

UNIVERSITY OF TARTU  
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Sol-gel preparation of controlled wall thickness high-quality  
nanoceramic microtubes

Master's thesis  
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## **Sol-gel preparation of controlled wall thickness high quality nanoceramic microtubes**

Miniaturization of technology offers many advantages as it enables manipulation with very small amounts of materials in a very precise manner. The development of miniature technology is currently a topical subject. Different fields of technologies already employ microfluidic systems, but for applications that require more extreme pressure and temperature conditions, such as plasma jet nozzles, spray heads or high temperature solid oxide fuel cells, there is a shortage of suitable materials and preparation methods of necessary parts. When looking more specifically at microtubes, the ones currently produced and used have significant limitations on their size and mechanical properties. In our research group a combination of extrusion and sol-gel technology has been used to produce nanoceramic microtubes with high structural homogeneity and excellent mechanical properties.. In the present work, the effect of different parameters on the properties of the material synthesis and tube preparation have been studied. As a result a method of microtube production has been developed that enables control of the diameter and wall thickness of the tubes. The outer diameters of these tubes are in the range of 100  $\mu\text{m}$  and inner diameter smaller than 1  $\mu\text{m}$  can be achieved. Due to the relatively uncomplicated preparation method, scalability and outstanding dimensions and properties, these microtubes are great candidates for using in microfluidic systems that operate under harsh conditions.

Keywords: sol-gel technology; yttria stabilized zirconia, YSZ; microtube; micronozzle; microfluidics; microtubular solid oxide fuel cell. CERCS: T153 Ceramic materials and powders.

## **Kontrollitava seinapaksusega kõrgekvaliteediliste nanokeraamiliste mikrotorude valmistamine sool-geel meetodil**

Tehnoloogia miniaturiseerimine võimaldab töötada väga väikeste materjalikogustega väga täpsel viisil ning seega avab mitmeid võimalusi vastavate tehnoloogiate efektiivsemaks muutmiseks. Miniatuursete tehnoloogiate arendamine on praegu aktuaalne teema ning muuhulgas on välja töötatud ka tehnoloogiaid, mis kasutavad mikrovedeliksüsteeme. Väga vähe on tegeletud aga lahendustega, mis sobivad kasutamiseks karmimates rõhu- või temperatuurioludes. Selliste rakenduste hulka kuuluvad näiteks mikrodüüsid, pihustussüsteemid ja kõrgtemperatuurised tahkeoksiidsed kütuseelemendid. Puudu on nii sobilikest materjalidest kui võimekusest valmistada sobivaid detaile. Näiteks eelnimetatud rakendustesse sobilike mikrotorude valmistamisel on praegu olulisi puudujääke nii torude suuruse kui mehaaniliste omaduste osas. Meie uurimisgrupis kombineeriti ekstrueerimine ja sool-geel tehnoloogia, et valmistada kõrge struktuurilise homogeensuse ja heade mehaaniliste omadustega nanokeraamilisi mikrotorusid. Käesoleva töö raames uuriti lähemalt erinevate sünteesiparameetrite otsest mõju valmistatavale materjalile ning sellest valmistatud torudele. Mikrotorude sünteesimeetodi täiustamise tulemusena on saavutatud algne võimekus kontrollida torude diameetrit ja seinapaksust. Valmistatud torude välisdiameetrid on suurusjärgus 100 µm ning vähim saavutatud sisediameeter on alla 1 µm. Valmistatud torud on suurepärased kandidaadid karmidel tingimustel töötavates mikrovedeliksüsteemides kasutamiseks, kuna kasutatav sünteesimehhanism on võrreldes enamlevinud meetoditega suhteliselt lihtne ja skaleeritav ning sünteesitud torud on äärmiselt heade mõõtmete ja mehaaniliste omadustega.

Märksõnad: sool-geel tehnoloogia; ütriumoksiidiga stabiliseeritud tsirkooniumoksiid, YSZ; mikrotoru; mikrodüüs; mikrofluidika; mikrotubulaarne kütuseelement. CERCS: T153  
Keraamilised materjalid ja -pulbrid.

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# 1 Introduction

Microtubes are miniature structures that have applications in a wide range of fields, including, but not limited to preparation and delivery of drugs [1], gas sensors [2], water monitoring [3]. There are several advantages to miniaturization as it can provide an extremely high level of precision in creation and manipulation of droplet-sized volumes of materials and reduce the overall amount of materials used in the process. For example, using microcarriers for administering drugs can help to raise safety and effectiveness of the drugs [1]. In the field of microelectronics, the development of microtubular solid oxide fuel cells is one way to achieve very high power densities, shorten start-up times and reduce thermal degradation [4].

While a lot of microfluidics-based applications that operate under mild conditions have been developed, there is a noticeable lack of systems that can operate under more extreme conditions, such as high pressure and temperature or thermal cycling. The need for materials that withstand these kinds of conditions is evident for miniature plasma sources [5], micro propulsion devices [6] and microtubular solid oxide fuel cells [4]. The main issues hindering the widespread use of such miniature technology are lack of suitable materials and engineering problems of miniaturization, like the difficulty to produce suitable sensors, valves and jet systems [3].

Ceramic metal oxide materials have the potential to overcome most of the mentioned difficulties. In this work, the unique method of yttria stabilized zirconia microtube preparation developed in our research group, has been significantly improved. Remarkable progress has also been made in understanding the synthesis mechanism on the structures. As a result of this progress, the properties of the obtained tubes, like their length, wall thickness and inner diameter can be controlled. A method of scaling up the production has also been demonstrated. As demonstrated earlier, tubes prepared using this method have good physical, optical and electric properties making them suitable for applications in various microfluidic systems, including under extreme conditions [7].

