of the thermal stresses, the determination of the temperature conductivity, and the determination of the moment of destruction of the specimen were all carried out with the complex. Using the variation in the temperatures between the internal and the external surfaces of the specimens at this moment we assessed the thermal-shock resistance of the materials under investigation. For specimens made from materials No. 3 this value was 785°C, and for No. 2 it was 825°C, which indicates its relatively high thermal-shock resistance. This result is also confirmed by data from research into the deformation of materials shown in Table 1.

Thus, a complex investigation was carried out of the strength crack resistance, and thermal-shock resistance of a number of compositions of cordierite design materials. It was established that cordierite K2, obtained by extrusion from plastic body, in its high coefficient of homogeneitry (m = 22.5) corresponds to metals. It is also explained that all the materials investigated are deformed nonlinearly both at normal and at elevated temperatures.

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DETERMINATION OF THE AMOUNTS OF INSOLUBLE RESIDUE IN FUSED MULLITE

BY THE DIELCOMETRIC METHOD

Yu. K. Shchipalov, A. N. Balyberdin,   UDC 666.762.14.046.512.017:537.72
and S. N. Spektor

Fused mullite, obtained by the induction fusion of a mixture of stoichiometric 3:2 composition from alumina grade G-00 and quartz concentrate, in recent years has been widely used as a refractory filler in the production of high-duty ceramics. The quality factor of the fused product consists of the concentration of insoluble residue which is mullite; this, where possible, contains a low concentration of alumina, which is incapable of reacting with other components. The content of insoluble residue in the fused mullite, depending on the melting schedule, is 93.0-98.5% (residual amount is used up on the glass phase, and, apparently, on the silica that is not capable of reaction). In the production of mullite by the method of arc or induction melting its crystals consist of intergrown, large, long-prismatic formations (in contrast to the needle crystals of mullite in porcelain).

The classical method of determining the amount of insoluble residue in ceramic materials consists in working the powder with particle sizes of 0.15-0.2 mm with 20% solution of HF for 1-4 h at 17-20°C, followed by washing the residue in 7.5% H_2SO_4 in a beaker and heating this mixture to boiling, after which the solution is filtered, and the residue is calcined to constant weight. Also recommended is the treatment of the powdered ceramic material with a mixture of HF and HCl in the ratio 1:1 or 20% solution of NaOH [1, 2]. The use of the classical method of determining the amount of insoluble residue in factory practice leads to more time being spent on each analysis, a substantial acid consumption, and the need to take care with the acids.
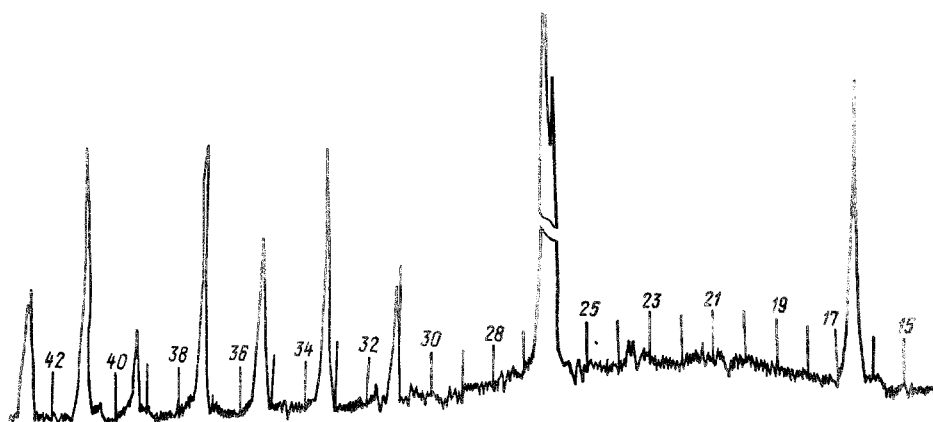
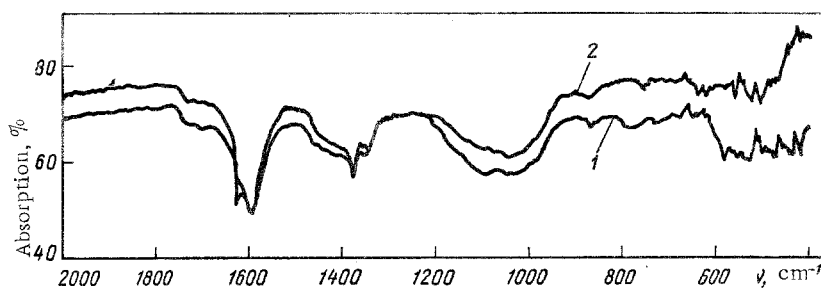Fig. 1. X-ray patterns of mullite (standard).

