Structure, morphology and mechanical properties of arrays of zirconia nanofibers at different heat treatment modes

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Abstract. Mats of yttria-stabilized tetragonal zirconia nanofibers were prepared in the present research. The effect of the mats calcination temperatures (600, 900, and 1200 °C) on their structure and morphology was investigated. It was found that phase composition of the fibers did not change in all range of the calcination temperatures, while the average grain size in fiber increased from 8 to 39 nm. Multi-cyclic and single loading-unloading nanoindentation testing of the ceramic mats showed that the hysteresis loop energy in samples decreases with higher calcination temperature. Hardness and the elastic modulus measured by spherical (with 10 and 250 μm radii) and sharp Berkovich indenters were the highest in the mats calcined at 900 °C. This calcination temperature can be considered an optimal one for preparation of nanofibers mats which mechanical properties are of importance for their application.

1. Introduction
It’s well known that electrospinning is the most commonly used technique for a large-scale nanofibers production due to its simplicity, versatility, high reproducibility and also the ability to manufacture filaments with a desired diameter, orientation, composition and morphology [1]. Polymer, composite, ceramic, metallic, carbon functional nanofibers can be produced using electrospinning [2]. Among ceramic nanofibers, ZrO$_2$ filaments occupy a special place due to their excellent thermal and chemical stability, oxygen-ionic conductivity, polymorphism, and amphoteric surface properties. Along with a high aspect ratio and a large specific surface area, this makes ZrO$_2$ nanofibers promising for bone tissue regeneration [3], solid oxide fuel cells [4], protection from electromagnetic interference [5], etc. While most zirconia nanofiber mats are functional, there is always a requirement for their mechanical properties. A nonwoven material containing spontaneously oriented ceramic nanofibers is a porous non-homogenized medium. The main local mechanical properties of the medium, such as hardness and elasticity, are up to several tens of MPa. Such values of hardness are typical for soft polymers [6]; they are well below ones reported for even highly porous ceramics [7]. The same is true for the elastic modulus [8].

Therefore, overcoming unnecessary fragility and improving the flexibility of ceramic fiber mats comes to the fore. It is well known that the greatest commercial value is 3Y-TZP bulk ceramics, which
is obtained by adding 3 mol% Y₂O₃ as a stabilizer agent in ZrO₂ and is a fully tetragonal fine-grained ceramic that is characterized by the best combination of hardness, fracture toughness, bending strength and Young's modulus [9]. But only bulk 3Y-TZP ceramics possess such outstanding characteristics. Typically, the Young's modulus of a 3Y-TZP nanofiber mat does not exceed units of MPa, which was significantly lower than the typical value of 210 GPa for bulk 3Y-ZrO₂ ceramics. This indicates 3Y-TZP nanofiber mat remarkable flexibility compared to traditional bulk 3Y-TZP ceramics. But other mechanical properties of the mats, such as hardness and elastic modulus were 4-5 orders of magnitude less than in bulk ceramics. Some authors [3, 10, 11] observed that the increase in annealing temperature led, first, to the partial loss of the ceramic mat flexibility and then to its fragility, but it has not been studied in detail. To study the mechanical properties of 3Y-TZP ceramic mats, we used nanoindentation [12]. We used the methods of single and multi-cycle loading with indenters of different sharpness and shape (spherical and pyramidal) to study the response of 3Y-TZP mats to such a load. The aim of this work was a comprehensive investigation of possible causes for the evolution of the mechanical strength and flexibility of ceramic mats made of nanofibers during nanoindentation with blunt (spherical) and sharp (pyramidal) indenters under the action of the same load and different annealing temperatures.

2. Materials and methods

3Y-TZP nanofiber mats were prepared from a solution of polyacrylonitrile (PAN, molecular weight Mw = 150,000, Sigma-Aldrich, USA) in N, N-dimethylformamide (DMF, Sigma-Aldrich, USA) followed by the addition of zirconium acetylacetonate (ZrAA, Sigma- Aldrich, USA) and yttrium nitrate hexahydrate (Sigma-Aldrich, USA) after stirred at 80 °C until the solution became transparent. Details of the preparation of ceramic nanofiber mats are described in [13]. The prepared solution was electrospun using electrospinning machine NANON-01A (MECC, Japan). The following operative parameters were chosen to fabricate smooth nanofibers: the accelerating voltage was 22 kV, the distance between the needle tip and the flat collector covered by aluminum foil was 20 cm. As-spun mats were calcined at temperatures 600, 900 and 1200 °C in air atmosphere.

