

AN ABSTRACT OF THE DISSERTATION OF

Richard E. Chinn for the degree of Doctor of Philosophy in Materials Science presented on June 15, 2015.

Title: Thermal Processing of Injection-Molded Silicon Carbide.

Abstract approved: _____

Sundar V. Atre

Silicon carbide is an important and versatile nonoxide ceramic. Powder injection molding (PIM) is a method of high-speed fabrication of complex near-net shapes of SiC and other powders. Green micro-machining (GMM) is used to extend the shaping capability of green ceramics and powder metallurgy to smaller feature sizes. Debinding—removal of organic additives—is the rate-limiting step in PIM. Sintering aids enable densification of sintered powders, especially in the absence of applied pressure during sintering. *Thermal Processing of Injection-Molded Silicon Carbide* presents a study of the effects of GMM, debinding, sintering aids and sintering on two size distributions of PIM α -SiC with 5% each of Y_2O_3 and AlN as sintering aids. The use of 10% 20-nm particles, i.e., a bimodal size distribution, to increase the packing density of the green bodies was found to have a small effect on the rate of debinding, the liquid-phase sintering (LPS) precipitates, the microstructural development and the mechanical properties of SiC compared to the conventional monomodal size distribution, where $D_{50} = 0.7 \mu m$. The nanoparticles and debinding methods did have a strong effect on the feasibility of GMM on SiC. The nanoparticles, debinding methods and GMM in combination significantly affected the sinterability of SiC.

The rates and effects of solvent debinding and thermal debinding were measured and compared by various kinetic models. The catalytic effect of the bimodal SiC, if any, was small compared to PIM SiC with monomodal particles. The activation energy for thermal debinding was similar to that of solvent debinding. Too rapid of debinding by either method was detrimental to sintering in the form of fracture in the green body by residual stress. The debinding mechanism shifted from surface dissolution to bulk diffusion as the solvent debinding progressed. Changes in thermal debinding mechanisms were also noted as a function of heating rate.

Thermal debinding was problematic in PIM bars with a large characteristic diffusion path length ψ , which led to fractures during sintering. Weak particle bonding and uncontrolled grain growth were observed in some cases after thermal debinding, and attributed to dissolution of aluminum in SiC, excess oxidation of the SiC and premature decomposition of polypropylene. Solvent debinding was less stressful, but not without fractures in some instances due to the swelling of the wax as it dissolved. Monomodal SiC was much more amenable to GMM than bimodal, whether solvent or thermally debound. The GMM swarf adhered to the monomodal more than to bimodal, even after the wax holding the swarf to the substrate was dissolved. The bimodal SiC had about one percentage point better densification than the monomodal. The grain size, precipitate content and Knoop hardness were about the same for monomodal and bimodal, whether solvent or thermally debound, with or without GMM, except in the case of thermally dewaxed bimodal SiC.

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Thermal Processing of Injection-Molded Silicon Carbide

by

Richard E. Chinn

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I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

Richard E. Chinn, Author

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CONTRIBUTION OF AUTHORS

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LIST OF ABBREVIATIONS AND ACRONYMS

Abbreviation or Acronym	Definition
AFM	Atomic force microscope/microscopy
CIP	Cold isostatic pressing
CPH	Close-packed hexagonal
CVD	Chemical vapor deposition
DSC	Differential scanning calorimeter/calorimetry
FCC	Face-centered cubic
GMM	Green micro-machining
GPS	Gas pressure sintering; overpressure
HIP	Hot isostatic pressing
HK	Knoop hardness
HP	Hot pressed
HTXRD	High-temperature X-ray diffraction
HV	Vickers hardness
ISE	Indentation size effect in hardness measurements
LDPE-g-MA	Low-density polyethylene-g-maleic anhydride
LPS	Liquid-phase sintering
MAT	Microwave assist technology; microwave sintering
MOR	Modulus of rupture; flexural strength; σ
PIM	Powder injection molding
PP	Polypropylene
PS	Pressureless sintering
PVT	Pressure-volume-temperature in feedstock rheology
RE	Rare earth elements; the lanthanide series
SENB	Single-edge notched beam
SEPB	Single-edge pre-cracked beam
SHS	Self-propagating high-temperature combustion synthesis
SPS	Spark-plasma sintering; field-assisted sintering
STP	Standard temperature and pressure, 25°C and 760 torr
TEM	Transmission electron microscopy
TGA	Thermogravimetric analyzer/analysis
WLF	Williams, Landel and Ferry rheological model
YAG	Yttrium-aluminum garnet, $Y_3Al_5O_{12}$ or $(Y_2O_3)_3(Al_2O_3)_5$
YAM	Yttria-alumina monoclinic, $Y_4Al_2O_9$ or $(Y_2O_3)_2(Al_2O_3)$
YAP	Yttrium-aluminum perovskite, $YAlO_3$ or $Y_2O_3 \bullet Al_2O_3$
XRD	X-ray diffractometer/diffraction

LIST OF SYMBOLS

Symbol	Name	Definition
K_{Ic}		Fracture toughness; critical value of the Mode I stress intensity factor
X_i		Mass fraction of component i
α	Alpha	Close-packed hexagonal SiC
β	Beta	Face-centered cubic SiC
γ	Gamma	Shear strain
η	Eta	Viscosity of feedstock
ρ	Rho	Density
σ	Sigma	Strength
τ	Tau	Shear stress
Φ	Phi	Consistency coefficient of feedstock
ϕ_i	Phi	Volume fraction of component i
ψ	Psi	Shape factor (volume/area) and characteristic path length

DEDICATION

This dissertation is dedicated to my wife Patsy, daughters Melissa and Heidi, grandson Ephraim, granddaughter Ilaria, mother Jackie Chinn, and parents-in-law Tony and Martha Mejia. It is also dedicated to the memory of my father, Bill Chinn, who left us in 2013.

PREFACE

My interest in ceramics processing dates back to the beginning of my professional career in a ceramic tape-casting factory. Ironically, perhaps, my master's degree in the 1990s was to have been a ceramic injection molding project but for canceled funding. My part-time pursuit of a Ph.D. at Oregon State University led me to an elective course in powder processing, IE534, taught by a professor I had not met previously, Sundar Atre. "The harder I work, the luckier I get," as the saying goes, and Dr. Atre took a chance on me to do the research for one of his projects. An initial project on spark-plasma sintering of silicon carbide did not pan out, but he stretched another project funded for one Ph.D. only into two candidates, and I was one of them.

I have tried to extend the trails blazed by Dr. Atre and his previous graduate students in the fields of powder processing, injection molding, green machining and several other topics in my research. *Thermal Processing of Injection-Molded Silicon Carbide* is the result of inquiries into sintering additives for SiC, the kinetics of dewaxing and the sintering of PIM SiC components.

My goals in this research include the degree itself, contributing to the body of knowledge in my profession by getting my research published in peer-reviewed journals, helping at least one professor get promoted and learning something new in materials science and engineering. I also hoped to get a patent or devise the next Big Thing, such as Chinn's Law, the Chinn Theorem, the Chinn Equation, and so on. All these would be named for my dad, of course. I am much too modest to name the Chinn Principle, whatever that may be, for myself. Any of my larger ambitions may yet happen. I take my research and other professional goals very seriously, but not at the expense of enjoying what I do for a living. The epigraphs that begin each chapter are meant to reflect that outlook, and also my thoughts about being a graduate student and grandfather simultaneously.

CHAPTER 1

1 General Introduction

The Simpsons: “Sideshow Bob!!!”

Sideshow Bob: “It’s *Doctor* Sideshow Bob!”

Homer Simpson: “*Real* doctor or a Ph.D.?”

Sideshow Bob: “Ph.D.!” — television’s *The Simpsons*.

Thermal Processing of Injection-Molded Silicon Carbide brings together studies of several diverse topics in materials science and engineering, including powder injection molding (PIM), nanomaterials, nonoxide ceramics, thermoplastic polymers, process kinetics, precision machining, liquid-phase sintering and microstructural development, among many others. Powder injection molding was used to fabricate ceramic-plastic composite test specimens.

In ceramic and powder metal fabrication, PIM is an alternative to the more common methods such as uniaxial pressing and cold isostatic pressing, and can produce shapes that are more complex and less symmetrical at a high production rate. Chapter 2 presents an overview of PIM, with emphasis on PIM of SiC. The four major steps of PIM—feedstock preparation, injection molding, binder removal and sintering—are described, along with the scientific principles that undergird each step. A fifth step pertinent to this thesis, green machining, is introduced. The methods of rheological analysis and PIM finite element simulation are mentioned in brief. Chapter 2 is in preparation for submission to *Powder Injection Molding International*.

Chapter 3, already published in *Ceramics International* in 2014, is an analysis of binder removal from SiC PIM feedstock by solvent extraction. Binder removal is usually the rate-limiting step in PIM, and can generate many defects that cannot be mitigated by subsequent steps. The use of nanoparticles to increase the particle packing efficiency in the feedstock was expected to affect the rates and mechanisms of debinding. The two-

step solvent debinding mechanism was delineated, and the effects of nanoparticles was smaller than expected from permeability estimates.

Thermal debinding in Chapter 4 is often the lowest-cost and simplest means of binder removal. The shaped PIM compacts are slowly heated in a furnace and held at a temperature where the binder components gradually become viscous and decompose without changing the shape of the compact, ideally, leaving the ceramic particles sufficiently bonded for the sintering step. Like solvent extraction, the melting and pyrolysis of the binder can also generate many defects and unpredictable results. An analysis of the kinetics of pyrolysis of the binder components used throughout this thesis is presented in Chapter 4, and compared to solvent debinding. The effect of nanoparticles was again small. Thermal debinding did not fit three kinetics models examined equally well. Chapter 4 has been accepted in the *43rd NATAS Conference* in 2015 and will be published in its proceedings. An extended version of Chapter 4 is in preparation for submission to *Powder Technology*.

A two-part review of the mechanisms and properties of sintering aids and nanoparticles used in SiC fabrication, from the literature, is presented in Chapters 5 and 6. The most common additives are carbon, B_4C , Al_2O_3 , MgO , AlN and Y_2O_3 . Part I in Chapter 5 is an analysis of these and other additives used in the low-cost pressureless sintering processes including PIM. Part II in Chapter 6 is an analysis of the additives used in pressure-assisted sintering processes. The additive-process combinations that yielded the highest density, strength, toughness, hardness and thermal conductivity are tabulated. The shortcomings of the less-successful additive-process combinations are examined. Chapters 5 and 6 are in preparation for submission to *Critical Reviews in Solid State and Materials Sciences* as a two-part paper.

The lessons learned from Chapters 2-6 were put to the test in Chapters 7 and 8, where a binder system of three thermoplastic polymers and an organic acid was extruded with two particle-size distributions of $SiC + AlN + Y_2O_3$, injection molded, debound by solvent and thermal methods, and liquid-phase sintered. The first particle-size distribution is monomodal, with 0.7- μm SiC. The second is bimodal, the monomodal powder with 10%

of 20-nm SiC and a higher packing density. Green micro-machining (GMM), a method of extending the fine-feature capabilities of PIM, is introduced in both chapters.

Chapter 7 compares the two particle-size distributions, thermal and solvent debinding, and GMM vs. not machined, in terms of phase stability during sintering, thermal expansion and contraction, densification, grain size and hardness. The monomodal coupons were highly amenable to GMM, both debinding methods and controlled grain growth. The bimodal coupons densified very well but were much less successful with thermal debinding and GMM. Chapter 7 is in preparation for submission to the *Journal of the American Ceramic Society*.

Chapter 8 examines thermal debinding in air and N₂, two sintering processes, two coupon sizes and fractography in addition to the three process variables in Chapter 7. The coupon size and thermal debinding, especially in air, had significant effects on the sinterability and microstructure of the coupons. Chapter 8 was presented at the *PowderMet 2015* conference and published in its proceedings.

The customary literature review can be found throughout Chapters 2, 5 and 6, as well as in the Introduction sections of Chapters 3, 4, 7 and 8. Conclusions are drawn in Chapter 9, and suggestions for future research in this field are provided. The appendices include the data used in Chapters 5 and 6, the injection-molding data for the bars in Chapters 7 and 8, and the feedstock properties for Chapters 3, 4, 7 and 8.

CHAPTER 2

2 Powder Injection Molded Silicon Carbide

Theodore "Beaver" Cleaver: "I could use my own money, the twenty-five dollars I got in the bank."

Wally Cleaver: "I thought you were saving that to go to college."

Beaver: "Larry says he never heard of a college you could go to for twenty-five dollars."

— television's *Leave It to Beaver*.

2.1 Introduction

Powder injection molding (PIM) of ceramics and metals dates back to 1932¹, but has been applied to SiC only sparingly since the 1980s. PIM is a near-net-shape process consisting of four major steps: feedstock preparation, injection molding, binder removal and sintering.² Of these four, binder removal is usually the slowest step by far.³ PIM is applicable to high-speed production of complex shapes, and pressureless sintering, but precise dimensional control and mold abrasion are significant obstacles to its more widespread use.⁴

Several similar and competing processes are in use, including gelcasting, robocasting, colloidal printing, centrifugal casting, pressure casting and so on. Each process has niche applications.

PIM is described in great detail in *Injection Molding of Metals and Ceramics* by German and Bose⁵, and *Ceramic Injection Molding* by Mutsuddy and Ford⁶, and is presented here only cursorily.

2.2 Feedstock Preparation

The feedstock preparation for PIM is essentially the same as for reinforced plastic composites, although PIM requires higher solids loading. Ceramic powders are blended in a high-shear mixer with one or more liquefied resin binders, with just enough resin to wet

the powder particles and fill the voids between particles. The binder increases the moldability of the powder and the strength of the greenware. The powder content greatly increases the viscosity of the resins, which affects the injection step. The viscosity of PIM feedstock is much lower than that of extrusion slip, but much higher than reinforced plastics. Two resin components of different molecular mass and glass transition temperature are often used, to facilitate maximum efficiency in the third step. Sintering additives, carbon sources, lubricants, mold releases, plasticizers, fatty acids and anti-foam agents may also be added. The resins are usually thermoplastic, although thermosetting (cross-linking) resins have also been used. Thermoplastic resins can be melted or dissolved and reconstituted, whereas thermosetting resins disintegrate irreversibly when subjected to excess heat or corrosion.

Feedstock mixer types include the twin-screw extruder, single screw extruder, twin cam, z-blade, double planetary and plunger extruder. The twin-screw co-rotating extruder is highly regarded for its high shear, brief residence time, feedstock homogeneity and scale-up potential.⁵ The heated extruder accepts the powdered or pelletized binder components first, melts them, and propels the fluidized binder mix to the ceramic powder feeder. The second feeder measures the ceramic powder by mass rate into the molten binder as the extruder blends and pushes the feedstock toward a heated die. The co-rotation of the side-by-side screws applies a high shear stress on the feedstock between the screws, for optimum mixing. A hot, viscous ribbon of semisolid feedstock is extruded onto a cooling conveyor belt and fed into a continuous chopping machine.

Once the powders and binders are sufficiently mixed and extruded, the feedstock must be pelletized or granulated for use by the injection molding machine. In pelletizing, the feedstock is extruded and chopped into small cylinders or brick-shaped units. In granulation, the feedstock is cut into random shapes that must pass through a sizing screen. In both cases, thermoplastic sprues, runners and scrap are recycled into the virgin feedstock. Pellets are considered more uniform and homogeneous than granules.⁵

A carbon source, such as char from the pyrolysis of organic binder, is useful for densifying carbide ceramics. Thermoplastics typically have a low char yield during burn-

out, and may be supplemented by a thermoset precursor such as epoxy, phenolic or especially polyphenylene.⁷

A key parameter in feedstock preparation is solids loading expressed as volume fraction ϕ or mass fraction X . If the ϕ is too low, the compact does not densify. If the ϕ is too high, the feedstock is too viscous and abrasive to inject. The maximum volume fraction, $\phi_{\max}$, where all particles are wetted by the binder and all the spaces between particles are filled, is *critical* solids loading, typically ~60 vol%. Dihoru et al.⁸ observed an *optimal* solids loading that was 7-8% less than the critical solids loading, when these parameters were measured by torque rheometry, as in Figure 2.1. Solids loading in SiC is limited to about 70-86 mass%, and Ohnsorg used 76-80% 1- μm α -SiC with B₄C additive, phenolic and 9-17% styrene.⁷ Whalen and Johnson¹ used 47 vol% α -SiC + 5% graphite in a binder of phenolfurfural and phenolformaldehyde in PIM RBSC. Renlund and Johnson⁹ used 40-60 vol% SiC, with B, C and B₄C additives, in a binder of ethylene and vinyl acetate. Zhang et al.¹⁰ used 56 vol% (80 mass%) 0.8- μm SiC in paraffin and a noncommercial resin called polycarbosilane (PCS). The PCS decomposed to SiC during pre-sintering. Yi et al.¹¹ used up to 75 vol% bimodal SiC in a cross-linked gelcast binder. Xu et al.¹² used 60 vol% SiC with Y₂O₃ and Al₂O₃ additives in a temperature-induced gelation (TIG) binder. Krug et al.¹³ tested 56 vol% alumina and 47 vol% yttria-stabilized zirconia, both in a polyoxymethylene binder. Lu et al.³ used 55 vol% SiC with Y₂O₃ and Al₂O₃ additives in a binder of polypropylene with paraffin and stearic acid.

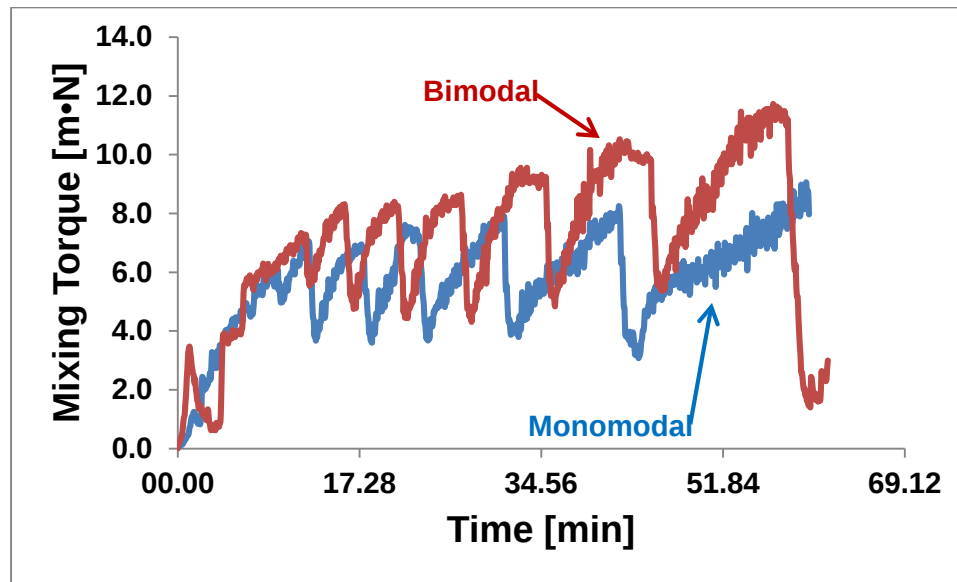


Figure 2.1: Torque rheometry of SiC feedstocks as a function of time as powder is added to molten binder. Each rise in each curve is a result of powder addition, until the rheometer can no longer mix in more powder.

The practical limit to solids loading in feedstock is a function of viscosity, which is a function of particle shape and size distribution. Spherical metal particles formed by melt-atomization processes have less of a viscosity-increasing effect and allow higher values of ϕ than angular ceramic particles formed by grinding processes. In the ideal case of smooth, spherical particles of one size, $\phi_{\max} \approx 64 \text{ vol\%}$.¹⁴ For SiC, $\phi = 60 \text{ vol\%}$ is equivalent to $\sim 85 \text{ mass\%}$.¹⁵

German¹⁴ reported an increase in packing density that reduced binder content and sintering shrinkage resulting from a bimodal PIM powder. Monomodal powders that contain only smaller (i.e., nano) particles densify easily but tend to agglomerate and shrink excessively. Monomodal powders that contain only larger (i.e., micro) particles have the opposite problems. The optimum bimodal compositions, in terms of minimum sintering stresses, consisted of 70-80% larger particles. Yi et al.¹¹ used a 70:30 mass ratio of micro to nano particles. Onbattuvelli et al.^{15,16} used a 90:10 mass ratio of micro to nano particles in a comparison of 58 vol% bimodal SiC to 51 vol% monomodal.

Lenk and Krivoshchepov¹⁷ evaluated the effects of surfactants on SiC with paraffin as the only binder, for low-pressure PIM. The 100-nm α -SiC particles and wax were stabilized by the addition of colloidal fatty amines and alkylsuccinimides, which improved the Bingham flow behavior of the feedstock.

Aggarwal et al.¹⁸, testing PIM niobium, found that irregular particle shape and a broad size range yield good shape retention during binder removal but lower packing density than equiaxed particles in a narrow size range. High shear rates were needed to mix the feedstock when its powder content approached critical solids loading, as indicated by the rising peak torques in Figure 2.1. A slight excess of binder was used to lower the viscosity near critical solids loading and increase the lubricity of the feedstock.

A critical problem of some feedstocks is phase migration or phase separation. If the uniform dispersion of the powder is unstable, the feedstock will not perform satisfactorily, and shrinkage will be nonuniform during binder removal and sintering. The powders can separate from the binder, or the powder particles can segregate by size or composition. A positive slope in the viscosity–shear rate curve, unlike Figure 2.2, is an indicator of phase separation.¹⁹ Solid particles in the feedstock, when flowing through a capillary tube, tend to migrate toward the centerline and away from the walls, in the Segré-Silberberg²⁰ effect.⁸ The phase separation is largely due to high shear gradients and shear rate gradients near boundaries, but may also be caused by chemical and physical forces at the capillary walls that repel the solids but attract the binder components.²¹ X-ray tomography is commonly used to evaluate phase separation in solidified feedstock.

2.3 PIM Rheological Properties

Rheological properties of feedstock such as viscosity as a function of temperature, shear rate, injection pressure and solids loading, are critical to successful PIM. The maximum packing density, or critical solids loading, can be determined by torque rheometry, e.g., ASTM D2538²², where the torque needed to mix molten binder and powder increases as powder is added, as in Figure 2.1.^{5,23} The viscosity of the feedstock as a function of temperature and shear rate is measured by capillary rheometry, ASTM

D3835²⁴, as in Figure 2.2. The specific volume (reciprocal of density) of the feedstock as a function of temperature and injection pressure is determined by high-pressure dilatometry, ASTM D792²⁵, as in the PVT (pressure-volume-temperature) diagram in Figure 2.3. The heat capacity is measured by differential scanning calorimetry (DSC), ASTM E1269.²⁶ The thermal conductivity can be determined by the transient line source method, ASTM D5930.²⁷ All these parameters are used in simulation software models.

The viscosities of polymer resins were rheometrically modeled by Williams, Landel and Ferry (“WLF”)²⁸ and Krieger and Dougherty²⁹ in the 1950s, and Cross³⁰ in the 1960s. The Tait³¹ constants originated with an equation of state pertaining to the compressibility of water, from the voyages of the *HMS Challenger* in the 1870s. The Tait and Cross-WLF models are developed in Osswald’s *et al.* book.³²

2.4 Injection Molding

Injection molding is done by sophisticated machinery that melts the feedstock, injects it into a reusable steel mold at low or high pressure, and ejects the molded components once they solidify.³³ The binder is typically pseudoplastic or shear-thinning, such that the viscosity decreases logarithmically with shear rate, as in Figure 2.2, where $\dot{\gamma} > 1$. Temperature gradients, phase migration and nonuniform solidification of the binder can result in defects such as incomplete fill, voids, knit lines, warpage and fracture. Porosity may be caused by aeration of the feedstock during mixing or mold fill. Residence time in the mold is on the order of 60 s. Abrasive wear of the equipment by the ceramic powder may cause rapid degradation. Thermoplastic sprues and runners can be recycled into virgin feedstock. Low-pressure PIM may be done with compressed gas as the piston instead of an auger, at $P \approx 0.3$ MPa.⁵

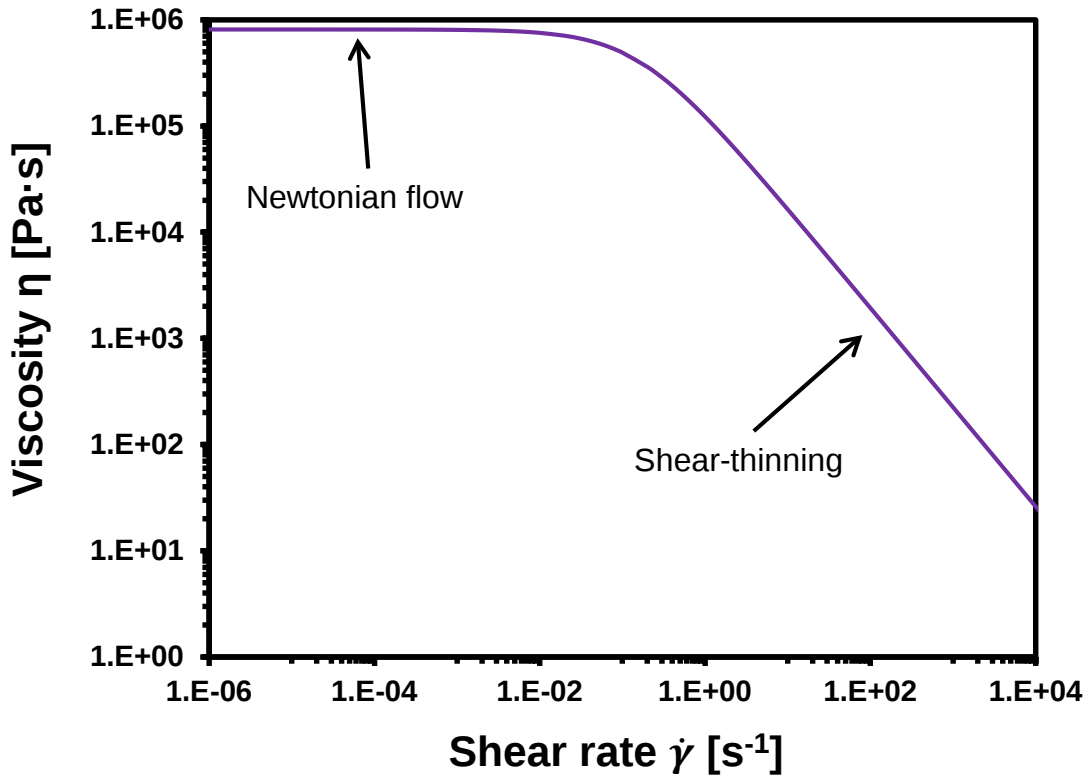


Figure 2.2: Viscosity as a function of shear rate of bimodal SiC feedstock, $\phi = 0.54$, at $T = 154^\circ\text{C}$.

Pseudoplastic binders obey the Ostwald-de Waele equation, in Equation 2.1, and the shear-thinning power law in Equation 2.2.³⁴

$$\tau = \Phi \dot{\gamma}^n \quad (2.1)$$

$$\eta = \Phi \dot{\gamma}^{n-1} \quad (2.2)$$

Where τ is the shear stress [MPa], Φ is the consistency coefficient, $\dot{\gamma}$ or dy/dt is the shear rate [s^{-1}] and n is the power law exponent or flow behavior index. For a Newtonian fluid, $n = 1$ and Φ is the shear rate-independent viscosity, as on the left side of Figure 2.2. For PIM feedstock, $n < 1$ and the viscosity is a function of shear rate, as on the right side of Figure 2.3 where $n = 0.072$. In PIM, $n > 1$ may be an indication of phase separation.¹⁹ A feedstock viscosity of $\sim 100 \text{ Pa}\cdot\text{s}$ is ideal for PIM, and the temperature, pressure and solids loading are selected accordingly.⁵

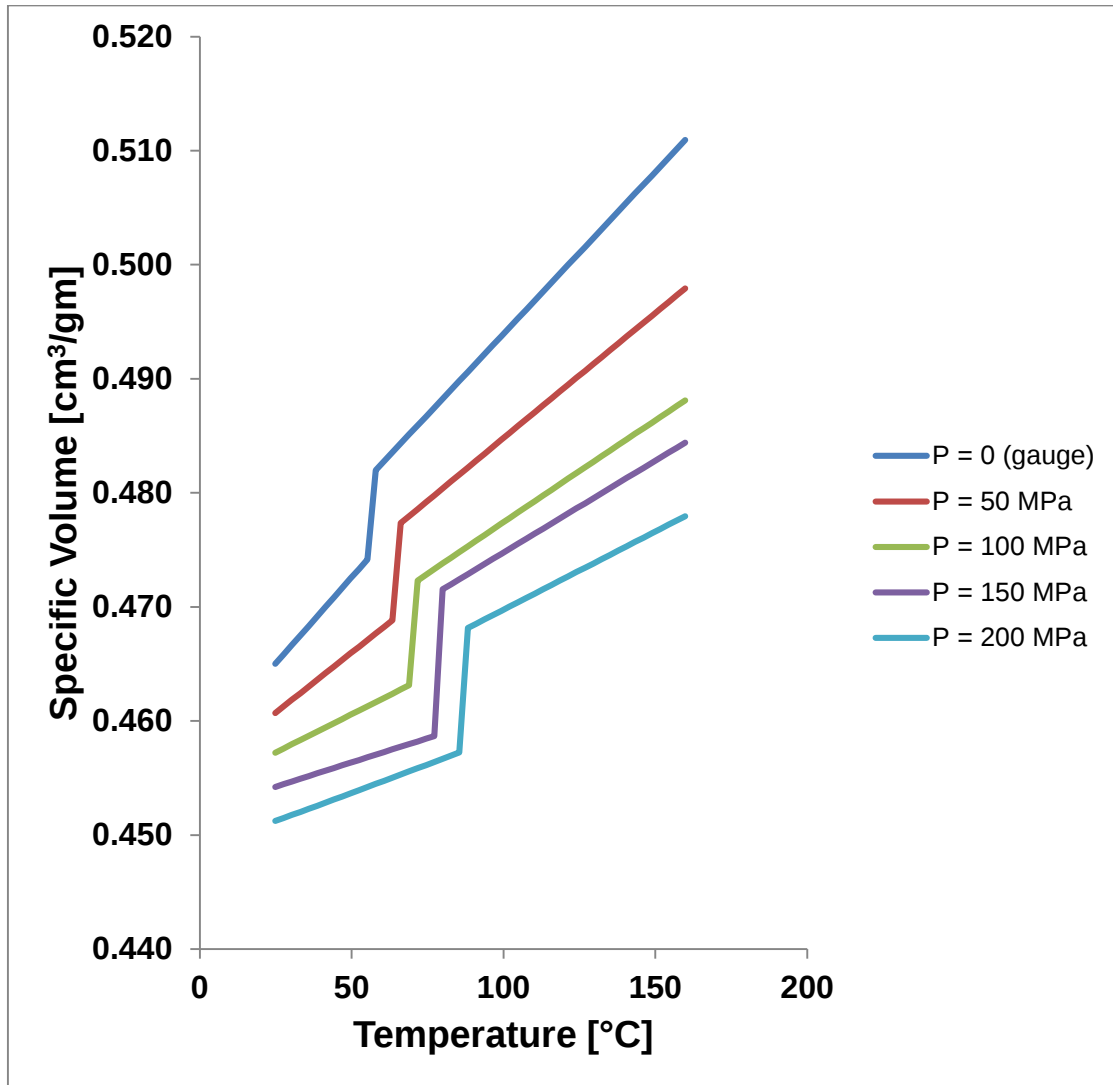


Figure 2.3: Linearized PVT plot of volumetric thermal expansion of bimodal SiC feedstock, $\phi = 0.53$, at various pressures.

