FABRICATION OF CERAMIC NANOFIBERS AND EFFECT OF CALCINATION PARAMETERS ON GRAIN GROWTH

A Thesis
Presented to
The Graduate Faculty of The University of Akron

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

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May, 2016
ABSTRACT

Electrospinning provides a straightforward method for generating continuous nanofibers. This technique has been used for many years to fabricate various types of nanofibers with different applications. Combining the electrospinning method and calcination process will result in fabrication of ceramic nanofibers.

The unique characteristics of ceramic nanofibers such as high surface to volume ratio, high porosity and semi-conductivity make these materials promising for advanced applications. Although they have unique characteristic behaviors, these nano materials have a major drawback; the brittleness has always been an issue for ceramic materials. According to the inverse Hall-Petch effect, it has been hypothesized that grain size has a direct effect on mechanical properties of ceramic nanofibers.

This work consists of three objectives. In the first phase, aluminum acetate nanofibers are fabricated by the electrospinning method. This step is followed by controlled calcination process to investigate the effect of calcination parameters on grain size growth. Scanning electron microscopy (SEM) is used to inspect the morphology of as-spun and calcined nanofibers. Energy dispersive X-ray spectroscopy (EDS) was utilized for elemental analysis. X-ray diffraction spectroscopy (XRD) is used for grain size calculation and study crystalline structure of calcined samples.
In the second phase, Mullite-like nanofibers are fabricated by using the electrospinning and calcination techniques and then characterized by SEM, EDS and XRD. The effect of surfactant on dispersion of nano silica powder has been studied.

In the final phase, alumina nanofibers are deposited on two different types of silicon carbide (SiC) composites for mechanical/thermal reinforcement in cyclic high temperature applications.
ACKNOWLEDGMENTS

I would like to express my sincere gratitude to my advisor, Dr. Edward Evans for all of his support, valuable guidance and for giving me this opportunity to make this happen.

I would like to acknowledge the entire Chemical and Biomolecular Engineering department professors and especially Professor George G. Chase for providing the opportunity for characterization of the samples and honoring me as a committee member.

I would like to thank Dr. Gregory Morscher for his support on this project, providing the silicon carbide composite samples.

I would like to thank Dr. Gary Doll for accepting my invitation and honoring me to be my committee member.

I would like to thank Mr. Tom Quick, Dr. John Senko and Dr. Lisa Park from Department of Geology for their help on obtaining the characterization data.

I would like to express my appreciation to my family for all of their support and encouragement.

Finally, I would like to express my greatest love to my wonderful wife for all of her support and kindness all the way through my study in the University of Akron.
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CHAPTER I

INTRODUCTION

1.1 Overview of work

Electrospinning is considered a straightforward method to fabricate nanofibers. This versatile technique can be utilized to produce nanofibers with different diameters and shapes, and functionalization. This technique has been used for over 80 years to produce continuous fibers in a straightforward manner. Various types of polymers and precursors have been electrospun by different research groups. Electrospun nanofibers have potential application in many different areas including biomedical, sensors, and catalyst support in energy conversion devices.

The electrospinning condition is affected by the process parameters, spinning solution characteristics, and ambient conditions. A schematic of a basic electrospinning setup is illustrated in Figure 1.1. It consists of a high voltage power supply to provide the necessary electric potential for fibers to form, a syringe pump to transfer the solution through a needle and a collector to collect the fibers.
Figure 1.1 Basic electrospinning setup

Another relatively new area of interest in the nanofiber field is the fabrication of ceramic nanofibers. Ceramic materials are known for their superior mechanical properties, thermal properties, and resistance to corrosion.\(^2\) Thanks to their high surface to volume ratio and potential extraordinary properties, ceramic nanofibers are being developed for variety of applications discussed in the next chapter.

Fabrication of ceramic nanofibers by electrospinning requires a further heat treatment step, which involves performing calcination of as-spun nanofibers at elevated temperatures in a furnace.

Among all research and studies related to ceramic materials, alumina has always been the area of interest for material scientists. Alumina has application in various fields owing to its unique characteristics including high thermal conductivity, high strength, and
chemical inertness. The applications of alumina are not limited to high temperature environment. Alumina materials can be used for abrasion resistance, catalyst support, and reinforcement for composites. Despite all of the beneficial characteristics of ceramic materials, brittleness has always been a major drawback for ceramic materials. This disadvantage becomes more of a concern when a mechanical property such as yield stress becomes a crucial factor. It is hypothesized that by reducing the grain size of alumina nanofibers to a certain range, the yield strength of nano structures will be increased, according to the inverse Hall-Petch effect.  

1.2 Project objectives

There are three objectives for this project:

1. The first objective is to fabricate alumina nanofiber structures and study the effect of calcination parameters on grain growth.

2. The second objective is to fabricate alumina/silica nanofibers including mullite-like ceramic nanofibers and study the effect of different surfactants on silica dispersion.

3. The third objective is to deposit the calcined alumina nanofibers on silicon carbide (SiC) matrix composites in order to study the survival of alumina nanofibers at multiple heating cycles.

1.3 Thesis outline

Chapter I gives the general overview of this work including project objectives, hypothesis, goals, and outline of this thesis.
Chapter II includes background information on electrospinning, ceramic nanofibers, grain growth theories and an introduction to silicon carbide composites.

Chapter III describes the fabrication and characterization of alumina nanofibers using the electrospinning and calcination methods, study the effect of calcination parameters on grain growth, followed by discussion of results.

Chapter IV describes the fabrication and characterization of alumina/silica nanofibers using the electrospinning and calcination methods, followed by discussion of results.

Chapter V describes the deposition of alumina nanofibers onto the silicon carbide (SiC) composites, followed by characterization data and a discussion of the results.

Chapter VI includes conclusion of the project and recommendations for future works.

Appendix A presents the scanning electron microscope images, energy-dispersive X-ray spectroscopy data of PVP/aluminum acetate and calcined alumina nanofibers and X-ray diffraction spectra of calcined alumina nanofibers.

Appendix B presents the scanning electron microscope images, energy-dispersive X-ray spectroscopy data of PVP/aluminum acetate/silica and mullite-like nanofibers.

Appendix C shows the statistical analysis of data for grain size for alumina nanofibers.

Appendix D presents the Scherrer equation and the assumptions that were made for grain size calculation.
CHAPTER II

LITERATURE REVIEW

2.1 Electrospinning

Electrospinning provides an efficient and straightforward method for generating non-woven fibers from 2 nm to several micrometers in diameter. Various kinds of nanomaterial that include polymers, composites, and ceramics can be fabricated with assistance of the electrospinning technique.  

2.1.1 History of electrospinning

Electrospinning was first observed in 1897 by Rayleigh, studied in detail by Zeleny (1914), and patented by Formhals in 1934; the first patent on electrospinning was issued for fabrication of textile yarns at a voltage of 57 kV to spin cellulose acetate using acetone, monomethyl ether and ethylene glycol as solvents. Simons in 1966 patented an apparatus for the production of non-woven fabrics that were ultra-thin and very light in weight. In 1971, Baumgarten made an apparatus to electrospin acrylic fibers with diameters in the range of 0.05–1.1 µm. Reneker and Chun, who revived interest in this technology in the early 1990s, showed that is possible to electrospin a wide range of polymer solutions. Reneker and Chun started using the “Electrospinning” term and now
this term is widely used in the science community. Polymeric nanofibers produced by electrospinning have become a topic of great interest for the past few decades. There are currently many research groups and companies working on the fabrication of nanofibers using electrospinning; for example nanofibers have been employed in filtration products at the industrial scale.9

2.1.2 Electrospinning process

Figure 2.1 illustrates a schematic of the two most common basic setups for electrospinning, vertical and horizontal. The basic apparatus consists of three major parts: 1) High-voltage power supply 2) Spinneret (metallic needle) and 3) Collector:
High voltage direct current (DC) in the range of several tens of kilovolts is necessary to charge a polymer solution, which is then accelerated towards a collector of opposite polarity. The spinneret is connected to a syringe containing the polymer solution or melt. With the use of a syringe pump, the solution can be fed through the spinneret at a constant and controlled rate. When the surface tension of the solution is overcome by repulsive electric force, a Taylor cone is formed at the tip of the needle. As this charged jet of polymer flies through the air, the solvent evaporates and fibers are collected on the grounded surface.10
2.1.3 Electrospinning parameters

In electrospinning, multiple parameters need to be controlled in order to fabricate nanofibers with desired properties. The parameters that have a direct effect on morphology and consistency of the nanofibers can be grouped in three categories:

1. Process parameters
   - Electric potential between needle and collector
   - Feeding rate of solution
   - Distance between collector and needle
   - Needle radius

2. Solution parameters
   - Viscosity of the solution (polymer concentration)
   - Surface tension of the polymer
   - Molecular weight of the polymer
   - Conductivity

3. Ambient parameters
   - Temperature
   - Humidity

Electrospinning can be used to fabricate solid nanofibers, hollow nanofibers, beaded nanofibers, nanofibers with porous structure and nanofibers with core/sheath structure. Many researchers have also reported fabricating aligned nanofibers by collecting nanofibers on a rotating drum or a thin wheel with a sharp edge.
2.1.4 Electrospinning applications

Thanks to their continuous length\(^{22}\), high surface to volume ratio\(^{23}\), and superior mechanical properties\(^{22}\), nanofibers can be used in multiple applications in a wide range of areas. For example, nanofibers can be applied in diverse industrial areas such as:

- **Biomedical**
  - Scaffolds for tissue engineering\(^{4}\)
  - Wound dressing and drug delivery\(^{24}\)
- **Sensors**
  - Optical sensors\(^{25}\)
  - Gas sensors\(^{5}\)
- **Electrodes**
  - Lithium battery\(^{6}\)
  - Supercapacitor\(^{26}\)
- **Filtration**\(^{9,22}\)
- **Reinforcement of composite materials**\(^{28,30}\)
- **Support for enzymes**\(^{30}\)
- **Catalysts**\(^{31,32}\)

2.2 Ceramic nanofibers

Ceramic materials are best known for their superior mechanical and thermal properties as well as their resistance to corrosion.\(^{7}\) Nano structured ceramics have
received attention in recent years because of their high surface area to volume ratio and their unique properties.

Different techniques have been proposed for ceramic processing which include sol-gel\textsuperscript{33}, pyrolysis\textsuperscript{34}, hydrothermal\textsuperscript{35} and electrospinning\textsuperscript{36}. Fabrication of ceramic nanofibers by electrospinning became more popular in recent decades. Research groups have successfully produced ceramic nanofibers of materials such as Al\textsubscript{2}O\textsubscript{3}\textsuperscript{2}, Fe\textsubscript{2}O\textsubscript{3}\textsuperscript{37}, Mn\textsubscript{3}O\textsubscript{4}\textsuperscript{38}, SiO\textsubscript{2}\textsuperscript{39}, SnO\textsubscript{2}\textsuperscript{40}, TiO\textsubscript{2}\textsuperscript{36}, V\textsubscript{2}O\textsubscript{5}\textsuperscript{41}, WO\textsubscript{3}\textsuperscript{42}, ZnO\textsuperscript{2} and mixture of these (i.e., Al\textsubscript{2}O\textsubscript{3}/TiO\textsubscript{2}\textsuperscript{43}, Al\textsubscript{2}O\textsubscript{3}/ZnO\textsuperscript{44}, SnO\textsubscript{2}/ZnO\textsuperscript{45}) using the electrospinning. Among all ceramic fabrication methods, electrospinning is one of the most straightforward and versatile techniques.

2.2.1 Fabrication of ceramic nanofibers

Fabrication of ceramic nanofibers by electrospinning consists of three main steps\textsuperscript{7}; The first step of making ceramic nanofibers by electrospinning is to prepare a homogenous spinnable polymer solution carrying the inorganic precursor. Examples of inorganic precursors include aluminum 2.4-pentanedionato\textsuperscript{46}, tin chloride\textsuperscript{40}, zinc acetate\textsuperscript{45}, titanium tetraisopropoxide\textsuperscript{36} and polymers such as polyvinyl pyrrolidone (PVP)\textsuperscript{46}, polyvinyl alcohol (PVA)\textsuperscript{37}, polyacrylonitrile (PAN)\textsuperscript{47} and polymethyl methacrylate (PMMA)\textsuperscript{41} are dissolved in a solvent to create a spinnable solution.

The second step is electrospinning of the solution under controlled conditions which is explained in detail in section 2.1.2 and the last step is calcination of as-spun fibers in the furnace at elevated temperatures to remove polymer and obtain the ceramic.
Figure 2.2 shows pictures of the materials produced during each step of the procedure for fabrication of aluminum oxide (Al₂O₃) nanofibers by electrospinning.