## **2 Author's role in the research**

The author prepared all the precursor materials, measured their viscosity and compared the effects of different synthesizing parameters on the properties of the precursor materials. The concept of the work was developed with supervisor Tanel Tätte PhD.

Scanning electron microscope images were captured by Siim Pikker; optical microscope images were captured by Tanel Tätte.

## **3 Overview of literature**

### **3.1 Yttria-stabilized zirconia**

Zirconium dioxide or zirconia is a ceramic material used in a variety of applications. It has a monoclinic lattice at low temperatures, but when temperature rises above 1170°C, it undergoes a phase transition to a tetragonal phase. The phase transition causes a volume change of 3-5% making the material more fragile and with several heat cycles can cause it to break. The phase transition can be avoided by adding dopants, such as yttrium oxide. Yttrium oxide stabilizes the tetragonal phase so when temperature drops under 1170°C, the material does not undergo a phase transition. This phenomenon gives name to the obtained material: yttria stabilized zirconia (YSZ). Doping also raises the ionic conductivity of zirconia. Since yttrium has a valence different from zirconium, it creates lattice defects allowing oxygen ions to move more freely inside the material. This makes the material suited for using as an electrolyte in a SOFC. [8]

Microtubes prepared from YSZ are nanohomogeneous and have very good mechanical properties: Young's modulus in the range 100-150 GPa, tensile strength 400-600 MPa and they withstand pressure up to 1000 atm in the tubes. Thanks to these properties they have been demonstrated to be applicable as microdimensional capillaries in a plasma jet device and have potential to be used in various other applications that require severe conditions [7].

### **3.2 Applications of microtubes**

#### **3.2.1 Micronozzles**

Micronozzles have applications in a variety of fields including drug administering [1], diagnostics [9], sensorics and monitoring [3]. Many of these applications have an early proof of concept, but are still under development and have no real life output due to problems of scaling up, reproducibility, high price or lack of suitable materials. Also for applications in more extreme pressure and temperature conditions, there is a lack of suitable materials. Nonetheless, there are already a few companies trying to find solutions and have entered the

market of micronozzle production. Mikros Technologies, a company originally founded to develop a micronozzle solution for two-phase cooling systems in a project with NASA Johnson Space Centre, has now expanded into developing solutions for industrial inkjet printing, micropropulsion systems and medicine and vaccine delivery and production. They use micro-electro discharge machining (micro-EDM) manufacturing process which can provide sub-micron accuracy in the placement and internal contouring of the nozzles. They work with electrically conductive materials, mostly stainless steel [10]. Crafts Technology also uses micro-EDM technology to produce micronozzles out of different ceramics and steels. Among others, they have worked on applications in medical and fluid-dispensing fields as well as laboratory testing [11]. While these solutions are already on the market, they are very expensive and nozzles or tubes with orifices with a diameter less than 20-10  $\mu\text{m}$  are not prevalent yet due to the absence of suitable technology.

### **3.2.2 Microtubular solid oxide fuel cells**

Microtubular solid oxide fuel cells (SOFC) are an example of microtube use under extreme conditions. SOFCs are one the most efficient ways to turn the energy released in a chemical reaction directly into electricity. Compared to other types of energy production, fuel cells in general have several advantages: they operate with no or very low environmentally harmful emissions, the efficiency and cost of energy production are not as dependable on the scale, fuel cells are quiet and have no moving parts. [12] In order to achieve better ionic conductivity, SOFCs usually work at rather high temperatures, which brings upon an important difficulty of building them: different materials have different thermal expansion coefficients so the range of materials that can be used as electrolytes and electrodes is rather limited, as they must be compatible. In addition, the electrolyte material needs to have high ionic but low electronic conductivity, it must be stable in both reducing and oxidizing environments and it must be possible to produce a thin film out of the material. YSZ has all these properties and is a popular choice for electrolyte material, including in microtubular SOFCs [8].

### 3.3 Preparation methods of microtubes

A simple and common method for microtube production is extrusion. In this process the precursor is pushed through a die of a desired size and shape and it then hardens by either a chemical reaction or cooling. This method is popular since it is inexpensive, scalable and has the possibility of co-extrusion of different layers. It is used to prepare tubes that have a diameter in the range of 1 mm and bigger [13;14]. A drawback of using extrusion for the production of microtubes is the lack of suitable technology to extrude microtubes with a diameter less than 1 mm.

Another common method for microtube preparation is using a template. It involves covering a small fiber with a ceramic material, letting it harden and then removing the fiber. The fiber can be covered using, for example sol-gel method or atomic layer deposition and the fiber can be removed by melting, burning or dissolving. Using a template enables better control of the size and shape of the obtained tubes, but it also has several drawbacks: the size of the tubes is limited by the size of the template, removing the template can damage the tube and most importantly, the obtained tubes are non-homogenous making the material mechanically weaker. [15]

Tubes can also be made by curling of the material used. Tubes with a diameter as small as 10  $\mu\text{m}$  and material sheet thickness of 200-400 nm have been using zirconium oxide. The curling happens due to tension gradient in the material sheet. However, these types of tubes are not suitable for use in many setups since they are not perfect tubes, but instead their cross-section is a spiral meaning they have an open side. [16]

