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Effect of Cellulose Supramolecular Structure on the Morphology of Aluminum Oxide Fibres Obtained *via* Sol-Gel Method

I. S. MARTAKOV¹, P. V. KRIVOSHAPKIN¹, M. A. TORLOPOV¹, E. F. KRIVOSHAPKINA¹ and V. A. DEMIN^{1,2}¹*Institute of Chemistry, Komi Science Centre, Ural Branch of the Russian Academy of Sciences, Ul. Pervomayskaya 48, Syktyvkar 167982 (Russia)**E-mail: gmartakov@gmail.com*²*Syktyvkar Forestry Institute, Branch of the Kirov St. Petersburg State Forest Technical University, Ul. Lenina 39, Syktyvkar 167982 (Russia)*

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Abstract

Micro-sized in the cross section aluminum oxide fibres, have been obtained by the sol-gel method with cotton cellulose as a template. The effect of the supramolecular structure of cellulose on the properties of ceramic fibres has been studied. It has been demonstrated that the initial morphology and supramolecular structure of cellulose have a significant impact on the template synthesis process.

Key words: aluminum oxide, fibre, cellulose, sol-gel method, template synthesis

INTRODUCTION

At the present stage of the development of chemical technology, ceramic fibres are of a special interest. On their basis, one could make the materials of a new generation, *viz.*, light, durable, wear-resistant, and suitable for using at high temperature values and in aggressive environments. As a promising material for the preparation thereof one could consider aluminum oxide. Its use would extend the scope of ceramic fibres and substantially reduce the cost thereof. In addition, aluminum oxide is produced from common naturally occurring minerals (bauxites, nepheline, and kaolinites). A high chemical and thermal stability and hardness inherent in the aluminum oxide are caused by its crystalline structure. Aluminum oxide can be crystallized in several modifications; the most stable among those is presented by α -Al₂O₃ (corundum). Industrial methods for forming such

high-temperature fibres usually, as a rule, include the preparation of metal oxide sols [1–3].

Ceramic fibres are made, in particular, by the method of template synthesis [4–7], that is based on the ability of polymeric fibres to swell in salt solutions or sols of hydrated metal oxides and absorb inorganic compounds or form complexes with them followed by burning the organic component [8]. After the sorption of the salts from solutions or nanoscale particles of sols of the fibres are dried and treat thermally to remove crystallization, hydrated water and template [9]. Oxide fibrous materials obtained in such a way remain the texture of the initial polymeric fibre.

Ceramic fibres obtained by the method of template synthesis, are characterized by a high reactivity in the adsorption interaction with gas and liquid environments, as well as by a chemical inertness with respect to the excited environment. Because of this, they could be used

as catalyst carriers, filtering media, thermal insulating layers and filling agents, means for capillary transportation. In addition, the ceramic fibres are characterized by a high dispersity level and mono-fractional composition of aluminum oxide, and therefore, they are promising for the development of high-strength ceramics, various composite materials for structural and functional purposes, having both improved and special properties [8]. In this context, the studies concerning the development of physicochemical and technological principles of the preparation of aluminum oxide fibres are relevant.

The authors of [4–8] obtained metal oxide fibres with transverse sizes from 4 to 10 μm using cellulose as a template; and demonstrated that in case of this method of synthesis the structure thereof depends on the morphology of cellulose fibres. However, the influence of the supramolecular structure of the template upon the morphology of metal oxides is poorly studied at the present time.

The purpose of this work consisted in studying the influence of the supramolecular structure of cellulose (template) that changes in the course of mercerization, upon the morphology of aluminum oxide.

EXPERIMENTAL

Materials

Sol of hydrated aluminum oxide. As a starting reagent we used chemical purity grade aluminum chloride hexahydrate $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, whereas as the hydrolyzing agent an ammonia solution was used with the concentration of 7 mol/dm³. The synthesis of the sol of hydrated aluminum oxide was performed using a controlled hydrolysis technique under permanent stirring and at a room temperature; the process was finished when the final pH value ranged within 5–5.5. Low molecular mass substances were removed from the sol *via* dialysis through a semipermeable polymeric membrane (CelluSep 1230-45); the completion of the reaction was monitored basing on a qualitative analytical reaction of chloride ions [10]. The resulting sol represented an opalescent aggregation-stable system; it was characterized by

the value of the dynamic viscosity, the content of dispersed phase, and by particle size.

