SOL-GEL PROCESSING OF CONTINUOUS MULLITE FIBERS

By

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DEDICATION

I dedicate this dissertation to my parents. Their love, support and wisdom have been and always will be a constant source of strength and inspiration.
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There is an increasing demand for materials that can withstand high temperatures without a deterioration in mechanical properties. Incorporation of fibers in metal or ceramic matrices can produce components that can maintain their integrity at high operating temperatures. Mullite fibers are a good candidate for such applications. Continuous fibers are a better choice for load bearing applications, as they provide higher strength than short fibers. Achieving continuous spinnability and producing glass free mullite fibers presented a challenge to researchers in the past.

The goal of this study was to determine the parameters necessary to produce a glass-free fibers with the ability to achieve continuous spinnability. To accomplish this goal, several experiments were conducted. The rheological conditions for continuous spinnability and the different factors that control the rheological behavior of the sol were determined. The optimum value for chelating agent/alumina
precursor molar ratio was determined. The effect of chelating agent on mullite transformation was investigated. Also, the role of aging and aging temperature in the processing of mullite fibers was determined. The effect of the chelating agent on the densification behavior and the porosity of the final product was determined. The grain growth of mullite fibers was also studied.

It was shown that fiber aging was crucial in achieving good quality fibers. It was also shown that mullite transformation was enhanced with increasing aging time, and it was shown that fiber grain size decreases with the increase of aging temperature. Also, shorter aging times were required at higher temperatures. Crystalline phase determination showed mullite was the only phase present. It was shown that no detectable amounts of intergranular glass phase were observed in the fibers processed in this study. In contrast, commercial fibers showed the presence of large intergranular glass phase. It was shown that the activation energy for grain growth was high. Grain growth was not significant for temperatures up to 1200°C for long annealing times (12 hours) or up to 1400°C for short annealing times (1 hour).
CHAPTER I
INTRODUCTION

The demand for materials that sustain high temperatures (in excess of 1200 °C) is increasing progressively. Many high-tech industries, particularly the aerospace industry, have numerous applications for such materials. Ceramic fiber composites have a major role in the manufacturing of components for high-strength, high-temperature applications. A candidate material for ceramic fibers is mullite. Mullite (3Al₂O₃·2SiO₂) is a crystalline ceramic that has an orthorhombic structure and with an alumina/silica molar ratio of 3/2. Mullite has excellent creep resistance and strength retention at high temperatures [Aks91]. In addition, mullite has good thermal shock resistance and chemical stability.

Sol-gel processing has been used in the production of mullite fibers due to the unique properties made available by using this technique. The sol-gel method permits precise control of properties and microstructure before and after heat treatment. By using this technique, fiber spinning can be accomplished at room temperature. Also, sol-gel processing provides better purity and control over homogeneity when compared to more conventional techniques.

The emphasis of this study was the production of continuous fibers. Continuous fibers are of special interest in load bearing structural composites.
Continuous fiber composites are generally stronger than short fiber composites when a load is applied in the direction parallel to fiber orientation.

The two primary challenges facing researchers in this area were achieving continuous spinnability and producing fibers without a glass phase. Researchers have been able to produce fully crystalline mullite fibers but were unable to achieve continuous spinnability [Ven90]. Commercially available mullite fibers are currently prepared with boria [Sow88]. This results in the presence of a glass phase. A glass phase can cause a catastrophic deterioration in the mechanical properties of the fiber at high temperatures.

In this study, several experiments were conducted to determine the factors that have an effect on sol-gel processing of mullite fibers. The role of pre-spinning hydrolysis on the properties of fibers in the green state was studied. In addition, the effect of pre-spinning hydrolysis on the final microstructure of fibers was investigated. The conditions for continuous spinnability for mullite sol was also investigated. The various factors that contribute to achieving continuous spinnability and the factors that determine the rheological behavior of the mullite sol were determined. The effect of chelating agents on organics removal, mullite transformation, and fiber microstructure was studied. The effect of varying the chelating agent/alumina precursor molar ratio on the sol rheology, sol stability, and fiber microstructure was also investigated.

Aging of mullite green fibers in humid air at different temperatures was studied. The effect of aging on the properties and the microstructure of fibers was
The role of aging on mullite formation was also investigated. In addition, the role of aging temperature on fiber microstructure and properties, and the advantages of high temperature aging were determined. Also, the densification behavior of aged fibers was determined.

The presence of an intergranular glass phase was investigated. A comparison between the commercial fibers and the fibers processed in this study was carried out to ascertain if there were differences in the intergranular glass phase content. The final study was on grain growth of mullite fibers. Grain growth as a function of time and temperature was determined.

**Statement of Problem**

To investigate the critical factors and their underlying mechanisms in the fabrication of single phase mullite fibers by a method of continuous spinning.

**Objectives**

The objectives of this study were as follows:

1. Determine the conditions for continuous spinnability for mullite sol and study the different factors that affect the rheology of the sol.
2. Determine the effect of pre-spinning hydrolysis on fiber properties and microstructure.
3. Study the effect of chelating agent on organics removal, mullite formation, and fiber microstructure.
4- Determine the optimum chelating agent/alumina precursor molar ratio.

5- Determine the effect of aging on mullite transformation. In addition, study the effect of aging on fiber microstructure and properties.

6- Investigate the effect of aging temperature on the properties and microstructure of fibers.

7- Determine the densification behavior of fibers.

8- Determine the factors critical to single phase formation and retention after spinning.

9- Determine if the fibers produced contain an intergranular glass phase and compare the results to those for commercial fibers.

10- Study grain growth as a function of time and temperature.
CHAPTER 2
LITERATURE SURVEY

Mullite Processing Via Sol-Gel

This study addresses the fabrication of mullite fibers using a sol-gel-based approach. Sol-gel processing was selected because of its unique characteristics which include excellent homogeneity, high purity, and low preparation temperatures [Mac82]. Large shrinkage, residual carbon (from sol components), and expensive raw materials are the main disadvantages. Mullite can be prepared using sol-gel from either single phase or diphasic gels.

Diphasic Gels

Gels that contain two different phases are often called diphasic gels. Mullite formation in diphasic gels exhibits a diffusion controlled growth mechanism by which the diffusion of the Al₂O₃ and SiO₂ components across the reaction layer controls the reaction rate [Li90a]. Aluminum species near the alumina particle surfaces diffuse along the mullite/alumina interface and react with the nearest available silicon species [Wei88b]. Silicon species may diffuse in the opposite direction toward aluminum species. Mullite crystals form on the interface and grow toward the diphasic region. The growth rate of the interface is limited by a short-range transportation rate and the amount of the reactants. The mullite formation...
temperature for this type of gels is high, about 1250 °C, compared to other approaches.

Diphasic gels were prepared by Prochazka and Klug [Pro83]. The aluminum precursor was aluminum isopropoxide, and the silicon precursor was ethylmetasilicate. Both precursors were dissolved separately in cyclohexane. Equivalent volumes of the solutions corresponding to the desired alumina-silica composition were measured and mixed in a blender. Fifty-five grams of water per mol of each alkoxide was mixed with twice its volume of t-butylalcohol and added to the cyclohexane solution. The resulting sol was agitated then aged for 24 hr. The solvent was evaporated at room temperature, and the residue was dried at 120 °C. The resulting powder was calcined at 750 °C.

The amount of residual carbon was observed to increase with increasing heating rate. The aluminosilicates prepared by this method were amorphous up to 950 °C where the formation of a crystalline phase was observed. The crystalline phase was determined to be either γ-alumina or an Al-Si spinel. Mullite formation was detected at 1200 °C.

Pask, Yoldas and co-workers used metal alkoxides to make diphasic mullite gels [Pas87]. The alumina sol was made by hydrolysis and polycondensation of Al(OC₄H₉)₃ (aluminum-sec-butoxide) followed by a peptization step. The resultant sol was a clear aqueous sol which contained AlO(OH) colloidal particles. These particles were reacted with Si(OC₂H₅)₄ (tetraethyl orthosilicate) in a water-ethanol medium forming a chemically-bonded silica layer around and in between the
particles. Gelation occurred after a short period of time yielding transparent granules about 5 nm in size upon drying at 500°C for 30 min.

Differential thermal analysis (DTA) results showed a shallow endothermic peak between 400°C - 1000°C which was caused by the gradual loss of hydroxyl groups. Broad diffraction peaks for spinel were observed using x-ray diffraction analysis (XRD) in a sample heated to 1000°C. A mullite formation exothermic differential thermal analysis (DTA) peak was observed at 1267°C. Upon heating to 1700°C, the grains had a prismatic shape and a glass phase was present, predominantly at the 3-grain junctions.

Mullite was also prepared from a diphasic gel by Ismail et al. [Ism87]. A boehmite sol was prepared using γ-\(\text{Al}_2\text{O}_3\), while the silica sol was prepared using colloidal \(\text{SiO}_2\). The mixture of the two sols was gelled at a pH of 3. The gelation rate was controlled by the addition of hydrofluoric acid (HF). Large additions of HF resulted in faster gelation [Ism90]. The dried gel was ground in an alumina-lined ball mill and calcined at 1400°C. The mullite formed was attrition milled using zirconia media. The DTA showed the crystallization of mullite at temperatures above 1290°C. The green compacts of mullite powder were isostatically pressed at a pressure of 200 MPa and sintered at a temperature of 1650°C. Transmission electron microscopy (TEM) micrographs for sintered bodies showed traces of a glassy phase but no glassy pockets at triple points.

Aluminosilicate gels with \(\text{Al}_2\text{O}_3/\text{SiO}_2\) composition ratio = 1, 1.5, and 2 were prepared by Wei and Halloran [Wei88a]. The precursors used were colloidal
pseudo-boehmite (AlOOH) and tetraethyl orthosilicate (TEOS). The TEOS, ethanol, and water with 0.018N HCl were mixed together in a ratio of 50 wt% : 30 wt% : 20 wt%. After the mixture was aged in a 50 °C bath for 3 hr, the colloidal pseudo-boehmite sol was introduced, and mixed for 30 min. This mixture was then aged in a 50 °C water bath. After 24 hr, the mixture formed a translucent white gel.

It was observed that the two discrete phases, pseudo-boehmite, and amorphous silica, transformed independently up to 1200 °C, then reacted to form mullite directly without the formation of a precursor (amorphous or spinel phase). Mullite was formed via nucleation and growth of single crystal grains by a process that was either interface or short range diffusion controlled [Wei88b]. It was found that the growth rate was time-dependent. The origin of the time-dependent character of the growth rate was not explained. It was also shown that Al2O3 particles that were larger than 30 nm did not react completely with SiO2, particularly at low temperatures. These alumina particles appeared to be entrapped in the mullite phase. Although the overall composition was stoichiometric, the transformation product was a silica-rich mullite phase with residual alumina particles.

Sundaresan and Aksay attempted to explain the time dependence of the growth rate found in the Wei and Halloran results [Sun91]. They argued that the growth rate of the mullite grains was controlled by the dissolution of alumina particles into the amorphous phase. When considering entrapment of alumina particles by the growing mullite grains, the number of transitional alumina grains
remaining in the diphasic region decreases slowly with time. Consequently, the total rate of alumina dissolution into the amorphous phase was not constant, but decreased slowly with time. This resulted in the time-dependent growth rate for mullite grains.

Mullite diphasic gels were also prepared by Sonuparlak [Son88]. Two processing methods were investigated. In both methods, the mullite sol was prepared by dropwise additions of TEOS into an aluminum monohydroxide (AlOOH) sol. The aluminum monohydroxide sol was prepared by dispersing boehmite powder in an aqueous solution using 0.07 mol HCl per mol of aluminum monohydroxide. In the first method, the sol mixture was stirred in the acidic condition until gelation was completed. In the second method, gelation was performed by the addition of a few drops of 0.1 M NH₄OH into the acidic aluminum monohydroxide - TEOS sol. Soft agglomerates as large as 25 to 30 μm were formed spontaneously.

Differential thermal analysis x-ray diffraction results showed that mullite formation occurs at a relatively high temperature (1280°C). The XRD analysis showed the presence of an amorphous phase and spinel phase below the 1280°C exotherm. The high mullite formation temperature enabled viscous sintering to occur at temperatures as high as 1250°C. As a result, high densification rates were achieved. Upon heating at 1250°C, 99% of theoretical density was achieved in the first method, while a uniaxial pressure of 441 MPa was needed to achieve the same density in the second method. The XRD pattern for samples from the first method showed the presence of a glass phase and a spinel phase together with mullite after
heating at 1300°C. No glass phase was detected in samples treated similarly from the second method.

A technique similar to the one developed by Sonuparlak was used by Li and Thompson [Li90a]. The diphasic gel was prepared by dispersing boehmite powder in a dilute HNO₃ solution. A suitable amount of TEOS together with an equal volume of ethanol were mixed with the boehmite dispersion to give the stoichiometric ratio of alumina/silica mullite. Gelation was accomplished in 12 hr inside a 60°C oven. Dynamic x-ray diffraction (DXRD) results showed that the silica phase in the diphasic gel remained amorphous throughout the heating process until it reacts with alumina to form mullite at 1250°C. The boehmite gel experienced the following transformation.

\[ \gamma\text{-AlOOH} \rightarrow \gamma\text{-Al}_2\text{O}_3 \rightarrow \delta\text{-Al}_2\text{O}_3 \rightarrow \Theta\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3 \]

Li and Thompson showed that mullite formation followed an Avrami type, diffusion-controlled growth mechanism with the nucleation process was complete before substantial growth took place. Samples fired at 1300°C showed rod-like crystals.

Seeded diphasic mullite gels were studied by Mroz and Laughner [Mro89]. The mullite seeds were prepared by calcining mullite gel at 1600°C for 2 hr. The mullite gel was prepared by peptizing pseudoboehmite and colloidal silica and gelling the sol using nitric acid. A 50 wt% acidic dispersion of calcined mullite powder was ball-milled and centrifuged to yield an agglomerate-free suspension of fine seed particles.
Seeded sols were produced by introducing different amounts of the seed suspension to the mullite sol before peptization was carried out. The sol was then gelled and dried at 90°C. The microstructure of the unseeded gel was compared to the microstructure of the seeded gel after firing at 1700°C. Most grains were acicular in the case of unseeded gel, while gels seeded with 4 wt% mullite seed showed equiaxed grains. No evidence of intergranular glass phase was found in the case of seeded gels.

A mullite seed content of 0.125 wt% gave different results. Seeds grew into acicular grains having aspect ratios as high as 12:1. The rest of the sample was a matrix of fine, nearly equiaxed grains with some intergranular porosity. The large grains resembled whiskers in a fine-grained matrix. It was not confirmed if the presence of the elongated fibers toughened the material.

The effect of precursor composition on mullite formation and the resulting structure was investigated by Li and Thomson [Li91b]. Diphasic gels with Al/Si atomic ratios of 6/1, 3.1/1, 3/1, 2/1, and 1/1 were used. Mullite formation was initiated at about 1300°C for all samples with only slight differences in temperatures. The mullite formation temperature was a minimum for an Al/Si ratio of 3 1/1 and increased as the Al/Si ratio of the gels increased or decreased. In the case of 6/1 gel, dissolution of alumina into the mullite solid solution was observed after the initial mullite formation. The dissolution was reversed above 1450°C with the formation of \( \theta\)-\( \text{Al}_2\text{O}_3 \) and then \( \alpha\)-\( \text{Al}_2\text{O}_3 \). A change of microstructure from equiaxed
to elongated mullite grain structures was observed within a narrow range of compositions near the Al/Si ratio of 3/1.

Li and Thomson developed another process to produce diphasic gels. The silica sol was prepared by hydrolyzing TEOS in water and a nitric acid solution with a pH of 2 [Li91a]. After hydrolysis was completed, aluminum nitrate was introduced. The solution was gelled in a sealed container at 60°C for 1 day. Mullite formation of this gel was detected above 1200°C. A 980°C peak observed in the DTA curve was attributed to the formation of Al Si spinel and/or mullite.

Single Phase Gels

Gels that have molecular scale mixing of the components are referred to as single phase gels. For mullite, single phase gels have molecular-scale mixing of alumina and silica through either coprecipitation of aluminum and silicon salts or hydrolysis of metal alkoxides [Li90a]. Mullite formation exhibits a nucleation-controlled mechanism. The mullite transformation temperature for single phase gels is below 1000°C.

One of the major obstacles in making homogeneous single phase (polymeric) mullite gel is the significant difference in the hydrolysis and self-condensation rates of aluminum and silicon alkoxides. Silicon alkoxide hydrolyzes at a much slower rate than aluminum alkoxide [Yol88]. Inhomogeneity arises from the formation of macromolecules that do not have mullite stoichiometry.
A process was developed by Yoldas and Partlow to circumvent the hydrolysis rate difference problem [Yo88]. The silicon alkoxide was partially hydrolyzed while the aluminum alkoxide was not hydrolyzed. Upon the addition of the aluminum alkoxide to the silica sol, a white precipitate formed, but this condensate dissolved forming a clear solution within hours at 60°C. The final hydrolysis was carried out either in the liquid state by adding water, which resulted in the formation of a gel or fine powder, or in the solid state after the sol was used for coatings or the deposition of thin films.

Mullite formation was observed to occur at 980°C in DTA measurements. Also, a large spontaneous densification occurred at 960°C. The low mullite formation temperature was attributed to the intimacy and homogeneity of alumina-silica bonding. The microstructure consisted of equigranular mullite grains about 2-4 microns in size, with no evidence of a secondary amorphous phase [Pas87].

Spark and Tucker developed a process to produce spinnable alumina-silica sols [Spa88]. The process consisted of two hydrolysis steps. In the first hydrolysis step, aluminum isopropoxide acetoacetic acid chelate was mixed with isopropyl alcohol, water and hydrochloric acid in a ratio of 1:3:1:0.01. To prevent the formation of precipitates, half of the alcohol was used to dilute the metal alkoxide, while the other half was mixed with the water and acid which was then slowly added to the alkoxide mixture. Tetraethoxysilane, isopropyl alcohol, water and hydrochloric acid in the molar ratio of 1:3:1:0.01 were added dropwise to the alumina sol in the second hydrolysis step.
After allowing the sol to gel in air, spinnability was achieved. The gel was fired at 1375°C after being dried at 130°C. Analysis via XRD showed that mullite was the only phase formed. The microstructure of the fired material and the presence of glass phase were not discussed in this study.

Li and Thomson also developed a process to produce single phase mullite gels [Li90a]. The aluminum precursor, Al(NO$_3$)$_3$·9H$_2$O, was dissolved in absolute ethanol. The solution was mixed with tetraethyl orthosilicate. The mixture was then gelled in a 60°C oven over a period of two weeks.

Dynamic X-ray diffraction (DXRD) results showed that the gel was completely amorphous up to approximately 1000°C, when mullite began to form. Mullite was the only crystalline phase detected, and the formation of a cubic spinel phase was not observed. Fourier transform infrared FT-IR analysis showed that at 500°C the gel has a mixture of amorphous silica and alumina, and at 900°C Al-O-Si bond formation was observed. Transmission electron microscopy (TEM) and BET results for powders heated at 950°C showed an average particle size of about 19 nm [Li90b].

Huling and Messing did a study on single phase gels derived from an aluminum nitrate nonahydrate-TEOS molecular sol [Hul89 and Hul92]. Two types of gel were produced: fresh gel and aged gel. The fresh gel was prepared by rapid dropwise drying of the molecular sol in a beaker heated to 120°C. The aged gel was prepared from the fresh gel by exposing it to a humid environment at 80°C.

Differential thermal analysis of the fresh gel showed an exothermic peak at 980°C [Hul92]. X-ray diffraction analysis for samples heated just above 980°C
showed nearly complete crystallization to the alumina rich tetragonal-mullite (2Al$_2$O$_3$·3SiO$_2$). Analysis using TEM showed the presence of a silica-rich amorphous phase enveloped by tetragonal-mullite.

