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26<sup>th</sup> Annual Conference on Composites, Advanced Ceramics, Materials, and Structures: B

> Hau-Tay Lin Mrityunjay Singh Editors

January 13–18, 2002 Cocoa Beach, Florida

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*Cover image*: SEM micrographs of carbon preforms from: A) cork, B) bamboo, C) beech, D) Spanish oak (axial), E) Spanish oak (longitudinal), and F) red eucalyptus. Image from F.M. Varela-Feria, M.J. López-Robledo, J. Martínez-Fernández, A.R. de Arellano-López, and M. Singh, "Precursor Selection for Property Optimization in Biomorphic SiC Ceramics," which begins on page 681.

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# Preface

The 26th Annual Cocoa Beach Conference and Exposition, an international meeting on advanced ceramics and composites, was held January 13-18, 2002. The conference attracted more than 450 attendees from 24 different countries. During the meeting, more than 385 technical papers covering a wide range of advanced ceramics topics were presented in nine topical focused areas and three symposia. Professor Victor Greenhut of Rutgers University, New Jersey, presented the 2002 James Mueller Lecture, the highest award granted by the Engineering Ceramics Division of The American Ceramic Society (ACerS). Professor Nils Claussen, Technical University of Hamburg-Harburg, Germany, delivered the Engineering Ceramics Bridge Building Award lecture.

We would like to thank the symposia and focused topical session organizers, session chairs, presenters, and conference attendees for their dedication, efforts, and enthusiasm in planning and participating in a vibrant and leading edge conference. Once again, "Cocoa Beach" has demonstrated why it is the premier conference on advanced ceramics and composites in the world. Also, a special thanks is extended to the ACerS staff for keeping things running smoothly.

The 199 technical presentations accepted for publication in the conference proceedings following a peer-review process are a tribute to this excellent meeting. These papers are included as issues 3 and 4 in Volume 23 of the *Ceramic Engineering and Science Proceedings*. Issue 3 includes papers under the broad topical headings of processing and thermomechanical property characterization; design, modeling, and reliability; impact testing and damage; ceramic matrix composites; processing and properties of fuel cells; and brazing and joining of ceramics. Issue 4 covers advanced processing, product development, and commercialization; engineering porous materials; diamond, wear resistant, and protection coatings; thermal and environmental barrier coatings; nanocrystalline materials and biomimetics; biomaterials; and functional ceramics. Subtopics for each of the areas are included in the appropriate Table of Contents.

We hope you find these papers technically stimulating and look forward to seeing you at "Cocoa Beach 2003".

Mrityunjay Singh Hua-Tay Lin

Advanced Processing, Product Development, and Commercialization

#### WATER-BASED TAPE CASTING WITH LATEX BINDERS

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## ABSTRACT

Water-based systems are the trend of the future in tape casting as well as in many other applications. One advantage of water-based systems is that the solvent is much easier to handle without risks of intoxication, explosions or fire. Some difficulties in using water-based systems in tape casting are that the tapes are more prone to cracking during drying and that the evaporation of water is slower. The solution to these problems is good dispersion and increased solids loading, which reduces the tendency to cracking and the amount of water that must be evaporated. Water-soluble binders tend to increase the viscosity of the suspension. Latexes, i.e. dispersions of non-water soluble polymer particles in water, have a less pronounced effect on the viscosity of the suspension. By using latex binders it is possible to develop water-based systems that have low viscosity and good casting properties. Tapes with latex binders are easy to laminate. If latex with a glass-transition temperature below room temperature is chosen it is possible to laminate the tapes at room temperature. Natural starches consist of particles with narrow size distributions and equiaxed shapes. These starches are easy to disperse in water and compatible with the latex binders. By laminating and sintering tapes with and without starches it has been possible to create dense/porous structures with crack-deflecting properties. These structures have been shown to have excellent damage resistance to thermal shock.

# INTRODUCTION

Whenever it is possible organic solvents are being replaced by water in all modern industrial processes. One advantage of water-based systems is that water is much easier to handle than an organic solvent without risks of intoxication, explosions or fire. Water-based systems generally have less impact on the general environment and are often less expensive.

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Although the benefits are great there are difficulties in changing to waterbased systems. Some of the possible problems that have been reported in the literature are foaming, presence of fisheye defects, cracking during drying and sintering, brittleness, viscosity problems, and difficulties in forming smooth green sheets [1]. Many of these problems are easy to solve. The main remaining difficulties are tape casting powders that react with water and cracking problems during drying of thick tapes. It has been shown that it is possible to tape cast ceramic powders that react with water in water. Hotza *et al.* [2,3] were able to tape cast AlN by adsorbing a protective layer of octadecanoic acid on the surface of the powder. Ceramic powders that do not react or dissolve can be dispersed in water when a suitable dispersant is found. There are three major groups of binders that have been tested in water-based tape casting: latex binders, cellulose ethers and polyvinyl alcohols (Fig. 1).



Fig. 1. Chemical structure of different binder types for tape casting in water (PVA – polyvinyl alcohol, HPMC – hydroxyethyl methyl cellulose).

#### LATEX BINDERS

Latex can be defined as a stable colloidal dispersion of a polymeric substance in an aqueous medium. Latexes are also referred to as polymer emulsions. The polymer particles have sizes ranging from 30-500 nm and volume fractions between 0.4 and 0.7. The polymer particles are dispersed in water with addition of electrolytes and surfactants. Both natural and synthetic latexes exist but only synthetic latexes are used for tape casting. The polymeric particles are dispersed in water by using surfactants. A surfactant consists of a hydrophilic head group and a hydrophobic tail. On the latex particle the hydrophobic tail is attached to the polymeric surface. The hydrophilic head group extends into the water phase. The hydrophobic tail is often an alkyl group of 8–18 carbon atoms. Surfactants are classified by type: anionic, cationic, nonionic and zwitterionic. The polar groups of anionic surfactants are typically carboxylate COO<sup>-</sup>, sulfate OSO<sub>3</sub><sup>-</sup>, sulfonate SO<sub>3</sub><sup>-</sup> or phosphate PO<sub>3</sub><sup>2-</sup> groups. Anionically stabilized latexes are electrostatically stabilized and as such they may be sensitive to high ionic strength and to polyvalent cations. Anionically stabilized latexes in general have low viscosity.

The polar groups of a nonionic surfactant are typically oxyethylene units  $[O-CH_2-CH_2-]$  with 5–10 units. Similar molecules are used as dispersants but in that case with much longer oxyethylene chains. The tail and head group are of a similar size. Nonionically stabilized latexes can tolerate high ionic strength and polyvalent ions as they are sterically stabilized. However, they may show temperature-dependent properties. When temperature is increased the solubility of the polar group decreases. This leads to a destabilization and hence flocculation of the latex.

## **Cellulose Ethers**

Unmodified cellulose polymer is insoluble in water. If the cellulose is modified so that hydroxyl groups are substituted for hydroxyethyl, methyl carboxymethyl or hydroxypropyl side groups (forming cellulose ethers) the polymer will be more soluble. The increased solubility comes from the bulkiness of the side groups that reduces the hydrogen bonding that normally takes place between the cellulose polymer molecules. The backbone of all cellulose type of polymers is much more inflexible than, for example, vinyls or acrylics. This means that the polymer is more outstretched in solution. This results in rather high viscosity solutions, and cellulose ethers are often used as thickeners because of this property. Nevertheless, the cellulose ethers have been used for tape casting. Chartier and Bruneau used hydroxypropylmethyl cellulose as a binder for tape casting of alumina [4] and Burnfield and Petersen [5] used hydroxyethyl cellulose instead. In both cases the green strength.

#### **Polyvinyl Alcohol**

Commercial polyvinyl alcohol (PVA) is often a mixture of polyvinyl alcohol and polyvinyl acetate. Hydrolyzing the polyvinyl acetate produces the alcohol. The degree of hydrolysation is often in the range of 87-89% and the PVA is then called partially hydrolyzed. The fully hydrolysed PVA has a degree of hydrolysation of 98-99%. The solubility in water increases with the number of acetate groups as a result of the weakening of the hydrogen bonding. Glasstransition temperature and tensile strength are lowered with a lower degree of hydrolysation. PVA is a common binder in pressing ceramics but it has also been used for tape casting [6]. In order to use PVA for tape casting it has to be plasticized. Common plasticizers for PVA include glycerol, polyethylene glycol and polypropylene glycol.

#### EXPERIMENTAL

A continuous tape caster (TC155 from AEM Inc.) with a stationary head was used in the experiments. This tape caster was specially designed to make thin tapes in the range of 4 to 400  $\mu$ m. Casting rates in the range of 10 to 50 mm/s were used. These casting rates correspond to total drying times of 1.3 to 6.2 min. The materials used are listed in Table I.

Material	Grade and Producer	Particle size [µm]	
Ceramic Powder			
Al <sub>2</sub> O <sub>3</sub>	AKP30, Sumitomo	0.4	
Al <sub>2</sub> O <sub>3</sub>	AKP50, Sumitomo	0.2	
Al <sub>2</sub> O <sub>3</sub>	AA04, Sumitomo	0.4	
$Al_2O_3$	AA2, Sumitomo	2	
$Al_2O_3$	A16SG, Alcoa	0.5	
ZrO <sub>2</sub>	DK4, Mandoval	1.5	
Mullite	SACR 193 Baikowski Chimie	2.3	
SiC	HSC059S, Superior Graphite	0.6	
SiC	A10, HC Starck	0.6	

Table I. Ceramic powders, binders and dispersants used in the experiments.

Binder		
Material	Grade and producer	Specifications
		Anionic, particle size 100–200
Acrylic-styrene latex	DM765, Perstorp Clariant	nm, $T_g - 16$ °C
		Nonionic, particle size $< 300$
Acrylic-styrene latex	LDM 7651, Perstorp Clariant	nm, $T_g = 10$ °C
A amilia atamana latav	DM76() Perstorn Clariant	Nonionic, particle size $20-200$
Act ync-styrene ratex	DM700, Perstorp Clariant	Anionic, particle size 370 nm.
Acrylic latex	B1035, Rohm and Haas	$T_{\rm g}$ –40 °C
		Anionic, particle size 320 nm,
Acrylic latex	B1001, Rohm and Haas	$T_g -6 °C$
Polyvinyl alcohol	KH17S, Nippon Gohsei	Degree of hydrolysis 80 %
Hydroxypropylmethyl		
cellulose	F4M, Dow	Mw 86000
Dispersant		
Polyacrylic acid	Dispex A40, Allied Colloids	Mw 10000, counter ion $NH_4^+$
Polyacrylic acid	D3021, Rohm and Haas	Mw 5000, subst. alkyl groups, counter ion NH4 <sup>+</sup>
Lignosulphonate	Wargonin Extra, Lignotech	Anionic PE, particle size 5 nm

# RESULTS

# **Comparing Binders**

Different types of binders were compared by measuring viscosity of slips at varying solids loading. The viscosity of the binder dissolved in water strongly influenced the viscosity of the tape casting slip. Slips with polyvinyl alcohol (PVA) and hydroxypropylmethyl cellulose (HPMC) had significantly higher viscosity (Fig. 2) [7]. To be able to use both PVA and HPMC in tape casting they must be used at much lower solids content. This means that much more water must be dried away during tape casting. To instead use a latex binder at a much higher solid contents increases the possible casting rate, reduces the cracking problems and decreases the energy consumption for drying in a large-scale production.

## Using latex binders in tape casting

Latex binders were found to be very useful for a range of ceramics. The viscosity of the latex will also affect the suspension (Fig. 3) [8,9]. Latexes are normally very low in viscosity since they are composed of particles rather than dissolved long molecules. The solids volume fraction (before addition of the latex particles) can range from 0.35 to 0.55. The viscosity of such slurries varies over a considerable range. The viscosity of the latexes also varies and this means that the

viscosity of the tape-casting suspension can be either unaffected or affected by the latex addition. Fig. 4 shows the viscosity range for the whole range that can be used to make good ceramic tapes. Below this range there is a tendency to form single droplets instead of wetting the whole tape, whereas above this viscosity there is a risk of producing uneven surfaces.



Fig. 2. Viscosity measurements of an alumina slip (A16SG) with a range of binders.



Fig. 3. Viscosity of alumina suspensions with and without latex binder at a volume fraction of 0.50 and 0.55 (alumina AKP30, latex Duramax B1035, dispersant Duramax D3021).



Fig. 4. Viscosity range that has been found useful for tape casting.

#### Optimizing dispersion with latex binders

Measurements on alumina powder at a solids loading of 0.50 and 0.55 showed that 0.2wt% added dispersant gave the lowest viscosity (around 1 Pa-s at 1 s<sup>-1</sup>,  $\phi = 0.55$ ). When an anionic latex was added an increase in viscosity could be observed at 0.2wt% addition. By increasing the dispersant concentration the viscosity could be reduced to approximately the same level as the slip without latex addition (Fig. 5). For the nonionic latex the increase in viscosity is even more dramatic. A slightly higher dispersant concentration is needed to reach the same viscosity (Fig. 6). The explanation for this behavior is that some of the dispersant is adsorbed on the latex causing a bridging flocculation. With an extra addition of dispersant this phenomena is overcome. It can also be noted that the increase in viscosity from the latex is negligible if the total solids content is kept constant.



Fig. 5. Relative viscosity (binder containing/binder free) as a function of amount of added dispersant (D3021) for slips with anionic latex.