Fig. 2. Spectrograms of mullite: 1) white mullite; 2) standard.

Papers have been published [3, 4] on the quantitative determination of mullite in porcelain and other ceramic materials by the x-ray method. The essence of the method is that the amount of mullite in the ceramic may be determined in unit proportions or percentages as the ratio of the height or area of the peak that is typical of mullite (or several peaks) on the diffractogram of the material to the height or area of a similar peak (with the same value for the interplanar distance) on the diffractogram of the absolutely pure mullite (standard). In this case, the standard should be prepared from the same batch of material as the powder being studied since it should preserve the morphology of the crystals, their composition, the number of defects, etc. [3]. It is noted that the most objective results are obtained when the particle size of the ceramic powders, subjected to x-ray analysis, is less than 5 µm. The standard is prepared by treating the material with hydrofluoric acid, rubbing the residue in a mortar, and secondary treatment in HF. In some cases these operations are repeated again [3].

However, the height and area of the typical reflexes on the diffractorgrams for the powders are determined not only by the amount of mullite in the ceramic, the dimensions, morphology, and degree of defectiveness of its crystals, but also by the mutual orientation of the powder grains, the coefficient of absorption of the x-rays by the sought-after and accompanying phases, etc. All this means that one and the same powder provides diffractograms different from each other because of the height and area of the typical peaks. Therefore, the most reliable quantitative characteristic of the mullite concentration in the ceramic is the ratio of the arithmetic mean of 10 or more measurements of the height and area of the typical reflex (peak) on the diffractograms of one and the same batch of powder to the height and area of the same reflex on the diffractogram of the standard. This method is very laborious.

Attempts have been made [5] to assess the contents of mullite in aluminosilicate articles by the IR-spectroscopic method (typical absorption band 1145–1178 cm^{-1}). The size of the particles of powder for these purposes should not exceed 2 µm. However, the reproduci-

bility of the results in the analysis is even worse than for the x-ray method. The IR-spectroscopic method is also very laborious.

In this work an attempt was made to find the quantitative relationship between the dielectric constant ε and the tangent of the angle of dielectric loss tan δ of fused mullite and its concentration of insoluble residue, and to use this relationship for practical purposes. The mullite powders from different meltings were analyzed for their contents of insoluble residue by treating them with a mixture of HF and HCl (1:1) using a method recommended by the Ukrainian Scientific-Research Institute of Refractories. In parallel we prepared a standard of insoluble residue (mullite and possible residues of unreacted alumina). The powder of fused mullite rubbed in a metal mortar and passed through mesh No. 008 (5476 apertures/cm^2) was subjected to magnetic treatment in the field of a permanent magnet (to remove the tramp iron), followed by etching in HNO_3 for 1 day, and then treated in hydrofluoric acid. The washed and dried powder was ground three times in an agate mortar, followed by a three-fold treatment in concentrated HF. The total time for treating the powder in HF was 24 h. The washed and dried powder was considered to be 100% insoluble residue. The recording of the diffractograms on the DRON-2 (Fig. 1) equipment and the IR spectra on the SPECORD-751R apparatus (Fig. 2) showed that the insoluble residue is actually pure mullite. Determination of the refractive indices n of the standard by the immersion method yielded a value of 1.655-1.656, which is close to the handbook data for n values of mullite (1.654).

