COMBINED THERMAL ANALYSIS OF DISPERSED AND FUSED SUBSTANCES

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A method is described for the combined thermal analysis of dispersed and fused substances in investigating the kinetics of heat- and mass-transfer processes in industrial materials such as glass, ceramics, cement clinker, etc., over a wide range of temperatures (20°–1000°C).

In order to investigate heat- and mass-transfer processes in materials undergoing heat treatment, an apparatus and a technique are necessary for the simultaneous combined determination of the kinetics of change of mass of material, specific heats, and heats of phase transitions, allowing for the physical state of the substance during heating up to 1000° C.

Because we did not have such an apparatus, we undertook the development of equipment by means of which, during heating of a material in the range 20°–1000° C, a simultaneous record could be made on the paper of a recording potentiometer of the following curves: the temperature curve of heating, the variation of the heat flux reaching the specimen from the surrounding medium, the electrical conductivity curve of the material, and the curve of variation of mass of substance during roasting, as well as the curve of rate of heating.

The equipment consisted of five basic units, indicated in Fig. 1 by dotted lines. The main part of the measuring unit was a calorimeter based on the principle of the diathermal shell [1]. It was made of stainless steel, of diameter 80 mm and height 65 mm, and had five cylindrical apertures of diameter 22 mm. In four of the calorimeter apertures diathermal shells were mounted with alumina cement. The shells were turned out of porous ceramic, and had an outside diameter of 20 mm, wall thickness 3 mm, and height 26 mm. On each shell was wound a thermopile consisting of 28 thermoelements of 0.3-mm-diam platinum/platinum-rhodium wire. The shells were protected inside by nickel sleeves of 0.5 mm wall thickness, and the thermopile was insulated by means of mica from the walls of the unit and the sleeve. Above and below the diathermal shells there were thermal-insulating pads to prevent heat reaching the interior of the shell through the end faces. The lower pads were fixed in position, and had platinum/platinum- rhodium thermocouples included in them, the ends of the thermopiles being brought out through the lower pads. For symmetry of heat flux, a similar shell of porous ceramic was mounted in the fifth aperture of the calorimeter, but without a thermopile. Inside two of the diathermal shells the substance being examined was located in nickel crucibles, while there was a reference substance inside the other two. Corundum, which does not undergo phase transitions on being heated to 1000° C, was used as a reference material. The thermopiles of the two shells in which the substance under examination was located, were connected in a differential manner with those of the reference shells (Fig. 2).

This method of correction excludes the effect of temperature fluctuations during the heating of the furnace. The use of two diathermal shells for the test material allows two specimens to be investigated at once. The position of the calorimeter in the furnace is rigidly fixed, by riveting it to the ceramic support.

The unit for carrying out the differential thermal analysis consists of three thermopiles connected in a differential circuit, the thermocouples, and a six-point recording potentiometer, the first and second points of which record the differential curves of heat flux variation, the third the heating rate, and the fourth the heating temperature. The rate of heating is proportional to the temperature drop in the shell with the inert substance [1].

The complex of instruments accomplishing the given heating schedule consists of an automatic electronic program control and setting equipment in an assembly with an electronic control unit (synchronized with the advance) and a single-point EPP-09 potentiometer with a feedback slidewire.

The controlling parameter in our scheme was assumed to be the heating rate. For this purpose the thermopile unit of the fourth shell, connected to the single-point potentiometer of the control instrument complex, was used. The use of the heating rate, which is a derivative of temperature, as the controlling parameter ensured that the given heating schedule was fulfilled to a high degree of accuracy. In this case the control accuracy was considerably greater than that to which the given schedule was reproduced, in terms of the parameter generally used—temperature.

To assess the physical state of the substance, its electrical resistance was measured and automatically recorded. In the electrometric analysis instrument complex there was an automatic recording ac bridge, calibrated in the range of measured resistances, 1–5000 ohm, using four scales (up to 10, 100, 1000, and 5000 ohm), and a PMT-type brush switch for range switching.

The measuring cell (electrodes), located in the crucible with the substance being examined, and inserted in the fifth socket of the unit (without a thermopile), was included in one arm of the bridge. A record of the curve of variation of electrical resistance was made on the bridge paper, and was duplicated by means of the feedback of the fifth point of the six-point recorder. The feedback was accomplished by a slidewire located alongside the scale of the instrument, and a silver contact fastened to the pen carriage of the bridge.

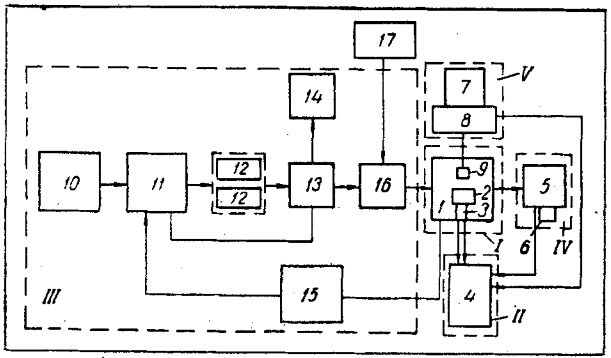

Fig. 1. Block diagram of the equipment: I) Measuring unit; II) instrument recording results of the combined thermal analysis; III) apparatus accomplishing the given heating schedule; IV) apparatus for electrometric analysis; V) equipment for recording change of mass of the substance; 1) electric furnace; 2) calorimeter; 3) ceramic support; 4) six-point automatic recording potentiometer with enhanced sensitivity; 5) automatic recording ac bridge; 6) PMT-type brush panel switch; 7) damped balance in an assembly with automatic recording ac bridge; 8) damped balance; 9) platinum crucible; 10) automatic electronic program control unit; 11) electronic control unit, synchronized with the advance; 12) intermediate relay; 13) operating mechanism; 14) position indicator of the control element; 15) EPP-09 type single-point potentiometer; 16) laboratory autotransformer; 17) voltage stabilizer, type 1834/V, 220/V, 2500 VA.