Cotton cellulose and mercerized cotton cellulose. As the starting material we used bleached cotton cellulose (SP-1400). The mercerized cellulose was obtained *via* treating the original cotton cellulose by sodium hydroxide solution with the concentration of 5.2 mol/dm³ with further washing and drying [11]. The mercerized cellulose is characterized by a high content of the α -form of cellulose (properly poly(1 \rightarrow 4)- β -D-anhydroglucopyranose), a very low content of hemicellulose and other related substances, a high polymerization level and a greater fibre length as compared with other cellulosic materials.

Aluminum oxide fibres. Ceramic fibres were obtained *via* impregnating the naturally occurring or mercerized cellulose fibres in the sol of hydrated aluminum oxide [8, 12] at a mass ratio $m(\text{Al}_2\text{O}_3)/m(\text{C}_6\text{H}_{10}\text{O}_5)_n = 1 : 25$. After the impregnation by the sol the fibres were dried in air at room temperature for 1 day, with further calcining. The calcination was performed stepwise through isothermal stages whose temperature corresponded to water desorption processes and the destruction of cellulose fibres. We chose the following mode of calcinations: heating rate from 20 to 600 °C equal to 2 °C/min, that from 600 to 1300 °C being equal to 5 °C/min, holding for 1 h at 200, 450, 600 and 1300 °C.

Methods

The density of sols was determined using the pycnometric method. The value of the dynamic viscosity was determined with the help of a VPZh-3 capillary viscometer (capillary diameter amounting to 0.56 mm). The mass fraction of the dispersed phase in the system was determined by gravimetric method. Particle size was measured using a Malvern ZetasizerNano ZS measuring unit basing on dynamic light scattering.

The X-ray phase analysis (XPA) of the samples was performed using a Shimadzu XRD-6000 X-ray diffractometer with $\text{CuK}\alpha$ radiation within the range of reflection angles $2\theta = 5\text{--}70^\circ$. The index of cellulose crystallinity I_{cr} was determined using a method by Segal [14]:

$$I_{\text{cr}} = I_{002} - I_{\text{sc}}/I_{002}$$

TABLE 1

Degree of ordering and crystallinity indices of the initial and mercerized cotton cellulose

Cellulose samples	Degree of ordering		Crystallinity index (I_{cr})
	K_1	K_2	
Original	1.5	1.0	0.82
Mercerized	1.3	1.0	0.53

where I_{002} is the intensity of reflex 002; I_{sc} is the scattering intensity at the angle $2\theta \approx 19^\circ$.

The IR spectra of the samples studied were registered using a Shimadzu IRPrestige-21 FTIR spectrometer within the mid-infrared region of $4000\text{--}400\text{ cm}^{-1}$ with pressing-in the samples in KBr pellets. The level of ordering the cellulose K_1 and K_2 were calculated by means of the Nelson and O'Connor method [15]:

$$K_1 = A_{1429}/A_{897}$$

$$K_2 = A_{1372}/A_{2900}$$

where A is the intensity.

The selection of the thermal treatment mode and evaluation of thermal effects were performed on the basis of the differential scanning calorimetry (DSC) data, that were obtained within the temperature range of $25\text{--}1250^\circ\text{C}$ at the heating rate of $5^\circ\text{C}/\text{min}$ (a Netzsch STA 409 PC/PG devise).

The morphology of the cellulose and aluminum oxide fibres was studied by means of scanning electron microscopy (SEM) using a VEGA3 TESCAN electron microscope in a BSE mode (backscattered electron mode).

RESULTS AND DISCUSSION

In the course of the mercerization, there occurs cellulose transition from structural modification I to structural modification II. The mercerized cellulose has a lower index of crystallinity, exhibits a higher degree of X-ray amorphism, has a less ordered packing of macromolecules as well as changed parameters of the crystal lattice. One of the measures of changing in the course of mercerizing is presented by crystallinity index that can be determined by means of XPA (Fig. 1) [13].

From Table 1 it follows that after the mercerization the crystallinity of cellulose decreases, *i. e.* the cellulose partially is transformed into the amorphous state. This is consistent with published data concerning the mercerization of cellulose [14].

Data concerning the level of cellulose ordering calculated from the IR spectra by means of the Nelson and O'Connor method, also indicate a significant reduction of the crystallinity index, which correlates with the XPA data (see Table 1).