A more high-technology approach to microtube preparation is micro-electro discharge machining. EDM as well as its variant micro-EDM is a method of carving a shape out of a workpiece using a series of electrical discharges between the cathode, usually tungsten materials, and the workpiece, anode, in a dielectric environment. The temperature at the point of discharge is 8 000 - 12 000 °C resulting in the vaporization of the material of the workpiece in that spot. It is used to create different types of structures, including microtubes and -channels with orifice diameter in the range of 10-20  $\mu\text{m}$  and submicron accuracy. This method can be used for a variety of materials, such as metals and alloys but has also been tested for carbides

and ceramics. The main drawback of this method is that it requires specific expensive machinery making the price of the obtained structures very expensive. [17]

In our laboratory, a unique method of producing microtubes has been proposed [7; 18; 19; 20]. Zirconium or titanium alkoxide, either butoxide or propoxide, is dissolved in different alcohols, yttria is added in the form of yttrium nitrate and the solution is vacuumated and heated to remove excess solvents. The obtained solution is viscous and spinnable into fibers. The material in the drawn fibers reacts with humidity in the surrounding air and via sol-gel transformation hardens and hollows to form microtubes. These microtubes have good mechanical and optical properties for applications including micronozzles, gas sensors or as optical waveguides. Furthermore, their electrical properties have been shown to be suitable for mSOFC applications [7; 21]. So far, the main drawing method has been using a glass rod [20], while some experiments with extrusion have also been made [7]. Recently progress using the extrusion method has been made and the combination of extruding a filament and employing sol-gel method to obtain tubes has so far proven to be the best way of producing tubes in the scale of tens to hundreds microns.

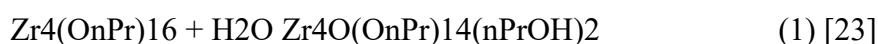
### **3.4 Colloidal solutions and sol-gel technology**

Colloidal solutions are two-phase systems, where nanosized solid particles are dispersed in a liquid. They differ from real solutions as the particles in the latter are molecular or ionic, not bigger nanoscale particles. These two types of solutions have similarities, like their flowing properties. But they also have differences due to the different size of the particles, like light scattering properties. Colloidal solutions also differ from suspensions, that have meso or macro scale particles dispersed in liquid. For example, the small size of the particles in a colloidal solution, as well as a dielectric double layer on their surface make the system more stable in comparison, as bigger particles in suspensions can precipitate more easily. However, the chemical balance of colloidal solutions is very delicate and when it is disrupted, for example by adding a tiny amount of an electrolyte, the stability is lost and the dispersed particles can coagulate and precipitate or gelatinate. This phenomenon is called sol-gel transition. The material obtained by this method, a gel, has properties similar to both liquids, like the speed of

diffusion in them, as well as solids, like elasticity. Technologies that use sol-gel transition for synthesis or material preparation, are called sol-gel technologies [22].

### 3.4.1 MTSAL theory

Metal alkoxides react readily with water, both from water bonded to other reagents and humidity in the air. The product of hydrolysis depends on the ratio of metal alkoxide and water. By adding small amounts of water into the system, the alkoxide molecules are re-structured and oligonuclear oxo-alkoxide species are formed. The microhydrolysis of zirconium propoxide follows reaction (1).



The products have complicated structures as shown in Figure 1. These particles have a core-shell structure that have metal-oxo particles with the structure analogous to the corresponding oxide on the inside and alkoxy layer forming the stabilizing shell on the surface [23].

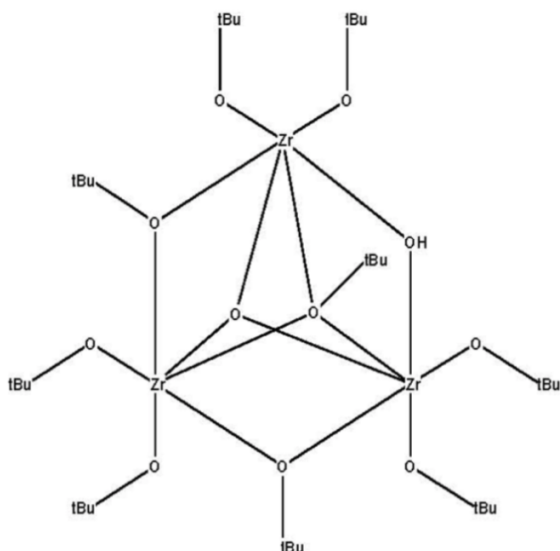


Figure 1. The product of microhydrolysis of zirconium alkoxide. [23]

If there is more water in the environment, the microhydrolysis continues as the stability of the particles is lost. Alkoxy groups are released from the outer layer and the metal oxo-alkoxide

species form into bigger clusters and can form new metal-oxide-metal bonds. The exact products of this reaction depend on the residual organic ligands in the particles: these ligands dictate the stability of the particles and the reactions on their surfaces. The products obtained via this route are called Micelles Templated by Self-Assembly of Ligands (MTSALs). It has been noted that although the exact size of the MTSAL particles is dependent on the interactions between ligands and solvents, their diameter is almost always in the range of 2-5 nm. MTSALs are primary products of the sol-gel transition and have a key role in determining the end products of the process. [23]

