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Metals and Ceramics Division

Fabrication of Whisker-Toughened Alumina Tubes

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FINAL REPORT

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ABSTRACT

A process has been developed to fabricate whisker toughened alumina composites by slip casting dense colloidal suspensions of Al_2O_3 -15% SiC_w . Optimum processing parameters for slip casting were developed with slip viscosity of 60-70 centipoise and solids content of 78-79 wt%. Slip-cast parts with green densities in the range of 65 to 68% of theoretical were achieved. Composite parts were pressureless sintered to 96-97% theoretical density with <1% open porosity. The composites exhibited strengths of 500 MPa, toughness of 6.5 MPa $\text{m}^{1/2}$, and hardness of 17.26 GPa (1765 kg/mm^2). High temperature strength retention was maintained up to 1200°C. Good thermal shock resistance with $\Delta T_{cr} = 500^\circ\text{C}$ was also achieved. The process technology was transferred into pilot scale for producing prototype heat exchanger tubing up to 4 inches in diameter at the facilities of Vesuvius/McDanel.

EXECUTIVE SUMMARY

The objective of this work was to develop the technology for fabricating large diameter silicon carbide whisker toughened alumina tubes and to fabricate prototype tubes with different diameters and lengths at the Vesuvius/McDanel facility to establish commercial feasibility. A further objective of this program was to identify and assess the potential market for the utilization of the whisker-toughened aluminum tubes in industrial applications such as the heat exchanger market. The marketing study results are the subject of a separate report.

Alumina ceramics exhibit excellent resistance to environmental attack up to relatively high temperatures; however, alumina tubes are susceptible to failures induced by thermal shock. Silicon carbide whisker (SiC_w) reinforcement was considered as a means to toughen the alumina and enhance its thermal shock resistance. The emphasis of this effort was on the development of practical technology using commercially viable production techniques that would readily lend themselves to scale-up. The ceramic processing, therefore, was limited to forming by slip casting and consolidation by pressureless sintering.

A forming process was developed with high loading of Al_2O_3 with 15 volume percent SiC_w . This was achieved by using dispersants, ultrasonication, aging, and pH adjustment. A slip of alumina with 15 vol% SiC_w with a solid content of up to 79 wt% with a low slip viscosity of 60 centipoise was consistently achieved and slip cast parts with green densities in the range of 65–68% of theoretical were obtained. The rate of slip casting, or tube wall thickness build-up, was relatively slow compared to that of alumina slips alone. This behavior resulted in whisker segregation and ultimately deformation during sintering.

Yttria was used as the sintering aid to provide for a sufficient amount of liquid phase to cause the pressureless sintering. Composite parts were pressureless sintered to 97% theoretical density with <1% open porosity using 2 vol% yttria. The type of kiln furniture, heating rate, sintering temperature and soak time at temperature were investigated. Except for the heating rate, all other sintering parameters were significant in optimizing the product final density. Optimum sintering conditions involved the use of high purity alumina kiln furniture and tubular alumina to protect the parts from carbon contamination, $10^\circ\text{C}/\text{min}$ heating rate, and 1825°C sintering temperature for 1–1.2 hours.

The optimum mechanical properties of the composites were a strength of approximately 500 MPa and toughness of $6.5 \text{ MPa}\cdot\text{m}^{1/2}$ at room temperature. High temperature strength retention was maintained up to 1200°C with excellent oxidation resistance at temperature. Also, excellent thermal shock resistance compared to alumina was observed up to $\Delta T=500^\circ\text{C}$. These properties are well within the identified performance requirements for the potential markets.

The technology developed in the laboratory was scaled up to fabricate tubes as large as 4" in diameter and 12" in length at the Vesuvius/McDanel facility. Green densities and sintered densities similar to the small scale results were achieved, but long tubes exhibited circumferential distortion. The tubes did not sinter concentrically along the entire length. This problem is likely due to green density non-uniformity and uneven distribution of whiskers as a result of the slow slip cast rate, and possibly due to a high liquid content at the sintering temperature as a result of yttria additions. The use of small aspect ratio whiskers (short with large diameters) or possibly SiC platelets could potentially solve both problems.

I INTRODUCTION

Waste heat from high-temperature flue streams is estimated at 23% to 67% of the input energy. This is estimated to be equivalent to 1-2 quads of energy lost each year from numerous industrial processes ^[1,2]. Waste energy from the aluminum, steel and glass-making industries are the most difficult to recover because the waste energy streams are: i) high temperature (up to 1400°C), ii) high fouling (particulate build up), and iii) corrosive environment.

Ceramic materials, as an alternative to metals, have higher potential to recover and recycle waste heat because they can provide high-temperature strength, oxidation resistance, and can withstand the corrosive constituents of many industrial waste streams. However, certain limitations exist which severely restrict the application of advanced ceramic heat exchangers. The most severe limitations are structural reliability and high cost.

Silicon carbide (SiC) is the most widely accepted ceramic material for advanced heat recuperation. Several prototypes of SiC ceramic heat exchanger systems have been developed in the past to provide service in waste streams with severe corrosion environments. The heat exchangers in the form of tubes were tested in the Ceramic Recuperator Analysis Facility (CRAF) at Oak Ridge National Laboratory ^[3]. The SiC tubular heat exchangers exposed to a maximum wall temperature of $\approx 1240^\circ\text{C}$, however, experienced severe corrosion. The SiC materials and coal slag reacted resulting in the formation of pits or channels in the SiC surface. Similarly, SiC materials exposed to steam reforming of material gas under pressure exhibited chemical instability.

Alumina has very high resistance to corrosion and wear. Even though it has a lower thermal conductivity than SiC its chemical stability in corrosive environments could make this material a viable system in heavy industry heat recuperation. However, primary problems with Al_2O_3 are low fracture toughness, and poor thermal-shock resistance, which limits structural reliability, and fast thermal-cycling operations. Accordingly, improvement in Al_2O_3 thermal-shock resistance, without changing its high chemical resistance, is desirable, and it is the subject of this report.

Ceramic materials are gaining increasing importance in many industrial applications because of their higher-melting temperatures, superior oxidation resistance and corrosion resistance over metals. However, monolithic ceramics have very low toughness or resistance to damage and pose severe problems regarding structural reliability. Toughness and hence reliability can be enhanced by the use of energy-dissipating micromechanisms which increase the work of fracture.

Fracture toughness and Weibull modulus of monolithic ceramics has been improved by incorporating a fine dispersion or reinforcement of a second phase in the form of particulates, whiskers, or fibers. Strengthening of monolithic ceramics has also been achieved by mechanisms such as load transfer from the matrix to the reinforcement. Toughening mechanisms identified in brittle materials are crack deflection, microcracking, crack bridging, and reinforcement pull out from the matrix. The crack bridging mechanism has been suggested to dominate in whisker toughened composites ^[4]. Whisker reinforced composites have been found to increase fracture toughness, decrease creep rate, and increase the thermal shock resistance of Al_2O_3 ^[5,6,7,8,9].

Significant increases in strength have also been observed ^[10]. These improvements make the Al_2O_3 -SiC whisker composite materials very suitable candidates for use in high-temperature heat exchangers for corrosive waste gas streams.

A. SiC Whisker Reinforced Alumina Composite

The mechanical and physical properties of Al_2O_3 and Al_2O_3 -SiC whisker composites have been reported in many literature references. Many different processing methods have been used to fabricate these materials, and the material properties can vary from one method to the other. The properties of these materials make them suitable for other applications of high industrial value such as cutting tools, wear parts, high-temperature insulators, etc. Whisker reinforced alumina composites have already found some very specialized applications especially in the cutting tool industry.

