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Composite ZrO_2 fibre-based materials with double ammonium–cobalt and ammonium–magnesium diphosphates

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The mechanism of solid-state interface interaction in systems of pure and stabilized zirconia fibres with ammonium–magnesium and ammonium–cobalt diphosphates has been studied. The investigation conducted makes it possible to control the preparation process of the composites. The optimal composition of dry slip was found to be 70 wt% of fibre and 30 wt% binder. The properties of the developed composite materials are presented.

1. Introduction

Refractory fillers and liquid phosphatic binders, including, for instance, alumophosphatic, alumochromphosphatic and alumoborophosphatic, are widely used for the production of high-temperature composite materials. However, technologically, the use of liquid binders is not always acceptable. For this reason, the production of ceramic composite materials for use as powder dry binders and fillers fabricated from refractory fibrous oxides, seems to be a prospect.

For scientific and practical purposes, it was interesting to investigate the interaction of the reinforcing component (zirconium oxide fibres) with powder phosphatic binders (double ammonium–magnesium and ammonium–cobalt diphosphates). During thermal treatment of such mixtures, gaseous products were evolved, the solid–phase reactions proceeded, compounds were formed, the crystal structure of the compounds changed, and the high-temperature porous ceramic material was prepared.

Previous works [1, 2] dealt with the thermolysis of double ammonium and divalent metal diphosphates. The authors showed that on heating, diphosphates underwent different thermochemical transformations: acidic monophosphates were formed between 350 and 400 °C, but cyclotetraphosphates were formed between 500 and 700 °C. Taking into account the intricacy and the variety of the processes during the preparation of fibre-reinforced ceramics, it was necessary to obtain information about the effect of the reinforcing component on hardening and sintering of the binder, and about their interaction at the phase interface.

The aim of this work was to study the effect of reactive ZrO_2 fibres of monoclinic and tetragonal structure on thermal transformations of powder phosphatic binders when the porous composite ceramic was formed.

2. Experimental procedure

The thermochemical and solid-phase transformations were studied by physicochemical analysis methods in the following systems: ZrO_2 m–$(NH_4)_2CoP_2O_7 \cdot 1.5H_2O$; ZrO_2t–$(NH_4)_2CoP_2O_7 \cdot 1.5H_2O$; ZrO_2 m–$(NH_4)_2MgP_2O_7 \cdot 4H_2O$; ZrO_2t–$(NH_4)_2MgP_2O_7 \cdot 4H_2O$.

2.1. Materials

As shown previously [3], a distinctive feature of fibrous oxides was their high reactivity stipulated by their structure. Their porosity was 70–90%, specific surface 100–150 $m^2 g^{-1}$; fibre diameter 7–9 μm, and grain size of oxide in the fibre 0.01–0.2 μm. The fibres were preliminarily subjected to thermal treatment in air at 900 °C. The tetragonal structure of zirconia fibres was stabilized by introducing additions of 18 mol% Y_2O_3 and 2 mol% MgO [4].

Ammonium-magnesium and ammonium–cobalt diphosphates were crystalline powders of white and pink colour. They contained 4 and 1.5 molecules of crystal water, respectively. They dehydrated on heating and fused at 1382 and 1240 °C, respectively [1].

2.2. Procedure

ZrO_2 fibres were mixed with binders in ratios from 90 : 10 to 50 : 50 wt %. The cylindrical and rectangular samples were pressed at 120 MPa. Half-finished products were annealed in air for 4 h at 100 °C intervals over the temperature range 200–1600 °C when pure zirconia fibres were used and 200–2000 °C when the compositions were reinforced with ZrO_2-stabilized fibres.

2.3. Measurement

The processes of thermal transformations, the structure of compounds and composites were examined on

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thermograph (Firm MOM), a diffractometer DRON-3 (where nickel is the filter, CuK_α radiation), a grating infrared-spectrophotometer (Perkin–Elmer, model 457), and an electron microscope SEM 100U. The strength was measured using an Instron press (Model 1195). M-1195, and the electrophysical characteristics were studied with the standard E-7 type equipment. All-Union state standard techniques were employed to determine the apparent density, porosity, and specific surface.