## 4 Experimental

### 4.1 Preparation of the precursor

Zirconium was used in the form of zirconium 1-propoxide (Sigma Aldrich, 70 wt% in 1-propanol) and it was dissolved in a mixture of propanol, butanol and pentanol. Per 1 mol of zirconium 1-propoxide approximately 2.3 mol of butanol and 1.3 mol of pentanol were added. About 4 moles of alcohols were added per 1 mole of propoxide, but propanol was added in small excess as it is simple to remove it later. Yttrium was added in the form of  $Y(NO_3)_3 \cdot 6H_2O$  (Novosibirsk Rare Metals Plant; 99.9%) dissolved in propanol. It was mixed with a small amount of distilled water and propanol. 0.04 mol of yttrium was added per 1 mol of zirconium 1-propoxide. The amount of water was varied so that the water-alkoxide mole ratio, R-value varied from 0.45 to 0.9. The obtained solution was dissolved in propanol so that the concentration of water in the solution was under 0.5 mol/l. The yttrium-water solution was added to the propoxide solution with the speed of 0.34 ml/min under constant stirring. Then the solution was vacuumed with Büchi V-700 vacuum pump using Büchi R-124 rotary evaporator and Büchi V-800 vacuum controller. During vacuuming the solution was in a 40°C water bath and the bulb was rotated so that the solution would flow inside and solvents would evaporate evenly from the whole material. When most of the solvents were evaporated and the solution was more viscous, the slowest possible speed of 5 rpm was applied. With this setup the pressure in the system was gradually brought to 20 mbar. Gradual lowering of the pressure is important to avoid intensive boiling in the bulb. For some samples, second vacuuming was carried out with an oil pump in order to study the effect of lowering the pressure in the system to under 1 mbar. After vacuuming with the Büchi vacuum pump the pressure in the system was raised to normal pressure in the laboratory, about 1000 mbar, the evaporated solvents were cleaned out and then the pressure was again gradually lowered to 20 mbar. After that the oil pump was attached to the system which enabled to lower the pressure to 0.1-1 mbar. Then the pressure was raised back to 1000 mbar by directing argon gas into the system. Argon was used in order to ensure no extra moisture is added to the precursor solution.

## 4.2 Choice of materials

Zr-1-propoxide was chosen as a metal source because its 1-propoxy groups are easily changed by 1-butoxy and 1-pentoxy groups by adding butanol and pentanol to it. The released 1-propanol can be easily evaporated in a vacuum pump. Less than 4 moles of butanol and pentanol combined were added per 1 mole of propoxide to ensure they would not be needed to remove later as it would be very difficult if not impossible with the setup used. Growing metal-oxo-alkoxide particles was initiated by adding small amounts of water to zirconium 1-propoxide. In order to ensure homogenous distribution of water, the propoxide was first diluted in propanol as propanol is a good solvent for water and any excess propanol can later be easily removed.

As mentioned in chapter 3.4.1, the products of sol-gel process depend on the MTSALs formed during the first stage of hydrolysis. If the stabilizing layers on these particles are similar enough, the material can crystallize [23]. If crystallization is unwanted, like in the case of this work, a mixture of different precursors can be used in order to avoid that. In previous works of our group, crystallization in the last stages of vacuuming has been a problem. This results in the material losing its spinnability and turning white or opaque instead of transparent. If Zr-1-propoxide is used as a metal source in the synthesis, adding butanol and pentanol into the mixture avoids the structural homogeneity and so far has successfully prevented crystallization.

Replacing some 1-propoxy groups with 1-butoxy and 1-pentoxy groups also helps to control both the viscosity as well as reactivity of the obtained precursor. Both of these are crucial parameters in the production of microtubes via this method. The more higher alcohols are in the solution, the less reactive and the more viscous it is. Material that has too high or too low viscosity is not easily spinnable into filaments and if filaments are formed, it is difficult to initiate their hollowing. If the material is too reactive, the drawn filaments are likely to break during curing. Thus tubes are either not formed at all or if they are, they are too curved, short or too brittle to be used in any applications. On the other hand, if the material is not reactive enough, the hardening takes place too slowly. This leads to the outer shell not being rigid enough to hold its structure, it shrinks with the material and the inner part will not become hollow to form a tube. The suitable proportions of butanol and pentanol used for the synthesis

were determined previously in the bachelor's thesis of the author [21] and were based on achieving optimal reactivity for the material.

### 4.3 Viscosity measurements

After the preparation of the precursor, it was left to flow into a 20 ml syringe overnight. The solution was allowed to rest for a couple of days before viscosity was measured using the falling ball method. Measurements carried out inside the 20 ml syringe using a metal ball with a diameter of 1 mm and mass of 4 mg. To measure the falling speed of the ball inside the precursor, materials were observed visually. Viscosity was calculated using the following formula:

$$\mu = \frac{2(\rho_{ball} - \rho_{mat})gr_{ball}^2}{9v_{ball}}$$

where:

$\mu$  - viscosity

$\rho_{ball}$  - density of the ball

$\rho_{mat}$  - density of precursor

$g$  - gravitational acceleration

$r_{ball}$  - radius of the ball

$v_{ball}$  - speed of the ball.

### 4.4 Drawing filaments

Two methods of filament drawing were used. First is the glass rod method. The precursor was in the reaction bulb, a round-tipped glass rod was immersed 1 mm into the precursor and when the rod was pulled out, the viscous solution formed a 15-50 cm long filament at the end of it. The filaments were set hanging on a horizontal rod in laboratory air at 22 °C and ~60 % relative air humidity. From the drawn filaments, ones with the most constant diameter were chosen within 10 seconds of drawing and separated. To initiate tube formation, approximately 1 mm

long ends of these tubes were broken off. The time between drawing the filament and breaking the end off varied from 20 s to 11 min.

The second method of filament drawing was through extrusion. After carrying out viscosity measurements, the precursor was pressed into a stainless steel syringe. A special apparatus was constructed which enabled the precursor to be pressed from the stainless steel syringe into laboratory air through a nozzle using Mitsubishi servomotors and controllers. Extrusion was carried out at 22 °C and ~60 % relative air humidity. To study the effect of the nozzle diameter on the obtained structures, different size nozzles were used with diameters varying from 100 to 600  $\mu\text{m}$ .