Processing of the SiC whisker reinforced Al_2O_3 composite has been studied by several investigators ^[9,11,12,13,14,15]. Mixing SiC whiskers with Al_2O_3 powder has proved to be very difficult because of the tendency of the whiskers to form strong agglomerates in the form of "nests," or "clumps" resulting in significant reduction in the packing efficiency. Colloidal processing is the most advantageous method capable of making a homogeneous dispersion of composite mixture of the whiskers and the matrix powder. Aqueous slurries are the most commonly used traditionally in most oxide ceramic processing and are most suitable for slip casting. Densification of Al_2O_3 -SiC_w composites is also very difficult without the aid of pressure at high temperatures. To a large extent this prevented the development of commercial application and, together with the inability to form complex near net-shape parts, have made their manufacturing cost very high and their applications very limited.

Porter et al ^[16] stated that no densification occurred for Al_2O_3 - 15% SiC_w composite sintered at 1550°C in vacuum for 30 minutes. Tiegs and Becher ^[11] used higher temperatures and reached a density of 83% of theoretical for Al_2O_3 - 10% SiC_w fired between 1700-1800°C. Densification by pressureless sintering to near full density (>96% of theoretical) can be achieved by the use of liquid phase sintering aids. The most commonly used sintering additives are Y_2O_3 and MgO ^[14,15,17].

Green-forming techniques of ceramics materials include conventional methods such as dry pressing, isostatic pressing, extrusion, tape casting, slip casting, and advanced methods such as injection molding and gel casting. Slip casting and extrusion are the most common methods used for large scale production of tubular shapes components. Yet other techniques are being developed such as colloidal pressing, which is considered a laboratory curiosity. Forming of Al_2O_3 -SiC_w to produce high green density is very critical to maximize density by pressureless sintering, however the forming techniques have to also be practical and economical for scale up. Slip casting offers the advantages of lower production cost and flexibility in shape and design. In addition, handling of the whiskers is safer in a slurry form as compared to the dry state.

Techniques traditionally used to break up soft agglomerates are ball milling ^[18], turbomilling ^[19], high shear mixing ^[20], and ultrasonication ^[21,22]. All mixing techniques except ultrasonication are highly abrasive and have been known to reduce whisker aspect ratio by reducing their length. These techniques are not very practical for dense colloidal suspensions of ceramic composites. Ultrasonic frequency sound energy can very effectively break down soft agglomerates contained in a dense slurry. The powerful local shear stresses introduced by the ultrasonic energy have become very effective in processing of dense ceramic suspensions ^[23,24].

Slip casting is a very traditional, economical tool which can produce complex shape parts in large quantities. The ceramic suspension directly affects the microstructure of sintered composites. A dense, stable, low viscosity slurry is necessary for successful slip casting operations. As demonstrated by Sacks et al. ^[17], fine Al_2O_3 powder and SiC whiskers can be codispersed in water under both acidic and basic conditions. It has been shown that the best conditions of the zeta potential/ionic strength equilibrium for SiC whiskers dispersed in water is at $\text{pH} = 4.0$ ^[22]. At lower pH values dense aqueous suspensions of alumina have a strong tendency to flocculate; for this reason a controlled acidic condition was chosen for processing these composites.

The flow behavior and stability of a slip are important in slip casting operations to achieve high green density with the minimum amount of defects. The rheological behavior of colloidal suspensions depends mainly on the following factors ^[25]:

- i. viscosity of the dispersion medium,
- ii. particle concentration,
- iii. particle shape, and
- iv. particle-particle and particle-dispersion medium interaction.

Usually liquids or particle/water mixtures do not show a purely viscous behavior. In most cases they exhibit a viscoelastic behavior, having properties of both solids and liquids. The needle shape of the SiC whiskers pose another problem into the homogenization and stability of these slurries. The definition of a fully dispersed, castable slip for this multicomponent system can be best defined by careful investigation into the experimental parameters that control its rheology, casting behavior, and sintering. It is the purpose of this subcontract to develop a process for optimum dispersion of the phases and rheological behavior suitable for slip casting operations. The development of an economically feasible process is the key parameter in reaching the goals of the subcontract and making the process attractive for commercialization. The ultimate objective of this subcontract is to manufacture prototype heat exchanger tubes for testing by industry.

In summary, waste-heat recovery for high-temperature, corrosive flue streams necessitates the use of ceramic heat-exchangers materials. Alumina appears to be one of the few chemically compatible ceramic materials to the corrosive environments of industrial processes such as glass, chemical, utility, and metal industries. However, alumina materials have exceedingly poor reliability because of low thermal-shock resistances. Whisker reinforcement in an Al_2O_3 matrix is a potential approach to enhance its thermal-shock resistance; however, the incorporation of whiskers into alumina necessitates the use of pressure-assisted (hot pressing or hot isostatic pressing) sintering. The latter is costly and impractical for producing complex near net shape components. Accordingly, the objective of this subcontract is to develop alumina-SiC_w composites to near full density, a mechanical property of ≥ 500 MPa in strength, and a fracture toughness of ≥ 6 MPa·m^{1/2} and thermal-shock resistance to $\Delta T \approx 500^\circ\text{C}$, using commercially practical forming and sintering techniques.

Previous attempts towards the fabrication of ceramic heat exchanger tubes of Al_2O_3 -SiC_w had been undertaken at Oak Ridge National Laboratory ^[27]. Extrusion was used as the forming method of the tubes. The mechanical properties and fired densities were relatively low, and the composites showed severe whisker agglomeration.

II. EXPERIMENTAL PROCEDURE

In this study, slip casting and pressureless sintering were selected as commercially practical processing steps to produce $\text{Al}_2\text{O}_3\text{-SiC}_w$ composites. The principal processing steps for the preparation of the $\text{Al}_2\text{O}_3\text{-SiC}_w$ composites by slip casting, are shown in the flow chart in Figure 1. The main steps are i) slurry preparation, ii) slip casting, and iii) pressureless sintering. Ceralox HPA 0.5 alumina with 500 ppm MgO was used almost exclusively in this study as the matrix materials. It should be noted that throughout this report, weight percent will be used for solid loading, and volume percent will be used for the composition of the composites. The Al_2O_3 was dispersed in water at a solids content of ≈ 80 wt% using dilute HNO_3 solution and an ultrasonic probe for stirring. The pH of the Al_2O_3 slurry was maintained at 4.0. The slurry was then ball milled for 4 hours to assure complete breakage of any agglomerates. During the 4-hour ball milling cycle the pH of the slurry was measured and maintained to $\text{pH} \approx 4.0$ by the addition of more nitric acid solution as needed.

The SiC whiskers were then weighted and placed into a plastic container and the Al_2O_3 slurry was then poured into the container along with a small amount of alumina grinding media to assist mixing during tumbling. All whisker handling operations were conducted inside a well ventilated hood. At this point, the $\text{Al}_2\text{O}_3\text{-SiC}$ whisker mixture became very thick and had no fluidity. It resembled a thick paste similar to the ones used for extrusion, and the whiskers were in big clumps at this stage. The mixture was then left to age and tumble on a rolling mill until it became very fluid and reached a viscosity of about 500 cps. A small amount of a dispersant was added during the tumbling cycle to assist in the breakage of the whisker agglomerates.

The sintering aid, Y_2O_3 , was then added to the acidic slip ($\text{pH} \approx 4.0 - 4.5$) and left to tumble for an additional time. During this time the slip had experienced dramatic change of the pH from acidic to basic reaching $\text{pH} \approx 9$. The viscosity also continued to drop at a constant rate, reaching a viscosity of about 350 centipoise. The pH of the slurry was then adjusted to ≈ 7.5 and ultrasonicated for $\frac{1}{2}$ hr. The pH adjustment and ultrasonication resulted in a reduction of viscosity from about 350 centipoise to ≈ 60 centipoise at a solids content of about 78-79 wt%, which is equivalent to about 48%. A plot of pH and viscosity of the slurry as a function of time at the various stages is shown in Figure 2.