**Differential thermal analysis** of the aged gel showed a prominent exothermic peak at 980°C. In addition, a broad weak peak was observed at 847°C. X-ray diffraction analysis of samples heated just below and just above 847°C showed that the DTA peak at that temperature corresponded to crystallization of 10 wt% orthorhombic mullite (3Al$_2$O$_3$·2SiO$_2$). It was observed that by increasing the heating rate at which the DTA was performed, the 847°C peak shifted to lower temperatures. Further, while the intensity of the 847°C peak increased with higher heating rates, the intensity of the 980°C peak decreased.

**Single phase gels** were also prepared by Schneider and co-workers [Sch92]. Aluminum butylate (72 wt%) was mixed with TEOS (28 wt%) in the presence of isopropanol as a solvent. Water was added droppwise to the mixture, and a white gel was produced. Differential thermal analysis showed a sharp exotherm of high intensity at 988°C, in addition to a weak exotherm at 1253°C. X-ray diffraction analysis for samples heated at 1100°C showed the presence of γ-Al$_2$O$_3$, mullite, and small amounts of cristobalite. Mullite was the only phase observed for samples subsequently heated to 1400°C and 1650°C.

The use of chelating agents in the processing of single phase mullite gels was studied by Heinrich and co-workers [Hei94]. Their system consisted of aluminum-sec-butylate, β-diketone, triethylorthosilicate, isopropanol and hydrochloric acid.
Acetylaceton (AcAc), methylacetoacetate (MAA), and ethylacetoacetate (EAA) were used as the \( \beta \)-diketone. The molar ratio, \( R \), of \( \beta \)-diketone to aluminum-sec-butylate was varied from 0.3 to 2.0. A solution of \( \beta \)-diketone and isopropanol was added dropwise to the aluminum-sec-butylate solution. A solution of TEOS and isopropanol was added thereafter. Hydrolysis was carried out by adding an aqueous HCl solution.

It was shown that particle size was a function of the amount of \( \beta \)-diketone used. The particle radius measured was a function of the number of condensation sites per aluminum atom which were blocked by \( \beta \)-diketones after hydrolysis. The more condensation sites blocked the smaller the particles.

The gelation time was found to be dependent on the amount and type of chelating agent. The gelation time increased as the amount of \( \beta \)-diketone increased and the larger the molecular size of the chelating agent. Nuclear magnetic resonance (NMR) results showed the presence of Al-O-Si bonds during all stages of gelation. The MAS-NMR spectra showed that it was possible to obtain homogeneous gels on a molecular scale using chelated aluminum alkoxides.

**Continuous Mullite Fibers Using Sol-Gel Processing**

The main problem associated with sol-gel processing is the difficulty in producing large shapes because of the cracking introduced by drying stresses associated with capillary forces, and shrinkage stresses during firing [LaC88]. These effects are minimized with fibers because the diffusion distances are small and
stresses can be relieved by local bending of the fiber. These factors are effective after forming the fibers from the sol, however, formation of fibers from the sol is a difficult task. Production of good quality continuous mullite fibers requires achieving certain rheological conditions that are essential for continuous spinnability.

Prior to the use of sol-gel processing, ceramic fibers were produced from molten oxides [Sow88]. The liquid phase required specific viscoelastic properties to undergo spinning of fibers, as a result, compositions were limited to certain oxides or mixture of oxides. Consequently, high percentages of SiO₂ were often needed in the fibers, and this limited their use at high temperatures.

Sol-gel processes can be used to produce fibers in the sol stage. This extends the range of compositions of ceramic fibers to include a variety of compositions that were not possible using the melt method. As a result, fibers that possess good creep resistance, chemical durability, and high tensile strength can be produced. Another advantage of sol-gel processing of fiber over spinning of molten ceramics is the lower processing temperature. Fiber spinning using the sol-gel method is usually carried out at room temperature which is more economical and technically more controllable than high temperature spinning.

Horikiri and co-workers investigated the processing of continuous mullite fibers from polymeric sols [Hor78]. The first step in the process was the production of polyaluminoxane. The polyaluminoxane was prepared by partially hydrolyzing and polymerizing an aluminum alkoxide. Triethylaluminum was polymerized in ether with an equimolar amount of water which was added dropwise at 20-80°C. The
polymerization process was monitored by measuring the amount of C₂H₆ produced. The degree of polymerization was controlled by changing the amount of water added. A polymeric silica sol was then mixed with the polyaluminoxane to form mullite sol.

The amount of silicon containing compound to be mixed into the solution of the polyaluminoxane was found to affect the spinnability of the sol. When a silicon containing compound with no spinnability was added in large amounts to the polyaluminoxane, the spinnability of the resulting solution was poor.

The mullite sol was spun through 30-100 micron holes. The atmosphere in which the spinning was carried out was controlled. Solvents contained in the fiber were removed during or after the spinning step. The spun fibers were hydrolyzed by moisture contained in the air and then were fired for the purpose of stabilization and sintering. Fibers produced at temperatures below 1250°C had good strength. On the other hand, fibers fired in the 1250°C-1500°C range were brittle and had low strength due to an exaggerated growth of mullite grains. As a result, the use of these fibers at high temperatures was limited.

Karst and Sowman investigated the processing of continuous mullite fibers from diphasic gels [Kar77]. The alumina sol was prepared by adding aluminum isopropylate to a mixture of formic acid and deionized water. Aluminum formoacetate was added to this mixture with subsequent heating to 60°C until the solution was clear. Following that, aqueous colloidal alumina, aqueous colloidal silica, and lactic acid were added to the mixture. The resulting sol was then concentrated under a vacuum. The sol was extruded through a spinneret after the
spinning viscosity was achieved. The extruded fibers were drawn vertically downward through the center of a dryer stack in a countercurrent stream of dry air introduced into the bottom end of the stack. The fibers were then fired at 200°C to remove physical water and other volatiles. Following initial firing, the fibers were heated to 870°C to remove residual volatiles and induce crystallization. After heating to 950°C, a toluene solution of 0.5 wt% butadiene-isoprene block copolymer rubber and 2.5 wt% mineral oil was applied to the fibers before winding them on a drum.

Samples fired at 1600°C had a tensile strength of about 0.86 GPa. X-ray diffraction analysis showed that fibers fired at 1500°C for less than 10 sec, showed a mullite phase with traces of alumina. After periods of time longer than 15 sec at 1500°C, mullite was the only phase detected.

Processing of continuous mullite fibers was also investigated by Tucker and co-workers [Tuc90]. The silica sol was prepared by hydrolyzing TEOS. The hydrolysis step was carried out in the presence of distilled water, hydrochloric acid, and isopropyl alcohol. The mixture was allowed to react at 40°C for 90 min. Hydrolysis of the aluminum mixture followed. The aluminum precursor was aluminum diisopropoxide acetoacetic ester chelate (ADC). The chelate provides a greater possibility for the formation of the linear polymers necessary for production of a spinnable fiber, as it allows two reaction sites for the ADC. The alumina sol components, ADC, hydrochloric acid, water, and isopropyl alcohol, were mixed slowly to form a homogeneous solution. The alumina and silica sols were then mixed at
40°C in a nitrogen atmosphere. Spinnable gels were attained from the sol in time periods ranging from 8 hours to 3 days.

In the spinning process, the fibers, after being extruded, were passed through an air gap to a bath containing deionized water and polyethylene imide. The pH of the bath was adjusted by adding sodium hydroxide. The bath was used to coagulate the fibers and to improve the structural integrity. Fibers with a large diameter, 110 micron, were spun. After firing at 1300°C, pure mullite fibers were attained. However, the fibers exhibited porosity and microcracks, and were very brittle, as a result.

The use of diphasic gels to produce mullite fibers was studied using two methods by Venkatachari et al. [Ven90]. The two methods differed in the choice of precursor materials used as the source of alumina and silica. Aluminum hydroxychloride hydrate and LUDOX AM colloidal silica were the starting materials for method I. Aluminum formoacetate and LUDOX C1 colloidal silica were the starting materials for method II. Another processing difference was that in method I fibers were drawn by hand, while in method II, fibers were prepared by centrifugal spinning.

Gas adsorption measurement indicated that the average pore size for method I fibers fired at 1000°C was about 4 nm. An average pore size of 2.2 nm was observed for method II fibers fired at 800°C. The finer pore structure of method II resulted in a more rapid densification. It was believed that densification of fibers occurred by a viscous flow mechanism in both methods.
X-ray diffraction analysis showed that mullite transformation occurred above 1200°C for both methods. Fibers from both methods fired at 1500°C showed grain sizes below 1 μm. Examination of grain boundaries of method I fibers via TEM did not show the presence of a glassy phase, no similar analysis was done on method II fibers. However, neither method could be used to produce solutions with the necessary properties for continuous fiber spinning.

Richards and co-workers investigated the effect of additives on microstructure and crystallization of mullite [Ric91]. The alumina sol was made by dissolving aluminum powder in a mixture of carboxylic acids. A commercial silica sol, NALCO 1034A, was added to the alumina sol. The additives investigated were B₂O₃, P₂O₅, and Cr₂O₃. They were added as boric acid, phosphoric acid, and chromium acetate, respectively. Lactic acid was added to inhibit gelation.

The sol was concentrated to a viscosity of 100 to 150 N.S/m², and then pressure extruded through a spinneret. The fibers were drawn after extrusion through a drying chamber to form continuous filaments. Differential thermal analysis was used to determine transformation temperature. For the unmodified mullite fibers, an exothermic reaction with a peak at 870°C was confirmed by XRD to correspond to the formation of a spinel phase. A second exotherm observed at 1295°C was confirmed to correspond to mullite formation.

Addition of low temperature glass formers such as B₂O₃ and P₂O₅ produced sharper exotherms and raised the spinel formation temperature to 911°C and 904°C, respectively. On the other hand, the addition of B₂O₃ and P₂O₅ lowered the mullite
formation temperature to 1222°C and 1283°C, respectively. Addition of Cr₂O₃ did not appear to have an effect on spinel and mullite formation temperatures.

Transmission electron microscopy micrographs of the unmodified mullite fibers heated to 1200°C and held for 1 hr showed grain size of 6000 Å, intergranular pore size of 250 Å, and intragranular pore size of 800 Å. Fibers that contained B₂O₃ had the smallest grains and the most uniform grain-size distribution. Grain sizes of 800-1000 Å, and pore size of 200 Å were observed for fibers containing B₂O₃. In addition, B₂O₃ fibers were denser than those of any other composition studied. On the other hand, addition of Cr₂O₃ or (P₂O₅ + Cr₂O₃) resulted in grain size larger than that of the unmodified mullite fibers.

Kim and co-workers studied formation of mullite fibers from polymeric sols [Kim93]. The alumina sol was prepared by mixing aluminum-sec-butoxide with iso-propanol, and acetylacetone. The mixture was then hydrolyzed and polymerized by adding water and hydrochloric acid. The silica sol was prepared by mixing TEOS, iso-propanol, water, and hydrochloric acid. After mixing the two sols, a condensation step was carried out inside an 80°C oven for 96 hr. The condensation time was reduced to 24 hr by using a rotary vacuum evaporator and a vacuum drying oven. Extrusion of fibers was accomplished by drawing fibers through a 200-600 μm hole spinneret.

Viscosity measurements of the mullite sol revealed that for the acetylacetone to aluminum-sec-butoxide molar ratio (R) of 0.5, the viscosity increased dramatically after 80 hr. Gradual increases in the viscosity were observed for R values of 1.5 and
0.1. The rheological behavior of the sol as a function of time was determined. Shear thickening behavior was observed after 48 hr, thixotropic behavior after 96 hr, and a pseudoplastic or shear-thinning flow behavior after 168 hr.

Differential thermal analysis results indicated that mullite formation occurred at 1080°C. X-ray diffraction analysis for samples heated to 1100°C showed the presence of a mullite phase. Micrographs taken by SEM showed that the fibers had a needle-like microstructure.

**Commercially Available Mullite Fibers**

Nextel 440 and 480 are among the commercially available mullite fibers. Nextel 440 fibers contain 70% Al₂O₃ + 2% B₂O₃ + 28% SiO₂ [Sow85]. They have a tensile strength of 1.72 GPa and modulus of elasticity of 207-241 GPa. Fibers heat treated at temperatures up to 1400°C retained their strength. Fibers heat treated beyond 1400°C showed a significant degradation of properties. Nextel 440 fibers contain very small crystallite in the range of 20 to 60 nm in size.

Nextel 480 fibers have a 3 to 2 molar ratio of alumina to silica [Job87]. The average grain size was shown to be 250 nm. The fibers retained about 75% of their strength through a heat treatment temperature of 1000°C, and 60% strength retention after 1400°C (these fibers were tested at room temperature). High temperature strength measurements showed that the strength remained almost constant up to about 800°C then fell to about 80% of its initial level at 1100°C. The fiber strength at 1250°C was about 0.5 GPa. The measurement of the elastic...
modulus at high temperatures showed a significant drop above 900°C. At 1350°C, the modulus was approximately 30% of its initial value. These fibers show a distinct intergranular glass phase.

Fine alumina-silica fibers were developed by Sumitomo chemicals. The composition of the fibers is 85 wt% alumina and 15 wt% silica [Les90]. The microstructure consists of very small \( \gamma \)-\( \text{Al}_2\text{O}_3 \) crystallites homogeneously mixed with an amorphous silica phase. The fibers were processed by polymerization of metal alkoxides. The fibers were heated to 760°C to remove organics. The final step was heating the fibers to 970°C to complete the formation of \( \gamma \)-\( \text{Al}_2\text{O}_3 \).

High temperature strength and elastic modulus measurements showed a drop in the strength and the modulus above 800°C. The elastic modulus at 1150°C was about 40% of its original value. Measurements of the creep rate indicated that the fiber crept at temperatures above 800°C, and that the creep rate increased rapidly with temperature. The degradation in the mechanical properties was attributed to the softening of the amorphous silica matrix in which the alumina crystallites were embedded. Transformation to mullite was noticed for fibers heated above 1127°C.
CHAPTER 3
SOL-GEL PROCESSING

Introduction

The term sol-gel is used to describe a variety of chemical synthesis of inorganic materials. The process owes its name to the rapid viscosity increase that occurs after sol fabrication or during aging [Bal93]. The sol is a system in which separate chemical species (solute and solvent) are metastable. If the solvation or suspension conditions are changed slightly, destabilization can occur [Jon88]. The destabilization of the sol can result in precipitation of the sol species as aggregated or unaggregated particles in the formation of a homogeneous gel.

The gel consists of a continuous solid network enclosing a continuous liquid phase [Bri90]. The gel has an elastic character which is introduced by the continuous solid network. The sol-gel technique involves physical and chemical processes associated with hydrolysis, polycondensation, drying, dehydration, and densification. The advantages associated with sol-gel processing are [Bal93]

- very high purity,
- better homogeneity compared to powder mixing technology,
- low processing temperature compared to traditional ceramic processing techniques,
- uniform phase distribution in multicomponent systems,
- easy preparation of coatings and thin films,
- better size control in powder synthesis, and
- the ability to produce new crystalline and non-crystalline solids

Although sol-gel processing has many advantages, it also has some disadvantages, such as [Mac82]

- the high cost of raw materials,
- large shrinkage during processing,
- residual porosity,
- residual hydroxyl groups and carbon,
- health hazards associated with the organic components, and
- long processing times.

Sols can be divided into two major categories, colloidal (particulate) sols and macromolecular (polymeric) sols. A colloidal sol is a solution that contains dense oxide particles [Jon89 and Bri90]. A macromolecular sol is a solution of macromolecules that are obtained by the hydrolysis and polycondensation of metal alkoxides.

Collids are solid particles with diameter of 1 nm to 100 nm [Wei38]. A colloidal system is a dispersed or heterogeneous system consisting of at least two phases, one of which is a dispersed phase and is uniformly distributed within a continuous phase (the dispersion medium) [Wei39].

A polymer or a macromolecule is a large molecule formed from monomers that are capable of forming at least two bonds [Bri90]. Metal alkoxides $M(OR)_x$ are derivatives of alcohols ($ROH$) in which the hydrogen of the hydroxyl group has been
replaced by a metal (M). Metal alkoxides can also be considered as derivatives of metal hydroxides, $M(OH)_x$ [Bra78]. Colloid stability is an important issue in the processing of colloidal sols. An understanding of the different forces acting on the colloids is essential when studying the stability of colloidal sols.

**Stability of Colloidal Sol**

The stability of colloidal sols is a function of a combination of factors. Those factors are presented in the following sections.

**Surface Energy**

From the first and the second law of thermodynamics, for systems with a plane interface separating the bulk phases [DeH93]

$$n_i dE = T dS - P dV + \gamma dA + \sum \mu_i d n_i$$

where

$E$ = internal energy,
$T$ = temperature, $S$ = entropy,
$P$ = pressure, $V$ = volume,
$\gamma$ = surface tension, $A$ = surface area,
$\mu_i$ = chemical potential of element $i$,
and $n_i$ = number of moles of element $i$. 
Introducing the Gibbs free energy $G$, where $G$ is

$$G = U + PV - TS$$ \hspace{1cm} 3.2$$

The derivative of the Gibbs free energy, $dG$, can be calculated as

$$dG = -SdT + VdP + \gamma dA + \sum \mu_i \, dm_i$$ \hspace{1cm} 3.3

The surface tension of a solid can be defined by the reversible work done in creating a new surface or by adding or removing atoms to or from the surface [Kn76]. The surface tension relative to the free energy and the internal energy can be defined as

$$\gamma = \left( \frac{\partial E}{\partial A} \right)_{T,V} = \left( \frac{\partial G}{\partial A} \right)_{P,T}$$ \hspace{1cm} 3.4$$

Where $\partial$ represents the partial derivative, and the subscripts refer to the independent variables which have to remain constant during the increase in surface area by a unit amount.

The source of the surface free energy arises from the broken or distorted bonds of surface atoms. These atoms are only partially surrounded by neighboring solid atoms. These broken or distorted bonds result in an increase in surface energy [Kn76]

From the above discussion it can be seen that the higher the surface area, the higher the energy state of the surface particles. Since systems tend to maintain a low energy state, there is a tendency to lower the surface area.
As mentioned earlier, colloids are very small solid particles with diameters of 1 - 100 nm. Assuming that the colloids are spherical, the surface area to mass ratio is

$$\frac{SA}{M} = \frac{3}{\rho \cdot r^3}$$

Where \(SA\) is the surface area, \(M\) is the mass, \(\rho\) is the density, and \(r\) is the radius. This means that for the same mass, the surface area of two spheres is larger than the surface area of one sphere. Therefore, there is a tendency for the colloids in the solvent to collapse, or to move to one another and coalesce to reduce surface area, and as a result, reduce the surface energy [Jon89].

The process of coalescence is driven by the difference in the solubility between surfaces of different curvatures. Particle surfaces have positive radii of curvature, while neck regions (formed during coalescence) have negative radii of curvature. The solubility is related to the radius of curvature by [Bri90]

$$S = S_o \exp \left( \frac{2\gamma_{SL}V_m}{RTr} \right)$$

where:

- \(S_o\) = solubility of a flat surface of the solid phase
- \(\gamma_{SL}\) = solid-liquid interfacial energy
- \(V_m\) = molar volume of the solid
- \(R\) = gas constant
This equation shows that positive radii have high solubility while negative radii have low solubility. As a result, the material dissolves from the particle surface and re-precipitates in the neck region. This process is similar to the evaporation-condensation process which will be discussed later in this study.

Colloids in suspension exhibit Brownian motion. Brownian motion is introduced by the constant collision of liquid molecules with colloids [Bri90]. The effect of these collisions on the movement of the colloids is inversely proportional to the size of the colloid. These moving colloids collide with each other and they may stick to each other due to the strong Van der Waals attractive forces.