## Wetting

A ceramic slurry has to wet the carrier film to a sufficient degree[10]. Insufficient wetting may cause pinhole defects in the ceramic tape. Three types of polymeric carrier films were tested and evaluated with regard to their wetting and tape-release characteristics with three different alumina systems (Table II). Too good wetting makes the release of the carrier film more difficult. With a tape-casting machine that forms the drying front rapidly it is possible to use a slip that does not wet as well and still get a well-formed ceramic tape.

Table II. Wetting and tape release behavior of an alumina slip (AKP30 powder, DM765 latex, 0.3 wt% D3021 dispersant) on different carrier films.

Carrier film	PET Polyethylene- therephtalate	PP Poly- propylene	Silicone Silicone coated PET
Wetting behavior	Good wetting	Intermediate wetting	Poor wetting
Release behavior	No release	Release	Easy release

#### Drying

One of the main difficulties in water-based tape casting is to dry the tape without cracking in a continuous process at a high speed. The latex does not form a continuous film until the discrete particles have coalesced. The thickest tape that can be cast without cracking, critical casting thickness (CCT), has been investigated for a number of systems (Table III). The most significant property that seems to control the CCT is the viscosity of the system at high solids loading.

System	Solids volume fraction	Latex particle size [nm]	T <sub>g</sub> of latex [°C]	CCT [µm]	Viscosity in mPas [Shear rate, s <sup>-1</sup> ]
SiC, DM760,					
lignosulphonate	59 wt%	20-200	1	60	623 (5)
SiC, DM765,					
lignosulphonate	63 wt%	100-200	-16	75	2410 (5)
Al <sub>2</sub> O <sub>3</sub> , AKP30, 7%					
DM765, Dispex	48 vol%	100-200	-16	410	522 (11.2)
Al <sub>2</sub> O <sub>3</sub> , AKP30, 10%					
DM765, Dispex	48 vol%	100 - 200	-16	370	1020 (11.2)
Al <sub>2</sub> O <sub>3</sub> , AKP30, 7%					
DM765, D3021	53.6 vol%	100 - 200	-16	460	463 (11.2)
Al <sub>2</sub> O <sub>3</sub> , AKP30, 7% LDM					
7651, D3021	53.6 vol%	<300	-10	700	350 (11.2)
Al <sub>2</sub> O <sub>3</sub> , A16SG, B1001,					
D3021	55 vol%	320	-6	~800	400 (11.6)
Al <sub>2</sub> O <sub>3</sub> , A16SG, B1035,					100.111.0
D3021	55 vol%	370	-40	~800	400 (11.6)
Mullite, SACR193,					
DM765, Dispex	45 vol%	100 - 200	-16	125	-
Mullite, SACR193,					
DM765, Dispex	51 vol%	100-200	-16	240	-

Table III. Critical cracking thickness for a number of systems.

In Table IV the effect on green density of anionic and nonionic latexes is shown for two types of powder. Using an anionic latex has a positive effect on the green density of the cast tape. At the same time if was found that there was a negative effect on the sintered density. The samples with anionic latex binder sintered to lower densities than the tapes with nonionic latex (Table III), even though the initial green density was higher.

The explanation for this could be found by observing the green tapes in the SEM. It seems that vertical channels formed in green tapes using anionically stabilized latex during drying. These channels form pores that are big enough to be stable during sintering and consequently lower the sintered density. Similar effects have been observed in latex paint systems with anionic latexes [11,12]. Although the reason for forming of drying channels with anionic latexes is not fully understood the following mechanism can be proposed. Due to phase separation between anionic surfactant and polymer in the latex during the drying process, the surfactant migrates to interfaces, e.g. air/liquid. There the surfactant stabilizes the pores forming during drying.

Table IV. Effect of falex type on green and sincled densit	Table IV.	Effect of	latex	type on	green and	sintered	density
--	-----------	-----------	-------	---------	-----------	----------	---------

Latex	Green density (%)	Sintered density (%)
Nonionic latex, DM765	51.6	94.3
Anionic latex, B1035	53.4	98.5 (99.7*)

\*Value in bracket with 0.05 % MgO addition.

#### Lamination

Latexes can be chosen with a wide range of glass-transition temperatures  $(T_g)$ . By choosing a transition temperature below room temperature cast tapes can be laminated at room temperature. Pressures in the range of 20-100 MPa have been used depending on the amount of binder added. There is usually a plastic deformation of the tape in the thickness direction. This plastic deformation coincides with an increase in green density of the laminated tapes.

After lamination the interface between the laminated tapes is indistinguishable on a SEM image. Laminated tapes of both alumina and silicon carbide were sintered and the fracture strengths were found comparable to those of slip-cast materials of the same compositions. Bending the tape during lamination can easily reproduce single curved tiles. It is also possible to produce tubes by wrapping tape around a core and isostatically press to laminate them.

# Producing Composites with Alternating Dense and Porous Structures

By producing dense and porous layers it has been possible to create a structure that deflects cracks. The porous layers are produced by adding starch to the ceramic slip. Starch particles are easy to disperse in a ceramic slurry. Since the particle size is relatively narrow they can be used to add porosity of a certain type (Table V). They burn out cleanly and can be used to add pores both to oxide and to non-oxide systems.

Starch type	Particle size range [µm]	Mean particle size [µm]	Particle shape
Rice	3-8	5	Polygonal, angular
Corn	5-26	15	Round, polygonal
Potato	15-100	33	Oval, spherical

Table V. Particle size and distribution of different natural starches.

The effect of adding starch to a slurry is mostly the same as the effect of adding extra powder of the same shape and size. At high shear rates where hydrodynamic forces dominate the suspension behavior there are small differences between the slurries with different starches. Composites made with alternating porous and dense layers have been found to have crack-deflecting properties [13]. Cracks are deflected by the porous layer and increase the work of fracture of the composite.



Fig. 7. Alumina laminate with alternating dense and porous layers using starch.

## DISCUSSION AND SUMMARY

Latexes have shown very promising properties in tape casting. By using latexes it is possible to tape cast with low viscosity at high volume concentrations making it possible to have a high production rate with a water-based system. It is however crucial to have good dispersion to be able to increase the solid content high enough. It should be noted that the dispersant could adsorb on some latexes making an increase in the concentration of added dispersant necessary. The ease of handling water-based suspensions together with lamination at room temperature makes latexes an interesting alternative. However there are some limitations that should be noted. When thick tapes are cast there is a tendency to cracking which makes it important to adjust such systems very carefully. However, tapes up to 400-800 µm have successfully been cast in water-based systems. With thinner tapes the release from the carrier film can be a problem. Latex-bonded tapes can have a large adhesion to the carrier film. Really thin tapes (below 20 µm) are difficult to remove. An alternative to removing these tapes is to laminate directly from the carrier film or to cast a second layer on the green tape with a first layer prior to removal. A practical problem that has to be considered is that dried latex can be difficult to clean out and that dried tapes with latex binder have to be burned out before redispersing the ceramic powder.

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#### RADIO FREQUENCY DRYING OF CERAMICS

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## ABSTRACT

Faster and more consistent drying is a common goal in today's ceramics industry. The use of Radio Frequency (RF) drying can offer many benefits over conventional drying, including faster drying, more uniform temperature gradients and moisture levels, lower drying temperature, and smaller equipment. Radio Frequency drying can be used alone or better yet it can be combined with conventional methods to get the best of both worlds. This paper will review how RF drying works, the benefits of RF drying, and hybrid RF-convection drying systems.

# INTRODUCTION

In today's competitive world, customers are constantly demanding higher quality at lower cost. For ceramic manufacturers, a key opportunity is to provide a more consistent product at faster line speeds. Radio Frequency (RF) drying provides both of these benefits. RF dryers allow ceramic manufacturers to change from older batch processes to lean continuous processes and drying times have been reduced from 24 hours to 90 minutes and from12 hours to 30 minutes. This paper provides an overview of how RF drying works and the significant benefits it provides to ceramic manufacturers in their quest for higher quality products at faster production speeds. In addition, it discusses how RF can be combined with convection drying to offer the benefits of both technologies in a hybrid system.

## DIFFERENCES BETWEEN RF AND CONVENTIONAL HEATING

Figure 1 shows the difference between conventional and RF heating. Conventional heating (i.e. conduction, convection, radiant) has a heat source on the outside and relies on transferring the heat to the surface of the material and then conducting the heat to the middle of the material. Radio Frequency heating is

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different; it heats at the molecular level so it heats from within the material and heats the middle as well as the surface.



Figure 1 - Solids Heating Comparison

The difference in the end result of a dried product is shown in figure 2. A conventionally dried product is hot and dry on the outside and cold and wet on the inside. Unfortunately, this is not efficient because the dry outer layer acts as an insulating barrier and reduces the conduction heat transfer to the middle of the product, especially with thermal insulating materials such as ceramics. This dry outer layer can cause quality problems, such as surface cracking, warping, a skin on coatings and uneven solids dispersion through wicking of sizing and binders from the middle to the surface.



Figure 2 - RF vs. Conventional Drying

With Radio Frequency drying, the heating is from within so there is no hot, dry outer layer. The product is heated throughout so the water in the middle will be heated and will move to the surface. In general, because of the heat losses at the surface, radio frequency dried products are hot and dry on the inside and cooler and wetter on the outside. The combination of these two technologies, using the RF heating to heat the inside and move the water to the surface where conventional methods are effective at removing it, offers some great potential benefits. The use of these hybrid systems will be discussed later.

# THE THEORY OF RADIO FREQUENCY HEATING (RF)

The basic theory of Radio Frequency heating is that dielectric materials are heated when placed in a high voltage, high frequency electric field. The best materials for RF heating are those that are neither good conductors nor good insulators (i.e. dielectrics). One of the key characteristics of RF heating is it "heats from within". Because it is heating at the molecular level, heating takes place throughout the whole material, from the middle to the surface. The material is heated through two heating mechanisms at work in RF heating, dipole rotation and ionic conduction.

In dipole rotation, the individual molecules rotate to align themselves with the electric field. Since the electric field is changing polarity millions of times per second, the molecules rotate millions of times per second, which causes friction and heat. Equation 1 shows the power (P) put into the material by dipole rotation is based on the voltage gradient in the material (V/d), the frequency of the electric field (*f*), and the loss factor of the material ( $\epsilon$ ''). It is important to note the relationship between frequency and loss factor in RF drying applications. In the frequencies used for RF drying (10-40 MHz), as the frequency increases, the loss factor of water decreases, offsetting most of the gain of the higher frequency.

$$P = (V/d)^2 f \varepsilon''$$
(1)

In ionic conduction, charged particles (ions) are always moving toward the opposite charged plate. Since the polarity is changing millions of times per second, these ions are constantly moving and colliding with other particles, similar to billiard balls. These collisions create friction and heat that warms the material. The power (P) put into the material by ionic conduction is based on the voltage gradient  $(V/d)^2$  in the material and the conductivity ( $\sigma$ ) of the material. The power is not based on the frequency as it is in dipole rotation.

$$\mathbf{P} = (\mathbf{V/d})^2 \,\sigma \tag{2}$$

In the drying of ceramics at RF frequencies, the majority of the heating is due to ionic conduction rather than dipole rotation. Thus the frequency has little effect on the heating rate of the water since frequency has no effect on ionic conduction and a very minor effect on dipole rotation.

# HOW RF ENERGY IS APPLIED

The RF dryer receives standard line power (i.e. 480V, 60 Hz) through the Switchgear. In the Power Supply section, line voltage is stepped up to high voltage AC through a transformer and then changed to high voltage DC through rectifiers. In the Oscillator section, high voltage DC is changed to high frequency, high voltage RF energy and transmitted to the applicator or electrodes where it is applied to the work. All of this is controlled by a modern control system.

The key to effective use RF energy for drying is the right applicator, or electrode design. Traditionally, heating was accomplished by creating a uniform electric field between two parallel plates. This approach is capable of heating thicker materials uniformly because a high voltage gradient can be established in the material. However, it does not work well for thin materials such as webs. In order to establish a high voltage gradient in a thin web material, the plates must be very close together which can cause arcing between the plates.

For thin materials, the strayfield electrode design was developed. This design creates an electric field between alternating parallel rods that gives a higher voltage gradient in the web for faster heating. A variation on this electrode design for thicker webs is the staggered strayfield design. This allows for more uniform heating of thicker webs. This has also been used for thin beds of ceramic powders. As a general rule, materials under 6 mm thick use the strayfield design, materials 6-12 mm use the staggered strayfield design, and materials over 12 mm use the parallel plate design. In all of these electrode designs, the material can be either self-supporting or can be transported on a conveyor (figure 3)



# THE EFFECT OF MATERIALS ON RF HEATING

Materials have a major effect on the success of RF heating. Some materials heat very well and some do not heat well at all. The key measure of "heatability" is the loss factor of the material. The loss factor is a material property that determines how well the material absorbs the RF energy. If the material has a high loss factor, it absorbs energy quickly and thus heats quickly. If a material has a low loss factor, it absorbs energy slowly and thus heats slowly. In general, polymers and ceramics tend to have low loss factor so it heats rapidly. This is why RF lends itself to drying so well, it heats the water quickly but does not heat most polymer and ceramic materials.

It is important to remember every material reacts differently and loss factors (the ability to absorb RF energy) can change with frequency and temperature. A material that does not absorb RF energy at room temperature might absorb the energy at higher temperatures. Likewise, the loss factor can vary with frequency (water is a good example of this). The complexity of the interaction between materials and the RF field makes it critical to consult with an expert in RF drying and conduct trials on your product.