The mechanical properties of fabricated zirconia nanofiber mats were measured by the nanoindentation method [14-19] using NanoIndenter® G200 (MTS Nano Instruments, USA) and TI-950 (Hysitron, USA) nanoindentometers. The nanoindenters operated in displacement control mode with a 0.05 s⁻¹ strain rate target and a 10 s hold at the maximum depth. Reduced elastic modulus and nanohardness were measured by diamond and zirconia spherical indenters with nominal radii of 10 μm and 250 μm, respectively. A sharper Berkovich indenter, the tip of which has R = 20 nm, was also used in this work.

The studies were carried out in a multi-cycle test mode [20-22], which makes it possible to effectively evaluate the properties of a ceramic fiber mat at various contact scales. In the process of multi-cycle testing, 5 repeated cycles loading and unloading are localized in the same indentation. The load on the indenter was proportionally varied from 0 to 5 mN. In this case, the residual load should keep the indenter in contact with the sample without side slip. At the end of unloading, a 20 s hold was provided to correct the thermal drift. To minimize thermal drift prior to testing, all tests were set to an initial drift rate of 0.08 nm/s. All the values were averaged over 10 measurements.

3. Results and discussion

Electrospun composite nanofibers are randomly distributed to form a nonwoven mat. They are initially cylindrical with a smooth surface. The average diameter of the produced filaments is 575 ± 65 nm. After calcinations at 600 °C the average diameter of the fibers reduced to 162 ± 15 nm due to ZrAA decomposition and PAN removal. Their surface remained smooth despite the relatively high temperature. The appearance and growth of ZrO₂ grains begins at temperatures above 650 °C that results in appearance of a rough surface. A further increase in the calcination temperature to 1200 °C is accompanied, on the one hand, by further growth of ZrO₂ grains, and on the other hand, leads to a
slight shrinkage of the fibers due to sintering. As a result of these processes, the average fiber diameter increases to 145 ± 16 nm, and their surface becomes even more rough.

The rise in fibers calcination temperature affects their specific surface area and porosity too. From nitrogen adsorption-desorption isotherms at 77 K of zirconia fibers prepared at different temperatures (figure 1) it can be seen that increase in calcination temperature results in hysteresis loop narrowing and the quantity of adsorbed nitrogen decrease. It indicates zirconia fibers porosity reduction with increase in calcination temperature due to ZrO$_2$ grain growth and sintering. In our case, pores are formed by the boundaries of adjacent ZrO$_2$ grains. These grain growths are also causes zirconia fibers specific surface area decrease with rise in calcination temperature.

![Nitrogen adsorption-desorption isotherms at 77 K of electrospun ZrAA/Y(NO$_3$)$_3$/PAN fibers calcined at 600 °C, 900 °C and 1200 °C.](image)

Figure 1. Nitrogen adsorption-desorption isotherms at 77 K of electrospun ZrAA/Y(NO$_3$)$_3$/PAN fibers calcined at 600 °C, 900 °C and 1200 °C.

The evolution of the grain structure of nanofibers with increasing calcination temperature is confirmed by XRD data. We saw that the fibers calcined at 600 °C have a crystalline structure and all the observed reflections correspond to t-ZrO$_2$. This indicates that these fibers are composed only of t-ZrO$_2$ grains. At a calcination temperature of 900 °C, the average grain size of t-ZrO$_2$ was 18 nm, and at a temperature of 1200 °C it reached 39 nm. No additional reflections from other 3Y-ZrO$_2$ phases are observed in the X-ray diffraction patterns with an increase in the calcination temperature. This is evidence that heat treatment of nanofibers in the range 600–1200 °C does not affect the phase composition of the fibers, although the average grain size of t-ZrO$_2$ increases by almost 5 times.

Two parameters can be relatively easily extracted from instrumental indentation tests: hardness $H$ and Young's modulus $E$, representing the plastic and elastic properties of the material, respectively. Both of these quantities depend in a rather complicated way on the testing conditions, in particular on the geometry of the indenter [23]. Typically, nanoindentation provides results from a locally homogenized volume at a micro- or nanoscale. It should be noted that the use of nanoindentation in the case of heterogeneous and porous materials, such as ceramic fiber mats, is very limited. This limitation is due to the fact that the theory is based on the assumption of a homogeneous and isotropic half-space without scale restrictions, and the data obtained are average values depending on the type of indenter and the depth of indentation. The general behavior of 3Y-TZP mats during nanoindentation directly depends on the formation of individual phases and their microstructures and is associated with
the possible mixing of unreacted components or the occurrence of chemical reactions that develop after such mixing [10].

