

Phase Morphology in Electrospun Zirconia Microfibers

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Electrospinning of sol-gels has been used to produce zirconiumdoped polymer microfibers from zirconyl chloride and poly (vinylpyrollidone) precursors. Calcination of these structures between temperatures of 370° and 930°C resulted in the formation of zirconia nanograined microfibers whose diameters ranged from 1200 to 800 nm at the higher temperatures and whose average grain size ranged from 9 to 33 nm. X-ray diffraction analysis revealed varying amounts of monoclinic and tetragonal zirconia present in the fibers and established how this varied with calcination temperature and time. The tetragonal phase was shown to be unstable and disappeared on heating the material beyond around 750°C. The amount of zirconia yielded from the precursor material was measured and was found to be consistently greater than the theoretical yield. Average grain size within the microfibers increased with increasing calcination temperature and is effectively doubled when a 10 kPa pressure was applied. The effect of pressure also results in the creation of new crystal structures within the nanofibers and, as with traditional zirconia processing, the addition of impurity ions was found to stabilize the tetragonal phase.

I. Introduction

NANOSTRUCTURED ceramic oxides are receiving significant research interest, due to the complex structural aspects that can be achieved on a relatively small scale. Also, nanocrystalline materials are often regarded as consisting of metastable phases due to the high interfacial and grain boundary energies present.¹ As a result, structure and associated properties will depend on processing history. In addition, grain size is an important factor insofar as grain size control can be used as a method to control many properties. One common method for the fabrication of nanostructured ceramics is the sol–gel approach. Here, a soluble ceramic precursor material is dissolved in an appropriate solvent that also contains an organic component, and subsequently annealed to create a ceramic oxide.

One system of interest is zirconia (ZrO₂). Traditionally, solgel-processed zirconia has been used in film form as a high refractive index coating or thermal barrier.^{2,3} However, the complex structural nature of this material has suggested that it may have other areas of application. Zirconia exists in three different polymorphs: monoclinic (ambient to 1175°C), tetragonal (1175°–2370°C), and cubic (2370°–2680°C). Zirconia, when processed using traditional methods, undergoes a morphological change from tetragonal to monoclinic as it cools to below 1175°C and the volume change associated with this causes the material to disintegrate. To counter this, a small amount of oxide impurity is added during the processing stage to stabilize the tetragonal structure at room temperature through a complex cation substitution mechanism.⁴ This leads to a material of quite complex structure. Techniques such as the precipitation method^{1,5} have been used to characterize crystal structure and grain size as a function of annealing temperature and dopant of zirconia nanoparticles, but recent studies⁶ have shown that hightemperature zirconia phases can be produced from sol-gels at relatively low annealing temperatures so long as the grain size is small enough. Interestingly, it has been shown⁷ that if the material is annealed at an insufficiently high temperature, then incomplete conversion of the precursor sol-gel into pure zirconia can result in point defects within the material that assist in the stabilization of the tetragonal structure and that subsequent removal of these defects causes tetragonal to monoclinic transformation. By stabilizing the high-temperature phase structure at room temperature, zirconia materials have been investigated for use in solid oxide fuel cells⁸ and as sensors.⁹ As has been shown with other systems, the electrical and mechanical properties are very dependent on crystal structure and dopant effects, thus suggesting that stabilized zirconia is a material of interest.

Sol–gel-processed ceramics in fibrous form are proving to be very interesting materials. Here, although the fiber diameters are not necessarily on the nanoscale (i.e., <100 nm), the crystals that constitute these fibers often are. There is overwhelming evidence to suggest that materials on this scale have unique physical, structural, electrical, and mechanical characteristics. For instance, the promising thermoelectric properties of doped cobaltite ceramics stem from complex layered structures within the ceramic grains caused by atomic misfits, and the smaller the grains, the greater the effect.¹⁰ Another example is the ferroelectric polarization properties of nanograined perovskite barium titanate.¹¹ Processing and characterization of polymeric microfibers, for instance, are now well-established phenomena, with polymeric microfibers being used as biostructural scaffolds, ¹² protective filters, ¹³ and polymeric batteries.¹⁴

A simple method of producing nano and microfibrous materials is electrospinning.¹⁵ The electrospinning process has been used for many years, but has reached a new level of interest recently as a method for creating one-dimensional structures of high aspect ratio. Electrospinning has seen extensive use in the production of polymeric and bio-materials for numerous applications, and in recent years, has been used to produce small-scale ceramic fibers¹⁶ through the use of sol–gels. The sol–gel method allows for the production of ceramic precursor fibers, which can then be annealed at relatively low temperatures to create ceramic oxide-based fibers of reasonable structural integrity.