Whalen and Johnson¹ got their best results with a highly symmetrical mold, and the injection site as central to the mold as possible.

Zhang et al.¹⁰ injected SiC + PCS binder into a mold at 20-50°C under a pressure of 108-141 MPa. Cracking was observed in the compacts due to differential shrinkage.

Krug et al.¹³ injected 170-175°C feedstock into a 135°C mold under a pressure of 95 MPa. The injection speed was $8 \times 10^{-5} \text{ m}^3/\text{s}$, and the filled mold was held at 5-120 MPa for 400 s.

Injection molding can be simulated by software such as Moldflow® (Autodesk Inc., San Rafael, California). The simulation of the process and its output greatly simplifies the design of the tooling and reduces the material waste from production trials. The simulations are developed from the rheological properties of the feedstock, the dimensions of the component and the process parameters such as temperature and pressure at each stage.³⁵ The simulated mold fill rate of a SiC armor tile, from $\phi = 53\%$ bimodal feedstock, is shown in Figure 2.4. The mold was filled in about 1.2 s by 160°C feedstock injected at 13.6 MPa and a maximum shear rate of 1990 s⁻¹. The tile solidified in 31 s but shrank about 6.1 vol%.

Aggarwal et al.¹⁸ noted the viscosity stability was important to the outcome of the injection molding step, and that weak temperature dependence of the viscosity minimized stress concentrations, cracks and distortion. The lowest injection pressure resulted in the lowest residual stresses.

Zauner³⁶ scaled down injection molding to produce compacts with microscopic features from 400-nm alumina. Micro PIM was considered more suitable for mass production than lithography-electroplating-molding (LIGA, in German) plus electrical discharge machining (EDM).

Onbattuvelli et al.^{15,16} reported lower viscosity in bimodal powder + binder than in monomodal, when the same volume fractions of powder were compared.

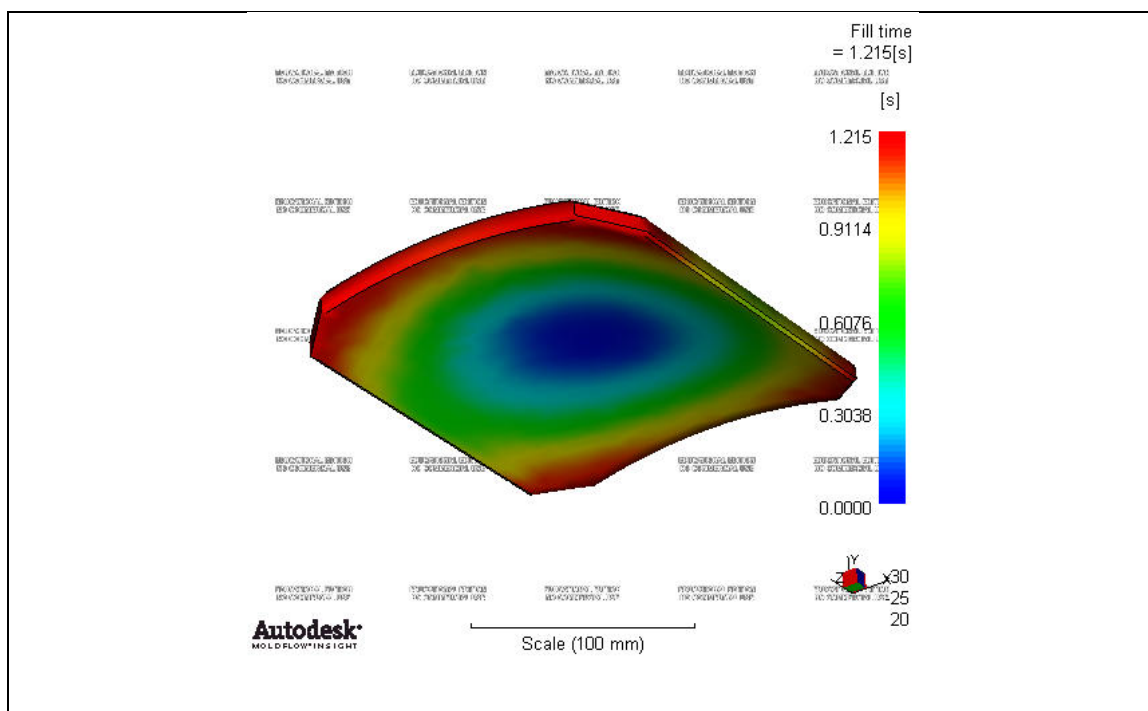


Figure 2.4: Simulated fill time of a 232 × 173 × 6 mm SiC curved armor tile.

2.5 Green Machining

Green machining, cutting and grinding done between the injection molding and binder removal steps, greatly reduces the time and expense of net shape achievement compared to post-sinter machining. Tooling wear is also greatly reduced, and process capability increased, by green machining.³⁷ While green machining via computer numerical control (CNC) tools is a mature process, green micromachining (GMM) is still novel, especially in polycrystalline SiC. The disadvantage of green machining is that green ceramics are very fragile and deformable.

The smallest structures that can be formed by PIM are about ten times the particle size, meaning that a 5- μm feature, such as a groove in a microchannel reactor, requires a mean grain size of no more than ~ 500 nm.³⁶ Christian and Kenis³⁸ fabricated alumina microdevices by gelcasting, where the smallest dimension was 30 times larger than the mean particle size D_p in the range of $0.3 \leq D_p \leq 3.0$ μm . In GMM, the particles are removed

whole; that is, the fracture is mostly in the binder, not the particles. This puts a lower limit on the size and smoothness of features that can be created by GMM.

Ceramic machining is not limited to conventional mechanical techniques. Electrical discharge machining (EDM), ultrasound, lasers, electrochemical etching, plasma etching, lithography and other methods have been applied to green machining and post-sinter machining.

GMM of PIM SiC components is described in Chapters 7 and 8 of this thesis.

2.6 Binder Removal

The binder's purpose is to facilitate molding, and it must be removed without disturbing the particles before sintering. Binder removal, baking, dewaxing or debinding, can be done by several methods. Defects such as cracks, pits, distortion and voids may result from debinding at too high of a rate. Solvent methods such as immersion extraction, supercritical³⁹ and condensation vapor, and thermal methods such as vacuum diffusion, capillary or wicking, gas permeation and oxidation have been used.^{3,7} The catalytic method is considered a combination of solvent and thermal debinding. Each technique has advantages and disadvantages, and niche applications. The cost of binder removal has been estimated as ten times the cost of the binder.⁴⁰ A common two-step debinding scheme is thermal or solvent removal of the lower molar-mass binder component such as paraffin, i.e., dewaxing, to create pores that enable thermal gaseous decomposition of the higher molar-mass "backbone" component, such as polyethylene, at a higher temperature.

In Ohnsorg's⁷ patent, the debinding time range was claimed as five days to two weeks. Phenol formaldehyde was added to the feedstock to provide carbon as a sintering additive. In Renlund and Johnson's⁹ patent, the defects caused by too-rapid debinding were minimized by the addition of stearic acid to the feedstock. The compacts were thermally debound while heated in vacuum to 400°C at 1.0 K/hr, and held at 400°C for 24 hr.

Barone and Ulicny⁴¹ observed a rise in internal pressure with heating rate. The thermal expansion of the binder induced hydraulic pressure in the compact. The two-

component binder was lost by evaporation and capillarity. The shrinkage associated with successful debinding was on the order of 0.5% in any dimension. The binder loss, with gas transport considered negligible, was modeled on Darcy's Law for water flowing through packed sand in Equation 2.3.

$$q = -\frac{\kappa}{\mu} \nabla P \quad (2.3)$$

Where q = volumetric flux [m/s], κ = permeability [m²] of the powder, ∇P = pressure gradient [Pa/m] and μ = viscosity [Pa·s] of the binder.

Zhang et al.¹⁰ pyrolyzed⁶ a pre-ceramic polymer binder, polycarbosilane, to form additional SiC and assist in the sintering step. The lower-melting component of the binder was paraffin. The compacts were heated to 150°C at 60 K/hr, and to 500°C at 2 K/hr during debinding.

Loh and German⁴ performed a statistical analysis of variance on the shrinkage associated with binder removal and sintering in Fe – 2% Ni powder. Solvent condensation debinding in heptane was compared to vacuum debinding for 12 hr at 70-150°C. The parameters were ranked from most to least significant: sintering heating rate, sintering hold temperature, sintering hold time, debinding method. Interactions between the four were mostly insignificant. Minimum length shrinkage was noted at a heating rate of 10 K/min, pre-sintering $T_{\text{hold}} = 1150^\circ\text{C}$, and $t_{\text{hold}} = 40$ min, after vacuum debinding. Solvent debinding resulted in the minimum thickness shrinkage. The shrinkage from debinding was anisotropic in all cases.

Maximenko and Van Der Biest⁴² applied finite element modeling to binder removal of a two-component binder, and noted that thermal debinding has a high risk of defect formation and component failure when the heating rate and weight loss rate are not optimized. Overpressure aided thermal debinding, both in practice and in one of the predictive equations.

Krug et al.¹³ removed polyoxymethylene binder by catalytic degradation in the solid state at 110°C for 5 hr in an atmosphere of N₂ purge gas and liquid fuming nitric acid from

a metered pump. Afterward, the compacts were heated in air at 2 K/min and held for one hour at 270°C, before sintering.

Lu et al.³ compared debinding and pre-sintering of PIM SiC in air to argon, at various pre-sintering temperatures. The heating rate was 1 K/min to 80°C, 0.5 K/min to 500°C, and 2 K/min to the pre-sintering temperatures. Two-hour isothermal holds were used at 180, 380 and 500°C. The binder was removed in air by thermal oxidation, and in argon by pyrolysis. Bending beam and disc specimens were pre-sintered at 550, 650, 750, 850 and 950°C for 2 hr in air, or 1200°C for 2 hr in Ar. No defects were detected in compacts debound in air at 500°C. The beams pre-sintered at 750 and 850°C in air had the same bending strength, 11-12 MPa, as the beams pre-sintered at 1200°C in Ar. The 950°C beams had strength >26 MPa, but were also distorted and heavily oxidized. The shrinkage in air and Ar was comparable, but an expected oxide skin, not necessarily deleterious, was noted on all the compacts pre-sintered in air.

German and Bose⁵ considered heating rates of 2 K/hr or less in thermal debinding to be unnecessarily slow, once the pores were partially opened by, say, solvent extraction of the paraffin. The capillary forces of the backbone binder component can be expected to maintain the shape of the compact and allow rapid heating on the order of a few hours. Furthermore, shape retention was assisted by a high-friction mixture of spherical and angular particles. The rate of solvent extraction was proportional to the square root of immersion time.

Enneti et al.⁴⁰ devised master debinding curves, similar to master sintering curves (MSC), to quantitatively compare different materials and debinding processes for design and optimization of PIM. The MSC approach and a shape factor were used to evaluate debinding activation energy, which was lower for solvent or wicking than for pyrolysis.

Onbattuvelli et al.¹⁶ observed a catalytic effect by nanoparticles in bimodal compacts on the degradation of binders when the debinding process was not diffusion-controlled. Binder removal was slower in the bimodal compacts than monomodal due to reduced pore size and porosity. The shrinkage was isotropic in both cases, in contrast to Loh and German's⁴ assertion of anisotropy.

Martin et al.⁴³ noted the slower degradation of paraffin + polypropylene binders in a mullite-zirconia composite when heated in N₂, compared to air.

Chapters 3 and 4 of this thesis examine the kinetics of solvent and thermal debinding, respectively, of SiC feedstock.

2.7 Sintering of PIM Ceramics

Pre-sintering or bisque firing is sometimes done to PIM ceramics after debinding. Once the binder is removed, typically at $\leq 500^{\circ}\text{C}$, the compact has negligible green strength unless it is heated to $\geq 850^{\circ}\text{C}$ for SiC and held at that temperature until bonds begin to form at particle contact points. Bisque firing is important for PIM ceramics that require stress relief, machining or other processing after binder removal. A pre-sintered compact is more rigid, but also more brittle and hard, than a fully green compact. Full sintering of PIM ceramics is essentially the same as for pressureless-sintered ceramics from any other shape-forming process.

Zhang et al.¹⁰ reported exaggerated grain growth after sintering in both PIM and dry-pressed compacts of the same composition, but it was not attributed to the PCS binder. The compacts had no sintering additives to control grain growth.

Loh and German⁴ observed anisotropic sintering shrinkage in rectangular tensile bars.

Krug et al.¹³ compared the sintering shrinkage of irregularly-shaped 0.6–0.8- μm alumina particles to equiaxed 0.3- μm zirconia. Shrinkage was greatest in the center of the compact and smallest along the surface in the mold-filling direction of the alumina, and opposite that in the transverse direction. Shrinkage was uniform in the zirconia. Evidence of the differential shrinkage due to the anisotropy of the ceramic powder was difficult to detect. Preferred orientation due to particle shape anisotropy occurred even at low shear rates.

Zauner³⁶ suggested that distortion in microcomponents during sintering could be minimized by long holding times at critical temperatures to relax induced stresses.

Onbattuvelli et al.¹⁵ witnessed the onset of densification at 1550°C in bimodal SiC, some 100 K lower than previously claimed for pressureless sintering. Nanorods formed in the monomodal SiC, but not in bimodal. The monomodal compacts had greater shrinkage, about 20 vol%, than bimodal, 15%. The shrinkage was isotropic in both cases. Weight loss and density reduction above 1950°C was attributed to the formation of volatile monoxides of Al and Y.

Chapters 5 and 6 of this thesis review the effects of sintering additives on SiC ceramics as reported by other authors. Chapters 7 and 8 report studies of debound and sintered PIM SiC components. Figure 2.5 illustrates the shrinkage of the tensile bars in Chapters 7 and 8 from fully green to fully densified by sintering.

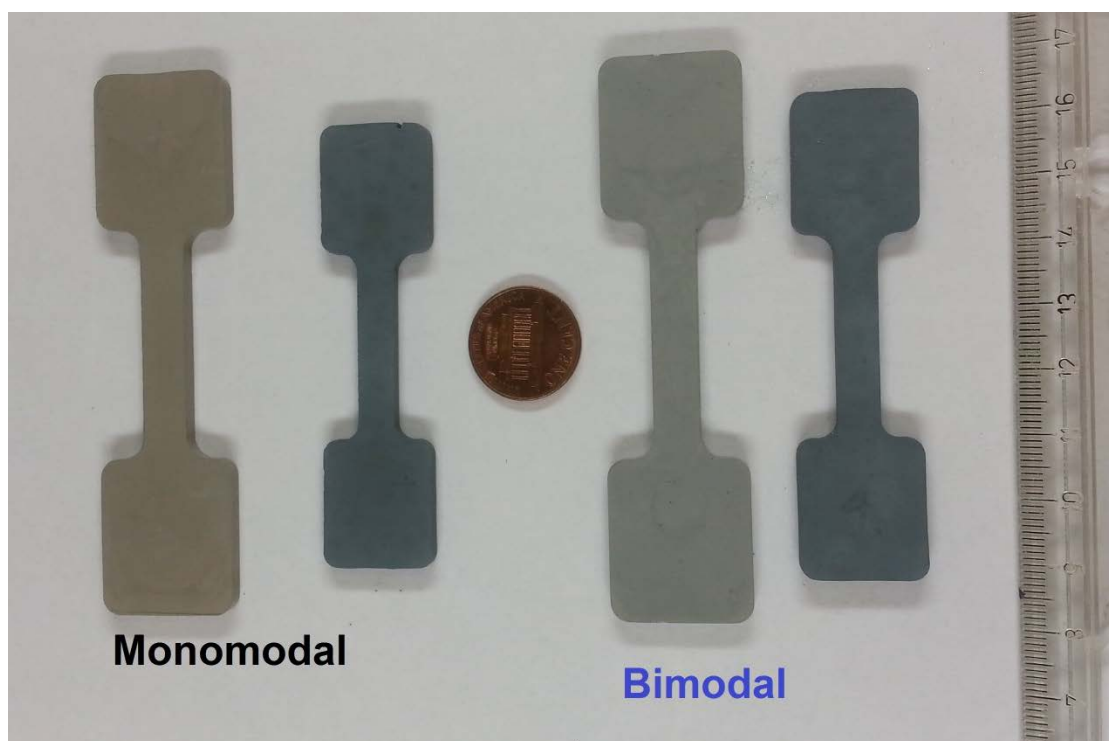


Figure 2.5: Sintering shrinkage in SiC tensile bars.

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CHAPTER 3

3 The Effects of Nanoparticle Addition on Binder Removal from Injection Molded Silicon Carbide

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Abstract

The effects of nanoparticle addition on the multi-step debinding of injection molded SiC samples were studied. Experiments varying the solvent debinding conditions (time, temperature and aspect ratio) were performed on monomodal, microscale (μ) and bimodal, micro-nanoscale (μ -n) SiC samples. Variations in the solvent debinding kinetics as a result of the reduced particle size and increased powder content were examined. The data showed solvent debinding to occur in two stages. The bimodal μ -n SiC samples showed a slower solvent extraction of binder components compared to monomodal μ -SiC samples. The activation energy for solvent extraction estimated from diffusion coefficients (Arrhenius equation) was in close agreement with the value estimated by the master debinding curve (MDC) method. An activation value around 50 kJ/mole was estimated by both the methods for μ and μ -n SiC samples.

“Though this be madness, yet there is method in it.” — William Shakespeare, *Hamlet*

3.1 Introduction

The selection of correct combinations of binders and powders is critical to developing a successful PIM process.^{1,2,3} Binder systems used in PIM typically include a high molecular weight polymer as well as a secondary phase that is easily removed by solvent,^{4,5,6,7} wicking^{8,9} and catalytic^{10,11} methods, following injection molding. Irrespective of the debinding technique used, the primary aim is rapid binder removal without any physical distortion of the injection molded green parts. In solvent debinding, binder removal leaves interpenetrating pore channels, which allow the decomposed gas to more easily diffuse out during subsequent thermal debinding. As a result, solvent debinding can reduce the debinding cycle significantly and has been widely accepted by the PIM industry.^{12,13,14} However, rapid binder removal may result in defects such as cracking, distortion, and slumping.^{13,14,15,16} A successful solvent debinding process thus depends on understanding and controlling diffusion-related factors such as temperature, time, solvent, and aspect ratio of molded parts.^{17,18,19,20,21,22}

Our prior reports on SiC injection molding demonstrated the use of bimodal μ -n powder mixtures as an effective way to increase the volume fraction of powder in the injection molding feedstock.^{23,24} The sintering behavior and properties of these systems have also been reported recently in the literature.^{25,26} However, there remains a concern that bimodal μ -n mixtures will have reduced pore size and porosity that will increase the tortuous path, thereby slowing the rate of binder removal from the injection molded “green” parts and increasing the formation of defects and carbon residue in PIM parts. In the current paper, the effects of nanoparticle addition on the solvent debinding kinetics of injection molded SiC samples were studied.

3.2 Experiment

Commercially available α -SiC, AlN and Y_2O_3 were used as the starting materials in as-received condition. A multi-component binder system comprising of paraffin wax (PW), polypropylene (PP), polyethylene-g-maleic anhydride (LDPE-g-MA) and stearic acid (SA) was used in the current study. The formulations and injection molding conditions for the monomodal and bimodal SiC powder-binder mixtures were discussed elsewhere.²⁴ Table 3.1 lists the composition of the SiC samples used in the present study. The binder composition was chosen in such a way to facilitate a multi-step (solvent, thermal) debinding. Heptane (Fischer Scientific) was used as the solvent to dissolve the soluble binder components without any further treatment. Injection molded green samples were machined to the dimensions ($l \times b \times h$ in mm) of $23 \times 13.2 \times 7.2$, $34.5 \times 6.6 \times 7.2$ and $25 \times 14 \times 2$, which correspond to a shape factor (ψ , volume-to-surface area ratio (V/SA)) of 1.94, 1.56, and 0.82 mm, respectively. Isothermal solvent debinding experiments utilizing five specimens of each dimension were performed in heptane at 20, 40 and 60 °C under slow and continuous stirring. Continuous solvent recycling at 2 ml/min was performed to avoid concentration effect of soluble components.^{17,18} All specimens were placed together into the solvent bath and were removed at each time-point for gravimetric analysis. The solvent debinding was monitored for up to 4 h. The fraction of the soluble binder remaining (f) can be calculated using Equation 3.1:

$$f = 1 - \frac{w_o - w}{f_o w_o} \quad (3.1)$$

where, f_o is the initial weight fraction of soluble binder, w_o is the initial mass of compact, and w is the instantaneous mass of compact. Thermogravimetric analysis (TGA) was performed (TA instruments Inc., Q500) under nitrogen atmosphere (50 ml/min) with a heating rate of 20 K/min, in order to verify the specimen weight losses during solvent debinding. Furthermore, scanning electronic microscopy (SEM) (FEI, QuantaTM) images were taken on both the surface and core of the samples to examine pore

evolution. Thermal debinding cycles of the solvent debound samples were performed under inert atmosphere in the CM 1212 FL furnace. TGA was once again performed on the thermally debound (brown) samples to determine the % residual carbon.

Table 3.1: Composition of SiC samples tested in the current study.

Sample	Avg. Particle Size (μm)	Solids Loading (vol%)	Soluble Binder Content	
			(vol%)	(wt%)
Monomodal SiC	0.7	51	27	11
Bimodal SiC	0.63	58	26	9

3.3 Results and Discussion

During the solvent debinding, heptane diffuses into the sample to dissolve wax and SA. As the molecular weight of the heptane is significantly lower than the molecular weights of the binders, heptane can diffuse into the sample faster than the wax + SA diffuse out of the sample. Consequently, the rate-limiting step is assumed to be the diffusion of the dissolved wax + SA molecules rather than the inward diffusion of the much smaller heptane molecules. Zaky et al.¹⁹ proposed a similar hypothesis for the dissolution of wax in hexane while Omar et al.⁷ suggested such a scenario for removal of polyethylene glycol in water. Thus, factors including ψ , immersion time and temperature that may affect the diffusion of the binder molecules are considered.

Figures 3.1 and 3.2 show the soluble binder extracted (%) in heptane at different time-temperature combinations from the SiC samples with different ψ ratio. As expected, increasing the ψ ratio signifies greater contact areas between solvent and binder and as consequence, lowers the debinding times. Oliviera et al.¹⁷ and Krauss et al.¹⁸ provided similar results for injection-molded alumina parts. Irrespective of the ψ ratio, the debinding rate was found to reduce with increase in the time. Such behavior has also been reported earlier by Oliviera et al.¹⁷, Krauss et al.¹⁸ and Zaky¹⁹ in stainless steel molded parts. With increasing solvent immersion time, the soluble components inside the samples diffuse through tortuous pathways, from inner regions to the

specimen surface, leading to a reduction in the debinding rate. Increasing the solvent temperature is found to exhibit an improvement in debinding process efficiency for all specimen dimensions. This may be due to an increase in solubility of wax and SA in heptane as function of temperature. Earlier reports by Omar et al.⁷ and Tsai et al.¹⁵ discussed similar effects of temperature on solubility.

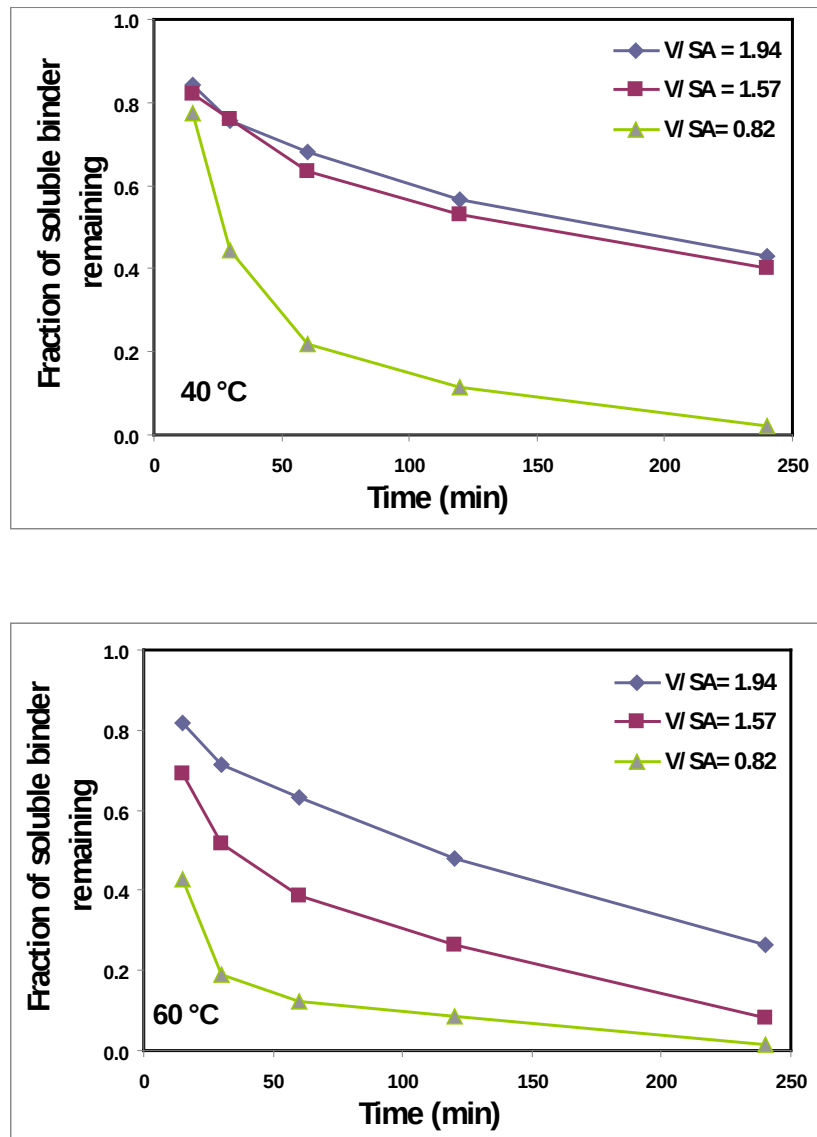


Figure 3.1: The effect of immersion time and temperature on the solvent debinding of monomodal μ -SiC samples with different ψ (V/SA) ratios.

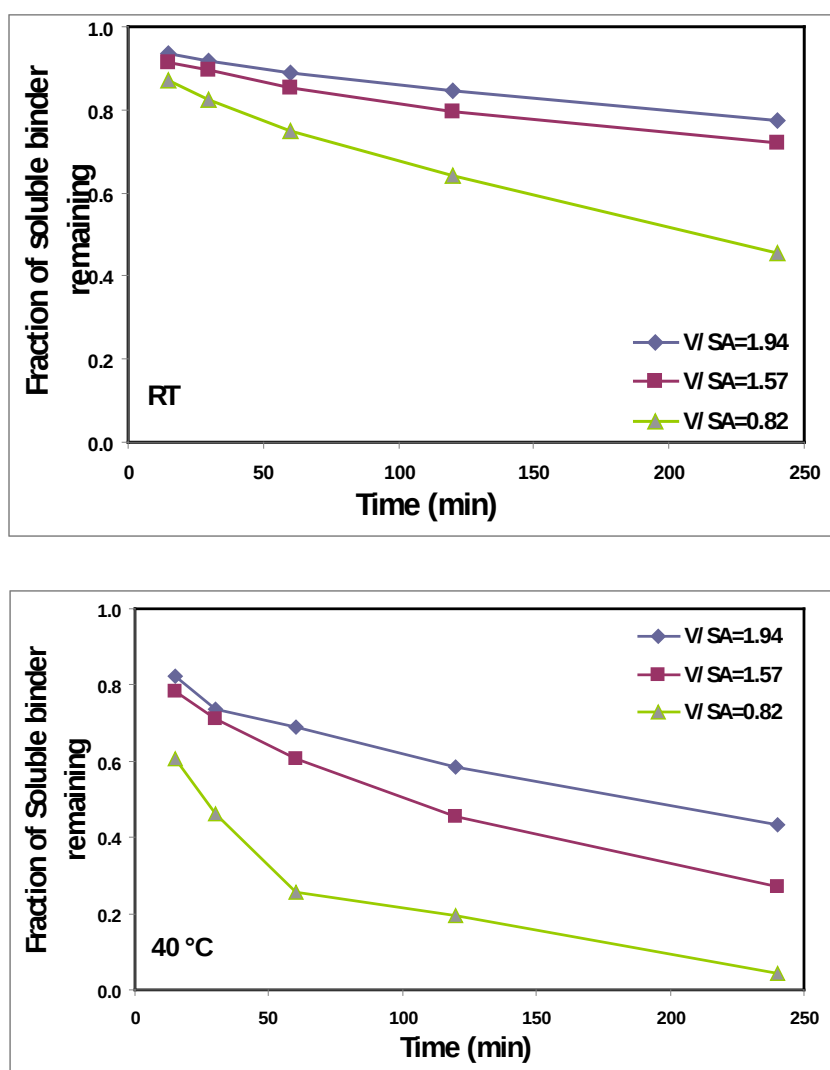


Figure 3.2: The effect of immersion time and temperature on the solvent debinding of bimodal μ -n SiC samples with different ψ (V/SA) ratios.

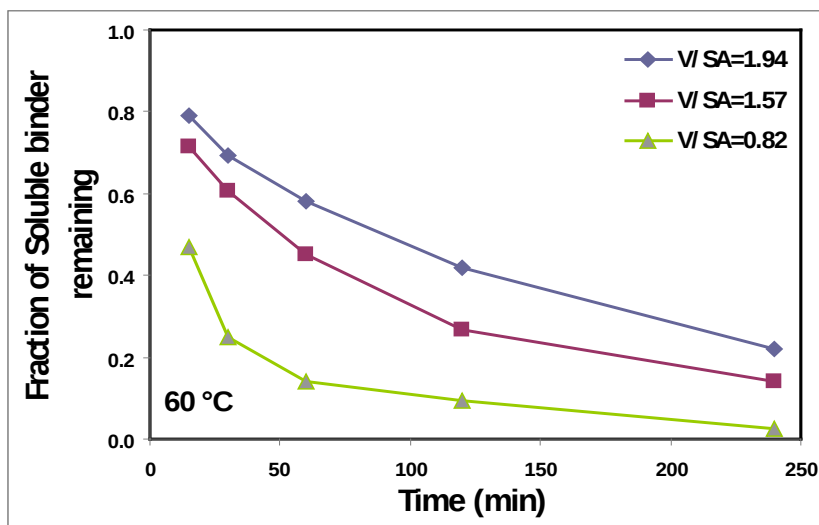


Figure 3.2 (continued): The effect of immersion time and temperature on the solvent debinding of bimodal μ -n SiC samples with different ψ (V/SA) ratios.

3.3.1 Confirmation Studies

No dimensional change was noticed with the samples irrespective of the solvent debinding conditions. These findings are in contradiction with those of Zaky¹⁹ and Wang et al.²¹ where dimensional change/swelling is reported when hexane is used as the solvent under similar conditions. To evaluate the total composition change in the samples during solvent debinding, thermogravimetric analysis (TGA) was performed. Figures 3.3 and 3.4 show the TGA curves for the samples with the ranges of 200–375°C and 380–490°C, respectively. The thermal analysis results agree with the initial proportion of binder components of the prepared feedstock. As immersion time increases, the composition varies due to a decrease in weight loss in the first degradation step, indicating the decrease in the soluble binder components. Similar TGA results were reported in the past by Oliveira et al.¹⁷ for injection-molded alumina samples. After 240 minutes, only the weight loss of the backbone polymer was observed, suggesting that nearly all soluble components were removed.