Figure 2.2 Fabrication process of ceramic nanofibers

2.2.2 Application of ceramic nanofibers

The unique characteristic behaviors of ceramic nanofibers such as high surface area to volume ratio, high porosity, and semi-conductivity have drawn attention in recent years. It has been shown that nano-grained ceramics have outstanding mechanical properties compared to their large-grained counterparts. Some studies on titania with nano structures indicate nano-sized titania has demonstrated improved bending stress, ductility at elevated temperature. They have also reported that compressive yield strength and hardness are influenced by both porosity and grain size.
Here are some current and potential applications of ceramic nanofibers:

- **Applications in catalysis**
  - Support for catalyst\(^{50}\)
  - Photocatalysts\(^{51}\)

- **Applications in environmental science**
  - Membrane for filtration\(^{52}\)
  - Gas sensors\(^{53-54}\)

- **Applications in energy**
  - Photoelectrodes for photovoltaic\(^{55}/fuel^{56}\) cells
  - Electrodes for lithium batteries\(^{57}\)

- **Thermal insulation\(^{58}\)**

2.3 **Aluminum oxide**

Aluminum oxide or alumina is a favorable material to work with owing to its high strength modulus, chemical inertness, low thermal conductivity and electrical insulation capability.\(^{59}\) Table 2.1 presents the physical properties of alumina.
Table 2.1 Alumina physical properties

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<tr>
<td><strong>Chemical formula</strong></td>
<td>Al₂O₃</td>
</tr>
<tr>
<td><strong>Molecular weight</strong></td>
<td>101.96 g/mol</td>
</tr>
<tr>
<td><strong>Appearance</strong></td>
<td>white solid</td>
</tr>
<tr>
<td><strong>Density</strong></td>
<td>3.96 g/cm³</td>
</tr>
<tr>
<td><strong>Melting point</strong></td>
<td>2072 °C</td>
</tr>
<tr>
<td><strong>Boiling point</strong></td>
<td>2980 °C</td>
</tr>
<tr>
<td><strong>Solubility in water</strong></td>
<td>insoluble</td>
</tr>
<tr>
<td><strong>Thermal conductivity</strong></td>
<td>30 W/m.K</td>
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Alumina exists in various phases including trigonal α phase, cubic γ and η phases, hexagonal χ phase, monoclinic θ phase, orthorhombic κ phase and finally δ phase could be in either tetragonal or orthorhombic phase. Among all these phases, only α-alumina is thermodynamically stable and occurs naturally as corundum or sapphire. Each phase has its own properties and characteristic. For example α and κ phases are used in wear-resistant environments thanks to their hardness and thermal stability. For instance, α-alumina has application in high temperature insulators and crucibles. Metastable γ and θ phases are suitable for catalyst purposes due to their low surface energies.

During the synthesis of alumina, findings indicated that transition phase from ceramic/polymer matrix to alumina, consisted of multiple steps. The first step is formation of boehmite (aluminum hydroxyl oxide) phase up to 450 °C then formation of γ-alumina up to 650 °C followed by formation of δ-alumina (1050 °C) and θ-alumina (1200 °C) and finally at temperatures above 1200 °C α-alumina can be achieved. It was demonstrated that adding silica (SiO₂) to alumina could hinder the phase transformation.
of $\gamma$-alumina to $\alpha$-alumina to above 1400 °C and it has prevented grain size growth of alumina.  

2.3.1 Aluminum oxide fabrication

Several methods have been proposed to fabricate alumina fibers: slurry spinning, melt spinning, induction heating, melt extraction, pyrolysis of cured polymer fiber and electrospinning.

Alumina-borate oxide fibers with 550 nm in diameter were fabricated using the sol-gel process and electrospinning technique. The solution was prepared by dissolving PVA in distilled water at 80 °C and stirring for 1h then adding the aluminum acetate stabilized with borate. A rotating drum was used to collect fibers on aluminum foil by employing electric potential of 19 kV and tip to collector (TTC) distance of 10 cm. As-spun fibers were calcined at 1000-1400 °C for 2h with 4 °C/min heating rate. For characterization purposes SEM, XRD and FTIR were used. Results indicated that $\text{Al}_4\text{B}_2\text{O}_9$ and $\text{Al}_{18}\text{B}_4\text{O}_{33}$ formed at 1000-1200 °C and became unstable at 1400 °C, at this temperature the dominant phase was $\alpha$-alumina. The grain size also increased significantly from 1000 to 1200 °C.

Effects of different precursors and parameters on fabrication of alumina nanofibers have also been studied. PVA and PEO have been used as the polymer part and aluminum nitrate and aluminum acetate as precursors. The spinning parameters were set as, tip to collector distance of 10 cm and voltage to 17-19 kV. Findings included aluminum nitrate fibers are difficult to spin due to the hygroscopic nature of nitrate anions and the ideal solution was selected as PVA/ aluminum acetate.
The impact of boric acid (2.7 wt. %) and sodium (2 wt. %) adducts in aluminum acetate precursor were investigated. In the first step PVA/aluminum acetate stabilized with boric acid solution was electrospun, then the as-spun fibers were calcined in order to observe the fate of these adducts (boric acid and sodium). The last step was to compare calcined fibers with pure α-alumina. The IR spectrum indicated that borate peaks at 1200-1400 cm\(^{-1}\) that differed from pure α-alumina spectrum. XPS results showed 2.7% sodium and 4.5% boron in fibers after annealing.

Transparent alumina nanofibers were successfully fabricated using aluminum 2,4-pentanedioionate and PVP by Azad. He used the term *cermer* to describe the ceramic polymer matrix. Electrospinning parameters maintained as electric potential 7-9 kV and TTC distance at 10 cm. Fibers were calcined at 1000 °C, 1300 °C and 1500 °C. The average grain size of alumina calcined at 1500 °C was measured only at 2.5 nm. Trace amount of carbon was also observed by Raman spectroscopy.

The sol-gel of aluminum isopropoxide (AIP) in ethanol was electrospan along with polyvinylpyrrolidone (PVP). Nanofibers with diameter range of 102-378 nm were obtained and were calcined at 500-1200 °C to observe the phase transition from boehmite to γ-alumina and α-alumina.

It has been also reported that γ-alumina nanofibers can be produced with 2-5 nm diameter by hydrolysis and dehydration of spherical Al nanoparticles.

2.3.2 Alumina applications

Alumina fiber is an important engineering material used in various applications including high-temperature insulation, catalyst support in high-temperature reactions, fire
protection, and aerospace application. Alumina fibers have been used in composites and as reinforcement agent for resins, metals and ceramics. There are also reports suggesting alumina application for adsorption/chemisorption of toxic metal ions and in water treatment. Removal of heavy metal ions (Pb2+, Cd2+) from water has been reported employing grafted thiol and octyl functional groups on alumina nanofibers. New potential application as biomedical implants for alumina nanofibers have been proposed thanks to its bioinert, biodegradable properties.

2.4 Grain Growth

Grain growth is defined as the increase in average grain size of crystalline compound. Grain growth happens when a material is heated and the free energy of the system decreases with increased grain size; to satisfy the conservation of matter, small grains may coalesce with other grains.

\[ \Delta G = S\Delta \gamma + V\Delta G_v \]  

Equation 2.1

Where, \( \Delta G \) is total free energy change, \( S \) is surface area of the grain, \( V \) is volume of the grain, \( \Delta \gamma \) and \( \Delta G_v \) are the differences in surface and volume free energy between initial and final phase respectively. According to Equation 2.1 during the annealing process, grain size grows until it reaches a size, which volume energy change is higher than surface energy change, then \( \Delta G \) becomes \( \leq 0 \). The grain is not thermodynamically stable beyond this point.

The grain boundary is the exterior layer between grains with thickness of 0.5 to 1 nm; this layer has higher energy than bulk grain itself, so it is considered as the driving
force in the grain growth process. The chemical potential gradient of the atoms make them diffuse from convex surface to concave surface.\textsuperscript{78}

Many properties of ceramic materials such as gas sensing, super conductivity and yield strength depend on grain size and size of grain boundaries.\textsuperscript{79} Understanding the grain growth and nucleation mechanism plays an important role in controlling the grain size and mechanical properties of materials. The difference in the free energy on the two side of a grain boundary is the driving force for grain growth which follows the Gibbs-Thomson equation (Equation 2.2). This equation also describes the variations in chemical potential across a curved surface or interface.\textsuperscript{80}

\[
\Delta F_m = \frac{A \gamma V_m}{r} \tag{Equation 2.2}
\]

Where, \(\Delta F_m\) is change in free energy, \(A\) is a constant from 1 to 3 depending on type of curvature, \(V_m\) is molar volume and \(r\) is the average radius of curvature of the grain.

2.4.1 Grain growth theory

Mass transport phenomenon in grain growth mechanism includes surface diffusion, grain boundary diffusion and/or volume diffusion. Mass usually transports from smaller grains to larger grains in order to decrease the system’s overall potential.

The sintering process is comprised of initial, intermediate and final stages. The last two stages are mainly controlled by boundary and lattice diffusion mechanism. At the very first step in sintering process, which is called consolidation, no volume change occurs and a bridge builds up between the elemental crystallites. The next step is
densification in which mass transport occurs between crystallites through the grain boundary.\textsuperscript{81}

Two types of grain growth mechanism have been proposed; normal grain growth and abnormal grain growth. The normal grain growth is mainly governed by the kinetic equation developed by Burke-Turnbull. They assumed that grain boundary migration is governed by pressure to the convex surface of the grain. This equation is also called curvature driven kinetics. The average grain size change is given by Equation 2.3.

\[ r_t^n - r_0^n = kt \quad \text{Equation 2.3} \]

Where \( r_t, r_0, n \) and \( k \) are the mean grain size at time equal to \( t \), initial average grain size, growth exponent and rate constant, respectively. The rate constant is given by the following equation.

\[ k = k_0 e^{-\frac{G}{RT}} \quad \text{Equation 2.4} \]

Where, \( k_0, G, R \) and \( T \) are material dependent factors as molar activation energy, ideal gas constant and temperature, respectively. It is implied from Equation 2.3 and Equation 2.4 that the average grain size increases as calcination temperature raises and average grain size is proportional to soaking time.

In abnormal grain growth, the microstructure of polycrystalline ceramic demonstrates abnormal (very large) grains between smaller grains. One good example of this behavior would be fine-grained \( \text{Al}_2\text{O}_3 \) matrix in which, single–crystal grain grows much faster than matrix grains. Grain boundary and grain orientation are two main factors that affect the mobility and energy of grain boundaries. Elimination of abnormal grain growth effect is vital in sintering to bring property advantages in some ceramic
materials. The abnormal grain growth mechanism does not comply with any mathematical equations.\textsuperscript{82}

2.4.2 Control of grain growth

Grain growth can be controlled by decreasing the boundary layer movement. Using additives (dopants) is a reliable method for this purpose; it will help to make a solid solution by integrating the particles. A report has shown that adding MgO to alumina improves the grain boundary roughness and grain growth.\textsuperscript{83}

The spark plasma sintering (SPS) technique has been used to fabricate dense ceramics with desired grain size. This technique is based on rapid heat generation with heating rate as much as (1000°C/min) and cooling rate of (350°C/min) and applying pressure on the specimen.

A study on grain growth of SrTiO\textsubscript{3} indicates that at low heating rate (10°C/min) the grain growth mechanism is controlled by 2D nucleation. In high heating rates (100°C/min) the grain growth mechanism is changed to coalescence of nanocrystals.\textsuperscript{84} There is disagreement on how heating rate will affect the grain size; some findings demonstrate high heating rate favors grain growth by increasing defect concentration.\textsuperscript{85,86} On the other hand some researches show that heating rate actually restrains grain size growth by avoiding the particle coarsening mechanism.\textsuperscript{87,88} A study showed at the temperatures above 1700 °C the average grain size of NiAl/Al\textsubscript{2}O\textsubscript{3} composite, shrinks to the fiber diameter which is called the ‘bamboo configuration’.\textsuperscript{73} Another study\textsuperscript{25} on zinc oxide (ZnO) nanofibers calcined at 400°C, 500°C, 650°C, and 800°C for 4 hours, showed a grain growth in crystalline structure by increase in calcination temperature. The length
to diameter ratio of single crystal alumina nanofibers with 50-100 nm diameters investigated for crystal growth and smallest possible diameter were calculated at 17 nm.

2.4.3 Hall-Petch effect

The Hall-Petch effect describes the correlation between grain size and yield strength in metal alloys\textsuperscript{90,91} and ceramics\textsuperscript{92,93}. The Hall-Petch effect predicts that by decreasing the grain size, yield strength and hardness should increase. The effect is based on dislocation movement within the grain boundaries. The relation between grain size and yield strength is demonstrated mathematically by the Hall-Petch equation:

\[
\sigma_y = \sigma_0 + \frac{k_y}{\sqrt{d}}
\]

Equation 2.5

Where \(\sigma_y\) is the yield stress, \(\sigma_0\) is a materials constant for the starting stress for dislocation movement, \(k_y\) is the strengthening coefficient (a constant specific to each material), and \(d\) is the average grain diameter.

2.4.4 Inverse Hall-Petch effect

Many studies have shown an inverse or negative Hall-Petch effect at grain sizes less than 50 nm.\textsuperscript{94,8} In negative Hall-Petch effect theory, yield strength and hardness of nanostructures increase relatively with grain size growth. This phenomenon usually happens when grain boundaries are unable to sustain the dislocation pile-ups.

When the grain size in a crystalline material goes to zero it becomes amorphous in shape and softer as a result. Since yield strength cannot be maximized by reducing the
grain size, it should be an optimum point where maximum strength is achieved. This critical grain size theory is graphed in Figure 2.3.