3. Results and discussion

3.1. Reinforcing component ZrO_2m fibres

According to the results of the thermal analysis obtained during thermal treatment of the compositions with pure zirconia fibres, first, between 140 and 160 °C the binders lost water of crystallization then between 205–215 °C, constitutional water was lost. The endothermic effects (the DTA curves, Fig. 1) corresponded to these processes. Over the temperature range 300–400 °C, the double ammonium–cobalt and ammonium–magnesium diphosphates dissociated to form acidic monophosphates and condensed phosphates in the X-ray amorphous state, the ammonia being evolved at this time. After annealing of compositions between 500 and 600 °C, the magnesium and cobalt diphosphates in the α-form and polyphosphates were formed in the binder (exo-effects in the DTA curves, Fig. 1). In the infrared spectra the absorption bands characteristic of these compounds in the 760–1160 and 1280–1300 cm^{-1} regions appeared (Fig. 2a). At this time, the zirconia fibres did not react. In the temperature range 850–1000 °C, cobalt and magnesium diphosphates were transformed into metal monophosphates, followed by the isolation. The zirconia fibres having a developed surface sorbed the isolated phosphorus oxide and reacted with it, forming zirconyl diphosphate. This process may be written as the total reaction $2ZrO_2 + Co_2P_2O_7 \Rightarrow 2Co_3\ (PO_4)_2 + (ZrO)_2P_2O_7$.

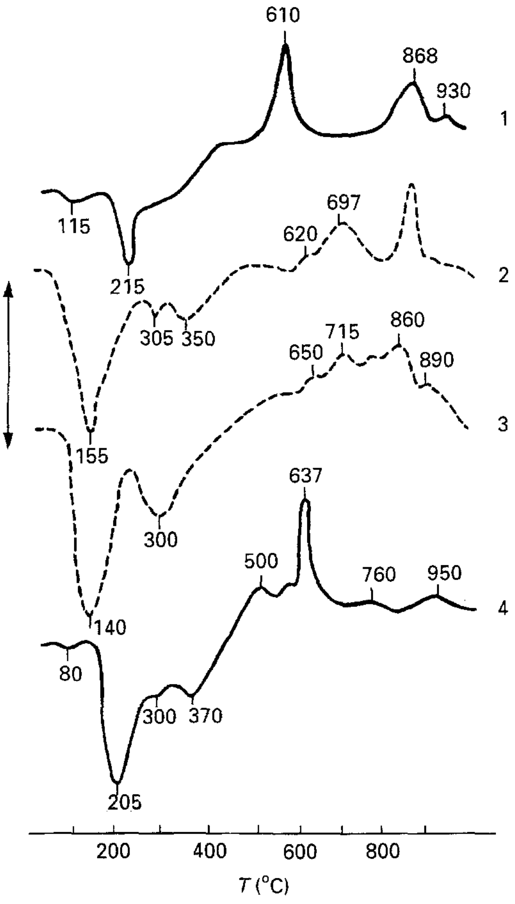

Figure 1 Derivatograms of compositions containing fibres of stabilized (1, 2) and pure (3, 4) ZrO_2 with dry binders (50 : 50 wt %): ammonium-cobalt diphosphate (1, 4) and ammonium–magnesium diphosphate (2, 3). Heated in air, heating rate 10 °C min^{-1}.