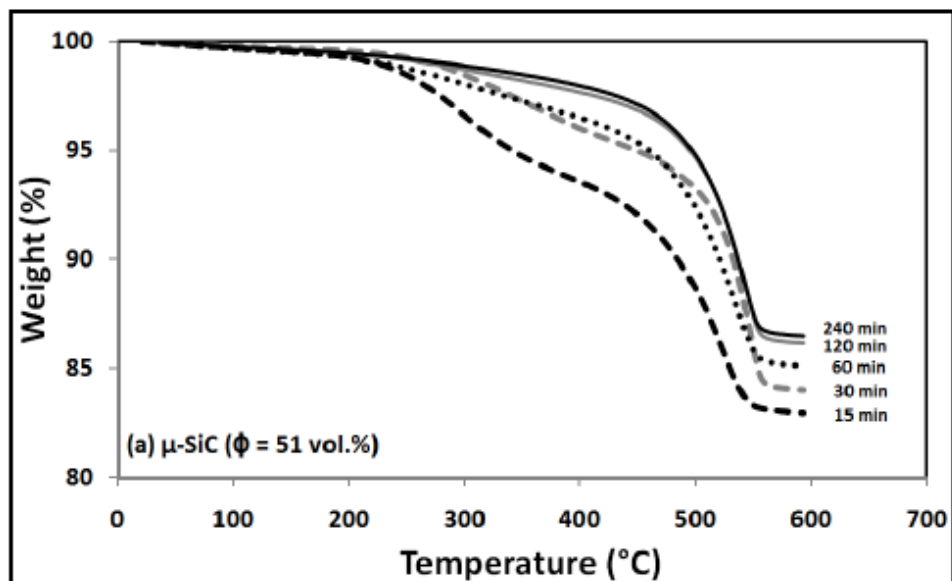


Figure 3.3: TGA runs on solvent-debound monomodal $\mu\text{-SiC}$ samples ($\psi = 0.82$) indicating the increasing removal of soluble binder components with increased immersion time.

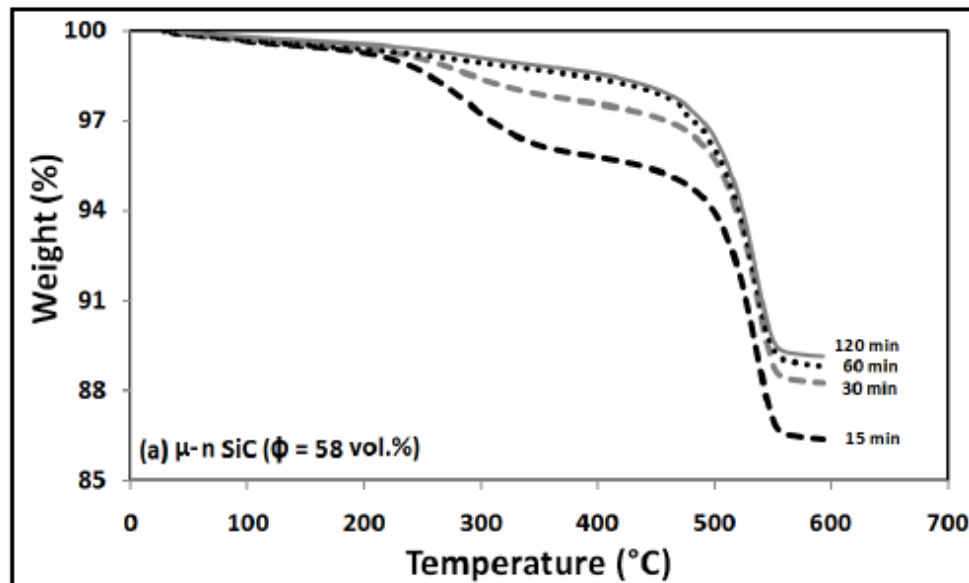


Figure 3.4: TGA runs on solvent-debound bimodal μ -n SiC samples ($\psi = 0.82$) indicating the increasing removal of soluble binder components with increased immersion time.

Figures 3.5 and 3.6 show the SEM micrographs of SiC samples after different solvent debinding times. The micrographs of all the green samples show a similar microstructure at regions close to the core and the surface. The surface micrograph of the region close to specimen surface after initial immersion in heptane (Figures 3.5c, 3.6c) show porous structure due to the elimination of soluble components, while no appreciable changes were observed in the micrograph of the specimen core (Figures 3.5d, 3.6d). Following increasing immersion times, the specimen microstructures at areas near the core and the surface become similar, indicating the removal of soluble components (Figures 3.5e, 3.6e and 3.5f, 3.6f).

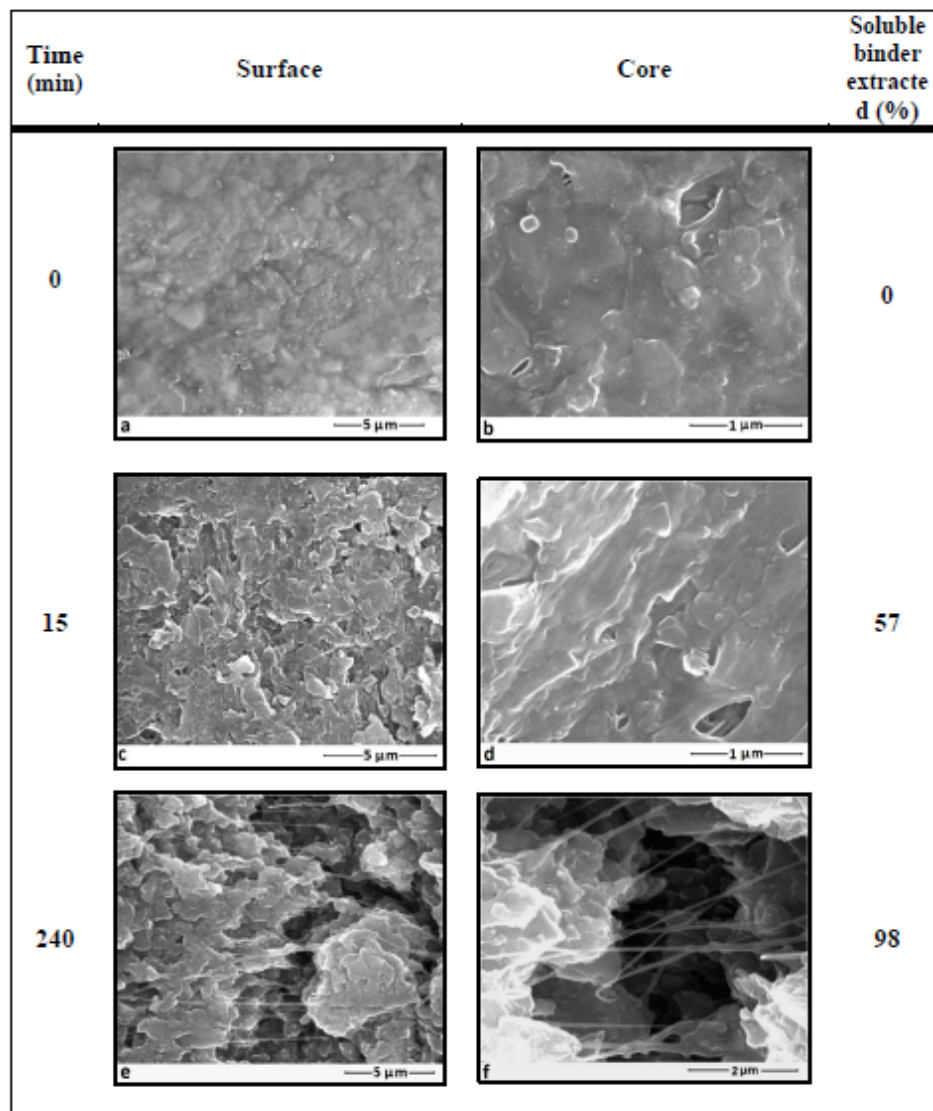


Figure 3.5: SEM micrographs of monomodal μ -SiC samples ($\psi = 0.82$) after debinding in heptane at 60 °C as function of immersion time.

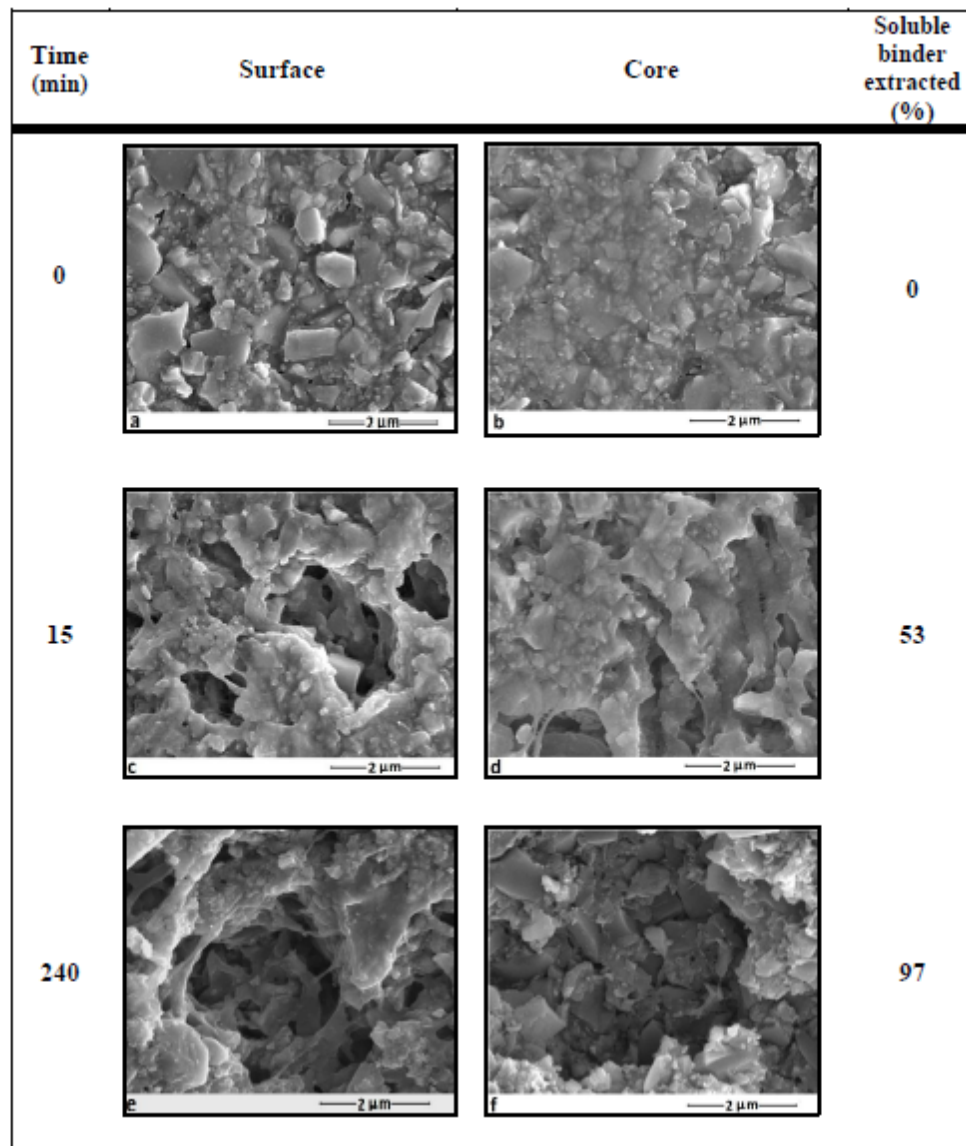


Figure 3.6: SEM micrographs of bimodal μ -n SiC samples ($\psi = 0.82$) after debinding in heptane at 60 °C as function of immersion time.

3.3.2 Effect of nanoparticle addition on the solvent debinding

From the Figures 3.1 and 3.2, it can be inferred that the bimodal samples exhibit a slightly slower polymer removal than the monomodal ones irrespective of the debinding conditions. This is due to the increase in the tortuous path to be followed by the binder components. Such behavior is an outcome of the combined effect of

increased solids loading (lower % porosity) and decreased pore size via nanoparticle addition. In order to analyze the effect of such nanoparticle addition, factors including powder particle content and particle size should be studied separately. For example, the Kozeny-Carman model (Equation 3.2) is used to determine the effect of varying the solids loading on the permeability, k .²²

$$k = \frac{2 * d_p^2 (1 - \varepsilon)^2}{75 * \varepsilon^2} \quad (3.2)$$

where, ε is the porosity ($= 1 - \text{solids loading}$) and d_p is the average particle size. In the present study significantly higher permeability values were estimated for monomodal μ -SiC compared to bimodal μ -n SiC samples. For example, at 51 vol% solids loading, the permeability value decreased from $1.04 \times 10^{-15} \text{ cm}^2$ to $0.42 \times 10^{-15} \text{ cm}^2$ with the addition of nanoscale SiC particles. It is interesting to note that in contrast to the large differences in permeability estimated by the Kozeny-Carmen relationship, the differences in solvent debinding rates for bimodal μ -n SiC and monomodal μ -SiC samples are relatively small. This indicates that despite the addition of nanoparticles and the higher solids loading, practical solvent debinding times can still be achieved without introducing defects in the samples.

At room temperature, the dissolution of the wax in heptane is the likely rate limiting step in the beginning of the debinding process over a leaching time of 60 min. Polymer removal during the dissolution controlled stage is twice as fast as the removal during the diffusion limited stage at later times. As the process proceeds, a longer diffusion distance through porous channels formed after initial debinding slows down the process and diffusion becomes the rate-determining step. Solvent debinding is predominantly diffusion-controlled process that can be represented by Equation 3.3, where F is the fraction of the remaining soluble polymer, D_e is the inter-diffusion coefficient of polymer and solvent, t is time and K represents the change in the mechanism controlling the debinding behavior.^{1,22}

$$\ln\left(\frac{1}{F}\right) = \frac{D_e t \pi^2}{\psi^2} + K \quad (3.3)$$

The plots of $\ln(1/F)$ and t/ψ^2 for extraction of paraffin wax at various temperatures showed two stages of debinding. The first stage of solvent extraction occurred up to 60 min and during this stage the major amount of paraffin wax was removed. The second stage of debinding occurred above 60 min. The first and second stage plots of $\ln(1/F)$ and t/ψ^2 for extraction of paraffin wax at 60°C for different size samples used in the present study are shown in Figures 3.7 and 3.8.

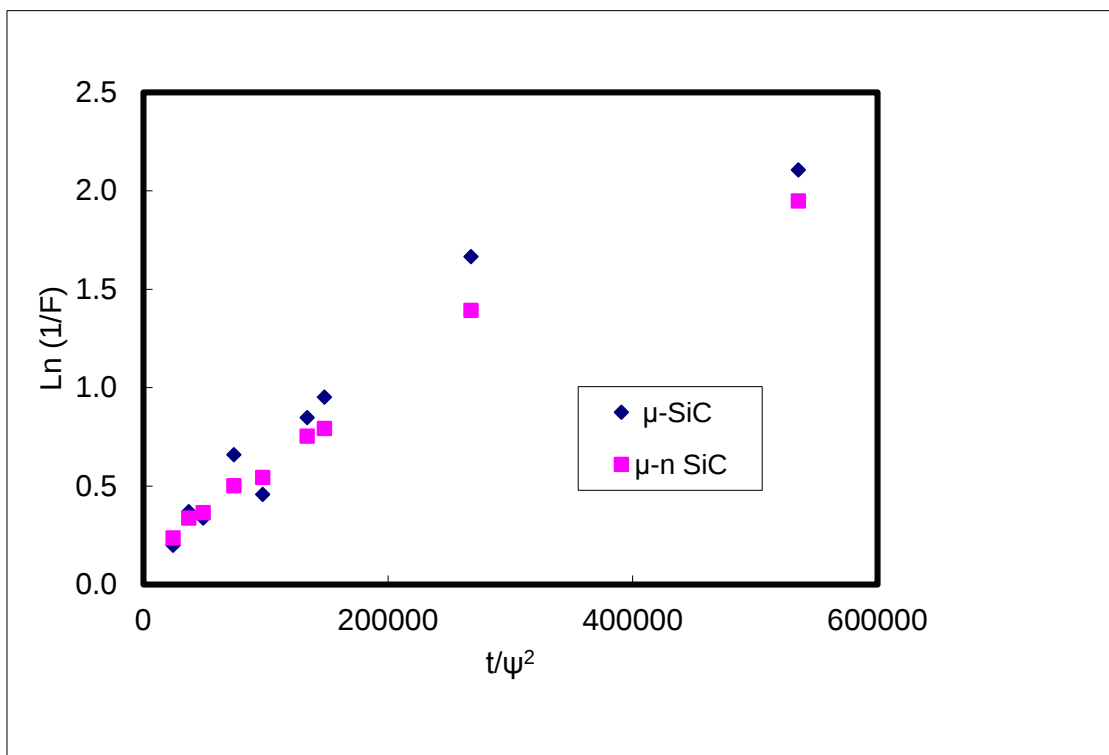


Figure 3.7: $\ln(1/F)$ vs. t/ψ^2 for extraction of paraffin wax at 60°C for different size samples for shorter times upto 60 min.

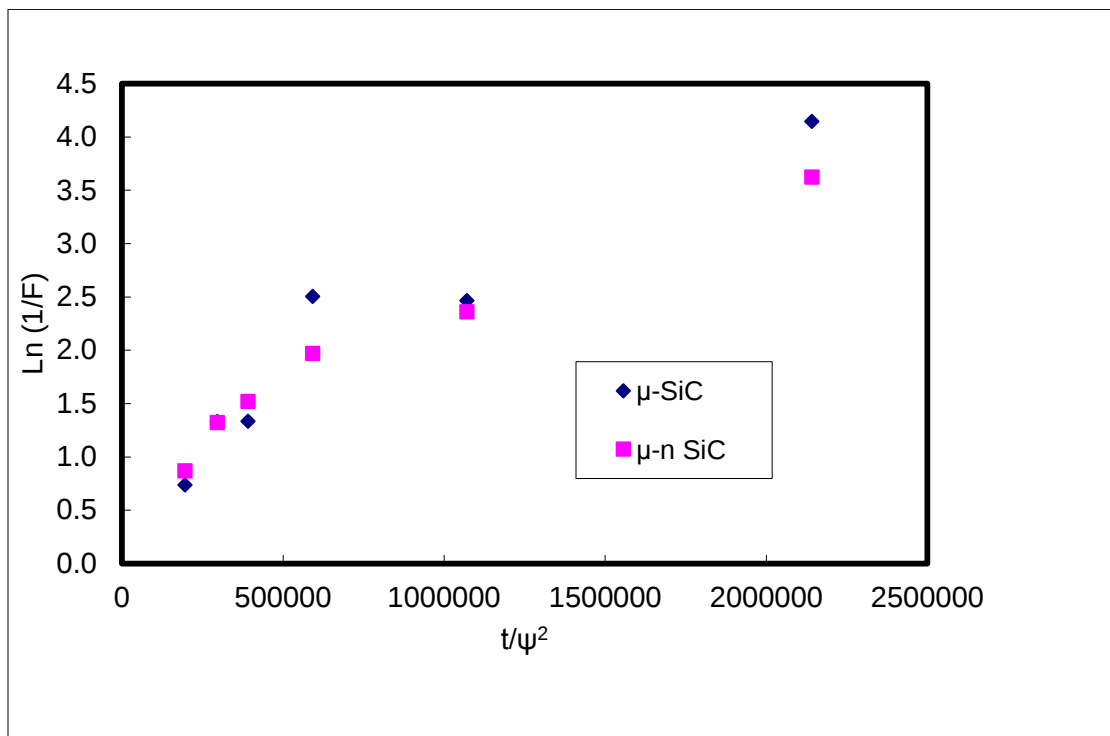


Figure 3.8: $\ln(1/F)$ vs t/ψ^2 for extraction of paraffin wax at 60°C for different size samples above 60 min.

The estimated diffusion coefficients D_0 , D_e and K for the two stages of solvent extraction calculated from the plot $\ln(1/F)$ as a function of immersion time of the samples in the present study are summarized in Tables 3.1 and 3.2. The data showed some interesting trends for SiC samples. The diffusion coefficient (D_e) increased with increase in temperature for both monomodal μ -SiC and bimodal μ -n SiC samples. Higher D_e values observed for increasing temperatures are possibly due to the increased diffusivity of the paraffin wax in heptane. The increase in diffusion coefficients with temperature was significant for the first stage compared to the second stage. Irrespective of the sample aspect ratio and solvent temperature, the bimodal μ -n SiC samples showed slightly lower D_e values than the corresponding monomodal μ -SiC samples. This may be due to the decreased rate of the binder-solvent interactions due to the nanoparticle inclusion. Similar results of decrease in diffusion coefficients with increase in temperature as well as lower diffusion

coefficients for bimodal μ -n samples were observed in a prior study of AlN.²⁷ The factor K represents the change in debinding mechanism and significant change for monomodal μ -SiC and bimodal μ -n SiC for the two stages of debinding. For any given temperature, the values of K for the second stage were higher than the first stage for both monomodal μ -SiC and bimodal μ -n SiC. For the first stage, the values of K ranged in between 0.08–0.26 for monomodal μ -SiC and 0.08–0.24 for bimodal μ -n SiC for different temperatures. The values of K increased to 0.14–0.85 for monomodal and 0.13–0.93 for monomodal μ -SiC and bimodal μ -n SiC during second stage of solvent extraction. The difference in values of K for the two stages clearly indicates a change in debinding mechanism during the first and second stage of solvent debinding. However, the values of K for both monomodal μ -SiC and bimodal μ -n SiC systems are quantitatively similar.

Table 3.2: Solvent debinding coefficients of monomodal and bimodal SiC samples.

Temperature (°C)	Dissolution coefficient, D_0 ($10^{-6} \text{ cm}^2/\text{s}$)		Diffusion coefficient, D_e ($10^{-6} \text{ cm}^2/\text{s}$)	
	monomodal	bimodal	monomodal	bimodal
25	0.04	0.04	0.03	0.03
40	0.30	0.20	0.20	0.10
60	0.41	0.30	0.20	0.10

The diffusion coefficients (D_e) data was further analyzed to estimate the activation energy for the extraction of paraffin wax as per the Arrhenius equation (Eq. 3.4)

$$D_e = D_0 \exp\left(\frac{-Q}{RT}\right) \quad (3.4)$$

Where Q is the activation energy for solvent extraction, R is the universal gas constant and T is the temperature. The activation energies for extraction of paraffin wax for μ and μ -n SiC for the first stage of extraction was estimated to be around $45 \pm 5 \text{ kJ/mol}$. The minor changes in D_e values with temperature limited accurate calculation of activation energy value for the second stage solvent extraction process.

The activation energy for solvent extraction was also estimated using Master Decomposition Curve (MDC) method. According to MDC concepts, the work for solvent extraction (Θ) is related to temperature as per Eq. 3.5²⁸

$$\Theta(t, T) = \left(\frac{1}{\psi^2} \right) \int_0^t \frac{1}{T} \exp\left(\frac{-Q}{RT} \right) dt \quad (3.5)$$

The value of Q at which F vs $\ln(\Theta)$ for samples of different sizes merge into one curve is estimated as the activation energy of the solvent extraction process.²⁸ The F vs. $\ln(\Theta)$ for μ and μ -n SiC samples for different values of Q is shown in Figure 3.9. The figure shows that the individual curves for samples of different sizes for both μ and μ -n SiC merge together for an activation energy value of 50 kJ/mol. Thus the activation energy for extraction of paraffin wax from μ and μ -n SiC samples is estimated to be 50 kJ/mol. The activation energy values estimated by the Arrhenius equation were similar to the estimated values based on the MDC method. The estimated activation energy values were also in general agreement to activation energies obtained for solvent debinding of other paraffin wax-polymer particulate systems in the literature ($\sim 42 \pm 5$ kJ/mol).²⁸ The absence of significant variations in activation energies between monomodal and bimodal systems indicate that there are no fundamental mechanistic changes in binder removal during solvent debinding owing to the addition of nano particles.

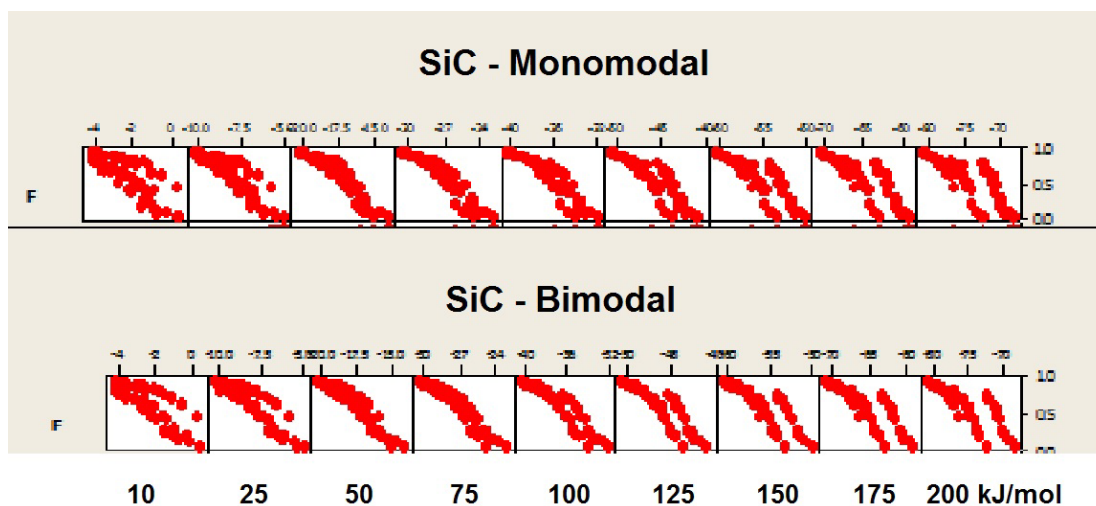


Figure 3.9: MDC curves for solvent extraction of paraffin wax from samples used in the present study at different values of Q .

3.4 Conclusions

The removal of binder by solvent extraction and thermal debinding from injection-molded monomodal and bimodal SiC samples was analyzed. The present study indicates that bimodal μ -n SiC samples had slightly lower debinding rates compared to μ -SiC samples. The combined effect of increased powder content and reduced average particle size via nanoparticle addition can be attributed as reasons for such behavior. However the differences in solvent debinding rates as a result of nanoparticle addition are much smaller than what permeability estimates suggest. The activation energy for solvent extraction estimated from diffusion coefficients and master decomposition curve concepts were in close agreement. No significant difference in activation energy for solvent extraction was observed for bimodal μ -n SiC samples compared to monomodal μ -SiC samples, indicating an absence of any major mechanistic changes in solvent debinding as a result of nanoparticle addition. The present study confirms that despite the addition of nanoparticles and the higher solids loading, practical solvent debinding times can still be achieved without introducing defects in the bimodal μ -n samples.

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CHAPTER 4

4 Kinetics of Thermal Debinding of Injection Molded Silicon Carbide

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Abstract

Powder injection molding (PIM) of SiC is a near-net shape, high-speed fabrication process that has been studied only lightly. Debinding is typically the rate-limiting step in PIM, and often a source of sintering defects. In this paper, the kinetic properties of thermally dewaxed and debound SiC PIM feedstocks by various models were compared to solvent dewaxed SiC from an earlier study. The activation energy E_a of pyrolytic dewaxing was 64 ± 12 kJ/mol for monomodal and 53 ± 7 kJ/mol for bimodal SiC powder size distributions, compared to ~ 50 kJ/mol for solvent dewaxing in both cases. The E_a of pyrolytic debinding of polypropylene was 103 ± 17 kJ/mol for monomodal and 109 ± 11 kJ/mol for bimodal by the Flynn-Wall (F-W) model. Some inconsistencies between the data here and the F-W model were noted. The Kissinger model yielded $\sim 20\%$ higher E_a values than the F-W model, but was very consistent within and between samples. The catalytic effect of nanoparticles on the debinding characteristics of PIM SiC was not statistically significant.

“Why, a four-year-old child could understand this! Run out and get me a four-year-old child, I can't make head or tail out of it!” — Groucho Marx in *Duck Soup*

4.1 Introduction

Powder injection molded (PIM) silicon carbide, SiC, is promising for a number of applications.^{1,2,3} The injectibility of PIM feedstock is dependent upon its thermophysical properties. In PIM, the binder system typically contains two resin components of different molecular mass and glass transition temperature, to facilitate maximum efficiency in the debinding step. Stearic acid, a lubricant, is used to enable debinding. A common two-step debinding scheme is removal of the lower molar-mass filler component such as paraffin, i.e., dewaxing, to create a network of pores that enable pyrolysis of the higher molar-mass “backbone” component, such as polypropylene (PP), at a higher temperature.⁴ Both steps of the debinding process are necessarily slow, to minimize damage from the stresses induced by the loss of organic components from the injection molding. Dewaxing methods include solvent, catalytic and supercritical, but thermal dewaxing is advantageous for its simplicity. The transport and deformation aspects of ceramic thermal dewaxing have been modeled by Shengjie et al.⁵ and Trunec and Cihlar.⁶

The ceramic particles provide a large amount of surface area, approximately 1–10 m²/gm for micro-particles and ~100 m²/gm for nanoparticles, for nucleation or catalysis of reactions, and also affect the thermal and rheological properties of the feedstock, such as thermal conductivity and viscosity. The optimization of a debinding process begins with an understanding of the kinetics of the polymer decomposition processes in the presence of the ceramic particles.

Thermal decomposition reactions are generally rate-modeled as Equation 4.1,

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (4.1)$$

where α is the fraction of substance converted, t is time, T is absolute temperature of the substance decomposing, $k(T)$ is an Arrhenius expression and $f(\alpha)$ is the reaction model. In

a first-order reaction, $f(\alpha) = 1 - \alpha$.^{7, 8} The temperature-dependent Arrhenius expression is given by Equation 4.2,

$$k(T) = Ae^{\frac{-E_a}{RT}} \quad (4.2)$$

where E_a is the activation energy, R is the ideal gas constant and A is the pre-exponential factor or rate constant. The two kinetic parameters in Equation 2 can be estimated by several methods; of interest here is the Flynn-Wall⁹ (F-W) non-isothermal method of thermogravimetric analysis (TGA). The activation energy and rate constant can be derived from TGA data by Equations 4.3 and 4.4,

$$E_a = \left(\frac{-R}{b}\right) \left(\frac{d(\log \beta)}{d\left(\frac{1}{T}\right)}\right) \quad (4.3)$$

$$A = \left(\frac{-\beta'R}{E_a}\right) \ln(1 - \alpha)10^a \quad (4.4)$$

where a is a constant ranging from about 5.4 to 29.6, b is a constant ranging from about 0.45 to 0.54, $\beta = dT/dt$, the heating rate of the TGA at a fixed conversion α that occurs at T , and β' is the value of β nearest the mean of the heating rates. E_a and A can be estimated from the slope and y-intercept, resp., of a semi-logarithmic plot of β versus the reciprocal of T . F-W data do not give any information about the reaction model, i.e., first-order, second-order, etc.