![Figure 2.3 Schematic of hardness versus grain size](image)

Significant yield strength reduction has been observed by decreasing the grain size for nanocrystalline and bulk TiO$_2$ from 30 μm to 10 nm.$^{95}$

Koch and Narayan$^{7-96}$ reviewed the inverse Hall-Petch effect and suggest this effect is valid only for grain size less than 10 nm. They believe due to porosity and amorphous inclusion in nanocrystalline material the conventional indentation measurement is not reliable. Several models have been proposed to describe the inverse Hall-Petch effect for example; the dependency of yield strength on strain rate and temperature below a critical grain size was explained by a model proposed by Carlton et al.$^{97}$
2.5 Silicon carbide composites

Ceramic matrix composite (CMC) is a general term for high performance ceramic structures with embedded fibers; this fiber-reinforcement technique adds extra toughness to the ceramic structure. Other properties that make this material on demand are high temperature capacity and environmental resistance. 98,99

Among ceramic matrix composites, silicon carbide (SiC) presents the best thermal properties. 100 It is the suitable option in gas turbines. 101 It can endure the temperatures up to 1200 °C especially when atmosphere is oxidizing and can withstand tensile stress up to 100 MPa. 100 SiC matrix composites are a promising option for thermal/environmental barrier coatings (EBC/TBC). SiC matrix composites have potential application in spacecraft, and aero jet engines due to their superior thermal shock resistance and durability at cyclic mechanical loading in oxidizing atmosphere. 102

2.5.1 Processing

There are three main methods to fabricate SiC/SiC composites102:

- Chemical vapor infiltration (CVI): In CVI, a carrier gas precursor is transported to and within a matrix at high temperature. This method produces composites with high porosity.

- Polymer impregnation and pyrolysis (PIP): In PIP, a polymeric SiC precursor is infiltrated into the SiC matrix at very high temperatures and pressure. This method could result in high crystallinity but shrinkage in the composite.
Melt infiltrated (MI): MI is a high temperature, high pressure process in which silicon melt infiltrates into the SiC matrix. This method provides lower porosity in the composite.

Generally, SiC/SiC system includes a chemically vapor infiltrated (CVI) SiC matrix around a woven SiC fibers, then infiltrated with molten silicon (Si). 100,103

2.5.2 Application

Environments exposed to thermal shocks, cyclic mechanical loading, corrosion and oxidation such as gas turbines, aero jet engines, brake systems, and spacecraft are promising application fields for CMC materials. Excellent thermal conductivity and durability against oxidation/corrosion of SiC matrix composite makes this material an excellent choice for environmental/thermal barrier coatings.102

In this chapter previous literatures and studies that have been done in the fields of electrospinning, fabrication of ceramic nanofibers and recalling the importance of aluminum oxide as an advanced engineering material has been reviewed. Considering the brittleness as the Achilles heel for ceramics, grain growth control is a promising approach to manufacture less brittle ceramics. In following chapters, experimental works in this regard are presented.
CHAPTER III

FABRICATION OF ALUMINA NANOFIBERS AND GRAIN GROWTH CONTROL

In this chapter, fabrication of aluminum oxide nanofibers and control of the grain size are discussed. Nanofibers containing different phases of alumina (Al_2O_3) were produced successfully with help of electrospinning. The process consists of three steps. The first step is making the electrospinning solution using aluminum acetate as precursor, the second step is to perform the electrospinning to fabricate PVP/aluminum acetate nanofibers and the last step is performing the heat treatment (calcination) at elevated temperatures in order to oxidize the nanofibers and decompose the polymer. Characterization results and calculated data are discussed for different nanofibers fabricated.

3.1 Materials

The materials that were used to fabricate aluminum oxide nanofibers include: polyvinylpyrrolidone (PVP) with molecular weight of 1,300,000 g/mol purchased from Sigma Aldrich, aluminum acetate, basic purchased from Strem Chemicals, glacial acetic acid purchased from EMD, ethyl alcohol 200 proof purchased from Decon Labs, formic
acid 98% purchased from Fluka Analytical. All chemicals were used without further modification.

3.2 Electrospinning

The electrospinning method was chosen in order to make a uniform sheet of as-spun nanofibers. The electrospinning parameters for this project were maintained as follows: relative humidity 10-25%, electric potential 13-15 kV, flow rate of 9-11 μl/min and tip to collector distance of 10 cm. All the experiments were conducted at room temperature measured at 20-22 °C.

3.2.1 Electrospinning setup

Electrospinning was performed in a humidity controlled box including the collector, WPI SP1011 syringe pump, Gamma High Voltage Research high voltage power supply, flat blunt tip needle 22 gauge, and humidity control setup to control the humidity. A rolling drum was used in order to collect uniform rectangular sheet of nanofibers. Figure 3.1 illustrates a schematic of the electrospinning setup including syringe pump, high voltage power supply, needle holder and collector. The actual electrospinning station (box) is pictured in Figure 3.2.
Figure 3.1 Schematic of electrospinning setup

The syringe pump pushes the electrospinning solution to the tip of the needle with controlled flow rate. The high voltage power supply creates an electric potential between the collector and the needle, and gives a charge to the solution. Counteraction between surface tension and electrostatic force results in elongation of the droplet on the tip of the needle; the elongated droplet is called the Taylor cone. When the electrostatic force overcomes the surface tension, the liquid flies over and sits on the collector. ¹
For controlling the relative humidity inside the electrospinning box, a simple setup (Figure 3.3) has been used. The humidification/dehumidification setup consists of two 250 ml vented Erlenmeyer flasks in series. The first flask was filled with either water or desiccant in order to humidify or dehumidify the electrospinning box respectively, air was passed through the flasks and into the electrospinning box.
Figure 3.3 Humidity control setup, humidification setup (top) dehumidification setup (below)

3.2.2 Electrospinning solution

The solution which was used for electrospinning consisted of PVP as the polymer and aluminum acetate as the inorganic precursor. To begin, aluminum acetate solution was prepared using the following weight ratios, 1:1:2.5 of aluminum acetate, citric acid and water. In the first step, all three ingredients were added into a 20 ml scintillation vial. The vial containing a white-colored solution was placed on a magnetic stirrer and stirred for 3 hours to achieve a clear solution.
In the next step, a polymeric solution was made by adding 10 wt% PVP to the previously prepared inorganic solutions followed by adding ethanol as the solvent. The vial was placed on a stir plate to be mixed overnight.

3.2.3 Fabrication of aluminum acetate/PVP nanofibers

In order to fabricate the alumina nanofibers, the first step is electrospinning the prepared solution described in section 3.2.2. The prepared solution was transferred to a 5 ml hypodermic syringe and placed on a syringe pump. The solution was pumped at a flow rate of 10.5 μl/min. The syringe was connected to the needle using 1/16 inch plastic tubes to deliver the solution to the tip of the needle. The distance between the tip of the needle and collector was 10 cm. The connector of high voltage power supply was attached to the needle and grounded to the collecting drum. The collecting drum was wrapped in aluminum foil. The rotating drum speed was set to 7 rpm. After checking all the tubes and connections, the syringe pump was started and voltage supply was turned on promptly after. The optimum relative humidity to fabricate beadless uniform fibers was determined to be in the 15%-25% range, which could be controlled by utilizing the (de)humidifier setup. The circulating fan in the lower section of the electrospinning box helped to keep the relative humidity steady. The tip of the needle needed regular checking and cleaning while spinning to eliminate blockage of the needle opening. During each run, about 5.5 ml of solution was electrospun and collected on a rectangular aluminum sheet.
3.3 Calcination

Calcination was performed on as-spun nanofibers in order to crystallize the mineral structure of the ceramics and remove the polymer. The main purpose of this process is to eliminate the polymer part of the as-spun nanofibers and to oxidize the inorganics to metal oxide. Two types of tube furnace were employed in this work. A high temperature SentroTech tube furnace (Figure 3.4) was used which has an operating temperature capacity of up to 1600°C with maximum heating rate of 7°C/min.

![Figure 3.4 SentroTech tube furnace](image)

A Thermolyne 21100 tube furnace (Figure 3.5) which has an operating temperature capacity of 1200°C and maximum heating rate of 10°C/min was also used.
Both furnaces were used interchangeably in order to calcine fibers at the desired condition.

![Thermolyne tube furnace](image)

**Figure 3.5 Thermolyne tube furnace**

Four different parameters were manipulated during the calcination process, including calcination temperature, heating rate, soaking time and cooling rate of the furnace. A rectangular crucible (4x10x2 WxLxH cm) was used to hold the specimens.

### 3.3.1 Calcination of aluminum/PVP nanofibers

The ultimate goal of calcining as-spun nanofibers was to remove PVP and oxidize the aluminum acetate to aluminum oxide. Calcination was performed at various temperatures from 900°C to 1350°C. PVP decomposition starts at 200°C and it will be over 95% decomposed above 500°C. As-spun nanofiber sheet obtained from
electrospinning was folded a couple of times to fit inside the crucible. Another same size crucible was placed on top of the first crucible to prevent the nanofibers from leaving the crucible during calcination. The heating rate range was set at 1-7°C/min and the furnace was started. When the temperature reached the plateau, it was kept steady for 1-6 hours (soaking time). The sample then cooled down in two different modes: high cooling rate by letting the furnace cool down by itself and low cooling rate by setting the cooling rate to 1°C/min. The cooling rate by unplugging the furnace was measured for both furnaces at 3.87°C/min and 3.29°C/min for SentroTech and Thermolyne furnace respectively. In both situations, samples were left overnight at room temperature before collecting.

Sixteen samples were made changing four variables with two levels each. Table 3.1 shows the calcination plan for as-spun PVP/aluminum acetate nanofibers, which were calcined using two types of furnace described in the previous section. All of the as-spun fibers were made using the same recipe and electrospinning condition described in sections 3.2.2 and 3.2.3.
Table 3.1 Calcination plan for PVP/aluminum acetate nanofibers

<table>
<thead>
<tr>
<th>No</th>
<th>Sample</th>
<th>Calcination Temp. (°C)</th>
<th>Ramping Rate (°C/min)</th>
<th>Soaking Time (h)</th>
<th>Cooling Rate (°C/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PVP-AA-MM-25-C3</td>
<td>1100</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>PVP-AA-MM-46-C4</td>
<td>1100</td>
<td>1</td>
<td>1</td>
<td>UP*</td>
</tr>
<tr>
<td>3</td>
<td>PVP-AA-MM-27-C1</td>
<td>1100</td>
<td>1</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>PVP-AA-MM-47-C2</td>
<td>1100</td>
<td>1</td>
<td>6</td>
<td>UP</td>
</tr>
<tr>
<td>5</td>
<td>PVP-AA-MM-25-C1</td>
<td>1100</td>
<td>7</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>PVP-AA-MM-36-C1</td>
<td>1100</td>
<td>7</td>
<td>1</td>
<td>UP</td>
</tr>
<tr>
<td>7</td>
<td>PVP-AA-MM-27-C3</td>
<td>1100</td>
<td>7</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>PVP-AA-MM-47-C1</td>
<td>1100</td>
<td>7</td>
<td>6</td>
<td>UP</td>
</tr>
<tr>
<td>9</td>
<td>PVP-AA-MM-46-C1</td>
<td>1350</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>10</td>
<td>PVP-AA-MM-25-C4</td>
<td>1350</td>
<td>1</td>
<td>1</td>
<td>UP</td>
</tr>
<tr>
<td>11</td>
<td>PVP-AA-MM-46-C2</td>
<td>1350</td>
<td>1</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>12</td>
<td>PVP-AA-MM-27-C4</td>
<td>1350</td>
<td>1</td>
<td>6</td>
<td>UP</td>
</tr>
<tr>
<td>13</td>
<td>PVP-AA-MM-36-C2</td>
<td>1350</td>
<td>7</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>14</td>
<td>PVP-AA-MM-25-C2</td>
<td>1350</td>
<td>7</td>
<td>1</td>
<td>UP</td>
</tr>
<tr>
<td>15</td>
<td>PVP-AA-MM-46-C3</td>
<td>1350</td>
<td>7</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>16</td>
<td>PVP-AA-MM-27-C2</td>
<td>1350</td>
<td>7</td>
<td>6</td>
<td>UP</td>
</tr>
</tbody>
</table>

UP: Furnace was cooled down by unplugging the power cord.

3.4 Characterization

In this section characterization of the electrospinning solution, as-spun PVP/aluminum acetate nanofibers and calcined nanofibers are discussed.

3.4.1 Characterization of electrospinning solution

The physical properties of the electrospinning solution were measured in order to explain the behavior of the solution. Viscosity was determined by using a Brookfield
viscometer DV2T. Surface tension of the solution was measured by a Central Scientific Interfacial Tensiometer using Du Noüy-Padday method.

3.4.2 Characterization of aluminum acetate/PVP nanofibers

The following characterization techniques were used in order to study the properties of as-spun aluminum acetate/PVP nanofibers. Scanning electron microscopy (SEM) by Hitachi model TM3000 was used to inspect the morphology of as-spun nanofibers. Energy dispersive X-ray spectroscopy (EDS) by Bruker Quantax 70 was utilized for elemental analysis. FiberQuant software was used to process the image and calculate the nanofiber diameters and diameter distribution.

3.4.3 Characterization of aluminum acetate/PVP nanofibers

The following characterization techniques were used in order to study the properties of calcined alumina nanofibers. Scanning electron microscopy (SEM) by Hitachi model TM3000 was used to inspect the morphology of as-spun nanofibers. Energy dispersive X-ray spectroscopy (EDS) by Bruker Quantax 70 was utilized for elemental analysis. FiberQuant software was used to process the image and calculate the nanofiber diameters and diameter distribution. A Rigaku Ultima IV X-ray diffraction (XRD) system with tube characteristic of 40 kV, 35 mA and copper as the target was used to determine the crystal structure of the samples and calculate the grain size. A Denver Instrument P-403 balance was used in order to weigh the samples before and after the calcination to determine the weight loss.
3.5 Results and discussion

Characterization results and data collected in the process of making as-spun and calcined fibers are discussed in this section. Data presented here include physical properties of the electrospinning solution, SEM images of both as-spun and calcined nanofibers revealing the morphology and fiber diameter, EDS results declaring the elemental composition of calcined samples, and XRD data to reveal the crystal structure of calcined alumina nanofibers and grain size comparison for calcined nanofibers that were presented in Table 3.1.

