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USE OF METHODS OF THERMAL ANALYSIS IN STUDYING CERAMIC MATERIALS ON THE BASIS OF Al_2O_3, ZrO_2, Si_3N_4, SiC AND INORGANIC BINDER

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Abstract

By thermoanalytical methods TG, DTG, DTA there have been investigated the processes occurring during the formation of ceramic materials on the basis of Al_2O_3, ZrO_2, Si_3N_4, SiC, and inorganic binder. IR spectroscopy has been an additional research method. It's been determined that with the use of H_3PO_4 as the binder for ceramic materials, the mechanisms of thermal decomposition are connected with the following processes: 1. removal of weakly tied and crystallized water in the temperature range of 120–230°C, the removal being characterized by the endothermic effect, 2. interaction of the initial powder components of the ceramic materials with orthophosphoric acid conditioned by a strong exothermic effect on the DTA curve in the range of 230–530°C, 3. overlapping of endo- and exo-effects, testifying to a complex mechanism of thermal transformations, 4. oxidizing of the non-reacted silicon at the temperature of 720(760)°C, an increase of mass is observed on the TG curve as a result of the formation of SiO_2 – crystoballite.

Keywords: ceramic materials, inorganic binders, IR spectroscopy, thermal analysis (TG, DTG, DTA)

Introduction

It is known [1, 2] that the dispersions of some substances in the orthophosphoric acid can form binding systems which are of interest for research and are of practical importance in various domains of material production. Such types of compositions are characterized by new technical properties like high-abrasive firmness, fireproof etc. Phosphate materials are compositions created as a result of the chemical reaction between the hard powdery substance (filler) and, usually, the liquid phosphate binder. Practically, any inorganic substance interacting with phosphate acid can be used as the powdery part of phosphate compositions. However, oxides are used more frequently. Compared to traditional ceramics, a distinctive feature of these materials is that the technology for their obtaining allows to use low temperatures (150–600°C) [3]. Using the data of DTA, IR spectroscopy and as chemical and X-ray phase analy-

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sis, the heat treatment regime for chamotte non-fired articles was chosen. It was shown that the desired strength and water resistance result from aluminophosphates insoluble in water [4]. In the work [5] are given the results of research on creeping in aluminosilicon concretes based on electrocorundum, fine milled alumina, pyrophyillite, and phosphate binders. The research deals with the deformation of concretes as a function of such technological parameters as specific pressure at pressing the temperature of processing, and the test conditions (time, temperature, load).

Investigations related to the thermal analysis of phosphate compositions are of interest since they allow to study not only the thermal properties and transformation of these systems, but also to use the obtained data in the interpretation of various high-temperature processes occurring in these systems, including creeping processes. An attempt to evaluate the structural changes observed in ceramic compositions based on aluminum oxide and phosphate H_3PO_4 at creeping with the used of IR spectroscopy, X-ray diffraction, and petrographic analysis was fulfilled by authors [6].

Aluminum oxide serves as raw material that is most frequently used as initial material for obtaining ceramic compositions. The mechanism of its interaction with orthophosphoric acid is investigated in several works [6–9]. If these data are generalized, then the occurring reactions are, mainly, as follows:

$$Al_2O_3+6H_3PO_4 \xrightarrow{150°C} 2Al(H_2PO_4)_3+3H_2O \tag{1}$$

$$Al(H_2PO_4)_3 \xrightarrow{236°C} AlPO_4{\cdot}xH_2O+2H_3PO_4 \tag{2}$$

Generally speaking, in normal conditions the products of such interaction are acid phosphates or hydrates of medium phosphates. When heated above 100°C, the new formations undergo polycondensation reactions in result of which various types of polymer phosphates are formed, the process being accompanied by the strengthening of the binding component. Data from literature often remind that Al is capable of building different compounds with the phosphate ion depending on the initial concentration of two reagents and pH.

