbacks of compressive or tensile testing is related to the need to convert uniaxial strain to shear strain, which for materials with complex structure leads to inaccuracies in the determination of these parameters. For example, dilatancy or asymmetry of the behavior of a material is not taken into account in tension and compression. On the other hand, it is extremely important to take this difference into account when simulating complexly shaped articles, since both shear strain and tensile strain may be dominant in different elements of the particular article (for example, in the handle of a semi-finished teapot).

Another major drawback associated with the use of methods of studying rheological behavior in the compression of a sample is the mutual influence of shrinkage and strain caused by an externally applied load, a factor that is not amenable to analysis. Since this effect may be significant [2], it is necessary to determine separately the load strain and the strain induced by sintering of the material (shrinkage) by means of direct methods. With such an approach it becomes possible to perform torsion tests of one end of a sample relative to the other. In the 1950s such tests were performed quite often for purposes of phenomenological analysis and estimation of the predisposition of comparable materials to strain. The samples were fabricated in the form of bars and full-body cylinders (E. Keller, 1939) or the actual shape of the samples was not specified [4].

Torsion load tests of ceramic materials are now performed only rarely as they are difficult to implement. Meanwhile, in the case of porous semifinished articles (sintered materials), rheological data may be obtained by means of such tests directly with the use of simple shear without the superposition of strain associated with shrinkage. In view of the active development of computer hardware that implement the method of finite-element simulation, the implementation of methods for the investigation of strain based on torsion of samples has grown significantly in recent decades.

PLANT FOR TESTING SAMPLES

The high-temperature features of the behavior and properties of sintered glass-ceramic materials were incorporated into the conceptual foundation of the method used to mount the samples to be subjected to torsion that was developed by the present authors. The method assured reliable operation of the plant used for rheological study of roasted semifinished articles in simple shear and in shear associated with axial strain induced by additionally applied compressive or tensile stresses. A schematic diagram of the plant is shown in Fig. 1. Its basic functional elements comprise two mechanisms for clamping the sample and corresponding systems of measurement of strain, a film editor, electric furnace, and furnace temperature regulator.

The clamping mechanism, which is intended for torsion loading of a sample *1*, comprises a shaft *3* mounted on rolling bearing *2* with disks that specify the arm *R* of application of the load force *4*; a ceramic tube (holder) *5* linked to the shaft *3* by a regulating flange assembly *6* by means of which the opposite end of the tube *5* may be adjusted for coaxial rotation. The mechanism used to clamp the sample, which serves to limit the freedom of displacement by translational motion, is mounted on guide rails by means of wheels *7*. The ceramic tube (holder) *8* transmits a compressive or tensile load specified by the load *9* to the sample by means of winches. Openings for feeding the tubes *5* and *8* are located in two of the walls of the chamber-type furnace *10*. Heating of the furnace is realized by means of silicon-carbide heaters *11*. Strain is read off relative to scales *12* and *13* with respect to the turning angle of arrows mounted on corresponding elements of the holders. The working part of the sample *1* is in the form of a small round tube (cf. Fig. 1*b*) that fits smoothly into the large-diameter bulging ends to prevent their deformation. The ends are supplied with openings for refractory ceramic dowels *14* which are situated in a criss-cross arrangement. When the furnace is functioning the metallic regulatory assembly *6* and metallic screws *15* remain practically unheated; the holders *5* and *8* and the dowels *14* are made of tightly caked corundum ceramic.

The use of the plant presupposes the availability of data on strain as a function of the specified stresses. The plant is designed for a static type of application of stresses. Torsional strain, moreover, corresponds to shear stress (tangential stress σ_{12}), developed by the moment of force *M* in the working section of the sample. Tensile and compressive strain corresponds to axial stress σ_{11}. Thus, a plane stressed state is realized in the sample in the case where tangential and axial stresses are simultaneously specified.

PREPARATION OF SAMPLES AND TEST CONDITIONS

Commonly used types of porcelain (household and sanitary porcelain) and semiporcelain, strain in which reaches