At $\text{pH} \approx 7.5$, viscosity of $\sim 60-70$, and solids loading of $\approx 78-79$ wt% the slips were found to be optimum for casting. Small amounts of defoaming agents were added to break air bubbles. Binder may be added at this stage of the process to give higher green strength. The colloidal slips were cast into plaster molds. For solid casting a funnel was attached to the mold which held excess slurry. After an overnight drying inside the mold the green parts were removed and left to dry for a few hours at room temperature and then dried completely in a drying oven maintained at $\approx 75^\circ\text{C}$. For drain casting of tubular shapes the mold was filled completely, and retained to full capacity by addition of more slurry as needed. Casting was done for time periods (15-45 minutes) depending upon the wall thickness desired. The slip was then drained out of the mold, and the parts were left in the mold to allow removal of the free water for 3-4 hours. Shrinkage of the parts during further drying makes for easy removal from the mold. These parts were also left to dry at room temperature after they were recovered from the mold, and then dried completely in the drying oven.

Figure 1. Process flow chart for the preparation of $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3\text{-SiC}_w$ composites by slip casting.

Figure 2. pH and viscosity history during slurry preparation for Al_2O_3 - 2%, Y_2O_3 - 15% SiC_w composition.

Low temperature organic volatiles such as dispersants and binders were burned out by calcination in an air furnace at 550°C for 6 hours. Green densities and dimensions were measured. Sintering was carried out in a resistance heated graphite furnace at temperatures between 1700 - 1850°C for 1 hour. The parts were placed into high-purity alumina crucibles for protection from contaminants and the highly reducing graphite furnace environment.

A variety of shapes and sizes of composites were formed by slip casting into plaster molds and fired to produce high density parts for property testing and process feasibility demonstration. The most common shapes formed were hollow tubes (1½ inches OD, 2 inches long, 0.05 - 0.10 inches wall thickness) for tube fabrication optimization and demonstration, and solid squares of 2 x 2 x 0.15 inches for mechanical and physical property measurements of these composites. The properties of $\text{Al}_2\text{O}_3\text{-SiC}_w$ composites prepared in the above optimized procedure is summarized in Table I.

Large size tubes (1½ inches OD by 16 inches long by 0.08 - 0.1 inches wall thickness) for prototype heat exchanger were produced at the facilities of Vesuvius/McDanel using slurries prepared at MER Corporation.

A. Equipment and Instrumentation

Slurry Preparation: The basic equipment necessary for the formulation of the slurry was an ultrasonic system type W-380 from Heat Systems - Ultrasonics, Inc., attached with an ultrasonic convertor, Model No. C-3. The system gave an average maximum output of 475 watts. pH measurements were made with a Corning pH meter Model 7. Calibration of the meter was done using pH calibrating buffer solutions. Viscosities of the slips were measured with a Brookfield Digital Viscometer Model DV-II using spindle #62 at 60 RPM. Ball milling of the alumina and tumbling of the composite slurries was done on a roller mill rotating at ≈ 400 RPM.

Slip Casting: Molds used for slip casting the composite slurries were made from No. 1 plaster. Molds for casting of tubes or crucibles were supplied by Vesuvius/McDanel. A variety of other molds were purchased from local shops.

Binder Removal: Green parts calcination was carried out into a static air furnace type Lindberg with MoSi_2 heating elements.

Sintering: Small samples were fired in an Astro furnace (Division of Thermal Technology, Inc.) with a hot zone of 4 inches in diameter by 6 inches long. The furnace is resistance-heated using graphite heating elements. Large size parts were fired into a home-made resistance heated graphite furnace with a hot zone of 1 foot by 2 feet by 1½ feet. In all cases the parts were fired into high-purity alumina crucibles. The alumina crucibles were replaced every 3-5 runs because of cracking and shrinkage at the high sintering temperatures.

Machining: Sintered samples were machined and polished using a variety of cutting and polishing wheels, equipment, and other metallographic consumables designed for advanced ceramic materials.

Testing and Characterization: For mechanical testing of the composites a 3- and 4-point bend test method was used to measure strength, and 4-point single edge notch beam method was used for toughness. For high-temperature testing the samples were heated by induction heating. Oxidation experiments were carried out in a MoSi₂ furnace. Hardness measurements were made on a Rockwell hardness system at the University of Arizona, Materials Science Department. Thermal conductivity was measured at Vesuvius/McDanel by the direct heating method.

**Table I. MER Optimized Pressureless Sintered Al₂O₃-SiC_w
Composite Specification Sheet**

COMPOSITION	Al ₂ O ₃ - 15% SiC _w
SPECIFIC GRAVITY	3.88 g/cc
DENSITY	96-97% of Theoretical
STRENGTH	500 MPa
TOUGHNESS	6.5 MPa m ^{1/2}
HARDNESS	17.26 GPa (1765 kg/mm ²)
THERMAL SHOCK RESISTANCE	500°C ΔT
THERMAL CONDUCTIVITY	18 W/mK @25°C

B. Process Development Parameters

The development of a procedure to fabricate whisker reinforced alumina composites by slip casting and pressureless sintering required a detailed examination of a wide range of experimental process parameters, and raw material variables. The major goals in developing this process was to be economically viable, offer flexibility in design, produce parts of near net shapes, and become transferrable into pilot-scale operations for prototype fabrication in a short time, and with low capital expense. The interaction with Vesuvius/McDanel and their feed back helped considerably in maintaining strict focus towards these goals.

A process development plan was carried out to optimize slip rheological properties and final composite properties. To optimize slip rheological properties for casting the following experimental parameters were investigated:

1. solid contents
2. pH
3. viscosity
4. aging
5. ultrasonication dispersion

To optimize composite density and properties during pressureless sintering the following parameters were investigated:

1. furnace kiln furniture and environment
2. sintering temperature
3. soak time
4. green density

To optimize the composite composition and overall properties for optimum performance the parameters investigated were:

1. Y_2O_3 content
2. SiC whisker content
3. MgO content

The research and development process plan was divided into seven main tasks as shown below:

- i. Raw Materials Selection
- ii. Slurry Preparation
- iii. Slip Casting
- iv. Calcination
- v. Pressureless Sintering
- vi. Composite Property Optimization
- vii. Testing, Characterization

The parameters examined to optimize properties of the slurries, and final composite performance are shown below for each task.

- i. **Raw Materials**
 - a. alumina matrix source and grade
 - b. whisker type
 - c. Y_2O_3 type, form
- ii. **Slurry Preparation**
 - a. preparation procedure
 - b. solid contents
 - c. slurry pH
 - d. slurry viscosity
 - e. dispersion
 - f. aging
- iii. **Slip Casting**
 - a. viscosity
 - b. pH
 - c. solid contents
 - d. binder and other organic additives
 - e. drying
 - f. green density
- iv. **Calcination**
 - a. temperature
 - b. soak time
 - c. heat rate
- v. **Pressureless Sintering**
 - a. furnace furniture and environment
 - b. sintering temperature
 - c. sintering soak time
 - d. heating rate
- vi. **Testing and Characterization**
 - a. density
 - b. shrinkage
 - c. microstructural
 - d. flexural strength
 - e. fracture toughness
 - f. oxidation resistance
 - g. thermal shock
 - h. thermal conductivity
 - j. high-temperature properties
- vii. **Composite Property Optimization**
 - a. Al_2O_3 type
 - b. whisker type
 - c. Y_2O_3 content
 - d. whisker content