Table 1 presents the results of chemical analysis of fused mullite and the standard. The analysis was done by fusing the powdered material with six times the amount of a mixture of sodium carbonate and potash (in a weight ratio of 1:1) in platinum curcibles at 1000°C for 40 min. The fusion was dissolved in hot water, and then the content of SiO_2 was determined by the gravimetric method, and the Al_2O_3 content by the gravimetric and volumetric methods (trilonometric). From Table 1 it is seen that in terms of composition the fused mullite, like the standard, differs from the original 3:2 stoichiometric mixture (71.8% Al_2O_3 and 28.2% SiO_2).

The powders of fused mullite with a known content of insoluble residue were subsequently used to determine ε' and tan δ' (apparent dielectric permeability and apparent tangent of the angle of dielectric loss of the heterogenous system solid phase—air). In [6] it is shown that with powder particle sizes of less than 0.25 mm the values of ε' become stable and do not depend on the amount of air in it. The powders of fused mullite passed through mesh No. 008 were poured into a cell consisting of a flat condenser with round copper electrodes fitted into a chuck made from plastic. The dielectric characteristics ε' and tan δ' were calculated from the equations

$$\varepsilon' = 144 \cdot 10^9 \frac{(C_1 - C_2) h}{d^2},$$

$$\tan \delta' = \frac{(Q_1 - Q_2)(C_1 + C_2)}{(C_1 - C_2) Q_1 Q_2},$$

where d and h are respectively the diameter of the electrodes of the condenser and the size of the gap between them, m; C_1 and Q_1 represent the capacitance of the condenser Φ and the quality of the contour with the condenser between whose electrodes air is located; C_2 and Q_2 represent the capacitance of the condenser Φ and the quality of the contour with the condenser between whose electrodes the powder being studied is located.
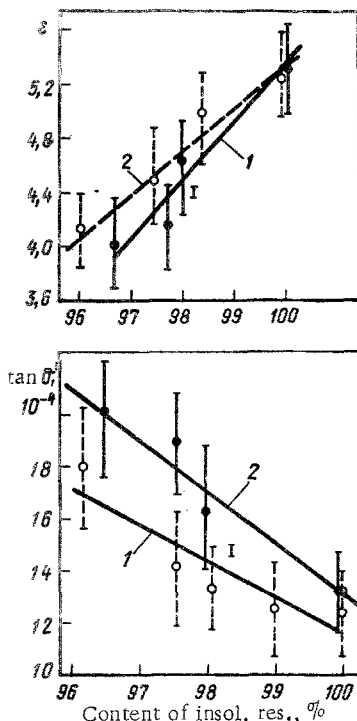
Fig. 3. Relationships between ε' and tan δ' and
the amount of insoluble residue in the mullite:
1) gray mullite taken from the starter region of
the casting; 2) white mullite.

The readings of the capacitance and the quality of the contour were taken on the quality
meter VM-560 with an electric field current of v = 100 kHz-10 MHz. Experiments showed that
the value of ε' does not strongly depend on the field frequency, and comes within the range
1.29-1.41, so it is quite adequate to determine ε' and tan δ' with a frequency of 1 MHz.

A nomogram exists [6] from which the values of the apparent dielectric permeability ε'
and the volume fraction V_S of the solid phase in the powder can be used to determine the
value of the true dielectric permeability ε, and moreover ε = kε', where k depends on V_S;

$$V_S = \frac{m}{\frac{\varrho}{Sh}};$$ m is the mass of powder in the cell of the condenser; ρ is the density of the solid

phase (fused mullite); Sh is the volume of the cell (S is the area of the electrodes; and
h is the distance between them).