For automatic recording of the loss of mass during heating, a damped balance was used in the unit with the ac bridge. Two photoresistors, which were included in the bridge arms, were fastened to the pillar of the balance. The bridge slidewire was disconnected. A black flag, glued to the balance indicator, occulted both photoresistors in the equilibrium position. From one pan of the balance was suspended a platinum crucible, lowered into the oven, on a fine platinum wire. To the other pan of the balance was fastened a compensating chain [2], which was joined at its other end, by means of a flexible cable and a pulley system to the sheaf of the reversible motor of the automatic recording bridge. When the equilibrium of the balance is disturbed, an unbalanced voltage arises in the bridge circuit and this leads to motion of the reversible motor. The chain rises (or drops) until the motor stops rotating and the unbalanced voltage equals zero, i.e., the balance reaches equilibrium. The losses in mass of the substance counterbalance part of the weight of the chain. The accuracy of operation of the electronic-mechanical balance corresponds to the accuracy of the damped balance (0.1 mg). While the test is being made, the calibration of the balance may be controlled. In addition to being on the bridge record, the curve of mass loss was reproduced on the six-point recorder (point 6), due to the feedback effected by means of the bridge slidewire.

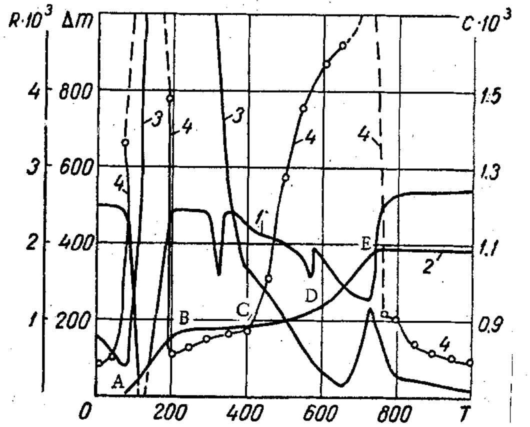

Fig. 3. Curves of combined thermal analysis of a soil-silicate mixture: 1) Thermogram; 2) curve of mass loss; 3) curve of electrical conductivity; 4) curve of variation of specific heat.

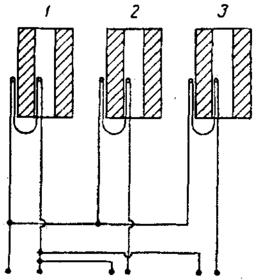

Fig. 2. Differential connection of the diathermal shell thermopiles: 1) diathermal shell with reference material; 2, 3) diathermal shells with material being examined.

In order to bring the temperature of the suspended crucible into line with that in the assembly, a platinum/platinum-rhodium thermocouple was located alongside the crucible. A temperature correction graph was constructed from the readings of the thermocouples in the assembly and in the furnace. The instruments of all units of the equipment received their voltage supply from a 1834/s, 220v, 2500VA type stabilizer.

Measurement of heat flux in the diathermal shell surrounding the specimen, the steady setting of the thermopiles, and the loss from the crucible with the substance being examined, allow a combined thermal analysis to be made for substances passing from a dispersed state to a molten one. To conduct the same investigations with the aid of the commonly used equipment for differential thermographic analysis is a matter of considerable difficulty, since the nature of the differential curves depends on the dispersion and packing density of the specimen and of the reference material, etc. [3]. When fusion occurs the indicated characteristics change, along with the relative position of the substance being examined and the thermocouple junctions. All this leads to a shift of the differential heating curve from its base value.

The appearance of fusion or sintering of the specimen leads to sealing in of the thermocouples and even to their being damaged.

Measurement of the heat flux in the equipment described makes it possible, when the calorimeter has been previously calibrated [1], to carry out quantitative measurements of specific heat and heat of phase transitions of the substance being examined.

Using the laboratory equipment described above, an investigation was conducted of heat- and mass-transfer processes during roasting of a soil-silicate mixture, which is used industrially for making new building materials—soil-silicates [4].

The soil-silicate mixture had the following composition: 3% Na_2O (introduced in the form of $NaNO_3$); 46.5% of medium loam; 46.5% of quartz sand, bonded with 6% of water. From the curve of variation of heat flux reaching the specimen (Fig. 3), it follows that at 130°, 310°, and 573° C, and in the range 600°–730° C, phase transitions occur, accompanied by endothermic effects. The nature of the curve of mass loss of substance indicates that in the range 80°–200° C (section AB) and in the range 600°–730° (section ED), very rapid reduction of the mass of substance occurs. The curve of electrical conductivity characterizes the change of physical state of the substance. Thus, the sharp fall of electrical resistance at 310° C points to the appearance of a liquid phase. A phase transition is also observed in the range 600°–730° C and at 800° C. Comparison of the data obtained allows conclusions to be drawn regarding the heat- and mass-transfer processes occurring in the soil-silicate mixture, which in turn explain the physical and chemical mechanism of the processes of roasting the given materials. For example, the endothermic effect (curve 1) in the range 600°–730°, the very rapid reduction in mass (2), the increase in electrical resistance (3), and of specific heat (4) in this same temperature range point to intensification of the heat- and mass-transfer processes connected with dehydration of the clay particles, a polymorphic transformation of quartz, dissociation of the niter, and the production of new forms.

The example given, and the great number of tests carried out on the equipment described, have enabled us to establish optimum technological conditions and parameters for the production of roasted soil-silicate materials [5, 6].

The equipment described may also be used for investigating heat- and mass-transfer processes occurring in other industrial materials in the temperature range 20°–1000° C.

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