III. RESULTS OF PROCESS DEVELOPMENT

A. Raw Materials Selection

The product information for this effort is shown in Table II.

i. Alumina

The selection of the matrix alumina with regard to purity is very critical to achieve high temperature properties of these composites. The presence of even small amounts of Na, Ca, or Si are known to generate a glass phase at temperatures of 1000°C. In advanced ceramic applications high purity is necessary to maintain high temperature properties. The type of matrix used primarily to make the composites was Ceralox HPA 0.5 alumina. The alumina has a purity of 99.97% (minimum), a median particle size of 0.47 μ m, and a surface area of 10 m²/g. The powder contains 500 ppm of MgO in the form of spinel. An additional type of alumina was also utilized to carry out some experiments for comparison purposes. The Reynolds low soda alumina, Grade: ERC-DBM (with 500 ppm MgO) was lower in cost compared to the Ceralox HPA 0.5. The powder has about the same particle size, lower surface area, 7.35 m²/g, and lower purity, 99.80%.

ii. SiC Whiskers

Two types of SiC whiskers were tested. The primary type which is also used in the final slurry formulation is SILAR^R SC-9 produced by ACMC, and SCW #1-2-105 produced by Tateho Chemicals. The Tateho whiskers were used for the first one third of this program, and a decision was then made to switch to the ACMC whiskers because of its higher performance. Material specification sheets for both types of whiskers are also shown in Table II.

iii. Y₂O₃

The primary form of Y₂O₃ used was 5 μ m (Coulter) powder from Unocal Corporation. Alternate form of Y₂O₃ investigated were yttrium nitrate liquid. A product specification sheet for the powder is also shown in Table II.

iv. MgO

Several forms of MgO were tested to prepare the composite slurries. The primary form was spinel supplied by the vendor of the alumina powder already mixed into the matrix. Pure MgO powder, MgCO₃, and MgNO₃ were also investigated. They were added in the form of fine powder or aqueous solutions.

TABLE II. Product Information for the Materials Used in this Study

A1.	<u>Alumina</u>	
	Supplier:	Ceralox, Tucson, AZ
	Median Particle Size:	0.47 microns
	Surface Area:	10m ² /g
	Purity:	99.97%
	Additives:	MgO 500 ppm (Spinel)
	Impurities:	Na: 22ppm, Si: 20ppm, Fe: 12ppm, Ca: 8ppm
B1.	<u>SiC Whiskers</u>	
	Supplier:	ACMC, Greer, SC
	Grade:	SILAR [®] SC-9
	Diameter:	0.6µm avg.
	Length:	10-80µm
	Whisker Content:	80-90%
	Crystal Phase:	alpha
	Surface Area:	3.0
	Impurities:	Ca: 3700 ppm Al: 1300 ppm Fe: 500ppm Mn: 2400 ppm Mg: 800ppm
C.	<u>Y₂O₃</u>	
	Supplier:	Unocal
	Avg. Particle Size:	FAPS 1.28µm Coulter 5.0µm
	Surface Area:	7.4 m ² /g
	Purity:	99.9%
A2.	<u>Alumina</u>	
	Supplier:	Reynolds Aluminum, Bauxite, AR
	Grade:	ERC DBM
	Medium Particle Site:	0.44 microns
	Surface Area:	7.25 m ² /g
	Purity:	99.80%
	Additives:	Na ₂ O: 0.060% SiO ₂ : 0.035% Fe ₂ O ₃ : 0.015% CaO: 0.035%
B2.	<u>SiC Whiskers</u>	
	Supplier:	Tateho Chemical Industries
	Grade:	SCW #1-S-105
	Diameter:	0.4 microns avg.
	Length:	20-200 microns
	Whisker Content:	80-85%
	Crystal Phase:	beta
	Surface Area:	—
	Impurities:	Mg: 0.2% max, Ca: 0.5% max., Al: 0.6%, Fe: 0.1% max

B. Slurry Preparation

The preparation of the composite slurry was proven to be the most important factor in the development of this process and in the determination of the final properties of the composites. The main difficulty in preparation of this type of composites is the complete dispersion of the SiC whiskers because of the strong tendency to form nests and clusters which are difficult to break, especially in dense slurries with solids contents of 80 wt%. The use of pure MgO and Y_2O_3 powders also posed great difficulties in preparation of the slurry due to their ionic dissociation in acidic solutions. In order to avoid changes in the slurry preparation procedure a suitable form of MgO and Y_2O_3 were selected, and added into the composite slurry in a timely sequence.

Dispersion of the whiskers was achieved by controlling the pH of the slurry, aging, tumbling, and ultrasonication. High-shear mixing was avoided because of the high solids content of the slurry, to avoid breakage of the whiskers, and to limit contamination from metal parts rotating at high speeds. Ultrasonication was found to be the most suitable method for dispersion.

i. Dispersion of the Al_2O_3

Dispersion of the Al_2O_3 can be done in both acidic solution (pH $\approx$ 4) and basic solutions (pH $\approx$ 11). In acidic solutions dispersion can be better because of the higher zeta potential, where lower viscosities of dense colloidal suspensions can be prepared. Based on the isoelectric points of Al_2O_3 and SiC whiskers the use of pH = 4.0 is most favorable. Slurries with basic pH were also prepared for comparison. A comparison in the slip properties and fired densities obtained suggested strongly that the acidic slurries were preferable. Comparison of these results are shown in Appendix 1, Table 1, in the report submitted by Vesuvius/McDanel. Dispersion of the alumina is most critical to avoid agglomerates which can grow dramatically at the high sintering temperatures. Dispersion of the alumina was achieved by the addition of dilute solution of HNO_3 . The pH was adjusted to $\approx$ 4.0 during mixing by magnetic stirring and ultrasonication. The slurry was additionally ball milled to avoid the presence of hard agglomerates. A verification of the dispersion was done by particle size measurement.

Measurements of the slurry viscosities as a function of solids content at pH = 4.0 is shown in Figure 3. Solid contents of Al_2O_3 of up to 82 wt% (53%) have stable castable viscosities of $\approx$ 150 centipoise. At solids contents of 83.2 wt% (55.5%) the viscosity rises to $\approx$ 312 cps, which reaches the upper limit of castability. Pure Al_2O_3 samples fired at 1550°C for 2 hours in air for comparison purposes had sintered density of 3.974 g/cc or 100% of theoretical density.

Slurries of Al_2O_3 - Y_2O_3 were prepared to investigate the effect of Y_2O_3 on the rheology of the slips. After dispersion of the pure Al_2O_3 at pH = 4.0 the Y_2O_3 was added at a concentration of 2.0%.

The pH of the slurry reached an equilibrium value of 8.0 after aging for 24 hours and had a viscosity of 180 cps at a solids content of 80 wt%. As the pH was reduced by the addition of nitric acid to lower values, and the viscosity was also reduced significantly. A plot of viscosity vs pH is shown in Figure 4. The pH could not be reduced below 7.0 by the addition of more HNO_3 even though the viscosity started to increase. A similar behavior of viscosity was observed with the whisker composite slurry. Accordingly pH adjustment by the addition of controlled amounts of acid was required to obtain optimum viscosity.

- * Al_2O_3 - 15% SiC_w
- Al_2O_3 - 2% Y_2O_3 - 15% SiC_w
- + Al_2O_3

Figure 3. Viscosity vs solid content of alumina and composite slurries.