3.5.1 Solution properties

The electrospinning solution was made using the recipe described in section 3.2.2. Shear stress and viscosity of this solution were measured by equipment described in section 3.4.1. Surface tension of the solution was measured three times, the average of these measurements was determined to be 10.65 mN/m with standard deviation of 0.27 mN/m. Dynamic viscosity of the solution was measured three times and the average of these measurements was 138.45 cP with standard deviation of 3.94 cP.

3.5.2 Weight loss

Nanofibers were weighed before and after calcination. As-spun fibers calcined at 1100°C and 1350°C in air, experienced on average 75.9% and 78.1% weight loss respectively during the calcination process. Nanofibers calcined for 1 hour and 6 hours have experienced 76.9% and 77.1% weight loss respectively. Nanofibers calcined with
1°C/min and 7°C/min heating rate, have experienced 76.8% and 77% weight loss and finally nanofibers calcined with cooling rate of 1°C/min have experienced on average 77.2% weight loss versus 76.8% for samples were cooled down by unplugging. No significant difference in weight losses were observed for different heating and cooling rates.

3.5.3 Nanofiber morphology

An SEM image of PVP/aluminum acetate nanofibers fabricated by using the same recipe described in section 3.2.2 is pictured in Figure 3.6. As-spun fibers tend to shrink after calcination due to the loss of the organic part and moisture.

![Figure 3.6 PVP/aluminum acetate nanofibers](image)

Figure 3.6 PVP/aluminum acetate nanofibers
PVP/aluminum acetate nanofibers are shown in Figure 3.6. Uniform and consistent nanofibers were achieved using the electrospinning method while controlling the humidity.

Figure 3.7 and Figure 3.8 present the alumina nanofibers calcined at 1100°C and 1350°C.

Figure 3.7 Calcined alumina fibers at 1100°C for 1 hour
Figure 3.8 Calcined alumina fibers at 1350°C for 1 hour

The nanofibers that were calcined at 1100°C shrunk dramatically but no significant change in morphology occurred. Fibers that were calcined at 1350°C, however, had considerable changes in morphology, the nanofibers were fused in junctions and less continuous long nanofibers were observed.

Fiber diameters were measured using the FiberQuant software. Table 3.2 shows the fiber characteristics for as spun PVP/aluminum acetate nanofibers and calcined alumina nanofibers at 1100°C and 1350°C.
Table 3.2 Fiber parameters for as-spun and calcined alumina nanofibers

<table>
<thead>
<tr>
<th>Fiber characteristics</th>
<th>As-spun</th>
<th>Alumina fibers calcined at 1100C</th>
<th>Alumina fibers calcined at 1350C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Fiber Diameter (nm)</td>
<td>417</td>
<td>211</td>
<td>183</td>
</tr>
<tr>
<td>Median Fiber Diameter (nm)</td>
<td>417</td>
<td>211</td>
<td>182</td>
</tr>
<tr>
<td>Standard Deviation (nm)</td>
<td>48</td>
<td>44</td>
<td>28</td>
</tr>
<tr>
<td>Fiber Diameter Range (nm)</td>
<td>296-510</td>
<td>135-309</td>
<td>108-260</td>
</tr>
</tbody>
</table>

After calcination, the fiber diameters decreased significantly for both calcination temperatures. Fibers calcined at 1350°C experienced more reduction in diameter than those calcined at 1100°C.

The alumina nanofibers diameter distribution histogram is presented in the next images; collected diameter data for fibers calcined at 1350°C had more precision than those calcined at 1100°C.
Figure 3.9 Nanofibers diameters distribution histogram from top left, as-spun PVP/aluminum acetate, calcined fibers at 1100°C and calcined fibers at 1350°C
3.5.4 Elemental analysis

Elemental analysis was collected by energy dispersive X-ray spectroscopy (EDS). The results indicated that elemental composition of fibers calcined at 1350°C were more in accordance with commercial alumina elemental composition (40% aluminum, 60% oxygen) than fibers calcined at 1100°C.

Table 3.3 Elemental composition of calcined fibers at different temperatures

<table>
<thead>
<tr>
<th>Average atomic %</th>
<th>Al</th>
<th>O</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina fibers calcined at 1100C</td>
<td>36.23</td>
<td>60.96</td>
<td>2.80</td>
</tr>
<tr>
<td>Alumina fibers calcined at 1350C</td>
<td>38.48</td>
<td>61.53</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 3.4 Elemental composition of calcined fibers at different heating rates

<table>
<thead>
<tr>
<th>Average atomic %</th>
<th>Al</th>
<th>O</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina fibers calcined at 1 C/min</td>
<td>38.57</td>
<td>59.70</td>
<td>1.74</td>
</tr>
<tr>
<td>Alumina fibers calcined at 7 C/min</td>
<td>36.14</td>
<td>62.79</td>
<td>1.06</td>
</tr>
</tbody>
</table>

Table 3.5 Elemental composition of calcined fibers at different soaking times

<table>
<thead>
<tr>
<th>Average atomic %</th>
<th>Al</th>
<th>O</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina fibers calcined for 1 hour</td>
<td>37.72</td>
<td>61.03</td>
<td>1.26</td>
</tr>
<tr>
<td>Alumina fibers calcined for 6 hours</td>
<td>36.99</td>
<td>61.46</td>
<td>1.54</td>
</tr>
</tbody>
</table>
Table 3.6 Elemental composition of calcined fibers at different cooling rates

<table>
<thead>
<tr>
<th>Average atomic %</th>
<th>Al</th>
<th>O</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina samples cooled down at 1 C/min</td>
<td>36.41</td>
<td>62.20</td>
<td>1.38</td>
</tr>
<tr>
<td>Alumina samples cooled down by itself</td>
<td>38.3</td>
<td>60.29</td>
<td>1.41</td>
</tr>
</tbody>
</table>

The average compositions reported in atomic percentages for alumina fibers calcined at different conditions are displayed in Table 3.3 through Table 3.6. All the measurements are in good accordance with commercial alumina values. There are no considerable differences between samples prepared at different conditions. Elemental analysis spectrum for two of the calcined fibers at 1100°C and 1350°C for 1 hour are shown in Figure 3.10 and Figure 3.11. Small quantities of sodium observed in elemental analysis for samples calcined at 1100°C; the sodium most likely came from the aluminum acetate precursor.
3.5.5 X-ray diffraction

X-ray diffraction data were collected using the Rigaku Ultima IV with 2theta range of 5-70 degrees. All of the samples were examined and data analysis on grain size was carried out.

The effects of four different parameters on XRD peaks were investigated in order to find a trend and track changes.
Figure 3.12 Effect of calcination temperature on XRD pattern

As can be seen in Figure 3.12, the sample that was calcined at 1350°C has a sharper peak at $\theta=42^\circ$ and peaks in $\theta < 30^\circ$ have been eliminated at higher calcination temperature.

Figure 3.13 Heating rate effect on XRD pattern for fibers calcined at 1100°C

The heating rate effect on XRD pattern is illustrated in Figure 3.13 and Figure 3.14 for fibers calcined at 1100°C and 1350°C respectively. Slightly sharper peaks were observed at higher heating rates but no notable change observed in peaks for 1100°C temperature.
Figure 3.14 Heating rate effect on XRD pattern for fibers calcined at 1350°C

Figure 3.15 Soaking time effect on XRD pattern for fibers calcined at 1100°C

Figure 3.16 Soaking time effect on XRD pattern for fibers calcined at 1350°C
The soaking time effect on XRD pattern is illustrated in Figure 3.15 and Figure 3.16 for fibers calcined at 1100°C and 1350°C respectively. Sharper peaks at 2θ=42° were observed for samples calcined for longer period.

![XRD pattern for fibers calcined at 1100°C](image1)

**Figure 3.17 Cooling rate effect on XRD pattern for fibers calcined at 1100°C**

![XRD pattern for fibers calcined at 1350°C](image2)

**Figure 3.18 Cooling rate effect on XRD pattern for fibers calcined at 1350°C**

The cooling rate effect on XRD pattern is illustrated in Figure 3.17 and Figure 3.18 for fibers calcined at 1100°C and 1350°C respectively. Sharper peaks at 2θ=42° were observed for samples that cooled down with slower rate.
Figure 3.19 XRD pattern for sample calcined at 1350°C with Miller indices

Samples calcined at 1350°C with heating rate of 7°C/min, soaking time of 6 hours and cooled down by itself had the most resemblance to α-alumina XRD spectrum.

Figure 3.19 graphs the XRD pattern for mentioned sample indicating the lattice planes.

Figure 3.20 graphs the XRD pattern for α-alumina obtained from Inorganic Crystal Structure Database (ICSD) for comparison purposes.

Figure 3.20 XRD pattern for standard α-alumina (ICSD)
3.5.6 Grain size

The grain size was calculated using the XRD peak spectrum and the Scherrer equation as described in Appendix D. PDXL software was also used in order to compare the peak intensities. All samples had peaks at $2\theta=35^\circ$ and $2\theta=42^\circ$ which are associated with $\alpha$-alumina. All the samples that were calcined at 1350°C, had no/minor peaks below $2\theta=30^\circ$ and have the main (sharpest) peak at $2\theta=42^\circ$. However, samples that were calcined at 1100°C had the main peak at $2\theta=16^\circ$. Samples were calcined at higher temperature experienced average grain growth as much as double of those samples were calcined at lower temperature. Longer soaking time resulted in slightly larger grain size on average. Heating and cooling rates did not have any considerable effect on grain size change. Table 3.7 demonstrates the average grain size calculated for each sample.
Table 3.7 Average grain size for alumina nanofibers

<table>
<thead>
<tr>
<th>No</th>
<th>Sample</th>
<th>Calcination Temp. (°C)</th>
<th>Ramping Rate (°C/min)</th>
<th>Soaking Time (h)</th>
<th>Cooling Rate (°C/min)</th>
<th>Average Grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PVP-AA-MM-25-C3</td>
<td>1100</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>21.6</td>
</tr>
<tr>
<td>2</td>
<td>PVP-AA-MM-46-C4</td>
<td>1100</td>
<td>1</td>
<td>1</td>
<td>UP*</td>
<td>26.7</td>
</tr>
<tr>
<td>3</td>
<td>PVP-AA-MM-27-C1</td>
<td>1100</td>
<td>1</td>
<td>6</td>
<td>1</td>
<td>22.8</td>
</tr>
<tr>
<td>4</td>
<td>PVP-AA-MM-47-C2</td>
<td>1100</td>
<td>1</td>
<td>6</td>
<td>UP</td>
<td>33.5</td>
</tr>
<tr>
<td>5</td>
<td>PVP-AA-MM-25-C1</td>
<td>1100</td>
<td>7</td>
<td>1</td>
<td>1</td>
<td>26.6</td>
</tr>
<tr>
<td>6</td>
<td>PVP-AA-MM-36-C1</td>
<td>1100</td>
<td>7</td>
<td>1</td>
<td>UP</td>
<td>23.3</td>
</tr>
<tr>
<td>7</td>
<td>PVP-AA-MM-27-C3</td>
<td>1100</td>
<td>7</td>
<td>6</td>
<td>1</td>
<td>39.6</td>
</tr>
<tr>
<td>8</td>
<td>PVP-AA-MM-47-C1</td>
<td>1100</td>
<td>7</td>
<td>6</td>
<td>UP</td>
<td>28.4</td>
</tr>
<tr>
<td>9</td>
<td>PVP-AA-MM-46-C1</td>
<td>1350</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>39.2</td>
</tr>
<tr>
<td>10</td>
<td>PVP-AA-MM-25-C4</td>
<td>1350</td>
<td>1</td>
<td>1</td>
<td>UP</td>
<td>42.7</td>
</tr>
<tr>
<td>11</td>
<td>PVP-AA-MM-46-C2</td>
<td>1350</td>
<td>1</td>
<td>6</td>
<td>1</td>
<td>44.2</td>
</tr>
<tr>
<td>12</td>
<td>PVP-AA-MM-27-C4</td>
<td>1350</td>
<td>1</td>
<td>6</td>
<td>UP</td>
<td>47.4</td>
</tr>
<tr>
<td>13</td>
<td>PVP-AA-MM-36-C2</td>
<td>1350</td>
<td>7</td>
<td>1</td>
<td>1</td>
<td>46.2</td>
</tr>
<tr>
<td>14</td>
<td>PVP-AA-MM-25-C2</td>
<td>1350</td>
<td>7</td>
<td>1</td>
<td>UP</td>
<td>35.9</td>
</tr>
<tr>
<td>15</td>
<td>PVP-AA-MM-46-C3</td>
<td>1350</td>
<td>7</td>
<td>6</td>
<td>1</td>
<td>53.3</td>
</tr>
<tr>
<td>16</td>
<td>PVP-AA-MM-27-C2</td>
<td>1350</td>
<td>7</td>
<td>6</td>
<td>UP</td>
<td>36.7</td>
</tr>
</tbody>
</table>

UP: Furnace was cooled down by unplugging the power cord.