## 5 Results and discussion

### 5.1 Reproducibility and viscosity

An important factor in raising the reproducibility of the experimental outcomes is how well excess solvents are removed. Any excess solvents left in the solution lower its viscosity and thus change the spinnability of the material. As an important innovation for controlling this, a two-step vacuuming with two different vacuum pumps was used. Compared to earlier one-step vacuuming until 20 mbar, this method enabled to achieve vacuum under 1 mbar, ensuring more complete removal of solvents. The effect of this can be seen in Figure 2: viscosities of materials vacuumated to 20 mbar, shown with black test points, have lower viscosities than the ones vacuumated under 1 mbar, shown with red test points. When vacuuming to 20 mbar the amount of solvents left in the precursor solution varies somewhat in different experiments affecting the properties of the obtained material. With vacuum as low as 1 mbar, the amount of excess solvents possibly left in the solution is negligible.

The amount of water added to the alkoxide-alcohols solution affects the growth of metal-oxo-alkoxide particles. In general, the more water is added, the bigger the particles grow and the more viscous the material is. This relation is shown in Figure 2. The most suitable viscosity for drawing filaments resulting in tube formation is 150-300 P. This was achieved with R-values up to 0.6 whereas the best samples were the ones with R-value in the range of 4.5-5.5 that underwent two-step vacuuming.

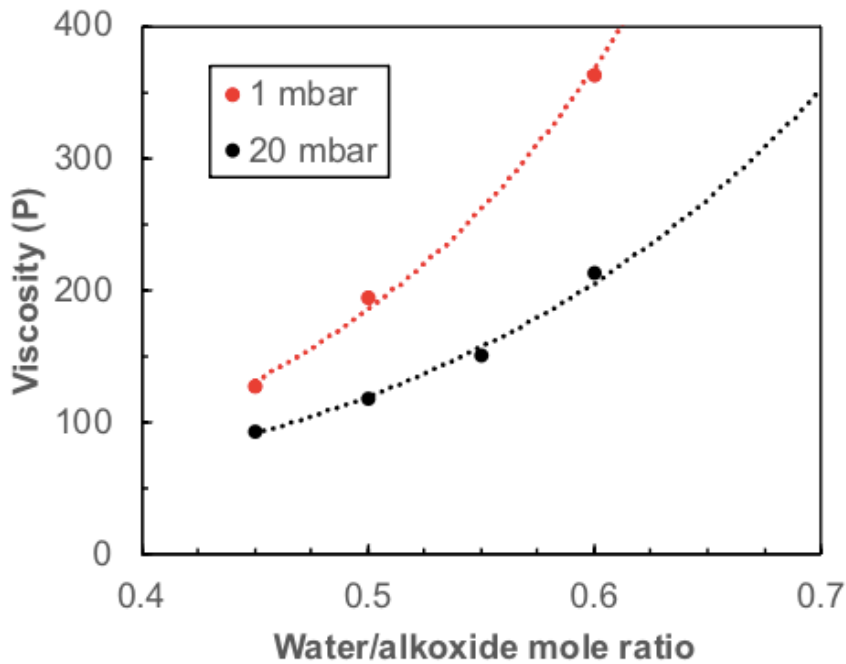


Figure 2. The dependence of precursor viscosity on water-alkoxide mole ratio and lowest pressure achieved in the system. Black test points were obtained with one-step vacuuming; red test points were obtained with two-step vacuuming. Dotted lines indicate fitting of experimental data.

## 5.2 Formation of the tubes

The formation takes place in three stages. First stage is the formation of the liquid filament by extrusion or pulling with a rod from the flask. Second stage is hardening of the outer layers of the filament. Third stage is hollowing of the filament and final hardening of the whole material leading to formation of a tube.

The outer layer of the drawn filament starts to harden when the alkoxide molecules react with water vapor in the environment forming a solid YSZ film on the surface of the filament. As the process continues, water molecules diffuse through the layer allowing the alkoxide molecules on its inner side to react and the film to grow thicker. The more the solid outer layer grows in thickness, the longer it takes the water molecules to diffuse through it, making the reaction slow down. The volume of the solid YSZ material is smaller than the volume of the liquid phase and accordingly the diameter of the solid shell is smaller than the diameter of the liquid

filament. This means the solid film pressurizes the liquid on the inside and when the pressure is higher than the strength of the solid film, cracks form on the surface of the film and some of the liquid phase is pushed out through them.

The hollowing of the filament begins as humid air can move inside of the tube through the formed cracks and the remaining liquid phase on the inside of the solid shell can react with the water molecules. Due to the reduction of volume, the inside of the tube is left hollow. This stage can be observed under an optical microscope. As air enters the tube, a meniscus is formed on the air-liquid surface and as the liquid material reacts with humidity in the air and solidifies onto the existing solid phase, the meniscus can be seen moving forward inside the tube. This stage of the formation of the tubes is faster when the humidity of the air is higher: in higher humidity the air-liquid meniscus inside the tube can be observed moving faster indicating a faster reaction.

Interestingly, when two filaments drawn from the same precursor have the exact same geometry and cracks form on one of them, that one usually forms a tube. At the same time the one without cracks stays a fiber. As a new understanding of the mechanism of the tube formation, it is proposed that the reason for this is that a thicker part of the filament near the glass rod acts as a liquid reservoir. Upon the direct drawing of the filament with a glass rod, the cross-section of the part of the filament near the end of the rod transforms from circular to ellipsoidal. Due to this, when the thinner part of the filament undergoes the initial fast solidification, the volume loss inside the material is compensated by the liquid flowing down from the reservoir and the orifice is not formed. The process is described in Figure 3. This explanation is supported by the fact that when cracks are formed, the filament fragmentizes and the partly hardened fragments fall onto a substrate under the setup, filaments made from a suitable precursor do form hollows. When the filament fragments are detached from the glass rod and thus the reservoir, the volume loss is not compensated and hollows form in the filaments.