**Van der Waals Forces**

"Van der Waals forces are short range secondary attraction forces which originate through electrical dipoles inside or on the surface of a material." [Van64]. In an electrical dipole, the centers of negative and positive charges are displaced with respect to each other. The presence of displaced centers of charges allow the columbic forces to become functional. Electrical dipoles are either inherent or induced. Electrical dipoles are inherent in asymmetrical molecules. Dipoles can be induced by an electric field that is either applied externally or applied by a neighboring ion, molecule or atom. This means that even symmetrical structures...
develop Van der Waals interactions. Van der Waals attraction forces are relatively weak for induced dipoles. Another type of dipole is the transitory dipole.

The Van der Waals forces result from three types of interactions [Bri90 and Hie77]:

- permanent dipole with permanent dipole (Keesom forces),
- permanent dipole with induced dipole (Debye forces), and
- induced dipole with induced dipole (London forces).

The third interaction occurs only when two atoms are in close proximity. The electrons of the two atoms will redistribute so as to minimize the energy of the system, producing two dipoles and resulting in a net attraction force. The total attractive force between molecules is the sum of all three mechanisms. The potential energy of attraction two spheres, $U_A$ is [Ree88]

$$U_A = -\frac{A_0}{24h}$$

where:

- $A$ = Hamaker constant
- $a$ = particle diameter
- $h$ = separation distance

The Van der Waals attraction forces can result in aggregation upon particle contact. Repulsive forces have to be induced to prevent aggregation of colloids.
Electrostatic Repulsion

One method used to prevent or reduce aggregation is the development of electrostatic repulsion. The net force between particles in suspension is assumed to be the sum of the attractive Van der Waals forces and the electrostatic repulsion created by the induced surface charges. The repulsive barrier depends on the types of ions in the electric double layer. The electric double layer is the region adjacent to the surface of the colloid which contains the charge-determining ions (those positioned on the colloid surface) and the counterions (those positioned on the adjacent surface). The counterions act to neutralize the surface charges.

Surface charge can be induced by the following techniques [Ree88]

1. Chemical reaction with an aqueous medium. In this process, the sign of the surface charge is determined by the pH of the solution [Kru49]. For hydrous oxides, the charge-determining ions are $H^+$ and $OH^-$. The charge is created by protonating or deprotonating the MOH (metal hydroxide) bonds on the surface of the particle. The pH at which the particle is neutrally charged is called point of zero charge (PZC).

In the case of pH less than PZC, i.e., acidic conditions, the MOH group is protonated and a positive charge is acquired [Bri90]

$$M-OH + H^- \rightarrow M-OH_2^+$$  38

When the pH is greater than the PZC (basic conditions), the MOH group is deprotonated and a negative charge is acquired

$$M-OH + OH^- \rightarrow M-O^- + H_2O$$  39
The magnitude of the surface potential, $\phi_0$, depends on the value of pH relative to PZC.

2- Adsorption of specific ions: In this process, the surface develops a charge due to the preferential adsorption of particular ions from the solution [Jon89]. Ions are adsorbed on oppositely charged surfaces [Ree88]. In some cases, complete adsorption of ions can lead to neutralization of the surface charge, as shown in this reaction:

$$MO + M^+ \rightarrow MOM$$

The adsorption of multivalent ions may lead to surface charge reversal:

$$MO + M^{n+} \rightarrow MOM^{(n-1)+}$$

Where $n > 1$

3- Desorption and dissolving: This process depends on the difference in the dissolution rate of the different ion in colloid particles [Jon89]. If the colloid is composed of two ionic species, then it is likely that the anions and cations will dissolve at different rates [Jon89]. The surface will have a high concentration of the ions with the lower dissolution rate, and a low concentration of the ions with the higher dissolution rate. As a result, the charge of the lower dissolution rate ions will dominate the surface charge.
The Structure of The Electric Double Layer

The distribution of ions and polar liquid molecules is influenced by the surface charge of the colloids in solution. Columbic forces repel like-charges and attract polar liquid molecules and oppositely charged ions into a region near the surface increasing their concentration relative to the average in solution [Ree88]. The potential gradient in the double layer is not sharp, because thermal vibrations of molecules in the liquid cause the diffusion of counterions. The diffusion of counterions due to molecule thermal vibrations is more significant at high temperatures. The double layer can be divided into two regions, the Stern layer and the Gouy or diffuse double layer [Br90]. The Stern layer is the region adjacent to the charged surface that contains a tightly bound layer of counterions. The diffuse layer is the region beyond the stern layer in which the counterions and polar liquid molecules diffuse freely. The plane separating the Stern and the Gouy layer is called the Helmholtz plane.

Charged colloids move when an electric field is applied [Br90]. As they move, they carry along the adsorbed layer and part of the counterion cloud. The rest of the counterions (the more distant portion of the double layer) move in the opposite direction. The plane that separates the fluid that moves with the particle from the region that flows freely is called the slip plane or plane of shear. The potential at the shear plane is referred to as the zeta potential. The point at which the pH is equal to zero is referred to as the isoelectric point (IEP) [Br90].
The potential drops linearly through the Stern layer. A model for the potential gradient in the diffuse double layer was developed by Gouy and Chapman [Ree88]. This model is based on a uniformly charged surface, a solution with uniform dielectric constant, and point charges. Assuming that the distribution of charges in the diffuse layer follows Boltzmann's equation, the concentration of counterions in the diffuse layer, $N_j$, relative to the concentration of counterions adsorbed on the surface, $N_{i0}$, is given by the following ratio:

$$\frac{N_j}{N_{i0}} = \exp\left(-\frac{U_p}{k_B T}\right)$$  \hspace{1cm} (3.12)

where $U_p$ is the potential energy of the ion, $k_B$ is Boltzmann constant, and $T$ is the temperature.

The potential in the diffuse layer $V$, where the surface potential $V_0 \leq 100$ mV, can be defined with respect to the surface potential as [Ree88]

$$V = V_0 \exp\left(-\frac{x}{k} \right)$$  \hspace{1cm} (3.13)

where $x$ is the distance from the charged surface, and $k$ is the Debye-Hückel screening length [Bri90]. The thickness of the double layer is the distance from the charged surface to the plane where $V = V_0 / 2.718$. The thickness of the double layer is calculated from the equation [Ree88]

$$k = \frac{\varepsilon \varepsilon_0 k_B T}{F^2 \sum N_i Z_i^2}$$  \hspace{1cm} (3.14)
Where \( \varepsilon \) is the solvent dielectric constant, \( \varepsilon_0 \) is the vacuum permittivity, \( F \) is Faraday's constant, \( N_i \) is the concentration of ions of type \( i \), and \( Z_i \) is the valence of counterions of type \( i \). Equation 3.14 shows that increasing the valence or the concentration of the counterions leads to compression of the double layer. On the other hand, increasing the temperature or the solvent dielectric constant leads to an expansion of the double layer.

The interaction of two particles with identically charged double layers is described by the DLVO theory [Bri90]. This theory assumes that the net force between particles is the sum of Van der Waals attraction forces and the electrostatic repulsion forces created by the interaction of the double layers. The form of the repulsion depends on the size and shape of the particle, the distance \( h \) between their surfaces, the double layer thickness, and the dielectric constant of the solvent. For two spherical particles of diameter \( a \), and for \( ka < 1 \), the potential energy of repulsion is [Ree88]

\[
U_r = \frac{\varepsilon a^2 \varepsilon_0^2}{4(h+a)} \exp\left(-\frac{h}{k} \right) 
\]

The repulsive energy increases with increasing surface potential, solvent dielectric constant, and double layer thickness.

The total potential energy, \( U_T \), is the sum of the attractive potential energy (from Van der Waals forces) and the repulsive potential energy:

\[
U_T = U_A + U_r
\]
Therefore, from equations 3.7 and 3.15, the total potential energy is

\[ U_r = -\frac{Aa}{24h} + \frac{\varepsilon a^2 V_e^2}{4(h+a)} \exp\left(-\frac{k}{k^1}\right) \]

For the case of \( ka > 1 \), the potential energy of repulsion becomes

\[ U_k = \frac{\varepsilon a V_e^2}{4} \ln\left[1 + \exp\left(-\frac{k}{k^1}\right)\right] \]

**Polymeric Stabilization**

Coagulation can be prevented by using polymers. The spatial extension of high molecular weight polymer molecules is usually comparable to or greater than the range of the Van der Waals attraction between colloids [Nap83]. Therefore, polymer molecules have the correct dimension to impart colloid stability. There are two types of polymeric stabilization: depletion stabilization and steric stabilization.

In depletion stabilization, colloidal particles are separated by free polymer chains (i.e., the polymer chains are not adsorbed on the colloid surface) [Nap83]. Depletion stabilization requires a high concentration of free polymer in the liquid. Low free polymer concentration may result in flocculation.

In steric stabilization, the macromolecules are adsorbed on the surface of the colloid. The adsorbed layer of macromolecules retards close approach of the particles in two ways, entropically and enthalpically [Bri90]. When colloids approach each other, the entropy drops as a consequence of the overlapping of chains from
different colloids. This reduced entropy results in a restraint of freedom of motion of the chains. In addition, when the polymer chains overlap, the solvent around the chains is compressed, expending energy. As a result, a pressure difference is created that pulls the solvent back into the space between the particles causing the particles to be pushed apart.

In order to have an effective steric barrier, certain requirements must be met. First, the polymer chains should be strongly attached to the surface, and second, the surface of the particle should be completely covered with the polymer. In addition, the polymer chains must be long enough to keep the point of closest approach outside of the range of the attractive Van der Waals forces.

**Sol-Gel Processing Stages**

Sol gel processing of materials requires following certain steps. Each step can have a significant effect on the properties of the final product. These steps are hydrolysis and polycondensation, gelation, aging, drying, dehydroxylation, and sintering.

**Hydrolysis and Polycondensation**

Hydrolysis and polycondensation are the reactions responsible for structure evolution in sol-gel processing. Hydrolysis and polycondensation can be used for processing of both, colloidal and polymeric sols. In order for polycondensation to occur, hydrolysis must first take place. Hydrolysis and polycondensation can occur to both inorganic precursors and metal-alkoxides.
Hydrolysis and Condensation of Inorganic Precursors

Hydrolysis of inorganic precursors is carried out by the dissolution of salts in water. The dissolution of salts yields anions and cations. The metal cations, interact with the water by the following reaction [Bri90]

\[ M^{z+} + H_2O \rightarrow [MOH_2]^{z+} \]

Depending on the water acidity, coordination number, valency, electronegativity of the metal and pH of the solution, the following hydrolysis reaction takes place [Bri90]

\[ [M(OH_2)]^{z+} \rightarrow [M-OH]^{z+} + H^+ \rightarrow [M=O]^{z-2} + 2H^+ \]

where M-(OH), M-OH, and M=O, are aquo, hydroxo, and oxo complexes respectively. The electronegativity is a measure of the atom's ability to attract electrons and it is proportional to the sum of the energy to add an electron and the energy to remove an electron from the neutral atom [Kio76].

At the same pH, different complexes can result depending on the metal valence [Bri90]. For a pH of 7, hydrolysis yields oxo complexes for a metal valence above +6 and aquo complexes for a metal valence below +3. Also, at the same valence, changing the pH results in different hydrolysis products. For example, hydrolysis of cations with \( z = +6 \) yields hydroxo complexes at low pH values (below 1.5), and oxo complexes at high pH values.

Condensation can occur by either nucleophilic substitution or nucleophilic addition in the processing of inorganic salts. Nucleophilic substitution takes place
when the preferred coordination is satisfied [Br90]

\[ M_1 -OX + M_2 -OY -M_1 -O -M_2 +OY \]

Nucleophilic addition takes place when the preferred coordination is not satisfied [Br90]

\[ M_1 -OX + M_2 -OY -M_1 -O -M_2 +OY \]

Condensation by nucleophilic addition occurs when one of the reactants has a maximum coordination number (N) lower than the oxidation state (z) (i.e., one of the reactants is coordinatively unsaturated). Except in the case of coordinatively unsaturated precursors, it is necessary to have hydroxo complexes to generate condensed species. This can be accomplished by adding a base to aquo complexes or by adding an acid to oxy complexes.

Condensation can take place through other reactions. Coordinatively saturated hydroxo-aquo precursors undergo a nucleophilic substitution reaction to yield a hydroxy bridge between two metal ions. This condensation reaction is called nolation [Br90]. Coordinatively saturated metals can also undergo a nucleophilic reaction followed by water elimination to yield an oxo bridge between the metal ions. This condensation reaction is called oxolation [Br90]. For coordinatively unsaturated metals, oxolation takes places by nucleophilic substitution.
**Hydrolysis and Polycondensation of Metal Alkoxides**

Metal alkoxides in general, and transition metal alkoxides in specific, are very reactive species. The high reactivity is due to the presence of highly electronegative alkoxy groups making the metal atoms vulnerable to nucleophilic attack [Bra78 and San88]. The hydrolysis of metal alkoxides results in the formation of hydroxides or hydrated oxides [Bra78]. When limited amounts of water are added, these metal alkoxides undergo partial hydrolysis reaction producing in some cases products of certain composition as oxide alkoxides.

Silicon alkoxides are considered far less reactive than transition metal alkoxides for the following reasons [Bri90]:

- Transition metals are more electrophilic due to their low electronegativity. This results in the transition metals being less stable toward nucleophilic reactions such as hydrolysis and polycondensation.
- Transition metals often possess several stable coordinations, and if coordinatively unsaturated, they are able to increase their coordination by condensation reactions.

The high reactivity of most metal alkoxides requires that they would be processed with strict control of moisture and other conditions of hydrolysis in order to prepare homogeneous gels. A comparison between silicon alkoxide and aluminum alkoxide is a good example of the effect of the electronegativity value. Silicon has an electronegativity value higher than that of aluminum [Kin76]. As a result, aluminum alkoxides have higher hydrolysis and condensation rates than silicon.
alkoxides. The difference in the hydrolysis and condensation rates between aluminum and silicon alkoxides is a serious problem in the processing of aluminosilicate sols.

Hydrolysis occurs by nucleophilic substitution mechanisms for coordinatively saturated metals in the absence of catalysts [Bri90]. A catalyst is a base or acid that is added to influence hydrolysis and polycondensation rates and is a result of the structure of the condensed product. The entire hydrolysis process depends on charge distribution in the alkoxide and the transition state. The metal atom and the leaving group have to be positively charged [San88]. The nucleophilic substitution mechanisms involve nucleophilic addition followed by proton transfer to the alkoxide or hydroxo-ligand within the transition state. Following that, the protonated species are removed as alcohol [Bri90].

$$\begin{align*}
H-O-H+M OR & \rightarrow H-O.M-OR \rightarrow HO-M.O-R \\
& \rightarrow M-OH+ROH
\end{align*}$$

The transition states are denoted with ( ).

Similar to the hydrolysis reaction, condensation occurs by nucleophilic substitution reactions. The condensation reaction is called alcoxolation if the alcohol was the by-product [Bri90].
If the condensation reaction by-product is water, then the reaction is called oxolation [Bri90]

$$M-OH + M-OR \rightarrow M-O\cdot M-OR \rightarrow M-O\cdot M-OH \rightarrow M-O-M+ROH$$

For coordinatively unsaturated metals, condensation occurs by olation [Bri90]

$$M-OH + M-OH \rightarrow M-O\cdot M-OH \rightarrow M-O-M+ROH \rightarrow M-O-M+H_2O$$

The kinetics of olation are faster than kinetics of alcoxolation and oxolation, since no proton transfer occurs in the transition state of olation. In addition, olation has faster kinetics because \((N-z) > 0\) [Bri90]

The reaction of metal alkoxides, before or during hydrolysis and polycondensation, with alcohols, \(\beta\)-diketones, alkannimines, and acid or base catalysts is of significant importance. Studying the reaction of these chemicals with metal alkoxides is important to understand growth and structure evolution in the sol-gel processes.
Metal Alkoxide Reaction with Alcohols

The type of solvent used in the sol-gel process has an important effect on reaction kinetics. Alkoxide reactivity can be modified by changing the solvent [San88]. The reaction of alkoxides with alcohols is called alcohol interchange reactions or alcobolysis which can be represented by the following equation [Bra78]:

$$M(OR)_n + xR'OH \rightarrow M(OR)_{n-x}(OR')_x + xROH$$  \hspace{1cm} 3.27

The ease with which the alkoxy group is interchanged is a function of the size of the alkoxy group. The ease of interchange decreases from primary to secondary to tertiary groups [Bra78]. The methoxy group has a higher interchangeability than the ethoxy group, which in turn has a higher interchangeability than the sec-butoxy group. Alcobolysis is also susceptible to steric factors. Bradley showed that the rate of exchange is slow in a mixture of titanium tert-butoxide and tert-butanol [Bra78]. On the other hand, the rate of exchange is fast in a mixture of titanium tert-butoxide and tert-butanol. The difference in the exchange rate was attributed to steric effects.

Reaction of Metal Alkoxides with $\beta$-Diketones

$\beta$-diketones are chemicals with molecules that have a reactive hydroxyl group. These molecules react readily with metal alkoxides through one of the following reactions [Bra78]:

$$M(OR)_n + xR^1COCH_2COR'' \rightarrow M(OR)_{n-x}(R^1COCHCOR'')_x + xROH$$  \hspace{1cm} 3.28
Acetylacetone (AcAc), benzoylaceton, and ethyl acetoacetate are examples of $\beta$-diketones.

$\beta$-diketone ligands are more resistant to hydrolysis and polycondensation than alkoxides groups. They are used to block hydrolysis sites, accordingly, they are called chelating agents. Chelating agents are used to prevent precipitation of rapidly reacting alkoxides. They can also be used to specify certain functionality for the metal atom, i.e. allow condensation to occur on certain sites in order to achieve a certain structure, like the growth of one-dimensional polymers which are suitable for fiber drawing.

The addition of chelating agents has an effect on gelation time [Hei90]. The gelation time increases with the increase of the amount of the chelating agent. Also, the gelation time increases with the increase of the molecular size of the chelating agent. The amount of chelating agent has an effect on particle size. Larger amounts of chelating agents result in smaller particle size due to the large number of blocked condensation sites.

**Reaction of Metal Alkoxides with Alkanolamines**

"Alkanolamines are derivatives of alcohols from which the hydrogen atoms of alkyl or alkenylene groups have been replaced by free amino or N-alkyl substituted amino groups" [Bra78]. Examples of alkanolamines are ethanolamine, diethanolamine, and triethanolamine (TEA). Like $\beta$-diketones, alkanolamines can
be used as chelating agent to control the degree of hydrolysis and polycondensation [Sel91 and Bri90].

Two types of results can be produced when alkanolamines react with metal alkoxides. Some metal alkoxides show reactivity with only the hydroxyl groups of the alkanolamines and simple derivatives are obtained [Bra78]

\[ M(OR)_n + xHORNH_2 \rightarrow M(OR)_{n-x}(ORNH)_2 + xROH \]  

In other metal alkoxides, both the hydroxylic as well as the amino groups of the alkanolamines undergo replacement reactions with metal alkoxides to form cyclic derivatives [Bra90]:

\[ M(OR)_n + xHORNH_2 \rightarrow (OR)_{n-2x}M(\cdot)R \cdot 2xROH \]

Role of Acid and Base Catalysts

Acid and base catalyst have an important role in sol-gel processing. Acid catalysts are used to enhance the process kinetics. The acid role is to protonate negatively charged alkoxide groups, eliminating the requirement for proton transfer within the transition state [Bri90]

\[ M-OR + H_3O^+ \rightarrow M^+ + H_2O \]

The ease of protonation varies for different alkoxide ligands. The facilitation of protonation decreases as the electrophilicity of the ligand decreases in the order, alkoxyl, hydroxyl, oxo [Bri90]. As a result, acid-catalyzed condensation is
directed toward the ends of the chain. This means that acid catalysis results in long polymer chains with little branching.

The role of base catalysts is to deproteinate the hydroxo ligands [Bri90].

\[ \text{M-OH} + \text{OH}^{-} \rightarrow \text{M-O}^{-} + \text{H}_2\text{O} \]

Generally, basic catalysis enhances condensation kinetics. The reactivity toward nucleophilic attack is higher in the middle of the chain than at the ends. This means that condensation is directed toward the middle rather than the ends of the chain. Consequently, more compact and highly branched species are produced.