Formation of slurries using MgO powder addition was not possible since the low concentration of MgO used can be readily dissolved in the acid slurry and washed away during slip casting. The stable form of MgO which was found not to affect the pH of the slurry and the slip formation procedure is spinel (MgAl_2O_4). The use of $\text{Mg}(\text{NO}_3)_2$, MgCO_3 , and $\text{Y}(\text{NO}_3)_3$ did not give stable slurries, and their use was not suitable in slip casting processes, since they dissolved in aqueous acidic media and were washed away during casting.

ii. Co-dispersion of SiC Whiskers and Al_2O_3

The Al_2O_3 -SiC whisker mixture can be dispersed at acidic pH as derived from their zeta potentials as a function of pH. During the first stage of the process development mixing and dispersion of the whiskers was done by slow and gradual addition of the whiskers with the aid of a magnetic stirrer and ultrasonication. This procedure was sufficient for whisker contents of up to 10% and small-size slurries. At higher whisker contents and larger slurry volumes, more practical ways were necessary to achieve good mixing and dispersion. At this point the effect of aging was examined. The whiskers were placed into another jar, and the dispersed alumina slurry was added. The result was a paste-like mixture with no fluidity. This was allowed to age by tumbling on a mill rotating at ≈ 400 RPM. The slurry was found to transform from a paste immediately after the addition of all of the whiskers down to a viscosity of ≈ 500 cps after about 36 hours of tumbling. During this time the pH had only changed slightly from 4.0 to about 4.5-5.0. A total of ≈ 20 alumina grinding media for 1 liter of slurry (density of slurry ≈ 2.38 Kg/liter) was added to enhance mixing during tumbling. No noticeable amount of grinding or breakage of the whiskers was observed during this time because of the high viscosity of the slurry and the small amount of media present. After 36 hours of tumbling the Al_2O_3 -SiC whisker composite, the Y_2O_3 was added. After the minimum viscosity had been reached by aging the slurry needed to be ultrasonicated to achieve complete dispersion of the whiskers and the alumina.

SEM analysis of the slurries, slip cast and dried during the various stages of processing, show a very rough, clustered morphology of the slurry for the Al_2O_3 - 15% SiC_w without any Y_2O_3 , as observed from Figure 5a. After the Y_2O_3 had been added to the slurry its morphology was smoother, as shown in Figure 5b. For the ternary composite slurry no whiskers were observed on the surface of the cast green parts. This can be explained since the movement of water can transfer the alumina which is finer in size, rather than the whiskers which are much larger in size and acicular in shape. From this observation, it is clear that Y_2O_3 is contributing positively towards an overall co-dispersion of the ternary composite.

iii. Dispersant

After the Al_2O_3 - SiC_w slurry has gained fluidity (after ≈ 30 hours) a homopolymer dispersant is added to assist the dispersion of the SiC whiskers. The dispersant is added at a concentration of 0.5-1.0 wt% and is left to dissolve by tumbling the slurry. At this time the slurry experiences no change in pH, and the viscosity is reduced only very slightly. Even though no visible effect on the properties of the slurries is observed (viscosity, pH), the dispersant may help in breaking the small whisker agglomerates during the ultrasonication stage.

Figure 4. Viscosity vs pH for Al_2O_3 - 2% Y_2O_3 slurry, 80% solids content.

Figure 5a. SEM micrograph of an Al_2O_3 - 15% SiC_w slurry before addition of Y_2O_3 showing clustering.

Figure 5b. SEM micrograph of an Al_2O_3 - 2%, Y_2O_3 - 15% SiC_w slurry showing smooth surface microstructure.

iv. Addition of Y_2O_3

At the 36-hour the Al_2O_3 - SiC_w mixture has reached the lowest possible viscosity by aging, tumbling, and dispersant addition. The Y_2O_3 is added and allowed to mix for an additional 6-8 hours. The Y_2O_3 has a dramatic effect on pH which changes from acidic pH = 4.5-5 to basic pH = 8.5-9.0. This change in pH, however, does not bring any dramatic change in viscosity which continues to drop to ≈ 250 . The drastic change in pH of the slurry comes from the dissolution of the Y_2O_3 into ions in presence of acidic solutions.

v. pH Adjustment

At pH of about 8.5 the slurry has a viscosity of about 250, the large whisker agglomerates have been well dispersed. The small agglomerates are broken by the adjustment of pH and final ultrasonication. The adjustment of pH and ultrasonication result in reduction of the viscosity from ≈ 250 down to ≈ 60 -80. It has been proven experimentally that pH adjustment or ultrasonication by themselves will result in moderate reduction of the slurry viscosity. The combination of both results in a combined reduction of viscosity and optimum dispersion. It has also been observed that sonication at high pH values > 8.5 can result in severe flocculation. The pH is adjusted before casting by means of dilute solution of HNO_3 to 7.5-7.8 where the minimum in viscosity is achieved. A plot of slip viscosity as a function of pH at this stage of the process is shown in Figure 6. The viscosity reaches a minimum at pH of ~ 7.5 . At pH values $< \approx 7.2$ the reverse effect occurs where the viscosity increases to values of > 300 CPS. At pH values < 6.8 the slurry is completely flocculated and its rheology is completely destroyed.

vi. Binder

After the adjustment of the pH to 7.5 and ultrasonication the slurry is ready for slip casting. A small amount of binder can be added (1-2 wt%) to the slurry to give better strength and handling of the green parts. Low molecular weight binders such as the polyethylene glycols (PEG 1450) result in no change in the viscosity of the slips. Higher molecular weight and harder binders are expected to cause significant change in the viscosity of the slurries. The addition of binder is not necessary for these composites as the whiskers themselves make the green parts very strong and easy to handle.

Other much smaller amounts of organic additives such as defoaming agents are added to remove air bubbles from the slip before casting. The slips are also allowed to rest for ~ 30 minutes before casting to allow for air bubbles to come to the surface. Air bubbles in the slips have been observed to be the major source of defects in solid casting of the composites. Vacuum casting of the composites is the best protection from the air bubbles. Such equipment, however, was not available during the course of this contract.

vii. Storage

Excess slurry can be sealed and stored for long periods of time. The pH and viscosity of the slurry will increase slowly and will reach equilibrium within 24 hours. Readjustment of the pH with ultrasonication will restore its optimum rheological properties and it can be ready for casting in very short periods of time. Readjustment of the pH was done up to five times over a period of 90 days and no statistically significant changes in green or fired densities were observed.

Figure 6. Viscosity vs pH of the composite slurry at the final stage of adjustment.

C. Slip Casting

A stable, well dispersed slurry with optimum rheological properties can result in optimum packing of the solids during removal of the water giving high green densities. A plot of green density and viscosity as a function of solid content is shown in Figure 7. Viscosity values of ≈ 60 -80 CPS at solid contents of 78-79 wt% for the composite Al_2O_3 - 2% Y_2O_3 -15% SiC_w were found to be optimum for slip casting, and result in the highest green densities for solid casting of square tiles. Despite the low packing density of the whiskers, green densities of the composites were identical to densities of pure Al_2O_3 . Green densities of 68% of theoretical have been achieved under the best conditions in casting for both pure alumina slurries and composite slurries. The effect of green density on fired density for solid cast pieces measures 2 in. x 2 in. x $\frac{1}{4}$ in. is shown in Figure 8. Solid block samples were preferred for this purpose because measurement of green and fired densities were more accurate. The green density has a strong effect on the fired density up to a green density of $\sim 67\%$ of theoretical. Above that the effect diminishes. For solid casting forming, defects such as air bubbles and voids due to incomplete casting are common but can be avoided with very careful control of the rheology of the slurry, and suitable casting operations. For drain casting such defects are very limited. A common defect from drain casting is warpage (differential shrinking) of the tubes during firing due to difference in wall thickness resulting from draining of the excess slip from the mold.

A variety of shapes and sizes are cast for the purpose of demonstrating the feasibility and commercial potential of the process to produce near net shape parts necessary for various applications. Various green and sintered shapes produced by slip casting are shown in Figure 9. Prototype heat exchanger tubes were manufactured by Vesuvius/McDanel using the process developed by MER.