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By definition, the aspect ratio of electrospun fibers, and in particular the fiber diameter, could provide an effective and simple way of introducing a sizing control into ceramic nanostructures. From a sol-gel precursor, electrospun fibers of known diameters can be easily obtained either in random or in aligned form, and subsequently annealed to produce oxide fibers. Several ceramic systems produced through the electrospinning technique have been studied in recent years^{11,16-18} with varying degrees of success. Recent work⁵ has shown that yttriastabilized zirconia can be successfully electrospun from a sol-gel precursor and that annealing at 1500°C for 1 h results in a nanofibrous structure of pure zirconia. Shao et al.¹⁹ have produced zirconia fibers of around 200 nm in diameter using poly(vinyl alcohol) as an organic precursor, whereas Dharmaraj et al.²⁰ used poly(vinyl acetate) to produce similar-sized fibers at varying calcination temperatures.

The work presented here is based on the production of solgel-derived zirconia fibers using poly(vinylpyrollidone) (PVP) as a precursor. Compared with other polymer precursors, PVP produces a prolific amount of electrospun material, suggesting it has potential for large-scale ceramic fiber production, and it is readily soluble in safe solvents, such as water. The study also establishes the effect of calcination temperature on average grain size, fiber diameter, and polymorphic composition.

II. Experimental Procedure

(1) Materials

The sol–gel precursor materials consisted of zirconyl chloride octahydrate (high purity grade, Sigma-Aldrich Pty. Ltd., Castle Hill, Australia) and PVP (M_w approximately 1 300 000, Sigma-Aldrich Pty. Ltd.) dissolved in deionized water and ethanol (absolute grade, Ajax Chemicals, Seven Hills, Australia). The composition used gave a clear, viscous liquid and contained 3.0 g ZrOCl₂ · 8H₂O, 0.3 g PVP, 1.3 g deionized water, and 0.7 g ethanol, giving a solution of approximately 57 wt% ZrOCl₂. The solution was stirred at ambient temperature for 24 h to ensure complete miscibility.

(2) Fiber Processing

The solutions were subsequently electrospun using standard electrospinning equipment at a feed rate of 0.3 mL/h through a needle of diameter 0.21 mm. The accelerating voltage used was 20 kV and the distance between the needle tip and the collector mechanism was 100 mm. To ensure fibers of reasonable consistency and quantity, a drum winder mechanism of rotational speed 80 rpm was used as the collector mechanism and a schematic showing the essential features of the electrospinning process is shown in Fig. 1. The viscosity of the solution coupled with the use of PVP as the organic precursor ensured a large quantity of fibers were obtained within a few minutes. The samples were subsequently oven dried for 48 h before calcination.



Fig. 1. Schematic showing the essential features of the electrospinning experimental setup. The Taylor cone is the phenomenon through which sol–gels are stretched electrostatically into small diameter fibers.

Calcination of the fibers was performed using a standard muffle furnace, with crucibled specimens placed in a cold oven, and then heated at approximately 8°C/min to the target temperature. Once the heating cycle had reached completion, the furnace was switched off and the specimens were left to cool overnight.

(3) Fiber Characterization

X-ray diffraction (XRD) experiments were performed using a Siemens D5000 Diffractometer (Siemens Ltd., Bayswater, Australia) at a wavelength of 1.5406 Å. Sharp XRD spectra were obtained by grinding the specimen with ethanol to form a slurry, which was poured onto a microscope slide and analyzed once the ethanol had evaporated off. A quantitative determination program (SIROQUANT-Sietronics Pty. Ltd., Belconnen, Australia), based on the Rietveld method,²¹ was used to determine the relative composition and the lattice parameters of the phases present in the annealed sample. The SIROQUANT program calculates a theoretical XRD profile and fits it to the measured pattern by full-matrix least-squares refinement of the following Rietveld parameters: phase scales, line asymmetry, phase preferred orientation, phase linewidths (U, V, W), instrument zero, the lineshape parameter for each phase, and the phase unit cell dimensions.