**Gelation**

As time proceeds after hydrolysis and polycondensation, clusters start growing either by aggregation of colloids (i.e., colloidal sols) or by linking polymer chains by condensation reactions (i.e., polymeric sols) [Bri90]. The clusters continue to grow until they collide and link together to form a single cluster. This single cluster is referred to as the gel. The gel can support stresses elastically, i.e., with no irreversible deformation [Hen90]. The time required to reach gelation point is called gelation time.

The rheological conditions of a gel include Newtonian behavior \((\sigma = \eta \gamma')\), shear thinning behavior \((\sigma = \eta \gamma'^n)\), and thixotropic behavior \((\sigma - \sigma_y = \eta \gamma^2)\), where \(\sigma = \) shear stress, \(\eta = \) viscosity, \(\gamma' = \) shear rate, and \(\sigma_y = \) yield stress [Jas76]. Sacks and Sheu investigated the changes in viscosity as a result of structure changes during
aging of silica gel [Sac87]. It was shown that initially, the sol exhibited Newtonian behavior (the viscosity is independent of shear rate). The sol behaved this way because there was no significant particle-particle interaction due to low particle concentration.

The Newtonian behavior was followed by shear thinning behavior (the viscosity decreases with the increase of the shear rate) for sols aged for a longer period of time. This behavior is due to the presence of large agglomerates that immobilize liquid resulting in high viscosity at low shear rates. At high shear rates, the agglomerates break releasing the entrapped liquid, and resulting in a decrease in the viscosity.

Further aging resulted in thixotropic behavior (yield behavior with hysteresis). The long aging time results in the formation of a three-dimensional network through condensation growth and agglomeration. A yield stress in the shear rate versus shear stress relation was observed due to the elastic character of the network. After the yield stress is exceeded, shear thinning behavior accompanied by hysteresis was observed. This behavior indicates that the network structure is broken down as the shear rate is increased, but full recovery does not occur when the shear rate is decreased.

Aging

The continuation of chemical reactions after gelation is referred to as aging [Hen90, Bri90]. Aging is carried out at room temperature or under hydrothermal
conditions by maintaining the gel in pore liquid. Aging results in strengthening, stiffening, and shrinkage of the network. Four processes are included in the aging process: polymerization, syneresis, coarsening, and phase transformation [Hen90]. These processes can occur singly or simultaneously.

The polymerization process involves condensation reactions that increase cross-linking in the gel structure [Bri90, Hen90].

\[ M-OH + HO-M \rightarrow M-O-M+H_2O \]  

(3.34)

In some gels (silica gel), polycondensation continues to occur after gelation due to the large concentration of silanol groups [Hen90, Bri90]. Further hydrolysis or re-esterification reactions can also occur during aging. The re-esterification reaction is the reverse of the hydrolysis reaction [Bri90].

\[ M-OH + ROH \rightarrow M-OR + H_2O \]

(3.35)

Re-esterification reaction can be suppressed by using excess water.

Syneresis can be defined as the shrinkage that takes place during aging as a result of condensation reactions [Bri90]. Gel shrinkage is accompanied by expulsion of pore liquid. The formation of bridging bonds by polycondensation causes syneresis [Hen90]. As the formation of bridging bonds proceeds, the contraction of the gel increases. The syneresis mechanism in particulate gels is somewhat different than that previously described. Gelation in particulate gels occurs as a result of the collapse of the electrical double layer, and Van der Waals attraction forces resulting in syneresis [Bri90].
Coarsening, or ripening, is a process by which dissolution and re-precipitation occur as a result of the solubility difference, S, between surfaces with different radius of curvature [Bri90]. Convex surfaces (which have positive radius of curvature) are more soluble than concave surfaces (negative radii) [Hen90, Bri90]. When a gel is immersed in a liquid in which it is soluble, dissolution occurs at the convex surfaces and re-precipitation occurs at the concave surfaces. That means that curved surfaces dissolve and necks grow between particles. As a result of the coarsening process, small particles disappear, and small pores are filled in. Neck growth provides the network with higher strength and stiffness.

After coarsening, the gel has a larger average pore size and a smaller surface area [Ile79]. The larger pore size results because the stiffer gel produced by aging does not shrink significantly under the capillary pressure [Bri90]. The reduction in the surface area is a result of the dissolution/re-precipitation process. Coarsening does not result in shrinkage, as the centers of the particles do not move toward each other. The rate of ripening is controlled by temperature, pH, concentration, and type of solvent.

Several types of phase transformations can occur during aging. These include microsyneresis and segregation. Microsyneresis is a solid/liquid phase separation that occurs on a local level. This phase transformation is driven by the affinity of the polymer for itself rather than the liquid. Segregation occurs when the liquid separates into two distinct phases. For example, the presence of an unreacted metal alkoxide in an isolated region within the pore liquid.
Crystallization is also observed in aged gels [Bri90]. Although most gels and precipitates are amorphous, aging permits the structure to rearrange by dissolution and re-precipitation, resulting in crystalline products. Crystallization can be accelerated under certain hydrothermal conditions.

**Drying**

Drying is the process of removing liquids such as alcohols and water from the gel [Jon89]. Drying under normal conditions gives rise to capillary forces which result in shrinkage of the gel [Bri90]. The resulting product is referred to as a xerogel [Heo90, Jon89]. When drying is carried out under hypercritical conditions, shrinkage does not occur and the resulting gel has a high surface area. This type of gel is referred to as an aerogel [Bri90]. Only drying under normal conditions is considered in this section. Drying can be divided into three stages: constant rate stage, first falling stage, and second falling stage.

**Constant rate stage**

In the constant rate stage, evaporation rate per unit area is independent of time. During this stage, the gel shrinks by an amount equal to the volume of liquid evaporated, and the liquid-vapor interface remains at the outer surface of the gel. As capillary forces affect the behavior of the gel during this stage, a brief discussion of relevant interaction follows.
If the solid-vapor interfacial energy, $\gamma_{SV}$, is higher than the liquid-vapor interfacial energy, $\gamma_{SL}$, the liquid tends to cover the solid surface and eliminate the solid vapor interface [Kin76]. The change in energy produced by spreading the liquid film is [Bri90]

$$\Delta E = \gamma_{SL} + \gamma_{LV} - \gamma_{SV}$$  \hspace{1cm} (3.36)

where $\gamma_{LV}$ is the liquid-vapor interfacial energy. If $\Delta E < 0$, the liquid will spread spontaneously to reduce the energy of the system.

The conditions for minimum energy can be specified using the contact angle. The contact angle, $\theta$, is the angle between the solid surface and the tangent to the liquid surface at the contact point. The interfacial energies are related to the contact angle by the equation [Kin76]

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL}$$  \hspace{1cm} (3.37)

When $\theta > 90$, nonwetting condition occurs in which liquid is depressed in the capillary. When $\theta < 90$, wetting occurs and the liquid is elevated in the capillary. When $\theta = 0$, spreading occurs and the liquid covers the solid surface completely.

Liquid rises in a capillary tube to replace the solid-vapor interface with a solid-liquid interface [Bri90]. The liquid rise results in an energy gain of $2\pi ah(\gamma_{SV} - \gamma_{SL})$, where $a$ is the tube radius and $h$ is the height to which the liquid rises. The work done by the liquid against gravity is equal to the product of the capillary pressure, $P_c$, and the volume of liquid moved, $\Delta V = \pi a^2 h$. By equating the energy gained to the work done, the capillary pressure can be calculated [Bri90].
where the negative sign indicates that the liquid is in tension.

Defining the radius of meniscus as [Bri90]

\[ r = \frac{a}{\cos(\theta)} \]  

the capillary pressure becomes

\[ \rho_c = -\frac{2 \gamma_{lv}}{r} \]  

The gel network support the tension in the liquid, and as a result, is placed in compression. Since alkoxide-derived gels have compliant networks, the compressive force causes these networks to contract into the liquid [Bri90]. Initially, the capillary pressure is low, and the radius of meniscus is much larger than the pore radius. As drying continues, the network stiffness increases due to the formation of new bonds and the decrease in porosity. As a result of the increased stiffness of the network, the tension in the liquid rises.

The end of the constant rate stage occurs when the radius of the meniscus becomes equal to the pore radius. This critical or "leatherhard" point occurs when the liquid exerts the maximum force on the pore wall [Hen90, Bri90]. Past the critical point, the tension in the pore liquid cannot overcome further stiffening of the network. As a result, the meniscus withdraws into the pores leaving air-filled pores near the outside surface of the gel. Therefore, during the constant rate stage, the
meniscus remains at the outside surface, and the meniscus radius decreases continuously.

**The first falling stage**

During the first falling stage, the evaporation rate per unit area decreases with time [Bri90]. The second stage begins when shrinkage ceases due to the increase in the stiffness of the gel. During this step, the liquid recedes into the interior and remains in the funicular condition, leaving air-filled pores near the surface. However, evaporation from the outside surface continues due to the presence of a continuous liquid film that supports flow to the exterior. The presence of adjacent pathways allows flow of liquid to occur.

Liquid flow in the first falling stage is driven by a capillary pressure gradient that is a result of a vapor pressure gradient within the pore. The liquid in the funicular state flows toward the exterior where evaporation occurs. Evaporation occurs at the outside surface because the vapor pressure is lower than it is at the inside of the pore. For a given vapor pressure, all menisci have the same curvature. Therefore, when gels contain variable pore sizes, larger pores empty first [Bri90]. If the large pores are interconnected, regions of drained pores will present. These regions may be large enough to scatter light, resulting in an opaque gel [Hen90 and Bri90]. These opaque gels are usually clear when fully saturated or fully dried. The presence of variable pore sizes can also result in cracking during drying due to the development of differential stresses [Jon89].
The second falling stage

In this stage isolated liquid pockets are formed, i.e. liquid enters the pendular condition, and drying continues by evaporation of the liquid within the body and diffusion of the vapor to the outside [Br90]. The drying front is characterized by a flow of liquid from the funicular region which evaporates at the boundary of funicular-pendular regions.

The isolated liquid pockets have a high capillary pressure, but do not exert a significant force on the solid network because they occupy a small volume fraction. As drying continues, the saturated region withdraws into the body, which in turn expands as the total stress on the network is relieved. As a result of the network being compressed more in the saturated region than near the drying surface, differential strain increases.

The development of a differential strain causes warping if only one side is being dried. This warping is permanent, which indicates that the unsaturated region of the gel retains some plasticity during the second falling rate stage. As the saturated region thickness decreases, its contraction is more effectively prevented by the larger unsaturated region. The resistance the saturated region encounters to contract increases the local network tension. This phenomenon accounts for the observed formation of cracks near the nondrying surfaces [Br90].
Dehydration

The dehydration process involves the removal of physically adsorbed water (physisorbed water) and chemically adsorbed water (chemisorbed water) [Hen90] Physisorbed water is bound to the gel surface, while chemisorbed water is hydroxyl groups associated with the gel surface If the physisorbed and chemisorbed water are not removed completely, poor optical properties or bloating during sintering can result [Hen90, Bri90]

Thermal dehydration

In thermal dehydration, hydroxyl (OH) groups are removed through a condensation reaction that is carried out at elevated temperatures. The rate of dehydration is a function of temperature and the concentration of remaining OH groups [Ile79] Physisorbed water is removed first at low temperatures, followed by the removal of weakly hydrogen bonded OH groups As the dehydration process proceeds, strongly bonded OH groups are removed, and finally, removal of isolated OH groups takes place Removal of isolated OH groups occurs at high temperatures because diffusion of protons is required for condensation to take place [Bri90] For systems that sinter at low temperatures, thermal dehydration is often not sufficient to avoid bloating, since densification begins before the complete removal of OH groups

Extensive thermal dehydration can be achieved by optimizing the gel microstructure and the thermal processing conditions [Bri90] Pore size, surface area,
and curvature are among the important microstructural variables that affect dehydration. Dehydration can be improved by increasing the pore size. Larger pores enhance the diffusion of the condensation byproduct, $\text{H}_2\text{O}$, and hamper sintering. Consequently, large pores permit complete dehydration to occur before pore closure.

High surface curvatures are achieved by selecting processing conditions that result in particulate rather than a polymeric microstructure [Bri90]. Particulate microstructures possess positive curvatures that facilitate dehydration due to reduced hydrogen bonding. Also, the low surface area to volume ratio associated with particulate microstructures leads to faster dehydration due to a reduced OH concentration on a per-gram basis. Large particles are advantageous from the standpoint of surface area to volume ratio and negative radii area. Large particles have low surface area to volume ratio and low negative radii surface area. On the other hand, large particles possess smaller curvature which can result in slower dehydration.

Chemical dehydration

Thermal dehydration normally does not reduce the [OH] sufficiently for certain applications (i.e., optical materials) [Bri90]. Consequently, finding another dehydration technique is necessary in order to achieve low OH content. Chemical dehydration has been investigated as a method to produce low OH content. This process employs the reaction between halogens and OH groups to dehydrate the surface.
Hair et al. investigated chemical dehydration of silica surface by replacing hydroxyl groups with chlorine atoms in a process referred to as chlorination [Hai67]. Chlorination can be achieved by using Cl\(_2\) gas. Chlorination using this method does not take place at temperatures < 700 °C.

\[ 2Cl_2 \rightarrow 4Cl \quad 3.41 \]

Chlorination of silica gel can also be carried out by using sulfuryl chloride (SO\(_2\)Cl\(_2\)) [Hai67]

\[ 2(\text{SiOH}) + SO_2Cl_2 \rightarrow 2(\text{SiCl}) + 2HCl + SO_3 \quad 3.42 \]

Although virtually complete dehydration of silica surface can be produced by chlorine treatment, foaming can occur when heating in the vicinity of the softening point [Sus86]. This foaming is a result of chlorine evolution as it replaces the OH groups during the dehydration process. Therefore, a dechlorination treatment (process to remove surface chlorine) is necessary to prevent foaming. In regions of incomplete chlorination, Cl may be removed by the following reaction [Sus86]

\[ \text{SiCl} + HOSi \rightarrow \text{Si} - O - \text{Si} + HCl \quad 3.43 \]

Dechlorination can be carried out by heating below the sintering temperature in dry oxygen environment [Sus86]. This oxidation treatment is diffusion controlled, and can result in a significant decrease in chlorine.

Since the chlorine content is proportional to the surface area of the gel, reduction of surface area prior to the chlorination treatment can result in a lower
residual chlorine content [Sus86]. Gels can be pre-sintered in order to reduce surface area. The degree of pre-sintering is controlled so that no closed pores are developed. The development of closed pores hinders the dehydration process.

Foaming can also be eliminated by using fluorine instead of chlorine [Bri90]. Fluorine can be introduced as HF, NH₄F, or SiF₄, and can replace OH groups in a manner similar to Cl [Bri90].

\[
Si_2OH + HF \rightarrow Si_2F + H_2O
\]

Foaming does not occur when using fluorine due to stronger Si-F bonds. However, fluorine is retained in the final gel.

**Sintering**

Sintering is a densification process that is driven by the tendency to decrease the surface area in order to reduce the surface free energy of the material [Kin76 and Bri90]. The surface free energy is reduced by the elimination of the solid-vapor interface. Gels generally have large surface areas, resulting in a relatively high driving force for sintering. The high driving force produces sintering at exceptionally low temperatures, where the transport processes are slow. Amorphous materials sinter by viscous flow, while crystalline materials sinter by solid-state diffusion [Bri90]. One of the important aspects in viscous and solid-state sintering is the effect of surface curvature on vapor pressure over the surface. This vapor pressure difference has an important role in the material transfer during sintering.
The pressure difference across a curved surface can be determined by considering a bubble being blown in a liquid bath by a capillary [Kin76]. If the gravitational effect is negligible, the only resistance to expansion of the bubble is the increased surface energy that is caused by the increase in the surface area. During equilibrium, the following equation must hold [Klo76]

\[ \Delta P dv = \gamma dA \]  

where \( \Delta P \) = the pressure difference across the curved surface, \( v \) = volume per unit area. The left hand side of the equation 3.45 represents the work of expansion, and the right hand side represents the increased surface energy. The values of \( dv \) and \( dA \) with respect to the radius of curvature, \( r \), are [Kin76]

\[ dv = 4\pi r^2 dr \]  
\[ dA = 8\pi r dr \]

Substituting the values of \( dv \) and \( dA \) in equation 3.45 results

\[ \Delta P = \gamma \left( \frac{2}{r} \right) \]  

Equation 3.48 is valid for spherical shapes. For more general shapes [Kin76]

\[ \Delta P = \gamma \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \]

where \( r_1 \) and \( r_2 \) are the principal radii of curvature.

The increase in vapor pressure due to an applied pressure of \( \Delta P \) can be calculated from [Kin76]
\[ V \Delta P = R T \ln \frac{P}{P_0} = \gamma \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \]  

where \( V \) = molar volume, \( p \) = vapor pressure over the curved surface, \( p_0 \) = vapor pressure over a flat surface, and \( R \) = gas constant. Rearranging equation 3.50

\[ \ln \frac{p}{p_0} = \frac{M \gamma}{p R T} \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \]

where \( M \) = molecular weight, \( p \) = density, and \( T \) = temperature. Equation 3.51 relates the difference in the vapor pressure to the curvature, and is called Thompson Freundlich (Kelvin) equation.

**Viscous sintering of amorphous materials**

The driving force for viscous sintering is a lowering of the surface energy by reducing the surface area. Considering the coalescence of a pair of spheres, Frenkel derived a model for viscous sintering [Kin76 and Brin90]. When two spherical particles in contact, there is a negative pressure at the small negative radius of curvature of the contact area \( (x) \) compared to the surface of the particle. This pressure difference causes a viscous flow of material to the neck region.

During viscous flow sintering, the neck widens and the centers of the particles approach one another causing shrinkage. The rate of growth of the neck area was obtained by Frenkel [Kuc49, Kin55, Kin76 and Brin90]

\[ \frac{r_n}{r_p} = \left( \frac{3 \gamma_1 \gamma_2}{\eta \gamma} \right)^{\frac{1}{2}} \]

where \( \gamma_1 \) and \( \gamma_2 \) are the surface tension coefficients, \( \eta \) is the viscosity, and \( r_p \) is the particle radius.
where \( r_n \) = neck radius, \( r_p \) = particle radius, \( \gamma_{sv} \) = solid-vapor interfacial energy, \( \eta \) = viscosity, and \( t \) = time. This relation was verified experimentally by Kuczynski, Kingery, and Berg [Kuc49 and Kin55]. The increase in the neck diameter is proportional to the square root of time. The rate determining factors for this process are surface tension, viscosity and particle radius. Higher sintering rates are achieved when the particle size and viscosity are small and surface tension is large.

The processing temperature has an important effect on the sintering rate. The sintering rate is proportional to \( \gamma_{sv}/\eta \). A change in the temperature results in changes in the content of the surface OH groups, and consequently, in the surface energy [Bri90]. However, the loss of OH occurs over a wide range of temperatures. Over the same range of temperatures, the viscosity changes by many orders of magnitude. As a result, the temperature dependence of the sintering rate is governed entirely by the viscosity [Bri90].

At low temperatures, the viscosity of glasses is represented by [Zar91, Bri90]

\[
\eta = \eta_0 \exp\left( \frac{\Delta G}{kT} \right)
\]

where \( \Delta G \) = activation energy for viscous flow, \( k \) = Boltzman's constant, \( T \) = temperature and \( \eta_0 \) can be calculated from [Zar91]

\[
\eta_0 = \frac{kT}{\nu V_m}
\]

where \( \nu \) is a frequency factor, and \( V_m \) is the volume occupied by a molecule. Equation 3.53 leads to an Arrhenius dependence for the viscosity [Zar91].
\[ \log \eta = A + \frac{B}{T} \]

where \(A\) and \(B\) are constants.

