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Ceric Oxide Effect on Heat-Induced Transformations of Zirconium Oxide Microfibers Prepared by Impregnation of Cotton Fiber

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Abstract—Thermal effects accompanying heat treatment of cotton fibers impregnated with mixed sols of zirconium and ceric oxides have been studied by thermogravimetric analysis and differential scanning calorimetry. Increase of ceric oxide fraction changes the temperature of zirconium oxide transition into the high-temperature tetragonal modification.

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Ceramic oxide fibers are widely applied as components of catalyst supports, filters to be used in aggressive media, gas sensors, solid fuel cells, high-temperature thermal insulators, reinforcing structures, and various composites [1, 2]. Polycrystalline fibers of zirconium oxide possess superior operation properties: high melting point (2700°C [3]) and excellent resistance against corrosion and oxidation.

Zirconium oxide fibers can be prepared by melt growth, chemical precipitation, extrusion of polymer solutions or sols, and via impregnation of natural or synthetic fibers. The latter approach is the most simple and cost-effective, the process examples are the impregnation of cellulose fibrous materials with zirconium salt solution [4] (sometimes with addition of magnesium, titanium, cerium, or yttrium salts [5]) followed by thermal treatment. In the course of heating of the impregnated fibers, below 600°C dehydration, oxidation, carbonization, and burning-out of cellulose fibers occur, the introduced salts suffer dehydration and turn to oxides, whereas above 600°C oxide particles are sintered, and the oxide crystal structure is finally formed.

Crystallization of amorphous zirconium oxide occurs via diverse pathways, and the transformation of the low-temperature modifications (t'-ZrO_2 and m'-ZrO_2) into the high-temperature monoclinic one (m-ZrO_2) can take place over wide temperature range (500–1000°C) depending on the precursor nature, the preparation method, and the heating rate [6–10]. Between 1100°C [8, 11] and 1170°C [1] the m-ZrO_2 modification is converted into the high-temperature tetragonal one (t-ZrO_2). The latter is further transformed into the cubic phase (c-ZrO_2, stable up to 2680°C [1]) above 2370°C.

The monoclinic phase transformation into the high-temperature tetragonal modification is a diffusion-free reversible martensite phase transition accompanied with the change in the unit cell volume. In order to prevent the overall material volume change and to stabilize the high-temperature tetragonal and cubic phases, certain additives are introduced into the precursor: maltose [12], mullite [13], or various metal oxides (Mg, Ca, Y, Ce, etc) [5]. Depending on the amount of stabilizer, the Fully Stabilized Zirconia (FSZ) [14, 15] and Partially Stabilized Zirconia (PSZ) [16–22] ZrO_2 are distinguished.

In the CeO_2–ZrO_2 system, a series of solid solutions can be formed, having monoclinic, tetragonal, or cubic lattice, whereas new chemical compounds are not formed [7].

In this work we studied the effect of ceric oxide additive on thermal properties of zirconium oxide ceramic fibers prepared by cotton fiber impregnation with sols of varied composition: $x\text{CeO}_2/(1–x)\text{ZrO}_2$, $x = 0–0.220$.