A second method for calculating the activation energy from constant heating rate TGA data is the derivative model given by Speyer.¹⁰ In this model, the second derivative of $f(\alpha)$ in Eq. 4.1 is used to derive Equation 4.5 for an n^{th} -order reaction. The first and second derivatives and α are calculated from TGA data. The slope of Eq. 4.5 gives the reaction order n , and E_a is proportional to the y-intercept. Only one heating rate is needed.

$$T^2 \frac{d^2\alpha/dt^2}{d\alpha/dt} = -n \left[\frac{T^2 \left(\frac{d\alpha}{dt}\right)}{1 - \alpha} \right] + \frac{E_a\beta}{R} \quad (4.5)$$

A third method for calculating the activation energy from constant heating rate TGA data is the derivative model devised by Kissinger.¹¹ The characteristic temperature T_{max} corresponds to the point where the conversion rate $d\alpha/dt$ reaches a maximum and

$d^2\alpha/dt^2 = 0$. The derivative of the first-order version of Eq. 4.1 is set to zero and rearranged into Equation 4.6.

$$\ln\left(\frac{\beta}{T_{max}^2}\right) = \left(\frac{-1}{RT_{max}}\right)E_a - \ln\left(\frac{E_a}{RA}\right) \quad (4.6)$$

The slope for a series of heating rates yields E_a and the y-intercept can be solved for A .

Gersten et al.¹², using the F-W method, measured an activation energy E_a of 250 kJ/mol for pure PP in a first-order, single-stage decomposition in argon. A 3:1 mixture of oil shale and PP resulted in $E_a = 242$ kJ/mol. The E_a for PP in papers cited by Gersten et al.¹² ranged from 130 to 324 kJ/mol. Peterson et al.¹³ observed a steadily increasing (with α) E_a for pure PP heated by TGA in N_2 , from 150 at $\alpha = 0.05$ to as much as 250 kJ/mol at $\alpha = 0.9$. In air, the E_a ranged from 85 to 270 kJ/mol. The mechanism of thermal degradation of PP was described as random scission followed by radical transfer resulting in pentane and other hydrocarbons. The degradation products formed simultaneously, manifested as a single step in the TGA curve or a single endotherm in a differential scanning calorimetry (DSC) curve. Shende and Lombardo¹⁴ noted the catalytic effect of solid particles on binder decomposition, which complicated the scale-up from the calculated kinetic parameters to the actual binder burn-out from a green compact, in a study of poly(vinyl butyral) binder in $BaTiO_3$ multilayer ceramic capacitors. Shende and Lombardo¹⁴ also modeled the build-up pressure within the pores during debinding, in an effort to predict the minimum amount of time for thermal binder removal. Saikrasun and Saengsuwan¹⁵ measured the kinetics of PP blended in a twin-screw extruder with various amounts of a liquid-crystal polymer, in N_2 and air. The E_a of PP in N_2 varied with α from about 60 to 140 kJ/mol. The reaction order, mechanism and A also varied with the fraction of PP in the mix, and the atmosphere.

Onbattuvelli et al. investigated the kinetics of dewaxing a paraffin-PP binder system in heptane solvent for monomodal and bimodal PIM AlN and SiC.^{16,17} The bimodal particle size distribution facilitated a higher solids loading in the feedstock than the conventional monomodal distribution, but also reduced the permeability of the compact and slowed the dewaxing rate slightly. The nanoparticles in the bimodal feedstock were observed to have a small catalytic effect on the pyrolysis of the PP.¹⁸ The activation energy of the paraffin

wax dissolution in liquid heptane was estimated to be around 50 kJ/mol by the master decomposition curve method.^{17,19}

The purpose of this paper is to evaluate the thermal debinding kinetics of green PIM SiC via TGA.

4.2 Experiment

Two α -SiC thermoplastic feedstocks were prepared and analyzed.^{18, 20} All percentages are mass%, except as specified. The first feedstock was monomodal, with $D_{50} = 0.7 \mu\text{m}$ and a solid fraction $\phi = 53 \text{ vol\%}$. The second was bimodal, with 90% of the monomodal powder and 10% of a finer powder with $D_{50} = 20 \text{ nm}$ and a solid fraction $\phi = 54 \text{ vol\%}$. The binder in both cases was 50% paraffin, 35% polypropylene, 10% low-density polyethylene-g-maleic anhydride, LDPE-g-MA, and 5% stearic acid. The polypropylene has a molecular weight of 42,600, and a melting point of 142°C. The LDPE-g-MA served as a bridging agent to help bond the ceramic particles to the polypropylene. The stearic acid acted as a lubricant. Each ceramic powder in the feedstock had 5% 1.1- μm AlN + 5% 40-nm Y_2O_3 as sintering additives.

The feedstocks were mixed and pelletized in a 27-mm twin-screw counter-rotating extruder described elsewhere.²⁰ The critical and optimum solids loading values were determined by torque rheometry in previous papers.^{18,20}

The solid : binder ratio and dewaxing kinetics were determined by thermogravimetric analyzer (Model 2950, TA Instruments Inc., New Castle, DE), and ASTM E1641-07.²¹ A flowing N_2 atmosphere of 60 ml/min and an aluminum pan were used in all TGA scans. All phase fractions are mass fractions, i.e., mass%, unless otherwise specified. Four or five TGA heating rates, $\beta = 5, 10, 15, 20$ and 30 K/min , were used to determine the temperature T where $\alpha = 4, 8, 12, 16$ and 20% of the wax or PP had pyrolyzed.

4.3 Results and Discussion

4.3.1 Paraffin Wax Pyrolysis

The wax pyrolyzed completely over the range of approximately 200 to 400°C, depending on β , for both feedstocks. Values of T at the selected values of α and β were taken from Figure 4.1 to construct Figure 4.2 for the monomodal feedstock, and the same data from Figure 4.3 to construct Figure 4.4 for the bimodal feedstock. The mean solid and binder content in the two green feedstocks, E_r , A and standard deviations s of E_r and A are shown in Table 4.1, from the plots in Figures 4.1–4.5, where E_r is the *refined* E_a from an iterative solution for b and a in Equations 4.3 and 4.4. The monomodal E_r was equivalent to Onbattuvelli's et al.¹⁷ results for the solvent dewaxing only at 4% conversion. At higher conversions, the E_r increased but with a decreasing slope, as indicated in Figure 4.5 and by the large s in Table 4.1. The bimodal E_r was virtually independent of conversion level, all within 0.6 kJ/mol of the mean, in Figure 4.5. The small difference in solids loading between the two feedstocks was taken into account in the amount-converted calculations.

The second plateaus in the curves in Figures 4.1 and 4.3 represent the transitions between the decomposition of paraffin and polypropylene. In the bimodal feedstock, the distinction between the paraffin decomposition range and the polypropylene decomposition range diminished as the heating rate increased. The 20 K/min curve in Figure 4.3, which has no plateau, was repeatable and had no nonlinear effect on the kinetics constants for the wax. The bimodal disassociation of E_a and A from α in Figure 4.5 may be an effect of the catalytic effect of the nanoparticles of SiC and Y₂O₃, although the mechanism is not clear.

The difference in E_r between thermal and solvent debinding is attributed to the different mechanisms of binder removal, sample size, temperatures and kinetics calculations. Thermal dewaxing was shown to be more stressful than solvent dewaxing in Chapters 7 and 8,²² to the point of fracturing the green compact even at heating rates of 1–2 K/min for components of size less than 50 gm.

The uncertainty in E_r was calculated as proportional to the uncertainty of the slopes of the best-fit lines in Figures 4.2 and 4.4. The mean monomodal uncertainty in E_r was 12.4

kJ/mol, and the bimodal 6.6 kJ/mol. The uncertainties decreased as α increased for monomodal, and were virtually independent of α for bimodal.

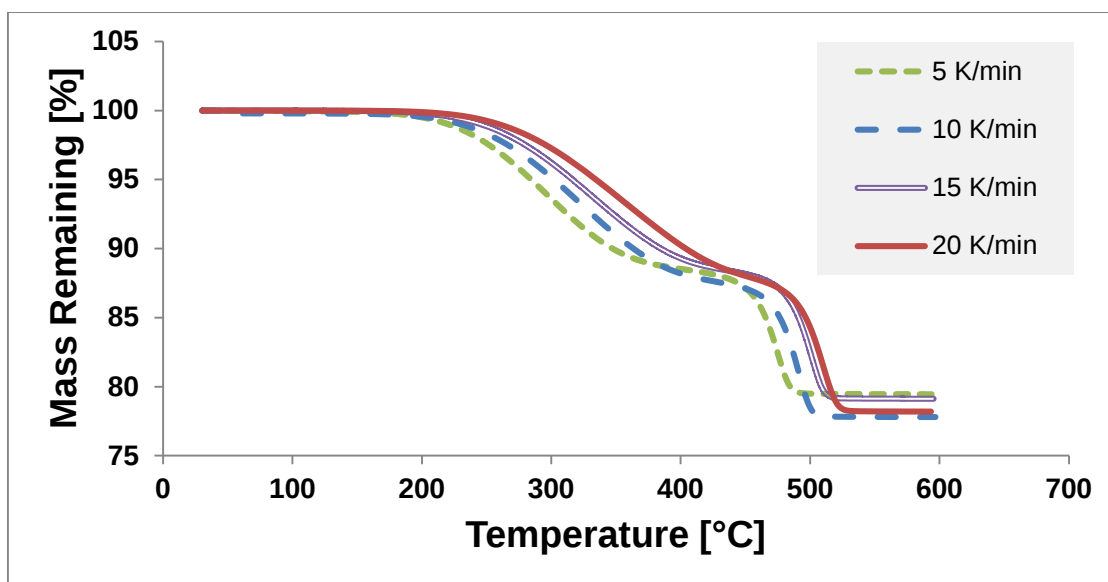


Figure 4.1: TGA plot of monomodal feedstock at various heating rates. The mean solids content is 78.6%.

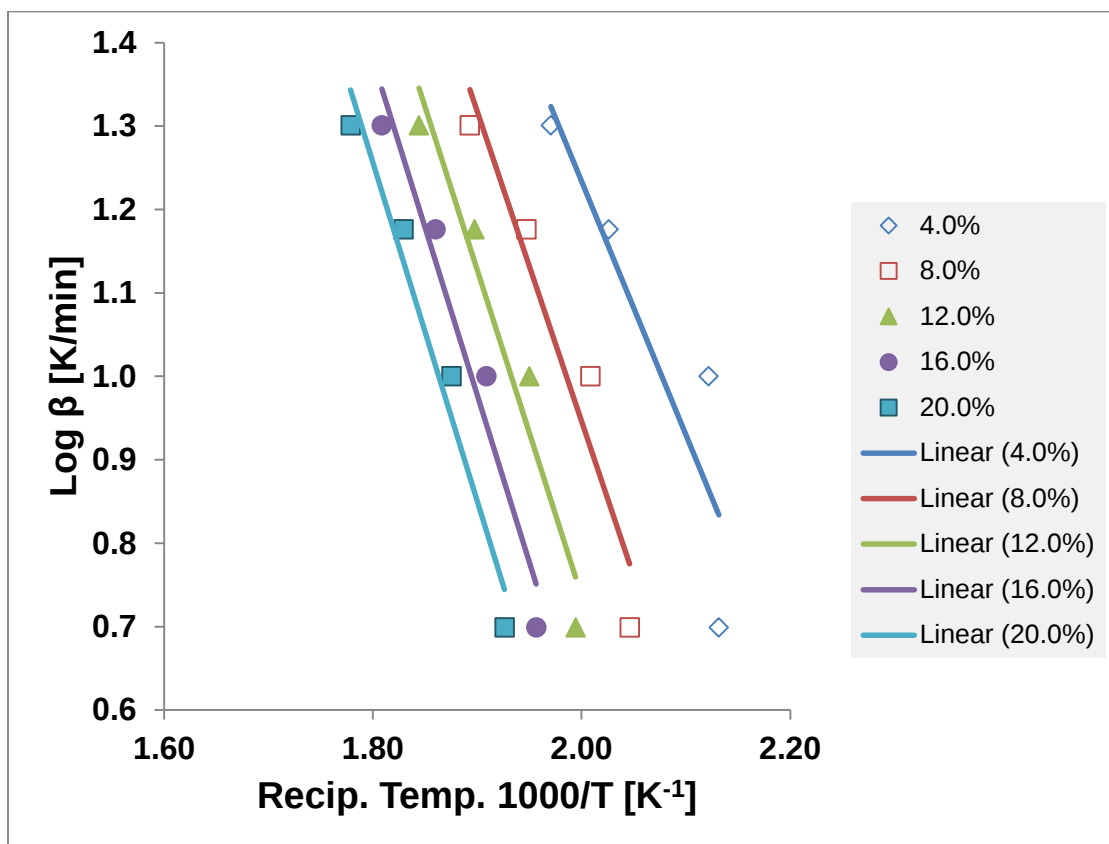


Figure 4.2: Flynn-Wall plot of paraffin decomposition kinetics in monomodal feedstock.

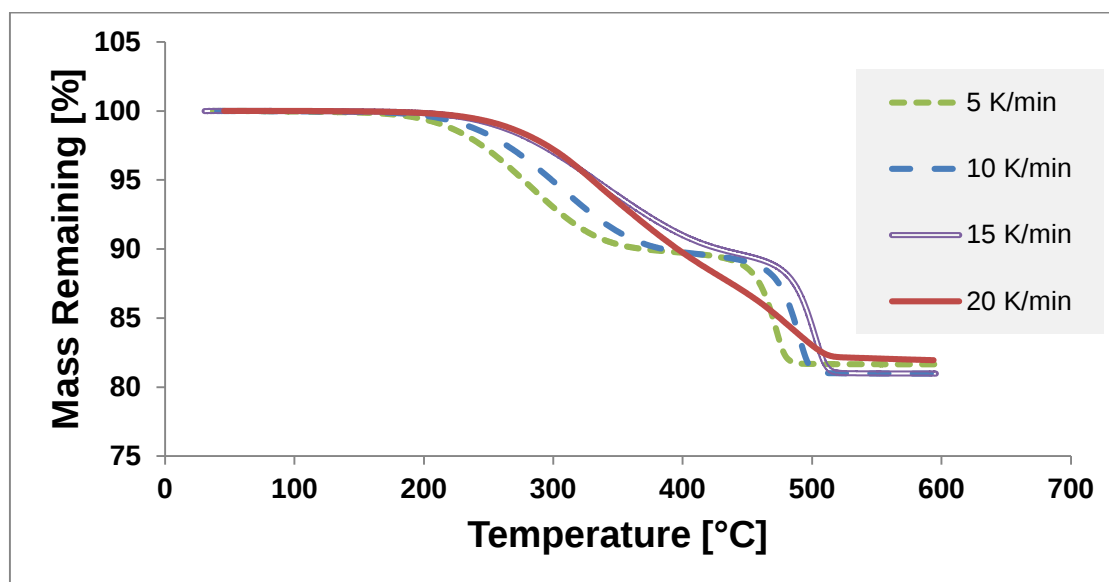


Figure 4.3: TGA plot of bimodal feedstock at various heating rates. The mean solids content is 81.4%.

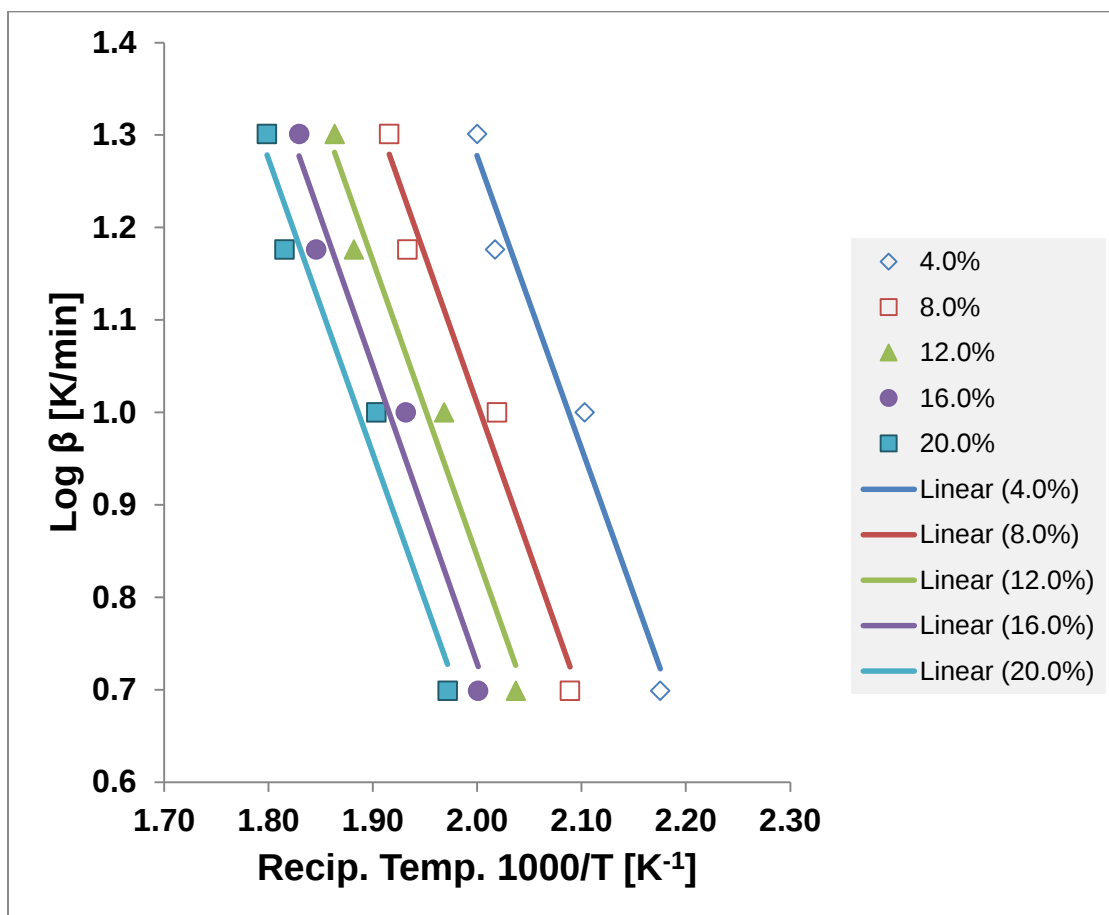


Figure 4.4: Flynn-Wall plot of paraffin decomposition kinetics in bimodal feedstock.

Table 4.1: Thermal debinding kinetics of PIM SiC.

Feedstock	Component	X_{solid}	X_{binder}	E_r	s	A	s
		mass%		kJ/mole		s^{-1}	
Monomodal	Paraffin wax	78.6	21.4	63.5	7.59	5.76×10^3	4.83×10^3
	PP (F-W)	88.0	12.0	103	11.0	3.25×10^6	5.74×10^6
	PP (Kissinger)			123	-	2.63×10^6	-
Bimodal	Paraffin wax	81.4	18.6	53.0	0.351	2.08×10^2	73.7
	PP (F-W)	90.1	9.9	109	24.0	1.09×10^6	1.17×10^6
	PP (Kissinger)			142	-	3.58×10^7	-
Polypropylene	PP (F-W)	0	100	129	22.1	1.10×10^8	1.84×10^8
	PP (Kissinger)			143	-	5.98×10^7	-

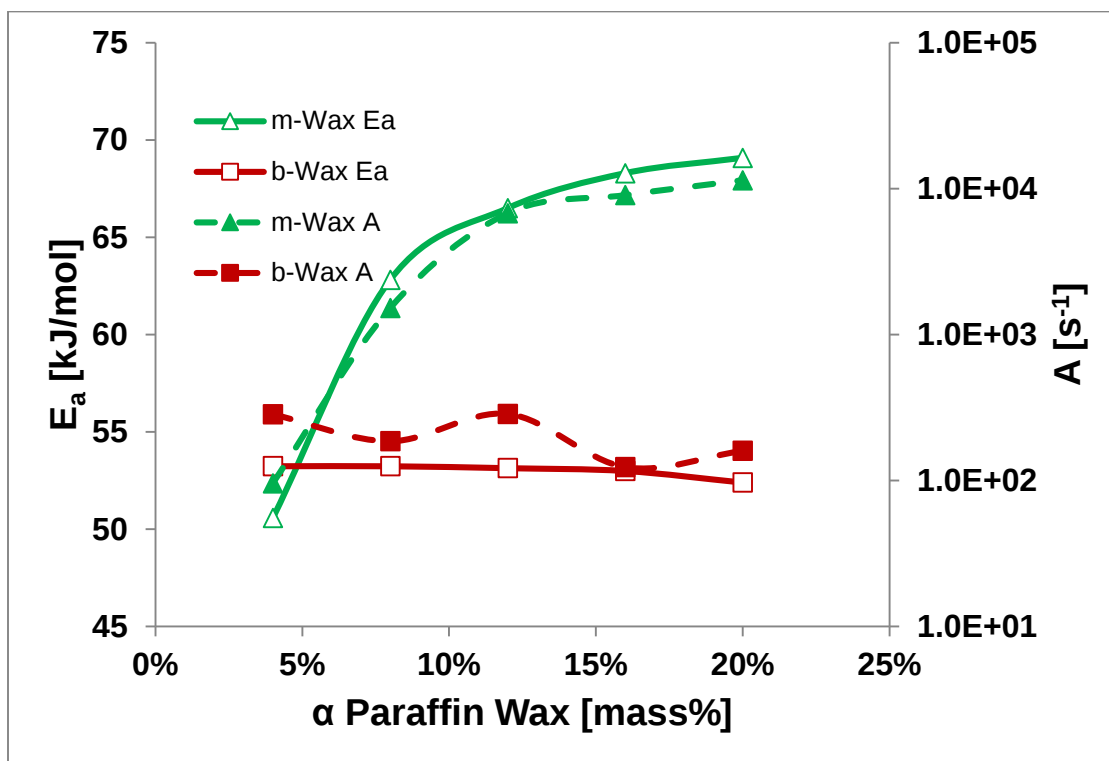


Figure 4.5: Activation energy and rate constant as a function of the amount of paraffin wax pyrolyzed.

4.3.2 Polypropylene Pyrolysis

To determine the kinetics of the PP decomposition, the feedstocks were first solvent-dewaxed in agitated heptane at 60°C for 4 hr. The residual heptane was evaporated overnight in a drying oven at 50°C. A strong sensitivity to sample size and shape required the dewaxed feedstocks to be ground to a powder. The sample size in each TGA test was 10.5 ± 0.5 mg. The same four heating rates were used, with the addition of 30 K/min.

The PP pyrolyzed completely over the range of approximately 260 to 530°C, depending on β , for both feedstocks. The mean solid and PP content in the two dewaxed feedstocks, E_r , A and standard deviations s of E_r and A are shown in Table 4.1, from the plots in Figures 4.6–4.10. The repeatable 5 K/min curve skewed the linearity of Figure 4.6, and was disregarded in the kinetics calculations. The 5 K/min curve yielded linear results with the other curves in Figure 4.8, although the 4% conversion line in Figure 4.9 had widely

scattered data, especially the 5 K/min point. The E_r and A values in Table 4.1 were calculated without the 4% conversion curve for the PP in the bimodal feedstock.

The uncertainty in E_r was calculated as proportional to the uncertainty of the slopes of the best-fit lines in Figures 4.7 and 4.9. The mean monomodal uncertainty in E_r was 16.7 kJ/mol, and the bimodal 10.9 kJ/mol. The uncertainties decreased as α increased. The E_r increased with α but with a decreasing slope for the bimodal feedstock in Figure 4.10. The monomodal E_r reached an apparent minimum at $\alpha = 12\%$, a phenomenon not reported in similar studies.^{13,15} The repeatability of the bimodal curve in Figure 4.5 and the monomodal curve in Figure 4.10 has not been confirmed.

The 5 K/min curve in Figure 4.6 suggested a multi-step decomposition, which is faintly visible in the other four curves of the higher heating rates in Figure 4.6. Two slope changes are apparent in the $\beta = 10\text{--}30$ K/min curves at approximately 250 and 450°C, which did not occur in Figure 4.8. The multi-step decomposition of PP was not reported in similar studies.^{13,15}

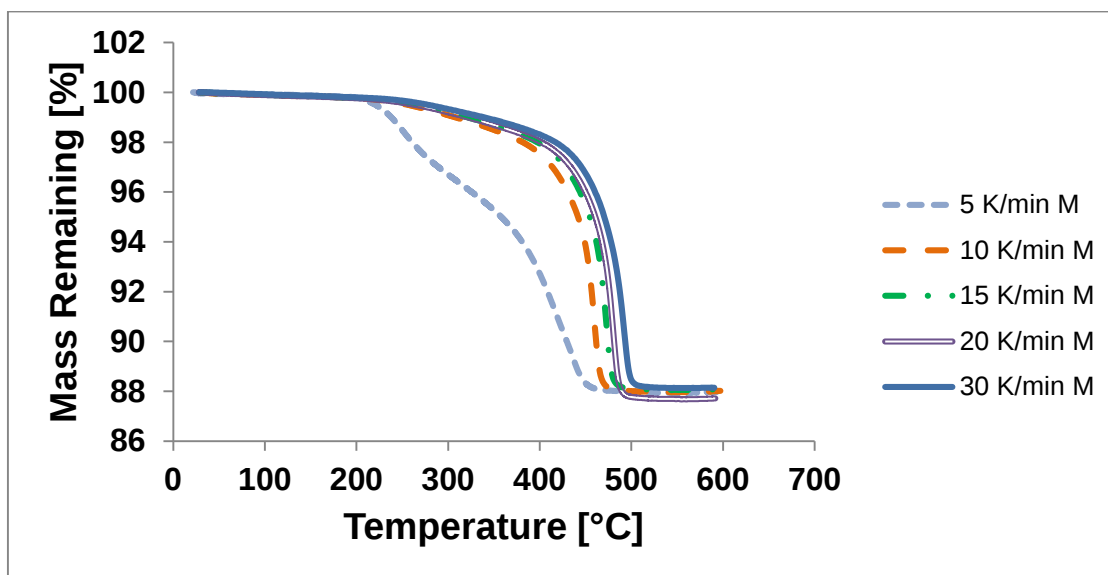


Figure 4.6: TGA plot of dewaxed monomodal feedstock at various heating rates.

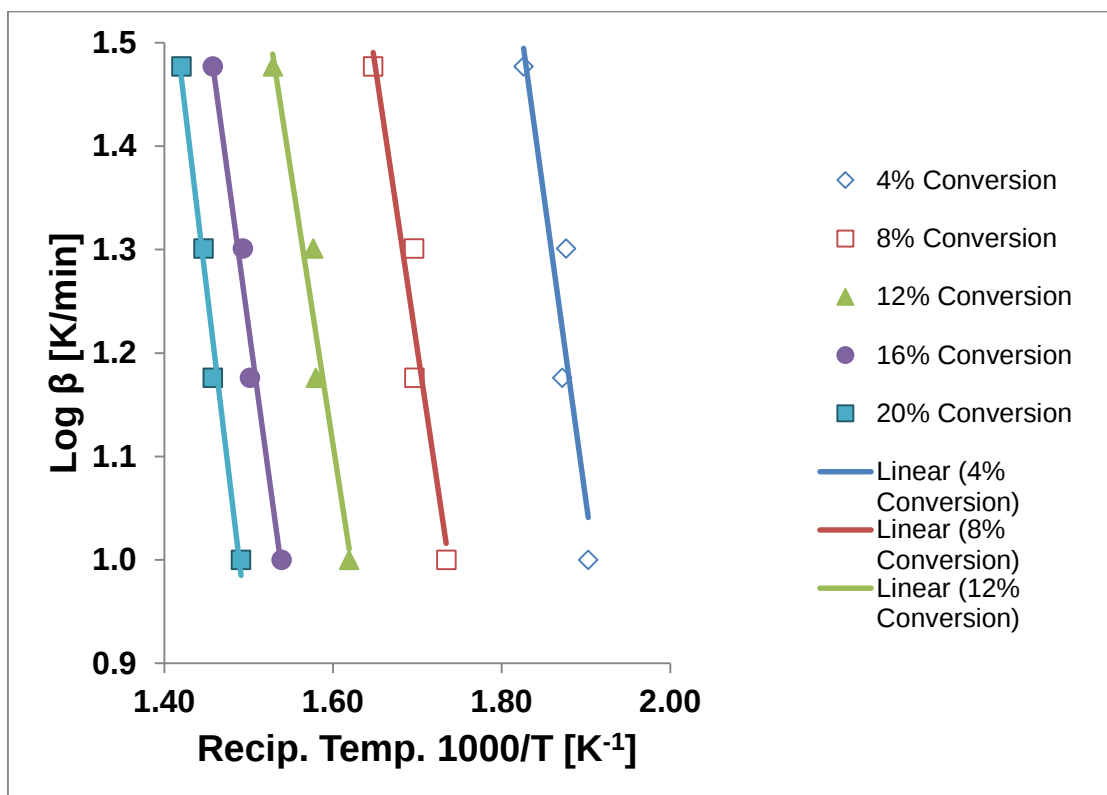


Figure 4.7: Flynn-Wall plot of PP decomposition kinetics in dewaxed monomodal feedstock, without the 5 K/min data in Figure 4.6.

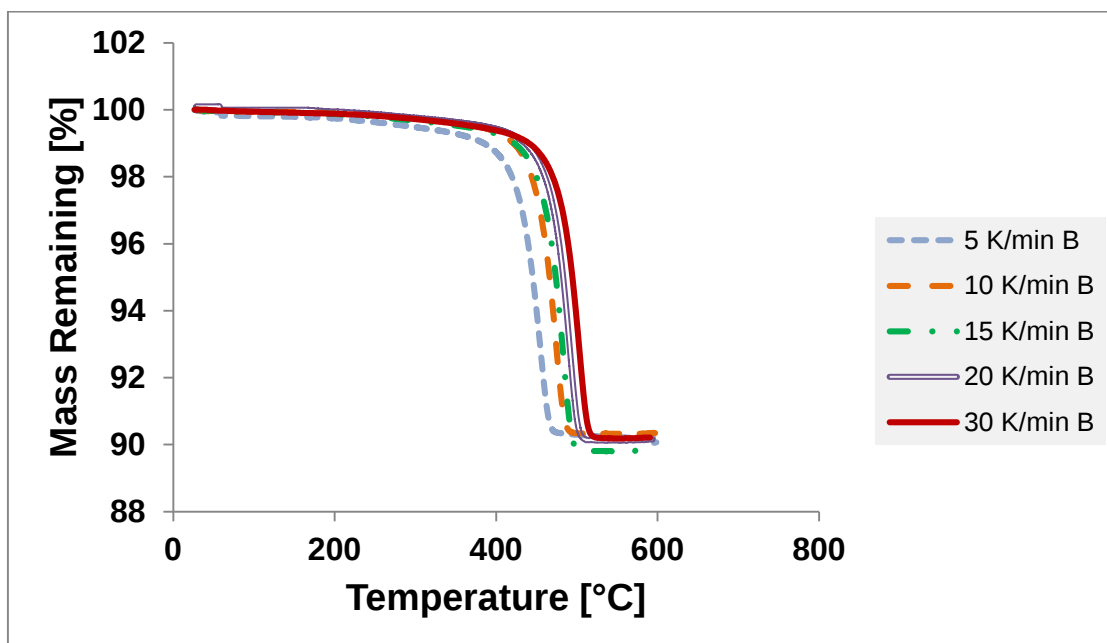


Figure 4.8: TGA plot of dewaxed bimodal feedstock at various heating rates.