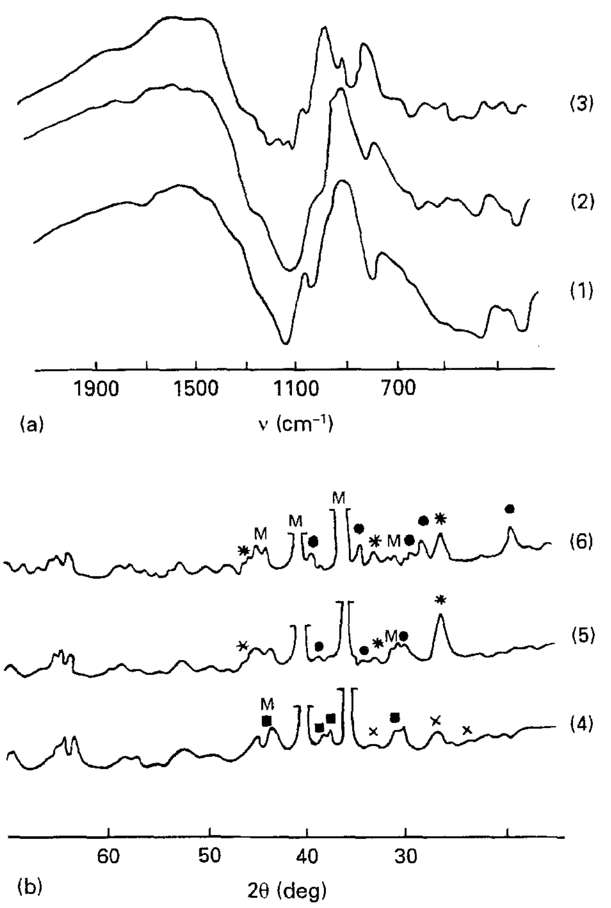

Figure 2 (a) IR spectra and (b) diffractograms of the composite $ZrO_2m + Co(NH_4)_2P_2O_7$ annealed at (1, 4) 600 °C, (2, 5) 900 °C, (3, 6) 1000 °C. (●) $(ZrO)_2P_2O_7$; (■) Co P_2O_7; (x) $Co(PO_3)_2$; (*) $Co_3(PO_4)_2$; M, ZrO_2m.

The formation of a new phase was confirmed by the X-ray phase and IR spectroscopic analyses (Fig. 2a, b).

Similar to this reaction, upon thermal treatment at 1000–1100 °C, the ammonia–magnesium composition contained ZrO_2m, $Mg_3(PO_4)_2$ and $(ZrO)_2P_2O_7$. This composition was preserved up to 1500 °C. As the temperature increased, the magnesium and cobalt monophosphate partially dissociated with the isolation of phosphorus oxide which interacted with free (unreacted) ZrO_2, forming zirconyl diphosphates on their surface. The interaction strengthened contact between the fibres and binders.

According to published data [1], magnesium and cobalt monophosphates fused at 1357 and 1160 °C, respectively. From the electron microscopic data it was seen that the binder did not fuse in the compositions. Particles of the cobalt monophosphate powder covering ZrO_2 fibres fused partially between 950 and 1000 °C and of the magnesium monophosphate one, between 1000 and 1050 °C. However, the binder did not spread, the samples preserved their shape, and shrinkage was 0.8%–1.2%. The latter was due to the developed surface and the elastic action of refractory fibres as well as to the formation of a thermostable compound (zirconyl diphosphate) at the fibre–binder interface, which improved the ceramic refractory properties. As the annealing temperatures increased up to 1600 °C, the material was sintered and the porosity character changed: the micro- and mesopores were closed, the macropores were preserved, and the density and the strength enhanced. For instance, the apparent density of the ZrO_2 fibre-based composition with ammonium–magnesium diphosphate after annealing at 600 °C was $1.8\,g\,cm^{-3}$ and after thermal treatment at 1600 °C, it was $2.5\,g\,cm^{-3}$.

3.2. Reinforcing component ZrO_2t fibres

Stabilized zirconia fibres containing 2 mol % MgO and 18 mol % Y_2O_3 were produced at 900 °C. They possessed a tetragonal structure with the parameters of an elementary cell: $a = 0.5164$; $c = 0.5194$ nm. The fibre diameter was equal to 8 μm and the fibre length was 10–100 mm. The fibres were crushed, a fraction of the 0.3–0.5 mm was sampled and mixed with powdered magnesium and cobalt diphosphates. The samples were prepared as described previously.