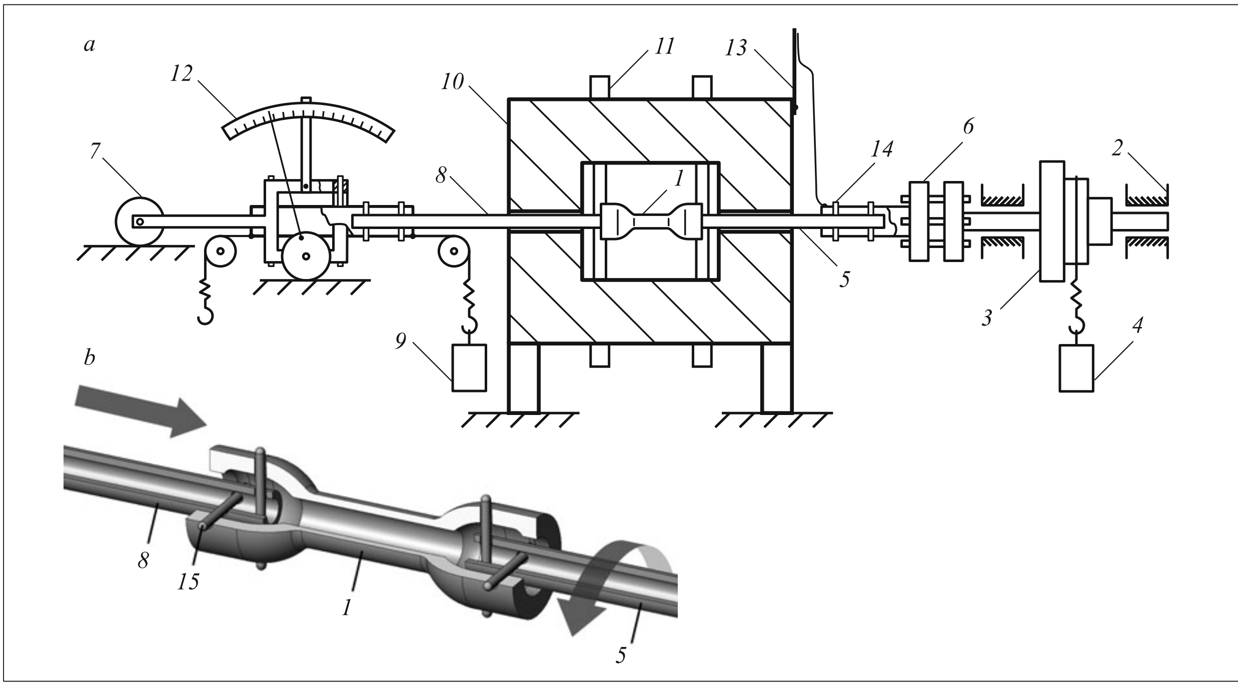

Fig. 1. Schematic diagram of plant (*a*) and mold and method of mounting of the sample (*b*).

significant levels in the course of roasting and is determined by processes of liquid-phase sintering and crystallization, were selected for study. Different types of complexly shaped articles (primarily vessels) and large articles (sanitary porcelain) were fabricated from these materials. High-density lithium aluminosilicate glass ceramic typical of electronic devices and used in large, complexly shaped articles were selected as the material with this type of glass-ceramic structure.

The samples were fabricated by means of overflow slip casting in gypsum molds made of porcelain, semiporcelain dross, and from highly concentrated aqueous slip based on lithium aluminosilicate glass. Each sample consisted of three parts (cf. Fig. 1), a working or middle part, and two adjustable parts. The working cylindrical part (25 – 35 mm in length) is molded with thickness of the wall around 2.5 mm, or one-third to one-half the thickness of the adjustable parts. The molded parts were glued together to overlap each other with the use of the same slip. Following drying, openings for the dowels were drilled in the adjustable parts. Moreover, sample tubes (~20 mm in length) were created from the remaining part of each billet to monitor free shrinkage in the course of roasting. The samples of semiporcelain and porcelain were preliminarily roasted according to the following regime: heating from room temperature to 900°C at a rate of 10°C/min, holding for 30 min at 900°C, and cooling together with the furnace.

The control samples were placed in direct proximity to the working part of samples that had been situated in the plant for torsion testing. A thermocouple is situated in such a way that its hot junction is inside the working part of the samples. A mechanical load is set next to the sample before the furnace is switched on and is removed after the end of the experiment from the cooled furnace. Experiments that differ in terms of the complexity of the stress state (simple torsion, simultaneous torsion and tension, and simultaneous torsion and compression) are conducted. The tests are performed in the following roasting regimes. For samples of semiporcelain and household and sanitary porcelain: heating to a temperature of 890°C at a rate of 10°/min, then to 1300°C (1350°C for household porcelain) at a rate of 2°C/min, cooling together with the furnace; and for samples of glass ceramic: heating to a temperature of 750°C at a rate of 10°C/min, then to 1270°C at a rate of 2°C/min, and cooling together with the furnace.