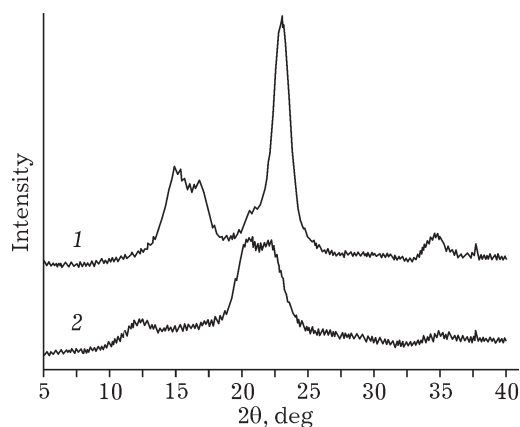


Fig. 1. X-ray patterns of original (1) and mercerized (2) cotton cellulose.

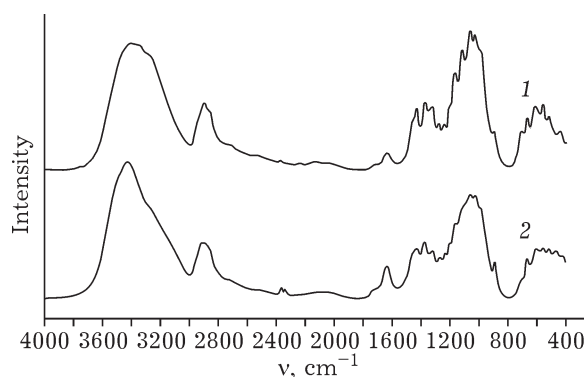


Fig. 2. IR spectra of the fibres of original (1) and mercerized (2) cotton cellulose.

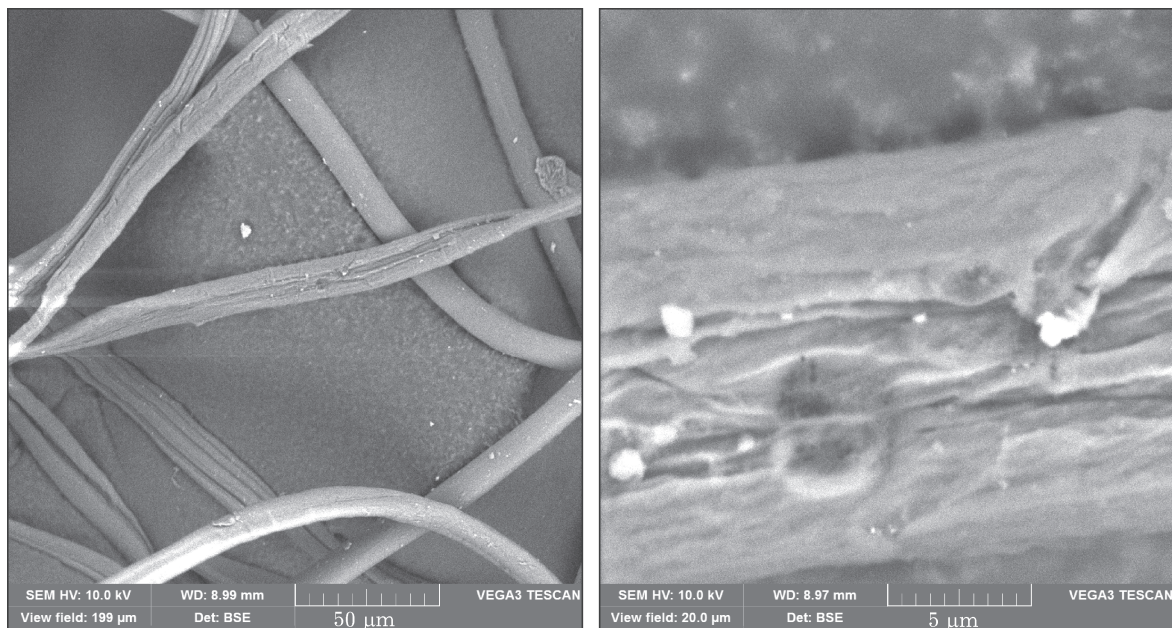


Fig. 3. Micrographs of the fibres of original cotton cellulose.