According to thermal analysis results, water of crystallization and ammonia were removed from the binders over the same temperature ranges, approximately equal to those in the case of the above-mentioned compositions (Fig. 1). Acidic monophosphates and condensed phosphates were formed in the compositions. At temperatures above 600 °C, these phosphates were decomposed involving the formation of cobalt diphosphate in the α-form and magnesium diphosphate in the β-form unlike previous results [2]; the presence of cyclic phosphates was not observed. By increasing the heating temperature of the composition to 850–900 °C, metal diphosphates were transformed into monophosphates. The phosphorus oxide was observed to isolate during this process, and to react with a fibrous solid ZrO_2-based solution to form yttrium and magnesium monophosphates. As a result of this process, the destabilization of tetragonal ZrO_2 took place and its monoclinic phase appeared. Owing to a high reactivity of fibres, the process with sufficient amounts of binder in the composite (40–50 wt %) developed so quickly that already at 1100 °C the solid ZrO_2-based solution was decomposed completely. Yttrium, cobalt or magnesium monophosphates, zirconia of the monoclinic structure and small amounts of zirconyl diphosphate in the compositions with ammonium–magnesium diphosphate, were found in the reaction products. As the samples were heated to 1000–1100 °C the binders partially fused. As the temperature increased to 1400 °C, the growth of yttrium monophosphate crystals occurred on the ZrO_2 fibre surface, shaped as tetragonal prism-bipyramids (Fig. 3). The phase composition of the composites was preserved during heating to 1600–1700 °C. Over the temperature range 1800–2000 °C a complete thermal dissociation of yttrium, magnesium and cobalt monophosphates, as well as a zirconyl diphosphate, occurred with the formation of metal oxides and phosphorus oxide, which sublimated. Zirconia again interacted with thermostable oxides to form a solid solution of the cubic structure. The composition ratio in a material exerted a significant influence on the temperature of thermal transformations and on the completeness of the reaction. The higher the diphosphate content in the composition, the lower was the decomposition temperature of the solid solution. When the binder concentration did not exceed 10–20 wt %, the solid solution did not completely decompose, even between 1500 and 1600 °C, due to the deficiency of phosphorous oxide. The parallel reactions typical of pure ammonium–cobalt and ammonium–magnesium diphosphates also proceeded when the binder in a material was in excess (more than 50%). They fused, the shrinkage increased, and the samples easily deformed on heating. It should be noted that the zirconia preserved its fibrous texture during thermochemical and structural transformations, although the fibre properties changed. As the annealing temperature increased, their porosity decreased, and they became harder and stronger. During sintering, in the presence of binders they formed a porous refractory ceramic material (Fig. 3).

3.3. Variation of the composite mass and properties as a function of thermal treatment temperature

The chemical and structural transformations occurring at the fibre–binder interface and in the binder itself determine production parameters of the composite materials: the character of the mass-loss curves during thermal treatment, sample shrinkage, changes in the apparent density, the strength, and in the electrophysical properties. In all cases, when the content of binder in the composite increased, the mass losses were raised, too (Fig. 4a).

The samples of the material reinforced with stabilized zirconia fibres had more mass losses than in the systems with pure ZrO_2 fibres due to the formation of refractory zirconyl diphosphate at the fibre–binder interface. Because at the initial stage of thermal treatment (100–400 °C) the composite materials lost water and ammonia, in the systems with ammonium–magnesium diphosphate the mass losses were higher because they contained 4 mol water of crystallization, while ammonium–cobalt diphosphate contained only 1.5 mol. In the temperature range 400–1000 °C the mass changes were negligible. However, they increased when the fusion process of the binder, as well as the partial dissociation and sublimation of P_2O_5, began (Fig. 4a).

The shrinkage of material samples was also negligible up to 1000 °C but began to increase in the temperature region of the chemical reactions and binder fusion. The variations of the apparent density as a function of thermal treatment temperature had