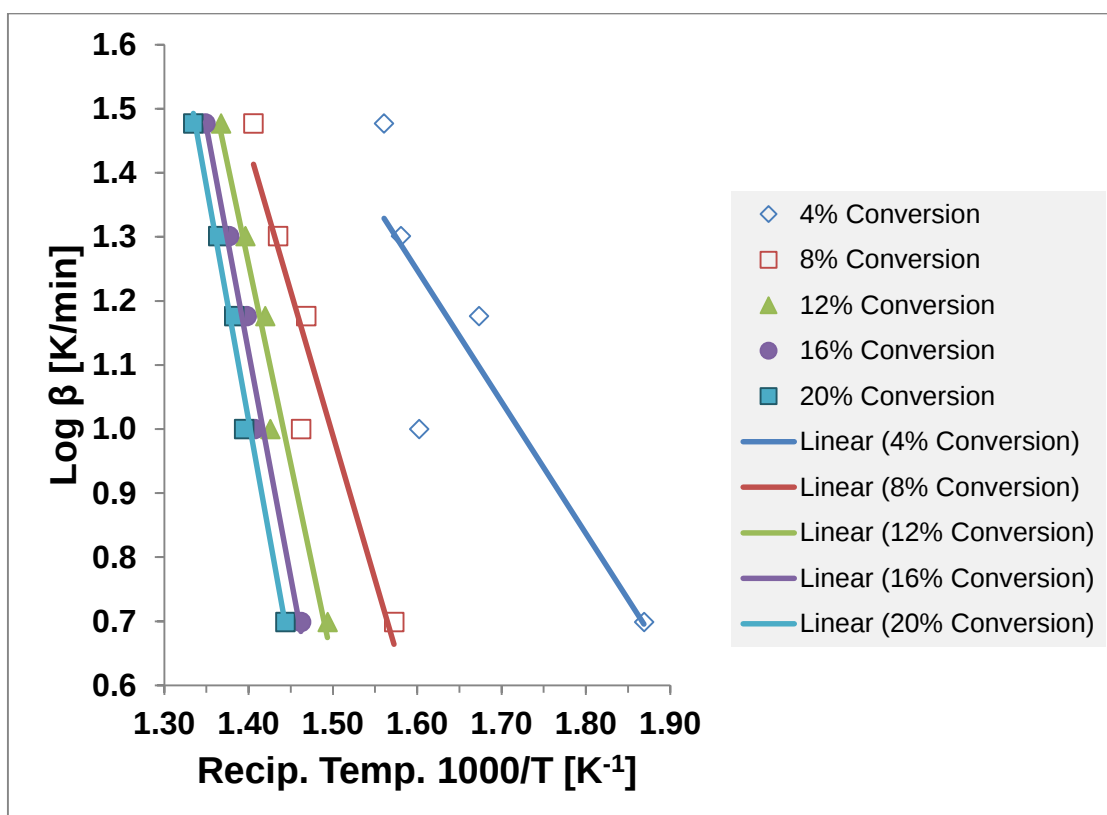


Figure 4.9: Flynn-Wall plot of PP decomposition kinetics in dewaxed bimodal feedstock.

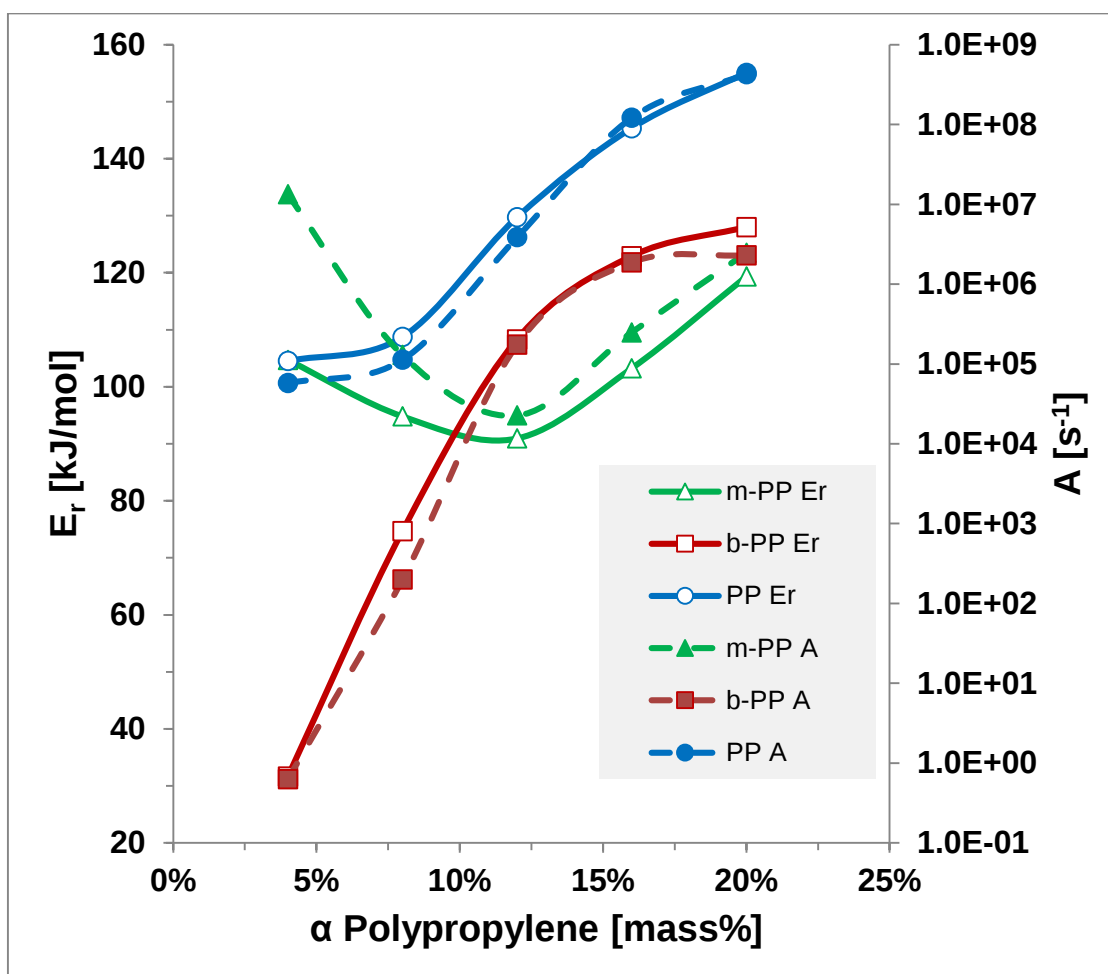


Figure 4.10: Activation energy and rate constant as a function of the amount of polypropylene pyrolyzed.

4.3.3 Pure Polypropylene, LDPE-g-MA and Stearic Acid

To assess the effects of the test method and instrumentation, pure PP and the other two binder additives were evaluated by TGA. The stearic acid in Figure 4.11, heated at 10.0 K/min in N₂, began to decompose at about 160°C and was virtually all gone by 260°C, in the early stages of the wax pyrolysis. The LDPE-g-MA in Figure 4.11, also heated at 10.0 K/min in N₂, decomposed in the late stages of the PP pyrolysis, about 450 to 500°C. The effects of the stearic acid on the wax pyrolysis and the LDPE-g-MA on the PP pyrolysis are not delineated by these data, but the wax and PP kinetics can be expected to have

been affected in some way by the two additives. That is, the additives might explain the deviations between these results and those reported in other studies.

The pure PP decomposed completely over the range of approximately 350 to 530°C, depending on β , in Figure 4.11. The E_r , A and standard deviations s of E_r and A are shown in Table 4.1, from the plots in Figures 4.11 and 4.12. The F-W plots in Figure 4.12 were very linear at all five conversion levels and all five heating rates. The E_r of pure PP was about 20% higher than for either of the feedstocks, and comparable to what was reported by Saikrasun and Saengsuwan¹⁵. These results were also comparable to the low end of what was reported by Peterson et al.¹³, and about half as much as reported by Gersten et al.¹² The mean uncertainty in E_r was 3.8 kJ/mol in Figure 4.12.

The apparent two-step decomposition of PP is also faintly visible in Figure 4.11, especially in the $\beta = 30$ K/min curve, with slope changes at approximately 350 and 450°C. The continuous decomposition of PP in the bimodal feedstock, as opposed to the apparent multi-step decomposition in pure PP and monomodal feedstock, might be a result of the catalytic effect of nanoparticles reported by Onbattuvelli et al.¹⁸

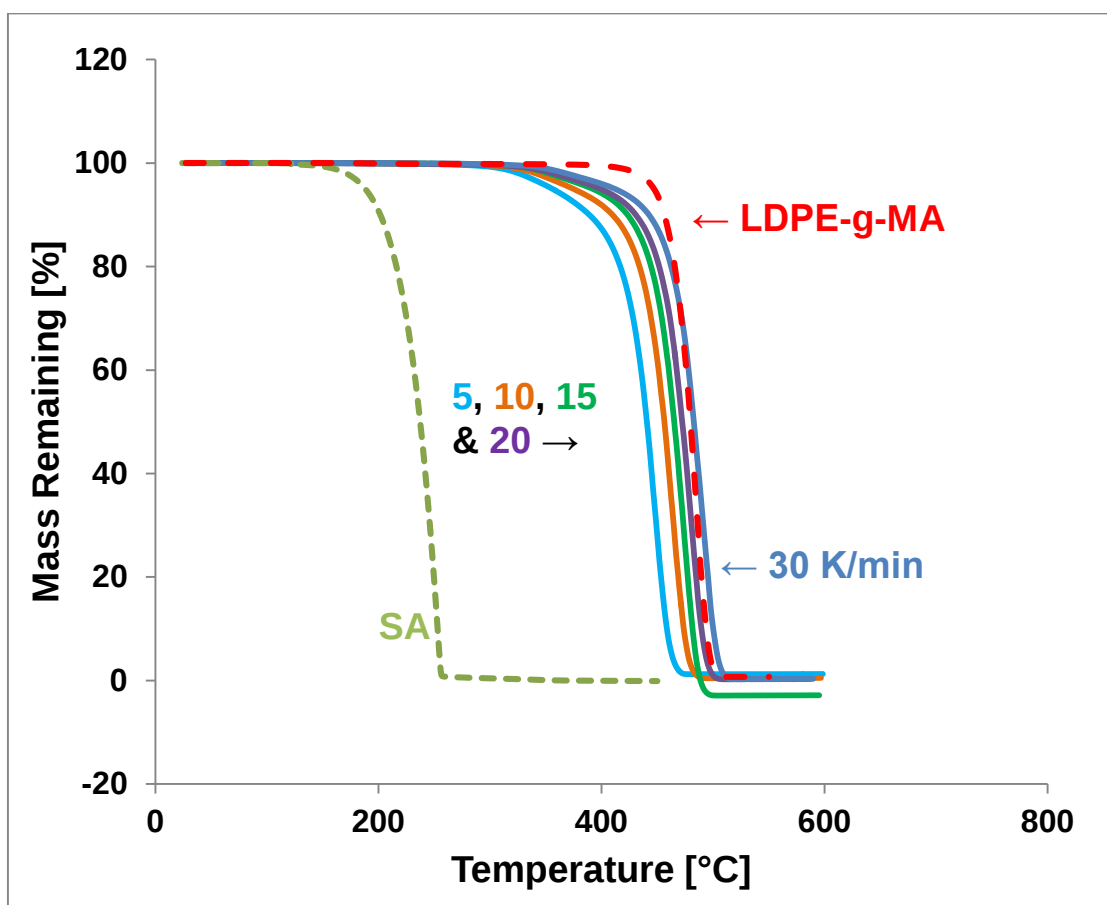


Figure 4.11: TGA plot of pure PP at various heating rates, and stearic acid (“SA”) and LDPE-g-MA at $\beta = 10.0$ K/min in N₂.

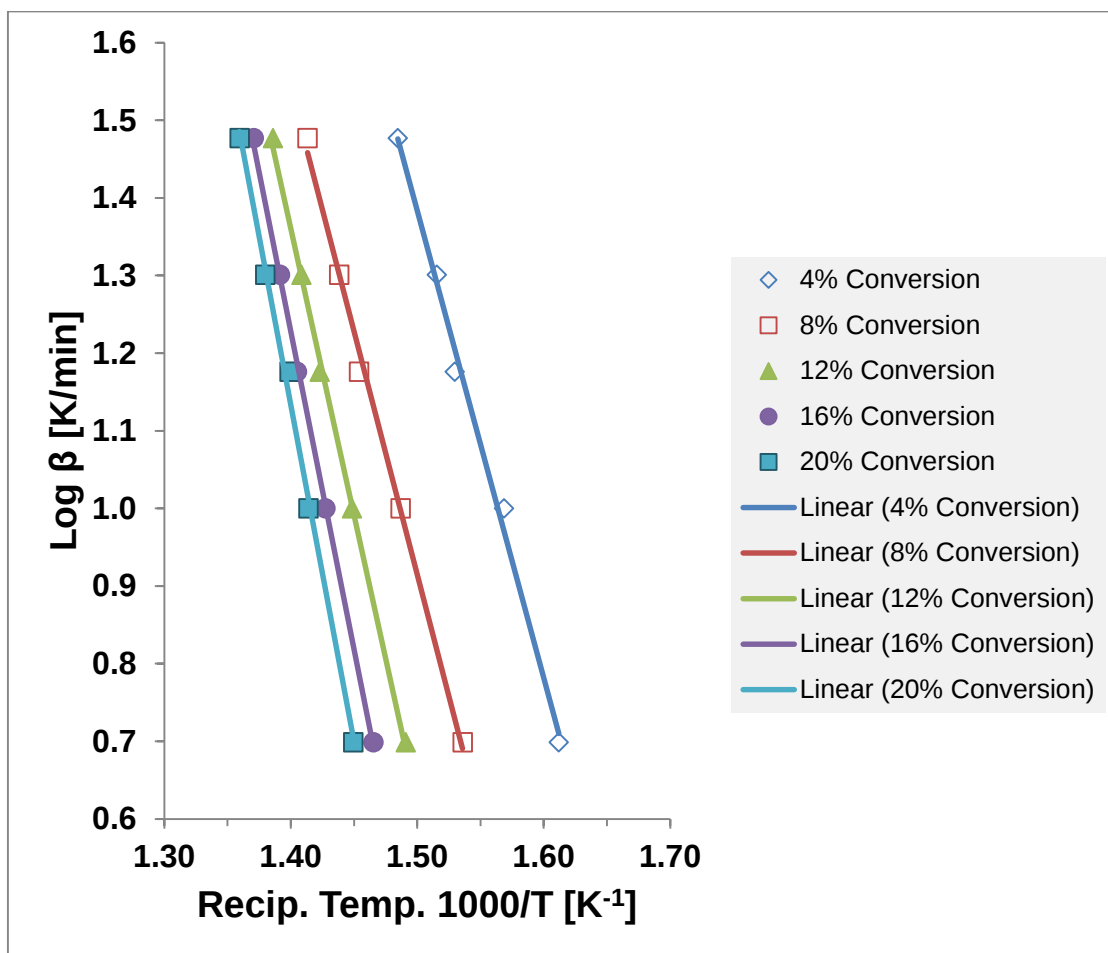


Figure 4.12: Flynn-Wall plot of pure PP decomposition kinetics.

The three $\beta = 15$ K/min curves from Figures 4.6, 4.8 and 4.11 were evaluated for the Speyer¹⁰ model in Figure 4.13. The first and second derivatives of α were smoothed over a period of ~ 0.8 min. The bimodal curve was remarkably linear over the narrow temperature range of about 470 to 520°C. The pure PP curve and especially the monomodal curve were much less linear. The slopes of all three curves were about two orders of magnitude less than the expected unity of a first-order reaction, suggesting, perhaps, a zero-order reaction. The E_a was 228 kJ/mol for monomodal SiC, 171 for bimodal, and 160 for pure PP. These figures were considered unreliable due to the lack of long-range linearity of the data.

The curves from Figures 4.6, 4.8 and 4.11 were evaluated for the Kissinger¹¹ model in Table 4.1 and Figure 4.14. The first derivative of α was again smoothed over a period of ~ 0.8 min. All three plots in Figure 4.14 fit the model very well with a correlation coefficient $R^2 > 0.99$. The E_a and A values were comparable to the F-W results at $\alpha \rightarrow 20\%$, and the lower end of Peterson's et al.¹³ results.

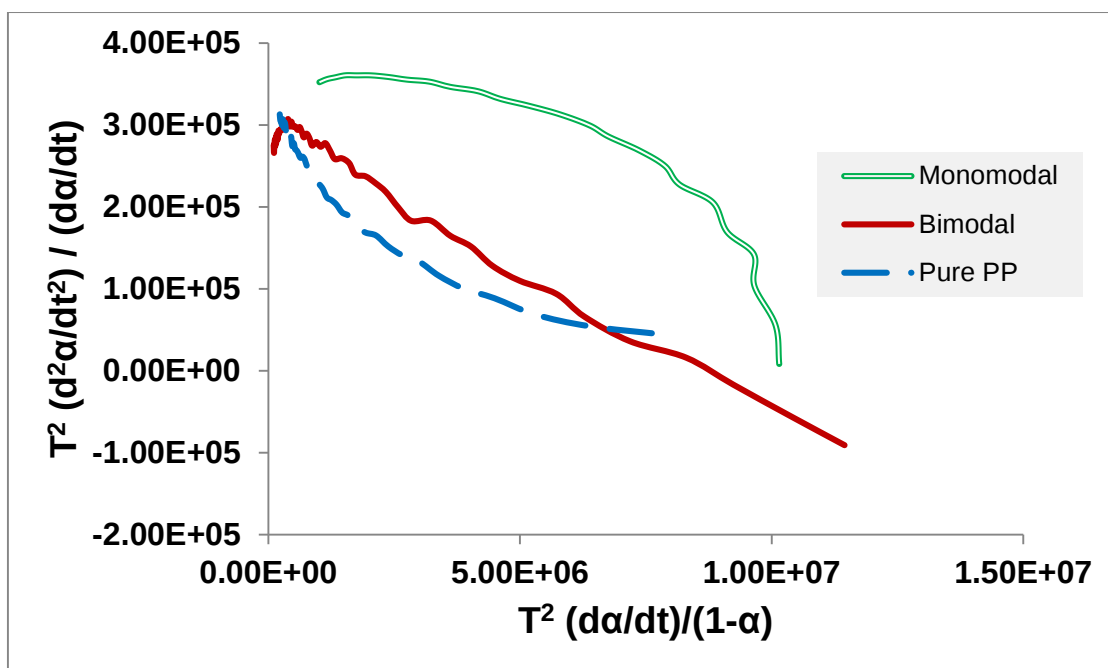


Figure 4.13: Speyer model of PP decomposition kinetics.

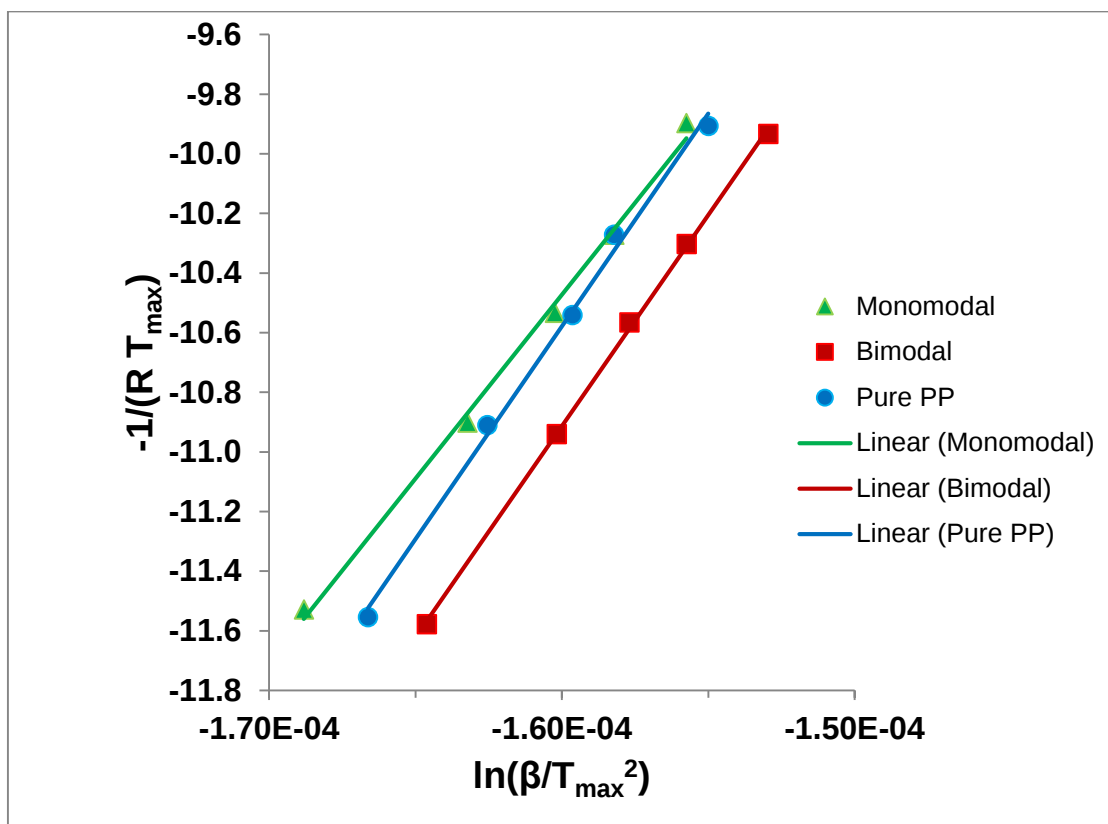


Figure 4.14: Kissinger model of PP decomposition kinetics.

The differences between pure PP and the PP in the feedstocks in this study can be attributed to the presence of SiC, AlN and Y₂O₃ particles, nanoparticles and LDPE-g-MA. The additional differences between this and similar studies by other authors can be attributed to the properties and amounts of the ceramic particles, feedstock preparation methods, sample size, metal of the sample pan acting as a potential catalyst, TGA characteristics, atmosphere, organic additives, calculation method, heating rates and conversion levels.

4.4 Conclusions

The activation energy by the F-W model of pyrolysis of paraffin wax from monomodal, 64 ± 12 kJ/mol, and bimodal, 53 ± 7 kJ/mol, SiC injection molding feedstock was similar to that of paraffin removed by dissolution in a liquid solvent.

The activation energy by the F-W method of pyrolysis of polypropylene from monomodal, 103 ± 17 kJ/mol, and bimodal, 109 ± 11 kJ/mol, SiC dewaxed feedstock was comparable to the lower end of ranges reported in other studies. The dependence of the activation energy on wax or polypropylene conversion was examined, but the mathematical relationship was inconsistent. The activation energy by the Kissinger model was similar to the F-W model only near 20% conversion, but was very consistent. The activation energy by the Speyer model was too scattered to be reliable in this study.

The differences between the two feedstocks, although small, were attributed to the additional nanoparticles in the bimodal feedstock. The differences between the dewaxed feedstocks and pure polypropylene were attributed to the particle properties and organic additives in the feedstocks. The differences between these results and those reported by other authors were numerous and included, in addition to the differences within this study, test methods and equipment, sample sizes, heating rates and conversion levels.

Future work in this study might include the evaluation of kinetics parameters at conversion levels higher than 20%, evaluations of the stearic acid and LDPE-g-MA with a possible rule-of-mixtures model for multi-component PIM binder, higher and lower heating rates, and further study of the outlier data such as the 5 K/min curve in Figure 4.6.

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CHAPTER 5

5 The Effects of Sintering Additives on the Properties of Silicon Carbide, Part I: Pressureless Sintering

Abstract

Silicon carbide is the most important and versatile non-oxide ceramic. SiC is useful for its strength, even at high temperature, hardness, corrosion and abrasion resistance, reflectance and many other properties. SiC is difficult to fabricate, but the obstacles can be mitigated with sintering additives. The additives enhance densification, lower the sintering temperature or time, enable fabrication techniques, or improve the properties of SiC. Misused additives can have the opposite effect, especially a reduction in properties. This paper reviews the many additives used with pressureless-sintered SiC, and assesses their efficacy in several applications and processes. The second paper reviews the effects of additives on SiC sintered under pressure.

Sir Donald Munger: "Tell me, Commander, how far does your expertise extend into the field of diamonds?"

James Bond: "Well, hardest substance found in nature. They cut glass, suggest marriages, I suppose it replaced the dog as the girl's best friend. That's about it."

M: "Refreshing to hear that there is one subject you're not an expert on."

— *Diamonds Are Forever*, 1971 movie.

5.1 Introduction

Silicon carbide, SiC, is a versatile ceramic with many high-performance applications, including armor^{1,2,3,4,5}, abrasives⁶, mechanical seals⁷, pump bearings⁸, aerospace optics⁹, mineral processing¹⁰, electric furnace elements^{11,12}, thin films¹³, microelectronics^{14,15,16}, nuclear fuel cladding^{17,18,19}, textiles²⁰, metal-matrix composites²¹, solar inverters²², molten metal processing²³ and refractories²⁴. SiC is the most used non-oxide ceramic in the world.²⁵ Some typical properties are given in Table 5.1. Of particular note are the strength and hardness of SiC, even at elevated temperatures; oxidation resistance; abrasion resistance; low neutron absorption; reflectance; wide bandgap and thermal conductivity. The drawbacks to SiC include difficulty of fabrication and limited toughness.

The purpose of this paper is to compile, examine and summarize the many sintering additives that have been investigated since the 1970s to densify, without pressure assistance, sintered SiC. The selection and processing of additives to facilitate the densification of a ceramic is an important aspect of grain boundary engineering. In addition to densification, the properties emphasized here are bending strength, fracture toughness, hardness, thermal conductivity and corrosion resistance. In the tables in this chapter, the additive compositions expressed as percentages are in mass %, unless otherwise specified. The properties are at room temperature, unless otherwise specified. Densities are expressed as percent of ideal density.

Table 5.1: Typical properties of densified SiC. All values are at room temperature, except as noted.^{26,27} More than one test method may be applicable to some properties.

Property	Symbol	Condition	Method	Range	Units
Density	ρ		ASTM C20	3.10 - 3.21	gm/cm ³
Modulus of rupture	σ		ASTM F417	462 - 540	MPa
Elastic modulus	E		ASTM C848	375 - 462	GPa
Poisson's ratio	ν		ASTM C848	0.21 - 0.38	—
Vickers hardness	HVN	1-kg load	ASTM C1327	24 – 27	GPa
Fracture toughness	K_{Ic}	notched beam	ASTM C1421	3.5 – 6.9	MPa m ^{0.5}
Thermal conductivity	k		ASTM C408	80 - 150	W·m ⁻¹ ·K ⁻¹
Thermal expansion	α		ASTM C372	3.3 – 4.6	10 ⁻⁶ K ⁻¹
Heat capacity	C_p	100°C	ASTM E1269	665 - 820	J·kg ⁻¹ ·K ⁻¹
Refractive index	η		refractometry	2.65 – 2.7	—
Birefringence	$\Delta\eta$		refractometry	0.042 – 0.097	—
Bandgap	ΔE		UV-visible spectrophotometry	2.2 – 3.3	eV
Electrical resistivity	ρ		ASTM D1829	>10 ⁶	$\Omega\cdot\text{cm}$

5.2 Applications and Properties

The hardness, strength, elastic modulus and toughness of SiC, combined with low density, make it a top choice for personal and vehicular armor, especially for larger-caliber projectiles.¹ Armor is subject to extremely high strain rates at the point of projectile impact. For most ceramic armor materials, brittleness increases with strain rate ($\dot{\epsilon}$), and toughness varies inversely with hardness. The brittleness associated with $\dot{\epsilon}$ is problematic for the intergranular silicon in reaction-bonded SiC, making it undesirable as armor. The toughness-hardness inversion represents a trade-off between SiC and B₄C.² No one property dominates the ballistic performance of ceramic armor, and the performance is not strongly indicated by all the properties considered as a set.⁴ The orders-of-magnitude difference in rates and pressures of ballistic tests versus the mechanical test procedures in Table 5.1 makes a correlation between the two tenuous at best.⁵

The low density and high refractive indices are keys to the application of SiC in anastigmat telescope mirrors. Large components such as pocketed mirrors can be fabricated from smaller pieces joined in the green state, or brazed with silicon as the filler. Taiwan's National Space Program Office used SiC optics in its ROCSAT-2 program.⁹

5.2.1 Toughness

Fracture toughness, or simply toughness, is resistance to crack growth, and can be measured or estimated in several ways. Anstis, Chantikul et al.^{28,29} devised toughness measurement techniques using a Vickers hardness indenter under large loads that were widely used in the 1980s and 1990s. The Vickers indentation methods were critically examined, and discredited, by Kruzic and Ritchie³⁰ and Quinn and Bradt³¹ in the 2000s. The low toughness of SiC compared to metals, cemented carbides and toughened zirconia limits the use of SiC in certain mechanical applications.

Toughness of ceramics is best determined by bending methods similar to the strength test, where the specimen has a precisely machined notch or “pre-crack” in the region of maximum tensile stress, such as ASTM C1421.³² These fracture mechanics methods are applicable to flat or rising R-curves (toughness as a function of crack extension) and are amenable to high-temperature tests.

SiC can be toughened by several mechanisms, including crack deflection and bridging, micro-cracking along weak interfaces, thermal expansion mismatch between SiC and precipitates, $\beta \rightarrow \alpha$ transformation (*in situ* toughening), elongated grain shape and coarse grain size. The anisotropy of hexagonal α -SiC grain growth in the $\beta \rightarrow \alpha$ transformation results in elongated grains and a jagged intergranular fracture path. Annealing can also increase toughness, by driving the $\beta \rightarrow \alpha$ transformation. Intergranular fracture corresponds to higher toughness and transgranular to lower toughness, due to the greater path length of intergranular fractures.

S.K. Lee et al.³³, MoberlyChan et al.^{34,35}, Rixecker et al.³⁶, Kim et al.³⁷, Zawrah and Shaw³⁸, Bothara et al.³⁹, S.H. Lee et al.⁴⁰, Hotta and Hojo⁴¹, Onbattuvelli et al.⁴² and Lomello et al.¹⁷ used indentation methods. She and Ueno^{43,44} used single-edge notched beam (SENB). Gubernat et al.⁴⁵ used both notched beam and indentation methods. Ray et al.⁴⁶ used the single-edge pre-cracked beam (SEPB) method. Keppeler et al.⁴⁷ used a high-temperature thermal shock method. The results of these papers by test method are summarized in Table 5.2, where SENB yielded the highest values and SEPB the lowest on

average. The indentation tests had the largest standard deviation. The thermal shock method was not tabulated due to the small amount of data.

Table 5.2: Summary of fracture toughness results of the papers cited in Tables 5.4–5.6 by method.

	Indentation	SENB	SEPB
Mean K_{Ic} [MPa m ^{0.5}]	4.55	6.23	4.02
Std. Dev. [MPa m ^{0.5}]	1.34	0.80	0.89

5.2.2 Strength

Pure tensile strength is difficult to measure in most ceramics.⁴⁸ Thus, the strength of ceramics is usually measured in 3-point or 4-point bending of a straight beam with beveled edges and a rectangular cross-section, as in ASTM C1161.⁴⁹ The 4-pt configuration subjects a larger volume of the beam to the maximum stress than does the 3-pt. The shear stress is zero between the two inner contact pins in 4-pt bending, but never zero in 3-pt. For these reasons, the 4-pt test is considered a better representation of the tensile strength than the 3-pt test. The bending strength is also known as modulus of rupture, MOR.