The rate of casting of the slip for the formation of hollow tubes $1\frac{1}{2}$ in. diam. by 2 in. long was determined during casting of Al_2O_3 - 2% Y_2O_3 -15% SiC_w into plaster molds at various times. The rate of casting was measured by the wall thickness of the crucibles produced. Measurements were taken from both the vertical walls of the crucibles and from the horizontal walls (bottom). A plot of crucible thickness in the vertical and horizontal walls as a function of casting time is shown in Figure 10, for a slurry with viscosity of 90 CPS, solids content of 78.3 wt%, and $\text{pH} = 7.5$. The wall thicknesses are almost identical in all directions up to about 40 minutes of casting. For casting times above 40 minutes the vertical walls do not increase in thickness while the horizontal walls continue to become thicker.

After cast parts have dried in the plaster molds for 2-3 hours, they can be removed from the molds. The parts are then dried further at room temperature for an additional 2-3 hours and then placed in a drying oven at 75°C to dry completely. The cast rate of Al_2O_3 - SiC_w slurry is relatively slow compared to pure Al_2O_3 , which could create problems for casting large parts. This is an area that needs to be further investigated.

Figure 7. Green densities and viscosities of composite slurries vs solid content.

Figure 8. Effect of composite green density on the final sintered density.

D. Binder Removal

Organic volatiles such as binders, dispersant, chemically bonded water, and dissociated or ionized Y_2O_3 are calcined in air at $550^\circ C$ for 6 hours. The parts are placed inside alumina crucibles and heated to temperature at a rate of $1^\circ C/min.$, soaked at temperature, and cooled at $1^\circ C/min.$ Measurements of green density and physical dimensions are taken after the binder burnout.

Thermal analysis of the calcination as a function of temperature and soak time is shown in Figure 11. The binder, PEG 1450, and all other volatiles have been volatilized by $550^\circ C$ where no more weight loss is observed. Small amounts of weight gain are observed for temperatures $>600^\circ C$. Thermal gravimetric analysis of samples at $550^\circ C$ as a function of soak time is shown in Figure 12. Soak times of up to 6 hours are acceptable, where at longer times the composites start to show small amounts of weight gain which may be resulting from the oxidation of the whiskers.

E. Pressureless Sintering

Pressureless sintering of the composites was done exclusively in a graphite heated furnace at a heating rate of $10^\circ C/min$ to temperatures of $1800-1900^\circ C$. The optimum firing temperature was found to be about $1825^\circ C$. The best furnace crucibles for firing the composites were found to be Al_2O_3 . A bed of tabular alumina was used most of the times around the samples for protection from furnace contaminants. The furnace kiln furniture and temperature had also a great effect on weight loss of the samples and fired densities. Graphite crucibles had the strongest negative effect resulting in weight losses as high as 5-8%. The combination of Al_2O_3 crucible with tabular alumina bed had the best results resulting in only weight losses of $<0.5\%$. Small weight losses were found to be necessary to achieve high fired density. A plot of fired density and weight loss as a function of temperature is shown in Figure 13. Samples fired above $1850^\circ C$ exhibited some reaction resulting in the degradation of the SiC whiskers. Mechanical properties of samples fired to temperatures $>1850^\circ C$ were significantly lower. An SEM micrograph of a composite fired to $1900^\circ C$ for 1 hour is shown in Figure 14. The whisker like structure of the composite was lost due to reaction of the whiskers with the alumina matrix. SEM micrographs of composites fired to $1825^\circ C$ for 1 hour are shown in Figure 15. The presence of porosity due to grain boundary pinning by the whiskers is also visible.

The heating rate of the samples to the sintering temperature had no significant effect on fired densities. Even at heating rates of $20^\circ C/min$ no significant difference in final densities were observed. A heating rate of $10^\circ C/min$ showed the most consistent results. A plot of fired densities as a function of sintering soak time is shown in Figure 16. The rate of densification was significant for up to 1 hour, after which it slows down, and the gain is not enough to compensate for the larger grain size of the composites ($8-10\mu m$). Optimum sintering of the composites was found to be between 1-1.2 hours.

F. Testing and Characterization

i. Density

The density and porosity of the samples were measured using the Archimedes method. Samples processed under optimum processing conditions with composition Al_2O_3 -2% Y_2O_3 - 15% SiC_w, have a density of 96-97% of theoretical and $<0.5\%$ open porosity. Values of density, porosity, and apparent specific gravity (ASG) of square tiles and crucibles are shown in Table IIIa and IIIb along with shrinkages.

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Figure 9. Various Al_2O_3 , and Al_2O_3 - 15% SiC_w shapes produced by slip casting.

Figure 10. Wall thickness of drain cast crucibles (1.5 inches diameter and 2 inches long with slurry of 95 cps viscosity and solid content of 78.5 wt%).

Figure 11. Calcination of composite parts. Plot of weight change vs temperature.

Figure 12. Calcination of composite parts. Plot of weight change vs soak time at 550°C.

ii. Shrinkage

Parts formed by either drain casting (hollow tubes) or solid casting (rods, square tiles, blocks) shrunk at an average of 8%. In most cases, shrinkage was not very uniform and tubes would deviate from circular shape, and squares experienced warpage. Shrinkages and densities of tubular shapes and square tiles are shown in detail in Table III. Square tiles had shrinkage of 5.9% along the length (x,y) but had a 20.9% shrinkage in thickness. Pure alumina square tiles fired to full density in air at 1550°C for 2 hours had more uniform shrinkages, 12.7% along the length and 11.0% in thickness. The shrinkages of pure Al_2O_3 were more uniform compared to the whisker composites. It is possible that this may originate from orientation of the whiskers in the composite microstructure as a result of slip casting. No correlation between slurry viscosity and shrinkage uniformity could be established. Such correlation may be possible where lower viscosities may result in enhanced orientation of the whiskers in one direction.

iii. Mechanical Properties

Rectangular bars of size 50 mm long by 6mm wide by 3mm thick were cut from 2 inches by 2 inches square tiles, polished down to 10 a micron surface finish and tested in 4-pt and 3-pt bending. Toughness of samples was determined by notched specimens (SENB) broken in 4-pt bending. Hardness is measured with a Rockwell system and the values are correlated to Vickers hardness.

Mechanical properties of these composites [Al_2O_3 - 2% Y_2O_3 - 15% SiC_w] processed under optimum conditions are: flexural strength of 500 MPa, fracture toughness of 6.5 $\text{MPa}\cdot\text{m}^{1/2}$, and hardness of 17.26 GPa (1765 kg/mm^2).

High-temperature flexural strength of the composites under a 3 point beam gave excellent strength retention up to 1200°C. It was not possible to test the composites at higher temperatures because of equipment limitations. A summary of the high temperature tests performed are shown in Table IV.

Figure 13. Fired densities of composites vs sintering temperature.

Figure 14. SEM micrograph of composites sintered to 1900° C indicating reaction resulting in the disintegration of the whiskers.

Figure 15. SEM micrographs of composites sintered to 1800°C for 1 hour.

Figure 16. Plot of fired densities of the composites vs soak time at the sintering temperature (heating rate at 10° C/min, soak temp. 1850° C).