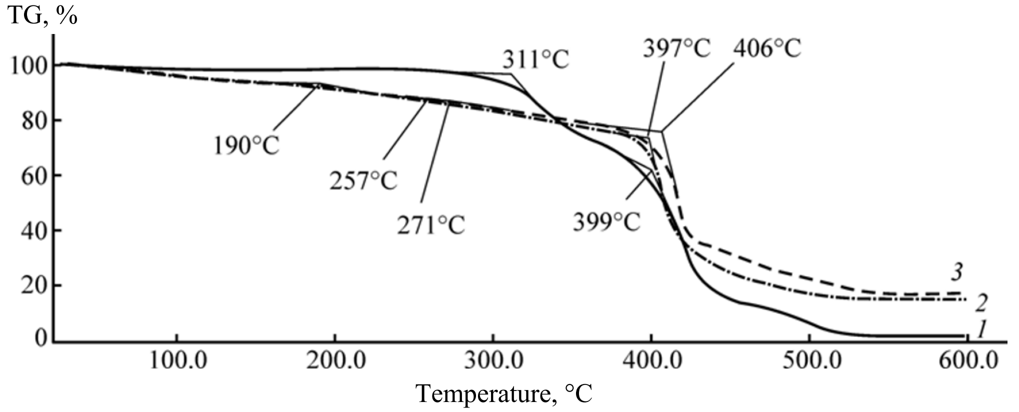

Fig. 1. TGA curves of initial cotton fiber (*1*) and cotton fibers impregnated with $ZrO_2/0.220CeO_2$ (*2*) and $ZrO_2/0.046CeO_2$ (*3*) sol.

TGA curves of the initial cotton fiber and the fibers impregnated with the sols (Fig. 1) represent the changes occurring at 25–600°C in air; no mass change was observed above 600°C.

Desorption of physically bound water occurred at 80–150°C; in the DSC curve this process was marked with poorly seen minimum at 80°C (Fig. 2, curve *1*). The mass loss at 150–540°C was due to the oxidative destruction of cellulose to give carbon as well as with dehydration of solvated zirconium and ceric oxides. Thermal destruction of initial cotton cellulose started at 311°C (Fig. 1, curve *1*); in the DSC curve that process was marked with exothermic peaks at 330, 366, 420, and 485°C (Fig. 2, curve *1*). The mass loss rate was decreasing at 540–600°C until carbon was completely burned out.

The content of inorganic ash as determined from TGA experiment is reported in Table 1 (recalculated into the oxides content).

At 100–300°C cerium and zirconium hydroxides were decomposed (Fig. 2, curves *2*–*4*). Cotton fiber treatment with sols of zirconium and ceric oxides decreased the onset of cellulose thermal destruction (275°C, treated with ZrO_2 sol; 271°C, $ZrO_2/0.046CeO_2$; 257°C, $ZrO_2/0.220CeO_2$; and 311°C, initial fiber) (Fig. 1). The same corresponds to the activation energy of thermal destruction (as determined with the Coats-Redfern method [23]): 52.82 kJ/mol (treated with ZrO_2), 37.46 kJ/mol ($ZrO_2/0.046CeO_2$), and 33.56 kJ/mol ($ZrO_2/0.220CeO_2$) compared with 113.38 kJ/mol (initial fiber). The exothermic process around 420°C (initial fiber) was also observed at lower temperature in the case of modified fibers (402°C, $ZrO_2/0.220CeO_2$; 415°C, $ZrO_2/0.046CeO_2$; and 408°C, ZrO_2) (Fig. 2). The splitting of exothermic peak was due to the overlap of exothermic cellulose destruction with endothermic removal of the destruction products from the reaction medium. The highest process rate was observed at 410°C (fiber modified with $ZrO_2/0.220CeO_2$), 420°C ($ZrO_2/0.046CeO_2$), and 430°C (ZrO_2).

The above observations pointed at possible catalytic effect of zirconium and ceric oxide on cellulose oxidative destruction.

The temperature of the exothermic effect corresponding to burning-out of the residual carbon (485°C in the case of initial cotton fiber) decreased (488°C, impregnation with $ZrO_2/0.220CeO_2$; 513°C, $ZrO_2/0.046CeO_2$; and 516°C, ZrO_2) with increasing ash content (Table 1) due to complicated burning of carbon.