Maximum strength and hardness in SiC and most ceramics are associated with microstructural uniformity, high relative density, low porosity, retardation of the $\beta \rightarrow \alpha$ transformation and a fine grain size. The size and concentration of defects, such as cracks and voids, is critical to the strength of SiC. Strength at high temperatures comes from an absence of secondary phases at the grain boundaries, in addition to the other characteristics.

Tanaka et al.⁵⁰, She and Ueno^{43,44}, Gubernat et al.⁴⁵, and Hotta and Hojo⁴¹ used 3-pt bending. Keppeler et al.⁴⁷, Rixecker et al.³⁶, Kim et al.³⁷, Goldstein et al.⁵¹, and Ray et al.⁴⁶ used 4-pt bending. Biaxial flexure of a circular or rectangular plate specimen is another method of measurement of ceramic strength, e.g., ASTM C1499⁵², but was not used in any of the research cited in this paper.

Tanaka et al.⁵⁰ measured the strength of the 0.29% Al-doped SiC at room temperature and at 1600°C. The high-temperature strength was about 90% of the room-temperature strength, in Table 5.3. Keppeler et al.⁴⁷ observed an increase in strength up to 1200°C in the pure- α globular microstructure, while the strength of the tougher $\beta+\alpha$ platelet microstructure dropped sharply above 1000°C in Table 5.3. Shinoda et al.⁵³ did not measure strength but observed high ductility in HIP SiC with B and C additives at 1600–1800°C. Kim et al.³⁷ compared the strength of two compositions at various temperature up to 1600°C in Table 5.3. The SiC with a rare earth oxide additive had 93% of its room-temperature strength at 1600°C in N₂. The SiC with Al₂O₃ and Y₂O₃ additives lost 40% of its strength at 1600°C. The N₂ atmosphere was used to suppress oxidative effects on strength as the temperature approached 1600°C, in comparison to Keppeler's et al.⁴⁷ mechanical tests done in air. High strength in SiC at ~1600°C suggests fitness for creep-resistant applications such as furnace fixtures.

Table 5.3: Summary of high-temperature strength in the papers cited in Tables 5.4–5.6.

Authors	Microstructure	Additives	Strength [MPa]	
			@Room Temp.	@T [°C]
Tanaka et al. ⁵⁰		0.29% Al + 0.1% B + 2.0% C	631	582 @ 1600
		0.29% Al + 0.1% B + 2.0% C	635	636@ 1600
Keppeler et al. ⁴⁷	Globular (α)	10 vol% (3 mole AlN : 2 Y ₂ O ₃)	564	725 @ 1200 324 @ 1400
	Platelets ($\beta + \alpha$)	10 vol% (3 mole AlN : 2 Y ₂ O ₃)	524	377@ 1400
Kim et al. ³⁷		2.7% AlN + 16.9% Er ₂ O ₃	588	551@ 1600
		13.5% Y ₃ Al ₅ O ₁₂	550	506 @ 1350 330@ 1600

While creep resistance indicates dislocation immobility and slow diffusion, both typical in carbide ceramics, Shin et al.⁵⁴ demonstrated ductile, plastic behavior in β -SiC at room temperature in sub-micron pillars. The 0.65- μ m diameter pillars, fabricated by CVD,

slipped on the $\langle 110 \rangle \{111\}$ slip system family of directions and planes under a critical resolved shear stress of 4.9–7.3 GPa in compression.

5.2.3 Hardness

SiC and most other ceramics are much too hard for the Brinell and most of the Rockwell scales. Rockwell 45N superficial hardness is applicable to some ceramics but not well suited for small specimens or study under a microscope. The two microindentation methods, Vickers (ASTM C1327⁵⁵) and Knoop (ASTM C1326⁵⁶) come from the same instrument and yield similar results but have different indenter configurations. The Knoop indentation, with twofold symmetry, has shallower penetration than Vickers and is less apt to nucleate cracks at the corners.⁵⁷ The Vickers indentation is a square-base pyramid that, by design, extends the range of the Brinell scale to very hard materials.⁵⁸ The Knoop calculation is based on the projected area of the indentation, while the Vickers is based on the contact area. This area difference precludes a mathematical conversion of one scale to the other. Both scales allow a variable indenter force, but the force can significantly affect the apparent hardness, as explained in the following paragraphs.

Both the Vickers and Knoop scales are subject to the indentation size effect (ISE), where the apparent hardness varies inversely with the indenter load. At some load, typically 10–20 N, the ISE levels off and the hardness becomes more or less independent of the applied force on the indenter. Cracking around the indentation increases with load, and at some point, obscures the indentation until it cannot be measured reliably. The ideal load is a balance between a load low enough to minimize surface cracking, yet high enough to minimize the ISE and make the indentation large enough to measure with the hardness instrument's microscope. Swab⁵⁹, investigating the hardness of a commercial SiC and other ceramics for armor applications, got optimum and ISE-independent results from the Knoop method with a 19.6-N (2 kgf) load, 19.8 ± 0.3 GPa for Cercom SiC (CoorsTek Inc., Vista, CA). The apparent Knoop hardness of SiC declined by ~25% over the range of 0.98 to 9.8 N due to ISE. Vickers ISE was indeterminate in SiC due to fractures surrounding the indentations, even at 0.98 N.

Majić et al.⁶⁰ evaluated the ISE on Knoop hardness of SiC over an indenter force range of 4.9 to 98 N. The ISE model was considered for its effect on the Knoop hardness (HK) in Equation 5.1:

$$HK = \alpha \frac{F}{d^2} \quad (5.1)$$

Where α is a geometric constant, F is the indenter force and d is the length of the longer diagonal of the Knoop indentation. The modified proportional specimen resistance (PSR) model in Equation 5.2 was amenable to the full range of indenter loads.

$$F = a_0 + a_1 d + a_2 d^n \quad (5.2)$$

The constant a_0 depends on the surface finish and material properties, a_1 is the specimen proportional resistance, a_2 the load-independent “true” hardness, and n is nominally equal to 2. Majić et al.⁶⁰ reported $a_0 = 1.321 \pm 1.059$ N, $a_1 = 4.392 \pm 16.004$ N/mm, and $a_2 = 1356 \pm 50.0$ N/mm² for Equation 5.2, with $n = 2$. If a_0 and a_1 are assumed to be zero due to the large scatter in the reported values, the PSR model is simplified to Meyer’s⁶¹ law, where a_2 represents the resistance of the material to the initial penetration and n is a measure of the effect of the deformation on the hardness of the material.⁶² If the Meyer index $n = 2$, the hardness is independent of the indenter load and there is no ISE. Normal ISE occurs when $n < 2$, and reverse ISE when $n > 2$. Reverse ISE, where $n \approx 2.5$ and the apparent hardness increases with load, occurs in annealed metal, i.e., materials with a large capacity for cold work, unlike SiC. The Meyer index for SiC was 1.8192, indicating substantial ISE.

When the indentation is entirely on one SiC grain, the hardness depends on the polytype and the crystal plane orientation. Balog et al.⁶³ measured 2525 kgf/mm² (24.8 GPa) on the 3C (100) planes and 2954 kgf/mm² (29.0 GPa) on 6H (0001) on the Knoop scale with a 100-gm (0.98 N) load.

She and Ueno⁴⁴ (98 N), Goldstein et al.⁵¹, Zawrah and Shaw³⁸ (98 N), Balog et al.⁶³ (9.8 N), Bothara et al.^{39,64} (9.8 N), S.H. Lee et al.⁴⁰ (98 N), and Mao-lin et al.⁶⁵ (1.96 N), used Vickers, with the indenter load in parentheses where provided. Gubernat et al.⁴⁵ and Ray et al.⁴⁶ (9.8 N) measured both Knoop and Vickers hardnesses. The effect of ISE on these results, if any, is unknown.

Balog et al.⁶³ also measured nanoscale indentations in SiC with a Berkovich indenter and an atomic force microscope (AFM). The Berkovich indentation is a tetrahedron with equilateral triangle facets, much too small for measurement in visible light, and a load typically about 0.1–100 mN.⁶⁶ The Berkovich test was also susceptible to ISE, as detailed in Chapter 6 of this thesis.

5.2.4 Corrosion Resistance

SiC is noted for its durability in many corrosive environments, such as spray nozzles for hot sulfuric acid⁶⁷, automobile engine components⁶⁸ and as refractory in acidic slag⁶⁹, basic slag and a reducing atmosphere.⁷⁰ Andrews et al.⁷¹ compared the corrosion resistance of three SiC compositions in 1.0-M HCl, HNO₃ and NaOH at room temperature, under Carbide Additives in §5.6.1 and Oxide Additives in §5.6.2 below.

Ray et al.⁴⁶ soaked bending-strength specimens of three compositions in either 49% hydrofluoric acid for 200 hr or 50% NaOH solution for 500 hr, at 80°C. Composition A, densified with 1.65% Al only, lost more than half its strength after the acid exposure and about one-third after the base exposure. Composition B, densified with 1% carbon and 0.25% B₄C only, was unaffected in both cases. Composition C, densified with 2.5% AlN only, was heated at three rates—2.5, 5 and 20 K/min—during hot pressing. The fastest heating rate had the highest mass loss in both liquids and lost nearly all its strength in the acid. The grain boundary chemistry, as-sintered strength and degree of strength degradation in each liquid were dependent upon the heating rate. The strength degradation in each case was attributed to corrosive attack on the grain boundary phases. Ray's et al.⁴⁶ investigation into the processing and mechanical properties of these and 23 more compositions is further reviewed in Chapter 6.

Herrmann et al.⁷² measured the corrosion resistance of EKasic® (ESK Ceramics GmbH & Co. KG, Kempten, Germany), solid-state sintered SiC with Al additives, in 0.5-M sulfuric acid at room temperature. The SiC formed a SiO₂ passivation layer 5–100 nm thick, which had a strong influence on the electrochemical behavior. The grain boundaries were less prone to corrosive attack than the grains, due to grain boundary resistivity as the

limiting factor of the corrosion rate. The SiO_2 passivation layer is soluble in hydrofluoric acid, but SiC is nonetheless highly resistant to HF compared to other silicon-based ceramics.

In a second paper, Herrmann et al.⁷³ measured the corrosion resistance of EKasic® in 1.0-M sodium hydroxide at room temperature. The nonuniform corrosion rate was 10–60 nm/min at 2 V, independent of grain orientation or polytype. As with H_2SO_4 , the grains were more susceptible to corrosion than the grain boundaries.

5.2.5 Thermal Conductivity

The thermal conductivity of single-crystal SiC is comparable to the most conductive metals, ideally, due to the size similarity of Si and C atoms.⁷⁴ Thermal conductivity by phonons is very sensitive to lattice defects such as grain boundaries, pores, precipitates, vacancies and solutes.⁷⁵ Oxygen and aluminum dissolved in the SiC lattice reduce the thermal conductivity by generating silicon vacancies, which scatter phonons. Although polycrystalline SiC is used for heat exchangers, the thermal conductivity of the ceramic is usually less than half the ideal value.

Liu and Lin⁷⁶ investigated the effects of SiC polytypes hot pressed with Al_2O_3 and Y_2O_3 additives, sintering temperature and test temperature on thermal conductivity. The highest conductivity, just over $90 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, was measured at room temperature in a composition that began as 20% α + 80% β but transformed to 88% 6H hexagonal during sintering. The conductivity decreased with increasing 4H content or test temperature. The 3C cubic $\rightarrow$ 4H hexagonal transformation was promoted by Al_2O_3 dissolving into the 3C lattice. The polytypes are discussed below under Structures of SiC.

Kinoshita and Munekawa⁷⁷ observed a maximum of $235 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ in thermal conductivity of SiC hot pressed with 0.25–0.40% Al_2O_3 content. The spike was explained by the solubility limit of Al_2O_3 in SiC of 0.40%, which also corresponded to a maximum d-spacing of SiC. Phonon scattering caused by grain boundary segregation of Al and O atoms above 0.45% Al_2O_3 brought the conductivity back down to $120 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. A secondary phase was not detected on the SiC grain boundaries.

Sigl⁷⁸ studied the effects of grain boundary phases on the thermal conductivity of SiC sintered with AlN, Al₂O₃ and Y₂O₃, limited to $\sim 85 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ by the additives. The thermal conductivity was determined from the thermal diffusivity by the laser-flash method.⁷⁹ The precipitates lowered the conductivity in a way that corresponded to Maxwell's rule-of-mixtures model for spherical particles. The amorphous layer at the grain boundaries lowered the conductivity by another $\sim 20\%$. Rare earth oxide additives with low solubility in SiC, in lieu of Al₂O₃, were suggested as a means of increasing the thermal conductivity of SiC ceramics.

Zhou et al.⁸⁰ used Y₂O₃ and La₂O₃ additives to densify β -SiC in Chapter 6 of this thesis. The additives gettered dissolved oxygen from the SiC lattice, stabilized the highly isotropic β -phase, and formed discrete crystalline precipitates at the triple points (where three grains intersect) rather than a continuous grain-boundary phase. A subsequent annealing step increased the grain size slightly. The thermal conductivity of the as-sintered compositions was about $134\text{-}169 \text{ W m}^{-1} \text{ K}^{-1}$, and $152\text{-}206 \text{ W m}^{-1} \text{ K}^{-1}$ for the same compositions after annealing.

Onbattuvelli et al.⁴² compared the thermal conductivity by laser-flash of two initial particle size distributions of injection molded SiC under Nitride Additives in §5.6.3 below. The thermal conductivity was as high as $73 \text{ W m}^{-1} \text{ K}^{-1}$ in the bimodal distribution sintered 4 hr at 1950°C.

Kim et al.⁸¹ achieved a thermal conductivity of $234 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ in SiC hot pressed with 1 vol% Sc₂O₃ and Y₂O₃. The additives reduced the oxygen concentration in the SiC lattice by forming a (Sc,Y)₂Si₂O₇ phase. The two additive cations, by being much larger than the Si atoms, could not dissolve significantly in the SiC. The additives minimized grain boundary segregation, and promoted crystalline intergranular phases as opposed to amorphous layers, all contributing to the unusually high conductivity.

5.3 Structures of SiC

SiC has a close-packed polymorphic structure that is highly susceptible to stacking faults, which give rise to polytypes, or one-dimensional variants.⁸² Close-packed hexagonal

α -SiC occurs in the wurtzite or 2H form, with the normal CPH stacking sequence of ABABAB. Some of the other 45-plus polytypes are 4H (ABCB), 6H (ABCACB) and 8H (ABCABACB). The 15R form is rhombohedral, but still considered α -SiC. The 6H form is the most common and most stable. Face-centered cubic β -SiC, also known as the 3C, sphalerite or zinc blende form, has the normal FCC stacking sequence of ABCABC. The 2H, 3C, 4H, etc., polytype designations are all Ramsdell notations.

The 1:1 stoichiometry was long thought to be the only compound form of silicon and carbon.⁸² Cubic Si_5C_3 was identified circa 1995 from a reaction between SiC and SiO_2 in a vacuum at 1750°C.⁸³ Both polymorphs and all polytypes of SiC have the same density and approximately the same Gibbs free energy. Unlike iron and many other polymorphic solids, the polytypes of SiC do not appear to have specific temperature-pressure ranges of stability.

The $\beta \rightarrow \alpha$ transformation of SiC annealed above 1800°C has been studied extensively by Heuer, Ogbuji et al.,^{84,85,86,87} who observed a two-step process in both hot pressed and pressureless-sintered SiC. In the first stage, composite grains with an α core in a β envelope grew rapidly from β grains. The α core grew into the coherent β envelope in the second stage. The coherent interface was the intersection of the close-packed planes, $\{111\}_\beta || (0001)_\alpha$, where the energy was lower than at random β/α interfaces. Impurities from the decomposition of a BN crucible assisted the growth of the partially transformed composite grains, compared to a graphite crucible. Lee and Kim⁸⁸ and MoberlyChan et al.³⁵ used the $\beta \rightarrow \alpha$ transformation to achieve *in situ* toughening by growing plate-like α grains from equiaxed β grains. Rixecker et al.³⁶ added α -SiC “seeds” to accelerate the $\beta \rightarrow \alpha$ transformation and thereby increase the toughness. Zhan et al.⁸⁹ retarded the $\beta \rightarrow \alpha$ transformation and grain growth in Al_2O_3 - Y_2O_3 -CaO doped β -SiC by applying uniaxial pressure during annealing. Hotta et al.⁴¹ noted a preference for the 2H polytype over 4H with increasing amounts of AlN additive, in the $\beta \rightarrow \alpha$ transformation. Aluminum from the decomposition of Al_4SiC_4 promoted $\beta \rightarrow \alpha$ in a paper by J.S. Lee et al.⁹⁰

SiC microstructures are prepared by conventional ceramographic methods, with water as grinding lubricant, coolant and solvent.⁵⁷ SiC can be etched by several methods:

chemically by boiling in Murakami's etchant; thermally in a vacuum or inert gas at 1300-1500°C for 1-3 hr⁹¹; in molten NaHCO₃ at 950°C for 10 min⁹²; in molten KOH + KNO₃ at 450°C⁹³, or by plasma in 400 mtorr CF₄ + 10% O₂ for 2-10 min.⁴⁶

SiC sintered with additives typically has secondary phases along the grain boundaries and especially at the triple points. The secondary phases may be vitreous, crystalline or some combination of the two, and provide a liquid transport mechanism at the sintering temperature. The liquid phase dissolves SiC to some degree, transports it to the necks and voids and precipitates it there upon cooling. The additives may also dissolve in the SiC or react with the SiO₂ on the SiC particle surfaces. The advantages of additives include: they lower the sintering temperature, usually by liquid phase formation; they can toughen the ceramic by thermal expansion mismatch and other mechanisms; they can control grain growth, which affects mechanical properties significantly; and they enable low-cost pressureless sintering in some cases. A disadvantage of additives is that residual grain-boundary glass enables creep, affects thermal conductivity and reduces strength at temperatures above the glass transition.

SiC sintered without additives requires very high process temperatures, usually in excess of 2000°C, and some form of high pressure to effect densification. Hot-press tooling may be expensive and wears out rapidly, making pressureless sintering very attractive for high-volume manufacturing. Grains in additive-free ceramics may grow uncontrollably, resulting in oversized grains with trapped pores that reduce strength, toughness or homogeneity. Ceramics without additives are advantageous in applications where: high-temperature degradation or creep is likely; secondary phases degrade key properties, such as optical transmission or thermal conductivity; or in corrosive environments where intergranular attack is possible.

5.4 Processing of SiC

Additives are selected in large part to improve the kinetics of sintering, but each additive must be thermodynamically compatible with SiC, and of low volatility in the sintering temperature range. Many other processing factors can be optimized to yield the

best combination of SiC properties for the lowest production costs. Processing variables include fabrication method, temperature, time, gas composition, gas pressure, die pressure, particle size, binders, deflocculents and heat sources, as well as additives. SiC powder is usually ground and wet-mixed in non-aqueous liquids such as alcohol or acetone to minimize further surface oxidation. SiC is sintered in inert gas, reducing gas or vacuum, to minimize oxidation and enhance densification mechanisms.

5.4.1 Additives and Thermodynamics

Negita⁹⁴ considered the reaction thermodynamics of additives with SiC intended for turbine engine components. Metals that do not decompose SiC in Reaction 5.3 near the sintering temperature were good candidates as additives:



B, Al, Fe, Co, Ni, Mg and Li substituting for *M* all favored Reaction 5.3 to the left at 2300-2400K, which is desirable for sintering SiC. Ti, Zr, Hf, Nb, Be and Ta all drove Reaction 5.3 undesirably to the right. The vapor pressure of metals at high temperatures and low pressures was another factor. Mg and Li boiled below the sintering range of SiC and required stabilization as compounds to serve as additives. Al, Fe, Co and Ni had high vapor pressures and easily evaporated during sintering. Boron had a low vapor pressure and performed well as an additive in both hot pressing and pressureless sintering. Metal oxides that do not decompose SiC included those of Al, Be, Y, Ce, La and Th, and were therefore promising as SiC additives. The effect of some oxides that do decompose SiC were tempered with the addition of carbon, which preferentially (to SiC) carburized CaO, ZrO₂ and HfO₂.

Neher et al.²⁵ investigated the ternary SiC-Al₂O₃-Y₂O₃ system, to evaluate the grain boundary phases apart from the SiC matrix. The melting points, measured with a simultaneous thermal analyzer, and phase stability compared favorably with literature and thermodynamic calculations. The SiC content had only a small effect on the melting temperatures, confirming the low solubility of SiC in Al₂O₃-Y₂O₃ compounds such as

$\text{Y}_3\text{Al}_5\text{O}_{12}$ ("YAG," for yttrium-aluminum garnet), $\text{Y}_4\text{Al}_2\text{O}_9$ ("YAM," monoclinic) and YAlO_3 ("YAP," perovskite).

Oxide additives typically react with the 2-nm thick SiO_2 layer on SiC, or other oxide additives, to form a binary or ternary eutectic liquid during sintering, to facilitate liquid phase sintering (LPS). Reaction between the additive and the surface oxide layer is known as reactive wetting. S.K. Lee et al.^{33,88}, She and Ueno^{43,44}, Can et al.⁹⁵, Gubernat et al.⁴⁵ and Ortiz et al.⁹⁶ used $\text{Al}_2\text{O}_3 + \text{Y}_2\text{O}_3$. Alumina and yttria additives frequently reacted to form intergranular YAG, YAM or YAP in these investigations. Foster and Thompson⁹⁷ used MgO , $\text{MgO} + \text{Al}_2\text{O}_3$, $\text{MgO} + \text{Y}_2\text{O}_3$, and $\text{MgO} + \text{Al}_2\text{O}_3 + \text{Y}_2\text{O}_3$. Zhan et al.⁸⁹ used $\text{Al}_2\text{O}_3 + \text{Y}_2\text{O}_3 + \text{CaCO}_3$. Huang et al.⁹⁸ used hydrated nitrate salts of Mg, Al and Y. Y.I. Lee et al.⁹⁹ and Zawrah and Shaw³⁸ used $\text{Al}_2\text{O}_3 + \text{Y}_2\text{O}_3 + \text{CaO}$. Tatli and Thompson¹⁰⁰ used MgO as a particle coating. Bind and Biggers¹⁰¹ and Mao-lin et al.⁶⁵ used Al_2O_3 only. Rare earth oxides were investigated by Kim et al.³⁷, Zhou et al.⁸⁰ and Balog et al.⁶³

Nitride additives, such as AlN and Si_3N_4 , affect the amount of vitreous phase at the grain boundaries and the growth of SiC grains. AlN and Al are soluble in SiC, but AlN is much more stable at the sintering temperature than metallic Al . Keppeler et al.⁴⁷, Rixecker et al.³⁶, Bothara et al.^{16,39,64}, Hotta and Hojo⁴¹ and Onbattuvelli et al.⁴² used $\text{AlN} + \text{Y}_2\text{O}_3$. Kim et al.³⁷ used $\text{AlN} + \text{Er}_2\text{O}_3$. Ray et al.⁴⁶ combined AlN and Si_3N_4 with various oxides, carbides and metals.

Carbide, metal, boron and carbon additives typically react with SiC to form a binary liquid phase just below the sintering temperature. Free carbon deoxidizes SiC particle surfaces, and reacts with free silicon to form additional SiC. Boron has low solubility in SiC but segregates to grain boundaries where it has a large effect on grain boundary energy. Both B and C can be provided by B_4C additive. Bind and Biggers¹⁰¹ densified SiC with B_4C and B separately. Prochazka⁹³ achieved solid-state sintering of SiC with B and C from a number of sources. Tanaka et al.⁵⁰ and MoberlyChan et al.^{34,35} used $\text{Al} + \text{B} + \text{C}$. S.H. Lee et al.⁴⁰ used $\text{Al} + \text{B} + \text{C}$ and ternary compounds thereof, and J.S. Lee et al.^{90,102} used Al_4SiC_4 and Al_4C_3 to densify SiC.

Pure SiC particles can form bonds amongst themselves, but not densify without sintering additives.⁷⁴ Commercial SiC powder typically contains up to ~5% free carbon and a smaller fraction of free silicon and dissolved oxygen, in some cases enough to preclude the need for additional sintering aids.

5.4.2 Micro vs. Nano Particles

The particle size of ceramic powders has a significant effect on sintering characteristics and the properties of the sintered component. A coarser or micro size, say ~0.1–10 μm , can be achieved with a ball mill at low cost and is suitable for a wide variety of applications. A finer or nano size, ≤ 100 nm, requires turbomilling and much more energy, at a much higher cost. The nanoparticles have much more specific surface area and higher capillary pressure to drive the densification process, and can yield a much smaller grain size after sintering. The high surface energy of nanoparticles promotes agglomeration, which must be counteracted by dispersant additives or other means to assure uniform dispersions of mixed powders.

Mechanical properties, especially strength and hardness, are dependent on the grain size and related by the Hall¹⁰³-Petch¹⁰⁴ relationship in Equation 5.4:

$$\sigma = \sigma_i + \frac{B}{\sqrt{d}} \quad (5.4)$$

Where σ is the tensile strength; σ_i is the friction stress, a measure of the lattice resistance to dislocation movement; B is the locking parameter, a measure of the hardening contribution of the grain boundaries; and d is the grain size as measured by, for example, ASTM E112.¹⁰⁵ The need for greater strength and hardness in ceramics demands the smaller grain size of nanoparticles.

Other factors that affect mechanical properties include porosity and especially defects. The additional costs of nanoparticles may be justified in production if the finer particles reduce porosity and defects significantly. Porosity can be measured by a number of methods, including stereological point fraction in the microstructure, e.g., ASTM E562.¹⁰⁶ Porosity can also be inferred from the Archimedes water-displacement methods

for density measurement, e.g., ASTM C20¹⁰⁷ or C373.¹⁰⁸ A ceramic is considered densified to closed porosity, i.e., the pores are discrete rather than form a continuous network, if the bulk density is at least ~95% of the theoretical density.⁷⁵

A combination of micro- and nano-sized particles in the green compact may be advantageous. Onbattuvelli et al.^{42, 109, 110} compared the pressureless densification of powder injection-molded (PIM) bimodal with monomodal SiC. The bimodal SiC was a mixture of 90% 0.7- μm and 10% 50-nm powders, and the monomodal was the larger particle size only. Better particle packing in the bimodal SiC yielded higher relative density after binder burn-out, which resulted in 15% linear sintering shrinkage compared to 19% for the monomodal. Both were 96–97% dense after sintering at 1950°C. The bimodal PIM feedstock also had rheological and solids-loading advantages.

5.4.3 Dies and Crucibles

Graphite is the hot-press die, furnace lining and crucible material of choice for SiC, as it is among the very few materials that can withstand the high temperatures and vacuum pressures of SiC sintering, does not contaminate SiC or react unfavorably with it, can be easily machined into a variety of shapes and sizes, has a low coefficient of thermal expansion and no phase changes, and is widely available at a modest cost. Graphite and SiC are both very susceptible to oxidation at high temperatures, requiring a vacuum, reducing or inert atmosphere.

Pressureless sintered SiC is often contained inside a graphite crucible with a threaded cap. The crucible can be lined with a cover mix of coarse powders similar in composition to the ceramic compact, to minimize evaporation of additives and inhibit absorption of contaminants. SiC and AlN crucibles may also be suitable, depending on the additives.

5.4.4 Sintering Powder or Foil

Ceramics in general are susceptible to reaction with the kiln furniture, dies, crucibles and furnace linings during sintering. Components in the ceramic compact can

evaporate at high temperature, especially in vacuum, and condense in cooler regions. These reactions can be minimized by protective barriers between the compact and the support structures, such as refractory metal or graphite foil, or loose powder. Refractory-metal foil may be useful in the research laboratory, but impractical for commercial production. SiC compacts are routinely packed in powders containing SiC, BN, MgO or carbon, known as cover mixes or mould powders. The carbon may be amorphous, such as lampblack, or graphite. The powder retards the evaporation of additives, metals and MgO in particular. Boron nitride is very compatible with both the SiC and the graphite components.

S.K. Lee et al.³³ used a cover mix of the same composition as the SiC specimens. Foster and Thompson⁹⁷ used combinations of BN with MgO, Al₂O₃ and Y₂O₃ (*M*, *A* and *Y* in Table 4) at various additive compositions and sintering temperatures. Goldstein et al.⁵¹ used 100-500 µm SiC grit in microwave sintering. Tatli and Thompson¹⁰⁰ had MgO in their cover mix to minimize Mg loss. Ortiz et al.⁹⁶ used a blend of 90% SiC and 10% Al₂O₃ inside a graphite crucible.

5.4.5 Sintering Atmosphere

The primary requirement of the atmosphere in SiC sintering is that it is non-oxidizing. Inert gases are frequently used, mostly argon and helium. Helium has higher thermal conductivity than argon, but is also more expensive. Vacuum on the order of <10 mbar is widely used. Nitrogen is used with nitride additives, such as Si₃N₄-bonded SiC, where it reacts with free Si or retards the evaporation of nitrides. Reducing gases, such as CO or H₂, are used for special purposes. Reactive gases, such as SiO, SiH₄, SiCl₄ and CH₄, are used when the SiC is synthesized by chemical vapor deposition or a gas-phase reaction.¹¹¹

It is advantageous in some situations for pressureless sintering to be done in higher than ambient pressure. The technique is called gas pressure sintering (GPS), or just overpressure. The excess pressure drives or retards certain gas-phase reactions, and controls the microstructure.³⁶ Keppeler et al.⁴⁷ used GPS in N₂ at 0.3 and 10 MPa. Rixecker

et al.³⁶ used GPS in N₂ at 10 and 200 MPa. Sigl⁷⁸ used Ar in GPS at 0.1 and 10 MPa. Can et al.⁹⁵ used Ar in GPS at 8 MPa. S.H. Lee et al.⁴⁰ used 0.1 MPa Ar overpressure, about twice the atmospheric pressure.

5.4.6 Hydrofluoric Acid Leaching

The high surface energy of microscopic SiC particles, and the presence of H₂O and O₂ in the air, result in a passivation layer of SiO₂ on the free surfaces of SiC powder. The SiO₂ layer inhibits densification of SiC by decreasing its surface energy below 1800 erg/cm² and interfering with diffusion of Si and C atoms at points of contact in a compact.⁹³

The SiO₂ layer can be leached away, temporarily, if the powder is soaked in hydrofluoric acid. HF leaching is commonly applied to processes where SiC is sintered without additives. Two disadvantages of HF leaching are the health hazards of HF, and the cost of an additional step in the production process. HF leaching was used by Nadeau¹¹², Datta et al.¹¹³ and Y.I. Lee et al.⁹⁹

HF leaching can be eliminated if additives are selected that reduce SiO₂, react with SiO₂ to form a liquid phase just below the sintering temperature, or take advantage of the SiO₂ layer in some other way to facilitate densification. The SiO₂ can also be decomposed to SiO_(g) by heating in a vacuum to ~1500°C.^{17,40}

5.4.7 Densification Mechanisms

Liquid-phase sintering (LPS) is an important densification mechanism of SiC, especially in pressureless sintering. In LPS, a liquid is present at the sintering temperature by the melting of an additive, or more often, by the eutectic reaction of two or more additives. In SiC systems, the eutectic reaction is often between one additive and the SiO₂ passivation layer on the SiC particles. The liquid must wet the SiC particles, and the SiC must have significant solubility in the liquid for LPS to occur. LPS enables particle rearrangement for closer packing, and aids the transport of Si and C atoms by capillary pressure. Upon cooling, the liquid may become a vitreous phase at the triple points and along grain boundaries, crystallize as a secondary phase, or dissolve into the SiC grains. If

the liquid changes composition or is consumed as the densification progresses, as in SiC with $\text{Al}_2\text{O}_3 + \text{Al}_4\text{C}_3$ additives, LPS becomes transient liquid sintering.⁷⁴

Solid-state sintering (SSS) is the primary densification mechanism of SiC with B or $\text{B}_4\text{C} + \text{C}$ additives. The difference in free energy between free surfaces and contact points between particles drives volume diffusion along grain boundaries and through the lattices to bring particle centers closer together. The surface energy, self-diffusion coefficient, temperature and particle size all affect the amount of shrinkage and the rate of densification.⁷⁴ Silicon and carbon both have relatively low self-diffusion coefficients in SiC.⁴⁵

5.4.8 Pressureless Sintering

Pressureless sintering, where ceramic compacts are essentially free-standing in the sintering furnace, is the easiest and least expensive way to densify most ceramics. The term is something of a misnomer, as the furnace may be evacuated, at atmospheric pressure or above ambient pressure. SiC compacts are typically pressureless sintered in a graphite crucible lined with cover mix, but the crucible does not apply pressure to the compact. The driving force is reduction of surface energy by forming and growing interfaces between neighboring particles that reduce the surface area. The interface growth has a number of mechanisms, including surface diffusion, grain boundary diffusion, volume diffusion, evaporation-condensation, plastic flow and viscous flow.