SIMPLE TORSION

The following formula, which was derived on the basis of Newton's law for viscous flow, was used to calculate the viscosity η from the results of tests of the tubular samples (Fig. 2):

$$\eta = \frac{4mgRx}{\pi(d^3 z - 3d^2 z^2 + 3dz^3 - z^4)} \frac{\Delta t}{\Delta W} \ (z \ll d), \qquad (1)$$

where m is the mass of the load (including the mass of the cable and the elements of the mounting); g, free-fall acceleration, $g = 9.82$ m/s^2; R, arm of application of load; x, z, and d, length and thickness of wall and outer diameter of tube (x, d, and z are determined by shrinkage in the course of roasting);

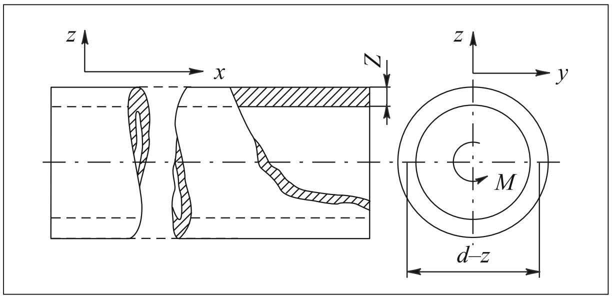

Fig. 2. Notation for dimensions of working part of sample.

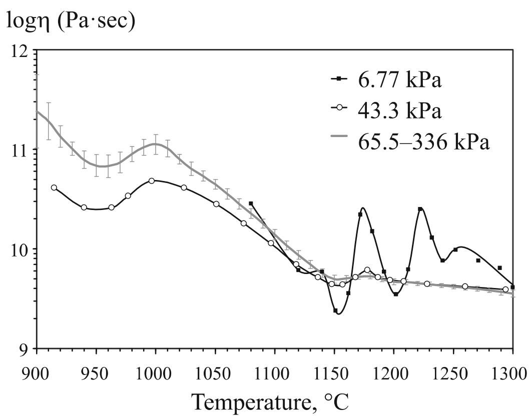

Fig. 3. Temperature dependence of logarithm of shear viscosity logη from results of experiments on torsion of thin-walled tubes of semiporcelain preliminarily heated to 900°C for different applied shear stresses (rate of heating 2°C/min, error bands calculated for a 0.99 confidence level.

Δt, time increment; and ΔW, angle of rotation of one end of the tube relative to the other, degrees.

Free shrinkage was calculated from the dimensions of the control samples measured before and after a test. This type of measurement of shrinkage free of externally applied stresses is more appropriate than with the use of contact dilatometers, as results from the use of such devices are affected by the pressure on the sample exerted by the clamping measurement system and the limited shrinkage at the end-faces of the sample [5]. The shrinkage produced by a load was similarly determined for the case of torsion from the dimensions of the samples. The results demonstrated that in samples made of materials belonging to the porcelain group, shrinkage along the shear axis (along the diameter of the sample) increased only slightly with an increase in the applied tangential stress and did not exert any effect on shrinkage along the other axes.

Significant shrinkage anisotropy was discovered. Samples that had been fabricated from different materials belonging to the porcelain group exhibited practically no difference in terms of magnitude of anisotropy. For a thin-walled cylindrical sample, shrinkage was ordered in terms of growth in the following sequence: along the axis (10%) < along the diameter (11%) < edgewise (16%). The greater edgewise shrinkage was a consequence of the anisotropy of the structure of the semifinished article caused by the morphological features of the particles of the raw material in the course of slip casting. Shrinkage anisotropy was not detected in the case of glass ceramic.

A significant difference (>30% for semiporcelain) was established between the viscosity calculated taking into account shrinkage of the sample and the viscosity obtained under the assumption that the dimensions of the sample remains constant, hence in calculating the viscosity, shrinkage of the sample in the course of roasting was taken into account. Functions that describe the dependence of the dimensions of the sample *l*, *d,* and *z*, on temperature used in calculating the viscosity were represented as regressions (polynomials) of dilatometric curves calibrated with respect to the ultimate shrinkages of freely sintered control samples.

Materials of the Porcelain Group

Despite the different compositions, it would appear that the rheology of household and sanitary porcelain and semiporcelain does not exhibit substantial differences and the graphs presented below, which characterize the rheology of semiporcelain in the course of roasting, may be considered typical for semifinished articles belonging to the porcelain group.

Graphic dependences of the viscosity of samples of semiporcelain on temperature, expressed in terms of semilogarithmic coordinates (Fig. 3), are similar to those presented previously for refractory clay [1]. More informative data on the viscosity of semiporcelain are shown in the form of a surface in Fig. 4.

It was established that in the range 910 – 960°C, stresses in the range 9.41 – 43.3 kPa exert no influence on viscosity. For the range 65.5 – 336 kPa, the viscosity curves exhibit slight statistical-type mutual deviations over the entire range of temperatures. A common graph with error bands for a 0.99 confidence level (cf. Fig. 3) was obtained after the curves had been processed by statistical methods. The presence of clear-cut viscosity minima at roughly 955 and 1133°C and viscosity maxima at 1000 and 1175°C is apparent for this graph. Analogous extrema are generally related to the start, respectively end of the evolution of the crystalline phases [4]. The viscosity graph has two well-formed descending rectilinear segments, a low-temperature segment in the region 1010 – 1145°C and a high-temperature segment in the region 1180 – 1300°C. In the region 1140 – 1300°C low stresses exert a greater influence on the viscosity and two pairs of minimum and maximum magnitudes at 1125 and 1137°C and at 1200 and 1223°C, respectively, are characteristic of these low stresses. A general trend to attenuation of the influence of stresses on viscosity as the temperature of 1300°C is approached is apparent. The temperature dependences of the viscosity of samples of sanitary and