Analysis of variance (ANOVA) was carried out using two bases: average grain size and highest peak grain size. According to ANOVA results, for both cases the calcination temperature had a significant effect on grain size change. Increase in calcination temperature will result in favor of grain growth. Heating rate, in both cases had minimal effect on grain size change. Soaking time had an effect on grain size, however it was not significant (p value = 0.079). Cooling rate also had some effect on grain size but it was not significant in both cases. Comprehensive data can be found in appendix C.
3.6 Discussion

Alumina nanofibers were fabricated using electrospinning and calcination methods. In order to study the grain size change during the calcination process, four different parameters were manipulated: calcination temperature, heating rate, soaking time and cooling rate. Among these four parameters, the calcination temperature definitely had a significant effect on grain size (p-value=0.000). According to Equation 2.3 and Equation 2.4 with increase in calcination temperature, rate constant (k) will also increase, this will be in favor of grain growth. Soaking time had an effect on grain size growth which was not statistically significant (p-value=0.079). According to Equation 2.3 when the soaking time increases, the grain size should also increases, which is in accordance with obtained result. Heating and cooling rates had null or minimal effect on grain size change, probably the effect of these parameters were surpassed by effect of other parameters. Almost all of the calculated grain sizes are in range of 10-50 nm, which according to Figure 2.3 are in the range for maximum hardness.

On average 75.9% and 78.1% weight loss experienced at calcination temperatures of 1100°C and 1350°C respectively. The other calcination parameters had no significant effect on weight loss. In 1100°C temperature main peaks observed below 2θ=30° which could be the result of sodium presence in the sample. XRD patterns for fibers calcined at 1350°C showed a single sharp peak (Figure 3.12) which could be an indication of grain growth in specific direction such as radial.
Calcination parameters can be sorted according to their importance of their effect on grain size change as follows:

Calcination temperature > Soaking time > Cooling rate > Heating rate
CHAPTER IV

FABRICATION OF ALUMINA/SILICA NANOFIBERS

In this chapter, fabrication of mullite-like, nanofibers is discussed. Nanofibers containing alumina (Al$_2$O$_3$) and silica (SiO$_2$) were produced successfully with the help of electrospinning. Alumina/silica nanofibers including mullite-like nanofibers may find use in oxidation resistant materials including environmental/thermal barrier coatings. The whole process of making the nanofibers consisted of three steps. The first step was to make the electrospinning solution using aluminum acetate and silica precursors. The second step was to perform electrospinning to fabricate the PVP/aluminum acetate/silica nanofibers and the last step was to calcine the fibers at elevated temperature in order to oxidize the inorganics and decompose the polymer. Characterization results and calculated data are included for the different nanofibers produced.

4.1 Materials

The materials that were used to produce alumina/silica nanofibers include: polyvinylpyrrolidone (PVP) with molecular weight of 1,300,000 g/mol purchased from Sigma Aldrich, aluminum acetate, basic purchased from Strem Chemicals, glacial acetic acid purchased from EMD, ethyl alcohol 200 proof purchased from Decon Labs, formic
acid 98% purchased from Fluka Analytical, silicon dioxide nanopowder 5-15nm purchased from Sigma Aldrich, and Ludox SK as the 25 wt% colloidal silica source purchased from Grace Davison. All chemicals were used without further modification.

4.2 Electrospinning

The electrospinning method was chosen in order to make a uniform sheet of as-spun nanofibers. The electrospinning parameters for this project were maintained as follows, relative humidity 10-15%, electric potential of 10 kV, flow rate of 8.5 μl/min and tip to collector distance of 10 cm. All of the experiments were conducted at room temperature measured at 20-22 °C.

4.2.1 Electrospinning setup

Electrospinning was performed in a humidity controlled box including the collector, WPI SP1011 syringe pump, Gamma High Voltage Research high voltage power supply, flat blunt tip needle 22 gauge, exhaust fan and piping connections to control the humidity. A rolling drum was used in order to collect uniform rectangular sheet of nanofibers. A complete description of the electrospinning setup is explained in 3.2.1.

The solution that was used for electrospinning consisted of PVP as the polymer part and aluminum acetate and silica as the inorganic precursor. To begin, aluminum acetate solution was prepared using following weight ratios, 1:1:2.5 of aluminum acetate, citric acid and water. In the first step, aluminum acetate was dissolved in deionized water and citric acid in a scintillation vial. The white-colored solution was put on a magnetic
stirrer and stirred for 3 hours to achieve a clear solution. In order to add silica precursor to the electrospinning solution two different silica sources were used. The first recipe was prepared by adding 1 wt% of silicon dioxide nanopowder to aluminum acetate solution. The second recipe was prepared by adding 4 wt% of colloidal silica (Ludox SK) to the solution and left on the stirrer for another hour to fully mix.

To prepare the polymeric solution 10 wt% PVP was added to the previously prepared inorganic solutions followed by adding ethanol as the solvent. Then the vial was put on a stir plate to be mixed overnight.

4.2.2 Fabrication of aluminum acetate/silica/PVP nanofibers

In order to fabricate the alumina/silica nanofibers, the first step is electrospinning the solution as described in section 3.2. Prior to the electrospinning process, the solution was placed in an ultrasonic bath for 20 minutes, in order to fully disperse the silicon dioxide particles. Soon after, the solution was transferred to a 5ml hypodermic syringe and placed in syringe pump with flow rate of 8.5 μl/min. The syringe was connected to the needle using plastic tubes to deliver the solution to the tip of the needle. The distance between the tip of the needle and the collector was maintained at 10 cm. The connector of the high voltage power supply was also attached to the needle and grounded to the collecting drum. The collecting drum was wrapped in aluminum foil. The rotating drum speed was set to 7 rpm. After checking all of the tubes and connections, the syringe pump was started and voltage supply was turned on promptly after. The optimum relative humidity was determined to be in 10%-15% range, which could be controlled by utilizing the (de)humidifier setup. At higher humidity, the fibers are prone to aggregate alongside
the jet stream (Figure 4.1). At lower humidity, the tip of the needle becomes blocked probably because the solvent evaporates too quickly.

Figure 4.1 Electrospinning at higher humidity

The circulating fan in the lower section of the electrospinning box helps to keep the relative humidity (RH) steady. The tip of the needle needed regular checking and cleaning while spinning to eliminate blockage of the needle opening. For each run, about 5.5 ml of solution was electrospun and nanofibers were collected on a rectangular aluminum sheet.
4.3 Calcination

Calcination was performed in order to crystallize the mineral structure of the ceramics and remove the polymer material. The main purpose of this process is to eliminate the polymer part of as-spun nanofibers and to oxidize the inorganics to metal oxide. A Thermolyne 21100 tube furnace (Figure 3.5) which has an operating temperature capacity of 1200°C and maximum heating rate of 10°C/min was also used.

![Thermolyne 21100 tube furnace](image)

Figure 4.2 Thermolyne 21100 tube furnace

Four different parameters were manipulated during the calcination process, including calcination temperature, heating rate, soaking time, and cooling rate of the furnace. A rectangular crucible (4x10x2 WxLxH cm) was used to hold the specimen.
4.3.1 Calcination of aluminum acetate/silica/PVP nanofibers

The ultimate goal of performing calcination on as-spun nanofibers was to remove PVP and oxidize the aluminum acetate/silicon dioxide to mullite. Calcination was performed at temperatures from 900°C to 1150°C. PVP decomposition starts at 200°C and it will be over 95% decomposed above 500°C. Heating rate range was set at 10°C/min. As-spun nanofiber sheet obtained from electrospinning was folded to fit inside the crucible. Another crucible was placed on top to prevent the nanofibers from leaving the crucible. When the temperature reached the plateau, it was kept steady for 6 hours. The sample was then cooled down by unplugging the furnace and letting it cool down by itself. The samples were left overnight at room temperature before collecting.

4.4 Characterization

In this section characterization of the electrospinning solution, as-spun PVP/aluminum acetate/silica nanofibers and calcined nanofibers are discussed.

4.4.1 Characterization of electrospinning solution

The physical properties of the electrospinning solution were measured in order to explain the behavior of solution. Viscosity was determined by using Brookfield viscometer DV2T. Surface tension of solution was measured by Central Scientific Interfacial Tensiometer using Du Noüy-Padday method.
4.4.2 Characterization of aluminum acetate/silica/PVP nanofibers

The following characterization techniques were used to study the properties of as-spun nanofibers of PVP/aluminum acetate/silica. Scanning electron microscopy (SEM) by Hitachi model TM3000 was used to inspect the morphology of as-spun nanofibers. Energy dispersive X-ray spectroscopy (EDAX/EDS) by Bruker Quantax 70 was utilized for elemental analysis. FiberQuant software was used to process the image and calculate the nanofibers diameters and distribution histogram. A Denver Instrument P-403 balance was used in order to weigh the samples before and after the calcination to determine the weight loss.

4.4.3 Characterization of aluminum oxide/silica nanofibers

For characterizing the calcined alumina/silica nanofibers, scanning electron microscopy (SEM) by Hitachi model TM3000 was used to inspect the morphology of calcined nanofibers. Energy dispersive X-ray spectroscopy (EDS) by Bruker Quantax 70 was utilized for elemental analysis. A Rigaku Ultima IV X-ray diffraction system with tube characteristic of 40 kV, 35 mA and copper as the target was used to compare the crystal structure of obtained samples to commercial mullite.

4.5 Results and discussion

Characterization results and data collected in the process of making as-spun and calcined fibers are discussed in this section. Data presented here include physical properties of the electrospinning solution, SEM images of both as-spun and calcined
nanofibers revealing the morphology and fiber diameter, and EDS results declaring the elemental composition of calcined sample

4.5.1 Solution properties

Electrospinning solution was made using the recipe described in section 4.2.1. Surface tension and viscosity of this solution were measured by equipment described in section 4.4.1. Surface tension of the solution was measured three times and average of these measurements was recorded 11.255 mN/m with standard deviation of 0.34 mN/m. Dynamic viscosity of the solution was measured three times and average of these measurements was 150.05 cP with standard deviation of 4.52 cP.

4.5.2 Nanofiber morphology

SEM images of aluminum acetate/silicon dioxide nanofibers prepared by silicon dioxide nanopowder are shown in Figure 4.3, as-spun fibers were calcined at 1000 °C for 4 hours with heating rate of 10 °C/min. 74.8% weight loss occurred during the calcination process. As-spun fibers tend to shrink after calcination due to loss of the organic part and moisture.
Figure 4.3 Aluminum acetate/silicon dioxide/PVP as-spun nanofibers (left) same fibers calcined at 1000 C for 4 hours (right)

Bead formation was observed in the SEM image of aluminum acetate/silicon dioxide/PVP samples (Figure 4.4). One of the main reasons of bead formation is the high surface tension in the solution.\textsuperscript{15} In order to overcome this issue, water (as the aluminum acetate solvent) with surface tension of 75 mN/m was partially replaced by acetic acid, which has surface tension of 27 mN/m. As it is clear in Figure 4.4 and Figure 4.5 after adding acetic acid as the solvent to the electrospinning solution, bead problem has decreased significantly.
Figure 4.4 Aluminum acetate/silicon dioxide/PVP nanofibers with water as solvent

Figure 4.5 Aluminum acetate/silicon dioxide/PVP nanofibers with acetic acid and water as solvent
As can be seen in Figure 4.5 there were still some small white spots visible in the nanofiber structure. EDS analysis indicated that these dots are mainly silicon dioxide. To address the concern of dispersing SiO\textsubscript{2} particles, surfactant-assisted dispersion was investigated.

4.5.3 Silicon dioxide dispersion

A non-ionic surfactant and a ketone were selected in order to improve the dispersion of silicon dioxide nanopowder in the electrospinning solution: Triton X-100 (TX-100) and cetrimonium bromide (CTAB). Separate solutions were prepared with equal amounts of aluminum acetate, PVP and nano SiO\textsubscript{2}, a few droplets of each additive (>1wt%) were added to each and electrospun at the same condition. Figure 4.6 and Figure 4.7 illustrates the SEM image of as-spun nanofibers treated with CTAB and TX-100 respectively.
As it can be seen in the images, TX-100 has the better dispersibility ratio than CTAB. Ludox SK, which is a commercial 25% colloid silica solution, is replaced later in experiments as the silicon dioxide source. In order to test the most appropriate solution
recipe for new Ludox SK, four different types of solutions were made using the following formula shown in Table 4.1.

Table 4.1 Recipes to make PVP/Ludox SK/aluminum acetate solution

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum acetate</td>
<td>1.45 g</td>
<td>1.45 g</td>
<td>1.45 g</td>
<td>1.45 g</td>
</tr>
<tr>
<td>DI water</td>
<td>3.2 g</td>
<td>3.2 g</td>
<td>3.2 g</td>
<td>2.95 g</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>-</td>
<td>1.45 g</td>
<td>-</td>
<td>1.45 g</td>
</tr>
<tr>
<td>Formic acid</td>
<td>1.45 g</td>
<td>-</td>
<td>1.45 g</td>
<td>-</td>
</tr>
<tr>
<td>Ludox SK</td>
<td>4 wt%</td>
<td>4 wt%</td>
<td>4 wt%</td>
<td>6 wt%</td>
</tr>
<tr>
<td>PVP</td>
<td>12 wt%</td>
<td>10 wt%</td>
<td>10 wt%</td>
<td>10 wt%</td>
</tr>
<tr>
<td>Ethanol</td>
<td>7.5 ml</td>
<td>7.5 ml</td>
<td>7.5 ml</td>
<td>7.5 ml</td>
</tr>
</tbody>
</table>

SEM images of aluminum acetate/silica nanofibers prepared by Ludox SK are shown in Figure 4.8. The concentration of aluminum acetate and ethanol was kept constant for all four solutions. A PVP concentration of 12 wt% or 10 wt% was used. Effects of acetic and formic acid were investigated. Ludox SK concentration was kept at 4 wt% for three of the samples, and 6 wt% the fourth sample.