Prior to pressureless sintering, ceramic specimens are formed in the green state most often by cold isostatic pressing (CIP) or uniaxial pressing, or both. CIP is also known as isopressing, and uniaxial as dry pressing or die compaction. S.K. Lee et al.³³ formed bars by CIP at 200 MPa in steel dies, to a green density that was 58% of theoretical density. Datta et al.¹¹³ applied CIP at 270 MPa to 62% density. Foster and Thompson⁹⁷ uniaxially pressed cylindrical SiC pellets at 94 MPa, followed by CIP at 172 MPa. She and Ueno⁴³ uniaxially pressed rectangular SiC bars at 3 MPa and CIP at 200 MPa. Gubernat et al.⁴⁵ used only uniaxial pressing. Keppeler et al.⁴⁷, Rixecker et al.³⁶ and Can et al.⁹⁵ used only CIP.

Zawrah and Shaw³⁸, Tatli and Thompson¹⁰⁰ and Ortiz et al.⁹⁶ used both uniaxial pressing and CIP, in that order.

Powder injection molding (PIM), an alternative to CIP and uniaxial pressing, is a near-net-shape process applicable to high-speed production of complex shapes and pressureless sintering. A review of PIM of SiC is provided in Chapter 2. Onbattuvelli et al.⁴² used PIM to fabricate green compacts.

Park and Kim¹¹⁴ studied the consolidation behavior of SiC powders in CIP and uniaxial compression with finite element analysis and various mathematical models. The effects of die friction, mandrels and other factors on green density uniformity were noted. The density distribution of a cylinder formed by CIP was more homogeneous than a similar shape from a uniaxial press.

Pressure-assisted sintering, including hot pressing, hot isostatic pressing and spark-plasma sintering, are described in Chapter 6 of this thesis, along with a review of papers pertaining to the effects of additives on pressure-sintered SiC.

5.4.9 Other Processes Used with SiC

Reaction-bonding is a low-cost method of fabricating SiC, especially for wear-resistance applications. Reaction-bonded SiC (RBSC) is the result of a compact of SiC and carbon particles exposed to molten or vaporized silicon. Additional SiC is formed *in situ* by reaction between the Si and free carbon, and the pores are filled with Si. RBSC shrinks ~1%, compared to 10-20% by other sintering methods.⁷⁴ Silicon nitride bonded SiC (SNBSC) is similar to RBSC, but with less free carbon and heated in an N₂ atmosphere to grow a Si₃N₄ bonding phase. While RBSC and SNBSC are important in the ceramic industry, they are of only passing interest in the scope of this thesis.

Annealing is a post-sintering heat treatment where a ceramic is held at high temperature for several hours, often to drive a slow transformation to completion. Keppeler et al.⁴⁷ and Kim et al.³⁷ increased the toughness of SiC by annealing. Zhan et al.⁸⁹ used annealing under pressure to retard the $\beta \rightarrow \alpha$ transformation. Zhou et al.⁸⁰ grew crystalline secondary phases in SiC by annealing at 1900°C for 4 hr, to improve the thermal

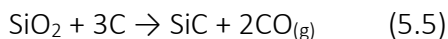
conductivity of the composite. Balog et al.⁶³ compared the hardnesses of individual SiC grains before and after annealing. S.H. Lee et al.⁴⁰ used annealing to enhance densification and mechanical properties. J.S. Lee et al.¹⁰² examined the decomposition of the additive at various annealing temperatures.

Sol-gel is a method of formation of high-purity, highly homogeneous ceramics. The sol is a dispersion of nano-sized particles in a liquid droplet. The gel is a polymer-like network of bonded particles after partial evaporation of the liquid. The gel network prevents segregation of particles and yields a very high surface area powder that can be densified at lower temperatures than conventional mechanical processing.⁷⁴ Ortiz et al.⁹⁶ used sol-gel to put a nano-layer of sintering additives on each SiC particle. Tatli and Thompson¹⁰⁰ used a similar hydrolysis process to coat SiC particles with magnesium methoxide in methanol.

Microwave assist technology (MAT) uses dielectric heating from a magnetron in addition to conventional radiant heating to densify ceramics.¹¹⁵ Microwave energy heats a compact from the center outward, the opposite of radiant techniques that heat from the surface inward. Most microwave furnaces use an industry-standard frequency of 2.45 GHz, which is not necessarily optimum for SiC.¹¹⁶ Microwave heating is very energy efficient, in that it heats the compact preferentially to the furnace insulation and kiln furniture, but has the disadvantages of inverse temperature gradients at high temperatures, and low susceptibility (ability to be heated by microwaves) of many ceramics at low temperatures. These two disadvantages are mitigated by MAT, where conventional heating in addition to microwave energy provides heating at low temperatures and keeps the external surfaces hot at the sintering temperatures. Some additives, such as carbon, and cover mixes behave as susceptors. MAT has found limited applications in SiC production, in part because of shallow penetration by microwaves in SiC.^{51,116}

5.5 Synthesis of SiC

Synthetic SiC was invented by E.G. Acheson in Pennsylvania circa 1892.¹¹⁷ In the Acheson process, high-purity coke and silica powders and additives are intimately mixed and packed into a resistance furnace around a graphite powder core between two electrodes, in Figure 5.1. The walls of the furnace are lined with SiC powder to minimize adverse reactions. The furnace is heated to approximately 2400°C for 40 hr. The silica is carbothermally reduced by Reaction 5.5:



A 32-Mg charge in a 12-m long cylindrical furnace yields 7200 kg of SiC.¹¹⁸ The SiC produced by the Acheson process requires further processing, such as crushing and fine grinding, before it is suitable for use as a ceramic powder.

Acheson named the product of his reaction carborundum on the assumption it was composed of carbon and corundum, Al₂O₃. The process and product were the foundation of the Carborundum Company, still a leading producer of SiC powder and SiC ceramic products. Several other processes have been developed to synthesize SiC, but 95% of all SiC is still produced by the Acheson process.¹¹⁸ Rice hulls¹¹⁹, gas phase reactions^{101,111}, chemical vapor deposition (CVD)¹¹⁶, self-propagating high-temperature combustion synthesis (SHS)^{120,121}, pack cementation¹²² and many other methods have been used to synthesize SiC. Most of these other methods are competitive with the Acheson process only in small-scale, specialty applications. Nadeau¹¹² attempted to synthesize and densify SiC simultaneously by hot pressing Si + C, which was described as reactive pressing. The result was β-SiC bonded by free silicon. Bind and Biggers¹⁰¹, Shinoda et al.⁵³, Lomello et al.¹⁷ and Noviyanto and Yoon¹²³ all synthesized the SiC in their research by methods other than the Acheson process.

SiC occurs naturally as the rare mineral moissanite, mostly in meteorites. Like most ceramics, commercial SiC must be synthesized from sources more abundant than its mineral occurrence. Moissanite is named for its discoverer, French chemist F.F.H. Moissan, a 1906 Nobel Prize winner in chemistry and a pioneer in carbide synthesis.¹²⁴

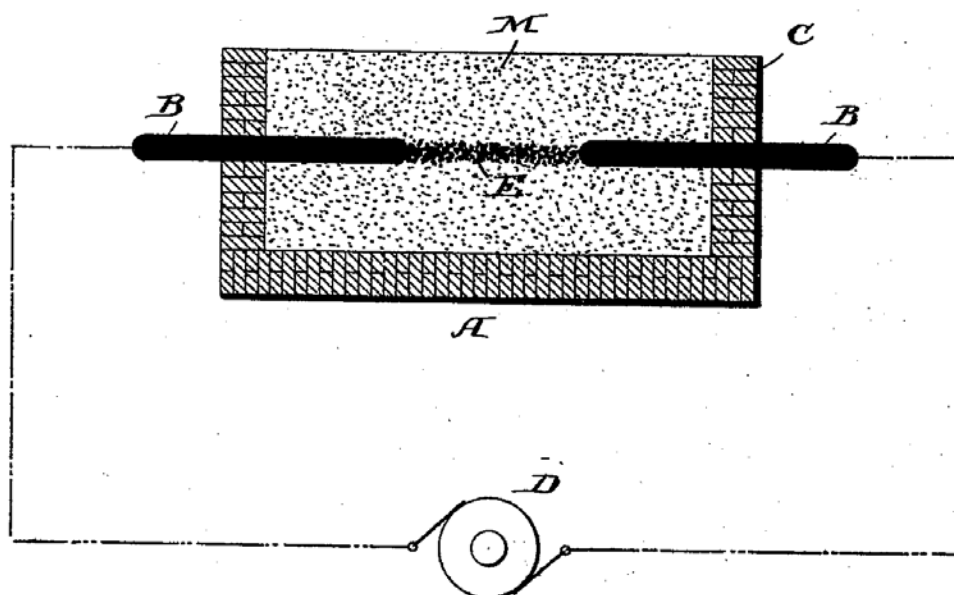


Figure 5.1: Diagram of the Acheson process for synthesizing SiC, consisting of (A) a furnace, (B) electrodes, (C) firebrick walls, (D) dynamo or other source of electricity, (E) graphite core, and (M) coke + silica + flux.¹¹⁷

5.6 Pressureless Sintering

Pressureless-sintered SiC compositions are summarized in Tables 5.4–5.6. Table 5.4 summarizes all compositions containing carbon, carbides, boron and metals as additives. These are referred to collectively as simply carbide additives in the Discussion §5.7 below. Table 5.5 is a compilation of oxide additives, and Table 5.6 of nitride additives.

5.6.1 Carbon, Boron, Metal, Carbide and Silicide Additives

Tanaka et al.⁵⁰ achieved full densification of CIP β -SiC with an addition of 0.29–0.49% Al, 0.1% B and 2% C. The carbon source was phenolic resin. The excess carbon, along with the boron and aluminum, were assumed to segregate to the grain boundaries and reduce the boundary energy. Very little $\beta \rightarrow \alpha$ transformation occurred, and the Al-

doping was deemed effective in preventing grain growth. The strength of the Al-B-C SiC was about 630 MPa in 3-point bending, and declined only to 580 MPa at 1600°C.

Datta et al.¹¹³ densified 37-nm α -SiC with 0.5% or more B₄C + 1% C by diffusion-controlled solid-state sintering at 2050°C for 15 min in a 3-mbar vacuum. The B₄C created vacancies that increased the self-diffusion coefficient of SiC by several orders of magnitude, up to the level of grain boundary diffusion coefficients, $\sim 10^{-6}$ – 10^{-5} cm²/s. The carbon reduced the silica layer on SiC particles by Reaction 5.5, increased the bulk self-diffusion coefficient of Si in SiC to that of C, and inhibited the growth of SiC crystals.

Andrews et al.⁷¹ compared the corrosion resistance of one SSS composition with B + C additives to two LPS SiC compositions described below under Oxide Additives. The amount of boron and carbon were not specified, but $2 \pm 0.4\%$ residual carbon was detected at the grain boundaries. Protective C and SiO₂ layers formed when the SSS SiC was exposed to 1.0-M HCl and HNO₃ at room temperature in an electrochemical cell. The protective C layer was again noted, along with soluble silicate ions, when the SiC was exposed to 1.0-M NaOH.

S.H. Lee et al.⁴⁰ synthesized Al₃BC₃ and Al₈B₄C₇ additives for both PS and SPS α -SiC. The SPS results are discussed in Chapter 6 of this thesis. The three PS compositions in Table 5.4 densified at $\geq 1950^\circ\text{C}$. The greater temperature and time in PS resulted in larger and more elongated grains than SPS, but not greater toughness. The 6H grains transformed to 4H in PS, and the fracture mode was transgranular.

Table 5.4: Additives of carbon, carbides, boron, silicon and metals; sintering parameters and properties of pressureless-sintered silicon carbide.

No.	SiC	Additive Composition	Sintering Conditions	Density	End Note
				% ρ_{ideal}	Year
1	0.27- μm β	0.018% Al, 0.10% B, 2.55% C, 0.37% SiO ₂ , 0.050% Fe	2100°C, 1 hr, Ar	75	50 Tanaka 1985
		0.018% Al, 0.15% B, 2.55% C, 0.37% SiO ₂ , 0.050% Fe		84	
		0.018% Al, 0.25% B, 2.55% C, 0.37% SiO ₂ , 0.050% Fe		99	
	0.28- μm β	0.027% Al, 0.1% B, 2.49% C, 0.36% SiO ₂ , 0.048% Fe		83	

No.	SiC	Additive Composition	Sintering Conditions	Density	End Note
				% ρ_{ideal}	Year
	0.28- μm β	0.050% Al, 0.1% B, 2.42% C, 0.30% SiO ₂ , 0.060% Fe		74	
	0.24- μm β	0.11% Al, 0.1% B, 2.19% C, 0.20% SiO ₂ , 0.040% Fe		82	
	0.26- μm β	0.29% Al, 0.1% B, 2.48% C, 0.43% SiO ₂ , 0.035% Fe		98	
	0.24- μm β	0.49% Al, 2.17% C, 0.35% SiO ₂ , 0.030% Fe		75	
		0.49% Al, 0.05% B, 2.17% C, 0.35% SiO ₂ , 0.030% Fe		93	
		0.49% Al, 0.1% B, 2.17% C, 0.35% SiO ₂ , 0.030% Fe		99	
		0.49% Al, 0.15% B, 2.17% C, 0.35% SiO ₂ , 0.030% Fe		99	
2	β	3% C + 1% B ₄ C	2100°C, 60 min, Ar	>98.5	33 S.K. Lee 1995
3	0.39- μm α (6H)	0.0% B ₄ C + 1% C	2000°C, 15 min, vacuum	62	113 Datta 2002
		0.5% B ₄ C + 1% C		81	
		1.0% or more B ₄ C + 1% C		89	
		0.0% B ₄ C + 1% C	2050°C, 15 min, vacuum	62	
		0.5% B ₄ C + 1% C		93	
		1.0% or more B ₄ C + 1% C		99	
		0.0% B ₄ C + 1% C	2100°C, 15 min, vacuum	62	
		0.5% B ₄ C + 1% C		98	
		1.0% or more B ₄ C + 1% C		99	
4	-	B + C	1950°C, 60 min	>96	71 Andrews 2007
5	α (6H)	7.5% Al ₃ BC ₃	1950°C, 2 hr, 0.1-MPa Ar	87.2	40 S.H. Lee 2009
		7.5% Al ₃ BC ₃	2000°C, 2 hr, 0.1-MPa Ar	96.8	
		7.5% Al ₃ BC ₃	2050°C, 2 hr, 0.1-MPa Ar	96.3	

5.6.2 Oxide Additives

Lee and Kim⁸⁸ added 6% Al₂O₃ + 4% Y₂O₃ to α - and β -SiC, pressureless liquid-phase sintered at 2000°C for 1, 2, 3 or 5 hr, and measured the fracture toughness. The four β -SiC starting powders partially transformed to α -SiC, the degree of transformation increasing with time. The grains in these four also became less equiaxed and more plate-shaped with time. The four α -SiC starting powders remained as the α -phase, equiaxed, after sintering. The grains in all compositions grew from submicron to as much as 16 μm ,

and the toughness increased from 4.5 to as much as 8 MPa m^{0.5}, with increasing sintering time. The plate-shaped, mixed α - β microstructures had the highest toughness. The toughness increase was attributed to crack deflection and bridging by the grains with the highest aspect ratio, i.e., the plate-shaped grains.

S.K. Lee et al.³³ added 6% Al₂O₃ + 4% Y₂O₃ to β -SiC, pressureless liquid-phase sintered at 2000°C, and observed rising R-curve behavior¹²⁵ when the SiC particles were elongated. The alumina and yttria formed a eutectic. The toughness ranged from about 5 to 7 MPa·m^{0.5}, and the exponent m was 0.135 in Equation 5.6:

$$K_R = k(\Delta a)^m \quad (5.6)$$

Where K_R is the fracture resistance, k is the toughening in a flat ($m = 0$) R-curve, and Δa is the crack extension in microns. A similar composition with 2.5- μ m equiaxed SiC grains had a much flatter R-curve with $m = 0.042$ and a maximum toughness of 5.5 MPa·m^{0.5}. A third composition in Table 4 with 3% C + 1% B₄C additive had a very flat R-curve and a toughness of 3 MPa·m^{0.5}. The densities ranged from 98.5 to 99.1% of theoretical. The 4-pt bending strengths were 480, 520 and 313 MPa in the three compositions prior to the toughness notch.

She and Ueno⁴³ attempted to improve the mechanical properties compared to Prochazka's⁹³ work, using 10% Al₂O₃ + Y₂O₃ as the additives to α -SiC in an 1850-2000°C pressureless sintering process in Table 5.5. A eutectic liquid between the two additives yielded density, strength and toughness as high as 98%, 625 MPa and 7.5 MPa·m^{0.5}, resp. Excess Al₂O₃ was needed to suppress its evaporation and increase the density. Strength and toughness decreased with increasing Y₂O₃ content, except at 2000°C sintering. The intergranular phase was primarily YAG, with a higher coefficient of thermal expansion than SiC, which left residual tension at the grain boundaries upon cooling. The toughening intergranular fracture was attributed to the thermal expansion difference between SiC and secondary phases. The increased toughening at 2000°C sintering was attributed to crack deflection.

In a second paper, She and Ueno⁴⁴ studied the effects of higher and lower 0.625 Al₂O₃ + 0.375 Y₂O₃ sintering aid contents on α -SiC again pressureless sintered at 1850-

2000°C. Density, strength, hardness (10-kg load) and toughness were optimized at 10% additives, compared to 5, 15 and 25%. Higher additive contents were largely lost to evaporation.

Goldstein et al.⁵¹, using microwave heating, densified 0.55- μm α -SiC with 1.4 vol% C + 5 vol% Al_2O_3 + 2.6 vol% Y_2O_3 to 98% at 1950°C. The microwave furnace applied 2.8-4.5 kW of forward power at 2.45 GHz for at least 30 min, in an atmosphere of Ar + 8% N_2 . The penetration by the microwaves was very shallow, estimated at just 3 μm at 700°C, but susceptors were not needed to assist the dielectric heating. Pure SiC under the same conditions did not densify. The densification uniformity was affected by spatial variations in the electromagnetic field intensity. Some alumina evaporated, but YAG formed at the grain boundaries. SiC grit lined the furnace chamber to improve hybrid heating and reduce cracking. The density, hardness (unspecified load) and strength were slightly less than conventionally sintered SiC of the same composition, leading to the conclusion that MAT had no advantage over conventional sintering techniques for SiC.

Y.I. Lee et al.⁹⁹ used 7% Al_2O_3 + 2% Y_2O_3 + 1% CaO as the additive in a two-step process with 20-nm β -SiC to achieve 95-99% density and much less grain growth than conventional pressureless sintering. In the first step, the pressurized furnace was heated to 1700°C in 20 MPa Ar. Second, the furnace was immediately cooled to 1550°C and held there for 8 hr. The additives formed a liquid at 1400°C. The control of density and pore size in the first step enabled full densification in the second step.

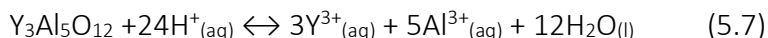
Zawrah and Shaw³⁸ used 7% Al_2O_3 + 2% Y_2O_3 + 1 or 3% CaO as the additive with 0.634- μm β -SiC to achieve 95% density as low as 1750°C. YAG liquid provided a rapid diffusion path along the grain boundaries in both compositions, and CaY_2O_4 was also present in the 3% CaO additive. The toughness was 3.9-5.7 $\text{MPa}\cdot\text{m}^{0.5}$, Vickers hardness (unspecified load) 19.2-23.2 GPa and elastic modulus 280-410 GPa, with the best properties in the 1% CaO composition sintered at 1800°C.

Gubernat et al.⁴⁵ investigated SiC at various sintering temperatures, additive fractions, and ratios of Al_2O_3 + Y_2O_3 and Al_2O_3 + Y_2O_3 + MgO additives. The precipitated phases included YAG, YAM, spinel and alumina. The best properties were obtained with

10-15% $\text{Al}_2\text{O}_3 + \text{Y}_2\text{O}_3$ in a 60:40 weight ratio, 15-20% $\text{Al}_2\text{O}_3 + \text{Y}_2\text{O}_3$ in a 40:60 weight ratio, and 10% $\text{Al}_2\text{O}_3 + \text{Y}_2\text{O}_3 + \text{MgO}$ in a 42:44:14 weight ratio. The use of coarse SiC mould powder at 1950°C for 2 hr minimized evaporation losses and yielded the highest relative densities for all compositions. The hardness and toughness values came from Vickers under a 5-N load and notched beam, respectively.

Tatli and Thompson¹⁰⁰ chemically coated α -SiC particles with a solution of magnesium methoxide in methanol to get a net addition of 5% MgO after hydrolysis. The compacts were pressureless sintered at 1450-1750°C, and compared to conventionally mixed SiC + MgO. A powder bed of 50% BN, 45% SiC and 5% MgO was used to minimize volatilization of the additive. The conventional mixture did not densify satisfactorily at any temperature. The coated SiC densified at 1550 and 1650°C, with Mg_2SiO_4 precipitating. The MgO coating was too porous at 1450°C, and evaporated at 1750°C.

Andrews et al.⁷¹ compared the corrosion resistance of two LPS SiC + 10% ($\text{Al}_2\text{O}_3 + \text{Y}_2\text{O}_3$) compositions to one SSS composition described above under Carbide Additives. The first oxide additive pair was in a 1:1 molar ratio, and formed YAG and YAM at the grain boundaries. The second was 4:1, and formed YAG and Al_2O_3 when pressureless sintered at 1950°C for 60 min. Details of the preparation were cited as the same as Can et al.⁹⁵ Exposed to 1.0-M HCl and HNO_3 at room temperature in an electrochemical cell, the YAG grain boundary phase decomposed according to the hydrolysis in Reaction 5.7 but the corrosion current was an order of magnitude lower than for the SSS SiC. A protective SiO_2 layer formed in HCl. In 1.0-M NaOH, $\text{Y}(\text{OH})_3$ precipitated on the surface but the corrosion rate was slower than in the two acids. The differences in corrosion characteristics between the two oxides, and between the two sintering mechanisms, were minor and did not lead the authors to declare any of the preparations more fit for a corrosion application than the others.



Ortiz et al.⁹⁶ prepared submicron α -SiC powder with 3.6 vol% $\text{Al}_2\text{O}_3 + \text{Y}_2\text{O}_3$ (5:3 mole, stoichiometric with YAG) additives as a colloidal suspension, i.e., sol-gel, for a wear-resistance application. The sol-gel and a mechanically mixed powder of the same

composition were densified by pressureless LPS at 1950°C for 1 hr in Ar. The sol-gel put a nano-layer of sintering additives on each SiC particle, resulting in the better distribution of additives. YAG precipitated in the colloidal SiC, but was negligible in the conventional SiC. The colloidal SiC had better sliding wear resistance and slightly higher density, while the hardness and toughness were about the same.

Table 5.5: Oxides additives, sintering parameters and properties of pressureless-sintered silicon carbide.

No.	SiC	Additive Composition	Sintering Conditions	Density	End Note
		mass%		% ρ_{ideal}	Year
1	0.27- μm β	6% Al_2O_3 + 4% Y_2O_3	2000°C, 1 hr	99.1	88 S.K. Lee 1994
			2000°C, 2 hr	99.2	
			2000°C, 3 hr	99.0	
			2000°C, 5 hr	98.7	
	α		2000°C, 1 hr	98.8	
			2000°C, 2 hr	98.8	
			2000°C, 3 hr	99.1	
			2000°C, 5 hr	98.5	
2	β	6% Al_2O_3 + 4% Y_2O_3	2000°C, 60 min, Ar	>98.5	33 S.K. Lee 1995
			2000°C, 180 min, Ar	>98.5	
3	α (6H)	9% (56 mol% MgO : 17 Al_2O_3 : 27 Y_2O_3)	1750°C, 180 min, BN+M+A+Y bed	73	97 Foster 1999
		9% (64 mol% MgO : 25 Al_2O_3 : 11 Y_2O_3)	1750°C, 180 min, BN powder bed	78	
		9% (76 mol% MgO : 10 Al_2O_3 : 13 Y_2O_3)	1750°C, 180 min, BN powder bed	78	
		9% (76 mol% MgO : 10 Al_2O_3 : 13 Y_2O_3)	1800°C, 140 min, BN+M+A+Y bed	78	
		9% (64 mol% MgO : 25 Al_2O_3 : 11 Y_2O_3)	1850°C, 120 min, BN powder bed	81	
		9% (76 mol% MgO : 10 Al_2O_3 : 13 Y_2O_3)	1850°C, 120 min, BN powder bed	80	
		9% (64 mol% MgO : 25 Al_2O_3 : 11 Y_2O_3)	2000°C, 60 min, BN powder bed	86	
		9% (53 Al_2O_3 : 47 Y_2O_3)	2000°C, 30 min, BN + Al_2O_3 + Y_2O_3	86	
4	0.6- μm α	10% (75% Al_2O_3 + 25% Y_2O_3)	1850°C, 1 hr, Ar	96	43 She 1999 MC&P
		10% (62.5% Al_2O_3 + 37.5% Y_2O_3)		96.8	
		10% (50% Al_2O_3 + 50% Y_2O_3)		95	
		10% (37.5% Al_2O_3 + 62.5% Y_2O_3)		93	
		10% (75% Al_2O_3 + 25% Y_2O_3)	1900°C, 1 hr, Ar	98	

No.	SiC	Additive Composition	Sintering Conditions	Density	End Note
		mass%		% ρ_{ideal}	Year
		10% (62.5% Al ₂ O ₃ + 37.5% Y ₂ O ₃)		98	
		10% (50% Al ₂ O ₃ + 50% Y ₂ O ₃)		97	
		10% (37.5% Al ₂ O ₃ + 62.5% Y ₂ O ₃)		95	
		10% (75% Al ₂ O ₃ + 25% Y ₂ O ₃)		98	
		10% (62.5% Al ₂ O ₃ + 37.5% Y ₂ O ₃)	1950°C, 1 hr, Ar	98	
		10% (50% Al ₂ O ₃ + 50% Y ₂ O ₃)		98	
		10% (37.5% Al ₂ O ₃ + 62.5% Y ₂ O ₃)		96	
		10% (75% Al ₂ O ₃ + 25% Y ₂ O ₃)		97	
		10% (62.5% Al ₂ O ₃ + 37.5% Y ₂ O ₃)	2000°C, 1 hr, Ar	97	
		10% (50% Al ₂ O ₃ + 50% Y ₂ O ₃)		97	
		10% (37.5% Al ₂ O ₃ + 62.5% Y ₂ O ₃)		96	
		5% (62.5 mass% Al ₂ O ₃ : 37.5% Y ₂ O ₃)	1850°C, 1 hr, Ar	95	
		10% (62.5 mass% Al ₂ O ₃ : 37.5% Y ₂ O ₃)		97	
		15% (62.5 mass% Al ₂ O ₃ : 37.5% Y ₂ O ₃)		96	
		25% (62.5 mass% Al ₂ O ₃ : 37.5% Y ₂ O ₃)		94	
5	0.6- μm α	5% (62.5 mass% Al ₂ O ₃ : 37.5% Y ₂ O ₃)	1900°C, 1 hr, Ar	97	44 She 1999 MRB
		10% (62.5 mass% Al ₂ O ₃ : 37.5% Y ₂ O ₃)		97	
		15% (62.5 mass% Al ₂ O ₃ : 37.5% Y ₂ O ₃)		97	
		25% (62.5 mass% Al ₂ O ₃ : 37.5% Y ₂ O ₃)		95	
		5% (62.5 mass% Al ₂ O ₃ : 37.5% Y ₂ O ₃)	1950°C, 1 hr, Ar	98	
		10% (62.5 mass% Al ₂ O ₃ : 37.5% Y ₂ O ₃)		98	
		15% (62.5 mass% Al ₂ O ₃ : 37.5% Y ₂ O ₃)		98	
		25% (62.5 mass% Al ₂ O ₃ : 37.5% Y ₂ O ₃)		95	
		5% (62.5 mass% Al ₂ O ₃ : 37.5% Y ₂ O ₃)	2000°C, 1 hr, Ar	97	
		10% (62.5 mass% Al ₂ O ₃ : 37.5% Y ₂ O ₃)		97	
		15% (62.5 mass% Al ₂ O ₃ : 37.5% Y ₂ O ₃)		97	