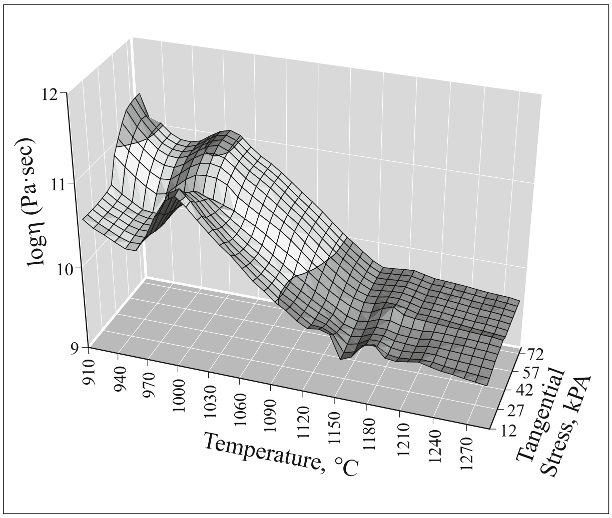

Fig. 4. Interpolated surface logη (in simple shear) from results of experiments on torsion of thin-walled tubes of porcelain preliminarily roasted at 900°C (rate of heating 2°C/min).

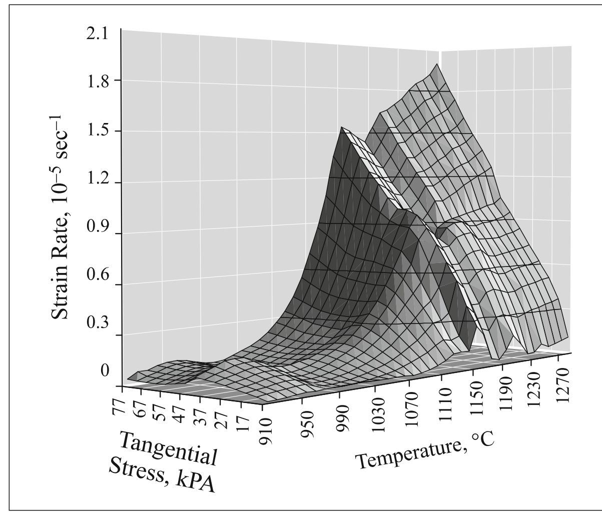

Fig. 5. Interpolated flow surface (in simple shear) from results of experiments on torsion of thin-walled tubes of semiporcelain preliminarily roasted at 900°C (rate of heating 2°C/min).

household porcelain exhibit a clear analogy to the viscosity graphs of semiporcelain. However, the viscosity graphs of samples of sanitary porcelain are distinguished by the absence of any clearly expressed viscosity maxima at low stresses. It may be suggested that the yield strength for household porcelain is below that for semiporcelain.

The series of curves presented in Fig. 5 in the form of a yield surface was calculated from a file of viscosity data for samples of semiporcelain. The curves that express the stress – strain rate dependence exhibit ascending rectilinear segments in the ranges of stresses 14 – 38 and 66 – 336 kPa. Extrapolation of the first rectilinear segments at 910 – 950°C yields a vanishing point roughly at the coordinate origin, and at temperatures from 960 to 1130°C, a conditional (static) yield strength with dominant values 2 – 6 kPa and maximum 10 kPa at 1000°C. The presence of yield strength is confirmed by the complete absence of strain (torsion) of the sample under a load of 6.77 kPa up to a temperature of 1080°C. Extrapolation of the second rectilinear segments yields a vanishing point at the coordinate origin for all the (temperature) graphs.

The curvilinear segment of the strain rate curves in the range of stresses from 34 – 43 up to 48 – 65 kPa attest to the presence of two flow mechanisms, where a change occurs from one to the other as a function of the applied stress and not on temperature. With increasing temperature the difference between the two strain mechanisms levels off, as is attested to by the fact that the slopes of both rectilinear segments tends to the same magnitude.