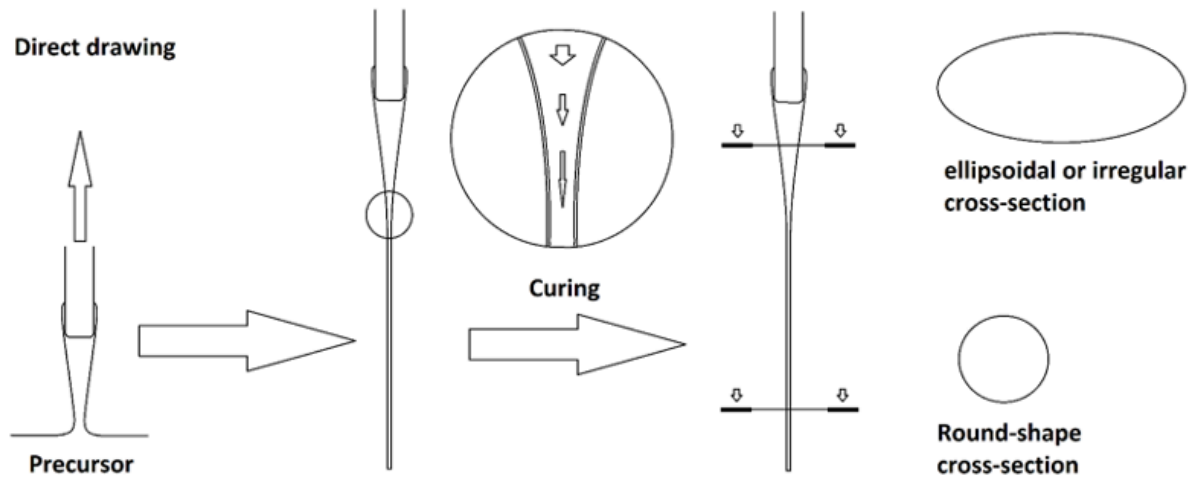


Figure 3. Direct drawing of filaments with a glass rod and the solidification of the filaments into non-hollow fibers.

### 5.3 Geometry of extruded filaments

Extruded filaments initially have circular cross-section throughout their length. During the curing process, both the shape and size of the cross-section can change. This is affected by two factors: the initial diameter and the break-off time of the filament.

Filaments with diameter less than 10  $\mu\text{m}$  do not form hollow tubes, most probably due to too rapid solidification. Filaments with diameters more than 200  $\mu\text{m}$  form a crumpled structure. This is because the initial shell that forms on its surface is not strong enough to sustain the circular cross-section as the volume of material inside the shell is reducing. As a result, the shell sinks in toward the central axis of the filament. Thus, the most suitable diameter of the initial filament for tube formation is between 10 and 200  $\mu\text{m}$ . The effect of the filament diameter is pictured in Figure 4. As the diameter of the filament may not be uniform throughout its length, it is important that the diameter in no part of the filament exceeds 200  $\mu\text{m}$  due to another phenomena as well. This size seems to be the critical threshold above which the wider part can start acting as a liquid reservoir, as described above. So although some parts of the filament may have a suitable diameter for tube formation, the hardening still results in a non-hollow fiber.



Figure 4. The effect of the initial diameter of the filament to the shape of the cured structure.

The break-off time has a direct effect on the wall thickness of the microtubes: the longer the time, the thicker the wall. This relation is seen on Figure 6. If the break-off time is too short, around 20 s, wall thickness is  $>10 \mu\text{m}$ , which is not enough to support the tube making it collapse. The smallest wall thickness while maintaining a regular round-shaped cross-section, was about  $10 \mu\text{m}$  and was obtained with a break-off time of 40 s. The longest break-off time tested resulted in a tube with wall thickness around  $50 \mu\text{m}$  and an orifice with a diameter about  $1 \mu\text{m}$ . Tubes with submicron inner diameter at one end could be well-suited for nanonozzle applications. Scanning electron microscope images of microtubes with different break-off times are in Figure 5.