SEM images (Figure 4.8) reveal that formic acid definitely is a better option as the solvent because fewer white spots were observed. When Ludox concentration was increased by 0.5% no change in the presence of white spots was observed. A PVP concentration of 12 wt% seems to result in more uniform and consistent nanofibers than the 10 wt% solution. The higher PVP concentration in the solution means higher overall viscosity and it has been shown $^{105}$ that optimum viscosity range is required to obtain uniform and smooth nanofibers.
Figure 4.8 PVP/Ludox SK/aluminum acetate nanofibers with different recipes

Table 4.2 Nanofiber parameters of PVP/Ludox SK/aluminum acetate

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Fiber Diameter (nm)</td>
<td>360</td>
<td>246</td>
<td>215</td>
<td>239</td>
</tr>
<tr>
<td>Median Fiber Diameter (nm)</td>
<td>359</td>
<td>241</td>
<td>211</td>
<td>230</td>
</tr>
<tr>
<td>Standard Deviation (nm)</td>
<td>68</td>
<td>69</td>
<td>66</td>
<td>51</td>
</tr>
<tr>
<td>Fiber Diameter Range (nm)</td>
<td>223-533</td>
<td>124-414</td>
<td>105-358</td>
<td>146-369</td>
</tr>
</tbody>
</table>
Fiber diameters are shown in Table 4.2 including average and median fiber diameter and fiber diameter range. The specimen with 12 wt% PVP (AA-SI-38) has the largest diameter among all because the spinning solution was more viscous. Figure 4.9 shows the fiber diameters distribution histograms. As it is seen in histograms nanofibers which are fabricated using 12 wt% PVP are more homogenous in diameter.

![Fiber Diameter Distributions](image)

Figure 4.9 Nanofiber diameters distribution of PVP/Ludox SK/aluminum acetate

4.5.4 Elemental analysis

Elemental analysis was collected by energy dispersive X-ray spectroscopy (EDS). The results revealed that atomic compositions of alumina/silica nanofibers calcined at
1100 °C for 6 hours are in good consistency with stoichiometric values for mullite.

(Table 4.3)

Table 4.3 Atomic percentages of AA/silica sample and stoichiometric mullite

<table>
<thead>
<tr>
<th>Atomic %</th>
<th>Al</th>
<th>Si</th>
<th>O</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA/silica sample</td>
<td>29.55</td>
<td>6.22</td>
<td>60.50</td>
<td>3.73</td>
</tr>
<tr>
<td>Mullite commercial</td>
<td>28.57</td>
<td>9.52</td>
<td>61.9</td>
<td>0</td>
</tr>
</tbody>
</table>

A small quantity of sodium observed in elemental analysis likely comes from aluminum acetate precursor.

![Elemental analysis spectrum by EDS](image)

Figure 4.10 Elemental analysis spectrum by EDS

4.5.5 X-ray diffraction

X-ray diffraction was collected for sample fabricated according to description in sections 4.2.2 and 4.3.1. Figure 4.11 shows the XRD pattern for mullite-like nanofibers and some peaks associated with mullite were marked with Miller indices in the pattern.
4.6 Discussion

Mullite-like nanofibers have been successfully produced using the electrospinning and calcination techniques. Two types of silicon dioxide source were used in order to fabricate mullite-like nanofibers, silica nanopowder and colloidal silica. Nanofibers fabricated using the colloidal silica 25 wt% (Ludox SK) were more uniform and beadless, probably because of better dispersion of silica. The colloidal silica (Ludox) is a promising precursor for fabricating silica nanofibers in more environmental friendly manner instead of using tetraethyl orthosilicate (TEOS). Silica nanopowder can also be used in fabrication of mullite-like nanofibers if silica is dispersed evenly throughout the solution. Surface tension of PVP/aluminum acetate/silica solution is slightly higher than PVP/aluminum acetate solution so either formic or acetic acid is needed at higher ratios in order to decrease the surface tension. Triton X-100 (TX-100) is a relatively suitable non-ionic surfactant to disperse nano silica powder in polymeric solution probably because of hydrophobic tail attached to the silica particles. Increasing the polymer concentration from 10 wt% to 12 wt% increased the fiber diameter 67%. Results obtained

Figure 4.11 XRD pattern of mullite-like nanofibers
from SEM images indicates consistent and bead-less nanofibers with average fiber
diameter of 233 nm. The EDS data confirms that the elemental composition of final
calcined sample is in accordance with commercial mullite. The XRD spectrum indicates
some peaks associated with commercial mullite.
CHAPTER V

DEPOSITION OF ALUMINA NANOFIBERS ON SILICON CARBIDE MATRIX

In this chapter, deposition of aluminum oxide nanofibers on two types of silicon carbide composites is discussed. The process consisted of electrospinning the PVP/aluminum acetate solution, calcining the as-spun fibers, dispersing alumina nanofibers in ethanol solution, coating the SiC composites surface with solution and heat treatment of the coated specimen. Silicon carbide (SiC) composites were coated with alumina nanofibers to reinforce these composites as barrier coatings and protection against oxidation. Characterization methods are mentioned afterward and eventually experimental results are discussed.

5.1 Materials

The materials that were used during this part of project include: polyvinylpyrrolidone (PVP) with molecular weight of 1,300,000 g/mol purchased from Sigma Aldrich, aluminum acetate, basic purchased from Strem Chemicals, glacial acetic acid purchased from EMD, ethyl alcohol 200 proof purchased from Decon Labs, formic acid 98% purchased from Fluka Analytical, melt infiltrated silicon carbide (SiC/SiC) composite coated with silicon (Figure 5.1) and SiC mini composites (Figure 5.2). All
chemicals were used without further modification. Both SiC composites were provided by Dr. Morscher (Mechanical Engineering, The University of Akron) and have been used without further processing.

5.2 Silicon carbide (SiC) coating

In collaboration with the Mechanical Engineering department, two types of silicon carbide composites were gathered to be coated with alumina nanofibers to be used as a modifier of the environmental/thermal barrier coatings (EBC/TBC). The nanofibers need to be able to survive at elevated temperatures (1350°C and above). Melt infiltrated composite (Figure 5.1) consists of a matrix phase and a fiber phase which is coated with silicon. These composites have maximum operational temperature of 1350°C. Silicon carbide mini composites (Figure 5.2) are made of tiny SiC rods (0.5 mm) attached together. These composites can be used at much higher temperatures.

Figure 5.1 Melt infiltrated silicon carbide sample
Two approaches were used to deposit nanofibers onto the SiC composites. The polymer nanofibers were electrospun directly onto the composites and calcined on the surface or they were electrospun, calcined, dispersed in ethanol and then added to the composite dropwise.

5.2.1 Electrospinning onto the SiC composite

The first approach used to add nanofibers to the SiC composite surface was by directly electrospinning of the nanofibers onto the surface. The electrospinning solution described in section 3.2.2 was used in order to directly electrospin the aluminum acetate and PVP nanofibers on melt infiltrated SiC composite (Figure 5.3). Electrospinning parameters were maintained at the conditions shown in Table 5.1.
Figure 5.3 Directly spun PVP/aluminum acetate on SiC composite

Approximately 6μl of solution were pumped for 40 seconds to cover the entire surface of the melt infiltrated SiC composite. Calcination was performed on the sample with the condition shown in Table 5.2.

Table 5.1 Electrospinning parameters for SiC coating

<table>
<thead>
<tr>
<th>Electric Potential</th>
<th>Feeding rate</th>
<th>Distance</th>
<th>Relative Humidity</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 kV</td>
<td>10 μl/min</td>
<td>10 cm</td>
<td>10%</td>
</tr>
</tbody>
</table>

Table 5.2 Calcination parameters for aluminum acetate/PVP coated SiC composite

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Heating rate</th>
<th>Soaking time</th>
<th>Cooling rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100 °C</td>
<td>1 °C/min</td>
<td>6 hours</td>
<td>unplug</td>
</tr>
</tbody>
</table>
Calcination results and SEM images indicated that the nanofibers did not survive this process, probably because of the fiber mat shrinkage.

5.2.2 Dispersion of nanofibers on SiC composites

The second approach was taken to calcine then disperse alumina nanofibers on SiC composites. Alumina nanofibers calcined at 1100 °C, 1350 °C and 1450 °C were dispersed in ethanol by utilizing ultrasonic bath made by SPER Scientific. The solution was placed over SiC composite using a dropper. The specimen was left aside for an hour for ethanol to evaporate. Figure 5.4 illustrates the calcined alumina nanofibers at 1350 °C on a melt infiltrated SiC composite. Figure 5.5 shows the calcined alumina nanofibers at 1350 °C on SiC mini composite.
Figure 5.4 Melt infiltrated SiC composite coated with calcined alumina nanofibers

Figure 5.5 SiC mini composite coated with calcined alumina nanofibers
5.2.3 Heat treatment on SiC composites

Coated samples were placed in the furnace for further heat treatment with the purpose of stabilizing the coating. The calcination temperatures were chosen according to operational temperature condition of these composites. The calcination parameters are shown in Table 5.3. Samples were left in the furnace overnight to be cooled down to room temperature.

Table 5.3 Furnace parameters for SiC heat treatment

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Heating rate</th>
<th>Soaking time</th>
<th>Cooling rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100-1450 °C</td>
<td>1 °C/min</td>
<td>1 hour</td>
<td>unplug</td>
</tr>
</tbody>
</table>

Figure 5.6 and Figure 5.7 demonstrate the specimen after the further heat treatment.
5.2.4 Dispersion of alumina nanofibers on silicon wafer

In order to verify the survival and investigate the adherence of nanofibers to the silicon surface the adhesion of alumina nanofibers to the substrate, a polished silicon wafer was coated with alumina nanofibers. Alumina nanofibers previously calcined at 1100 °C were dispersed in ethanol using the same procedure described in section 5.2.2.
The coated silicon wafer specimen was calcined in the furnace with conditions shown in Table 5.4.

Table 5.4 Furnace parameters for coated silicon wafer

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Heating rate</th>
<th>Soaking time</th>
<th>Cooling rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100 °C</td>
<td>2 °C/min</td>
<td>6 hours</td>
<td>unplug</td>
</tr>
</tbody>
</table>

5.2.5 Characterization of SiC samples

The following characterization techniques were used in order to study the properties of SiC samples. A Hitachi TM3000 scanning electron microscopy (SEM) was used to inspect the surface adherence of applied alumina nanofiber coatings. A Bruker Quantax 70 energy dispersive X-ray spectrometer (EDS) was utilized for elemental analysis of the SiC surface before and after the coating was applied. Images were analyzed for untreated SiC sample, SiC coated with calcined alumina nanofibers and the coated SiC samples following the heat treatment.

5.3 Results and discussion

Characterization results and data were collected in the process of deposition of alumina nanofibers onto the SiC composite is discussed in this section. Data presented here include, SEM images of before and after further heat treatment of the samples, revealing the morphology and adherence of nanofiber to the SiC surface and EDS results showing the elemental composition of the samples.
5.3.1 Silicon wafer

Silicon wafers were examined by SEM after deposition of alumina nanofibers calcined at 1100 °C. SEM results show a solid adherence and bonding between the silicon wafer and alumina nanofibers. Figure 5.8 shows both uncoated silicon wafer and deposited sections. Figure 5.9 shows an inset of the previous image at higher magnification.

![Silicon wafer deposited with alumina (x2k magnification)](image)

Figure 5.8 Silicon wafer deposited with alumina (x2k magnification)
Elemental analysis results also confirmed the deposition of alumina nanofibers onto the silicon wafer.
Figure 5.10 EDS spot in silicon wafer deposited with alumina

Figure 5.11 Elemental analysis graph of silicon wafer deposited with alumina

The yellow circle in Figure 5.10 illustrates the exact spot of the performed elemental analysis, where both alumina and silicon are present. Figure 5.11 shows the elemental analysis graph, which indicated that elemental composition of the yellow circle as 44.6 wt% oxygen, 35.6 wt% silicon, 16.4 wt% aluminum and 3.4 wt% sodium. The
EDS results revealed that during the heat treatment process, silicon was oxidized to silicon dioxide.

5.3.2 Melt infiltrated silicon carbide

Figure 5.12 shows a very thin layer PVP/aluminum acetate nanofibers directly spun on to a melt infiltrated SiC sample. After calcination performed at 1100 °C for 6 hours there were no visible nanofibers detected by SEM. However, the elemental analysis confirmed the presence of 1 wt% aluminum. This result indicated that directly electrospun nanofibers did not survive onto the SiC surface due to the significant shrinkage and weight loss during the calcination.
Figure 5.12 Directly spun PVP/aluminum acetate nanofibers on MI-SiC

Figure 5.13 shows the alumina nanofibers on melt infiltrated SiC. On the left picture, already calcined alumina nanofibers at 1100 °C are deposited on melt infiltrated SiC. On the right picture, the same specimen was heat treated at 1100 °C for 6 hours. SEM images revealed that alumina nanofibers that were previously calcined at 1100 °C can survive the second heat treatment at the same temperature for long hours.
Heat treatment on a second sample was run at 1300 °C for 6 hours, but no visible nanofibers were detected by SEM. The elemental analysis results confirmed the presence of alumina at a level of 5.47 wt% and 4.42 wt% for heat treatments at 1100 °C and 1300 °C respectively.