# HOW RF DRYING CAN IMPROVE YOUR CERAMIC DRYING PROCESS

All of the information on how RF drying works and how it interacts with materials is interesting, but what really matters is how it can improve your drying process. Because RF drying differs from conventional drying methods, it has some significant advantages in drying materials such as ceramics. These include:

- Faster drying times and reduced labor cost with continuous versus batch processing. Because the energy is absorbed directly by the water throughout the product, heating and drying is faster. This means faster cycle times and lower labor costs with a continuous process.
- More uniform temperature gradient through the product due to heating from within, resulting in more consistent product quality. This uniform heating prevents a dry outer layer and provides a more uniform dispersion of sizing and additives throughout the product.
- No overheating of the base ceramic material since most materials are self-limiting, i.e. they won't heat once the material is dry. This prevents scrap product and improves product quality.
- Selective heating allows water to be heated with less heating of the base ceramic material. This improves the quality of the product through lower drying temperatures (normally these do not exceed 100°C).
- Moisture leveling in the product, resulting in more consistent product quality and lower cost by not over drying some areas to meet required moisture levels in others.
- Instant on and off power and heating, reducing costs by eliminating warm up and cool down cycles associated with conventional systems.
- Efficient energy usage because energy used is proportional to the amount of work being done (water being evaporated). This reduces cost, as lower production volume will have lower operating cost.
- Fewer environmental issues as there are no combustion by-products to exhaust. This improves quality by keeping the dryer cleaner and reduces costs by reducing permits and approvals for process emissions.

It is interesting to note that almost all of these benefits are a direct result of the unique way RF energy interacts with materials. These are benefits that are only available through the use of RF drying.

# HOW RF AND CONVECTION CAN BE COMBINED FOR THE MOST EFFICIENT DRYING

Conventional heating methods work very well at removing moisture from the surface of materials and RF works very well at heating the middle of a product and driving the moisture to the surface. It is only natural to then look at combining these two technologies to take advantage of the benefits each provides. In fact, the combination of RF and conventional drying has been done in several different ways to significantly improve drying processes. There are four main RF-conventional combinations, RF pre-heat, RF boost, RF finish, and full RF/conventional. Each of these will be discussed in more detail.

# **RF PREHEAT**

One possible combination of RF and conventional drying is using RF at the beginning of a process. This heats the material quickly, evenly and helps move the moisture to the surface. The overall time is shortened in the falling rate zone because the whole product has been heated, not just the surface. The even heating avoids a dry outer layer that causes uneven dispersion of sizing and additives in the product. Another application for RF pre-heat is curing processes. The RF is very good at quickly heating the product to a consistent temperature, after which conventional methods are very good at maintaining the temperature for a dwell or cure time.

# **RF BOOST**

RF energy can be added in the middle of a process line to give an RF "boost" to the conventional drying process. In this case, the RF heats the inside of the product and drives the moisture to the surface where conventional methods are

effective. As with the other combinations of RF and conventional drying, the overall drying time is reduced with the use of the RF boost.

# **RF FINISH**

Another combination of RF and conventional drying is using RF to do the finish drying. This is used with good thermal insulating materials such as ceramic fiber mat where the dry insulating surface inhibits the drying process.

# FULL RF AND CONVENTIONAL

The first three combinations of RF and conventional drying use RF in part of the process cycle with some significant reductions in drying times. It makes sense that another option is to use RF and conventional methods simultaneously during the whole process. This offers the largest potential reduction in drying time of all the methods, although it does complicate equipment design. This is a common design for ceramic dryers and has enabled tenfold reductions in drying times.

# CONCLUSION

Radio Frequency drying offers many benefits today's ceramic manufacturers need to stay competitive, namely higher quality at lower cost. Any ceramic drying process has the potential to be significantly improved with RF drying. Specific benefits offered include:

- Faster drying times to reduce cycle times and reduce labor with continuous versus batch processing.
- More uniform drying throughout the product due to heating from within, resulting in more uniform dispersion of sizing and additives.
- No overheating of the material since most ceramic materials are selflimiting, i.e. they won't heat once the material is dry. This prevents scrap product and improves product quality.
- Selective heating allows water to be heated with less heating of the ceramic material. This lower temperature drying improves the quality of the product.
- Moisture leveling in the product, resulting in a more consistent product quality and lower costs.
- Instant on and off power and heating, reducing costs by eliminating warm up and cool down cycles associated with conventional systems.
- Efficient energy usage because energy used is proportional to the amount of work being done (i.e. water being evaporated). This reduces costs as lower production volume has reduced operating costs.
- Fewer environmental issues as there are no combustion by products to exhaust. This improves quality by keeping the dryer cleaner and reduces costs by reducing permits and approvals for process emissions.

In addition to stand-alone RF drying, RF can be combined with conventional drying methods such as convection and conduction to gain even greater improvements in line speed and product quality. There is great synergy with these hybrid systems where RF excels at heating evenly within the material and pushing the moisture to the surface and conventional methods excel at removing moisture from the surface. Whether the RF is used as a pre-heat, boost, finish, or a full RF application, drying ceramics can be much more effective with these systems.

For anyone in the ceramic industry interested in improving their quality and lowering their costs at the same time, Radio Frequency drying belongs at the top of their list.

## LASER CVD SYSTEM DESIGN, OPERATION, AND MODELING

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A gas-jet laser chemical vapor deposition (LCVD) system has been designed and developed for the manufacture of small, complex ceramic, metallic, and composite parts. In the past two years, direct writing and fiber growth mechanisms have been demonstrated for several materials. Thermally controlled experiments have permitted the optimization of process parameters and the growth of three-dimensional muti-layer structures. Extensive modeling in the areas of chemical kinetics, thermodynamics, heat transfer, fluid flow, and mass tranport have lead to a better understanding of the LCVD process.

#### INTRODUCTION

Chemical vapor deposition (CVD) is a coating process that is noteworthy for the synthesis of metals and ceramics and has been used industrially for many decades. A variant, laser chemical vapor deposition (LCVD), holds great potential for the manufacture of small and complex metal, ceramic, and composite parts. The production of physical parts using LCVD involves generating solid deposits on the surface of a substrate by inducing localized chemical reactions in a suitable vapor reactant through the use of a laser beam. Materials prepared by CVD, and presumably by LCVD, typically possess high purity, low porosity, and a high degree of crystallinity. These attributes are the result of deposition occurring one atom at a time, leading to materials having excellent mechanical properties and thermal stability.

Pyrolytic LCVD is a thermally driven process in which the energy of a laser beam is used to heat the surface of a substrate to the temperature required for chemical deposition. It allows superb spatial resolution ( $\sim 5 \,\mu$ m) because the chemical reactions are restricted to the heated zone created by the focused laser spot. In contrast to the localized heating used in LCVD, a traditional CVD furnace heats the entire surface of the substrate to the temperature required for reactions to proceed. The deposition rate for CVD processes may be limited by diffusion of gases into and out of the reaction zone. Since the chemical reaction occurs simultaneously across the surface of the substrate, the diffusion path for reactive gases is typically one-dimensional in the direction normal to the reaction plane. By contrast, the diffusion zone for LCVD techniques is a hemisphere centered about the focused laser spot. This point-source chemical reaction opens three-dimensional diffusion paths for gases to diffuse into and out of the reactive zone. These diffusion paths are compared in Figure 1. This and perhaps other unknown factors permit deposition rates

for LCVD techniques to be orders of magnitude higher than for traditional CVD.

Another obvious advantage of LCVD over CVD is the ability to generate



Figure 1. CVD and LCVD diffusion paths.

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patterned deposits without the use of lithography. There are two methods for producing threedimensional parts via pyrolytic LCVD. Direct writing deposits a pattern of thin lines on the substrate by moving the substrate perpendicular to the axis of the laser beam. These twodimensional patterns can be formed upon previous deposits to create a layered three-dimensional part (similar to most rapid prototyping techniques). Fiber depositions are also possible. In this case, the substrate is moved away parallel to the laser beam axis at a rate equal to the deposition rate of the fiber. Direct writing and fiber growth methods can be combined to produce such structures as coiled springs, fibrous scaffolds, or, in principle, fiber-reinforced laminar composites.

### BACKGROUND

In the past 25 years, LCVD technology has progressed considerably. Fiber growth rates exceeding 2 mm/s have been reported for numerous metals and ceramics.<sup>1</sup> A linear growth rate of 200 mm/s, or a volumetric deposition rate of 50 mm<sup>3</sup>/s, was recently achieved for carbon.<sup>2</sup> For perspective, this corresponds to fabricating a component the size of a penny in 10 seconds, ignoring time delays for movement required to build complex shapes. Spatial resolution is below 10  $\mu$ m in fiber diameter and down to 5 nm in layer thickness. Numerous materials have been deposited with pyrolytic LCVD techniques including Cu, Au, Si, AI, W, C, WC, B, TiC, TiN, SiC, and Si<sub>3</sub>N<sub>4</sub>. A comprehensive list of materials and structures deposited using pyrolytic LCVD is available.<sup>1,3</sup>

Understanding and modeling the LCVD process is not a trivial matter. The deposition process occurs at the atomic level and is restricted to an area on the substrate on the order of micrometers. Across this reaction zone, the temperature can exceed 2000°C and there are large thermal gradients. The process may also include high-velocity fluid flow, which affects the local temperature and reagent concentration. Since the deposition rate depends on both of these, predicting growth rates and shapes can be challenging.

Several efforts have been made to model the chemical kinetics of the LCVD process. The models differ somewhat depending upon the nature and location of the material growth. When deposition occurs near the original substrate surface, the models rely on an Arrhenius relationship describing growth in the kinetically limited regime, with allowances for diffusion limitations as well as some other effects such as desorption and thermodynamics.<sup>4-6</sup> Models have also been made to predict fiber growth, including axial and lateral growth.<sup>7</sup> Maxwell<sup>8</sup> developed a model for fiber growth through the transient regime close to the substrate. For longer fibers, the temperature field was assumed to be constant, since the effects of heat conduction through the substrate were assumed to be negligible.<sup>9</sup>

A number of analytical and numerical attempts have been made over the years to model the temperature variations within and around the laser heated zone.<sup>1,5</sup> The majority assumed a Gaussian distributed laser beam and emphasized conduction as the primary heat transfer mode. A few thermal models have included the effect of forced flow convection. As early as 1977, Steen<sup>10</sup> developed a finite element model that included a non-reacting gas jet that was coaxial with the laser beam and normal to the substrate surface. He found that forced convection and radiation heat transfer losses were indeed significant for a temperature sensitive process. Excluding our earlier efforts,<sup>11,12</sup> no model has estimated the effects of a high velocity angled jet configuration.

Some LCVD thermal models have also been extended to include the mass transport of reagent gases and the prediction of deposition rates. Zhang and Faghri<sup>13</sup> recently proposed a three-dimensional model of the SALD process that included heat transfer, mass transport, and the loss of reagents to the deposition reaction. However, no model has addressed the viscous flow contribution of an impinging gas-jet to the mass transport of reagent gases.

## GAS-JET LCVD SYSTEM

System Design

The main body of the Georgia Tech LCVD system consists of two stainless steel cylindrical chambers (Figure 2). The upper chamber contains the substrate and reagent gases and provides

numerous ports for laser entry and sensing and control devices. It measures 15 cm in diameter by 20 cm high. The lower chamber houses the stage assembly, which moves the substrate in the reaction chamber using flexible а bellows feedthrough. The lower chamber measures 55 cm in diameter and both height.

Figure 3 is a



Figure 2. CAD model and photo of LCVD chamber.

cross-sectional view of the LCVD chamber and is helpful in understanding how the LCVD system works. A CO<sub>2</sub> laser beam enters the reaction chamber through a ZnSe window in the chamber top. The laser beam is focused to a 200  $\mu$ m spot on the surface of the substrate. Note that the laser could also focus on a previously deposited material to begin construction of the next layer. The energy of the laser is absorbed and heats the surface to the desired deposition temperature



Figure 3. Cross section of LCVD chamber.

(typically 500 to 2000°C). A stream of reactive gas is directed onto the substrate at a 45° angle through a gas-jet delivery system. The gas is heated as it approaches the substrate and is adsorbed onto the deposition surface, where it reacts to form a chemically pure solid deposit. The gaseous byproducts of the reaction are carried away from the deposition site and are evacuated from the chamber through the vacuum If a different material is port. desired to form a composite structure, the reagent stream flowing through the gas-jet is changed.

The substrate sits on top of a shaft that extends into the lower chamber. In order to achieve a patterned deposit, the substrate is rotated and translated by the stage assembly in the lower chamber. Directly beneath the substrate is a resistive heating element. This heater can be used to raise the global temperature of the substrate to within  $\sim 200^{\circ}$ C of the deposition temperature. This not only reduces the amount of time and energy required for the laser to locally heat the deposition zone to the deposition temperature, but it also reduces the stresses in the material due to thermal shock.

This versatile design permits for three modes of operation (Figure 4). For the primary mode, the substrate is heated globally and the laser raises the temperature locally to trigger the CVD reaction. In this mode, the reagent is supplied by the gas jet. For a second mode, a laser is used for local heating, but the chamber is filled with reagent rather than being delivered locally. For the third mode, the laser is not used. The substrate is heated globally to the deposition temperature and the reagent is supplied by the gas jet. This multiple mode approach not only introduces two novel systems, but also allows inter-system comparisons.