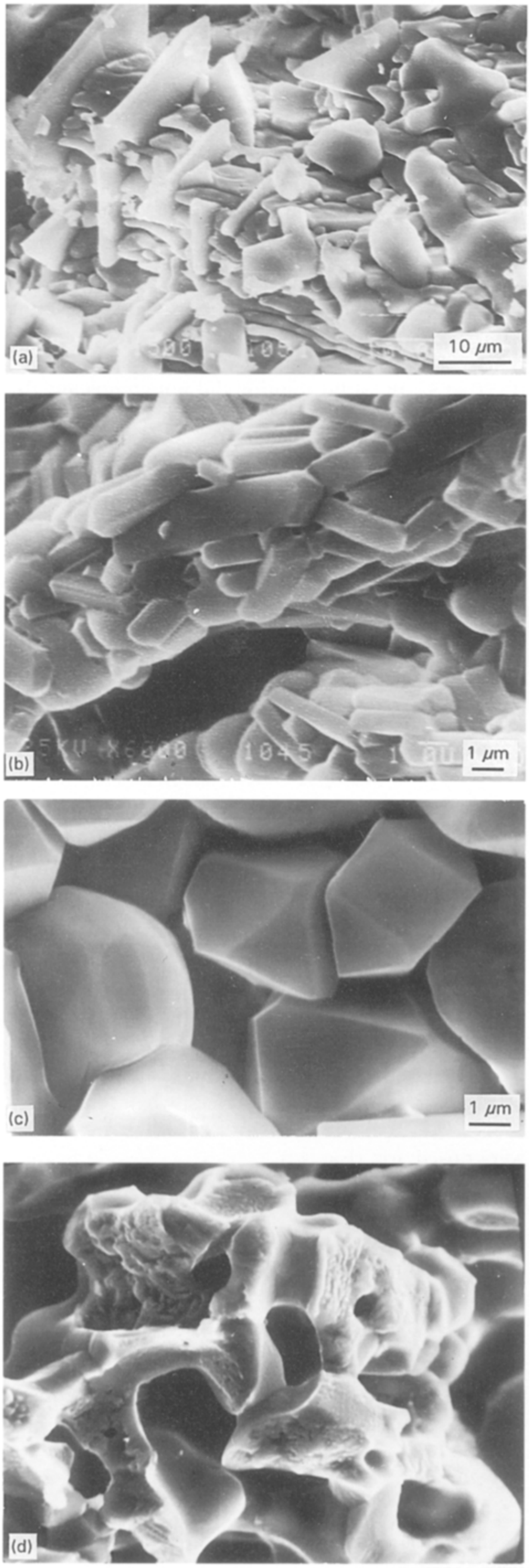

Figure 3 Microstructure of the substances annealed at 1400 °C: (a) pure binder $Co(NH_4)_2P_2O_7$; (b) composite $ZrO_2t + Co(NH_4)_2P_2O_7$ (70:30 wt %): the crystals of YPO_4 on zirconia fibres; (c) crystals of $Co_3(PO_4)_2$ in this composite and ceramics annealed at 2000 °C: (d) $ZrO_2t + Co(NH_4)_2P_2O_7$; (e) $ZrO_2t + Mg(NH_4)_2P_2O_7$.

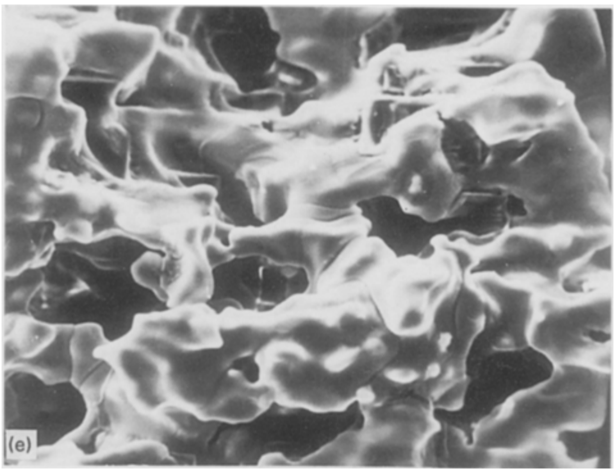

Figure 3 (Continued).

a good correlation with the curves for mass losses and material shrinkage. A marked growth of the density was observed in the samples undergoing thermal treatment at temperatures above 1000–1100 °C. The apparent density of materials with ammonium–cobalt diphosphates varied from 1.5–2 $g\,cm^{-3}$ (800 °C) to 4–4.5 $g\,cm^{-3}$ (1600 °C). Samples with 10% binder had a maximum density, but composites with 50% binder had a minimum one, which was caused by the formation of numerous pores and channels during its partial decomposition. Its density was 2.5–2.8 $g\,cm^{-3}$ and porosity 25%–28%. Composite samples with 30% binder had the highest compression strength of 185 MPa, while the strength properties of samples with 10% and 50% binder were practically the same and equal to 140 MPa when the mean total porosity was equal to 25%.

The apparent density of composites with ammonium–magnesium diphosphate after their thermal treatment at 1600 °C was somewhat lower and equal to 2.8–3.5 $g\,cm^{-3}$, while the compression strength was equal to 175 MPa. The sample porosity was higher and varied from 30%–45% depending on the component ratio in the composite. Use of the compositions containing a magnesium phosphatic binder permits the production of materials with a higher refractoriness (up to 1800 °C) whereas those with a cobalt phosphatic binder may be used up to 1600 °C.