III. Experimental Results

(1) Processing Observations

Originally, fibers were collected through the use of a horizontal square collector plate. However, there were problems associated with this method, typically caused by the ionic nature of the solution and the relatively high stiffness of the fibers when compared with polymeric electrospun fibers. The presence of the zirconvl chloride gave the solution an ionic characteristic, which caused the fibrous material to preferentially align along the electrical field. As this field acted perpendicular to the collector plate, fibers tended to stand vertically between the plate and the needle, a phenomenon enhanced by the high fiber stiffness. Eventually, enough fiber mass would form so as to collapse the fibrous structure onto the collector plate, but this would occur after significant bunching and random coalescence of the fibers close to the needle, leading to a very distorted, random collection of fibers. Use of a horizontal rotary collection mechanism (e.g., drum winder) actually gained benefit from some of these issues, resulting in homogeneous, reasonably well-aligned fibers.

(2) Percentage Yield of Fiber

The thermal decomposition mechanism of zirconyl chloride is unclear. However, it is believed²² that the structure of this compound is quite complex, consisting of constitution water rather than hydration water. This would suggest that the structure of zirconyl chloride is best represented as being $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ and $8Cl^-$ rather than $ZrOCl_2 \cdot 8H_2O$. With this structure in mind, a likely decomposition would be according to the following equation:

$$[Zr_4(OH)_8(H_2O)_{16}]^{8+} + 8Cl^- \rightarrow 4ZrO_2 + HCl + 16H_2O$$
 (1)

This might also account for some of the complex hydroxylbased intermediate stages that are believed to occur during this decomposition process.⁷ It is unclear what, if any, role the PVP plays in this decomposition reaction, but assuming that all solvents have been subsequently removed during the electrospinning and drying process, zirconyl chloride octahydrate should constitute 91% of the weight of the electrospun fibers. From Eq. (1), 1 g of ZrOCl₂ · 8H₂O should yield 0.383 g of ZrO₂. Sample weights before and after annealing at temperatures between 270° and 930°C for 1 h revealed that the yield was consistently underestimated by around 10%–17%. This could have two reasons: incomplete removal of the PVP or incomplete conversion of the ZrOCl₂ · 8H₂O.

At low annealing temperatures, the fibrous specimens showed a dark tinge that was not apparent at higher temperatures. This suggests that residual PVP is still present.





Fig. 2. Scanning electron microscope images of sol-gel-processed zirconia nanofibers annealed at (a) 370°C, (b) 450°C, (c) 540°C, and (d) 930°C.

However, high-quality XRD spectra were obtained at these temperatures, suggesting that the presence of the polymer was not interfering with the creation of zirconia crystals. One anecdotal piece of evidence to propagate this view is that samples annealed at temperatures higher than 630°C displayed significantly more brittleness than material processed at lower temperatures. At this stage, any effect from the decomposition of PVP on the calcination mechanism is unclear, although carbon or carbon-based compounds were not spectroscopically detected, other than at temperatures where calcination is yet to commence.

The second reason is probably due to the presence of impurity hydroxide OH^- ions.⁷ These ions are a known impurity in zirconia. It is very likely that there are OH^- ions present in the samples, as the mode of synthesis used is susceptible to incorporation of such impurities. Annealing zirconia from zirconyl chloride octahydrate creates an environment where freed water molecules can react with the chlorine ions to form hydrochloric acid and OH^- ions. Therefore, if the hydroxide ions were present in the final product, they would contribute to the higher than expected yields.

(3) Fiber Morphology

Figure 2 shows scanning electron microscope images of fibers annealed at 370° , 450° , 540° , and 930° C. These images reveal that fiber diameter quickly reaches a threshold minimum value of around 850 nm, as shown in Fig. 3, and suggests that the polymer has essentially been eliminated at temperatures of 540° C and higher. In addition, Fig. 2(d) reveals a distinctly granular structure, absent from other images, which is most likely due to larger grain size, rather than a polymer-based phenomenon.

(4) XRD Analysis

Figure 4 presents XRD patterns obtained from specimens annealed at various temperatures for 1 h. Annealing temperature was the only experimental variable in this analysis. The units of intensity are arbitrary and hence are excluded from the ordinate. Zirconia nanocrystals do not form from this precursor at temperatures below 400° C,²³ so the amorphous trace at 370° is as expected. At temperatures of 450° and 540° C, the peaks are representative of a tetragonal phase (characterized by the asymmetry and slight splitting of the 110 and 112 peaks at 35° and 50°). At temperatures of 540° and 630° C, the tetragonal phase starts to transform into a monoclinic pattern, and at temperatures of 730° C and higher, the transformation is virtually complete. This is clearly revealed in Fig. 4 through the increasing size of the characteristic 111 and 111 peaks and the gradual disappearance of the tetragonal 011 peak as a function of increasing temperature.