#### Process Control

The production of high quality three-dimensional objects using LCVD requires precise process control.14 In the current design, the deposition rate is controlled by varying the laser intensity, reagent composition /

concentration, and stage speed to produce the proper height and width of



Laser. On Gas-Jet: On



deposit. Since LCVD is a thermally activated process in which the deposition rates may follow an Arrhenius relationship with respect to temperature, it is critical to monitor and control the absolute temperature and temperature variations across the deposition zone. The current system uses a



Figure 5. Thermal image of fiber growth.

high-resolution thermal imaging system that is capable of processing over 300,000 temperature readings at a rate of 30 times per second. The imaging system can record temperatures from 720 to 2050°C to within 1°C. The spatial resolution is 3.5  $\mu$ m and the field of view is 2 mm wide. A thermal image during fiber growth is shown in Figure 5. The data from this imaging system are reported to the control program that regulates laser power. The resulting thermal control loop allows the deposition process to be controlled within 5°C.

Gas-Jet: On

In addition to controlling the local temperature, it is also important to monitor

the geometric quality of the deposit. A laser triangulation device has been used that is capable of precisely measuring the deposit height through an observation port in the upper chamber. This device has a resolution of 10  $\mu$ m at a standoff distance of 35 cm. By measuring the deposit height while rotating and translating the substrate, it is possible to generate a three-dimensional surface map of the exterior of the deposit geometry. This surface map can then be compared to the part's CAD model in order to identify irregularities or flaws in the deposit shape. Since this is a technique that can be accomplished without removing the sample from the deposition chamber, further processing steps can be taken to correct any manufacturing flaws.

In addition to monitoring the temperature and geometry during the deposition process, each aspect of the LCVD system is controlled through a Labview computer program. A number of electronic sensors and valves permit complete automation, which includes controlling the deposition pressure, differential pressure between chambers, reagent gas flow rates, and the removal of gaseous by-products.

## MATERIAL DEPOSITION

#### Direct Writing, Fiber Growth, and Nano-Structures

Operation of Georgia Tech's LCVD system began in October 1999.<sup>15</sup> Carbon was chosen as the initial material for deposition because the reagents (methane, propylene, and acetylene) were



Figure 6. Direct writing of carbon.



Figure 7. Carbon fiber.

thermal control program. The 250  $\mu$ m diameter fiber grew at a linear growth rate of 78  $\mu$ m/min. Figure 8 shows that multiple fibers can be grown at an angle to the substrate and form a robust connection at their point of intersection. This behavior makes it feasible to construct complicated fibrous scaffolds without the use of an underlying substrate.

The LCVD system has also been used to deposit carbon in the form of nanofibers on catalyzed substrates such as Grafoil® and silicon. The structures shown in Figure 9 have outer diameters on the order of 100 nm. Numerous applications using these nano-scale materials are being proposed in a wide variety of industries. In addition to depositing carbon on a variety of substrates, the LCVD system has also been used to deposit materials such as boron, boron nitride, and molybdenum.<sup>16.17</sup>



1300°C

non-toxic

and

at

inexpensive.

and

demonstrates the ability to direct write carbon lines on a graphite substrate. The scanning speeds were in the range 50-100  $\mu$ m/s

typical

dimensions were 300  $\mu$ m wide by 50  $\mu$ m tall. Fiber growth has also been successfully demonstrated. The fiber in Figure 7 was deposited from propylene

also

line

using the

Figure 6

Figure 8. Carbon fiber scaffold.

## Multi-Layer Deposits

Lines can also be deposited on top of previous lines to generate multi-layer wall structures. Process control is extremely important when depositing multiple layers of materials. Since the underlying deposit may exhibit irregularities, proper control is needed to insure that these irregularities are not amplified with each successive layer. The implementation of automatic temperature control has permitted significant advances in the ability to deposit uniform multi-layer carbon structures.

A number of structures have been created using a multiple pass process whereby the substrate was either translated along one axis in alternating directions or in a continuous circular pattern.<sup>18</sup> The resulting structures were multi-layered carbon walls or cylinders. Figure 10 illustrates a typical laminated carbon wall generated from a reagent gas mixture of 75 % methane and 25 % hydrogen at 101 kPa (1 atm). The wall is composed of 20 layers. The straight-sided walls and a flat top of this structure make it a promising building block for future threedimensional objects.

Theoretically, this construction technique creates layers that are intimately bonded producing a final structure that could exhibit either bulk solid or laminated solid properties. Figure 11 shows a cross section of the multi-layered wall. The interior structure appears very dense with few pores or defects. The individual layers are evident in Figure 11 and appear to be well bonded. It is believed that some of

the less defined black marks in the of photo are artifacts sample preparation such as residue from the polishing operation. The lower layers exhibit a characteristic volcano shape,<sup>1</sup> appears to diminish with which increasing numbers of layers. The diminishing of the volcano effect with height is evidence that a temperature controlled process can eliminate sizeable interlayer voids. Small cracks can also be observed in the cross section and are believed to result from thermal induced stresses between layers of deposit.



Figure 9. Carbon nanofibers.



Figure 10. Cross section of carbon multi-layer wall.



Figure 11. Cross section of carbon multi-layer wall.

#### KINETIC AND THERMODYNAMIC MODELING

The chemical kinetics of carbon fiber deposition using the LCVD system were studied for two separate precursor gases, methane and propylene.<sup>19,20</sup> The deposition rate was modeled as  $kC^n$ , where k is the rate constant according to the Arrhenius equation  $(k=k_oe^{-Q/RT})$ , C is the local concentration, and n is the order of the reaction. The kinetic modeling presented here uses the peak temperature at the center of the laser spot rather than an average, and this peak temperature was measured using the thermal imager rather than calculated. Traditional CVD kinetic analyses probably do not apply directly to LCVD since the heating time is shortened and the elevated temperatures of LCVD may lead to different reaction paths.

Twelve fibers were grown using methane at four different concentrations (50, 60, 70, and 80 % methane, with the remainder hydrogen) and three different average temperatures (1300, 1350, and 1400°C). The time elapsed during fiber growth was recorded, and this was used to determine the growth rate. Using methane as the precursor at a total pressure of 78.4 kPa, a multiple regression analysis resulted in an activation energy of 176 kJ/mol, a pre-exponential constant of  $2.66 \times 10^{15}$  cm/s, and an order of the reaction of 3.47.

Twelve fibers were also grown using propylene at four different concentrations (40, 50, 60, and 70 % propylene, with the remainder hydrogen) and three average different temperatures (1300, 1350, and 1400°C). Using propylene as the primary reagent at a total pressure of 21.3 kPa, a multiple regression analysis resulted in an activation energy of 286 kJ/mol, a pre-exponential constant of  $3.54 \times 10^{12}$ , and an order of the reaction of 1.90.

This analysis was also designed to determine if thermodynamics could explain the volcano effect experienced at elevated temperatures. The thermodynamics of the CVD reaction to deposit carbon was modeled using the SOLGASMIX-PV program, which predicts the equilibrium assemblage of known elements by minimizing the free energy. The input to the model was 3 moles of carbon and 14 moles of hydrogen. Since the final result of the model was at equilibrium,

the initial structure of the molecules was not important, only the relative amounts of carbon and hydrogen. The solid amount of carbon deposited at various temperatures was determined along with the equilibrium concentrations of the various hydrocarbons in the gas phase. The results of the thermodynamic calculations are given in Figure 12 and show that the amount of solid carbon decreases from almost three moles at 2000 K, down to zero at 2500 K. The model implies that solid carbon does not exist in equilibrium above 2500 K (in



Figure 12. Species at equilibrium versus reaction temperature.

the presence of hydrogen), and any solid carbon would react with hydrogen to produce acetylene and other hydrocarbons. In general, the results support the theory of etching at high temperatures, and predict this etching reaction to occur above  $2500 \text{ K} (2227^{\circ}\text{C})$ .

## THERMAL AND FLUID MODELING

Both two-dimensional and three-dimensional thermal and fluid flow models were developed using a commercial CFD package called FLUENT. The basic geometry and boundary conditions for the models are illustrated in Figure 13. For both cases, a user-defined function simulated laser heating as a Gaussian distributed energy source in the uppermost layer of elements of the substrate volume.

The two-dimensional model served as a platform for comparing the thermal behavior of various substrate materials when heated by a Gaussian laser beam. The two dimensional model was axisymmetric and did not account for fluid movement. The thermal and optical properties of the substrate materials were considered constant with respect to temperature, excluding thermal conductivity. The model was evaluated for three different substrate materials: graphite, silicon, and tungsten. The model was empirically verified for the first two materials over a range of flow rates. Figure 14 shows the peak temperature on each substrate as a function of laser power. Note that peak temperature increases as thermal conductivity decreases. Not only does the peak temperature change due to the material properties, but the shape of



Figure 13. Thermal/fluid model.

the temperature distribution changes as well. Note in Figure 15 how the temperature profile for silicon is much more narrow than that of tungsten. With regard to LCVD, this means that it is more difficult to achieve high resolution deposits on highly conductive substrates such as tungsten.

The three-dimensional model was extended 25 mm above the graphite substrate to include fluid movement associated with the gasjet inlet. The reagent flow was specified at the inlet as a normal

velocity corresponding to flow rates of 0 to 5000 sccm. The flow was composed of 80 % methane and 20 % hydrogen. Figure 16 demonstrates a typical velocity magnitude profile for the gas-jet along the vertical symmetry plane of the model. The effects of flow rate on the temperature profiles for a graphite substrate are shown in Figure 17. Figure 18 quantitatively illustrates the velocity profiles at the center of the laser spot as a function of the vertical distance from the substrate. The height from the substrate is measured directly above the center of the laser spot in each case. Figure 18 shows that the maximum horizontal velocity imparted by the gas-jet occurs less than 400 µm from the surface. The maximum for the vertical component of flow, directed downward onto the substrate surface, occurs at roughly twice this distance.



Figure 14. Substrate peak temperature vs. laser power.



Figure 15. Temperature distribution.



Figure 16. Velocity magnitude (m/s) above substrate.

Figure 17. Temperature profile vs methane flow.

## MASS TRANSPORT MODELING

A gas-jet delivery system is expected to aid mass transport of reagent gases to the deposition zone, thus increasing the deposition rate. In order to judge the effectiveness of such a system, a steady state, two-dimensional finite difference code has been developed. The governing equation



Figure 18. (a) Horizontal and (b) vertical velocity vs. distance from substrate surface.

for mass transport includes macroscopic fluid flow, diffusion, and a sink term that represents the consumption of reagents at the surface. The temperature and fluid velocity throughout the domain were accepted as input from the threedimensional thermal and fluid flow model The diffusion term was previously described. calculated at each node using the Chapman-Enskog method. At the surface, the sink term was nonzero and equal to kC''. After applying the boundary conditions in Figure 19, the governing equation was solved iteratively for the concentration throughout the domain. Although this model is simplistic in nature, it is a valuable qualitative tool for estimating the effects of the gas-jet on the deposition process.



Figure 19. Concentration model conditions.

Currently, the mass transport model is in the early stages of empirical verification. Preliminary results were in agreement with recent experiments involving the deposition of carbon fibers from a mixture of 80 % methane and 20 % hydrogen at 1 atmosphere.<sup>19</sup> Both the experimental data and the mass transport model indicated that fiber growth was kinetically limited at peak temperatures around 1500°C. Therefore, the model predicted minimal concentration gradients during steady state growth.

#### CONCLUSION

An LCVD system has been designed, fabricated, and tested during the past four years. Several novel features are advantageous in terms of build time, accuracy, resolution, and flexibility. A high velocity gas-jet is used to deliver reagent gases directly to the substrate surface. Patterned deposits are generated by rotating and translating the substrate in a spiral fashion, which avoids high reversal forces and associated vibrations. A thermal imaging system is used to control the deposition temperature to within 5°C and can document two-dimensional thermal gradients in real time. A laser triangulation distance device is also used to evaluate deposit uniformity and overall shape.

This system has been used to deposit several materials. Both direct writing and fiber growth have been demonstrated with carbon on various substrates. For the first time, careful thermal control has permitted the fabrication of uniform multi-layer structures that can be used as building blocks for larger three-dimensional objects.

Kinetic models were presented that predict the growth rate of carbon fibers via LCVD at a given peak temperature, for methane or propylene precursors. The kinetics of the deposition were studied based on the measured peak temperature of the fibers during growth. The apparent activation energy for carbon growth from methane was 176 kJ/mol, and the order of the reaction was found to be 3.47. The apparent activation energy of carbon growth from propylene was 286 kJ/mol, and the order of the reaction was 1.9. In general, the fiber growth rates increased with increasing reagent concentration and increasing temperature, up to approximately 2100°C when the volcano effect appeared. The cause of volcano shaped deposits was also explored through experimentation and thermodynamic modeling, and found to be an etching reaction induced by the elevated temperatures at the center of the laser spot.

An angled gas-jet has been shown to have a significant impact on both the peak temperature and temperature profile of a laser-heated substrate. The maximum velocity imposed by the gas-jet occurs just 400  $\mu$ m above the surface and varies with flow rate. It can be assumed that the fluid in this high velocity zone is composed of fresh reagent gases, supporting the concept that a gas-jet could aid in mass transport and diffusion. Although the effect of the gas-jet on a diffusion-limited deposition process has yet to be determined, the mass transport model has been empirically verified for a kinetic limited process and will serve as a valuable tool in future work.

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# NEAR NET SHAPES BY CERAMIC INJECTION MOLDING

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# ABSTRACT

Ceramics and their composites are extremely difficult to machine and form into complex shapes. Ceramic Injection Molding (CIM) has emerged as an ideal process for producing near net shaped ceramic components in moderate to high volumes. The process of CIM involves the mixing of the ceramic powder with an organic binder to form a feedstock, injection molding the feedstock into the desired shape, debinding, and finally consolidating the material by sintering. This paper will discuss some of the critical aspects of the ceramic injection molding process and also touch on some of the current applications.