At high temperatures, the viscosity of glass departs from Arrhenian behavior to follow what is called Vogel Fulcher-Tamman empirical equation [Zar91, Bri76]:

\[ \log \eta = A_1 + \frac{B_1}{T - T_o} \]

where \(A_1\), \(B_1\), and \(T_o\) are constants.

Kingery and Berg developed a procedure to derive the shrinkage rate [Kin55].

Considering the volume of the neck region [Kin55]:

\[ V_n = \frac{\pi x^4}{2r} \]

Substituting equation 3.52 in 3.57 results in:

\[ V_n = \frac{9\pi r y^2 t^2}{4\eta} \]

Taking the derivative of \(V_n\) with respect to \(t\):

\[ \frac{dV_n}{dt} = \frac{18\pi r y^2 t}{4\eta^2} \]

where the negative sign indicates the decrease in volume. The volume decrease in the sphere at each contact is [Kin55]:

\[ \frac{dV_n}{V_0 dt} = -\frac{27y^2 t}{8r^2 \eta^2} \]
where \( V_o \) is the initial volume of the sphere. Considering each sphere has a number of contacts = \( n \), and by integrating equation 3.60 [Kim55],

\[
\frac{\Delta V}{V_o} = \frac{27n\gamma^2 r^2}{16\pi^2 n^2}
\]

Equation 3.61 represents the shrinkage rate during viscous flow sintering. This expression is expected to hold to a volume shrinkage of 2% with reasonable precision.

**Sintering of crystalline materials**

As with viscous flow sintering of amorphous materials, sintering of crystalline materials is driven by the tendency to lower the surface free energy by reducing the surface area [Brn90 and Kim76]. The surface free energy is reduced by replacing the high-energy solid-vapor interface by a lower energy solid-solid interface. Material transfer during sintering of crystalline materials is influenced by the pressure difference and changes in free energy across a curved surface.

Evaporation-condensation and solid-state diffusion are the mechanisms by which material can be transported in a crystalline material. Evaporation-condensation and solid-state diffusion paths are illustrated in Figure 3-1. Material transport by solid-state diffusion is divided into the following mechanisms [Kim76, Brn90].
Figure 3-1  Matter transport paths during solid-state sintering. 1) Surface diffusion; 2) Lattice diffusion from the surface, 3) Vapor transport, 4) Boundary diffusion, 5) Lattice diffusion from the grain boundaries and 6) Lattice diffusion from the bulk. Adapted from [Kin76]
- Surface diffusion in which the surface is the source and the path of the transported material
- Lattice diffusion in which the surface, grain boundary, or dislocations is the source and the surface is the path
- Grain boundary diffusion in which the grain boundary is the source and the path of the transported material

**Evaporation-condensation mechanism**

In the evaporation-condensation mechanism, material is transported from the region of high vapor pressure (the particle surface) to the region of low pressure (the neck). The evaporation-condensation process results in a decrease in the energy of the system, but it does not produce densification [Bri90]. Changes in pore-shape are produced during this process, but shrinkage does not occur.

In order to determine the growth rate of the neck between two particles, consider the Thomson-Freundlich equation for two bonded particles [Kin55, Kin76]

\[
\ln \frac{p_1}{p_o} = \frac{\gamma M}{\rho RT r_n} x - \frac{1}{2}
\]

where \(p_1\) is the pressure over the small radius of curvature of the neck. The pressure difference \(p_o - p_1\) is small, and \(r_n > x\). As a result, to a good approximation, \(p_1/p_o = \Delta p/p_o\), and equation 3.62 becomes [Kin55]
\[ \Delta p = \frac{\gamma M p_o}{\rho \pi RT} \]

where \( \Delta p \) is the difference between the vapor pressure of the small negative radius of curvature and the vapor pressure over the nearly flat particle surface.

Using the Langmuir equation for the rate of material transfer, \( m \) [Kin55],

\[ m = \alpha \Delta p \left( \frac{M}{2\pi RT} \right)^{\frac{1}{2}} \]

where \( \alpha \) is an accommodation coefficient that is approximately equal to 1. The rate of condensation is equal to the volume increase [Kin55],

\[ \left( \frac{m}{\rho} \right) A = \frac{\delta V}{\delta t} \]

From the geometry of the two spheres in contact, Figure 3-2, \( x = \frac{r_n^2}{2r} \), \( A = \frac{\pi}{2} r_n^2 / r \), and \( v = \pi r_n^4 / 2r \). Substituting values for \( m \), \( A \), and \( v \) in equation 3.65 and integrating, the relationship for the rate of growth of the bond area between particles is obtained [Kin55, Kin76]

\[ \frac{r_n}{r_p} = \left( \frac{2\sqrt{\pi M^2 \gamma p_o}}{\sqrt{2} \rho^2 R^2 T^2} \right)^{\frac{1}{3}} \left( \frac{1}{3} \right)^{\frac{1}{3}} \left( \frac{\frac{2}{3} \frac{1}{3}}{\frac{3}{3} \frac{3}{3}} \right)^{\frac{1}{3}} \]

In addition to time, the main variables that affect the rate of pore-shape change through this process are the particle radius and the vapor pressure. The vapor pressure increases exponentially with temperature, resulting in a strong dependency of evaporation-condensation process on temperature [Kin76]
Figure 3-2. Schematic of the initial stages of sintering by evaporation/condensation mechanisms. Adapted from [Km55]
Solid state mechanisms

The difference in the free energy between the neck area and the surface of the particle provides the driving force for material transfer [Kin76]. Matter can move from the surface, from the grain boundary, or from the bulk by surface, grain boundary, or lattice diffusion. Similar to evaporation-condensation, the transfer of material from the surface to the neck by surface or lattice diffusion does not lead to shrinkage or densification [Bri90 and Kin76]. Shrinkage and densification take place when material is transported from the particle volume or from the grain boundary between particles.

Considering the case of matter transport from the grain boundary to the neck by lattice diffusion, and from the geometry of the neck region as shown in Figure 3.3, the following is obtained [Kin55]

\[ \rho = \frac{r_a^2}{4\pi}, \quad V = \frac{\pi r_a^4}{2\rho} \]

The surface energy produces an excess of vacancies in the regions of negative curvature [Bri90]. This excess of vacancies results in a flux of vacancies away from the perimeter of the neck. The vacancy flux per unit time per unit length, J, can be written as follows [Kin55]

\[ J = 4D_v \Delta N \]

where \( D_v \) = vacancy diffusion constant, \( \Delta N \) = the excess concentration of vacancies. The excess concentration of vacancies is determined from [Kin55].
Figure 3-3 Schematic of initial stages of solid-state sintering. Adapted from [Kin55]
where \( a \) = atomic radius, and \( N_0 \) = vacancy concentration at a plane surface. The self-diffusion coefficient is related by [Kin55]:

\[
D_s = a^3 D_N
\]

Also, the rate of volume change, \( dV/dt \), is related to the vacancy current, \( J \), by [Kin55]

\[
\frac{dV}{dt} = 2\pi r_n a^3 J
\]

Substituting equations 3.69, 3.70, and 3.71 into equation 3.68 and integrating yields the neck growth rate [Kin55]

\[
\frac{r_n}{r_p} = \left( \frac{40\gamma a^3 D_s}{kT} \right)^{1/2} \frac{T}{5\pi^2}^2
\]

The shrinkage rate is determined through the same procedure that was used for viscous sintering [Kin55]

\[
V_s = \frac{3}{2} \left( \frac{40\gamma a^3 D_s}{kT} \right)^{1/2} \frac{T}{5\pi^2}^2
\]

and

\[
\Delta V = \frac{3n}{8} \left( \frac{40\gamma a^3 D_s}{kT} \right)^{4/3} \frac{T}{5}\]

Equation 3.74 is expected to hold to a volume shrinkage of 2%
Equations 3.72 and 3.74 indicate that the neck growth rate is proportional to $t^{1/5}$, and that the shrinkage rate is proportional to $t^{2/5}$ [Kin76]. Control of particle size is important, since the sintering rate is roughly proportional to the inverse of the particle radius. This means that as the particle size is increased, the sintering rate is decreased.

The mobility of atoms is high within the grain boundary. Consequently, diffusion in the grain boundary is rapid. However, the flux of diffusing atoms is small because the grain boundary cross-sectional area is very small [Bri90]. Diffusion through the lattice, on the other hand, is very slow, but the flux can pass through a larger area. As a result, the net rate of transport by lattice diffusion may be greater than that of grain boundary diffusion.

The particle size can determine which transport mechanism is dominant. Grain boundary diffusion is dominant in case of small grains due to the large volume fraction occupied by the grain boundary. The activation energy for lattice diffusion is higher than that of grain boundary diffusion [Bri90]. However, the lattice diffusion coefficient increases rapidly with temperature. As a result, lattice diffusion becomes more important at high temperatures. It has been observed that surface diffusion is most important during the early stages of sintering. This diffusion affects the neck diameter but not the shrinkage or porosity [Kin76]. Grain boundary and lattice diffusion become important following the early stages of sintering.

As shown in equations 3.61 and 3.74, the sintering rate is proportional to $t^2$ for viscous sintering, and is proportional to $t^{4/5}$ for lattice or volume diffusion. This
means that viscous flow sintering is much faster than solid-state diffusion sintering. The difference in the sintering rate for the two mechanisms can have significant effects on the densification behavior of some systems. Sacks and Pask reported very rapid densification in aluminosilicates with compositions that contained large amounts of liquid phase [Sac82]. High densification rates persisted up to an alumina content of 74 wt%, at which a sharp decrease in the densification rate was observed. This sharp decrease in densification rate occurred at the transition from mullite-mullite region to a mullite alumina region. This transition was associated with the elimination of the glassy phase. The drop in the densification rate was attributed to absence of viscous sintering and the activation of solid-state sintering.
CHAPTER 4
COMPOSITE MATERIALS

Definitions and Characteristics

Composites are materials that consist of two or more chemically and physically distinct constituents on a macroscale level [Aga80, Hul81]. Composites can be made by mixing the separate constituents in such a way that the dispersion of one constituent in the other can be done in a controlled way to optimize properties. Since the constituents may be individually tailored to enhance separate physical or chemical characteristics, the properties of the composite should be superior to those of the individual components. Composites consist of one or more discontinuous phases, called the reinforcing material, embedded in a continuous phase, called the matrix. In general, reinforcing materials are stronger and harder than the matrix.

Properties of composites are highly dependent on the properties of their constituent materials. The properties of composites are also influenced by the distribution of the constituents and the interaction among them [Aga80]. These properties may be the volume fraction sum of the properties of the constituents, or the properties of the composite work together to provide properties that are not accounted for by the volume fraction sum of the constituents properties. Composites can be described by the geometry of the reinforcement. The geometry of the reinforcement is described by size, shape, and size distribution. Composites with
identical reinforcement geometry may differ in concentration, concentration
distribution, and orientation.

Concentration is considered the most important parameter influencing the composite properties [Aga80]. It is considered as controllable manufacturing variable used to dictate the properties of the composite. The concentration distribution can be used to determine the homogeneity of the composite material system [Aga80]. Particles may be uniformly dispersed in a composite without touching each other. Particles can also be arranged in a way to form a network with a continuous path connecting all particles.

The orientation of the reinforcement has a great influence on the isotropy of the system [Aga80]. In the case of spherical reinforcement particles, the composite behaves as an isotropic material. For reinforcement particles with unequal dimension, isotropy is obtained if they are randomly oriented, an example is the randomly oriented, short-fiber reinforced composite. In some cases, anisotropy is desired in order to improve a certain property in a specific direction. Continuous-fiber-reinforced composites can be anisotropic, if the fibers are aligned in one direction or woven in stacked planes. Anisotropy can also be introduced by using certain manufacturing processes, such as extrusion of short-fiber composites.

The majority of structural composites have been fabricated to improve the mechanical properties, such as strength, toughness, stiffness, and high-temperature performance [Aga80]. The geometry of the reinforcement has a strong influence on the strengthening mechanism. Consequently, reinforcement phase geometry can be
considered as a basis for classification of composites. Composites can be divided into two major categories [Aga80]. The first category is called particle-reinforced composites (particulate composites). This category includes all composites with particles that are nonfibrous in nature. The particles may be spherical, platelet-shaped, cubic, tetragonal, or any other regular or irregular shape that is approximately equiaxed. The second category consists of fiber-reinforced composites (fibrous composites). A fiber is distinguished by its length being much greater than its cross-sectional dimensions [Aga80]. The emphasis in this study is on unidirectional fiber composites, other composites are beyond the scope of this study.

**Unidirectional Fiber Composites**

Unidirectional fiber composites contain fibers that are aligned parallel to each other in a single direction. These composites have two important features; their high strength to weight ratio, and controlled anisotropy [Aga80]. Unidirectional fiber composites are divided into discontinuous (short) fiber unidirectional composites and continuous-fiber unidirectional composites. In discontinuous-fiber unidirectional composites, the fiber orientation cannot be controlled easily. In these composites the load bearing capability is a function of the fiber length.

Continuous-fiber composites have a higher strength and modulus values in the direction of the fiber axis than the strength and modulus of short-fiber composites [Aga80]. However, these composites are very weak in the transverse direction.
Therefore, continuous-fiber composites are superior to short-fiber composites when load is applied in the longitudinal direction (parallel to fibers).

The use of fibers in high-performance engineering materials is based on the following characteristics [Cha87]:

- A high aspect ratio \((L/d)\) that facilitates the transfer of a major part of the applied load by the matrix to strong fibers.
- A small fiber diameter with respect to grain size. This allows a higher fraction of the theoretical strength to be attained than that possible in a bulk form, because the smaller size has a lower probability of having large surface flaws.
- A high degree of flexibility that is a characteristic of a material with high modulus and small diameter. This flexibility allows a variety of techniques to be used in manufacturing composites with these fibers.

Unidirectional composites consist of parallel short or continuous fibers embedded in a matrix. Several unidirectional layers (each referred to as a lamina) can be in a specified orientation to fabricate a laminate [Pig80, Aga80]. Figure 4-1 shows a continuous-fiber composite lamina. Laminae are considered building blocks that are used to make high-performance structural elements. Since the main application of unidirectional composites is for load bearing, understanding the mechanics of these composites is essential.
Figure 4-1 Unidirectional continuous fiber composite lamina. Adapted from [Aga80]
Mechanics of Fiber Composites

Designing composites to sustain high loads for various applications requires a thorough understanding of composite mechanics. The behavior of unidirectional composites is a result of the behavior of the interface between the fiber and the matrix, and the behavior of the fiber and the matrix themselves [Cha87].

The fiber interface is responsible for transmitting the load from the matrix to the fibers [Aga80]. The fibers contribute the greater portion of the composite strength. This means that the efficiency of load transmission from the matrix to the fibers can have a large influence on the strength of the composite. There are two types of bonding that can exist at the fiber-matrix interface, mechanical bonding and chemical bonding [Cha87]. Mechanical bonding can occur by simple mechanical keying effects between two surfaces. The mechanical keying can be produced by having a rough fiber-matrix interface. It can also be produced by the contraction of the matrix against the fibers. In most cases, mechanical bonding alone is not enough to have an effective reinforcement. However, mechanical bonding can add to the overall bonding, in the presence of reaction bonding.

Chemical bonding can be divided into two types, dissolution and wettability bonding, and reaction bonding [Cha87]. In dissolution and wettability bonding, interaction between components occurs at an electronic scale. The bond strength varies from weak Van der Waals to strong covalent bonds. Intimate contact is required between the fiber and the matrix to achieve this kind of bonding, since
these interactions are short range. This implies that no contaminants on the fiber surface, or entrapped air or gas bubbles at the interface, should be allowed to exist.

Reaction bonding occurs by transport of atoms from the fiber and the matrix to the interface, which is considered the reaction site [Cha87]. The reaction products and the reaction rates depend on the matrix composition, reaction time, and temperature. The thickness of the interface reaction zone (x) is generally described by the formula [Cha87]

\[ x = \sqrt{Dt} \]

where \( D \) = diffusion coefficient, \( t \) = time. The diffusion coefficient is determined by the formula [Cha87]

\[ D = D_0 \exp\left(-\frac{Q}{kT}\right) \]

where \( D_0 \) = constant, \( Q \) = activation energy, \( k \) = Boltzmann constant, and \( T \) = temperature.

Mechanics of Unidirectional Continuous Fiber Composites

Consider the case of a continuous fiber composite with parallel fibers under a longitudinal tensile load. Assuming a perfect fiber to matrix bonding, the longitudinal strains in fibers (\( \varepsilon_f \)), matrix (\( \varepsilon_m \)), and composite (\( \varepsilon_c \)) are equal [Aga80 and Mal88].
\[ \varepsilon_f = \varepsilon_m = \varepsilon_c \]

From linear elasticity theory, the stress and the strain are proportional to each other according to Hook's law [Tew78]:

\[ \sigma = E \varepsilon \]

where \( \sigma \) is the stress, which is the amount of load applied per unit area, and \( E \) is Young's elastic modulus. Assuming both fibers and matrix behave as linearly elastic materials [Mal88]:

\[ \sigma_f = E_f \varepsilon_f = \sigma_f \]
\[ \sigma_m = E_m \varepsilon_m = \sigma_m \varepsilon_c \]

where \( \sigma_f \) = fiber stress, \( \sigma_m \) = matrix stress, \( E_f \) = fiber elastic modulus, and \( E_m \) = matrix elastic modulus.

The tensile load applied on the lamina, \( P_c \), is shared by the matrix and the fibers [Mal88]:

\[ P_c = P_f + P_m \]

where \( P_f \) = load applied on fibers, and \( P_m \) = load applied on matrix. Using the definition of stress, equation 4.7 becomes [Aga80 and Mal88]:

\[ \sigma_c = \frac{A_f}{A_c} \frac{\sigma_f}{A_f} + \frac{A_m}{A_c} \frac{\sigma_m}{A_m} \]

where \( \sigma_c \) = average tensile stress in the composite, \( A_f \) = net cross-sectional area for fibers, \( A_m \) = net cross-sectional area for matrix, \( A_c \) = cross-sectional area of the
composite, i.e. $A_c = A_f + A_m$. Defining fiber and matrix volume fractions [Agar80 and Mal88],

$$V_f = \frac{A_f}{A_c}$$

$$V_m = \frac{A_m}{A_c}$$

Thus equation 4.8 becomes [Agar80]:

$$\sigma_c = \sigma_f V_f + \sigma_m V_m$$

or

$$\sigma_c = \sigma_f V_f + \sigma_m (1 - V_f)$$

Dividing equation 4.11 by the strain yields [Mal88]:

$$E_c = E_f V_f + E_m (1 - V_f)$$

where $E_c =$ average composite elastic modulus. Equations 4.12 and 4.13 indicate that the contributions of the fibers and the matrix to the average properties of the composite are proportional to their volume fraction. Such a relationship is referred to as the rule of mixture [Agar80 and Mal88].

The fraction of load carried by the fibers in a unidirectional continuous fiber lamina can be determined by dividing the load applied to the fibers by the load applied to the composite [Mal88].
Equation 4.14 indicates that in order to attain high stresses in the fibers and thereby use the fibers efficiently, it is necessary for the fibers modulus to be much greater than the matrix modulus [Aga80]. Figure 4-2 shows the fraction of the composite load carried by the fibers. As shown in the figure, the fraction of the total load carried by the fibers increases with the increase in ratio of fiber modulus to matrix modulus and the increase in the volume fraction of fibers. However, when fiber volume fraction exceeds 80%, properties start deteriorating due to the inability of the matrix to infiltrate the bundles of fibers resulting in poor fiber matrix bonding and void formation in the composite.