Figure 5.14 and Figure 5.15 show the already calcined alumina nanofiber at 1350 deposited on melt infiltrated SiC after heat treatment at 1300 °C for 1 hour at different magnifications. The elemental analysis results indicated that average composition of 53.15 wt%, 22.12 wt%, 19.75 wt% and 4.98 wt% for oxygen, aluminum, silicon and sodium respectively.

Figure 5.13 Alumina nanofibers on MI-SiC composite before (left) and after heat treatment (right)
Figure 5.14 Alumina nanofibers on MI-SiC composite after heat treatment at 1300 °C (x2.5k mag.)

Figure 5.15 Alumina nanofibers on MI-SiC composite after heat treatment at 1300 °C (x6.0k mag.)
A second step heat treatment was performed on the same sample from the last section (Figure 5.14) at 1350 °C for 1 hour. The SEM results show some fiber-like structures (arrows in Figure 5.16) but no consistent nanofibers structure were detected.

![Image](image.png)

**Figure 5.16** Second stage heat treatment on MI-SiC composite coated with alumina nanofibers on at 1400 °C

Alumina nanofibers that were already calcined at 1450 °C were deposited on melt infiltrated SiC and then the sample heat treated at 1350 °C for 1 hour. Figure 5.17 shows these nanofibers on SiC substrate before the heat treatment. After performing the heat treatment, no visible nanofibers can be seen on the surface, although elemental analysis confirmed the presence of alumina at same levels before and after heat treatment.
Figure 5.17 Alumina nanofibers calcined at 1450 °C on MI-SiC composite before heat treatment

For the final sample, five layers of calcined alumina nanofibers were deposited on melt infiltrated SiC samples with 30 min time intervals, and then the sample was heat treated at 1350 °C for 1 hour. It can be seen in Figure 5.18 that the nanofibers survived at 1350 °C, which is the operating temperature limit for melt infiltrated SiC composite. Figure 5.19 shows the same nanofibers at higher magnification. The diameter of the alumina nanofibers were measured at 250nm.
Figure 5.18 5-layer alumina nanofibers on MI-SiC composite after heat treatment at 1350°C

Figure 5.19 5-layer alumina nanofibers on MI-SiC composite after heat treatment at 1350°C (x25k magnification)
As the last experiment on melt infiltrated SiC composites, the previously made sample underwent a second heat treatment process at exactly the same condition (1350°C for 1 hour) and nanofibers survived after second heat treatment as can be seen in Figure 5.20.

![Image](image_url)

Figure 5.20 Second heat treatment at 1350 on alumina coated MI-SiC composite

5.3.3 SiC Mini composites

In the first step, PVP/aluminum acetate nanofibers were directly spun on the SiC mini composites surface. The calcination was done at 1100 °C for 6 hours and no fibers were detected with SEM. Figure 5.21 shows the as-spun, PVP/aluminum acetate nanofibers on SiC mini composites substrate.
Figure 5.21 Directly spun PVP/aluminum acetate nanofibers on SiC mini composites

In the next step, alumina nanofibers previously calcined at 1100 °C were deposited on SiC mini composites, and then the sample was heat treated at 1300 °C for 6 hours. Figure 5.22 shows the dispersed alumina nanofibers before heat treatment on SiC mini composites surface. Although no fibers could be seen by the SEM after the heat treatment, the elemental analysis proves the presence of the aluminum before and after heat treatment. Figure 5.23 shows the elemental analysis graph of SiC mini composites coated with alumina nanofibers calcined at 1100 °C and Figure 5.24 shows the elemental analysis graph of the same SiC mini composites coated with alumina nanofibers after heat treatment calcined at 1300 °C.
Figure 5.22 Alumina nanofibers previously calcined at 1100 °C on SiC mini composites

Figure 5.23 Elemental analysis graph for SiC mini composites coated with alumina nanofibers before the heat treatment
In the next step, alumina nanofibers calcined at 1350 °C were deposited on SiC mini composites, and then the sample was heat treated at 1300 °C for 1 hour. Figure 5.25 shows the nanofiber morphology on SiC mini composites after heat treatment at 1300 °C.
Figure 5.25 Alumina nanofibers on SiC mini composites after heat treatment at 1300 °C

In the next step alumina nanofibers already calcined at 1450 °C were deposited on SiC mini composites in order to be heat treated at 1350 °C for 1 hour. Figure 5.26 shows alumina nanofibers on SiC mini composites substrate after heat treatment at 1350 °C.
Figure 5.26 Alumina nanofibers on SiC mini composites were heat treated at 1350 °C.

In the next step, the same specimen from the last section was heat treated at the same condition to observe the survival of the fibers. Figure 5.27 shows the alumina nanofibers on SiC mini composites after second heat treatment at 1350 °C. Figure 5.28 and Figure 5.29 show the elemental analysis of the untreated SiC mini composites before deposition of the alumina nanofibers and after the second heat treatment at 1350 °C. Most of the silicon was oxidized to silicon dioxide and mass percentages of the final sample were measured at 54.3% oxygen, 32.7% silicon, 6.8% aluminum and 6.2% sodium.
Figure 5.27 SiC mini composites coated with alumina fibers after second heat treatment at 1350 °C

Figure 5.28 Elemental analysis of untreated SiC mini composites
In the final step, SiC mini composites coated with alumina nanofibers were heat treated at 1450 °C for 1 hour. This temperature is very close to the operation limit for the SiC mini composites. Figure 5.30 shows the SEM image of SiC mini composites coated with alumina nanofibers after heat treatment at 1450 °C. Some fiber-like shapes were observed but no consistent nanofiber structures were detected.
Figure 5.30 SiC mini composites coated with alumina nanofibers after heat treatment at 1450 °C

5.4 Discussion

Alumina nanofibers have been successfully deposited onto the SiC mini composite and melt infiltrated SiC composite using the electrospinning and heat treatment processes. Results indicated that directly electrospinning on SiC composites is not an applicable manner to deposit alumina nanofibers because of shrinkage of the as-spun fibers during the calcination. Results obtained from SEM images indicated that adherence and incorporation of alumina nanofibers into the SiC structure were achieved. The EDS data confirmed that the elemental composition of alumina material. Multiple heat treatments on coated melt infiltrated SiC and SiC mini composites indicated that alumina nanofiber coatings can survive after calcination at 1350 °C for 2 times and makes these nanofibers suitable option for cyclic high temperatures application. Alumina
nanofibers need to be calcined prior to deposition on SiC composite at a higher
temperature than the heat treatment temperature; otherwise, these nanofibers will not
survive this temperature increase. This happens probably because of the difference
between free energy of alumina phase at different temperatures, which makes nanofibers
calcined at lower temperatures less stable. Deposition and characterization of calcined
alumina nanofibers on SiC mini composites was more challenging because of the uneven
surface of this composite.

In future work, it is recommended that a more uniform and perhaps thicker
nanofiber coating of mullite-like nanofibers to be applied to the SiC composites.
Alternative deposition techniques such as plasma spray coating might be used in order to
disperse ceramic materials evenly onto the SiC surface.
CHAPTER VI

CONCLUSIONS AND FUTURE WORK RECOMMENDATIONS

6.1 Conclusions

In this work, three projects were studied including fabrication of alumina nanofibers followed by grain size study, fabrication of alumina/silica nanofibers, and deposition of alumina nanofibers on silicon carbide (SiC) composites. Based on the findings of this work the following conclusions can be made:

1. Alumina nanofibers were fabricated using electrospinning and calcination methods. The average diameter for as-spun fibers was 417 nm, which reduced to 211 nm and 183 nm after calcination of 1100°C and 1350°C respectively. The grain size for calcined alumina nanofibers was in the range of 10-50 nm. On average 77% weight loss occurred during the calcination.

2. Among four calcination parameters manipulated, calcination temperature has a significant effect on grain size. An increase in calcination temperature, leads to an increase in the grain size. Soaking time has an effect on grain growth but it is not statistically significant (p value = 0.079). Heating and cooling rates had no effect on grain size growth.
3. Mullite-like nanofibers have been successfully fabricated using the electrospinning and calcination techniques. Colloidal silica 25 wt% (Ludox SK) is a promising precursor for fabricating silica nanofibers in more environmental friendly manner instead of using tetraethyl orthosilicate (TEOS). Non-ionic surfactant was used to improve silica nanopowder dispersion in the electrospinning solution. Fiber morphology can be adjusted by changing the solvent type and polymer concentration. The ideal relative humidity was found out to be in 10%-15% range in order to make uniform fibers.

4. Alumina nanofibers have been successfully deposited onto the SiC mini composite and melt infiltrated SiC composite using the electrospinning and heat treatment processes. The results indicated that alumina nanofibers deposited onto SiC composites can survive high temperatures cyclic operations as long as the fibers are heat treated at a higher temperature prior to deposition onto the SiC composite.

6.2 Future work

Recommendations for future work based on the results of this study are as follows:

1. In order to investigate the calcination parameters in detail, performing mechanical characterization techniques such as shear or tensile strength on alumina nanofibers is suggested.

2. High resolution transmission electron microscopy (HR-TEM) is recommended to verify the grain size measurements.
3. For further investigation of heating and cooling effects, calcination studies can be done with rapid heating and cooling rates such as microwave annealing or plasma heating.

4. Ceramic nanofibers can be dispersed more evenly onto the SiC composite matrix using other techniques such as plasma spray coating.

5. Alumina/silica nanofibers can also be deposited on composites as additives to the thermal/environmental barrier coatings.
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APPENDICES
APPENDIX A

ALUMINA NANOFIBERS ADDITIONAL DATA

This appendix includes the SEM images, EDS data and XRD raw data for as-spun PVP/aluminum acetate and alumina nanofibers.

Figure A.1 PVP/aluminum acetate nanofibers trial1
Figure A.2 Calcined alumina nanofibers at 200°C for 4 hours and 5°C/min heating rate

Figure A.3 Calcined alumina nanofibers at 300°C for 4 hours and 5°C/min heating rate
Figure A.4 Calcined alumina nanofibers at 740°C for 4 hours 10°C/min heating rate

Figure A.5 Calcined alumina nanofibers at 1100°C for 4 hours 10°C/min heating rate
Figure A.6 EDS alumina nanofibers at 200°C for 4 hours 5°C/min heating rate

Figure A.7 EDS alumina nanofibers at 300°C for 4 hours 5°C/min heating rate
Figure A.8 EDS alumina nanofibers at 740°C for 4 hours 10°C/min heating rate

Figure A.9 EDS alumina nanofibers at 1100°C for 4 hours 10°C/min heating rate
Figure A.10 PVP/aluminum acetate nanofibers trial4

Figure A.11 PVP/aluminum acetate nanofibers trial4
Figure A.12 PVP/aluminum acetate nanofibers trial6

Figure A.13 PVP/aluminum acetate nanofibers trial6 (x30k magnification)
Figure A.14 Alumina nanofibers calcined at 1100°C, 7°C/min heating rate, 1h soaking time and 1°C/min cooling rate

Figure A.15 Alumina nanofibers calcined at 1350°C, 7°C/min heating rate, 1h soaking time and fan cooled
Figure A.16 Alumina nanofibers calcined at 1100°C, 1°C/min heating rate, 1h soaking time and 1°C/min cooling rate

Figure A.17 Alumina nanofibers calcined at 1350°C, 1°C/min heating rate, 1h soaking time and fan cooled
Figure A.18 EDS PVP/aluminum acetate nanofibers trial1 mm-25

Figure A.19 EDS alumina nanofibers calcined at 1100°C, 7°C/min heating rate, 1h soaking time and 1°C/min cooling rate

Figure A.20 EDS alumina nanofibers calcined at 1350°C, 7°C/min heating rate, 1h soaking time and fan cooled
Figure A.21 EDS alumina nanofibers calcined at 1100°C, 1°C/min heating rate, 1h soaking time and 1°C/min cooling rate.

Figure A.22 EDS alumina nanofibers calcined at 1350°C, 1°C/min heating rate, 1h soaking time and fan cooled.
Figure A.23 PVP/aluminum acetate nanofibers trial1 mm-27

Figure A.24 Alumina nanofibers calcined at 1100°C, 1°C/min heating rate, 6h soaking time and 1°C/min cooling rate
Figure A.25 Alumina nanofibers calcined at 1350°C, 7°C/min heating rate, 6h soaking time and fan cooled

Figure A.26 Alumina nanofibers calcined at 1100°C, 7°C/min heating rate, 6h soaking time and 1°C/min cooling rate
Figure A.27 Alumina nanofibers Alumina nanofibers calcined at 1350°C, 1°C/min heating rate, 6h soaking time and fan cooled

Figure A.28 EDS PVP/aluminum acetate nanofibers trial1 mm-27
Figure A.29 EDS alumina nanofibers calcined at 1100°C, 1°C/min heating rate, 6h soaking time and 1°C/min cooling rate

Figure A.30 EDS alumina nanofibers calcined at 1350°C, 7°C/min heating rate, 6h soaking time and fan cooled
Figure A.31 EDS alumina nanofibers Figure calcined at 1100°C, 7°C/min heating rate, 6h soaking time and 1°C/min cooling rate

Figure A.32 EDS alumina nanofibers Alumina nanofibers calcined at 1350°C, 1°C/min heating rate, 6h soaking time and fan cooled
Figure A.33 PVP/aluminum acetate nanofibers using formic acid as solvent

Figure A.34 PVP/aluminum acetate nanofibers trial11 flow rate 11μl/min, voltage 15kV, and 10cm distance
**Figure A.35** EDS PVP/aluminum acetate nanofibers trial 11 flow rate 11 μl/min, voltage 15 kV, and 10 cm distance

**Figure A.36** PVP/aluminum acetate nanofibers trial 14
Figure A.37 PVP/aluminum acetate nanofibers trial15

Figure A.38 Alumina nanofibers calcined at 1350°C, 1°C/min heating rate, 6h soaking time and 1°C/min cooling rate
Figure A.39 Alumina nanofibers calcined at 1100°C, 1°C/min heating rate, 1h soaking time and fan cooled

Figure A.40 Alumina nanofibers calcined at 1350°C, 7°C/min heating rate, 6h soaking time and 1°C/min cooling rate
Figure A.41 EDS alumina nanofibers calcined at 1100°C, 1°C/min heating rate, 1h soaking time and fan cooled

Figure A.42 EDS alumina nanofibers calcined at 1350°C, 7°C/min heating rate, 6h soaking time and 1°C/min cooling rate
Figure A.43 EDS alumina nanofibers calcined at 1350°C, 1°C/min heating rate, 6h soaking time and 1°C/min cooling rate.