## **INTRODUCTION**

Ceramic Injection Molding (CIM) can be considered a part of a more broad material shaping technique known as Powder Injection Molding (PIM). PIM is currently a commercial technology that is used for producing complex shaped parts from numerous high performance materials [1,2], including ceramics and ceramic-based composites. The technology builds on the attributes of plastic injection molding to form complex shapes from plastics, and expands it into the area of high performance materials, including metals, alloys, ceramics, cermets, ceramics and composites [1].

Though the era of ceramic injection molding appeared during the early part of the last century (Patent granted as early as 1929), one of the major spurts in growth for CIM came with the need for fairly complex shaped spark plugs in the 1930's [2]. The technology somehow took a backseat for a while till the advent of the jet age when ceramic injection molding was used as the process for producing large complex shaped cores for complex jet engine components. This business still remains one of the biggest users of ceramic injection molded parts. During

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the last 20 years, the tremendous development in the area of MIM (metal injection molding) significantly overshadowed the growth and development of CIM. However, during that timeframe, CIM had quietly made inroads into numerous industries and had established itself firmly as the process of choice for making small and extremely complex shaped parts. This paper will discuss the critical steps in CIM and some of the uses of ceramic injection molded components.

# **CIM PROCESSING STEPS**

The process of CIM, in its most general form, consists of mixing an organic binder (typically thermoplastics, waxes, oils, acids, etc.) with the desired ceramic or ceramic-based powder(s). The mixing is usually carried out at an elevated temperature where the organic binder is in the form of a liquid. The powder and organic binder mixture is usually palletized to produce small uniform pieces of the mixture generally known as the feedstock. The palletized feedstock can be fed into the hopper of a injection molding machine, where it is again remelted in the barrel, moved to the front of the machine near its exit nozzle, and then pushed into an oversized die cavity by the reciprocating screw (in general injection molding machines). Other types of injection molding machines with different processing schemes are also frequently used in this process.

The molded shape or the "green part" is usually an oversized replica of the final product. The tool is built with a precise knowledge of the shrinkage that the "green" or as-molded part will undergo once the organic portion of the binder is fully removed and the part is consolidated to almost full density. Based on this precise knowledge of shrinkage and proper process control, it is possible to produce parts with high degree of consistency and dimensional accuracy.

Generally, the as-molded part is subjected to a step known as debinding. During this step, the organic portion of the green part is extracted. Ideally, debinding results in the gradual and complete removal of the organic phase without leaving behind any residual contamination, and the by-products of the debinding process is environmentally friendly in nature. In general, the binder system is not a single organic material but consist of several different components that serve different purposes. The main constituents are the backbone binder, the filler phase and a surfactant. The filler phase is removed during the early part of the debinding process and the backbone is removed at the end typically by thermal means.

After the removal of the organic binder, the part is subjected to a thermal treatment known as sintering which results in the densification of the part to the desired level. In some cases, post sinter secondary processes can be applied for a variety of different reasons.

The general CIM process can be divided into several core steps that are shown schematically in Figure 1. The core processing steps are feedstock, molding, debinding, and consolidation. Even though the figure shows the core steps in a generic form, it should be realized that the process has numerous variants. The numerous variations are a reflection of the different combinations of powders, organic binders, mixing process (twin screw, double planetary, sigma blade, etc.), molding techniques (reciprocating screw, low pressure injection molding, medium pressure injection molding, etc.), numerous debinding routes (wicking, thermal, catalytic, solvent, etc.) that are again dependent on the initial binder choice, and numerous different sintering techniques.

# **BRIEF DESCRIPTION OF THE CRITICAL PROCESSING STEPS**

As described in the earlier section, the general process of CIM can be divided into the following critical steps: feedstock formulation, injection molding, debinding, and consolidation of the parts. The following sections will briefly discuss some of the details of the critical processing steps.

# FEEDSTOCK FORMULATION

The feedstock consists of two main parts. The first part is the organic binder that is needed to produce the complex shape while the other part is the actual material that will form the ceramic or ceramic-based composite part. The two different materials need to be uniformly mixed together to form the feedstock. In CIM, several different mixing equipments have been used. Some of the common mixing equipment includes kneader-extruder, twin-screw extruder, twin roll mill, double planetary mixer, etc.

The ceramic powder, it should be realized, is usually quite a bit different from its metal and alloy counterpart. The ceramic powders are considerably finer than the metal powders typically used for powder injection molding, and the powders are generally more irregular or angular in nature (of course ceramic powders can vary widely in shape). This characteristic of the ceramic powders makes them more difficult to load to high volume fractions in the organic binder. In general, the typical D50 of the ceramic powders used in CIM are usually below 1  $\mu$ m while all the MIM powders have a D50 greater than 1  $\mu$ m. Powders finer than 1  $\mu$ m are preferred in CIM to achieve better sintered density and carry out sintering at a relatively low temperature. In some cases, bimodal powder distribution has provided improved properties due to improved powder packing. However, in this case, care needs to be taken in tailoring the powders such that the finer powder fraction fits into the interstecies of the larger particles, thus, increasing the packing density.



Figure 1. Flow chart showing the major steps in CIM [1].

The organic portion of the feedstock is responsible for the homogeneous packing of the powders into the desired shape and the retention of the shape till some degree of strength is attained in the part. Thus, the feedstock has several diverse requirements, and hence, is made up of several constituents. There is, however, no universally perfect binder that works for all powders. Thus we see the proliferation of numerous and diverse binder systems. However, most binder systems have several common constituents. One constituent of the binder that is also the primary constituent is the one that imparts the flow characteristics and can be removed early on in the debinding step. To this, a plasticizer is often added to make the polymers more flexible. This filler phase is removed during the early stages of debinding, thus, leaving behind open pores through which the remaining binder can be removed during the subsequent processing step. The filler phase may be removed using a variety of different debinding techniques such as catalytic reaction, solvent extraction (including water), thermal evaporation, sublimation, etc. The other constituent is the backbone polymer that is often retained as the filler phase is removed and holds the shape together. Later, during pre-sintering, the remaining binder is removed through the open pore channels already left behind by the filler or primary phase. The other constituent, commonly known as the processing aid, is usually a very minor part of the binder volume, but it has a major role in the overall functioning of the binder system. They basically act as a bridge between the binder and the powder and significantly reduce the viscosity of the feedstock thus making it easily moldable. These additives also acts as lubricants allowing easier release of the molded part from the mold cavity. In ceramic injection molding, since the particles are very fine, the powders are usually agglomerated. The agglomerates are broken up during the process of high shear mixing, but to retain the deagglomerated state, the use of processing aid is also necessary. Coupling agents, also part of the processing aid, is often used to improve the bonding of polymer to the ceramics. Thus, it is possible to imagine the complex nature of the binder systems that are used for CIM. Given below are examples of some of the commonly used materials in the binder systems: Polypropylene, polyethylene, polyvinyl chloride, paraffin wax, microcrystalline wax, polyethylene glycol, cellulose, polycarbosilane, several alcoxides, agar, vegetable oil, stearic acid, stearates, olates, silanes, titanates, etc.

Some of the ideal binder attributes are low viscosity, low viscosity change around the molding temperature but rapid change in viscosity during cooling, high strength of binder after cooling, minimum flow orientation, good adherence to powder, leave little or no harmful residue after debinding, can be recycled, does not produce toxic or environmentally detrimental by-products during the debinding cycle, and is low cost. It can, therefore, be realized that there is no universal binder system suitable for all ceramic materials.

# MOLDING

The molding process involves the use of a pre-designed tool that is the accurate oversized replica of the final part. The pre-calculated shrinkage is built into the tool itself. This tool is usually placed in a position where the molten feedstock can flow into the die cavity from the injection molding machine barrel. There are several types of injection molding machine that are in use at the current time. It would not be possible to discuss the details of the all the machines that are typically used for molding. It would be useful simply to discuss the generic principal of the machines. The two broad classes of injection molding machines are the screw type and the plunger type. The reciprocating screw type machines are a direct adaptation of the plastic injection molding machines to CIM. In this machine, palletized feedstock is fed into the heated barrel of the machine through a hopper. The feedstock is heated and plasticized by the action of the screw, which also results in moving the molten feedstock to the front of the barrel. The actual molding happens when the screw is thrust forward in the barrel and pushes the molten shot through the sprue, runner, and gate in to the die cavity. The tooling can be heated so that the shot does not prematurely freeze up in the die. Usually the fill times are also kept short to allow little time for the material to freeze before the cavity is completely filled. Once the mold is filled, it cools in the die cavity. To counter the shrinkage, typically a pressure is maintained till the gate freezes off. The molded part is then ejected and the cycle is repeated. Thus a typical molding cycle would consist of the following steps: filling the mold, packing, cooling, mold opening and part ejection, and closing of the mold.

The plunger type machines generally have no screws and a plunger pushes the accumulated molten feedstock into the die cavity. The pressure on the ram can be through hydraulic or pneumatic. Depending on the maximum pressure that can be applied, the injection molding machines can be classified as medium or low pressure injection molding. Thus, for injection molding, the pressure can vary over a wide range (from 0.1 MPa to more than 100 MPa). Some large low-volume ceramic parts have been made using the low or medium pressure machines as the use of such pressures allows the use of less expensive tooling material.

The capability of an injection molding machine can be specified by a number of different parameters. Some of them are outlined below:

Shot size, injection pressure, clamping force, open or close loop control, cycle time, mold opening size, etc.

Some special consideration should also be given to the barrel and screw of CIM machines due to the abrasive nature of the CIM feedstock. In high abrasive wear applications, some of the vanadium carbide containing tool steels or boride clad steels are found to be superior.

# DEBINDING

This step is perhaps the most complex and critical step in the CIM process. Any defects that are generated during this step are only exaggerated during the subsequent processing steps. The defects that can be generated during the debinding process are numerous and include blistering, pin hole formation, distortion, slumping, molding weld line separation, powder-binder segregation, reside from the binder, cracking, etc. It is extremely important to pay careful attention to the debinding details in order to produce good CIM parts.

The debinding process, in general, consists of two stages. The first stage is the removal of the filler and the second is usually the removal of the backbone binder phase (by thermal means). There are numerous variations in debinding that is again dependent on the choice of the original binder system. Some of the commonly used debinding practices include organic solvent extraction, catalytic reaction, water extraction, evaporation of a portion of the binder, supercritical debinding, wick debinding, and thermal debinding. Early debinding cycles relied on total thermal degradation, which was very long and prone to defects. The aim of debinding is to remove the organic binder with the least impact on the part in the shortest period of time in an environmentally friendly manner.

Binder extraction involves fluid flow through pore channels in the compact. The fluid could be either a liquid or gas. The flow through the pore channel is dependent on the porosity, pore size, and permeability. For vapors to come out, it is important to have open pore channels, which are connected to the exterior surface. For thermal debinding, faster debinding occurs at elevated temperatures, but this can also be the cause of defects. Most debinding processes are developed to reduce the long times that are needed for pure thermal debinding. The practice of wick debinding is quite often used in CIM. In this process the compact is embedded in a wicking medium and heated to a temperature where a part of the binder forms a liquid phase and is quickly removed by the wicking medium. In other cases, to afford faster debinding, a major part of the binder is removed by organic solvents, water, or by a catalytic reaction. In some special cases of debinding, such as supercritical fluid extraction, a gas such as carbon dioxide can act as a fluid that is responsible for the extraction of a part of the binder. The final debinding atmosphere also plays a role in the debinding rate. A small amount of retained binder is needed to maintain the shape of the compact, and this is almost always removed by the application of thermal energy. This is the final binder burnout stage. It is usually important to carry out experiments to determine the critical temperatures for this last stage of debinding as the heating rates to be used is dependent on this. Among the numerous debinding processes that are currently in use, it is really difficult to come up with a comprehensive cost model to determine the most economical debinding route.

# **CONSOLIDATION**

Once the binder has been removed from the green part the next step in the CIM process is consolidation. The consolidation is generally achieved by a thermal treatment, often termed as sintering. The purpose of sintering is to provide structural integrity to the CIM part. During this step, usually the pores are removed as increased particle bonding takes place and the part shrinks as a result of the reduction of the porosity. The process of pore elimination and particle bonding is also accompanied by a concomitant increase in most engineering properties such as strength, hardness, toughness, etc. The driving force for sintering is the stress associated with a curved surface. Mass flow occurs during the process to eliminate the porosity. The mass flow may occur through any one or more of the following mechanisms: surface diffusion, grain boundary diffusion, volume diffusion, and evaporation-condensation. The sintering may be purely solid-state or in some cases there may be the presence of some liquid (liquid phase sintering). The sintering process is quite often pressureless, but in several occasions, pressure assisted hot consolidation is used to attain better properties. Some typical examples of pressure-assisted consolidation conditions for ceramic materials are given below:

Aluminum Nitride:	2500°C /100MPa / 1 hour
Aluminum Oxide:	1650°C /100MPa / 1 hour
Silicon Carbide + Boron:	2000°C /200MPa / 0.8 hour
Yttria Stabilized Zirconia:	1400°C /200MPa / 2 hour

# **APPLICATIONS**

The applications of CIM are wide and varied. Industrial ceramics are widely used in areas of sensors, thermocouples, crucibles, setters, thermal barriers, etc. Most companies in ceramics often use some variance of the technology. Some of the more specific applications are in the areas of textile fabrication machines (alumina-chromia; zirconia), sound transducers (lead-zirconia-titanate), microelectronic packaging (AlN), cutting tools (silicon carbide/alumina), abrasive jet nozzles, gas turbine heat engine component (silicon carbide), casting cores, etc. It is expected that the applications will continue to grow and CIM will become one of the key process in the Ceramics Age.