An extrapolation of one of the typical shear rate graphs obtained is presented in Fig. 6 (a typical curve for a solid-phase structured system is shown for comparison). Systems with analogous flow type may be encountered in the studies published by Yu. Ye. Pivinskii [6], for example, for a suspension of TiO_2 in white alcohol, though a complete qualitative correspondence is not found in the scientific literature. In Fig. 6 the segment in the range of stresses 14 – 38 kPa is approximated quite accurately by a straight line that passes through the coordinate origin. Therefore, the existence of minimum Newtonian viscosity on this interval may henceforth be assumed. The perpendicular to the horizontal axis dropped from the first point of the curve (which is justified by the established presence of limiting stresses) supplies the magnitude of the yield strength. The provisional nature of this degree of yield strength (the presence of regions of creepage may be attributed to such yield strength) should be noted in a rigorous interpretation. Following the rectilinear segment the sharp downward bend in the curve attests to the development of dilatant behavior in the system (in the range 40 – 60 kPa), which is replaced with increasing stress by Newtonian flow with maximum viscosity. Moreover, in the interval of stresses 30 – 60 kPa and of temperatures

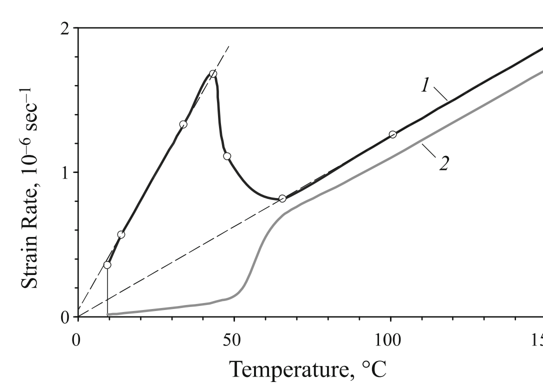

Fig. 6. Extrapolation of flow curve (*1*) at 940°C from results of experiments on torsion of thin-walled tubes of semiporcelain preliminarily roasted at 900°C (see text for explanation) and comparison with the model flow curve (*2*) for a solid-phase structured material.

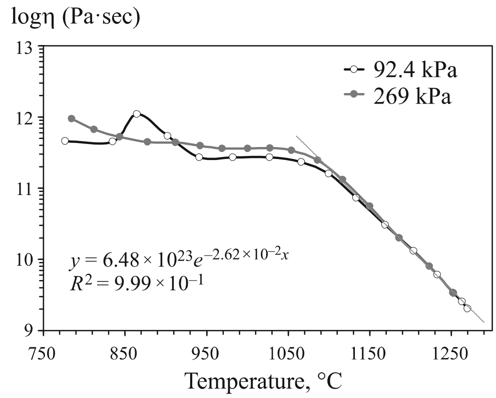

Fig. 7. Temperature dependence of logη in simple shear, constructed from the results of experiments on torsion of thin-walled tubes of semifinished glass ceramic articles and their approximation (1100 – 1270°C) by an exponential function (y, viscosity, Pa·sec, x, temperature, °C; R^2, reliability of approximation).

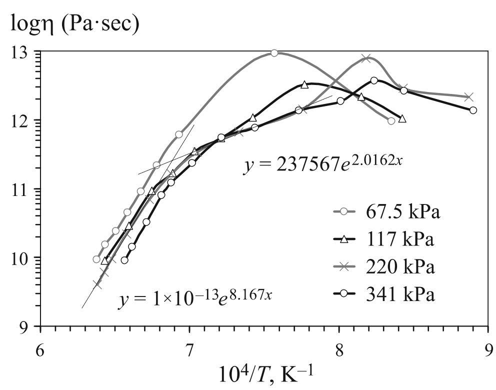

Fig. 8. Temperature dependences of logη in simple shear constructed from results of experiments on torsion of sintered thin-walled tubes of semiporcelain.

1040 – 1100°C there also exists a type of dilatant flow in which viscosity varies in direct proportional to stress and, consequently, the strain rate remains constant.

Thus, four characteristic stress intervals may be identified: critically low (<10 kPa), low (10 – 35 kPa), and intermediate and high (50 kPa).

Semifinished Glass Ceramic Articles

The rheological behavior of semifinished lithium aluminosilicate glass ceramic upon heating differs substantially from that of semifinished porcelain articles. Segments of each of the temperature curves of the viscosity logarithm that are shown in Fig. 7 and that are calculated from the results of torsion tests may be approximated by two sloping lines. Moreover, the high-temperature segments (from 1100 to 1270°C) of both curves coincide in a single straight line, whereas the low-temperature segments differ (their approximation is not shown in Fig. 7). An exponential equation that reflects Newtonian flow of the material in the high-temperature interval is given in Fig. 7. At the intersection of the two lines in the region near 1000°C, the dominant strain mechanism changes. The sharp rise in viscosity at 850°C (cf. Fig. 7) corresponding to the low test stress is probably associated with processes of crystallization. The most intensive shrinkage is observed in the range 1150 – 1270°C; above 1270°C expansion of the material occurs as a consequence of overburning.