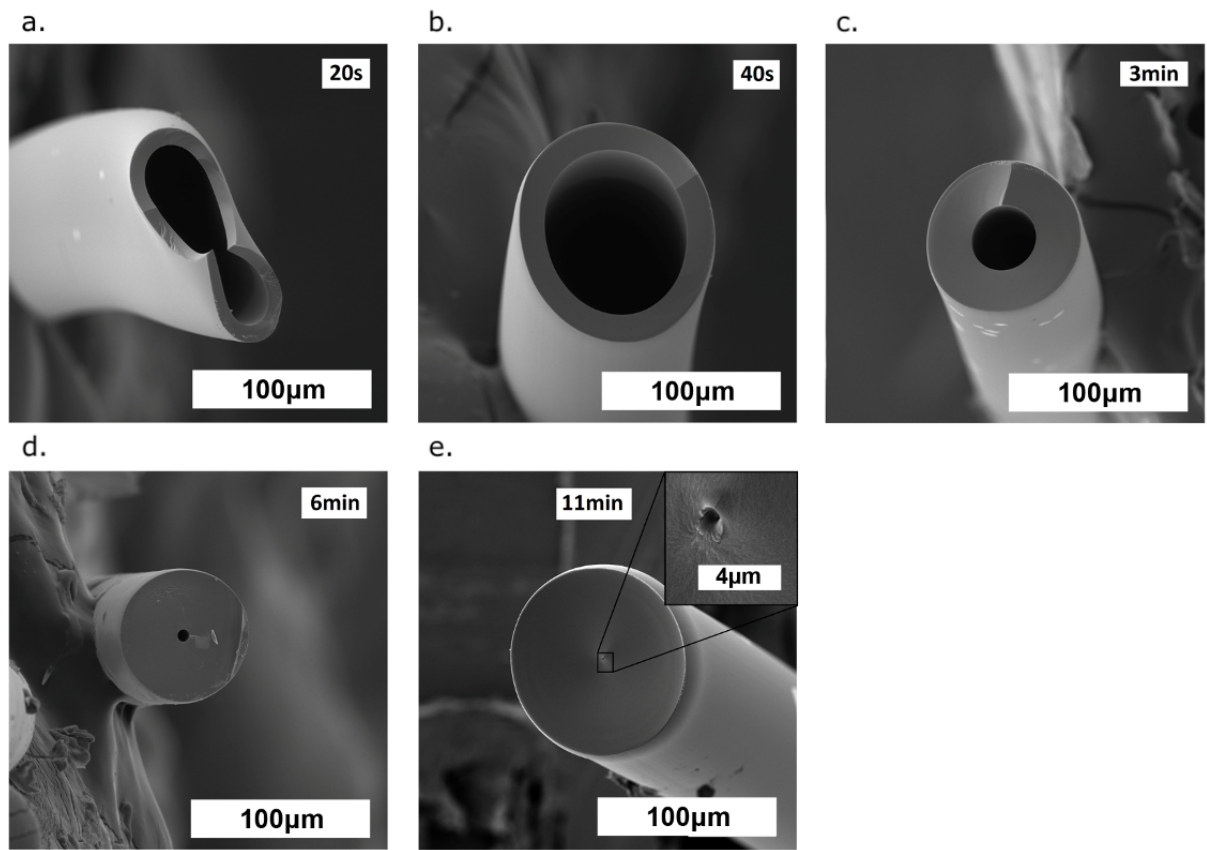


Figure 5. Scanning electron microscope images of tubes that were broken off at different times after drawing the filaments. a. shows a collapsed tube; inset on e. shows submicron sized hollow core.

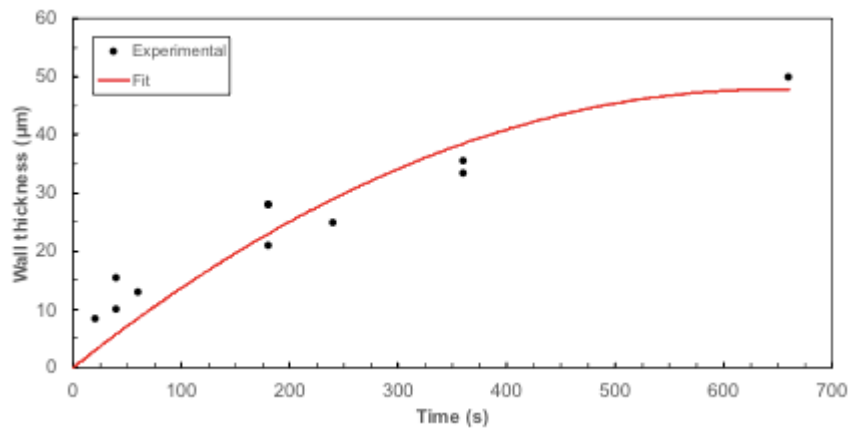


Figure 6. The relation between break-off time and wall thickness.

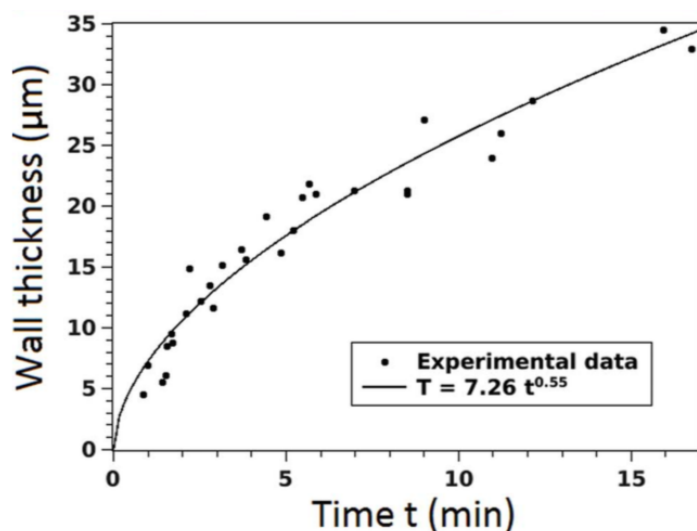


Figure 7. The relation between ageing time and wall thickness of 3-5 cm long TiO<sub>2</sub> fibers [18].