Based on the determined electrophysical properties, it was found that the composites with ammonium–cobalt diphosphate were highly electrosensitive to water vapour. Thus, the specific electrical resistance of the pure ZrO_2 fibre-based composites was decreased by the order of 1–1.5 when the moisture content in the atmosphere was increased by 5%–6% at room temperature. As a whole, the specific resistance of the materials was enhanced as the temperature of thermal treatment increased. That was logical, because their density was enhanced (Fig. 4b). However, when the stabilized zirconia fibres were used in the composite, the magnitude of the specific resistance was lower and did not exceed 10^{10}–10^{11} $\Omega\,cm$. This was associated with the ionic character of conduction inherent to solid ZrO_2-based solutions. A complex relationship between the magnitude of the dielectric permittivity of

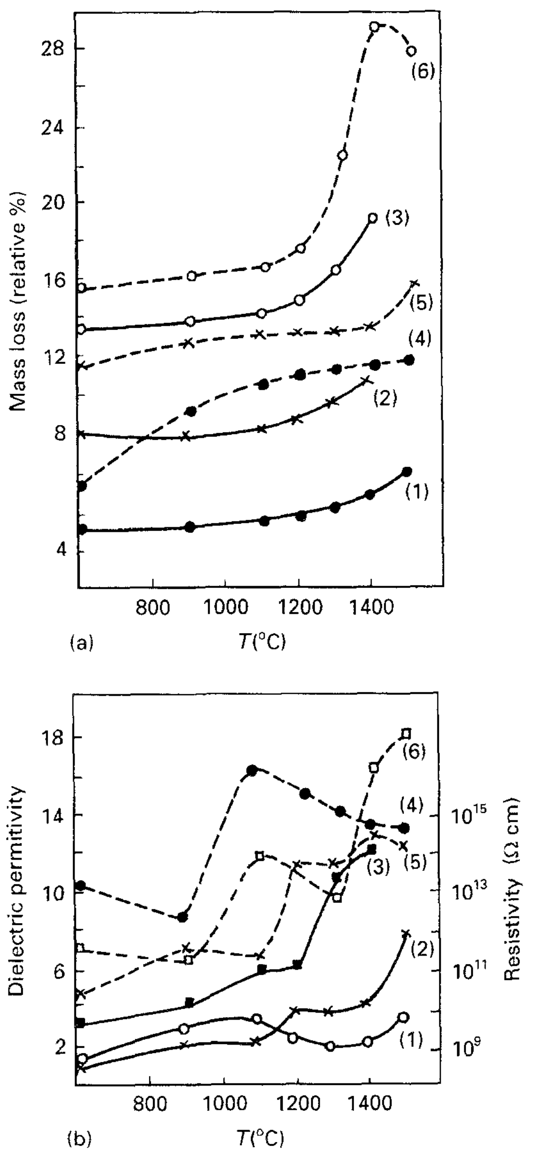

Figure 4 Thermal treatment dependence of mass losses in the samples of ammonium–cobalt diphosphate with pure ZrO_2 fibres (1–3) and with stabilized ZrO_2 (4–6) with the component ratio: 10:90 (1, 4); 30:70 (2, 5); 50:50 (3, 6) (a), and of the specific resistance (1–3) and the dielectric permittivity (4–6) in the composite $ZrO_2m + Co(NH_4)_2P_2O_7$ with the same component ratio (b).

the composites and the increase of their thermal treatment temperature was observed. The maximum values of ε of the compositions annealed between 1000 and 1100 °C were observed, and may be attributed both to the reversible transformation transition $ZrO_2m \rightleftharpoons ZrO_2t$ in the indicated temperature range, and to the formation of the tetragonal ZrO_2 phase (Fig. 4b).

4. Conclusions

1. The interaction of pure and stabilized zirconia fibres with double ammonium–cobalt and ammonium–magnesium diphosphates has been studied.
2. The interaction of monoclinic ZrO_2 at temperatures above 1000 °C results in the formation of zirconyl diphosphate at the fibre–binder interface.
3. In the temperature region 1000–1300 °C, the solid-phase reaction with a binder proceeds when the stabilized zirconia fibres are used. This causes the formation of yttrium and magnesium monophosphates, the decomposition of the solid solution and the appearance of ZrO_2m. At heating of composites above 1800 °C, the dissociation of metal monophosphates and the regeneration of cubic structure solid ZrO_2 solution, take place.
4. The optimal fibre-to-binder ratio in the composites is equal to 70:30 wt %.

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