Samples of Sintered Semiporcelain

Torsion tests in the same roasting regime were conducted with sintered samples of semiporcelain that had already been subjected to torsion under a tangential stress of 110 kPa. The graphs describing the dependence of the viscosity logarithm on inverse temperature shown in Fig. 8 all have a single maximum at relatively low temperatures along with two rectilinear segments.

As the tangential stress is increased from 67.5 to 341 kPa, the viscosity maximum on the curves shifts from 1040°C towards low temperatures down to 940°C. This most likely attests to the fact that the maximum is caused by competition between processes of thermally activated “healing” of microcracks (ascent of viscosity curve) and brittle failure of the microstructure of the material (descent of viscosity curve), the intensity of which also depends on the magnitude of the applied stress. Thus, higher tangential stresses assure early hardening and subsequent dominant failure of the strength relations in the microstructure of porcelain below 940°C. In this case we may speak of complex rheological behavior, the nature of which in the range 940 – 1040°C changes from dilatant to thixotropic. Towards low temperatures starting from the viscosity maximum, processes of hardening dominate failure processes; depending on the attained temperature, the applied stress either amplifies these processes or weakens them.

A more detailed analysis may be performed on the basis of the flow curves shown in Fig. 9. The dependence of the strain rate on tangential stress in the low-temperature region (940°C) characterizes dilatant behavior, while in the region of intermediate temperatures, a behavior that is close to the Bingham model (1010, 1050°C) and dilatant behavior (1110, 1160°C), while in the high-temperature region (1210, 1240, 1270°C), behavior that corresponds to the Shvedov model [7]. Linear extrapolation of the curves to the horizontal axis makes it possible to estimate the yield strength (except for the curve at 940°C). The magnitude of the yield strength decreases from 60 to 40 kPa as the temperature is increased from 1000 to 1300°C. Since it is significantly greater than in preliminary roasting (sintering), the introduction of intermediate cooling stages (until a sufficiently low temperature is reached) into the traditional regime of roasting of materials in the porcelain group could substantially reduce the ultimate strain of the articles.

The rectilinear segments of the viscosity graphs (cf. Fig. 8) were extrapolated by means of exponential functions represented by the Arrhenius equation $\eta = \eta_0 \exp(Q/RT)$ in order to determine the magnitude of the coefficient Q, usually referred to as the apparent activation energy. For the low-temperature and high-temperature segments Q amounted to 2.4 and 9.8 kJ/M, respectively (for 220 kPa). Due to the formation of a rather large quantity of melt in the course of roasting of materials from the porcelain group (roughly 60% of the glass phase is present in the ultimate composition of the material), it is reasonable to compare their rheology to that of glasses. The rectilinear segments of the viscosity graphs, separated by an intermediate region around 1170°C (cf. Fig. 8) are analogous to the corresponding graphs of glasses for a temperature region lying below the glass-transition temperature (for example, the rheology of low-temperature metaphosphate glass with shear viscosity at T_g on the order of 10^8 Pa·sec [8]).

COMBINED TORSION WITH AXIAL TENSION OR COMPRESSION

As a rule, when an article is subjected to roasting the material of the article is in a complexly stressed state. In the case of relatively slight strains under the effect of deadweight, when the nature of the deformation of shape is maintained, the field of stresses may be considered to be locally constant during the roasting process. Thus, the relationship between the principal stresses remains invariant and therefore, according to the classification presented in a previous monograph [9], it may be assumed that the roasted article experiences “simple loading.” It remains for us to determine the mutual influence of the components of the strain rate tensor, which may be a consequence of dilatant behavior, anisotropy developed in the course of strain, asymmetry of the response to tension/compression, etc. For this purpose, the difference between the viscosity obtained in simple shear and the magnitude of the viscosity determined by the same method, but with the added application of an axial tension/compression load, were determined under the assumption that the influence exerted by axial tension on viscosity is different from that of axial compression.

The viscosity graphs constructed from the results of tests of samples of semiporcelain in a complex stress field are shown in Fig. 10 by comparison with the graph of Fig. 3, which was constructed following tests in the absence of any axial load. Torsional stress in tests with added compression or added tension reached 90 kPa, a magnitude that was selected from the range of stresses for which the viscosity graph of Fig. 3 was constructed, while the choice of axial load was limited by possible warping of the sample.