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#### FABRICATION OF CERAMIC COMPONENTS FOR MICRO GAS TURBINE ENGINES

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## ABSTRACT

Assembly Mold SDM (Shape Deposition Manufacturing) has been used in combination with Gel Casting to fabricate ceramic micro gas turbine components. Full 3-dimensional ceramic turbines and compressors with a feature size down to 200  $\mu$ m were built. The turbine has been tested and been spun up to 456,000 rpm. During the research, it was found that the development of a ceramic air bearing is desirable. Thus, a process utilizing MEMS techniques has been developed to fabricate patterns with 125  $\mu$ m feature size. In this paper, the techniques used to fabricate functional rotor groups, improve accuracy, and pattern micro features will be discussed.

#### INTRODUCTION

Assembly Mold SDM (Shape Deposition Manufacturing) is a derivation of Mold SDM [1, 2], an additive-subtractive layered manufacturing process developed at Stanford University. A mold design is decomposed into several geometrical features, and then SDM is applied to fabricate each mold feature. After all the geometrical features are made, a complete mold is built by assembling the mold features. Figure 1 illustrates the fabrication of an example mold. In this project, the mold material is KC3230A wax from Kindt-Collins Company in Ohio, the support material is Soldermask<sup>TM</sup>, a UV curable, water-soluble polymer resin from Advanced Ceramics Research (Tucson, AZ).

There are several advantages of Assembly Mold SDM compared to competing processes. First, complicated mold geometries are split into several less complex geometrical features. This provides a solution to build molds which are difficult to make by Mold SDM; second, for each split geometrical feature, one can choose the best fabrication strategy to apply, depending on the complexity of the geometry; third, each piece of the mold assembly can be fabricated in a parallel process, therefore, the overall fabrication time is reduced; the last point, but not the least, the change of design can be reflected rapidly in this process.

The major drawback of the Assembly Mold SDM is the possibility to have geometrical inaccuracy during the mold assembly process. The detail of the inaccuracy introduced in this process will be discussed in the FABRICATION PROCESSES section.

Once a fugitive assembly mold has been made, the gel casting process is applied to build a monolithic ceramic part. Gel casting is a ceramic forming technique first developed by Oak Ridge

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National Laboratory in the 1990s [3]. The basic concept of this process is to make a slurry of desired ceramic powders with gel precursors (monomers and cross-linkers). The polymerization process is initiated right before casting and completes afterward to form a solid gel network that holds the powders. The green part is then going through processes such as demolding (remove the mold), drying (remove water or solvent), debinding (remove polymeric binders), and sintering, in order to acquire the final part. Comparing with other ceramic forming techniques, gel casting has advantages such as short molding time, high green state strength, good mold material compatibility, minimal molding defects and minimal warpage in green and brown state [3].



Figure 1. Principal process steps for Assembly Mold SDM

#### MICRO GAS TURBINE ENGINE DESIGN AND REQUIREMENTS

By combining the assembly Mold SDM and gel casting processes, the Rapid Prototyping Laboratory (RPL) at Stanford University is developing a miniature ceramic gas turbine with its industrial partners. M-DOT Aerospace Inc. (Arizona, USA) designed the engine and RPL's responsibilities include the fabrication of ceramic components. The goal of this project is to develop a higher power density energy source by making palm-size gas turbine engines with ceramic components. The rotor group (a monolithic body of turbine, compressor, and shaft) is designed to spin at 800,000 rpm to generate 100 watts. Among several engineering ceramic materials, silicon nitride (Si<sub>3</sub>N<sub>4</sub>) has been chosen because of its good combination of thermal properties, corrosion resistance, and mechanical strength.

Figure 2 shows the design of this micro gas turbine and the major component to be made by silicon nitride. Due to the high rotating speeds, the straightness of the shaft and the shape accuracy is crucial for a functioning device. The target turbine inlet temperature (TIT) is above 1000°C, with an operation time of 100 hours.

#### FABRICATION PROCESSES

#### Overview of Rotor Group Fabrication

The rotor group is a unitary rotating component that consists of turbine, compressor, and shaft. There is an interconnect structure between turbine and compressor, a short shaft connects to turbine and a long shaft on the compressor side. Due to the complexity of the geometry, this casting mold is decomposed into five pieces: cap, turbine, interconnect, compressor, and shaft. Each mold piece was made individually by the best strategy chosen form its geometry. Figure 3 (A) shows the schematic of the rotor group mold consists of 5 pieces. The turbine and compressor geometry are made using the SDM process, while the rest of the mold is made by CNC machining. Assembly Mold SDM allows a quick reflection of design change. For example, we can change the diameter of shaft or the shape of blades by replacing the specific mold pieces, without modifying the other mold pieces.



Figure 2. Design of rotor group and inlet nozzle. Both components are made of silicon nitride

Sources of Geometrical Inaccuracy

After the rotor group is sintered, it is found that the geometry features are shifted from the concentric center. An obvious example is shown in Figure 3 (B), the shaft of the rotor has shifted and has eccentricity of 0.5 mm. This indicates the two possible sources of geometrical inaccuracy: the error from the shaping of each mold piece; the error from the mold assembly process.



Figure 3. (A) Rotor group mold assembly. (B) As-sintered rotor shows the eccentricity. (C) The schematic shows the drifting of Soldermask during wax casting.

A careful inspection of the fabrication processes indicates that the Soldermask compact geometry drifted during embedding with hot wax. This is illustrated in Figure 3 (C). During the fabrication of turbine and compressor molds, a Soldermask compact is deposited on a wax base. The Soldermask is machined on the wax base and a new layer of the wax is cast on it. Thus, the machined geometry of Soldermask is transferred onto the wax and after the Soldermask is sacrificed, the wax holds the negative geometry. (I don't think this sentence is necessary.) The new layer of molten wax on the Soldermask compact softens the wax base underneath the Soldermask compact and the following shrinkage during the wax solidification drags the Soldermask compact away from the original position and also tilts it out of plane.

#### Improvements of Geometrical Accuracy

To remove the errors from fabrication and mold assembly, the rotor group fabrication process has been modified to provide a better geometry support. Figure 4 shows the two major changes in the process: metal base for Soldermask, and metal guide for assembly.



Figure 4. Improvements of fabrication. (A) Metal base for Soldermask. (B) Metal guide for mold assembly.

The metal base provides a rigid support of the Soldermask material during both the CNC machining and the following wax casting steps. The replacement of the base from wax to aluminum alloy minimizes the possible tilting and drifting of turbine and compressor geometry. Once mold assembly pieces are separately made, each piece is turned on lathe to remove the eccentricity before being assembled. The assembly strategy has been modified to use external metal guide instead of the geometrical features on adjacent mold pieces. The metal guide is expected to provide a solid fixture for assembly alignment, and the external guiding for alignment is superior to the original method using interconnect features. Both metal base and metal guide are designed to work best with the dimensions of rotor group, however, the same concepts apply to the fabrication of other components. Furthermore, the metal guide assembly method provides a universal fit for any future design of the rotor group. For example, given the same alignment feature of the mold assembly, one can quickly change the shaft diameter or the turbine geometry by only changing the specific mold assembly piece. For conventional mold fabrication and any other rapid prototyping techniques that produce one-piece molds, a whole new mold has to be fabricated even there is a tiny change in design. Table I and II present the comparisons of measured geometrical inaccuracy of molds with different fabricating strategies.

## Overview of Inlet Nozzle Fabrication

The silicon nitride inlet nozzle of the micro gas turbine engine is also fabricated using the Assembly Mold SDM process. The mold pieces are prepared using the SDM process with Soldermask support material and wax part material.

Component	Base Material	Eccentricity (mm)		
		Minimum	Average	Maximum
Turbine	Wax	0.10	0.27	0.41
Turbine	Metal	0.06	0.08	0.09
Compressor	Wax	0.11	0.19	0.27
Compressor	Metal	0.03	0.13	0.19

Table I. Effect of metal base for the eccentricity of turbine and compressor mold geometry

Table II. Effect of metal base for the tilting of turbine and compressor mold geometry

Base Material	Tilt angle (°)
Wax	0.42 ~ 0.54
Metal	0.12 ~ 0.17

The mold for the inlet nozzle is decomposed into 5 pieces. The decomposition was done so that the position of the layer boundaries has minimum effects on the part quality and the mold pieces align by themselves.

The lower disk of the inlet nozzle green part is 0.76 mm thick and its diameter is 34 mm. To avoid the warpage of the disk sintering fixtures to support the disk are prepared and shown in Figure 5 (A).

The thin inlet nozzle vanes support the upper part of the inlet nozzle and the upper part of the inlet nozzle can sag due to its own weight during sintering. The cone with curved surface at the center of the lower sintering fixture is designed so that the sintering fixture rather than the inlet nozzle vanes supports the weight of the upper part.



Figure 5. Ceramic inlet nozzle. (A) Cross-section of sintering fixture and inlet nozzle. (B) Assintered inlet nozzle.

The sintering fixtures are used in the brown state so that they can shrink with the same rate during sintering, causing no relative motion or friction between the part and sintering fixture. If the shrinkage rate of the fixture differs from that of the part, however, the mismatch in shrinking will produce constraint stress thus cause cracks during sintering. Inspections with fluorescent paint indicate the existence of micro-cracks on the bottom of inlet nozzle where the fixture might have smaller shrinkage rate and therefore constrained the shrinking of nozzle part.

#### FUNCTIONALITY TESTS

The functionality of the rotor group fabricated with Assembly Mold SDM process has been demonstrated by a series of tests of the turbine and compressor.

The simplified rotor spun up to 456,000 rpm with room temperature pressurized nitrogen gas [4]. The turbine is designed to spin at 800,000 rpm under 1,000°C air. Comparing the speed of the sound and energy of room temperature nitrogen and 1,000°C air, the performance of the turbine is satisfactory.



Figure 6. (A) Simplified rotor. (B) Rotor group spin tested up to 420,000 rpm.

The functionality of compressor has been demonstrated by the test of the whole rotor group. The rotor group is mounted on a test rig and pressurized nitrogen (N<sub>2</sub>) was used as the driving gas. The compression ratio and flow rate of the compressed gas have been measured to characterize the compressor. The characterization result of the compressor up to 420,000 rpm shows that the performance of the compressor reasonably matches with the designed performance. The estimated efficiency of compressor using the pressure and mass flow data falls between 54 - 57%. The CFD estimation of compressor efficiency is 63%.

The rotor group was mounted on miniature ball bearings. The vibration measurement of the rotor group during the compressor characterization and rotor-bearing dynamics analysis suggested the bearings, as well as the use of the room temperature nitrogen as driving gas, are responsible for the limiting the current maximum speed.

The measure for the performance of ball bearing is surface speed, denoted as DN valued. It is defined as the pitch diameter in mm and rotation speed in rpm. It is commonly accepted in ball bearing industry that 2E+6 mm rpm is practical limit of miniature ball bearings. The performance of the ball bearings used in the rotor group test rig corresponds to DN = 2.0E+6 mm rpm<sup>†</sup>. The spinning of the rotor group at higher speed requires bearings with higher number assuming the diameter of the shaft cannot be reduced. Since air bearings operate at higher surface speeds compared to ball bearings, the development of technologies for the fabrication of micro air bearings is attractive for the implementation of micro gas turbine engines.

<sup>\*</sup> Pitch diameter of a ball bearing is approximately defined as the average of inner and outer diameter.

<sup>&</sup>lt;sup>+</sup> Pitch diameter = 4.76 mm, rotation speed = 420,000 rpm.

### MICRO CERAMIC BEARING PATTERN

An individual research activity of RPL demonstrates the capacity to fabricate the micro pattern for air bearing by combining gel casting and a MEMS related process called "Soft Lithography" [5]. The overall processes to fabricate the tilting pad bearing pattern is shown in Figure 7. The master pattern of tilting-pad bearing is generated by DRIE (Deep Reactive Ion Etching) silicon process. PDMS (Polydimethylsiloxane) is cast onto master to replicate the pattern; a gel casting process transfers the features from PSDM to ceramic part. PDMS is flexible and helps to minimize the damage during removal of molds.



Figure 7. The soft lithography process used to fabricate bearing patterns.

Figure 8 presents the details of tilting-pad bearing patterns under SEM (Scanning Electron Microscopy) inspection. The straight sidewall shows a good definition of micro pattern, and the smallest feature is less than  $125\mu$ m (the tilting pad) and has an aspect ratio of higher than 8. This work provides a potential to make ceramic air bearings for the micro gas turbine system.



Figure 8. The SEM pictures show the details of sintered ceramic tilting-pad bearing pattern. Left: sintered silicon nitride (Si<sub>3</sub>N<sub>4</sub>). Right: sintered alumina (Al<sub>2</sub>O<sub>3</sub>).

## CONCLUSIONS

In this paper, we have discussed the fabrication of ceramic gas turbine components by the combination of Assembly Mold SDM and gel casting techniques. The processes have been

examined and the sources of geometrical inaccuracy are identified. New mold manufacturing strategy is applied to reduce the error in geometry features.

The rotor group has been tested for its functionality. The turbine rotor spun up to 456,000 rpm and the compressor (tested with the whole rotor) spun up to 420,000 rpm with pressured N<sub>2</sub> at room temperature. The characterizations of the rotor demonstrated the performance that follows the design intention.