Table IIIa. Shrinkage and Densities of Slip Cast 2 by 2-Inch Squares

Sample ID	Green Density (g/cc)	Sintered Density (g/cc)	ASG (g/cc)	Open Pores (%)	Linear Shrinkage (x) (%)	Linear Shrinkage (y) (%)	Linear Shrinkage (z) (%)
*101-1	2.66	3.69	3.706	0.48	5.01	4.96	15.4
*110-1	2.70	3.69	3.708	0.46	4.90	4.34	15.3
*97-6	2.618	3.70	3.807	2.8	5.47	4.95	--
*96C-1	2.616	3.76	3.957	2.46	5.70	6.2	20.9
●Al ₂ O ₃ -1	2.682	3.974	3.974	0.0	11.70	12.0	9.6
●Al ₂ O ₃ -2	2.682	3.974	3.974	0.0	13.33	13.71	12.32
*98-1	2.622	3.735	3.790	1.49	4.83	5.48	21.7
*R98-1	2.486	3.708	3.780	1.91	8.36	9.35	19.5

Table IIIb. Shrinkage and Densities of Slip Cast 2 Inches Long by 1½ Inches in Diameter Crucibles

Sample ID	Green Density (g/cc)	Sintered Density (g/cc)	ASG (g/cc)	Open Pores (%)	Length Shrinkage (%)	Diameter Shrinkage (%)
*87C-1	--	3.724	3.744	0.5	4.26	7.12
*110-1	--	3.662	3.710	1.34	4.0	7.43
*97-6	--	3.790	3.805	0.44	4.0	7.46
●96C-1	--	3.794	3.794	0.0	8.6	11.63

* Fired at 1825°C for 1 hour in Argon. Al₂O₃-15% SiC_w w/Y₂O₃.

● Fired at 1550°C for 2 hours in Air. Pure Al₂O₃ [Ceralox HPA 0.5].

Table IV. High Temperature Strength of Al₂O₃ - 2%, Y₂O₃ - 15% SiC_w Composites

Temperature	Flexural Strength (MPa)
RT	513
1000°C	614
1200°C	578

iv. Physical Properties

a. Thermal Conductivity

Thermal conductivity of Al_2O_3 - 2%, Y_2O_3 15% SiC_w composites was measured by the direct heating method. Thermal conductivity data as a factor of temperature for composites with 94% are shown in Table V.

Table V. Thermal Conductivity of Al_2O_3 - 2%, Y_2O_3 - 15% SiC_w Composites (94% Density) as a Function of Temperature

Temperature ($^{\circ}\text{C}$)	Thermal Conductivity (W/m.K)
25	17.9
250	13.4
300	12.6
350	11.4
400	10.5

Regression Equation with R^2 of 0.99 is $K = 18.41 .0198 \text{ Temp } (^{\circ}\text{C})$

b. Thermal Shock

Thermal-shock tests were conducted by heating mechanical test bars to test temperature, soaking for 10 minutes at temperature, and dropping into boiling water. The resultant flexural strength of the bars was measured in 4-pt bending. A summary of the strength as a function of ΔT is shown in Table VI. The strength of the composites is retained up to ΔT at values of 500°C . At ΔT of 700°C a significant drop (16%) in strength was measured.

Table VI. Flexural Strength of Thermally Shocked Composites

Temperature ($^{\circ}\text{C}$)	Flexural Strength (MPa)
RT	509
400°C	481
500°C	503
700°C	421

v. Oxidation

Oxidation of the samples was done in static air environment at temperatures up to 1400°C. Oxidation rates at temperatures up to 1200°C were extremely slow and no weight changes were detected for exposure times up to 72 hours. Oxidation rates above 1200°C started to rise rapidly and continued at a parabolic rate. Results of oxidation experiments for 1300°C and 1400°C are shown in Figures 17 and 18. The rate of oxidation was found to be strongly proportional to the density and open porosity of the samples. The rate of oxidation of a 95% dense sample is about 50% higher than the rate of oxidation of a 97.5% dense sample. A plot of the weight gain due to oxidation at 1400°C as a function of time for a 97.5% sample and a 95% sample is shown in Figure 19.

vi. Microstructure

Composite samples were exposed to 1400°C in air over a period of 24 hours. These samples were tested for strength in 4-pt bending. The composites showed a maximum in strength after oxidation for 8 hours. A plot of the strength as a function of oxidation time is shown in Figure 20. This large (54%) increase in strength observed is believed to occur by the healing of surface defects on the composites, and possibly due to the compressive stress generated by the volume expansion during oxidation of the SiC whiskers.

Specimens cut from square tiles were polished to 1 micron finish to reveal details of the microstructure of the composites, grain size, dispersion of the SiC whiskers, and pore size. Optical micrographs of the composites showing whisker distribution are shown in Figure 21. SEM micrographs of polished surface and fracture surface for the composites are shown in Figure 22.

Failure analysis of broken bars was done to identify failure initiation of the composites. The most common failure points were voids from slip casting believed to originate from air bubbles trapped in the slurry, generated during casting of the slurry into the molds, or incomplete casting. Other defects observed were large alumina grains, grown to $>10\text{ }\mu\text{m}$ at the high sintering temperatures. The bars used for mechanical testing were from samples solid cast into 2 x 2 x 1/4-inch pieces. These samples when compared to drain cast tubes had a much higher probability of containing air bubble related voids, and incomplete casting in the center of the parts. It was also found that solid casting with the aid of high frequency vibration resulted in the reduction of the number of defects significantly, this assisted in the removal of the air bubbles during casting.

X-ray diffraction was used to identify the stability of the phases and the formation of the liquid phase that assisted in densification. The Al_2O_3 and SiC phases were well maintained as the original crystal structures. The liquid phase formed from the reaction of Al_2O_3 and Y_2O_3 was found to be $\text{Al}_5\text{Y}_3\text{O}_{12}$.

Figure 17. Weight gain of composites during oxidation vs time at 1300°C and 1400°C.

Figure 18. Weight gain of composites vs square root of time indicating parabolic rate of oxidation.

Figure 19. Weight gain of composites during oxidation at 1400°C vs time for two different sintered densities.

Figure 20. Room temperature flexural strength of composites oxidized at 1400°C at various oxidation times.

G. Composite Property Optimization

i. Al_2O_3 Type

The slurry preparation process was developed and optimized based on the Ceralox HPA 0.5 alumina. Slurries prepared with the Reynolds ERC-DBM, even though similar to the Ceralox alumina, did not have the same rheological properties. The slurries had viscosities of 195 CPS at solids content of 76.43 wt%, while the Ceralox alumina based slurries have viscosities of ≈ 60 -70 CPS at 78-79wt% solids. Green densities of these samples were considerably lower (64.1%) as compared to the Ceralox samples (67.5%). During pressureless sintering the Reynolds ERC-DBM samples shrunk much more; the samples had also slightly lower densities. A summary of the density and shrinkage of these samples appear on Table VII.

**Table VII. Shrinkage and Densities of Slip Cast Blocks
of Al_2O_3 - 2%, Y_2O_3 - 15% SiC_w Composites for Two Types of Aluminas**

TYPE OF ALUMINA	GREEN DENSITY	SINTERED DENSITY (g/cc)	ASG (g/cc)	OPEN POROSITY (%)			
					X_1 (%)	Y_1 (%)	Z_1 (%)
Ceralox HPA	2.62	3.735	3.790	1.43	4.83	5.48	21.7
Reynolds ERC-DBM	2.486	3.708	3.780	1.91	8.36	9.35	19.5

ii. Whisker Type

During the first four months of this program Tateho SiC whiskers were used to produce the composites. With a whisker content of 10% slurry weight, solid contents of 82wt% were possible with viscosities of 100-120 CPS. However, it was noticed that after pressureless sintering the population of whiskers was relatively low, while the count of particles was high. It was suspected that many of the whiskers may have disintegrated into powder during the high sintering temperature. The presence of large voids in the samples were believed to have originated from some reaction taking place during sintering. An experiment into the thermal stability of the Tateho and APMC SiC whiskers was made. The two types of whiskers were placed into SiC crucibles and fired to 1800°C in argon. Both types of SiC whiskers survived the temperature and the furnace environment. The weight gain for the APMC whiskers was 4.71%, while for Tateho whiskers was 0.68%. In another run in vacuum (-28 in Hg), 1800°C, 30 minutes, the APMC whiskers experienced a weight loss of 21.1%, and the Tateho 18.8%.