Fiber failure strain is generally lower than the matrix failure strain [Mal88]. The tensile rupture of fibers will result in a tensile rupture in the composite. From equation 4.12, the longitudinal tensile strength of a unidirectional continuous fiber composite can be calculated as [Aga80, Hul81, Mal88]

\[
\sigma_m = \sigma_f V_f + (\sigma_m)_{ef}(1-V_f)
\]

where \(\sigma_m\) = the longitudinal tensile strength of the composite, \(\sigma_f\) = fiber tensile strength, and \((\sigma_m)_{ef}\) = matrix stress at the fiber failure strain. The strengthening
Figure 4-2  Fraction of composite load carried by fibers as a function of fiber modulus/matrix modulus ratio for different fiber volume fractions. Adapted from [Mal88, Aga80].
effect is not achieved unless the strength of the composite exceeds that of the matrix alone [Aga80]

\[ \sigma_{cm} = \sigma_{fu} V_f + (\sigma_{mu})_{off}(1-V_f) \geq \sigma_{mu} \]  

4.16

where \( \sigma_{mu} \) = the strength of the matrix. Using equation 4.16, a critical volume fraction of fibers, \( V_{fc} \), is defined [Aga80 and Mal88]

\[ V_{fc} = \frac{\sigma_{mu} - (\sigma_{mu})_{ef}}{\sigma_{fu} - (\sigma_{mu})_{ef}} \]  

4.17

This critical volume fraction of fibers has to be exceeded in order for strengthening to occur.

**Mechanics of Discontinuous Parallel Fiber Composites**

When a load is applied to a discontinuous fiber lamina, it is transferred to the fibers by shear stresses acting at the fiber/matrix interface [Mal88]. The lower modulus for the matrix results in the longitudinal strain in the matrix being higher than that in adjacent fibers. As a result, a shear stress distribution across the fiber/matrix interface is established, if perfect-fiber matrix bonding is assumed.

The normal stress distribution in a discontinuous fiber can be calculated by equilibrium analysis. Considering an element with length \( dx \), at a distance, \( x \), from a fiber end (as shown in Figure 4-3), the force equilibrium equation for \( dx \) is [Mal88]
Figure 4-3 Longitudinal tensile loading of a discontinuous fiber in a unidirectional composite. Adapted from [Mal88].
\[
\left(\frac{\pi}{4} d_f^2\right) (\sigma_f + \sigma_i) = \left(\frac{\pi}{4} d_f^2 \sigma_i\right) + \pi d_f dx_t
\]

where \(\sigma_f\) = longitudinal stress in the fiber at a distance \(x\) from one of its ends, \(\tau_i\) = shear stress at fiber-matrix interface, \(d_f\) = fiber diameter. Equation 4.18 can be simplified to [Mal88]

\[
\frac{d \sigma_f}{dx} = \frac{4 \tau_i}{d_f}
\]

4.19

Ignoring the stress transfer at the fiber ends, and assuming the interfacial shear stress is constant and equal to the matrix yield shear stress, integration of equation 4.19 yields [Mal88]

\[
\sigma_f = \frac{4 \tau_i x}{d_f}
\]

4.20

Equation 4.20 indicates that the fiber stress is not uniform. The fiber stress is zero at the ends and increases linearly to the maximum value at the central portion of the fiber. For short fibers, the maximum fiber stress occurs at \(x = L/2\), thus [Aga80 and Mal88]

\[
\sigma_{fm} = 2 \tau_i \frac{L}{d}
\]

4.21

"The minimum fiber length in which the maximum fiber stress can be achieved" is referred to as load-transfer length \((L_t)\) [Aga80]. The load is transferred from the matrix to the fiber over the load-transfer length, which is given by [Aga80]

\[
\frac{L_t}{d} = \frac{\sigma_{fm}}{2 \tau_i}
\]

4.22

Since \(\sigma_{fm}\) is dependent on the applied stress, the load-transfer length is also dependent on the applied stress. A critical fiber length \((L_c)\) can be defined as the
minimum fiber length in which the fiber strength \( (\sigma_{fu}) \) can be achieved [Aga80, Mal88]

\[
\frac{L_{c}}{d} \frac{\sigma_{fu}}{2\tau_{f}}
\]

4.23

The critical fiber length is independent of applied stress. The maximum value for the load-transfer length is the critical length.

Figure 4-4 shows the significance of the critical fiber length on the longitudinal stresses of the fiber. In the case of fiber length smaller than the critical length, the maximum fiber stress may never reach the value for fiber strength [Mal88]. As a result, either the matrix or the fiber-matrix interfacial bond may fail before fibers reach their potential strength. In the case of fiber length equal to the critical length, the maximum fiber stress reach as the fiber strength at the middle of the fiber. The last case is when the fiber length is greater than the critical length. The maximum fiber stress may reach the fiber strength over much of its length. However, the fiber remains ineffective over a distance equal to \( L_{c}/2 \) from each end. For effective strengthening, the selected fiber length should be much greater than the critical length.

The average fiber stress can be calculated from the formula [Aga80 and Mal88]

\[
\sigma_{fm} = \frac{1}{L} \int_{0}^{L} \sigma_{f} \, dx
\]

4.24

The quantity represented by the integral is the area under the curve of fiber stress
Figure 4-4  Significance of critical fiber length on the longitudinal stresses of a discontinuous fiber [Mal88]
versus length (Figure 4-5) Therefore, the average fiber stress is [Mal88, Aga80]

\[ \sigma_{fuv} = \sigma_{fu} \left(1 - \frac{L}{2L} \right) \]  

4.25

In the case of \( L > L_c \), equation 4.25 becomes

\[ \sigma_{fuv} = \sigma_{fu} \left(1 - \frac{L_c}{2L} \right) \]  

4.26

and in the case of \( L < L_c \), equation 4.25 becomes:

\[ \sigma_{fuv} = \frac{\sigma_{fm}}{2} \]  

4.27

For \( L > L_c \), the longitudinal tensile strength of the composite is determined by substituting \( L_c = L_c \) and \( \sigma_{fm} = \sigma_{fu} \) and using the following rule of mixture [Mal88]:

\[ \sigma_c = \sigma_{fu} V_f + \sigma_{fm} V_m \]  

4.28

Thus, the longitudinal tensile strength of a unidirectional discontinuous fiber composite is [Aga80, Hnl81, and Mal88]

\[ \sigma_{cm} = \sigma_{fu} \left(1 - \frac{L_c}{2L} \right) V_f + \sigma_{fm} (1 - V_f) \]  

4.29

For the case of \( L >> L_c \), equation 4.29 becomes identical to equation 4.15, which is used for continuous fibers. A comparison between equation 4.15 and equation 4.29 shows that continuous fibers always strengthen a matrix more effectively than short fibers.
Figure 4-5. Longitudinal stress distribution along a discontinuous fiber under longitudinal tensile loading [Mal88].
In the case of $L < L_c$, no fiber failure occurs. Instead, failure occurs by one of the following failure modes [Mal88]

- Fiber matrix interface bond failure followed by fiber pullout. In this case, the longitudinal tensile strength of the composite is [Mal88]

$$\sigma_m = \tau_m \frac{L}{d} V_f + \sigma_{mp} \left(1 - V_f \right)$$

where $\tau_m$ = shear strength of fiber-matrix interface, $\sigma_{mp}$ = matrix stress at the instant of fiber pullout.

- Matrix failure, in which the longitudinal tensile strength of the composite is [Mal88]

$$\sigma_m = \tau_m \frac{L}{d} V_f + \sigma_{mp} \left(1 - V_f \right)$$

where $\sigma_m$ = tensile strength of the matrix. Which mode is responsible for the failure is dependent on the relative values of $\tau_m$ and $\sigma_{mp}$.

The discontinuities caused by the presence of fiber ends result in stress concentrations. The stress concentrations are produced because the load that is not carried by the fiber due to the discontinuity must be carried by other fibers. These stress concentrations can have detrimental effect on the strength of the composite.

**Failure of Unidirectional Composites Under Longitudinal Tensile Loads**

Failure of unidirectional composites that are subjected to longitudinal tensile load is initiated by fiber breakage [Aga80]. Fiber strength in reality is not a single value [Mal88]. Fiber strength follows a statistical distribution due to the presence of defects. Consequently, it is expected that a few fibers will fail at stress levels
below the average strength. The remaining fibers will carry higher stresses, and may not fail simultaneously.

The stress distribution in a fiber changes when breakage occurs. The stress at each of its broken ends becomes zero [Mal88]. However, the stress builds back up to reach the average value over a distance of $L_c/2$ from each end. The stress states in the region of the broken ends contain the following [Mal88]:

- high shear stress concentrations in the matrix within the fiber end region,
- stress concentrations at the void created upon breakage of the fiber, and
- an increase in the normal stress in the neighboring fibers.

The presence of these stresses can result in failure of the composite.

Failure Processes

Fracture toughness of a unidirectional composite is the sum of the energies consumed by several failure processes. These failure processes are fiber debonding, fiber pullout, fiber fracture, and matrix cracking or yielding [Mal88]. An advancing crack always has a longitudinal stress concentration at its tip. The stress component perpendicular to the longitudinal stress and the shear stress component may reach high values slightly ahead of the crack tip. Depending on the strength of the fiber-matrix interface, these stress components can cause debonding of the fibers from the surrounding matrix by breaking the chemical and secondary bonds between the fibers and the matrix [Aga80, Mal88]. Fiber debonding is more probable to occur than fiber tensile failure when the interfacial bonding is weak and fiber strength is high.
A debonding crack may run at the interface or in the adjacent matrix depending on their relative strengths. In both cases, a new surface is created, which results in an increase in the fracture energy.

When a load is applied, fibers start breaking randomly at various locations due to the statistical distribution of surface flaws [Mal88]. The opening of the matrix crack causes broken fibers to pull out from the surrounding matrix rather than fibers breaking again at the plane of composite fracture [Aga80, Mal88]. Fiber pullouts occur when brittle or discontinuous fibers are used to reinforce a tough matrix. Fiber pullouts occur in the case of fibers whose ends are within a distance of \( L_c/2 \) of the composite fracture surface. Fiber pullout is opposed by friction at the fiber-matrix interface which results in an increase in the fracture energy. For cases when the fiber length (or broken fiber length) is greater than \( L_c/2 \) or the interfacial strength is high, fiber failure or fiber debonding occurs first followed by fiber pullout.

The difference between fiber pullout and fiber debonding is that fiber pullout occurs when a crack initiated at the fiber is unable to propagate into the tough matrix, whereas fiber debonding takes place when a matrix crack is unable to propagate across a fiber [Aga80]. Fiber pullouts are usually accompanied by matrix deformation. In fiber debonding, on the other hand, no matrix deformation takes place. Both mechanisms, fiber debonding and fiber pullouts, significantly enhance fracture energy, and consequently, the toughness of the composite. Figure 4-6 shows fiber debonding and fiber pullouts in a unidirectional continuous fiber composite.
Figure 4-6  Fiber pullouts and debonding in a unidirectional continuous-fiber composite [Aga80]
Fibers break when their fracture strain is reached [Aga80]. When a crack propagates in a direction normal to the fibers, fiber failure will eventually take place for complete separation of the laminate. Brittle fibers have low energy-absorbing capability because they have a low fracture strain. Although fibers are responsible for enhancing the strength of the composite, fiber fracture accounts for only a small fraction of the total energy absorbed.

In order for the fracture of the composite to be completed, the matrix material surrounding the fiber has to fracture [Aga80]. Brittle matrices can undergo only a limited deformation, while ductile matrices can undergo extensive plastic deformation. Both cracking and plastic deformation absorb energy. However, the energy required for plastic deformation is much higher than that for cracking. Therefore, the contribution of ductile matrices to the total absorbed energy is significant, whereas the contribution of brittle matrices is relatively insignificant.
CHAPTER 5
EXPERIMENTAL PROCEDURE

Mullite Sol Preparation

Tetraethyl orthosilicate (TEOS) was used as a precursor for silica, and aluminum-sec-butoxide (ASB) was the precursor for alumina. Two types of solvents were tested for the silica sol: sec-butanol and ethanol, while for alumina sol, only sec-butanol was used as a solvent. It has been observed that there is large difference in the hydrolysis and polycondensation rates between TEOS and ASB [Yol88]. Hydrolysis and polycondensation rates of ASB is much higher than that for TEOS [Yol88]. In order to circumvent the difference in the hydrolysis and polycondensation rates, alumina precursor is not generally hydrolyzed prior to mixing with silica sol while, the silica precursor is partially hydrolyzed. A chelating agent was added to the alumina sol to control hydrolysis and to assist in forming a polymeric sol. Two types of chelating agents were used in the process, triethanolamine (TEA) which is an alkanolamine, and acetylacetone (AcAc) which is a 1,1-diketone.

Figure 5-1 shows the experimental procedure for this study. Alumina sol preparation was done in a controlled environment (drybox) in which the humidity was maintained at very low levels. The controlled environment was needed to prevent the hydrolysis of ASB by humidity. First, the chelating agent and ASB were diluted separately with sec-butanol. Chelating agent/ASB molar ratio (R) was varied
Figure 5-1. Flowchart for the experimental procedure
in different experiments. Second, the chelating agent solution was added drop-wise to the ASB solution which was being stirred vigorously. After adding the chelating agent solution, the solution was stirred for 24 hours to ensure homogeneity.

The silica sol was prepared by diluting TEOS in a solvent. A mixture of DI water and solvent was then added to the solution. The water to TEOS molar ratio was 2. The hydrolysis step was carried out by heating the sol to 60°C for 60 minutes in a water bath and was allowed to cool. Finally, the silica sol was added drop-wise to the alumina sol inside the drybox while stirring. The sol mixture (mullite sol) was stirred for 24 hours to ensure homogeneity. Solution concentrations were selected to yield an 72-75 wt% alumina/28-25 wt% silica composition after heat treatment. Table 5-1 shows the composition of the different sols used.

The mullite sol was condensed by heating to 50°C-60°C and simultaneously applying a vacuum. Condensation was interrupted and the sol was filtered through a 1 micron filter. The filtration step was introduced to remove impurities and, in some cases, precipitates. Precipitate and impurity-free clear sols were required for successful fiber spinning. The sol was further condensed until the rheological conditions for continuous spinnability were achieved.

Fiber Spinning and Aging

The sol with the right rheological conditions was poured into a container inside the spinneret. A cup-shaped spinneret with 40 μm holes was used.
Table 5-1 Sample Identification of Sols Used in this Study with Their Compositions

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Silica Sol Solvent</th>
<th>Chelating Agent</th>
<th>R-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>STO.3</td>
<td>sec-butanol</td>
<td>TEA</td>
<td>0.3</td>
</tr>
<tr>
<td>ETO.3</td>
<td>ethanol</td>
<td>TEA</td>
<td>0.3</td>
</tr>
<tr>
<td>ET1</td>
<td>ethanol</td>
<td>TEA</td>
<td>1.0</td>
</tr>
<tr>
<td>EAO 15</td>
<td>ethanol</td>
<td>AcAc</td>
<td>0.15</td>
</tr>
<tr>
<td>EAO.3</td>
<td>ethanol</td>
<td>AcAc</td>
<td>0.3</td>
</tr>
<tr>
<td>EAO.6</td>
<td>ethanol</td>
<td>AcAc</td>
<td>0.6</td>
</tr>
</tbody>
</table>
nitrogen pressure of 2 - 4 MPa was then applied on the sol inside the sealed spinneret. The fibers extruded from the spinneret were wound on a rotating drum (winder) with 15.2 cm diameter. The fiber spinning rate varied between 9.42 m/min and 42.41 m/min. The spinning rate was controlled by the motor speed. A schematic of the fiber spinning assembly is shown in Figure 5.2.

After completing the spinning process, the fibers were removed from the drum and were placed inside a 100% humidity chamber for aging. Aging was carried in this study using vapor rather than a liquid. Room temperature and high temperature aging were carried out. The room temperature aging was conducted in a sealed plastic box with water containers inside. High temperature aging was conducted in a sealed furnace with water containers inside. Different aging times and temperatures were tested.

**Firing and Characterization**

After aging was completed, the fibers were placed in a furnace on an alumina substrate and heated in air. The fibers were heated to 600°C (5°C/min heating rate) and held for 2 hours to remove organics. Following that, the fibers were heated to 900°C (10°C/min heating rate) and held at that temperature for 30 minutes to complete sintering. The fibers were then heated to 1500°C (15°C/min heating rate) and held for 10 minutes to complete crystallization and densification. Other heating schedules were used in different parts of this study.
Figure 5-2. Schematic of fiber spinning assembly
Various characterization techniques were used in different steps of the process. These include:

- Fourier transform-infrared spectroscopy (FT-IR),
- viscosity measurements,
- thermogravimetric analysis/differential thermal analysis (TGA/DTA),
- x-ray diffraction (XRD),
- chemical (acid) etching,
- sink-float density measurement,
- transmission electron microscopy (TEM),
- scanning electron microscopy (SEM), and
- tensile strength measurement.

The FT-IR was used in transmission to detect hydrolysis in silica sol (i.e., if silanol groups were present). A rotary viscometer was used to measure the viscosity and shear stress change with shear rate for the mullite sol. Viscosity measurements were used to determine sol structure and the conditions for continuous spinnability. Viscosity measurements were also used to determine the effect of different factors (R value, time, etc.) on sol rheology. Organics removal and mullite formation were investigated using TGA/DTA. Determination of the crystalline phases was carried out using XRD. Glass phase detection was carried out by chemically etching fibers. Chemical etching was carried out by immersing the fibers in 52% HF solution for 15 minutes.
Sink-float density measurements on short fibers were used to determine the densification behavior of fibers. Transmission electron microscopy was used to detect the presence of intergranular glass phase. TEM samples were prepared by casting fibers in an epoxy matrix. The body was cut into thin slices, polished down to 100 microns, then thinned further by dimpling and ion milling.

Scanning electron microscopy was used on short fibers to observe the microstructure of fibers prepared under different conditions. This technique was used in combination with chemical etching to determine the presence of a glass phase. It was also used to determine grain growth as a function of time and temperature.

Tensile strength measurements were used to characterize fiber strength after sintering. Single fibers were fixed on a rectangular sheet of paper using wood glue, as shown in Figure 5-3. The center part of the paper was cut out, and the edges were left to hold the sample. After mounting the sample on the tensile test instrument, the paper edges were cut so that the fiber would carry the complete load during the measurement. A gauge length of 1 in was used for the fibers.
Figure 5-3 Schematic of a tensile strength test specimen.
CHAPTER 6
RESULTS AND DISCUSSION

Chapter Outline

This chapter describes the experimental investigation into process development for producing continuously spinnable mullite fibers via the sol-gel process. A discussion of the results of the investigation is presented. The first section deals with the different aspects of the chemical processing of mullite sol components with emphasis on the effect of silica pre-spinning hydrolysis on fiber properties.

In the second section, the results of the rheology study are presented. This study investigates the following:

- effect of solvent content and continuous spinning conditions.
- change of rheological conditions with time
- silica sol solvent effect on mullite sol rheology
- role of R value

The third section discusses the TGA/DTA results for various sols. The effect of aging on properties, mullite formation, and fiber microstructure is discussed in the fourth section. This section also discusses high temperature aging.

The fifth section deals with the densification behavior of fibers and the effect of aging temperature on fiber density. In the sixth and seventh sections, crystalline

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phase determination and glass phase detection results are presented. The eighth section discusses grain growth in mullite fibers as a function of time and temperature. In the ninth section, strength measurement results are presented. In the final section, the results of this study are compared to the results achieved by other investigators.

**Chemical Processing of Mullite Sol**

The effect of different types of solvents on silica sol characteristics and on the final properties of mullite fibers was investigated. The goal was to determine the effect of pre-spinning hydrolysis of silica sol on the properties of fibers spun. The two solvents tested were sec-butanol and ethanol. These two solvents were selected because TEOS has different hydrolysis rates in them. When sec-butanol was used as a solvent, no significant hydrolysis was observed. The FT-IR results for silica sol heated at 60°C for 60 min, as shown in Figure 6-1, indicate that hydrolysis did not take place. The associated 3675 cm\(^{-1}\) absorption band which corresponds to the silanol O-H stretching vibration (indicative of hydrolysis) was not observed. Similar results were observed when the silica sol was heated at 60°C for 2 and 4 hr.