Some authors [8] suggest the idea that the hardening process is due to the following scheme:

$$2Al(H_2PO_4)_3+Al^{3+} \xrightarrow{H_2O} 3AlH_3(PO_4)_2{\cdot}xH_2O+3H^+ \tag{3}$$

The solution of mono-aluminum phosphate is unstable and it can be considered to be an acid salt of aluminum orthophosphate with two molecules of orthophosphate acid:

$$Al(H_2PO_4)_3 \rightarrow AlPO_4{\cdot}2H_3PO_4 \tag{4}$$

According to literature data, at higher temperature the following transformation occurs:

$$\begin{gathered} AlPO_4\ \text{(berlinit)} \xrightarrow{586°C} AlPO_4\ \text{(high temperature berlinit)} \xrightarrow{815°C} \\ AlPO_4\ \text{(trialfit)} \xrightarrow{1065°C} AlPO_4\ \text{(crystobalite)} \qquad (5) \\ 2AlPO_4 \xrightarrow{1300°C} Al_2O_3+P_2O_5 \end{gathered}$$

Investigations related to thermal analysis of phosphate compositions are of interest since they allow to study not only the thermal properties and principles of potential ceramic systems, but also to use the obtained data in the interpretation of various high-temperature processes occurring in them, including the process of high-temperature creeping.

Experimental

Materials

Aluminum oxide Al_2O_3, ZrO_2, Si_3N_4, and SiC have been used as initial materials for obtaining compositional materials on the basis of phosphate bondings. To serve as non-organic bonding, use has been made of phosphoric acid H_3PO_4 (85%). Conditions for conducting the thermoanalytical experiment: freshly prepared solutions of Al_2O_3–P_2O_5 (H_3PO_4), Si_3N_4–P_2O_5 (H_3PO_4), ZrO_2–P_2O_5 (H_3PO_4), SiC–P_2O_5 (H_3PO_4) have been used as samples for thermal analysis.

Methods

TG, DTG and DTA curves in air were obtained by means of derivatograph Q-1500 D (Figs 1–4) and derivatograph OD-103 (MOM) Hungary (Fig. 5). The parameters during the test were as follows; ceramic crucible; inert material aluminum oxide, the sample masses were 1.0 g (Figs 1, 2, 5), 1.390 g (Fig. 3), 0.740 g (Fig. 4); heating rate 10°C min^{-1} (Figs 1, 5), 15°C min^{-1} (Figs 2, 3, 4) and sensitive DTA and DTG 250 and 500 μV respectively. The DTA and temperature measuring thermocouples were made of Pt–Pt/Rh wire. Infrared (IR) absorption spectra of compositions were registered using an UR-20 spectrophotometer (Germany) (Fig. 6). Samples were prepared by grinding in an agate mortar and mixing vaseline oil. The crystal solidification product content was defined on a DRON-3 diffractometer with CoK_α radiation (iron filter).

Results and discussion

Thermoanalytical curves of freshly prepared Al_2O_3–H_3PO_4 composition are given in Fig. 1. It should be noted that the interaction of orthophosphoric acid with aluminum oxide is a complex process which depends on the type of the oxide its own composition, time of interaction and temperature [8–10]. Depending on these on the factors, the reaction products as well as the intermediate stages can be identified. However, it should be noted that the process of fireproof phosphate bindings formation includes the formation of phosphoric acid, which, later on, while heated in the presence of aluminum oxide abundance, react with the oxide and lead to the formation of crystalline and amorphous phosphates.

Stable forms are those that are formed at 300°C. The final form is almost always $AlPO_4$ in its various polymorphous modifications. Such phosphate compositions are obtained on the basis of aluminum oxide and have the shape of bricks and other special forms. They display unusual properties such as fireproof, highly-abrasive strength load proof, stable dimensions, all these making them preferable for various applications. Since the properties of these phosphates are rather close, it is sometimes difficult to identify and distinguish them.

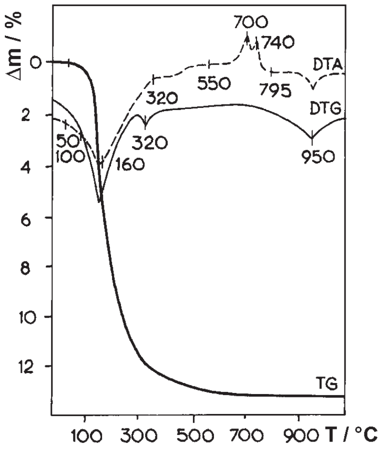

Fig. 1 Thermoanalytical curves of Al_2O_3–P_2O_5 system

The analysis of obtained thermoanalytical curves for the Al_2O_3–H_3PO_4 (Fig. 1) shows the beginning of the loss of the mass as a result of the dehydration of $AlH_3(PO_4)_2{\cdot}H_2O$ formed at the temperature of 50°C. According to [8, 11], during the interaction Al_2O_3, with H_3PO_4, $Al(H_2PO_4)_3$ is initially formed, while during interaction with Al_2O_3 sediment of hydrated phosphate $AlH_3(PO_4)_2{\cdot}xH_2O$ is formed, where x changes from 1 to 3. Probably, first occurs the reaction:

$$AlH_3(PO_4)_2{\cdot}3H_2O \xrightarrow{-2H_2O \text{ at } 80\,^\circ C} AlH_3(PO_4)_2{\cdot}H_2O$$