According to Fig. 2, the IR spectra of the original and mercerized cotton cellulose exhibit the absorption maxima to be almost coinciding. The broad absorption band at $3700\text{--}3100\text{ cm}^{-1}$ in the IR spectrum of cellulose is connected with the stretching vibrations of hydroxyl groups involved in the hydrogen bonding. It should be noted that there is a slight shift of

the band maximum of the sample of mercerized cellulose, the stretching vibrations of OH groups toward a high frequency range. Changing the contour of the band with shifting the maximum toward higher frequencies indicates a decrease in the fraction of groups included in a stronger hydrogen bonding, *i. e.* a loosening of the structure of mercerized cellulose as

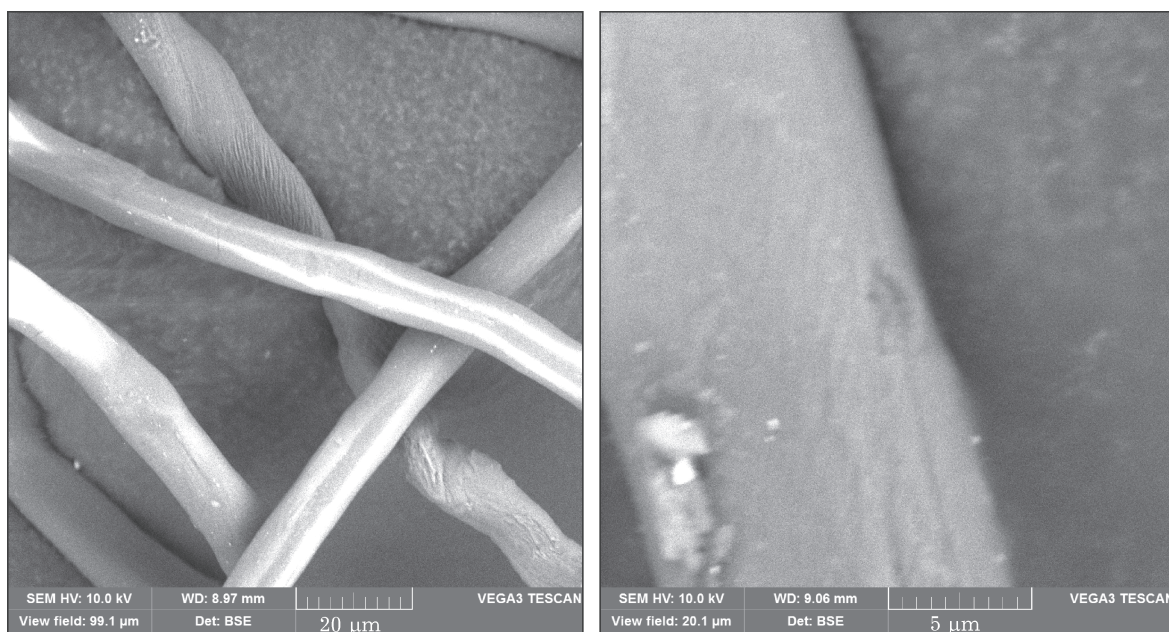


Fig. 4. Micrographs of the fibres of mercerized cotton cellulose.

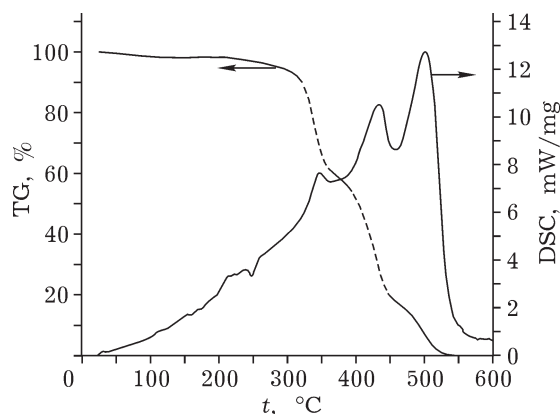


Fig. 5. TG and DSC curves for the sample of mercerized cotton cellulose.

compared to the original cotton cellulose. The ratio between the intensities of the bands at 1429 and 897 cm^{-1} as a measure of the ordering level to a better extent reflects the changes those occur in the cellulose under mercerizing and correlates with the index of crystallinity.