The absence of silanol groups had an adverse effect on the formation of the polymeric structure (which is required for fiber spinning) via polycondensation after mixing with the alumina sol. The mullite sol made from this silica sol was labeled "ST0.3." Fibers drawn from this mullite sol had a very poor green strength. The term "poor green strength" was used to categorize fibers that broke into small pieces prior to firing. The term "good green strength" was used to categorize fibers which
Figure 6-1  FT-IR spectrum for silica sol with sec-butanol solvent heated at 60°C for 60 minutes
maintained integrity before firing. The fibers in which hydrolysis and polycondensation reactions were incomplete were characterized by weak, brittle failure past firing at 1200°C. Poor green strength was a result of the absence of polymeric chains. The poor quality of fired fibers was a result of a poorly connected and homogenized green structure.

Figure 6-2 is a SEM micrograph of a fiber made from the ST0.3 sol with a silica hydrolysis time of 4 hours. As shown in the micrograph, a large whisker-shaped grains and large pores were present. The poor mechanical properties observed for these fibers can be attributed to the microstructure of the fiber, which resulted from the absence of molecular-scale mixing due to the poor hydrolysis of TEOS.

When ethanol (which is normally used in preparing silica sols) was used as a solvent, a pronounced hydrolysis was observed. Results obtained by FTIR for the silica sol heated at 60°C for 60 min showed the presence of the 3675 cm⁻¹ absorption band, as shown in Figure 6-3. The formation of silanol groups, as a result of hydrolysis, is essential to the formation of the polymeric structure produced when mixing with alumina sol. A maximum water/TEOS molar ratio of 2 was required to form the desired polymeric structure. A 3-dimensional network structure is produced at higher water/TEOS molar ratios [Sae87]. Mullite sols made from this silica sol were labeled "ET0.3." Fibers extruded from this mullite sol had good green strength, were flexible, and straight after firing at temperatures above 1200°C.
Figure 6-2. SEM micrograph of a fiber made from STO.3 sol with silica hydrolysis time of 4 hours, fired at 1400°C.
Figure 6-3  FT-IR spectrum for silica sol with ethanol solvent heated at 60°C for 60 minutes.
The good green strength can be explained by considering hydrolysis and polycondensation reactions. The bi-functionality of the partially hydrolyzed TEOS groups (which is a result of using water/TEOS ratio of 2) and the high polycondensation rate of aluminum alkoxide promote the formation of polymeric chains by the polycondensation of partially hydrolyzed silicon atoms and the unhydrolyzed aluminum atoms. The good characteristics of the fired fibers were due to the homogeneity obtained from having extensive hydrolysis and polycondensation reactions. Figure 6-4 shows a SEM micrograph of a mullite fiber made from the ET0.3 sol. The grains were mostly equiaxed and no whisker shape grains were observed.

The difference in the TEOS behavior for the two different solvents can be explained by considering the interchangeability and the hydrolysis resistance of the different alkoxy groups. When sec-butanol is used as a solvent the following reaction takes place:

\[
\text{Si(OCH}_2\text{CH}_3)_4 + x\text{C}_4\text{H}_9\text{OH} \rightarrow \text{Si(OC}_2\text{H}_5)_x + x\text{C}_4\text{H}_9\text{OH} 
\]

The interchangeability of the \( \text{OC}_2\text{H}_5 \) is greater than that of \( \text{OC}_4\text{H}_9 \) [Bra78]. Therefore the concentration of \( \text{OC}_4\text{H}_9 \) ligands increases progressively after mixing. Since the resistance to hydrolysis increases with an increase in length of the alkoxy group [Bra78], a slower hydrolysis is expected when the metal ligand is \( \text{OC}_4\text{H}_9 \) rather than \( \text{OC}_2\text{H}_5 \). When ethanol is used as a solvent, the metal ligand \( \text{OC}_2\text{H}_5 \) does not change, since the interchange of the ligand with the solvent yields the same product as the reactants. Consequently, hydrolysis is faster.
Figure 6-4. SEM micrograph of a mullite fiber from ETO.3 sol with silica sol hydrolysis time of 1 hour, fired at 1500 °C.
when \( \cdot \text{OC}_2\text{H}_5 \) is the metal ligand due to the relative short length of the ethoxy group.

To investigate the possibility of performing hydrolysis after spinning, a silica sol was prepared without water. The silica sol was mixed with an alumina sol and condensed to the proper viscosity for spinning. The fibers spun from the mixed sol were difficult to handle due to very low green strength. This may show that the evolution of an interconnected polymeric structure prior to spinning is necessary to produce good quality fibers.

For all the methods used to prepare the mullite sol, a precipitate free and transparent sol was a prime consideration. The presence of precipitates has a detrimental effect on the continuity of the fiber spinning process since the precipitates flocculate and clog the spinneret holes, impeding the spinning process. Precipitates were formed when water was introduced along with triethanolamine (TEA) to the aluminum-sec-butoxide (ASB) solution, and when water was added to the mullite sol.

It is believed that the formation of precipitates is attributed to the rapid hydrolysis and condensation of ASB:

\[
\text{Al(OC}_2\text{H}_5)_3 + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + 3\text{C}_2\text{H}_5\text{OH} \tag{6.2}
\]

\[
\text{Al(OH)}_3 + \text{Al(OH)}_3 + (\text{OH})_2 \text{Al} - \text{O} - \text{Al(OH)}_2 + \text{H}_2\text{O} \tag{6.3}
\]
Rheology Study

Effect of Solvent Content and Continuous Spinning Conditions

The rheological behavior of the mullite sol as a function of solvent content was investigated. In addition, the rheological conditions for continuous spinning were determined. A variety of viscosity ranges were attained by evaporating solvent during the condensation step. Figure 6-5 shows plots of shear stress versus shear rate and viscosity versus shear rate for the mullite sol ET0.3 which had ethanol as silica sol solvent and TEA as the chelating agent with a chelating agent/ASB molar ratio (R) of 0.3. The three plots shown in Figure 6-5 correspond to three ET0.3 sols with different amounts of solvent removed. The sol with high volume content of solvent exhibited Newtonian behavior (plot 1), in which the viscosity was shear rate independent. This behavior was due to the insignificant interaction between sol clusters.

When the solvent amount was decreased by condensation, the sol exhibited a shear thinning behavior (plot 2), in which the viscosity decreases with increasing shear rate [Sac87]. The decrease in the viscosity with the increase of shear rate can be attributed to the release of the immobilized solvent within clusters after they break [Sac87]. Further condensation resulted in a sol with thixotropic behavior (plot 3). Thixotropic behavior occurs when a three-dimensional network is formed. Solts with thixotropic behavior have an elastic character. After the yield stress is exceeded,
Figure 6-5. Plots of a) shear stress versus shear rate, b) viscosity versus shear rate for ETO.3 sol. Plot 1 corresponds to high solvent content, Plot 2 corresponds to medium solvent content and Plot 3 corresponds to low solvent content.
shear thinning behavior is accompanied by hysteresis [Sac87]. This behavior indicates that the broken network was not recovered when the shear rate was decreased.

It was observed that in order to achieve continuous spinning, slightly shear thinning behavior is required. The sol corresponding to plot (2) exhibited excellent spinnability. Also, the fibers spun from this sol had very good green strength. Sol with thixotropic behavior exhibited poor spinnability but reasonable green strength. On the other hand, sols with Newtonian behavior exhibited reasonable spinnability but broke into small pieces prior to firing. This poor green strength is due to the absence of a continuous structure. These results are also consistent with previous observation for silica sol [Sac87]

Change of Rheological Conditions with Time

The change of rheological behavior of mullite sol aged at 6°C with aging time was studied. Figure 6-6 shows plots of shear stress versus shear rate and viscosity versus shear rate for ET0.3 sols immediately after condensation and 5 days after condensation. It was observed that the viscosity increased with time. However, the shear thinning behavior was maintained. Sol made with acetone (AcAc) as a chelating agent with \( R = 0.15 \) (labeled "EA0.15") exhibited a different behavior. Figure 6-7 shows that EA0 15 sols did not show a significant change in viscosity even after 18 days. However, a change was observed in the viscosity behavior and the sol became highly thixotropic after 18 days. This change in behavior may be attributed to the low R value used in the solution. Small R values generally result in a smaller
Figure 6-6. Plots of a) shear stress versus shear rate, b) viscosity versus shear rate for ETU.3 sol. Plot 1 measurement taken immediately after condensation, Plot 2 measurement taken 5 days after condensation.
Figure 6-7  Plots of a) shear stress versus shear rate, b) viscosity versus shear rate for EA0.15 sol. Plot 1 measurement taken immediately after condensation, Plot 2 measurement taken 18 days after condensation.
fraction of hydrolysis sites being blocked. As a result, hydrolysis and polycondensation can continue and lead to a three-dimensional network with thixotropic behavior.

Silica Sol Solvent Effect on Mullite Sol Rheology

The effect of silica sol solvent on mullite sol rheology was investigated. Figure 6-8 shows the rheological behavior of mullite sols with two different silica sol solvents, sec-butanol and ethanol. The mullite sol made with sec-butanol as silica sol solvent and TEA as chelating agent with R = 0.3 was labeled "ST0.3". This sol showed a Newtonian behavior, while ET0.3, which used ethanol instead of sec-butanol as the silica sol solvent, exhibited shear thinning behavior. These results can be explained by considering the effect of silica sol solvent on the hydrolysis of TEOS that was presented in the preceding section. When sec-butanol was used, no significant hydrolysis was observed. As a result, structure evolution was very limited, and cluster interaction was minimal, which resulted in Newtonian behavior. On the other hand, when ethanol was used, hydrolysis was observed, and cluster growth took place as a result. The breaking of these structures and the release of the entrapped liquid resulted in the shear thinning behavior.

The Role of R Value

The effect of the molar ratio R on the sol rheological behavior was studied using acetylacetone and triethanolamine as chelating agents. When AcAc was used
Figure 6-8  Plots of a) shear stress versus shear rate, b) viscosity versus shear rate for ET0.3 and ST0.3 sols.
as the chelating agent, low values of R (<0.3) resulted in thixotropic sols which gelled readily when exposed to air. On the other hand, high values of R (>0.5) resulted in approximately Newtonian behavior. In addition, precipitate formation was observed in these sols. The optimum R value for continuous spinning and good stability of the sol was approximately 0.3. Figure 6-9 shows that the sol with R=0.3 (EA0.3) exhibits a slightly shear thinning behavior. The figure also shows that sols with R=0.15 (EA0.15) exhibit thixotropic behavior, and sols with R=0.6 (EA0.6) display Newtonian behavior. The thixotropic behavior was a result of the small fraction of hydrolysis sites blocked by the chelating agent, and the Newtonian behavior was a result of the large fraction of blocked hydrolysis sites.

When TEA was used as the chelating agent, similar results were observed. Figure 6-10 shows that for sol ET1, which had a R=1, Newtonian behavior was observed. No precipitate formation was detected in this sol. Sol with R=0.3 (ET0.3) exhibited a slightly shear thinning behavior, and possessed a very good spinnability.

The effect R value has on the behavior of sols with different solvent contents was investigated. Figure 6-11a shows that ET0.3 sol exhibited a change in behavior from Newtonian to shear thinning upon condensation of the sol. Sol with R=1 (ET1) on the other hand did not show any change in the rheological behavior (from Newtonian behavior) upon condensation (Figure 6-11b). This result can be explained by considering the role played by the chelating agent. As mentioned previously, the chelating agent acts as a barrier toward the hydrolysis process by blocking hydrolysis
Figure 6-9 Plots of a) shear stress versus shear rate, b) viscosity versus shear rate for EA0 15, EA0.3, and EA0 6 sols.
Figure 6.10 Plots of a) shear stress versus shear rate, b) viscosity versus shear rate for ET0.3 and ET1 soils.
Figure 6-11. Plots for viscosity versus shear rate for a) ET0.3 sol and b) ET1 sol.
the solvent content was decreased and cluster growth took place. When R = 1, the sites. As R increases, the fraction of available hydrolysis sites decreases. The smaller the fraction of available hydrolysis sites, the more limited the growth of clusters. For the sols with a R = 0.3, the fraction of blocked hydrolysis sites was small. As a result, cluster growth was not restricted. Shear thinning behavior resulted when fraction of blocked hydrolysis sites was large. Consequently, cluster growth was restricted and the behavior remained Newtonian when the liquid content was decreased.

**Thermal Analysis Study**

Thermal analysis study was carried out using simultaneous TGA (thermal gravimetric analysis) and DTA (differential thermal analysis) analyses. Results of TGA/DTA analysis were used to determine the temperature range over which weight loss of fibers took place due to removal of organics and dehydroxylation. In addition, DTA results were used to determine mullite transformation temperature. Figure 6-12 shows TGA/DTA results for fibers from ET0.3 sol aged for 24 hours at room temperature. As shown in the figure, the weight loss ceases at approximately 650 °C. Mullite transformation occurred at about 980 °C, which is shown as the sharp exothermic peak. This mullite transformation temperature is typical for single phase mullite gels.

While chelating agents play a beneficial role in developing the desired rheological characteristics for fiber spinning, they induce other effects during
Figure 6-12. a) TGA and b) DTA results for ET0.3 fibers aged for 24 hours at room temperature.
Figure 6-13  a) TGA and b) DTA results for EA0.3 and ET0.3 fibers aged for 24 hours at room temperature.
subsequent processing. Therefore, the effect of chelating agent on weight loss and mullite formation was investigated using TGA/DTA analysis. Figure 6-13a shows removal of organics was completed at lower temperatures with AcAc than with TEA. At 200°C, the EA0.3 fibers had lost approximately 77% of the total weight loss, while the ET0.3 fibers had lost only 42% of the total weight loss. Removal of organics and hydroxyl groups at low temperatures is important because it reduces the possibility of foaming and residual porosity due to gas entrapment. Foaming, or bloating, can occur if sintering takes place before the complete removal of volatile. Figure 6-14 shows bloating and the presence of porosity in ET0.3 sol fibers that was heated quickly to 1500°C without allowing organics to be removed.

The effect of the chelating agent on mullite transformation was also investigated. As shown in Figure 6-13b, both samples, ET0.3 and EA0.3, have mullite transformation peaks at approximately 980°C. However, the peak intensity is about 8 times larger in the case of AcAc (sample EA0.3). These results indicate a significant enhancement in mullite formation when the AcAc is used. This enhancement in mullite formation may be attributed to more uniform mixing (on a molecular scale) achieved in sols prepared with AcAc.

**Aging Study**

Prior to fiber spinning, the sol is only partially hydrolyzed. Consequently, an aging step following spinning is of significant importance. The aging step aids in completing hydrolysis and polycondensation of the gel, and it can have an influence
Figure 6.14 SEM micrograph for ET0.3 fiber aged for 24 hours at room temperature and fired at 1500°C with heating rate of 15°C/min.
on the properties of the fired fiber. It was observed in this study that fibers that were not aged were curly, brittle, and very weak. These fibers retained a black color, indicative of the presence of residual carbon at temperatures as high as 1100°C.

Figures 6-15 shows the microstructure of a EA0.3 sol fiber that was not aged. The presence of a significant porosity and irregular large grains is evident. The porosity can be attributed to the removal of volatiles at high temperatures rather than low temperatures (below sintering temperature). This can cause incomplete sintering. Figure 6-16 shows weight loss continued above 1000°C for the unaged fibers. The presence of large irregular grains among small equiaxed grains may be attributed to the absence of molecular-scale homogeneity in the gel prior to crystallization. Aging can help in lowering the temperature of volatile removal. Figure 6-16 shows that while volatile removal for unaged fiber continued to above 1000°C, weight loss was ceased at about 600°C for aged fibers. Figure 6-17 shows the microstructure of EA0.3 sol fiber aged at 100°C. The microstructure of the aged fiber does not show the presence of porosity. Also, a majority of the grains were small and equiaxed. No exaggerated grain growth, similar to that in the unaged fiber, was observed.

The role of aging time on mullite formation was investigated. Figure 6-18 shows DTA results for ET0.3 sol fibers with different aging treatments. For unaged fibers, the 980°C peak was not detectable. Fibers aged for 5 hours exhibited a small exothermic peak at temperature slightly above 980°C, and a larger peak was detected for fibers aged for 24 hours. Both samples were aged at room temperature.
Figure 6-15  SEM micrographs for unaged EA0.3 fiber fired at 1500°C for 10 min.
Figure 6-16. TGA results for aged and unaged ET0.3 fibers.
Figure 6-17  SEM micrograph of an EA0.3 fiber aged at 100° with no hold time and sintered at 1500°C for 10 min.
Figure 6-18. DTA results for ET0.3 fibers with different aging times.
These results indicate that longer aging times enhance mullite formation. These results can also be explained in terms of fiber homogeneity. Absence of micro-scale homogeneity resulted in an undetectable mullite transformation for the unaged fibers because of the lack of local stoichiometry at the reaction temperature. The enhancement in the mullite formation with increasing aging time can be attributed to the improvement in the micro-scale homogeneity. This improvement in homogeneity is a direct result of hydrolysis and polycondensation reactions taking place during aging.

The role of aging temperature on fiber microstructure was studied. It was observed that aging temperature had an important effect on fiber grain size. High aging temperatures produced smaller grain sizes. Figure 6-19 shows the microstructure of room temperature aged ET0.3 sol fibers (24 hr aging time), and the microstructure of the same fibers aged at 100°C (with no hold time). A significant difference in the grain size was observed. Similar microstructure was attained for EA0.3 sol fibers aged at 100°C (Figure 6-20). Fibers from EA0.3 sol aged at 80°C showed a significantly larger grain size (Figure 6-21).

Upon examination of both types of fibers aged at 100°C, the EA0.3 fibers (that were made with AcAc as the chelating agent) were found to be strong and flexible, while ET0.3 sol fibers (that were made with TEA as the chelating agent) were weak and brittle. Density of the ET0.3 fibers was 2.7 g/cm³ while the density of EA0.3 fibers was 3.1 g/cm³. Examination of ET0.3 fiber ends showed a significant separation between an outside tabular shell and an inside fiber core.
Figure 6-19. SEM micrographs of ET0,3 fibers a) aged at room temperature for 24 hours b) aged at 100 °C with no hold time. Both fibers were sintered at 1500 °C for 10 min.
Figure 6.20  SEM micrograph of an EA0.3 fiber aged at 100°C with no hold time and sintered at 1500°C for 10 min.
Figure 6-21. SEM micrograph of an E0.3 fiber aged at 80°C with no hold time and sintered at 1500°C for 10 min.
This structure resulted in the poor mechanical properties of these fibers. Figure 6-23 shows a uniform microstructure across the fiber and the absence of large pores in EA0.3 fibers.

These results can be attributed to the difference in the aging (hydrolysis and polycondensation) rate between the two fibers. Fibers made with AcAc as a chelating agent complete aging faster than fibers made with TEA. The variation in the extent of aging across the fiber in the case of ET0.3 fibers resulted in a dense outside shell and a porous inside core. In contrast, EA0.3 fibers did not show a difference in the microstructure across the fiber, since no significant variations in aging existed. These results indicate that AcAc is a better choice of chelating agents if high temperature aging is to be used.

Maintaining a constant aging temperature, the effect of R value on grain size was investigated. Fibers from sols EA0.3 and EA0.6 (corresponding to R=0.3 and R=0.6 respectively) were aged at 80°C and fired at 1500°C. A comparison between Figures 6-21 and 6-24 show that EA0.3 fibers had a significantly larger grain size than EA0.6 fibers. The small grain size of the EA0.6 fibers was a result of the chelating agent's effect on hydrolysis. High R values resulted in a smaller fraction of hydrolysis sites, and consequently, a smaller fraction of polycondensation sites. The small fraction of polycondensation sites restrained cluster growth in the sol. As a result, small grains were produced upon firing.