Pressureless sintering of the two types of whisker composites showed similar behavior. The Tateho whisker composites showed a consistently slightly better densification as the fired densities obtained were about 0.5-1% higher. However the best mechanical properties obtained were with the APMC whisker composites. A plot of sintered densities as a function of whisker content for the two types of whiskers is shown in Figure 23.

Figure 21. As-Polished Photomicrographs of Composites Polished to 10 Micron Finish.

(a)

(b)

Figure 22. SEM Micrographs of Composites (a), Polished Surface and (b) Fractured Surface.

iii. Y_2O_3 Content

The Y_2O_3 content was varied to find the minimum amount necessary for maximum densification and high-temperature mechanical property retention. Densification of composites for up to 5% SiC whiskers is possible (98% theoretical density) without the presence of any Y_2O_3 . Above 5% whiskers densification is slowed down considerably in the absence of sintering aids.

Preparation of Al_2O_3 - 15% SiC_w with various amounts of Y_2O_3 content showed different rheology. A plot of maximum equilibrium pH of the slurry and viscosity as a function of Y_2O_3 content is shown in Figure 24. The viscosities measured for the slurries were at pH = 7.5 for those which had equilibrium pH > 7.5. The best rheological properties were for slurries prepared with Y_2O_3 content between 1.5 - 2.25%.

Slurries prepared with various amounts of Y_2O_3 were slip cast and fired to 1800°C for 1.5 hrs. A plot of fired and green densities as a function of Y_2O_3 content is shown in Figure 25. Both green and fired densities showed optimum properties for Y_2O_3 content of 1.5 - 2.25%. A summary of the densities and porosities of these samples is shown in Table VII. A similar trend in mechanical properties is also observed as shown in Figure 26. Based on these observations the amount of Y_2O_3 was maintained to 2.0%.

Samples containing 2.0% Nd₂O₃ as sintering aid were also examined. The samples showed significantly higher green density, but the fired density was very low, 90.1%. A summary of the results is also shown on Table VIII for the sample identified 93D-2.

iv. Whisker Content

The whisker content was varied for the ACMC whiskers from 5% - 20%. The slurry rheology was optimized for whisker content up to 15%. Densities of composites with 15% SiC_w (ACMC) and 2% Y_2O_3 at optimum dispersion conditions were 97% of theoretical. Slurries prepared with 20% SiC_w and 2% Y_2O_3 had densities of 93.5% of theoretical.

For whisker content of up to 5% high densities were achieved without any sintering aids. For whisker contents of 10% and 15% densification was very low without the use of sintering aids. A plot of fired density as a function of whisker content is shown in Figure 27. A summary of the results of density, porosity, and apparent specific gravity is shown in Table IX.

IV. VESUVIUS/MCDANEL PROTOTYPE FABRICATION

Slurries prepared at the facilities of MER Corporation were shipped to Vesuvius/McDanel for casting prototype tubes for heat exchangers. Vesuvius/McDanel was able to achieve fired densities of 95-96% of theoretical as had been claimed by MER. Distortion of the tube diameter during firing has been reported to be still an unresolved technical problem. Preparation of the slurries at the facilities of Vesuvius/McDanel was decided to be a more appropriate, and MER is providing the necessary support. A report on the work performed by Vesuvius/McDanel is attached as Appendix 1.

Figure 23. Comparison of Fired Densities of Composites Prepared with Tateho and ACMC Whiskers.

Figure 24. pH and Viscosity of Composite Al₂O₃ - 15% SiC_w Slurries with Various Amounts of Y₂O₃.

Figure 25. Fired and Green Densities of Composites (Al₂O₃ - 15% SiC_w) Containing Various Amounts of Y₂O₃.

Figure 26. Mechanical Properties of Composites (Al_2O_3 - 15% SiC_w) Containing Various Amounts of Y_2O_3 .

Figure 27. Fired and Green densities of Composites Containing Various Amounts of Whiskers.

**Table VIII. Densities and Porosities of Composites
as a Function of Y_2O_3 Content**

Sample ID	Y_2O_3 Content (Vol%)	Green Density (g/cc)	Green Density (%)	Sintered Density (%)	Sintered Density (%)	Open Porosity (%)	ASG (g/cc)	Sintered Wt. Change (%)
93-1	0	2.4385	65.8	3.146	84.9	13.09	3.620	-0.74
95Y15-1	1.50	2.600	67.2	3.707	95.7	0.52	3.726	-0.83
9Y20-2	2.0	2.605	67.2	3.704	95.5	0.78	3.733	-0.76
95Y225-1	2.25	2.6318	67.8	3.707	95.5	2.53	3.803	-0.85
95Y30-1	3.0	2.563	65.9	3.607	92.7	6.16	3.844	-1.64
95Y40-1	4.0	2.571	65.7	3.551	91.0	8.03	3.862	-2.02
93D-2	2% Nd_2O_3	2.698	68.7	3.540	90.1	6.82	3.8	-0.77

Fired at 1825°C for 1 hour in Argon. Whisker Content 15%.

**Table IX. Densities and Porosities of Composites
as a Function of Y_2O_3 and Whisker Content**

Sample ID	Y_2O_3 (vol%)	SiC_w Content (vol%)	Green Density (g/cc)	Sintered Density (g/cc)	Open Porosity (%)	ASG (g/cc)	Sintering Wt Change (%)
94A-1	0	0	2.649	3.886	1.21	3.94	-0.75
94E-1	0	5	2.606	3.813	0.10	3.816	-0.46
95B-1	0	10	2.652	3.454	7.95	3.752	-0.63
93-1	0	15	2.4385	3.146	13.09	3.620	-0.74
94B-1	2	0	2.693	3.801	0.63	3.825	--
93B-1	2	10	2.625	3.720	3.24	3.844	-0.90
87-2	2	15	2.584	3.709	3.05	3.825	-0.6
111-4	2	20	2.534	3.576	1.47	3.630	-0.3

Fired at 1825°C for one hour in Argon.

V. CONCLUSIONS

1. A process has been developed to fabricate whisker toughened alumina composites by slip casting and pressureless sintering. Dense colloidal slurries of Al_2O_3 - 15% SiC_w composites have been prepared. The developed slip was demonstrated to be stable for over 90 days.
2. Optimum slip casting properties were found to be a viscosity of 60-70 cps, pH of 7.5, at a solids content of 78wt% (47.7%). Optimum green densities by slip casting were 67% of theoretical.
3. Densification to 97% of theoretical was obtained at a whisker content of 15%. Higher whisker contents resulted in densities of <95% of theoretical, which are considered unsatisfactory for the goals of this contract.
4. Tubular shapes were formed by slip casting and pressureless sintered to densities of 97% of theoretical and open porosity of <0.5%. Optimum sintering conditions were found to be at 1825°C for 1 hour in an argon atmosphere.
5. The composites produced under this contract (standard composition Al_2O_3 - 2%, Y_2O_3 - 15% SiC_w) showed strengths of 500 MPa, toughness of 6.5 $\text{MPa}\cdot\text{m}^{1/2}$, hardness of 17.26 GPa (1765 kg/mm^2), high-temperature strength retention to 1200°C, good oxidation resistance to 1200°C, and thermal shock resistance significantly improved compared to pure alumina.
6. The process has demonstrated an excellent potential to be scaled-up from bench scale to pilot scale for the production of large-diameter, long heat exchanger tubes.

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