The mercerized cellulose, despite of profound swelling in alkaline solution exhibit the original geometric dimensions of cotton cellulose fibres to be conserved after subsequent washing and drying (Figs. 3 and 4). The surface of the mercerized fibre is more smooth and flat.

Figures 5 and 6 demonstrate the curves of TG and DSC in the course of heating the cellulose in an atmosphere of air. The DSC curves for the sample of the original cotton cellulose are not presented because they are generally similar to the data for the samples of mercerized cotton cellulose. Upon heating the cellulose in the oxygen environment the DSC curve (see

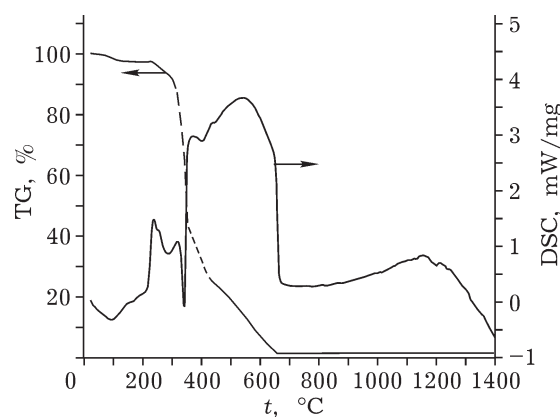


Fig. 6. TG and DSC curves for the sample of mercerized cotton cellulose impregnated with a sol of hydrated aluminum oxide.

Fig. 5) exhibits endothermic effects. Within the temperature range of $90\text{--}100\text{ }^{\circ}\text{C}$ there occurs a desorption of water absorbed earlier; at $200\text{--}250\text{ }^{\circ}\text{C}$ there occurs dehydration, beginning the destruction of cellulose glycoside bonds is observed (*i. e.* depolymerisation); at $300\text{--}350\text{ }^{\circ}\text{C}$ one can observe developing the processes of profound thermal cellulose destruction, as well as the formation and volatilization of levoglucosan accompanied by a significant loss of the mass. Within the range of $420\text{--}450\text{ }^{\circ}\text{C}$ the exothermic effect is associated with the condensation of volatile products, the formation of new bonds, with appearing the aromatic structures. The highest rate of mass loss is observed within the temperature range of $380\text{--}540\text{ }^{\circ}\text{C}$, which is connected with the oxidation of the organic matrix and with the formation of volatile compounds. This process corresponds to exoeffects exhibited by the DSC curve.

For the sample of cotton cellulose impregnated with the sol, the DSC curves demonstrate similar effects within the mentioned intervals, which effects are inherent in the cellulose proper (see Fig. 6). However, the character of the DSC curve for this sample is different. At $320\text{--}350\text{ }^{\circ}\text{C}$ there appears an endothermic effect associated with the decomposition of the residual amounts of ammonium chloride (a product of aluminum chloride hydrolysis). When the temperature increases from 540 to $600\text{ }^{\circ}\text{C}$, the rate of mass loss is markedly reduced, the carbon burnout is stopped and metal oxide begins to form with a fibrous texture. Further increasing the temperature of heat treatment up to $1300\text{ }^{\circ}\text{C}$ does not lead to changing the sample mass. In the course of the thermal oxidation of cellulose impregnated with the sol of hydrated aluminum oxide there occurs nucleation and growth of the grains of aluminum oxide. They form a linear chain structure that reproduces the shape of the original cellulose fibre.

As the impregnating system we used a sol of hydrated aluminum oxide having the following characteristics: the mass fraction of aluminum oxide ($5.8\pm 0.3\%$), the dynamic viscosity ($5.9\pm 0.7\text{ mPa}\cdot\text{s}$), particle size ($76.5\pm 1.2\text{ nm}$).

The reflexes on the XRD pattern of aluminum oxide fibres indicate the formation of a stable α -aluminum oxide phase. The formation of crystalline aluminum oxide starts at the cal-