Later, on DTA there occurs a strong endothermic effect with the minimum at 160°C as a result of reaction:

$$2AlH_3(PO_4)_2{\cdot}H_2O \xrightarrow{-H_2O \text{ at } 160\,^\circ C} Al(H_2PO_4)_3{+}AlPO_4$$

Further, on the DTG curve one can see the decrease of the mass with the minimum at 320°C in result of the following reaction:

$$Al(H_2PO_4)_3 \leftrightarrow AlPO_4{\cdot}xH_2O{+}2H_3PO_4$$

Exothermal effects (Figs 2, 3) at 550, 700, 740, >850, 1230°C are the result of polymorphous transformations:

$$AlH_2P_3O_{10} \xrightarrow{-H_2O} Al(PO_3)_3(B) \xrightarrow{800\,^\circ C} Al(PO_3)_3(A) \rightarrow$$
$$\text{Metaphosphate glass} \xrightarrow{1230\,^\circ C} \text{crystobalite}$$

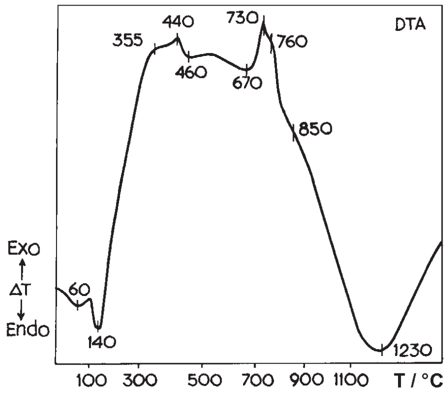

Fig. 2 DTA curve of Al_2O_3–P_2O_5 system

Composition on the basis of ZrO_2

Zirconum dioxide a refractory (2680°C) white substance is used for obtaining fireproof materials of various destination, including perspective phosphate materials. One of the methods for obtaining the $2ZrO_2 \cdot P_2O_5$ composition is the gradual heating and annealing the mixture consisting of a stoichiometric quantity of zirconium dioxide and the solution of ortophosphoric acid. The material for investigations has been obtained by interaction of ZrO_2+H_3PO_4, where ZrP_2O_7 is formed.

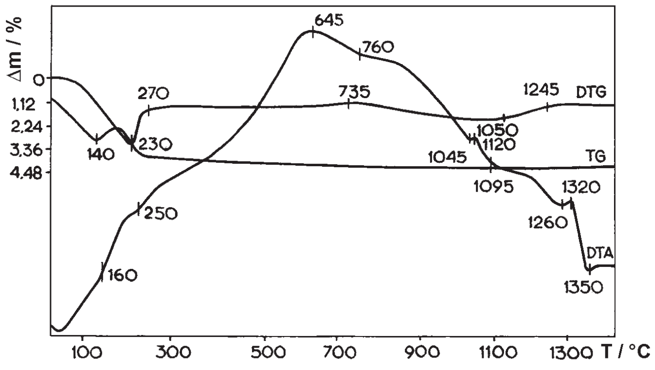

Fig. 3 TG, DTG, DTA curves ZrO_2–P_2O_5 system

Analysis of TG, DTG, DTA curves (Fig. 3) shows the two-stage transformation of two endopeaks at 140 and 230°C with formation of ZrP_2O_7.

The formation of the pyrophosphate is accompanied by the exothermal effect with the maximum at 645°C (DTA curve). Since the zirconium of phosphate materials contains much free zirconium dioxide, the thermal effect at 1050°C (Fig. 3) can be the result of the polymorphous transformation of monoclinic ZrO_2 in tetragonal ZrO_2 [12, 13].