Figure 5 reveals the percentage present of each phase as a function of annealing temperature as determined by the SIROQUANT software package. Clearly, the tetragonal phase dominates at lower annealing temperatures, and the monoclinic phase predominates at the higher temperatures. At an annealing temperature of 540°C, the fibers are very much a composite structure of the two crystal types. To investigate further the crystal structure of the fibers in the intermediate temperature range, the effect of annealing time on the percentage of monoclinic material present was determined at two sample temperatures. Between annealing times of 30 min and 4 h, a slight



Fig. 3. Influence of the annealing temperature on the average fiber diameter of sol-gel precursor electrospun zirconia nanofibers.



Fig. 4. Comparison of X-ray diffraction analysis patterns of specimens annealed at various temperatures for 1 h. The material is essentially tetragonal at low temperatures and monoclinic at high temperatures. There is a range of temperatures at which both crystal phases exist.

increase in the monoclinic phase was detected at 450°C, whereas no discernable variation in monoclinic phase amounts was detected at 630°C. These results are consistent with the observations reported by Whitney,²⁴ who showed that at 597°C and beyond, conversion is effectively complete after 30 min, whereas conversion at lower temperatures continues slowly for several hours. This analysis suggests that for the heating regime adopted (i.e., sample placed in a cold oven and then slowly heated over a period of several hours), the time spent at the thermal soak (annealing) temperature does not significantly affect the crystallographic composition of the zirconia fibers.

(5) Effect of Varying the Heating Regime

Studies were performed to establish the effect of multi-stage heating regimes on the final crystal structure of the nanofibers. Two regimes were adopted at two temperatures: regime A involved annealing at 450° C for 1 h and then subsequent heating to 730° C for 1 h followed by a furnace cool; regime B involved cooling to room temperature between the two heating stages, as detailed in Fig. 6. The reason for this was to establish if annealing at lower temperatures is final, or if it could be superseded by a higher temperature annealing treatment. This would show if the tetragonal transformation is a permanent one. Figure 7



Fig.5. Percentage of monoclinic phase present versus annealing temperature (annealing time = 1 h).

presents the XRD spectra obtained from both heating regimes, and from reference spectra obtained at 450° and 730° C. This analysis shows that although tetragonal zirconia can be easily formed at 450° C, it is metastable, and is converted to monoclinic zirconia through subsequent heating processes.

(6) Crystal Size Effects

One possible explanation for the presence of the tetragonal phase is the influence of crystal size. It has been suggested²⁵ that the size of an unconstrained zirconia crystal affects the stability of the tetragonal phase, and that for crystals smaller than 30 nm, the excess energy provided by the inner surface energy of the crystal is sufficient to stabilize the tetragonal phase. Therefore, as crystal size increases, this would suggest that the tetragonal structure eventually transforms into more stable monoclinic phase as the inner surface energy changes.

The average crystal size of the zirconia nanofibers obtained at different annealing temperatures can be approximated by the Scherrer method. This method relies on smaller crystals producing broader XRD peaks than larger ones and relates the size



Fig. 6. Schematic representation of the multi-stage heating regimes used in this study. Regime A involves a staged heating process and regime B involves an intermediate cooling stage.



Fig. 7. X-ray diffraction analysis patterns for multistage heating regimes A and B and reference spectra taken at 450° and 730°C. Both regimes create a mostly monoclinic material.

of the crystal (t) to the width of the peaks at 50% of their height (B), i.e.,

$$t = \frac{K\lambda}{B\cos\theta_{\rm B}}\tag{2}$$

where K is a constant depending on the crystallite shape, λ is the X-ray wavelength, and θ_B is the Bragg angle. By comparison of the characteristic monoclinic peak at approximately $\theta_B = 28^\circ$, approximate average grain sizes were obtained as detailed in Table I. Clearly, average grain size increases with increasing annealing temperature, strengthening the previous hypothesis. However, the "transformation size" of 30 nm is not achieved in this study. Although the Scherrer method is only an approximate method, there is still most likely a cause other than energy factors for the tetragonal to monoclinic transformation. Perhaps the most likely influence is the presence of hydroxide impurities, as detailed previously.