A comparison of the graphs shows that in the range 950 – 1020°C, shear viscosity in the case of added tension (+67 kPa) of the sample is twice as great as viscosity with added compression (–36 kPa). Moreover, the viscosity curve

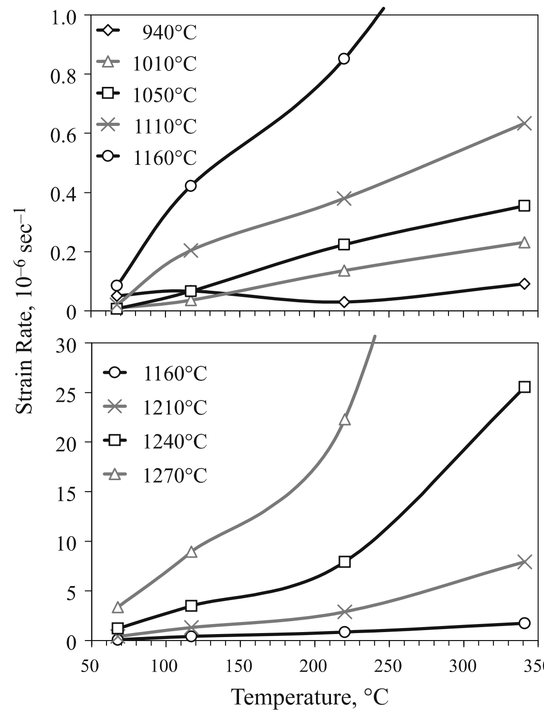

Fig. 9. Flow curves in simple shear constructed from results of experiments on torsion of sintered thin-walled tubes of semiporcelain.

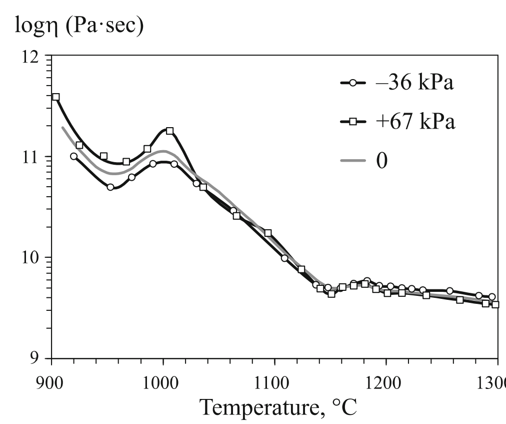

Fig. 10. Temperature dependences of logη constructed from results of experiments on torsion with added axial compression or added tension loading of thin-walled tubes of semiporcelain that have been preliminarily roasted at 900°C (90 kPa torsion loading).

determined without axial loading lies between the two curves characterized by axial stress. Consequently, there exists a qualitative difference in the influence of the nature of an axial load on the torsional viscosity in the given temperature interval. The results show that the proposed method may be used to discover asymmetry in the mechanical response of a material to tension/compression. Above 1020°C the differences between the viscosities are not great and the nature of the graphs is, on the whole, the same. Therefore, it may be

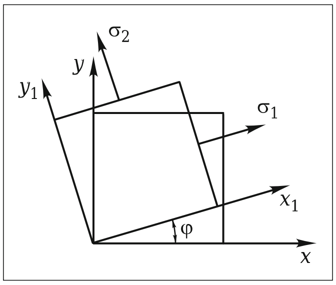

Fig. 11. Position of principal axes of stress tensor relative to axes of sample.

concluded that in the region of high shear stresses (90 kPa), axial loading does not exert any influence on torsional strain of a sample in the temperature range 1030 – 1300°C, whereas strain of a semifinished article of semiporcelain leading to ultimate distortion of its shape obeys the law of Newtonian flow and a single rheological parameter of the material, namely the viscosity coefficient determined in simple shear, is sufficient for arriving at a complete description of the strain.

The direction of the principal axes of the stress (strain) tensor and the maximal tangential stress τ_{max} were determined in order to arrive at an exact representation of the stress state of the material of a sample in combined torsional loading and application of an axial load; note that in the present case τ_{max} is not equal to the torsional stress ("simple" shear) σ_{12}.

Let us consider development of a thin-walled tube into a plane (Fig. 11). Suppose that one axis of the stress tensor is directed along the *z*-axis (edgewise) while the other two axes (x_1 and y_1) lie in the plane of development of the tube. Then it is only necessary to find the angle φ between axis x_1 and the *x*-axis of the tube. Here the angle between axis y_1 and the axis *x* of the tube will be $\varphi + \pi/2$. The angle φ and the maximum tangential stress are determined from the formulas [6]

$$\tan 2\varphi = \frac{2\sigma_{12}}{\sigma_{11}}, \quad (2)$$

$$\tau_{max} = \frac{1}{2}\sqrt{\sigma_{11}^2 + 4\sigma_{12}^2}. \quad (3)$$

Thus, for –36 kPa and φ = –39°, the maximum tangential stress amounts to 92 kPa. For 67 kPa and φ = 35° the maximum tangential stress will be 96 kPa. In simple torsion of a thin-walled cylindrical sample the shear plane is perpendicular to its axis (*x*) while the angle φ = ±45°. Upon application of an axial load of –36 kPa or 67 kPa (in addition to a torsional stress of 90 kPa), the shear plane deviates in modulus from the perpendicular position by 6 and 10°, respectively.