Figure 2 illustrates depth-dependencies of the elastic modulus and hardness of the 3Y-TZP nanofibers mats tested by indenters with different sharpness and shape. As we seen on figure 2(b, c), the effect of the calcination temperature on the elastic modulus is non-monotonous, with the highest values observed for the mats calcined at 900 °C. At this calcination temperature, the average size of tetragonal grains usually does not exceed 18 nm, and with a further increase in temperature to 1200 °C they reach 39 nm in diameter. Such a rearrangement of the grain structure is accompanied by a simultaneous decrease in the porosity of nanofibers. It should be noted also that the elastic modulus obtained at calcined 1200 °C is equal \( E = 0.55 \pm 0.06 \) MPa is below the typically reported values [3, 10, 11]. In this case, \( E \) is lower, and the elasticity of the mats at this annealing temperature is even higher than at \( T = 600 \) °C, and this is observed for both spherical indenters, the radii of which differ by a factor of 25. We also see that the absolute values of hardness for a spherical tip with \( R = 250 \) µm differ by 2 times from the higher values obtained with a 10 µm indenter tip. This is because a blunt spherical indenter has a higher contact surface, allowing more material to be integrated under the same load.

Berkovich pyramidal indenter is much sharper than spherical indenters. The spherical blunting tip of such an indenter does not exceed 20 nm. Figure 2d shows how the elastic modulus and hardness change as a function of the calcination temperature during nanoindentation with a Berkovich tip. All the regularities of the indentation scale effect (ISE) in hardness are also fulfilled here: the sharper the indenter used, the greater the obtained hardness value. The elastic modulus has the highest value equal to \( 1.56 \pm 0.65 \) MPa for \( T = 1200 \) °C.

Figure 2. \( P-h \) diagram (a), elastic modulus and hardness of a mat of ceramic 3Y-TZP nanofibers under indentation for different annealing temperatures by: (b) spherical indenter \( R = 250 \) µm, (c) spherical indenter \( R = 10 \) µm, (d) Berkovich indenter \( R = 20 \) nm.
From the energetic point of view, the method of multi-cycling loading is most suitable for indentation of ceramic fiber mats. As seen in figure 3, multi-cycling load-unload-reload-unload tests contain both unloading and reloading curves. The beginning of the reloading curve has a lesser effect on the formation of material pop-in around the indentation, that contributes to a stricter observance of the Oliver-Pharr conditions [14]. We see that the loop energy (the loop area) decreases with the increase in calcination temperature. In the last load-unload cycle on the mats calcined at 1200 °C the hysteresis loop energy was approximately 2.5 times lower than the one registered in the 600 °C calcined mats. It was found earlier that the hysteresis observed under multicycle nanoindentation may appear because of quasi-brittle fracture, phase transformation, viscoelastic or viscoelastic deformations. It was experimentally proved that all these processes increase the area of the hysteresis loop. But as we have seen in figure 4, at the present research the hysteresis loops narrow with the increasing calcination temperature. In our case it can be assumed that increase in crystallinity of the fibers and growth of the average grain size may serve as such mechanism.

![Figure 3](image1.png)

**Figure 3.** (a) - dependence of the load (1) and the indentation depth (2) on the time of the multi-cycle test; (b) - Ph-diagrams of 5 loading-unloading cycles at different annealing temperatures:
1 - 600 °C, 2 - 900 °C, 3 - 1200 °C.

![Figure 4](image2.png)

**Figure 4.** Dependence of the energy of the hysteresis loop on the annealing temperature of ceramic fiber mats: 1 – 600 °C, 2 – 900 °C, 3 – 1200 °C.

The highest mechanical properties are achieved in mats calcined at 900 °C. It was previously shown that at this temperature, micro-roughness begins to appear on the surface of nanofibers due to grain growth, which affects the elasticity and hardness of the mats.
4. Conclusion
The mats of ceramic nanofibers were prepared from solution of PAN in N,N-dimethylformamide with addition of zirconium acetylacetonate and yttrium nitrate hexahydrate by the electrospinning technique. Their were calcined at 600, 900, and 1200 °C; the resulting fibers had a diameter of 145±16 nm. The phase composition of the mats at these temperatures was 100 % tetragonal zirconia phase. It was found that the average grain size increases from 8 to 39 nm with an increase in the calcination temperature to 1200 °C.

Some mechanical properties of the mats were determined by the nanoindentation method. Experiments with indenters of different sharpness have shown that mats calcined at 900 °C have the highest hardness and modulus of elasticity. Optimal mechanical properties are believed to occur at a calcined temperature of 900 °C due to the balance between sufficient grain growth and little or no fiber cross-sintering. This annealing temperature can be considered optimal for the manufacture of nanofiber mats, the mechanical properties of which are important for their application.

Acknowledgments
The research was financially supported by the Russian Fund for Basic Research: projects № 18-29-17047 (synthesis, study of the microstructure and of the mechanical properties) and № 19-03-00634 (investigation of the phase composition), and by TSU named after G.R. Derzhavin, order No. 591-3 of February 25, 2020 (nanoindentation tests). The research was carried out with the use of equipment of G.R. Derzhavin Tambov State University Common Use Center.

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