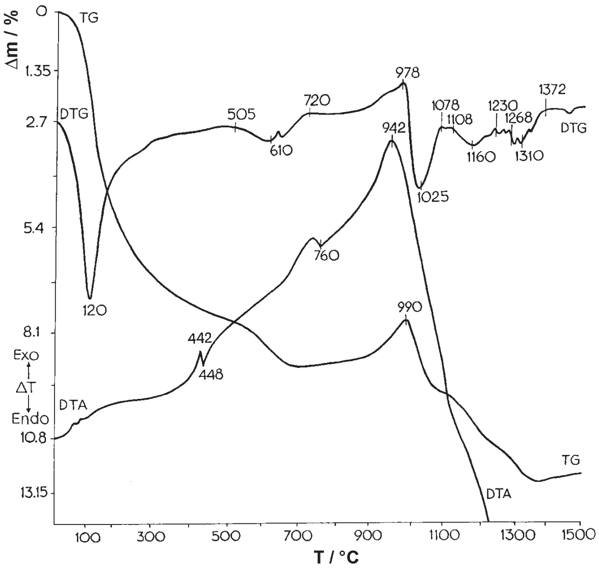

Fig. 4 TG, DTG, DTA of $SiC–H_3PO_4$

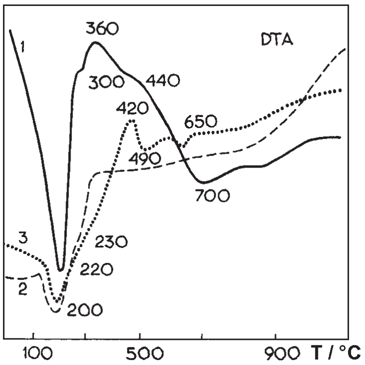

Fig. 5 DTA curves of 1 – $Si_3N_4–H_3PO_4$; 2 – $Si_3N_4–Al_2O_3–H_3PO_4$; 3 – $ZrO_2–H_3PO_4$

The thermal processes of interaction in studying systems $Si_3N_4–H_3PO_4$ (1), $Si_3N_4–Al_2O_3–H_3PO_4$ (2); $ZrO_2–H_3PO_4$ (3); are shown in Fig. 5. We obtain samples applying the method of closing powder with phosphoric acid. By thermal analysis it has been established that when heating the $Si_3N_4+H_3PO_4$ composition there occurs the removal of water and NH_3, this being proved by endothermal effects on DTA at 200°C. Later on the exoeffect is observed at 360°C, which is connected with the interaction of acid with free Si. At temperatures above 700°C one can observe the increase of the mass due to oxidation of non-reacting silicon followed by formation of SiO_2 – crystobalite.

Composition on the basis of SiC

In the initial mixture SiC (85–86%) and the mixture of H_3PO_4, H_2O (other) – at temperature increase within 100–130°C (minimum on DTG 120°C) one can notice a sharp decrease of mass (water evaporation) – endoeffect which immediately turns into a number of exoeffects with peaks on DTA curves at 380, 442, 760 and 942°C which, probably, refer to the process of interaction of SiC with phosphoric acid: the first three effects are the result of mass decrease while the fourth is due to mass increase by about 1% (Fig. 4). It is worth noting here that the mechanism of interaction of $SiC+(H_3PO_4 \rightarrow H_4P_2O_7 \rightarrow HPO_3 \rightarrow P_2O_5)$ and possible intermediate products is much more complicated since the analysis of TG and DTG curves reveals several other processes – at 610, 800, 980, 1025, 1160, 1310°C etc., which are difficult to identify due

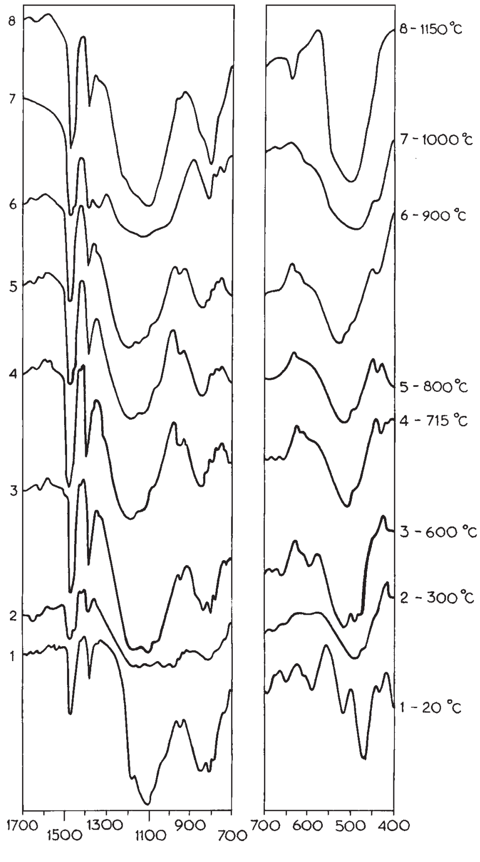

Fig. 6 IR spectra of system SiC–H_3PO_4 (temperature depending)

to overlapping of close endo- and exoeffects. Total decrease of mass up to 1372°C is 13–14%.