The spin test suggests the possible improvement in the rotor performance with a better bearing system. An effort of fabricating micro tilting-pad bearing pattern is presented and demonstrates the capability to make ceramic components on a micro scale.

## ACKNOWLEDGEMENT

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# LOW PRESSURE INJECTION MOLDING PROCESS FOR NEAR-NET SHAPE, HOT GAS FILTER COMPONENTS

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## ABSTRACT

Advanced, coal-fueled, power generation systems require low cost, high efficiency, and durable hot-gas filtration systems. The requirement of a high surface area-to-volume ratio filter implies non-trivial shapes. Conventional filters are based on a candle design and more recent innovations involve a cross-flow design. COIC has been developing low pressure injection molding (LPIM) for low cost production of complex-shaped ceramic filters and other advanced ceramic components. Through a DOE-funded Phase II STTR, COIC has developed the LPIM technology for the fabrication of high-purity mullite based candles, 30" long, and roughly 4" x 4" x 8" cross flow filters. Highlights of this study are presented here.

## INTRODUCTION

Advanced coal-fueled power generation systems utilizing Pressurized Fluidized Bed Combustion (PFBC) and Integrated Gas Combined Cycle (IGCC) technologies are currently being developed for high efficiency, low emissions and low-cost power generation<sup>1,2</sup>. In spite of the advantages of these promising technologies, the severe operating environment often leads to material degradation and loss of performance, particularly in the barrier filters used for particle entrapment. These aggressive environments include temperatures up to 1000°C, pressures up to 20 atmospheres, thermal transients, and highly corrosive effluent gases containing micron-sized ash particulates. For these reasons, new and innovative hot gas filtration devices are needed to address the challenges with these state-of-the-art coal-fueled power generation systems.

The filter should capture more than 99% of the flyash particles while providing a minimal pressure drop. As the ash layer builds up on the filter surface, the pressure drop across the filter increases and hence the ash layer must be dislodged and collected. A clean gas stream is pulsed from the downstream side of the filter element to perform this operation. This pulse cleaning and other process transients expose the filter element to cyclic mechanical and thermal stresses. The filter elements must have excellent thermal shock resistance in addition to superior mechanical integrity and chemical resistance.

There are several types of filter designs under consideration for hot-gas filtration application. Two of the prominent designs are the candle and cross-flow filter designs (see figure 1). Candle filters are currently in use for hot-gas filter applications in PFBC and IGCC processes. The candle filter typically consists of a large tube with one closed end and a supporting flange at the open end.

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The hot process gases pass through the porous media of the tube, which captures the flyash and allows the passage of air. Back-pulsing is used to flush the build-up of flyash from the filter in order to maintain peak performance capability.

The cross-flow design<sup>3,4</sup> consists of two sets of flow channels that are perpendicular in an alternating stack. The hot process gases pass through one set of channels in either a series or parallel setup and the porous media of the walls between the two sets of channels allows the passage of air and blocks the passage of flyash. This design has several advantages over the existing candle filter system. The main advantages are that the design is more efficient system due to the fact of the filter media is parallel to the gas flow direction, which results in less blockage, rather than perpendicular as in the candle system. As compared to the candle design, the cross-flow design also provides the higher surface area per unit volume of the filter. Next, the manifolding necessary for this design places the filter in compression, which inherently favors a ceramic body, rather than tension. Finally, due to the compact size of the filter, this design is more resistance to thermal shock from process upsets and backpulsing.

Whatever be the filter design of choice, there is one major challenge and that is, filter fabrication. Typically, a cross-flow filter is fabricated by laminating several layers of hollow channels in orthogonal directions. As a result, such filters tend to delaminate and are susceptible to breakage during operation. In the case of the candle filter, tailoring a uniform distribution of the required porosity all along the length of the candle filter is critical not only for filtration efficiency but also for mechanical integrity required to survive backpulsing or any process upsets.



Figure 1: Schematic of (a) candle filter and (b) cross flow hot-gas filter design concepts.

To address the processing challenge associated with the hot gas filter designs, especially the cross-flow design, COI Ceramics has developed a unique, low pressure injection molding (LPIM) process during the course of a Phase II STTR funded by DOE. Using high purity mullite, which was determined to be the most suitable ceramic material for hot gas filtration applications, both candle and cross flow filter components incorporating porosity suitable for optimum filtration characteristics were successfully developed. This paper describes important aspects of the development work performed to successfully produce the filters using LPIM.

# BACKGROUND AND EXPERIMENTAL APPROACH

## Low Pressure Injection Molding of Filters

The injection molding process is an excellent method for fabricating ceramic bodies with complex geometries. LPIM utilizes a proprietary wax blend as both a binder and liquid medium for fabricating ceramic bodies. The binder, typically 15 - 25 w%, is mixed with ceramic powder.



Figure 2: Flowchart describing the sequence of key steps for the wet filter fabrication process.

This mixed slurry is injected into a mold with low-pressure air and cooled while under pressure. The temperature in the mixing tank controls the viscosity of the slurry and the temperature at the die controls the set-up time. The temperature at the tank and the die along with injection pressure and hold time are manipulated to ensure complete production of a well-formed part. Figure 2 shows a flow chart of the overall injection molding process.

Low-pressure injection molding process is very similar to conventional ceramic injection molding, with one critical difference: the pressures employed are in the range of 0.35-0.7 MPa (50-100psi) vs. 7-70 MPa (1000-10,000psi) for conventional ceramic injection molding. A number of technical differences also result from the lower injection pressures and from the configuration of the machine system, as shown in the schematic of Figure 3:

- The lower injection pressures result in lower tooling deflections, which, in turn, result in highquality, defect-free components.
- The flow into the die cavity can be controlled at low rates, which, combined with the bottom injection, allows the development of a laminar melt front without the need for complex tooling design.
- The mixing portion of the machine allows for easy de-airing of the molding mix prior to injection. Which is necessary to eliminate internal voids and other defects.
- The lower injection-hold pressure place reduced amounts of internal stress on molded parts resulting in components with fewer defects (external cracks) after binder removal.



Figure 3: Schematic of the low – pressure injection molding machine.

For this program, in order to fabricate intact filter components of the candle and cross-flow types, an optimum LPIM process had to be developed, for which the following experimental parameters were varied and optimized:

- ➤ Tank Temperature ➤ Mixer Velocity ➤ Degassing Conditions ➤ Injection Pressure
- ► Injection Temperature ► Injection Time ► Mold Temperature

## Filter Porosity Development

From Phase I research conducted at Oak Ridge National Lab (ORNL) by Dave Stinton et. al, high purity mullite (Duramul EG from Washington Mills, NY) was found to be one of the best candidates for hot-gas filter applications. Besides the LPIM processing of high purity mullite based filters, in order to meet the filtration requirements, adequate porosity having the right pore characteristics for hot gas filtration had to be incorporated. Two different techniques: particle size selection and the addition of fugitive organic materials were evaluated for porosity development.

Two different mullite starting particle sizes and varying amounts of C granules or whiskers as fugitive binders were investigated. Duramul mullite powders screened to: (a) -100 mesh size, which resulted in an average particle size of  $125\mu$ m and a particle size distribution of 5 -  $150\mu$ m and; (b) to -80 + 100 mesh size, which yielded an average size of  $160\mu$ m for a size distribution ranging from 120 to  $180\mu$ m, were used. Between 10 and 20v% (varying in steps of 5v%) of the fugitive C binder was mixed in to the IM slurry. 5w% and 10w% sub-micron mullite was added as a sintering aid to the -100 and -80 + 100 mesh powders, respectively.

Disk samples containing nominal amounts of COIC's proprietary wax binder, the fugitive binder, and the sintering aid were fabricated by LPIM. The green disks were debindered and sintered using a carefully controlled heat treatment regime. Microstructural analysis was conducted to characterize the porosity in the sintered filter samples. Mechanical durability and permeability of samples was evaluated at Siemens Westinghouse STC in Pittsburgh by subjecting porous disks (60mm dia. x 6.25mm thick) to air pressure and measuring pressure drop across.

# **RESULTS AND DISCUSSION**

## Filter Porosity Development

Of the two different pore forming methods that were investigated to obtain the desired permeability and open porosity, it was found that particle size selection approach yielded the best results. Samples containing any amounts of the fugitive binder in the -100 mesh mullite powder containing 5w% submicron mullite resulted in samples that had inadequate permeability and inhomogeneous porosity. From the sintered disks, it was found that the wide particle size distribution allowed for better particle packing as the smaller particles filled the void spaces between larger particles. This resulted in reduced (and sometimes non-uniform) porosity and lower than adequate permeability, despite the presence of the fugitive binder.

On the other hand samples of the -80 +100 mesh size mullite containing 10w% submicron mullite sintering aid and no fugitive (C) binder yielded filter samples with acceptable porosity, permeability, and integrity for hot gas filtration. (SWSTC's acceptable threshold for candle filter use is a pressure drop of <10 in-wg/10 fpm without disk failure.). Figure 4, below shows the shows the microstructure of the optimum filter samples that met test requirements.




Low Pressure Injection Molding - Process Optimization & Filter Fabrication

As described in the experimental background, key injection molding process variables were varied and the optimum set of process parameters for fabricating cross flow filters of high purity mullite was arrived at. A listing of the experimental ranges over which such fabrication processing was optimized is provided in Table I below.

Process Variable	Property Affected	Typical Conditions
Tank temperature	Slurry viscosity	155 – 175 °F
Injection pressure	Fill density & porosity	30 – 50 psi
Orifice temperature	Flow characteristics	140 – 165 °F
Die temperature	Solidification time	70–110 °F
Injection time	Fill uniformity	20 - 240  sec

Table I: Key Processing Parameters for Injection Molding Process.

Even though the processing parameters listed in Table I appear distinct, to some extent they are inter-linked – changing one parameter affects more than one property. For example, increasing the tank temperature decreases the viscosity, which helps the slurry fill the die completely and evenly. However, because of the higher temperature of the slurry the part cools down slower, the rate of which is also controlled by the orifice temperature, die temperature, and injection time. Green disks were produced by varying the parameters over the range of processing conditions so as to produce acceptable parts. Acceptable parts were those that first met the visual criteria for physical imperfections and then the weight criteria for maximum solids filling. Some of the acceptable green disks were sectioned to examine the interior for the presence of defects such as voids or cracks.

The acceptable disks were then subjected to a single cycle debindering/sinter heating schedule. This schedule had multiple segments that were designed to control the manner in which the binder was removed from the green body and also enable consolidation to required densities at higher temperatures. In arriving at the optimum ramp rates and hold times at each of the critical debindering regimes (corresponding to binder melting, vaporization, decomposition, and oxidation in sequence), results of combined DTA & TGA testing done at Harrop Industries in Ohio were utilized. It was seen that in the decomposition and initial oxidation regimes, the majority of the binder loss (~50%) occurred. Accordingly, the ramp rates in these regimes were the slowest.

#### Cross-Flow Filter Prototypes

In addition to initial optimization of the injection molding process to produce intact, porous mullite disks, the process had to be further refined – primarily, with respect to debindering and sintering - in order to fabricate cross flow filter prototypes. Figure 5 shows the picture of a typical cross-flow filter that has been produced using the optimized LPIM process. This filter prototype has 9 x 9 array of orthogonal channels and is roughly 4" x 4" x 8" in dimensions.

#### Candle Filter Prototypes

After obtaining candle filter specifications from Mary Anne Alvin of SWPC, the design and manufacture of an injection molding die to produce candle filters was targeted. Owing to the size and weight of the die along with space constraints of the low pressure injection molding machine at COIC, the overall length of the candle filter was scaled down from 1.0m to 0.75m. Even so, die design was extremely critical to achieving a complete and uniform filling of the mold and a good

release of the 0.75m long candle from the molds. Going from the cross-flow filter to the candle prototype, the tank, tube, and orifice temperatures, the hold times and the injection pressure had to be optimized over again. Figure 6 shows photographs of the green forming sequence for the high purity mullite-based candle filters that were successfully fabricated using LPIM.



Figure 5: Picture of 9 x 9 (4" x 4" x 8" size) cross-flow hot-gas filter fabricated by LPIM.



Figure 6. Photographs of: (a) as-molded green candle, (b) candle removed from the mold.

Besides the necessary changes in the injection processing conditions, some important modifications had to be made to the debindering and sintering conditions for the candles. The biggest challenge in the heat treating process was to prevent slumping and cracking of the large candles. As the binder is removed, it goes through a molten phase where the it flows and causes the candle filter to slump simply from its weight.

Several iterations of heat treating had to be done prior to arriving at the optimum conditions for successfully sintering the large candle. Particular attention had to be paid to the settering/bedding of the candle, which actually consisted multiple layers of materials. After the settering, the entire heat treatment was performed in a single stage where the first stage was designed for carefully-controlled binder removal at relatively low temperatures (60 - 500°C) and the second stage for sintering of the coarse mullite body, at 1600°C.

Figure 7(b) shows the photograph of a candle that has been sintered using a single stage heat treatment process to the required density ranges for hot gas filter applications. Fig. 7(a) shows the candle in its green state for comparison purposes. It can be noted that there is little shrinkage or warpage of the sintered candle as compared to the green one. However, the green forming and sintering process needs to be further optimized to improve surface texture of the sintered candles.



Figure 7. LPIM processed: (a) green candle and (b) intact and straight sintered candle.