CONCLUSION

Through the use of the proposed method of application of torsion to thin-walled tubes it becomes possible to investigate at the necessary theoretical level the rheology of materials that become self-sealing when subjected to high-temperature treatment. In particular, with the use of the method it becomes possible to determine the mutual influence of the components of the strain rate tensor, which may be a consequence of dilatant behavior, anisotropy that has developed in the course of strain, asymmetry of the mechanical response of the material to tension/compression, etc. The computational basis of the method derives from formulas for determining the viscosity and shear modulus that are easy to use in practical applications.

Substantial anisotropy of the ultimate shrinkage as a consequence of the technology employed in molding is characteristic of samples that have been fabricated from slip with a significant fraction of asymmetric particles (in the form of flakes). For samples consisting of isometric particles, no shrinkage anisotropy is observed. The ultimate shrinkage (irrespective of the initial structure of the material) is practically independent of the applied tangential stress (strain and rate of shearing strain). Four temperature domains of roasting of semifinished articles belonging to the porcelain group in which the samples exhibited distinct rheological behavior were determined: 955 – 1000°C, 1125 – 1137°C, 1153 – 1175°C, and 1200 – 1223°C.

The existence of four characteristic stress intervals was established for these materials: a domain of critically low stresses (up to 10 kPa), a domain of low stresses (10 – 35 kPa), and a domain of intermediate and high stresses (50 – 300 kPa and higher). The domain of critically low stresses is bounded above by the magnitude of the discovered yield strength, which reaches a maximum at 1000°C. This domain is characterized by high slope of the viscosity extrema as a function of temperature. In the low-stress domain there exists flow with minimum Newtonian viscosity. The rheology of the material in the domain of intermediate stresses is determined by dilatant behavior. The domain of high stresses is characterized by flow with maximum Newtonian viscosity.

The results of tests of the samples in the complex stress field showed that in the range 950 – 1010°C additionally applied axial tensile stress increases the effective torsional viscosity of semiporcelain while at the same time the analogous shear stress decreases it. In the region of high stresses, axial loading does not have any effect on torsional strain of the sample in the temperature interval 1030 – 1300°C.

We may suppose that a single rheological parameter of the material — the viscosity coefficient determined in simple shear — is sufficient for calculating the residual strain of semiporcelain. Up to 1050°C strain of semifinished articles is relatively low and simplified calculations may be applicable here. The required temperature dependence of viscosity (for stresses >15 kPa) may be represented by only two exponential functions that reflect segments that are rectilinear in viscosity graphs expressed in terms of semilogarithmic coordinates.

Among the distinctive features of the rheology of sintered samples of semiporcelain may be cited the elevated yield strength, a transitional region of behavior around 1170°C, and a viscosity maximum at relatively low temperatures. Models that take into account the existence of substantial yield strength and the phenomenon of dilatancy must be used to describe the rheological behavior of sintered semiporcelain at high temperatures. Newtonian flow of the material at temperatures from 1100 to 1270°C has been established for semifinished articles fabricated from highly concentrated aqueous slip based on lithium aluminosilicate glass. The rheology of such articles in the course of roasting may be represented by means of two exponential equations.

REFERENCES

1. T. Kraft, H. Reidel, R. Raether, and F. Becker, "Simulation des Brennprozesses bei der Herstellung von Gebrauchskeramiken," *Keramische Zeitschrift*, **54**, 374 – 381 (2002).
2. P. Z. Cai, G. L. Messing, and D. J. Green, "Determination of the mechanical response of sintering compacts by cyclic loading dilatometry," *J. Amer. Ceram. Soc.*, **80**(2), 445 – 452 (1997).
3. E. A. Olevsky, "Theory of sintering: from discrete to continuum," *Mater. Sci. Eng.*, **R 23**, 41 – 100 (1998).
4. V. F. Pavlov, "The connection between viscosity and the physical-chemical processes occurring during refiring of refractory clays," *Refractories and Household Ceramics*, **3**(5/6), 179 – 181 (1962).
5. A. Mohanram, S.-H. Lee, G. L. Messing, et al., "A novel use of constrained sintering to determine the viscous Poisson's ratio of densifying materials," *Acta Materialia*, No. 53, 2413 – 2418 (2005).
6. Yu. E. Pivinskii, *Theoretical Aspects of Ceramic and Refractories Technology. Selected Studies* [in Russian], Vol. 1, Stroiizdat, St. Petersburg (2003), 544 pp.
7. K. K. Strelov, *Theoretical Foundations of the Technology of Refractory Materials* [in Russian], Metallurgiya, Moscow (1985), 480 pp.
8. H. Takahashi and Y. Hiki, "Study on the shear viscosity of several inorganic glasses," *J. Applied Physics*, **84**(1), 213 – 218 (1998).
9. A. A. Il'yushin, *Plasticity. Part One. Plastoelastic Strain* [in Russian], OGIZ, Moscow (1948), 378 pp.