From thermogravimetric data it follows that the residual mass after heating up to 1372°C, within the limits of the experiment's error, is equal to the initial mass of SiC. This is also confirmed by the general picture of IR spectra of the initial mixture SiC+(H_3PO_4+H_2O) and of all other samples heated up to 300, 600, 715, 800, 900, 1000 and 1150°C, respectively. These samples still retain the absorption bands related to SiC at 1100, 830, 800, 780, 700, 650, 600, 500 cm^{-1} etc. (Fig. 6).

Thus the investigation of processes of SiC interaction with binding on the basis of phosphoric acid IR spectroscopy and thermogravimetric method, shows that the SiC mass in the initial mixture (with H_3PO_4, H_2O) and after its heating up to 1372°C, is the same – i.e. SiC either doesn't interact with the phosphoric binding at all, or the created intermediate products again turn into SiC at further temperature increase, this being in agreement with author's data [14].

Figure 6 shows IR spectra of SiC+H_3PO_4 samples heated at various temperatures. On their basis one can judge about the structural transformations of the investigated system as a result of heating. The bands in IR spectra of the mixture which are not related to SiC and which gradually vanish when approaching 1000–1200°C, are the bands of the products of transformation $H_3PO_4 \rightarrow H_4P_2O_7 \rightarrow HPO_3$; ν(PO), δ(O–P–O), ν(HOP) etc.

The statement are confirmed by XRD data: on the diffractograms we have noticed the following peaks of α-SiC: 0.282, 0.251, 0.2349, 0.2175, 0.142, 0.1329 (ASTM 11-500). We have also noticed the SiO_2 peaks at 0.424, 0.333, 0.1812 nm. The peaks at 0.199, 0.1329 are related to another form of SiC, which correlates with the result indicated in [15]. The changes observed in IR spectra and in respect to XRD data prove that the impact of temperature leads to phase transformations, to the formation of SiO_2.

The results of scanning electron microscopy investigations are shown in Figs 7 and 8. The microstructure of non-porous part of the composition prior to testing consists of loose crumpled aluminum phosphates. After testing, the structure becomes

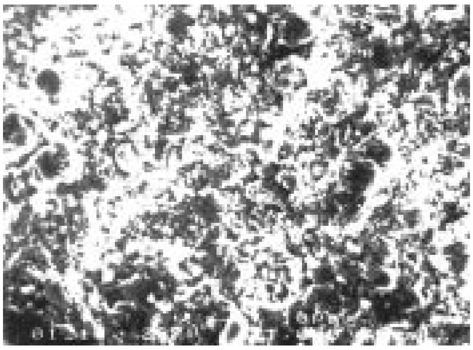

Fig. 7 Scanning electron micrograph of system Si_3N_4–H_3PO_4 after treatment at 300°; ×1000

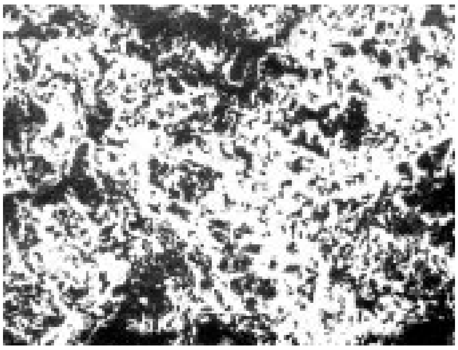

Fig. 8 Scanning electron micrograph of system Si_3N_4–H_3PO_4 after testing for creeping at 1400°C

framed, i.e. more dense than the crumpled one (after 300°C). The element analysis done on the longitudinal and diametrical cross-section of samples, after testing for creeping at 1450°C, 0.2 MPa load and 55 h exposure, has shown the availability at phosphorous migration toward the external surface of the sample.

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