Furthermore, the value of k can be found, knowing the value of the true ε for the speci-
fied dielectric (e.g., corundum or β-quartz) and by determining the value of ε' for this di-
electric by the stated method with the same degree of dispersion. Then $k = \varepsilon_{SiO_2}/\varepsilon'_{SiO_2}$.
In our case the value of k found in this way proved to be equal to 2.98.

The pouring of the powder into the condenser and the measurement of the capacitance of
the condenser and the quality of the contour on the quality meter VM-560 take a period equal
to 5-10 min, which is much less than the time required on the x-ray or IRS apparatus and in-
terpreting the diffractograms and spectrograms.

Figure 3 shows the relationships between ε and tan δ' for fused mullite and the amounts
in them of insoluble residue. Each point on the graphs is the average of six measurements.
As seen from Fig. 3, these relationships, as a first approximation, are linear and can be
expressed by the equations (for white mullite taken from the center of the cast block):

$$\varepsilon = 5.3 - 0.31(100 - K),$$

$$\mathrm{tg}\,\delta' = 13 \cdot 10^{-4} + 2 \cdot 10^{-4}(100 - K),$$

where K is the amount of insoluble residue, %.

Attempts to construct similar relationships with data from the x-ray patterns and IR
spectrometric data did not give the desired results because of the significant spread in
the results obtained.

Obviously, in such a narrow range of concentrations of insoluble residue (95.0-98.5%) these methods cannot ensure the required accuracy in determining the specified factor (K). At the same time, the method of dielcometry is more sensitive to the ratio of crystalline and glassy phases in fused mullite. As Fig. 3 shows, ε falls and tan δ' increases with a reduction in the amount of insoluble residue, which completely agrees with the position confirming the rise in tan δ with increase in the amount of glass phase in the ceramic.

The greatest expenditure of time in determining the amount of insoluble residue in fused mullite by the dielcometric method is taken on constructing the calibration graph (see Fig. 3). In the presence of such relationships the method can be considered to be a rapid method of determining the amount of residue in the mullite in comparison with x-ray and IR methods.

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QUESTION OF DETERMINATION OF THE DISTRIBUTION OF ERRORS IN X-RAY

FLUORESCENT ANALYSIS OF NONMETALLIFEROUS RAW MATERIAL

V. A. Shibanov, N. V. Khlyustov,   UDC 543.42:666.32
and V. D. Konev

X-ray fluorescent methods of analysis of nonmetalliferrous raw materials are finding increasing use since they possess unquestionable advantages over other methods. They are very rapid and possess relative simplicity in their operations in conducting analyses and sufficiently high accuracy and sensitivity. However, the use of the x-ray fluorescent method in determining the components of a raw material with an atomic number of less than 20 is complicated as a result of increased requirements for identity of the analyzed samples with respect to density, dimensions of the particles of the investigated material, and surface quality. In addition, in making measurements in air, which to a significant degree weakens the characteristic radiation of light elements, there is an increase in the requirements for constancy of the geometric parameters of the measurements. There is also an increase in the requirements for stability of the power supply voltages of the x-ray apparatus.

We have conducted investigations on determination of the distribution of errors in x-ray fluorescent analysis of refractory clays for Al_2O_3 content for a BARS-1 crystalless x-ray analyzer.

The total mean-square deviation of the results of observations may be represented in the form

$$S = \sqrt{S_1^2 + S_2^2 + S_3^2 + S_4^2},\tag{1}$$

where S_1, S_2, S_3, and S_4 are the mean-square deviations of the results of observations caused by the random process of interaction of the x-ray radiation with the substance and of recording of the photons of the secondary radiation, the geometric factor of the measurements, the instability of the apparatus, and the method of preparation of the samples, respectively.

Depending upon the method of preparation of the samples the analyzed samples differ in density, surface geometry and surface finish, and dimensions of the material particles. In working with a thick emitting layer [1] a change in the thickness of the irradiated sample does not lead to a change in the intensity of the recorded radiation.