It is interesting to compare the effect of curing time on YSZ structures prepared with the method described in this work to the effect of it on TiO<sub>2</sub> structures described in our group's earlier work [18]. The TiO<sub>2</sub> structures were synthesized using the same method as described in this work, but used titanium butoxide as metal source, didn't have added yttria and were vacuumated at 70 °C with 1-2.5 mbar being the lowest pressure achieved. The curve of time dependence of thickening for these samples is shown in Figure 7. It is clear that the wall thickness grows faster for YSZ samples: after 3 minutes the tubes had wall thickness around 20-30 μm, whereas in the same time, walls in TiO<sub>2</sub> fibers had thickness around 10-15 μm. By the 11 minute mark, the YSZ structures are almost fully hardened and further growth of wall thickness is very minimal, while in TiO<sub>2</sub> samples the wall thickness clearly grows even after 10 minutes of drawing. This indicates that the reaction taking place between zirconia compounds and water is much faster. Moreover, the processes that take place during the hardening of the wall are actually different as indicated by the solubility test also carried out with both zirconium and titanium filaments [18]. When immersed into hexane, zirconium based filaments do not dissolve and since hexane cannot break covalent bonds, it indicates the presence of covalent metal-oxygen-metal bonds. These filaments do not dissolve even when immersed in hexane immediately after drawing. On the other hand, titanium based filaments not only completely dissolve in hexane, but freshly drawn filaments also start to liquify in hexane vapor if held 0.5-1 cm above the surface of hexane. This means that in the Ti-oxo-alkoxide material a covalent network is not formed. Comparing these two materials, zirconium based material may be more difficult to handle and needs faster manipulation, but is in general more suited for different applications.

## 5.4 Initiating the formation of the microtubes

The understanding of the solidifying mechanism gave the idea to initiate the final stage of tube formation in a controlled way, without the spontaneous formation of cracks. Some time after the drawing of the filament, when a solid shell is formed on its surface, the filament can be broken off to desired length allowing the air to enter the tube and the rest of the process continues as described above. Break-off time is the time between the formation of the filament and breaking off the part of interest from the rest of the filament. The longer the break-off time is, the thicker the walls of the obtained tube are. So by alternating the time the outer shell is allowed to form, the wall thickness of the final tubes can be controlled. Since the solidifying reaction itself also takes time, the wall thickness changes along the tube: the part of the tube that is formed the earliest has the smallest wall thickness and vice versa. This phenomenon is seen in the images in Figure 8. When these microtubes are to be used as micronozzles, this feature is very useful as the wider end could be connected to other parts of the system as an inlet and the narrow end used as a precise outlet.

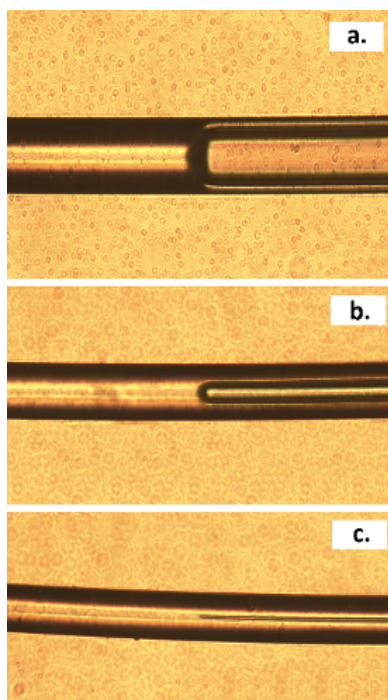


Figure 8. Transition of a partly solid filament into a microtube. Image a. is taken near the place of the cut just after cutting off the pictured part of the filament; the cut itself is on the far right, outside of the image. Image b. is taken in the middle of the tube formation process. Image c. is taken at the end of the process. The meniscus is moving from right to left in all the images; between taking each picture, the filament was moved under the lens in accordance with the moving of the meniscus.

## 6 Conclusion

As a result of this work, the synthesis mechanism of nanoceramic microtubes was further studied, the preparation method of them was significantly improved and the direct effects of different parameters of the preparation process on the prepared material and the structures obtained were described. The use of an improved two-step vacuuming helps to have better control over the removal of excess solvents of the precursor liquid thus helping to better employ the effect of water-alkoxide mole ratio on its viscosity. Choosing extrusion as the drawing mechanism of filaments enables us to prepare microtubes with different controlled diameters.

It was demonstrated that the formation of tubes from filaments can be initiated by breaking off the ends of filaments. Changing the time between drawing the filament and breaking its end off determines the wall thickness of the tube. Using this technique it was possible to prepare microtubes with inner diameter less than 1  $\mu\text{m}$ . In combination with extrusion, this makes it possible to scale up the production while also having good control over the parameters of the obtained microtubes.

Compared with other methods of microtube preparation, including traditional extrusion techniques, sol-gel approach is cheaper, less complicated and enables to achieve significantly smaller inner and outer diameters. When also taking into account their high structural homogeneity and excellent mechanical properties, these microtubes make very good candidates for nozzles in plasma jet devices, spray heads or electrolyte material in microtubular solid oxide fuel cells. As the dimensions of the microtubes are well-controlled, they can now be tested for these applications. In addition to that, the next step should be assembling a production prototype that would make it possible to scale up the production.

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## 9 Extras

An article by our research group on the same topic is soon to be sent to Scientific Reports for publishing. The introduction of the article is following.

### **Controllable sol-gel filament templated method for preparation of sub-100 $\mu\text{m}$ nanoceramic microtubes**

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#### **Abstract**

Microtubular solid oxide fuel cells ( $\mu\text{SOFC}$ ) have enabled record-high volumetric power densities in direct conversion of chemical energy into electricity. However, the lack of suitable methods for preparation of thin-walled (10  $\mu\text{m}$  or less) microtubular ceramic electrolytes has hindered development of these technologies. Currently available methods do not allow to prepare ceramic tubes finer than around 1 mm in diameter with wall thickness in some hundred microns. The current work expands upon our previously published technological pathway for truly microscale yttria stabilized zirconia microtubes with diameter ranging from 20 to 100  $\mu\text{m}$  and wall thickness from 7 to 30  $\mu\text{m}$ . The mechanism of tube formation process is clarified. The proposed method potentially allows large scale production of these materials.

Keywords: microtubes, sol-gel technology, SOFCs

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