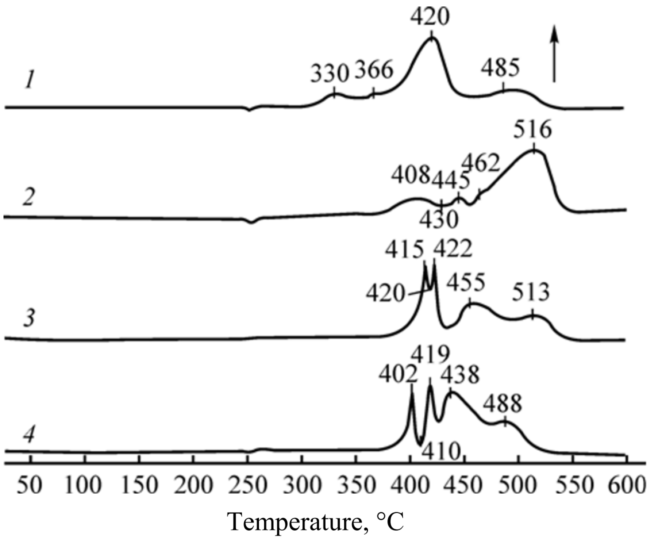

Fig. 2. DCS curves of initial cotton fiber (1) and microfibers containing ZrO_2 (*2*), $ZrO_2/0.046CeO_2$ (*3*), and $ZrO_2/0.220CeO_2$ (*4*) at 50–600°C.

Table 1. Ash content in the fibers before heat treatment

Sample	Ash content, wt %
Cotton fiber	1.40
ZrO_2-containing cotton fiber	19.0
$ZrO_2/0.046CeO_2$-containing cotton fiber	16.6
$ZrO_2/0.220CeO_2$-containing cotton fiber	14.5

Table 2. Physical properties of the initial sols

Sample	pH	Density, g/cm^3	Average particle size, nm
ZrO_2	1.88±0.02	1.053±0.001	18±2
$ZrO_2/0.046CeO_2$	3.31±0.02	1.052±0.001	20±2
$ZrO_2/0.220CeO_2$	3.07±0.02	1.108±0.001	18±2

Formation of t'-ZrO_2 was exothermic, the corresponding DSC peak was observed at 462°C (ZrO_2), 455°C ($ZrO_2/0.046CeO_2$), and 438°C ($ZrO_2/0.220CeO_2$); thus, in the presence of ceric oxide the onset of low-temperature tetragonal ZrO_2 phase was decreased. Temperature of the t'-ZrO_2 → m-ZrO_2 transformation (DSC: 895°C, ZrO_2; 870°C, $ZrO_2/0.046CeO_2$; and 870°C, $ZrO_2/0.220CeO_2$) was independent of ceric oxide presence (Fig. 3). The results coincided with the published data [7, 10–13, 24].

The diffusion-free reversible martensite transformation m-ZrO_2 → t-ZrO_2 was assigned to the exothermic effects at 1100°C (ZrO_2), 1085°C ($ZrO_2/0.046CeO_2$), and 990°C ($ZrO_2/0.220CeO_2$). The transformation was thus observed at much lower temperatures than in the presence of other stabilizing additives, 1100–1170°C [1, 8, 11].

Solid solution formation in the studied dioxides mixture was accompanied with endothermic effects at 1200, 1230, 1328, and 1363°C [7]. The reverse partial transition of t-ZrO_2 into m-ZrO_2 was accompanied with endothermic effect at 472°C ($ZrO_2/0.046CeO_2$) and 499°C ($ZrO_2/0.220CeO_2$).

The presence of tetragonal and monoclinic modifications of zirconium oxide in the prepared microfibers was confirmed by X-ray diffraction data (Fig. 4). With increasing content of ceric oxide, fraction of the high-temperature tetragonal phase grew. Phase composition of the microfibers was stable during prolonged incubation.

To conclude, DSC studies of CeO_2 effect on zirconium oxide stabilization in the sol-impregnated cotton microfibers revealed that increase of ceric oxide content resulted in lower temperature onsets of t'-ZrO_2, m-ZrO_2, and t-ZrO_2 formation. The catalytic effect of the dioxides on the thermal oxidative destruction of cotton cellulose was demonstrated as well.