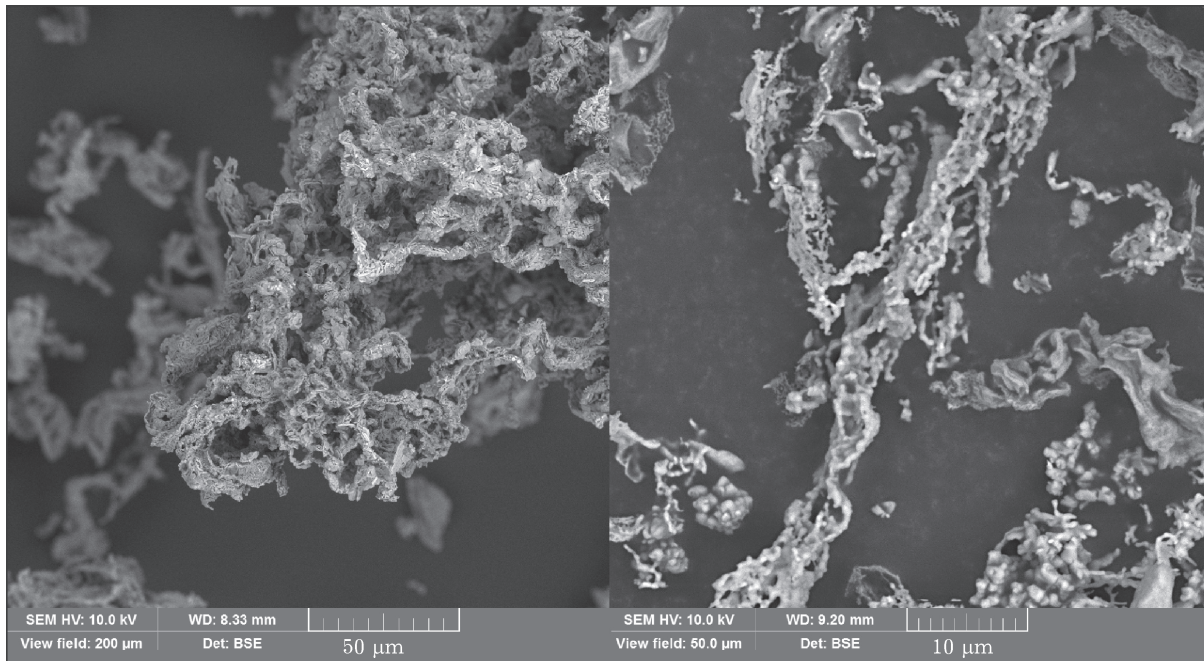


Fig. 7. Photomicrographs of aluminum oxide obtained *via* calcining the cotton cellulose impregnated with a sol of hydrated aluminum oxide.

cination temperature of $\sim 600^\circ\text{C}$ in the form of γ -phase, at a higher temperature than 1100°C a diffusion-free transformation of γ -alumina into $\alpha\text{-Al}_2\text{O}_3$ (corundum) that remains unchanged in the course of the further heating-cooling cycles occurs.

Figure 7 demonstrates that the initial shape of cellulose, remains unchanged, however, when using non-mercerized cellulose as a template, the corundum fibre consists of poorly sintered crystallites. On the contrary, in case of mercerized cotton cellulose, well-sintered aluminum oxide fibres