(7) Stabilization of the Tetragonal Phase and the Influence of Pressure

Although tetragonal zirconia is obtainable from zirconyl chloride sol–gel by calcination at temperatures of around 500°– 600°C, this phase is metastable and will transform to monoclinic phase on subsequent heating at higher temperatures. In traditional zirconia processing, the tetragonal phase is stabilized by the addition of small amounts of impurity oxide, such as calcium and yttrium. Figure 8 presents three XRD patterns obtained from material calcined at 800°C. Figure 8(a) is obtained from the pure zirconyl chloride-based sol–gel used throughout this study and reveals the predicted monoclinic-dominated structure.

Table I.Average Crystallite Thickness Versus AnnealingTemperature According to the Scherrer Equation (annealing
time = 1 h)

Annealing temperature (°C)	Average crystallite thickness (nm)
450	9.00
540	10.80
630	16.20
730	23.13
830	26.99
930	32.39

Figure 8(b) was obtained from a sol–gel containing 5 wt% calcium acetate, thus introducing a small amount of calcium impurity to the calcined material. Clearly, this material is tetragonal, and subsequent heating of the specimen showed this material to be stable. Figure 8(c) was obtained from the pure sol–gel, pressure-fired at 800°C for 4 h under 10 kPa pressure in a graphite capsule. The material is clearly mostly monoclinic, but there are several differences between this material and the standard material worth discussing.

The monoclinic lattice parameters appear to have slightly changed as a result of the pressure firing. Initial calculations have shown that the unit cell shrinks by between 0.5% and 0.9%. In addition, basic analysis of the peak widths shows that pressure firing effectively doubles the average grain size of the material, whereas addition of 5% calcium impurity has negligible effect on the grain dimensions. Clearly, increased pressure has the effect of promoting intergranular diffusion, leading to larger grains. This would therefore suggest that if firing could occur in a vacuum, then grain size may be reduced. This would be of great importance for materials such as cobaltites, whose properties are very dependent on the size of the complex layered oxide structures formed during calcination.

A major difference between the pressure-fired zirconia and the normally calcined zirconia is the presence of extra diffraction peaks, most notably at $2\theta = 45^{\circ}$ and at $2\theta = 55^{\circ}$ where a doublet is seen to occur. These peaks may correspond to orthorhombic zirconia whose presence has been reported elsewhere^{26,27} in materials processed with impurities through traditional or thin film deposition techniques, and usually through high-pressure means. It is rare to detect orthorhombic zirconia in pure, dopant-free material, and the stability of this phase is not fully known. These peaks are also characteristic of perovskite-type structures, but as there are no impurity metallic cations in the material, the existence of this structure is unlikely.

The process of pressure firing involves placing the material in a porous graphite capsule, and initial XRD analysis of the final product revealed a large quantity of residual carbon present in the material. The pattern presented in Fig. 8(c) has been created by removal of the characteristic hexagonal graphite lines, so there is the possibility that these extra peaks are in fact caused by the presence of zirconium carbide or zirconium carbonate in the material. This is to be investigated further.

The effect on mechanical and electrical properties of these various structures is the subject of future work.



Fig. 8. X-ray diffraction analysis patterns for (a) standard zirconia (ZrO₂) nanofibers calcined for 1 h at 800°C, (b) standard ZrO₂ nanofibers containing 5 wt% calcium oxide impurity calcined for 1 h at 800°C, and (c) standard ZrO₂ nanofibers calcined at 800°C for 4 h under a pressure of 10 kPa.

IV. Conclusions

A study has been performed to assess the key structural characteristics of zirconia microfibers produced by the electrospinning and subsequent annealing of a zirconium-based sol-gel. It showed that at room temperature, typically unstable tetragonal zirconia was found to be dominant in zirconia microfibers when processed at low annealing temperatures. This was attributed to the small crystallite size, as well as the likely presence of stabilizing impurities, such as hydroxide ions. The monoclinic content of the nanofibers increases with increasing temperature, as does the average grain size. There is evidence to suggest that the polymer precursor is not completely removed during the conversion process at the lowest temperatures. The fibers at lower annealing temperatures are less brittle than those formed at higher temperatures; the grains at the higher temperatures appear better defined and the fiber diameter decreases with annealing temperatures increasing to 540°C. This suggests that at temperatures higher than 540°C, the polymer has been completely removed, and the main change is in the conversion of tetragonal to monoclinic structure caused by increasing average grain size. Tetragonal zirconia can be introduced in a stable form by the addition of small amounts of calcium oxide impurity, and high-pressure processing of the sol-gel zirconia precursor reveals the possible presence of orthorhombic zirconia.

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