## SUMMARY AND ACCOMPLISHMENTS

- This process development research program has been successful in pushing the envelope on the capabilities of the injection molding process for fabricating ceramic components.
- Low-pressure injection molding (LPIM) is an excellent method for fabricating both cross-flow and candle filters.
  - ✓ Injection molding process has been successfully developed at COI Ceramics, Inc.
  - ✓ Other complex and large scale parts can be produced using optimized processing.
  - ✓ This LPIM process resulted in sintered, 30" long candle filters that met the permeability specifications of Siemens Westinghouse (SWSTC) for hot gas filters.

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# NEAR NET-SHAPE SiO<sub>2</sub>-TiO<sub>2</sub>-GLASS COMPACTS WITH REDUCED THERMAL EXPANSION

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## ABSTRACT

 $ULE^{TM}$  glasses show negligible thermal expansion in the useful temperature range. In this paper, colloidal sol-gel alternative to costly flame hydrolysis is presented. Colloidal gel processing of pure silica powders leads to greenbodies with open pores. Near net-shape SiO<sub>2</sub>-TiO<sub>2</sub>-glass production can base on this technique as it can be combined with penetration of the fluid titanium compound. After removing organic compounds by calcination, purely anorganic greenbodies can be sintered to dense glassbodies. The transparent samples show a smaller coefficient of thermal expansion (CTE) than fused silica.

#### **INTRODUCTION**

Fused silica glasses containing about 7 wt% of titanium dioxide show extremely low coefficients of thermal expansion (CTE) in a temperature regime from room temperature to 1000 °C. Historically, ultra-low-expansion glasses (ULE<sup>TM</sup>, Trademark by Corning Inc.) have been produced by flame hydrolysis of volatile silicon and titania compounds since the 1960's. Recently, also sol-gel techniques are applied for production. Disadvantages in these processes are found in comparatively high cost of manufacture.

Alternative route for production of silica-titania glasses is the sintering of green bodies consisting of nanosized silica particles. Before sintering, the titania compound can be added by soaking. Comparable processes are already used for the formation of pure silica glasses on an industrial scale 1,2.

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#### **EXPERIMENTAL SET-UP**

Nanosized particles of different diameters are formed by flame hydrolysis of silicon compounds, e.g. of SiCl<sub>4</sub>. Pure silica powders like OX50 (trademark of DEGUSSA) are produced on a very large industrial scale. These are transferred into a colloidal slurry, where particles cross-link at low temperature in a given mould. After drying, porous, but mechanically stable green bodies are obtained.

The porous green bodies can be soaked with titania containing compounds, e.g. titaniumisopropoxide <sup>3, 4</sup>. In this case, after hydrolysation to titaniumhydroxide, water is set free and condensation occurs to silica-titania network. After a second drying step, residual organic compounds can be removed from the samples by calcination at 500 °C in air for two hours. After this step, samples are sintered in a vacuum furnace (Thermal technology, type 0010-9306) until dense samples are obtained.

## **RESULTS AND DISCUSSION**

Figure 1 shows relative sintering density vs. temperature, where comparison to pure silica green bodies (unsoaked OX50) is made. Soaked samples sinter at temperatures about 50 K lower than pure silica porous green bodies. So  $TiO_2$  works as a "fluidizer" in the sintering process. At 100 % relative sintering density, samples are transparent and clear.



Fig. 1: Relative sintering density of soaked samples (approx. 4 wt% TiO<sub>2</sub>) and non-soaked OX50 – green bodies. Relative density was normalized to 2.2 g/cm<sup>3</sup> after <sup>6</sup>.

EDX-Analysis of sintered samples shows a  $TiO_2$ -content of about 4 wt%. Gravimetrically, 3.9 wt% of  $TiO_2$  were calculated in advance. X-ray diffractometry detected no crystallinity in the glass. Additionally, Raman spectroscopy is done on these samples. Fig. 2 shows spectra from fused silica, silica glass with about 4 wt%  $TiO_2$  and pure  $TiO_2$ -powder (Degussa P25).



Fig. 2: Unpolarized Ramanspectra of fused silica, SiO<sub>2</sub> with about 4 wt% TiO<sub>2</sub> and pure TiO<sub>2</sub> –powder (Degussa P25)

The sample with about 4 %weight of titanium dioxide shows an additional peak at 945 cm<sup>-1</sup> compared with the pure fused silica sample. Literature data <sup>5</sup> identify this peak as Ti-O-vibration (Ti<sup>4+</sup> on Si<sup>4+</sup>-site). Comparing this spectrum with a pure TiO<sub>2</sub>-powder spectrum (P25) shows no correspondence of peaks. So there is no hint on phase separation or significant crystallinity.

Determining the coefficient of thermal expansion (CTE)

Thermal expansion of was determined corresponding to DIN 52358 with an arrangement as shown in Fig. 3. The sample is heated in a furnace, elongation is



Fig. 3: Setup for CTE-determination, Netzsch TMA 402



Fig. 4: Relative elongation when heating a SiO<sub>2</sub>-TiO<sub>2</sub>-sample

detected by an inductive displacement pickup. The samples are about 25 mm in length and 2 to 5 mm in diameter.

Results of the measurement are shown in fig. 4. The sample analysed in this case contains about two percents  $TiO_2$ . Pure fused silica shows about twice the thermal expansion of this sample.

## CONCLUSIONS

Nanosized pure silica powder (OX50 by DEGUSSA) was processed by colloidal gel technique to form greenbodies with open pores. Simultaneously, a suitable organic titanium compound was prepared in a liquid to penetrate the green body by soaking. After drying the soaked green body, a calcinations step removes organic compounds leading to a purely anorganic body in the appropriate composition of titania and silica.

After sintering in a vacuum furnace transparent  $SiO_2$ -TiO<sub>2</sub> glasses were achieved. Powder diffractometry and Raman spectrometry showed no significant crystallinity in the samples. Thermal expansion was reduced as expected according to literature. By the additional feature of near-netshape processing, soaking of OX50-green bodies is a promising alternative to conventional flame hydrolysis techniques. With colloidal gel processing, moderate cost of manufacture meets with high quality of the resulting glasses.

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# AN APPROACH TO EXAMINATION OF THERMAL DECOMPOSITION BY NOVEL EVOLVED GAS ANALYSIS

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## ABSTRACT

Pyrolysis behavior of remained carbon substances in hydrolysis products of aluminum alkoxides has been investigated with comparison of EGA-MS using capillary and skimmer interfaces. The technique with skimmer interface has a possibility to present new information on elimination processes of impurities in ceramic starting materials during its firing or sintering processes. As the pyrolysis, ethyl group were eliminated at higher temperature than butyl group. In the measurement with skimmer interface it results a possibility of polymerization of the ethyl group, since the skimmer has much less adsorption than the capillary.

#### **INTRODUCTION**

It is very important to understand firing and sintering processes as step-by-step for systematic design of the processes. As a technique to approach to understand thermal behaviors, EGA (evolved gas analysis) has received attention as not only the EGA itself but as TDS (thermal desorption spectroscopy), TPD (temperature programmed desorption spectroscopy) and TG-MS (thermogravimetry-mass spectrometry) which is a combination of thermal analysis and EGA-MS technique.

On the other hand, the impurities in the fine ceramic materials have also received increasing attention, since the impurities exert considerable effects on such features as the sintering process, the properties of the final products, etc. The impurities of carbon substances due to the sol-gel method have been successfully analyzed with our trial type EGA-MS apparatus [1]. After that, we have developed our apparatus with a new interface between a heating furnace (atmospheric pressure) and a vacuum chamber with a mass spectrometer [2].

In this study, we have compared two types of interfaces between the

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furnaces and the mass spectrometer, which interfaces connect with a same vacuum chamber, with measurements of hydrolysis products of aluminum alkoxides.

## EXPERIMENTAL

For sample preparation, we have referred to a report [3] on sol-gel processing as follows: the molar ratio between the aluminum alkoxides (methoxide, ethoxide, i-propoxide and sec-butoxide) and water kept at 1:100 in all cases. The hydrolysis was carried out with deionized and distilled water kept at the hydrolysis temperature. The hydrolysis temperature was kept at 90 °C with a water bath. The precipitates were suction-filtered, washed with the alcohol that corresponded to its alkoxyl group, and dried with CaCl<sub>2</sub> at the hydrolysis temperature. As a result of this sample preparation, pseudoboehmite was obtained on each Al alkoxide.



Figure 1 Schematic diagram of the instrumental model EGA-MS apparatus. [1]Furnace, [2]Q-MS, [3]Capillary interface, [4]Skimmer interface, [5]Gate valve, [6]Turbo molecular pump, [7]Rotary pump, [8]Sample

The EGA-MS apparatus was constructed with two gold image furnace (MR-39H, Shinku-Riko) and a quadrupole mass spectrometer (M-400QA-M, ANELVA) as shown in Fig. 1. In capillary-interface mode, the two devices are connected with a fused-silica capillary coated with polyimide. Its length and inner-diameter are 700 mm and 0.10 mm respectively. The pathway of gaseous

species was heated at 200 °C. The carrier gas is high-purity helium of which plumbing is with a liquid nitrogen pool to trap traces of water and the other impurities. In the other skimmer-interface mode, two conic quartz tubes with orifice connected the two devices at atmospheric pressure or under vacuum. Since the carrier gas used was also high-purity helium, the evolved gaseous species with higher masses were enriched after the second orifice, consequently as a principle of a jet separator as shown in Fig. 2. It is due to difference of diffusion velocity.



To rotary pump

Figure 2 Principle of a jet separator.

#### **RESULTS AND DISCUSSION**

The quartz tube had no special heating, except infrared from the furnace lamp and radiant heat from the sample. In fact, the image furnaces of the capillary and skimmer modes were subtly different. While a single lamp type was used in capillary mode, a double-lamp type was used in skimmer mode because we were afraid that the skimmer would make shadow which would lower its maximum temperature.

The major gaseous species by the thermal desorption e.g.,  $H_2O$  due to the dehydration from aluminum hydroxide to aluminum oxide, were excluded in this study. Paying attention to gaseous species with very small amounts, Figures 3 and 4 show EGA-MS curves obtained from the hydrolysis product of Al sec-butoxide with capillary and skimmer interfaces respectively. The fragments of carbon substances remained due to alkoxyl group not reacted, were detected at about 289 °C in both interface modes. The fragments of 15, 26, 41 and 56 amu are identified as CH<sub>3</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>3</sub>H<sub>5</sub> and C<sub>4</sub>H<sub>8</sub> respectively. The species were produced by electron impact that is ionization source of the quadrupole mass spectrometer, though the desorped one from the sample is  $-CH_2CH(CH_3)_2$ .

Figures 5 and 6 show EGA-MS curves obtained from the hydrolysis product of Al ethoxide with capillary and skimmer interfaces respectively. The  $C_2H_2$  fragment due to ethoxyl group was detected. On the other hand, the larger fragments such as 41 and 56 amu were detected. The detection temperature of the larger fragments is different from that of 26 amu fragment. Therefore there is a possibility that remained ethoxyl group non-reacted and the other carbon substances exist. The temperature of 26 amu peak was at about 347 °C that is higher than that in the case of butoxyl group.



Figure 3 EGA-MS curves obtained from hydrolysis product of Al sec-butoxide with capillary interface.



Figure 4 EGA-MS curves obtained from hydrolysis product of Al sec-butoxide with skimmer interface.



Figure 5 EGA-MS curves obtained from hydrolysis product of Al ethoxide with capillary interface.



Figure 6 EGA-MS curves obtained from hydrolysis product of Al ethoxide with skimmer interface.

methoxyl	ethoxyl	i-propoxyl	sec-butoxyl
290 °C	345 °C	270 °C	290 °C

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Table 1 shows the comparison of thermal decomposition of each alkoxyl group non-reacted and remained in the each hydrolysis product. The temperature is independent to the length of the carbon chain, provided that methoxyl group is polymerized in aluminum methoxide.

As a comparison between capillary and skimmer interfaces, obtained peaks were broader in skimmer mode measurement. We have thought that the reason is turbulence in the furnace. The gas flow design in the capillary-mode furnace is well-conditioned by using by quartz tube to avoid the turbulence of the carrier gas. However the quartz tube cannot be set in the skimmer-mode furnace because of the interface and the furnace designs.

# Conclusion

As the pyrolysis behavior of the alkoxyl group non-reacted and remained in the hydrolysis products, the elimination temperature of ethyl group from remained ethoxyl group is higher than that of sec-butoxyl group. On the newly interfaced EGA-MS, developed design of carrier gas flow is expected.

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# COST-EFFECTIVE SYNTHESIS OF SILICA AEROGELS FROM WATERGLASS/TEOS BY AMBIENT DRYING AND THEIR APPLICATIONS

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#### ABSTRACT

Cost-effective ambient drying processes for synthesizing silica aerogels from waterglass/TEOS have been developed. The waterglass-based process was applied to produce aerogel-PVB composites for the thermal insulation. The aerogels were obtained by solvent exchange/surface modification of wet gels using IPA/TMCS/n-Hexane solution. The aerogel-PVB composites were fabricated by hot pressing. The aerogel-smart glazing could be manufactured from wet gel films dip/spin-coated with the silica sol prepared via TEOS-based processing. The thermal conductivities of aerogel products will be discussed.

#### INTRODUCTION

The silica aerogels are nanoporous materials with high surface area (500 ~ 1200 m<sup>2</sup>/g), high porosity (75.0 ~ 99.8 %), low density (0.003 ~ 0.350 g/cc), low dielectric constant (< 2.0), low reflective index (1.0 ~ 1.08), and low thermal conductivity (0.01 ~ 0.03 W/(m·K)).<sup>1.2</sup> Because of their excellent heat insulation properties, silica aerogels have received significant attention.

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