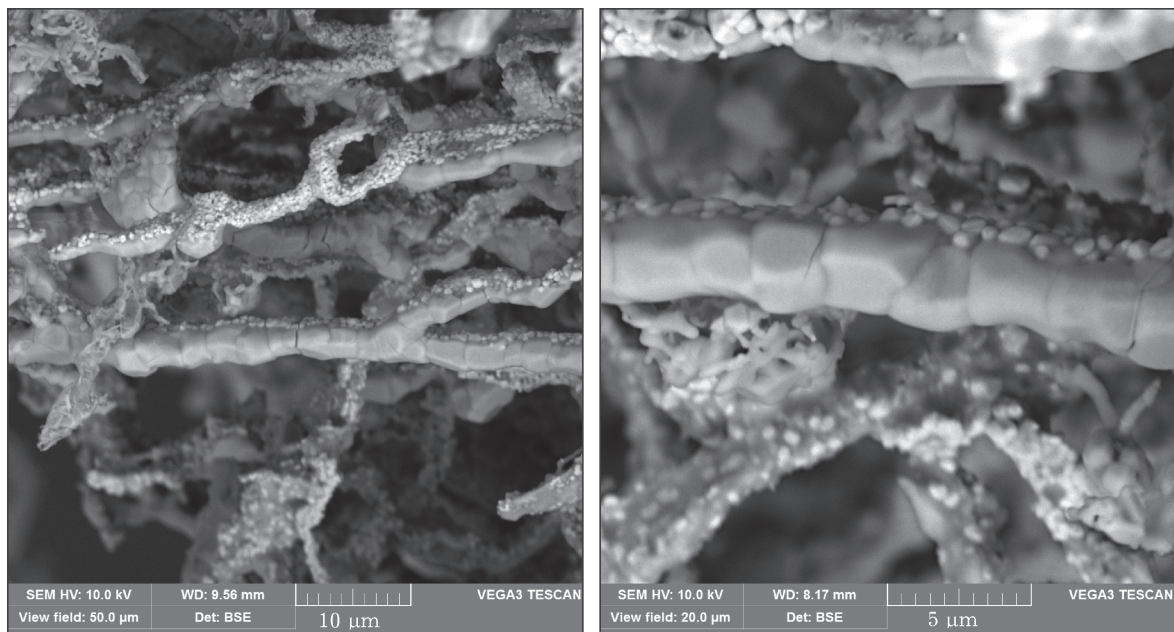


Fig. 8. Photomicrographs of aluminum oxide obtained *via* calcining the mercerized cotton cellulose impregnated with a sol of hydrated aluminum oxide.

with a diameter of 2–5 μm , preserving the shape of template, are formed (Fig. 8). This makes it possible to set the texture of the oxide fibres at the early stages of template synthesis with the use of cellulosic materials.

CONCLUSION

The method of the template synthesis of ceramic fibres has been developed, the essence of which consists in the impregnation of cellulose fibres by the sol of hydrated aluminum oxide followed by a thermal treatment. This allows to synthesize aluminum oxide fibres with a wide spectrum of applications.

It is demonstrated that the mercerization crucially affects the supramolecular structure of cellulose. As the result, the inner surface of cellulose increases, which, in turn, affects processes of filling capillaries, pores and sorption of cellulose nanosized sol particles by.

It has been found that the mercerization improves properties of the resulting corundum fibre. When using the mercerized cellulose as a template aluminum oxide with a well-formed fibrous structure, is formed, what is caused by template properties. The fibres have the diameter from 2 to 5 μm . In case of non-mercer-

ized cotton cellulose poorly sintered loose Al_2O_3 fibres are formed, which, undoubtedly, impairs their physicomechanical indicators.

REFERENCES

- 1 Afanasov I. M., Lazoryak B. I., Vysokotemperaturnye Keramicheskiye Volokna, Izd-vo MGU, Moscow, 2010, 51 p.
- 2 Claus B., Schwaller D., *Adv. Sci. Technol.*, 50 (2006) 1.
- 3 Bunsell A. R., Berger M. H., Fine Ceramic Fibers, Marcel Dekker Inc., NY, 999 p.
- 4 Yermolenko I. N., Ulyanova T. M., Vityaz P. A., Fyodorova I. L., Voloknistye Vysokotemperaturnye Materialy, Nauka i Tekhnika, Moscow, 1991.
- 5 US Pat. No. 3 385 915, 1968.
- 6 Fan T. X., Chow S. K., Zhang D., *Progr. Mater. Sci.*, 54 (2009) 542.
- 7 Liu W. W., Zeng C. F., Zhang L. X., Wang H., Xu N., *Mater. Chem. Phys.*, 103 (2007) 508.
- 8 Sun R. Q., Sun L. B., Chun Y., Xu Q.-H., Wu H., *Micropor. Mesopor. Mater.*, 111 (2008) 314.
- 9 Hall S. R., Biotemplating: Complex Structures from Natural Materials, World Sci. Publ., Singapore, 2009.
- 10 Petrukhin O. M., Analiticheskaya Khimiya. Khimicheskiye Metody Analiza, Khimiya, Moscow, 1992.
- 11 Rogovin Z. A., Khimiya Tsellyulozy, Khimiya, Moscow, 1972.
- 12 Vityaz P. A., Fyodorova I. L., Yermolenko I. N., Ulyanova T. M., *Ceram. Int.*, 9 (1983) 46.
- 13 Karlivan V. P., Metody Issledovaniya Tsellyulozy, Zinatne, Riga, 1981.
- 14 Nikitin V. M., Obolenskaya A. V., Shchegolev V. P., Khimiya Drevesiny i Tsellyulozy, Lesn. Prom-st', Moscow, 1978.
- 15 Nelson M. L., O'Connor R. T., *J. Appl. Polym. Sci.*, 8 (1964) 1311.