Figure A.44 PVP/aluminum acetate nanofibers trial15
Figure A.45 PVP/aluminum acetate nanofibers trial16

Figure A.46 Alumina nanofibers calcined at 1450°C, 1°C/min heating rate, 1h soaking time and fan cooled
Figure A.47 Alumina nanofibers calcined at 1400°C, 1°C/min heating rate, 1h soaking time and fan cooled

Figure A.48 Alumina nanofibers calcined at 1100°C, 1°C/min heating rate, 6h soaking time and fan cooled
Figure A.49 EDS alumina nanofibers calcined at 1400°C, 1°C/min heating rate, 1h soaking time and fan cooled

Figure A.50 EDS alumina nanofibers calcined at 1100°C, 1°C/min heating rate, 6h soaking time and fan cooled

Figure A.51 EDS alumina nanofibers calcined at 1450°C, 1°C/min heating rate, 1h soaking time and fan cooled
Raw X-ray diffraction data for alumina nanofibers calcined at different conditions are presented in following tables.

Figure A.52 XRD spectrum for alumina nanofibers calcined at 1100°C, 7°C/min heating rate, 1h soaking time and 1°C/min cooling rate

Figure A.53 XRD spectrum for alumina nanofibers calcined at 1350°C, 7°C/min heating rate, 1h soaking time and fan cooled
Figure A.54 XRD spectrum for alumina nanofibers calcined at 1100°C, 1°C/min heating rate, 1h soaking time and 1°C/min cooling rate

Figure A.55 XRD spectrum data for alumina nanofibers calcined at 1350°C, 1°C/min heating rate, 1h soaking time and fan cooled
Figure A.56 XRD spectrum data for alumina nanofibers calcined at 1100°C, 1°C/min heating rate, 6h soaking time and 1°C/min cooling rate

Figure A.57 XRD spectrum for alumina nanofibers calcined at 1350°C, 7°C/min heating rate, 6h soaking time and fan cooled
Figure A.58 XRD spectrum for alumina nanofibers calcined at 1100°C, 7°C/min heating rate, 6h soaking time and 1°C/min cooling rate

Figure A.59 XRD spectrum for alumina nanofibers calcined at 1350°C, 1°C/min heating rate, 6h soaking time and fan cooled
Figure A.60 XRD spectrum for alumina nanofibers calcined at 1100°C, 7°C/min heating rate, 1h soaking time and fan cooled

Figure A.61 XRD spectrum data for alumina nanofibers calcined at 1350°C, 7°C/min heating rate, 1h soaking time and 1°C/min cooling rate
Figure A.62 XRD spectrum for alumina nanofibers calcined at 1350°C, 1°C/min heating rate, 1h soaking time and 1°C/min cooling rate

Figure A.63 XRD spectrum for alumina nanofibers calcined at 1350°C, 1°C/min heating rate, 6h soaking time and 1°C/min cooling rate
Figure A.64 XRD spectrum for alumina nanofibers calcined at 1350°C, 7°C/min heating rate, 6h soaking time and 1°C/min cooling rate

Figure A.65 XRD spectrum for alumina nanofibers calcined at 1100°C, 1°C/min heating rate, 1h soaking time and fan cooled
Figure A.66 XRD spectrum for alumina nanofibers calcined at 1100°C, 7°C/min heating rate, 6h soaking time and fan cooled.

Figure A.67 XRD spectrum for Alumina nanofibers calcined at 1100°C, 1°C/min heating rate, 6h soaking time and fan cooled.
APPENDIX B

ALUMINA/SILICA NANOFIBERS ADDITIONAL DATA

This appendix includes the SEM images, and EDS data for as-spun PVP/aluminum acetate/silica and mullite-like nanofibers.

Figure B.1 PVP/aluminum acetate/silica nanofibers trial1
Figure B.2 EDS PVP/aluminum acetate/silica nanofibers trial1

Figure B.3 PVP/aluminum acetate/silica nanofibers trial2
Figure B.4 Calcined alumina/silica nanofibers mm7-c1

Figure B.5 EDS calcined alumina/silica nanofibers mm7-c1
Figure B.6 PVP/aluminum acetate/silica nanofibers mm-13

Figure B.7 PVP/aluminum acetate/silica nanofibers mm-14
Figure B.8 Calcined alumina/silica nanofibers mm13-c2

Figure B.9 EDS calcined alumina/silica nanofibers mm13-c2
Figure B.10 PVP/aluminum acetate/silica nanofibers mm-19a

Figure B.11 PVP/aluminum acetate/silica nanofibers mm-19b
Figure B.12 PVP/aluminum acetate/silica nanofibers mm-19c

Figure B.13 PVP/aluminum acetate/silica nanofibers mm-21
Figure B.14 Calcined alumina/silica nanofibers mm21-c1

Figure B.15 EDS calcined alumina/silica nanofibers mm21-c1
Figure B.16 PVP/aluminum acetate/silica nanofibers with 4 wt% Ludox SK

Figure B.17 EDS PVP/aluminum acetate/silica nanofibers with 4 wt% Ludox SK
Figure B.18 PVP/aluminum acetate/silica nanofibers electrospun at 10μl/min flow rate, 14 kV, 10 cm distance and 0% humidity (trial 12)

Figure B.19 Calcined alumina/silica nanofibers at 1100°C with 2°C/min heating rate and 6 hours soaking time fan cooled (trial 12)
Figure B.20 EDS calcined alumina/silica nanofibers at 1100°C with 2°C/min heating rate and 6 hours soaking time fan cooled (trial 12)
APPENDIX C

STATISTICAL ANALYSIS DATA

In this appendix, analysis of variance (ANOVA) report generated by Minitab software is presented. General linear model is used to analyze the data. Average grain size and highest peak grain size data are analyzed separately.

**General Linear Model: Avg Grain Si versus Calcination, Heating Rate, ...**

<table>
<thead>
<tr>
<th>Factor</th>
<th>Type</th>
<th>Levels</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcination Temp.</td>
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<td>2</td>
<td>1100, 1350</td>
</tr>
<tr>
<td>Heating Rate</td>
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<td>2</td>
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<tr>
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Analysis of Variance for Avg Grain Size, using Adjusted SS for Tests

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Seq SS</th>
<th>Adj SS</th>
<th>Adj MS</th>
<th>F</th>
<th>P</th>
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</table>

S = 56.3541  R-Sq = 75.86%  R-Sq(adj) = 67.08%

<table>
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<tr>
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<th>SE Coef</th>
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<th>P</th>
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<tbody>
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<tr>
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<td>14.09</td>
<td>-1.94</td>
<td>0.079</td>
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<tr>
<td>Cooling Rate 1</td>
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<td>14.09</td>
<td>0.84</td>
<td>0.420</td>
</tr>
</tbody>
</table>

Least Squares Means for Avg Grain Size
Calcination | Mean | SE Mean
--- | --- | ---
1100     | 278.1 | 19.92
1350     | 432.0 | 19.92
Heating Rate |          |      
1     | 347.6 | 19.92
7     | 362.5 | 19.92
Soaking Time |          |      
1     | 327.7 | 19.92
6     | 382.4 | 19.92
Cooling Rate |          |      
1     | 366.9 | 19.92
4     | 343.3 | 19.92

Grouping Information Using Tukey Method and 95.0% Confidence

Calcination
Temp. | N   | Mean | Grouping
--- | --- | --- | ---
1350 | 8   | 432.0 | A
1100 | 8   | 278.1 | B

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

Heating Rate | N   | Mean | Grouping
--- | --- | --- | ---
7   | 8   | 362.5 | A
1   | 8   | 347.6 | A

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

Soaking Time | N   | Mean | Grouping
--- | --- | --- | ---
6   | 8   | 382.4 | A
1   | 8   | 327.7 | A

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

Cooling Rate | N   | Mean | Grouping
--- | --- | --- | ---
1   | 8   | 366.9 | A
4   | 8   | 343.3 | A

Means that do not share a letter are significantly different.

Residual Plots for Avg Grain Size

Plots for Average Grain Size
General Linear Model: Highest Peak versus Calcination, Heating Rate, ...

Factor            Type   Levels  Values
Calcination Temp.  fixed       2  1100, 1350
Heating Rate       fixed       2  1, 7
Soaking Time       fixed       2  1, 6
Cooling Rate       fixed       2  1, 4

Analysis of Variance for Highest Peak Grain Size, using Adjusted SS for Tests

Source             DF  Seq SS  Adj SS  Adj MS      F      P
Calcination Temp.   1   98596   98596   98596  18.55  0.001
Heating Rate        1    2070    2070    2070   0.39  0.545
Soaking Time        1   13806   13806   13806   2.60  0.135
Cooling Rate        1   10712   10712   10712   2.02  0.183
Error              11   58463   58463    5315
Total              15  183648

S = 72.9028   R-Sq = 68.17%   R-Sq(adj) = 56.59%

Term            Coef  SE Coef      T      P
Constant      323.13    18.23  17.73  0.000
Calcination  1100  -78.50    18.23  -4.31  0.001
Heating Rate  1      11.37    18.23   0.62  0.545
Soaking Time  1   -29.38    18.23  -1.61  0.135
Cooling Rate  1    25.88    18.23   1.42  0.183

Least Squares Means for Highest Peak Grain Size

Calcination    Mean  SE Mean
1100          244.6    25.78
1350          401.6    25.78

Heating Rate  Mean  SE Mean
1            334.5    25.78
7            311.8    25.78

Soaking Time  Mean  SE Mean
1            293.7    25.78
6            352.5    25.78

Cooling Rate  Mean  SE Mean
1            349.0    25.78
4            297.3    25.78

Grouping Information Using Tukey Method and 95.0% Confidence

Calcination
Temp.    N  Mean  Grouping
1350    6  401.6  A
1100    8  244.6  B

Means that do not share a letter are significantly different.
Heating
Rate  N  Mean  Grouping
1     8  334.5 A
7     8  311.8 A

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

Soaking
Time  N  Mean  Grouping
6     8  352.5 A
1     8  293.7 A

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

Cooling
Rate  N  Mean  Grouping
1     8  349.0 A
4     8  297.3 A

Means that do not share a letter are significantly different.

Residual Plots for Highest Peak Grain Size
Figure C.1 Calcination parameters effect on average grain size

Figure C.2 Calcination parameters effect on highest peak grain size
### General Linear Model: Highest Peak versus Calcination, Heating Rate, ...

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#### Analysis of Variance for Highest Peak Grain Size, using Adjusted SS for Tests

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\[ S = 72.9028 \quad \text{R-Sq} = 68.17\% \quad \text{R-Sq(adj)} = 56.59\% \]

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#### Least Squares Means for Highest Peak Grain Size

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<td>25.78</td>
</tr>
<tr>
<td>4</td>
<td>297.3</td>
<td>25.78</td>
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#### Grouping Information Using Tukey Method and 95.0% Confidence

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<th>Mean</th>
<th>Grouping</th>
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<td>A</td>
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<tr>
<td>1100</td>
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Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

**Heating**

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<th>Grouping</th>
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</thead>
<tbody>
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<td>8</td>
<td>334.5</td>
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<tr>
<td>7</td>
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<td>311.8</td>
<td>A</td>
</tr>
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</table>

Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

**Soaking**

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<th>Grouping</th>
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<tbody>
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<td>6</td>
<td>8</td>
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<tr>
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Means that do not share a letter are significantly different.

Grouping Information Using Tukey Method and 95.0% Confidence

**Cooling**

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</tr>
<tr>
<td>4</td>
<td>8</td>
<td>297.3</td>
<td>A</td>
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</tbody>
</table>

Means that do not share a letter are significantly different.

**Residual Plots for Highest Peak Grain Size**
APPENDIX D

GRAIN SIZE CALCULATION

In this appendix, Scherrer equation is presented which used in order to calculate the grain size employing the XRD data.

\[ \tau = \frac{K \lambda}{\beta \cos \theta} \]  

Equation D.1

Where \( \tau \) is crystal (grain) size of alumina nanofibers (nm), \( \lambda \) is the wavelength of X-ray beam (nm), \( \beta \) is full width at half maximum FWHM for the main alumina peaks (radians), \( \theta \) is Bragg angle, \( K \) is a crystal shape constant from 0.9~1.

For grain size calculation in this study, these assumption were made, \( K=0.94 \) and instrumental line broadening factor is already subtracted by the manufacturer’s software.