High temperature aging has the following advantages when used in processing of EA0.3 fibers:
Figure 6.22  SEM micrograph of ET0.3 fibers aged at 100°C with no hold time and sintered at 1500°C for 10 min.
Figure 6-23  SEM micrograph of an EA0.3 fiber aged at 100°C with no hold time sintered at 1500°C for 10 min.
Figure 6-24  SEM micrograph of an EA0 6 aged at 80°C with no hold time and sintered at 1500°C for 10 min.
- improves reaction kinetics, and as a result, aging time can be reduced. This point is crucial when considering a continuous spinning process.
- improves micro-scale homogeneity, and as a result, fibers are produced with relatively small grain size. Small grain size fibers are desirable when achieving high strength is required

**Densification Study**

Apparent density measurements were carried out for the EA0.3 and ET0.3 fibers aged at room temperature for 24 hours and fired at different temperatures with a heating rate of 10°C/min. Figure 6-25 shows the densification behavior for both types of mullite fibers. The error bars were not shown in the figure due to the very small value of the standard deviation (σ = 0.00177). At temperatures below 800°C, EA0.3 fibers had lower density than ET0.3. This may be a result of the removal of organics at a lower temperature as was the case for EA0.3 fibers, as discussed earlier.

Significant increase in the density occurred in both samples above 800°C due to viscous flow sintering. The sintering rate was faster for the EA0.3 fibers. At a temperature of 1000°C, EA0.3 reached about 96% of its final density, while the ET0.3 fibers reached approximately 90% of final density. Figures 6-26 and 6-27 show polished sections of EA0.3 and ET0.3 fibers fired at 1500°C. Some porosity was observed in the ET0.3 fiber, but none was observed in the EA0.3 fibers. Figure 6-28 shows an unpolished section of ET0.3 fiber with large pores present.
Figure 6-25  Densification curves for EA0.3 and ET0.3 fibers aged for 24 hours at room temperature
Figure 6-26. SEM micrograph for a polished-cross section of EA03 fiber sintered at 1500°C for 10 min.
Figure 6-27  SEM micrograph for a polished cross section of ET0.3 fiber sintered at 1500°C for 10 min
Figure 6-28  SEM micrograph of an ET0.3 fiber sintered at 1500°C for 10 min.
It was observed that the final apparent density depends on aging temperature. Fibers aged at 80°C and 100°C had apparent densities of 2.9 and 3.1 g/cm³, respectively after sintering at 1500°C for 10 min. This change in density with aging temperature is attributed to the extent of aging reached at a certain temperature. The higher the aging temperature, the higher the vapor pressure. Also, aging reaction kinetics are enhanced at high temperatures. Therefore, high aging temperatures produce fibers with less organic content, and consequently, less organic material was removed during firing providing higher densities.

**Crystalline Phase Determination**

Crystalline phase determination was carried out using X-ray diffraction (XRD). The XRD pattern for pure mullite powder shown in Figure 6-29 was used as a reference to determine if mullite was the only phase formed in the fibers. Fibers from EA0.3 and ET0.3 sol were fired at 1000°C, which is slightly above the exotherm observed in the DTA curve. Both samples showed patterns (Figure 6-30 and 6-31) identical to the pure mullite pattern shown in Figure 6-29. Fibers from the same sols were fired at 1500°C and showed patterns identical to the ones in Figures 6-30 and 6-31. These results show that there was no phase transformation above 1000°C from another crystalline phase to mullite. The results indicate that the 980°C exotherm corresponds to mullite formation, and that mullite was the only crystalline phase present. The positions of XRD peaks and their intensities for ET0.3 fibers fired at 1500°C, for pure mullite powder, and for the standard ASTM peaks are presented in Tables 6-1, 6-2, and 6-3. The results shown in Tables 6-1 and 6-2 indicate that
Figure 6-29  XRD pattern for pure mullite powder
Figure 6-30. XRD pattern for EA0.3 fibers fired at 1000°C.
Figure 6-31. XRD pattern for ET0.3 fibers fired at 1000°C.
Table 6-1  Positions of XRD peaks and their intensities for ET0 3 fibers

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Table 6-2  Positions of XRD peaks and their intensities for pure mullite powder

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<td>52.64</td>
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<tr>
<td>6</td>
<td>35.348</td>
<td>75.42</td>
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<tr>
<td>7</td>
<td>37.095</td>
<td>18.05</td>
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<tr>
<td>8</td>
<td>39.328</td>
<td>28.90</td>
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<td>9</td>
<td>40.953</td>
<td>100.00</td>
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<td>10</td>
<td>42.670</td>
<td>34.84</td>
</tr>
<tr>
<td>11</td>
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<td>17.10</td>
</tr>
<tr>
<td>14</td>
<td>53.933</td>
<td>28.90</td>
</tr>
<tr>
<td>15</td>
<td>57.645</td>
<td>35.28</td>
</tr>
<tr>
<td>16</td>
<td>58.415</td>
<td>13.30</td>
</tr>
</tbody>
</table>
Table 6-3  Positions of XRD peaks and their intensities for the standard ASTM peaks:

<table>
<thead>
<tr>
<th>Peak Number</th>
<th>Angle (Degree)</th>
<th>Intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16.432</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>23.554</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>25.971</td>
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<td>26.267</td>
<td>100</td>
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<tr>
<td>5</td>
<td>30.960</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>33.228</td>
<td>40</td>
</tr>
<tr>
<td>7</td>
<td>35.278</td>
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<td>38.992</td>
<td>4</td>
</tr>
<tr>
<td>10</td>
<td>39.276</td>
<td>20</td>
</tr>
<tr>
<td>11</td>
<td>40.874</td>
<td>60</td>
</tr>
<tr>
<td>12</td>
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<td>21</td>
<td>57.561</td>
<td>20</td>
</tr>
<tr>
<td>22</td>
<td>58.412</td>
<td>12</td>
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</tbody>
</table>
mullite fibers peaks match all mullite powder peaks with very small difference in peak position (maximum difference in peak position = 0.09°). Comparing Table 6-3 to Table 6-1, all peaks with intensity > 8 in the ASTM file matched the mullite fiber peaks with very small difference in peak position (maximum difference in peak position = 0.09°).

**Glass Phase Detection**

The presence of an intergranular glass phase in mullite fibers can result in detrimental effects on high temperature properties of the fibers. The intergranular glass phase causes a deterioration in the creep resistance of the fibers, this limits their use at high temperatures. Since the main application for mullite fibers is at high temperatures, production of glass-free mullite fibers is crucial.

Two techniques were used for glass phase examination, chemical etching and transmission electron microscopy (TEM). The chemical etching technique is based on the large difference in the dissolution rate of the siliceous glass phase and mullite in hydrofluoric acid (HF). The silica phase dissolves readily in HF while mullite has a very low dissolution rate [Sac79]. The chemical etching experiments were carried out by immersing fibers in 52% HF solution for 15 minutes. Micrographs were taken using SEM before and after the etching treatment to determine if there were differences in the microstructure. Fibers produced by the processes developed in this study were compared to commercially available mullite fibers.

Figures 6-32a,b and 6-33a,b show ET0.3 and Nextel 480 fibers before etching at different magnifications. Figures 6-34a,b and 6-35a,b show the fibers after the
Figure 6-32. SEM micrograph of an ET0.3 fiber before etching a) at 2000X and b) at 15000X.
Figure 6-33 SEM micrographs for a Nextel 480 fibers before etching a) at 2000X and b) at 15000X.
Figure 6-34 SEM micrograph for an etched ET0.3 fiber a) at 2000X and b) at 15000X.
Figure 6-35  SEM micrograph for etched Nextel 480 fibers a) at 2000X and b) 15000X.
etching treatment. No detectable difference was observed in the microstructure of ET0.3 fibers after etching, indicating that there was no significant amount of glass phase present. In contrast, Nextel 480 fibers exhibited a significant difference in the microstructure after etching. The etched Nextel 480 fibers showed a network of porosity that resulted from the dissolution of the glass phase. These results indicate that Nextel 480 fibers contain a large amount of glass phase. Figure 6-36 shows the microstructure of an etched Altex fiber produced by Sumitomo company. Altex fibers contain 15 wt% silica and 85 wt% alumina. Although the Sumitomo fiber composition has a lower silica content than the fibers produced in this study, the etching treatment resulted in the dissolution of an intergranular glass phase, as shown in Figure 6-36. Results for EA0.3 fibers were similar to those obtained for ET0.3 fibers. Figure 6-37 indicate that there was no detectable amount of glass phase present in these fibers.

Micrographs taken by TEM confirmed the results achieved by chemical etching for ET0.3 fibers. Figures 6-38 and 6-39 show that no glass phase was present at the grain boundaries or at the triple junction points. Fibers made with sec-butanol as the silica solvent (ST0.3 sol) which, as mentioned previously, had a poor homogeneity, showed the presence of an intergranular glass phase Figure 6-40. It was observed in this study that the absence of molecular-scale homogeneity of the gel may lead to the presence of an intergranular glass phase.
Figure 6-36  SEM micrograph of an etched Altex fiber at 15000X.
Figure 6-37. SEM micrograph of an etched EA0.3 fiber at 15000X.
Figure 6.38. TEM micrograph of an ETO,3 fiber at 200,000X. Samples were prepared and micrographs were taken by A. Morrone.
Figure 6-39. TEM micrograph of an ET0.3 fiber at 1500,000X. Samples were prepared and micrographs were taken by A. Morrone.
Figure 6-40  TEM micrograph of ST0.3 fibers at 100,000X. Samples were prepared and micrographs were taken by A. Morrone.
Grain Growth Study

Grain growth can result in detrimental effects on fiber strength if large grains are produced. The strength of polycrystalline ceramics is inversely proportional to the grain size [Km79]. Since mullite fibers are primarily used at high temperatures, grain growth is expected due to the strong dependency of grain growth on temperature. The grain growth follows the Arrhenius equation [Km79]

\[ U = U_0 \exp \left( -\frac{Q}{kT} \right) \]

where \( U \) = growth rate, \( U_0 \) = constant, \( Q \) = activation energy for grain growth, \( k \) = Boltzmann constant, \( T \) = temperature.

The change in the grain size as a function of temperature and time was examined. The grain size was measured using SEM. To measure the grain growth as a function of temperature, EA0.3 fibers (pre-sintered at 1500°C) were annealed at different temperatures, but with constant annealing time (1 hour). The results are presented in Figure 6-41. The figure shows that up to 1400°C, there was no measurable increase in grain size for 1 hour hold period. However, a significant increase in the grain size was observed at 1500°C.

The grain growth as a function of time was investigated using EA0.3 fibers (pre-sintered at 1500°C). The fibers were annealed at 1200°C for different periods of time. Figures 6-42 and 6-43 show the change in the grain size with annealing time at 1200°C and 1400°C. No significant change in the grain size was observed even
Figure 6-41 Grain size versus annealing temperature for EA03 fibers (pre-sintered at 1500°C) with 1 hour annealing time.
Figure 6-42  Grain size versus annealing time for EA0.3 fibers (pre-sintered at 1500°C) with annealing temperature of 1200°C.
Figure 6-43. Grain size versus annealing time for EA0.3 fibers (pre-sintered at 1500°C) with annealing temperature of 1400°C.
for annealing times as long as 12 hours at 1200°C. However, for annealing temperature of 1400°C, grain growth was observed after annealing time of 8 hours. These results show that the process for grain growth has a high activation energy so that time-dependent growth is not observed at temperatures up to 1200°C. A significant change occurs in 1 hour at 1500°C or in 8 hours at 1400°C.

Tensile Strength Measurements

The tensile strength of ET0.3 and EA0.3 fibers was measured. Both types of fibers were sintered at 1500°C. However, ET0.3 fibers were aged for 24 hours at room temperature, while EA0.3 fibers were aged at 100°C with no hold time. Many of the ET0.3 and EA0.3 fibers failed near the area where the glue was applied. No strength values were reported for these fibers as the results were not representative of the tensile strength of the fiber. Results are reported only for fibers that failed at regions other than the glue interface.

The tensile strength of fibers was calculated by this equation

\[ \sigma_f = \frac{P}{r^2\pi} \]

where \( \sigma_f \) = tensile strength, \( P \) = applied tension force at fracture, and \( r \) = fiber radius. Fiber diameters were 15-25 microns for ET0.3 fibers and 11-20 microns for EA0.3 fibers.
The measured tensile strengths for the two types of fibers were as follows:

- For ET0.3 fibers: $\sigma_t = 0.26$ GPa
  
  number of samples = 27
  number of samples that broke at the middle during testing = 5
  standard deviation = 0.05

- For EA0.3 fibers: $\sigma_t = 0.44$ GPa
  
  number of samples = 20
  number of samples that broke at the middle during testing = 3
  standard deviation = 0.1

Only the samples that broke in the middle were taken into account in measuring the fiber strength and the standard deviation. The difference in the tensile strength can be attributed to the difference in grain size and porosity. The average grain size of ET0.3 fibers was about 1.23 microns, while the average grain size for EA0.3 fibers was 0.37 micron. Also, it was shown in a previous section that ET0.3 fibers exhibited some porosity due to the high temperature required for organics removal. The EA0.3 fibers did not exhibit porosity. Preliminary measurements on EA0.3 fibers sintered at 1200°C yielded tensile strength data as high as 1.15 GPa. This is presumed to result from an even smaller grain size.
Comparison Study

In this section, the results achieved in this study are compared to the results reported previously in the area of sol-gel processing of mullite as well as processing of mullite fibers. It was shown in this study that there was a single phase transformation that occurred at 980°C to form mullite. Some previous studies showed more than one phase transformation before forming mullite.

- Prochazka and Klug results showed a phase transformation at 950°C to form $\gamma$-Al$_2$O$_3$ or spinel, and another phase transformation at 1200°C to form mullite [Pro83].

- Pask and co-workers results showed a phase transformation at 1000°C to spinel followed by transformation to mullite at 1200°C [Pas87].

- Richards and co-workers results indicated a phase transformation at 870°C to spinel followed by transformation to mullite at 1295°C [Ric91].

One of the main objectives of this study was to produce single phase mullite fibers with no intergranular glass phase. Results indicate this objective was achieved. However, other studies reported the presence of more than one phase:

- Pask and Ismail showed the presence of a glass phase [Pas87, Ism87].

- Hulling and Messing showed the presence of tetragonal mullite and glass phases [Hul89].

- Wei and Halloran showed that mullite produced contained alumina particles [Wei88b].
Schneider and co-workers indicated the formation of $\gamma$-$\text{Al}_2\text{O}_3$, cristobalite and mullite in the system they studied [Sch92].

Sonuparlak showed the presence of spinel and glass phase [Son88].

Tests of commercial Nextel fibers conducted in this study showed an appreciable glass phase.

Production of fibers with equiaxed grains was achieved in this study. Previous studies carried out by Mroz and Laughner and Li and Thomson produced acicular grains [Mro89, Li91b, and Kim93]. The grain size of fibers produced in this study (EA0.3 fibers) was 0.37 microns compared to the 2-4 micron grain size produced by Yoldas and Partlow [Yo188].

Venkatachami and co-workers were able to produce single phase mullite fibers with small equiaxed grains. However, these fibers were short because continuous spinnability could not be achieved [Ven90]. In this study, continuous spinning of fibers was achieved. Tucker and co-workers were able to produce mullite fibers. However, fiber diameters were large (110 microns), the fibers were brittle, exhibited porosity and microcracks [Tuc90]. Fibers produced in this study (EA0.3) had small diameter (10-20 micron). These fibers were flexible and did not have porosity or microcracks. Mullite fibers produced by Kim and co-workers had needle-like grains compared to equiaxed grains achieved in this study [Kim93]. No reference for grain size, fiber diameter, or fiber strength was found in Kim’s work. Also, the presence of an intergranular glass phase was not investigated.
A process was developed to produce continuous mullite fibers. The conditions to achieve continuous spinnability and the factors that affect the rheological behavior of mullite sol were determined. The optimum value for chelating agent/alumina precursor molar ratio was determined. Also, the effects of changing the chelating agent on organics removal, mullite formation, fiber aging, fiber densification, and fiber microstructure were investigated. The role of aging in mullite transformation and its effect on the properties and microstructure of fibers were determined. In addition, the effect of aging temperature on properties and microstructure was obtained. The fibers were tested to determine if there was an intergranular glass phase and were compared to commercial mullite fibers. The grain growth was determined as a function of time and temperature.

Conclusions

The following conclusions were drawn from the work done during this study:

- The conditions for continuous spinnability of mullite sol were determined. Continuous spinnability was achieved when the sol flow behavior was slightly shear thinning.
- Sol viscosity increased significantly with time but flow behavior remained...
the same for sols with moderate values of $R$ ($R=0.3$). For low values of $R$ ($R<0.3$), viscosity did not change significantly, but flow behavior was altered

- Shear thinning behavior was observed when silica hydrolysis occurred, and Newtonian behavior was observed when silica hydrolysis did not occur

- Sols with low $R$ values exhibited thixotropic behavior, while those with intermediate and high $R$ values exhibited shear thinning and Newtonian behavior, respectively.

- Change of solvent content resulted in a change in flow behavior for sols with moderate $R$ values ($R=0.3$), but it did not result in a change in behavior for sols with high $R$ values ($R=1$)

- Pre-spinning hydrolysis of silica sol was important to achieve good strength for green fibers and good microstructure for sintered fibers. Also, pre-spinning hydrolysis of silica sol aided in avoiding the formation of an intergranular glass phase

- Lower temperature of organics removal and significantly enhanced mullite transformation were achieved when AcAc was used as a chelating agent.

- Fiber aging was shown to be crucial in attaining quality fibers. Un-aged fibers showed significant porosity and large irregular grains, while aged fibers did not show the presence of porosity and the grains were equiaxed and small

- Aging assisted in enhancing mullite formation.

- The grain size increased with increasing aging temperature

- Fiber density increased with increasing aging temperature
• Fibers made with AcAc aged more efficiently at high temperatures than those made with TEA.

• The densification rate was higher for fibers made with AcAc than those made with TEA.

• Mullite was the only crystalline phase present above 1000°C.

• Neither fibers made with TEA nor fibers made with AcAc showed the presence of an intergranular glass phase.

• Intergranular glass phase was present when pre-spinning hydrolysis of silica was not accomplished.

• Commercial mullite fibers showed the presence of intergranular glass phase.

• Grain growth was not significant for temperatures up to 1400°C.

• Grain growth was not significant for periods as long as 12 hours at 1200°C

Future Work

Although extensive research has been conducted on the processing of mullite fibers, additional research is proposed in several areas. These include:

• Examine different techniques to inhibit grain growth in mullite fibers.

• Investigate the possibility of using the microwave energy in processing of mullite fibers. This study could include
  • measure the dielectric properties of fibers at different temperatures,
  • design microwave cavities for the different processing stages (i.e., organics removal, dehydration, and sintering),
- study the change in reaction kinetics compared to conventional heating, and
- examine the effect of microwaves on: drying and organics removal, sintering, mullite transformation, and grain growth.
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<table>
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<th>Reference</th>
<th>Authors</th>
<th>Title</th>
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BIographiesKetch

Salwan Al Assafi was born in Baghdad on November 14, 1965. He was raised in Hay Al-Adil on the western side of Baghdad. In 1983 he was admitted to the University of Mosul and majored in mechanical engineering. In 1984 he transferred to the University of Baghdad where he continued his studies in mechanical engineering. In 1986 Salwan was selected to continue his education in the Department of Nuclear Engineering. He completed his undergraduate studies in 1988, receiving a bachelor of science degree in nuclear engineering. In 1989 he was awarded a government scholarship to continue his graduate education in the United States. He was admitted to the University of Florida in May of 1990 where he joined Dr. Clark's ceramic processing group. His research focused on the microwave joining of alumina ceramics with alumina gels and he was awarded his Master of Science degree in May, 1992. Salwan joined Dr. Simmons' research group in 1992 where his studies focused on processing of continuous mullite fibers prepared using sol-gel techniques. He is a member of the American Ceramic Society, the National Institute of Ceramic Engineers and Keramos, the ceramic engineering honor society. His hobbies include racquetball, tennis, bowling and travel.
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality as a dissertation for the degree of Doctor of Philosophy.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality as a dissertation for the degree of Doctor of Philosophy.

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