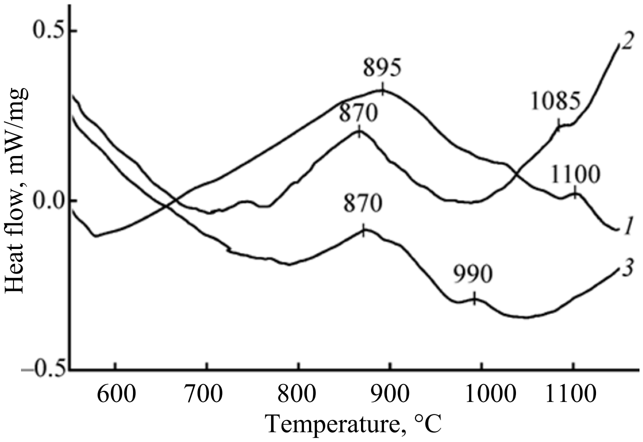

Fig. 3. DCS curves of microfibers containing ZrO_2 (*1*), $ZrO_2/0.046CeO_2$ (*2*), and $ZrO_2/0.220CeO_2$ (*3*) at 550–1200°C.

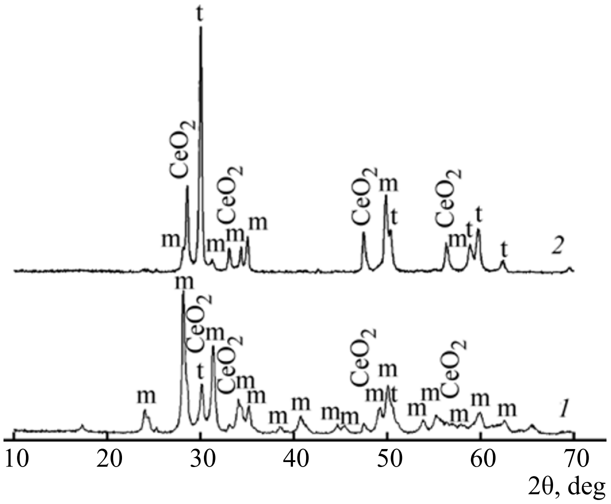

Fig. 4. X-ray diffraction patterns of microfibers produced at 1250°C: $ZrO_2/0.046CeO_2$ (*1*) and $ZrO_2/0.220CeO_2$ (*2*). Indexes assign the peaks to corresponding ZrO_2 phases: (m) is high-temperature monoclinic and (t) is high-temperature tetragonal.

EXPERIMENTAL

Zirconium oxide sols were prepared via controlled hydrolysis of zirconium(IV) oxochloride in the aqueous solution with slowly added aqueous ammonia (room temperature, at stirring). The mixed sols of ceric and zirconium oxides were prepared using the single-phase sol method, hydrolysis of mixed solution of zirconium(IV) oxochloride and cerium(IV) chloride with aqueous ammonia. The initial salt solutions were filtered through paper filter, the salts concentration was 1 mol/L. Parameters of the prepared sols are given in Table 2. Particles size was determined by dynamic light scattering (Zetasizer Ver.7.01).

Cotton fiber was impregnated with the prepared sols, dried in air, and then thermally treated. The samples were coded similarly to the sols used: ZrO_2, cotton fiber impregnated with pure zirconium oxide sol, $ZrO_2/0.046CeO_2$, cotton fiber impregnated with the mixed sol (CeO_2 molar fraction 4.6%), and$ZrO_2/0.220CeO_2$, cotton fiber impregnated with the mixed sol (CeO_2 molar fraction 22%).

Heat-induced transformations of zirconium oxide were studied by TGA and DSC (NETZSCH STA 409 PC). The experiments were run in platinum crucible in the range of 25–1400°C at 10°/min heating rate; then, the sample was then cooled down to 200°C (either in air or under argon), and burned in air at up to 1250°C with subsequent 1 h of isothermal annealing.

X-ray diffraction studies of the microfibers were performed with Shimadzu XRD-6000 (powder method, CuK_α).

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