No.	SiC	Additive Composition	Sintering Conditions	Density	End Note
		mass%		% ρ_{ideal}	Year
		25% (62.5 mass% Al ₂ O ₃ : 37.5% Y ₂ O ₃)		94	
6	0.55- μ m α	1.4 vol% C + 5 vol% Al ₂ O ₃ + 2.6 vol% Y ₂ O ₃	Microwave, 1900°C, 90 min, Ar + 8% N ₂	95.0	51 Goldstein 2002
			1900°C, 90 min, Ar + 8% N ₂	98.5	
7	20-nm β	7% Al ₂ O ₃ + 2% Y ₂ O ₃ + 1% CaO	1500°C, 8 hr	76	99 Y.I. Lee 2003
			1550°C, 8 hr	85	
			1750°C, 5 min	90	
			1750°C, 30 min	98	
			1700°C, 0 hr	77	
			1750°C, 0 hr	85	
			1800°C, 0 hr	90	
			1850°C, 0 hr	98	
			1650°C, 0 hr + 1500°C, 8 hr	80	
			1700°C, 0 hr + 1500°C, 8 hr	85	
			1700°C, 0 hr + 1550°C, 2 hr	88	
			1700°C, 0 hr + 1550°C, 8 hr	95	
			1750°C, 0 hr + 1550°C, 8 hr	99	
8	0.634- μ m β	1% CaO + 7% Al ₂ O ₃ + 2% Y ₂ O ₃	1750°C, Ar	96	38 Zawrah 2004
			1800°C, Ar	97	
			1900°C, Ar	95	
		3% CaO + 7% Al ₂ O ₃ + 2% Y ₂ O ₃	1750°C, Ar	95	
			1800°C, Ar	96	
			1900°C, Ar	89	
9	α	10% (4 mol Al ₂ O ₃ + 1 mol Y ₂ O ₃)	1875°, 30 min; GPS, 1925°C, 60 min, 8 MPa, Ar	97	95 Can 2006
		10% (5 mol Al ₂ O ₃ + 3 mol Y ₂ O ₃)		98	
		10% (1 mol Al ₂ O ₃ + 1 mol Y ₂ O ₃)		98	
		10% (1 mol Al ₂ O ₃ + 2 mol Y ₂ O ₃)		97	
		10% (1 mol Al ₂ O ₃ + 4 mol Y ₂ O ₃)		90	
10	1- μ m α	5% (60% Al ₂ O ₃ : 40% Y ₂ O ₃)	1900°C, 1 hr, Ar	90	45 Gubernat 2007
		10% (60% Al ₂ O ₃ : 40% Y ₂ O ₃)		94	
		15% (60% Al ₂ O ₃ : 40% Y ₂ O ₃)		91	
		20% (60% Al ₂ O ₃ : 40% Y ₂ O ₃)		93	
		15% (40% Al ₂ O ₃ : 60% Y ₂ O ₃)		95	
		20% (40% Al ₂ O ₃ : 60% Y ₂ O ₃)		94	
		10% (42 Al ₂ O ₃ : 44 Y ₂ O ₃ : 14 MgO)		82	
		10% (12 Al ₂ O ₃ : 61 Y ₂ O ₃ : 27 MgO)		80	
		5% (60% Al ₂ O ₃ : 40% Y ₂ O ₃)	1950°C, 1 hr, Ar	94	
		10% (60% Al ₂ O ₃ : 40% Y ₂ O ₃)		94	
		15% (60% Al ₂ O ₃ : 40% Y ₂ O ₃)		95	
		20% (60% Al ₂ O ₃ : 40% Y ₂ O ₃)		93	

No.	SiC	Additive Composition	Sintering Conditions	Density	End Note
		mass%		% ρ_{ideal}	Year
		15% (40% Al ₂ O ₃ : 60% Y ₂ O ₃)		91	
		20% (40% Al ₂ O ₃ : 60% Y ₂ O ₃)		95	
		10% (42 Al ₂ O ₃ : 44 Y ₂ O ₃ : 14 MgO)		89	
		10% (12 Al ₂ O ₃ : 61 Y ₂ O ₃ : 27 MgO)		81	
		5% (60% Al ₂ O ₃ : 40% Y ₂ O ₃)	1950°C, 2 hr, Ar	95	
		10% (60% Al ₂ O ₃ : 40% Y ₂ O ₃)		94	
		15% (60% Al ₂ O ₃ : 40% Y ₂ O ₃)		93	
		20% (60% Al ₂ O ₃ : 40% Y ₂ O ₃)		92	
		15% (40% Al ₂ O ₃ : 60% Y ₂ O ₃)		93	
		20% (40% Al ₂ O ₃ : 60% Y ₂ O ₃)		93	
		10% (42 Al ₂ O ₃ : 44 Y ₂ O ₃ : 14 MgO)		77	
		10% (12 Al ₂ O ₃ : 61 Y ₂ O ₃ : 27 MgO)		81	
		5% (60% Al ₂ O ₃ : 40% Y ₂ O ₃)	1950°C, 2 hr, Ar, SiC mould powder	94	
		10% (60% Al ₂ O ₃ : 40% Y ₂ O ₃)		96	
		15% (60% Al ₂ O ₃ : 40% Y ₂ O ₃)		95	
		20% (60% Al ₂ O ₃ : 40% Y ₂ O ₃)		95	
		15% (40% Al ₂ O ₃ : 60% Y ₂ O ₃)		95	
		20% (40% Al ₂ O ₃ : 60% Y ₂ O ₃)		94	
		10% (42 Al ₂ O ₃ : 44 Y ₂ O ₃ : 14 MgO)		96	
		10% (12 Al ₂ O ₃ : 61 Y ₂ O ₃ : 27 MgO)		93	
		5% (60% Al ₂ O ₃ : 40% Y ₂ O ₃)	2000°C, 1 hr, Ar	85	
		10% (60% Al ₂ O ₃ : 40% Y ₂ O ₃)		84	
		15% (60% Al ₂ O ₃ : 40% Y ₂ O ₃)		82	
		20% (60% Al ₂ O ₃ : 40% Y ₂ O ₃)		83	
		15% (40% Al ₂ O ₃ : 60% Y ₂ O ₃)		86	
		20% (40% Al ₂ O ₃ : 60% Y ₂ O ₃)		81	
		10% (42 Al ₂ O ₃ : 44 Y ₂ O ₃ : 14 MgO)		79	
		10% (12 Al ₂ O ₃ : 61 Y ₂ O ₃ : 27 MgO)		74	
11	α (6H)	5% MgO coating on SiC	1450°C, 30 min	87	100 Tatli 2007
			1450°C, 120 min	88	
			1550°C, 30 min	96	
			1650°C, 30 min	94	
			1650°C, 60 min	96	
			1750°C, 30 min	65	
		5% MgO mixed with SiC	1450°C, 30 min	64	
			1450°C, 120 min	62	
			1550°C, 30 min	63	
			1650°C, 30 min	62	
			1650°C, 60 min	63	
			1750°C, 30 min	64	

No.	SiC	Additive Composition	Sintering Conditions	Density	End Note
		mass%		% ρ_{ideal}	Year
12	-	10% (1 mol Al_2O_3 : 1 mol Y_2O_3)	1950°C, 60 min	98.8	71 Andrews 2007
		10% (4 mol Al_2O_3 : 1 mol Y_2O_3)		97.6	
13	0.5- μm α	Colloidal 3.6 vol% (5 mol Al_2O_3 + 3 mol Y_2O_3)	1950°C, 1 hr, Ar	>99	96 Ortiz 2012
		3.6 vol% (5 mol Al_2O_3 + 3 mol Y_2O_3)		95	

5.6.3 Nitride Additives

Keppeler et al.⁴⁷ compared the thermomechanical properties of a globular α -SiC with a platelet-forming composition that began with 99% β + 1% α SiC. The globular composition was sintered in N_2 at 0.2-0.3 MPa pressure at 1980°C for 30 min. The platelet composition was sintered at atmospheric pressure in N_2 at 1990°C for 30 min, at 10 MPa overpressure another 30 min, and annealed 6 hr at 1970°C and 0.5 MPa to drive the $\beta \rightarrow \alpha$ transformation. The secondary phases, grain size and grain shape were significantly different between the two compositions. The globular composition was slightly stronger, especially at 1000°C, but the platelet composition was tougher, as much as 5.5 compared to 4.1 MPa·m^{0.5}, from 400 to 900°C.

Rixecker et al.³⁶ achieved fully dense α - and β -SiC with AlN + Y_2O_3 sintering aids. The AlN additive combined with an overpressure of N_2 precluded the need for a powder bed to prevent evaporation of grain-boundary components during pressureless LPS. The toughness was about 4-6 MPa·m^{0.5}, and the 4-pt bending strength was 500-550 MPa. Annealing at 1950°C for up to 32 hr drove the $\beta \rightarrow \alpha$ transformation and affected the toughness. The excess N_2 stabilized AlN at high temperatures, which inhibited a SiC decomposition reaction. This use of N_2 is somewhat contradictory to Chia's et al. patent, where "... N_2 retards the sintering of silicon carbide and requires an increase in the sintering temperature and/or time for conventional silicon carbides to achieve equivalent densities." ¹²⁶ The results are compiled in Table 5.4.

Sigl⁷⁸ synthesized YAG, combined it with AlN in a 4:1 molar ratio, and added it to α -SiC in volume fractions from 0 to 30 vol%, in a study of thermal conductivity as a function

of additives and rule-of-mixture models. The 0% additive was EKasic® D, for comparison to a commercial SiC. LPS was the sintering mechanism in a GPS process where 0.1-MPa Ar was applied at 1970°C for 30 min, followed by 10-MPa Ar for 10 min to achieve maximum densification in all compositions. All the thermal conductivity values declined with increasing additive content and temperature. The thermal conductivity of the experimental compositions ranged from about 20 W m⁻¹ K⁻¹ for 30 vol% additives at 1000°C to 85 W m⁻¹ K⁻¹ for 3 vol% additives at room temperature. The thermal conductivity of the commercial SiC at ~40–105 W m⁻¹ K⁻¹ was a little higher than the experimental compositions over the same temperature range.

Onbattuvelli et al.⁴² injection molded 0.7-μm α-SiC with 5% each AlN + Y₂O₃ sintering aids, in both monomodal and bimodal (with 10% 50-nm α-SiC) particle size distributions. Both compositions were sintered in Ar for 2 or 4 hr at 1800–2000°C in 50-degree increments. Full densification was achieved only above 1900°C. A weight loss that reduced the density slightly was observed at 2000°C, and attributed to the formation of SiO, Al₂O, YO and CO gases. Therefore, 1950°C was the optimum sintering temperature for either soak time or size distribution. The bimodal shrank less at 1950°C, about 15% isometric linear shrinkage compared to 19% for the monomodal. The bimodal had slightly higher thermal conductivity at 73 W m⁻¹ K⁻¹ than the monomodal at 68 W m⁻¹ K⁻¹.

Table 5.6: Nitride + oxides additives, sintering parameters and properties of pressureless-sintered silicon carbide.

No.	SiC	Additive Composition	Sintering Conditions	Density	End Note
		mass%		%ρ _{ideal}	Year
1	99% β + 1% α	10 vol% (3 AlN : 2 Y ₂ O ₃)	GPS, 1990°C, 30 min, 10 MPa N ₂ , anneal	~99	47 Keppeler 1998
	α	10 vol% (3 AlN : 2 Y ₂ O ₃)	GPS, 1980°C, 30 min, 0.3 MPa N ₂	~99	
2	90% β	10 vol% (20 mol% AlN + 80 mol% Y ₂ O ₃)	GPS, 2010-2030°C, 60 min, 10 MPa N ₂ , anneal	94.9-96.4	36 Rixecker 2000
	90% β	10 vol% (20 mol% AlN + 80 mol% Y ₂ O ₃)	GPS, 2000°C, 60 min, 200 MPa N ₂ , HIP	99.4	
	90% β	10 vol% (40 mol% AlN + 60 mol% Y ₂ O ₃)	GPS, 1980°C, 60 min, 10 MPa N ₂ , anneal	≥99.6	

No.	SiC	Additive Composition	Sintering Conditions	Density	End Note
		mass%		% ρ_{ideal}	Year
	90% β	10 vol% (60 mol% AlN + 40 mol% Y ₂ O ₃)	GPS, 2010°C, 60 min, 10 MPa N ₂ , anneal	>99.9	
	96% β	10 vol% (60 mol% AlN + 40 mol% Y ₂ O ₃)	GPS, 1980°C, 60 min, 10 MPa N ₂ , anneal	>99.9	
	90% β	7 vol% (60 mol% AlN + 40 mol% Y ₂ O ₃)	GPS, 2020°C, 60 min, 10 MPa N ₂ , anneal	>99.9	
	100% α (6H)	10 vol% (60 mol% AlN + 40 mol% Y ₂ O ₃)	GPS, 1950°C, 60 min, 10 MPa N ₂	>99.9	
	100% α (6H)	10 vol% (80 mol% AlN + 20 mol% Y ₂ O ₃)	GPS, 2000°C, 60 min, 10 MPa N ₂	>99.9	
	100% β	10 vol% (60 mol% AlN + 40 mol% Y ₂ O ₃)	GPS, 1980°C, 60 min, 10 MPa N ₂	>99.9	
	100% β	10 vol% (60 mol% AlN + 40 mol% Y ₂ O ₃)	GPS, 1980°C, 60 min, 10 MPa N ₂	>99.9	
3	12.5 m ² /gm α	3 vol% (4 mol YAG : 1 mol AlN)	GPS, 1970°C, 30 min, 0.1 MPa + 10 min, 10 MPa Ar	>95	78 Sigl 2003
		5 vol% (4 mol YAG : 1 mol AlN)		>95	
		10 vol% (4 mol YAG : 1 mol AlN)		>95	
		20 vol% (4 mol YAG : 1 mol AlN)		>95	
		30 vol% (4 mol YAG : 1 mol AlN)		>95	
		30 vol% (4 mol YAG : 1 mol AlN)		>95	
4	0.7- μ m α	5% AlN + 5% Y ₂ O ₃	1800°C, 2 hr, Ar	<90	42 Onbattuvelli 2012
			1800°C, 4 hr, Ar	<90	
			1850°C, 2 hr, Ar	<90	
			1850°C, 4 hr, Ar	<90	
			1900°C, 2 hr, Ar	<95	
			1900°C, 4 hr, Ar	<95	
			1950°C, 2 hr, Ar	96	
			1950°C, 4 hr, Ar	96	
			2000°C, 2 hr, Ar	95	
			2000°C, 4 hr, Ar	95	
	90% 0.7- μ m α + 10% 50-nm α	5% AlN + 5% Y ₂ O ₃	1800°C, 2 hr, Ar	<90	
			1800°C, 4 hr, Ar	<90	
			1850°C, 2 hr, Ar	<90	
			1850°C, 4 hr, Ar	<90	
			1900°C, 2 hr, Ar	<90	
			1900°C, 4 hr, Ar	<95	
			1950°C, 2 hr, Ar	97	
			1950°C, 4 hr, Ar	97	
			2000°C, 2 hr, Ar	95	
			2000°C, 4 hr, Ar	95	

5.7 Discussion

Oxide additives yielded >95% densities as low as 1550°C, in Figure 5.2. At the same time, a number of oxides sintered at higher temperatures were inadequately dense. The nitride additives generally required at least 1950°C for densification, but yielded consistently >95% densification. The carbide additives resulted in both >95% density at lower temperatures and <95% density at higher temperatures, indicating that these additives behave less predictably than the others. Like the nitrides, 1950°C was a reliable starting point for densification of SiC with carbide additives. Higher temperatures can be detrimental to density, as additives may evaporate with increasing temperature. Figure 5.2 contains over 100 data points and represents a large swath of PS SiC ceramics.

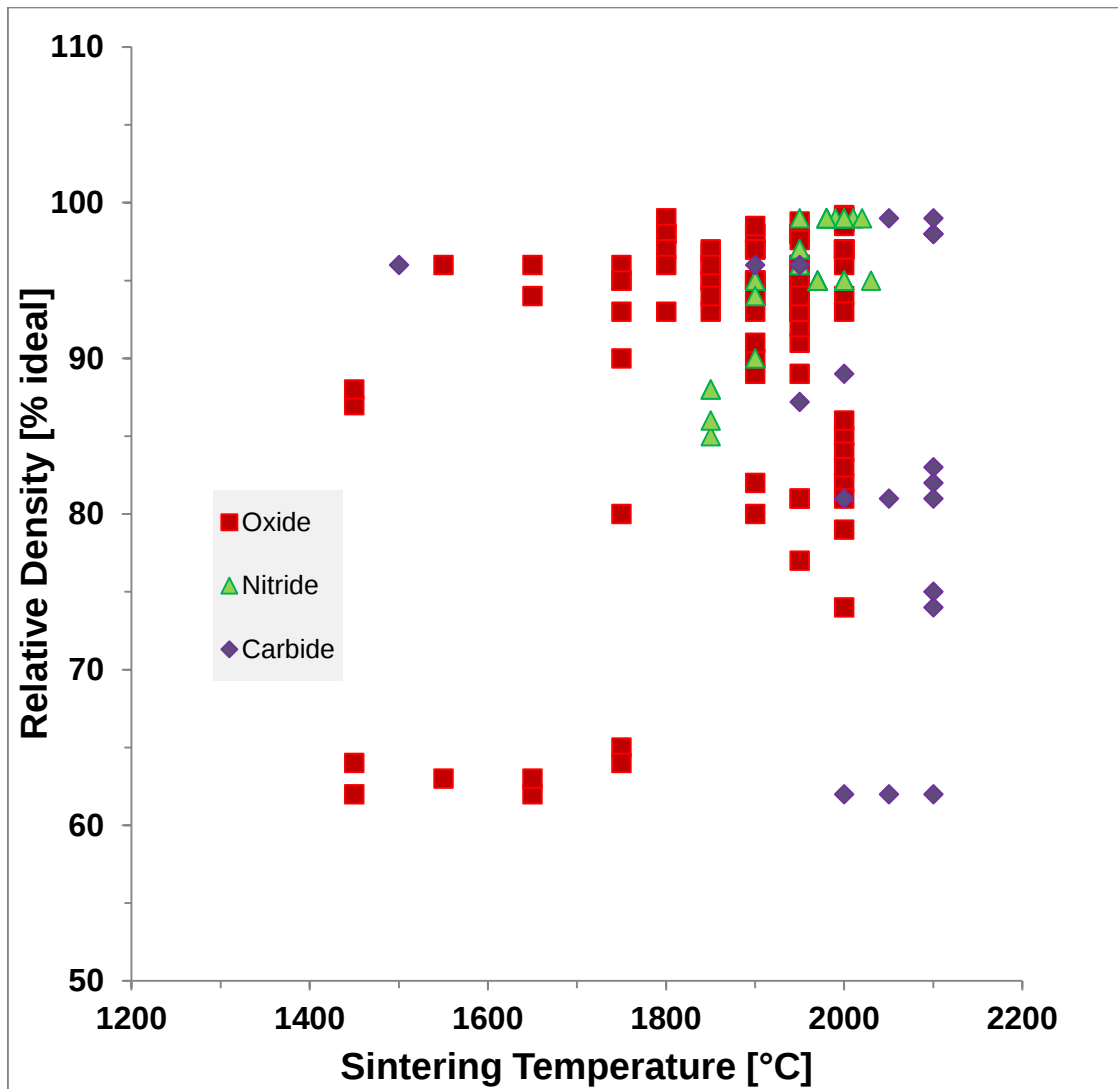


Figure 5.2: Map of relative density as a function of sintering temperature and additive family from the data in Tables 5.4–5.6.

The carbide additives yielded >95% densities at the lowest total additive amounts, in Figure 5.3. Several of the carbides were densified with 2–3% additives. Most of the oxide and nitride compositions needed 5–10% additives for densification. Additives of any kind exceeding about 10% brought few if any advantages in densification.

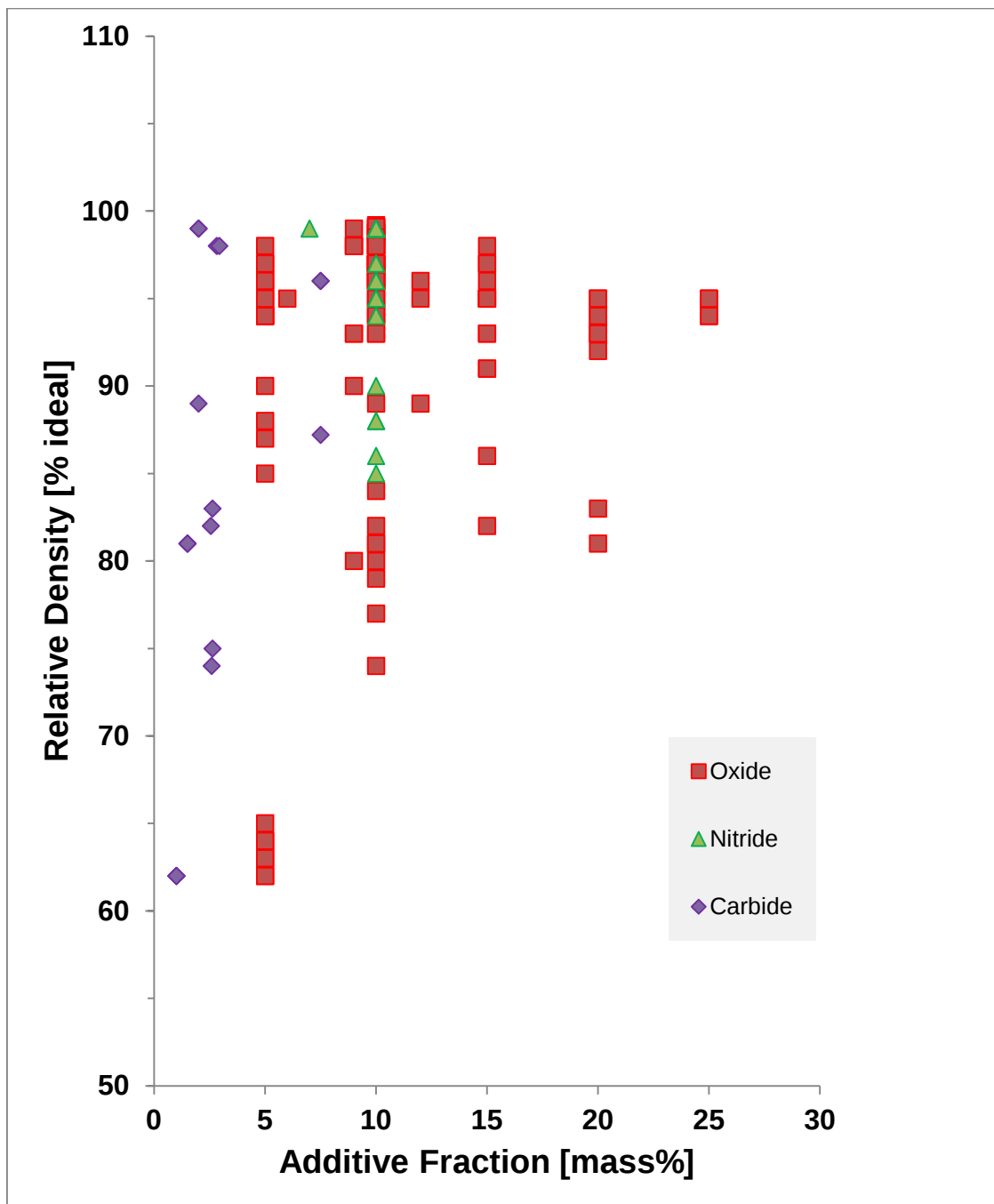


Figure 5.3: Map of relative density as a function of total additive content and additive family from the data in Tables 5.4–5.6.

The thermal conductivity in Figure 5.4 appears to increase with increasing sintering temperature. A better explanation is that the conductivity increases with relative density, which tends to increase with temperature and pressure, as the conductivity is highly

susceptible to microstructural defects, pores in particular. The rare earth oxide additives provided the most consistently high thermal conductivity, all more than $133 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, and nitrides the lowest at $85 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ or less. The thermal conductivity decreased with increasing additive content in Figure 5.5, as increasing additive content tends to promote secondary phases that decrease the mean free paths of phonons in SiC. All the rare earth oxide and other oxide compositions were hot pressed in Figures 5.4 and 5.5, whereas all the nitrides were GPS or pressureless sintered. None of the no-additive or carbide papers cited in Chapter 5 or 6 provided thermal conductivity data.

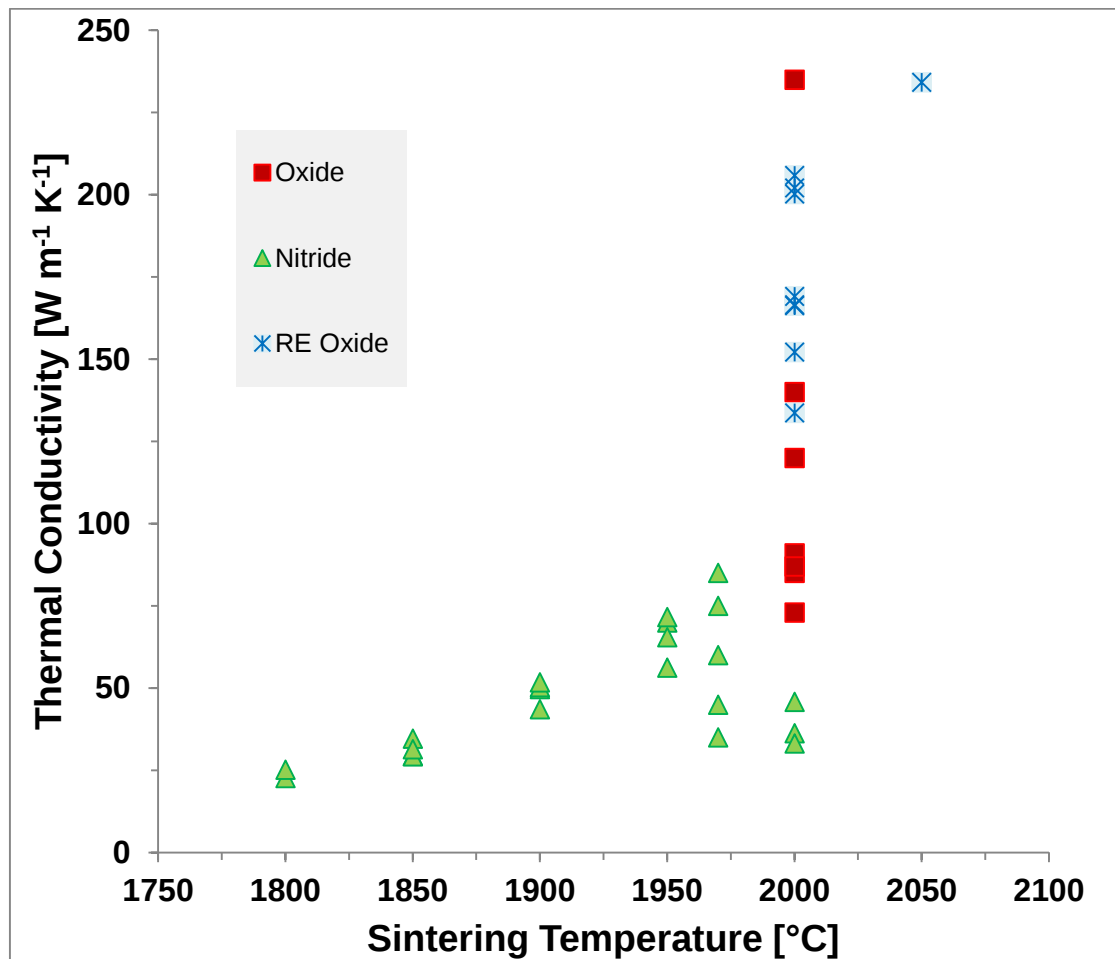


Figure 5.4: Map of thermal conductivity of SiC as a function of sintering temperature and additive family from the papers cited under the Thermal Conductivity heading.

Due to the small pool of data for mechanical properties of PS SiC, these data were combined with the pressure-assisted SiC and are graphically presented in Chapter 6, except for the high-temperature strength of pressureless-sintered SiC in Table 5.3. Similarly, the combined thermal conductivity data are presented here in Figures 5.4 and 5.5.

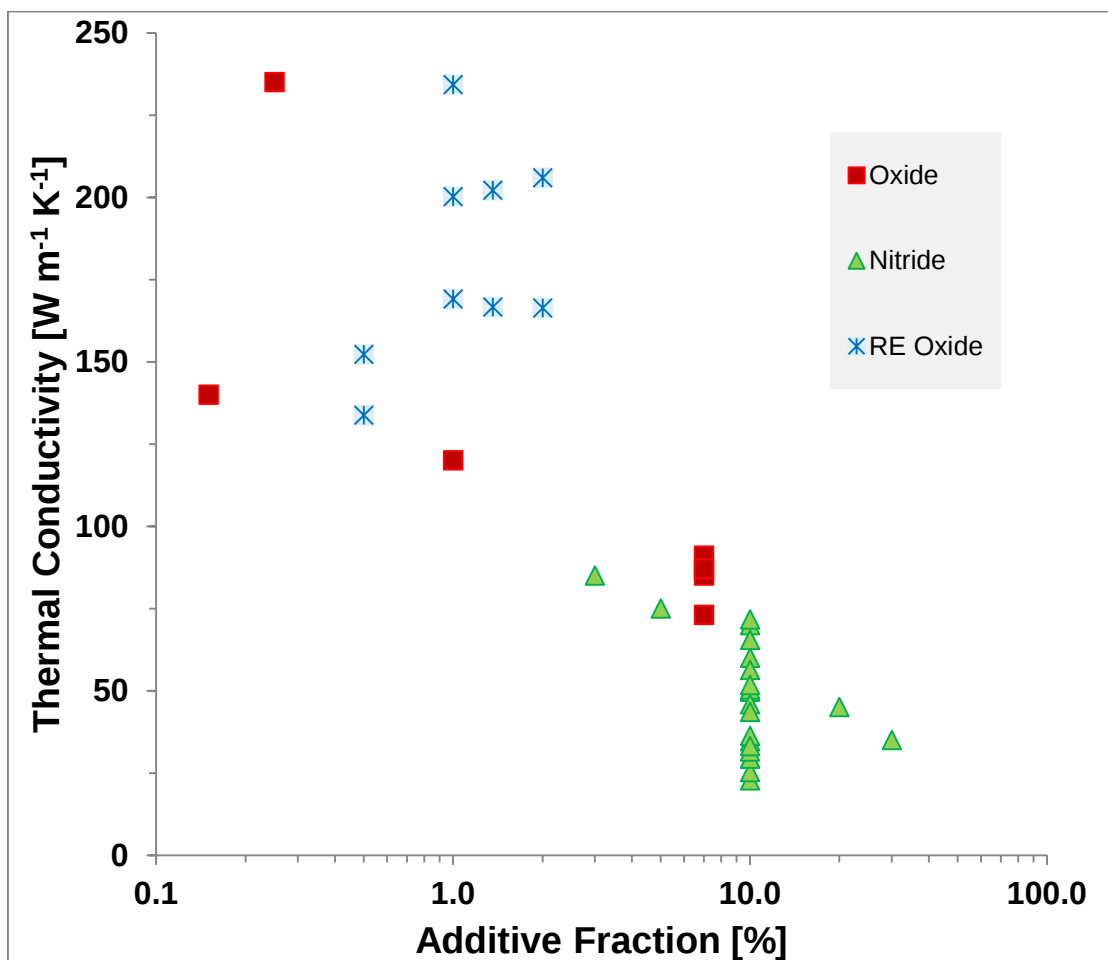


Figure 5.5: Map of thermal conductivity as a function of total additive content and additive family from the papers cited under the Thermal Conductivity heading.

Selections from the best properties from each additive group are highlighted in Table 5.7. Several other compositions and processes besides those given in Table 5.7 achieved approximately 100% densification, for example. Corrosion data were limited and not suitable for a quantitative comparison. In each citation in Table 5.7, the results were

somewhat dependent upon the measurement method, such as 3-pt vs. 4-pt bending for strength, indentation vs. fracture mechanics for toughness, and ISE for hardness. The citations in Table 5.7 were also selected for their high density, typically >95%, and low additive amounts.

Table 5.7: Selected property values in the papers cited in Tables 5.4–5.6.

Objective	Value	Additives	Process	End Note
Density	>99%	1.0% or more B ₄ C + 1% C	2050°C, 15 min, vacuum	Datta ¹¹³
		6% Al ₂ O ₃ + 4% Y ₂ O ₃	2000°C, 1 hr	S.K. Lee ⁸⁸
		10 vol% (60 mol% AlN + 40 mol% Y ₂ O ₃)	GPS in 10-MPa N ₂ , 2010°C, 60 min, anneal	Rixecker ³⁶
Strength [MPa]	631	0.29% Al, 0.1% B, 2.48% C, 0.43% SiO ₂ , 0.035% Fe	2100°C, 1 hr, Ar	Tanaka ⁵⁰
	640	5% (62.5 mass% Al ₂ O ₃ : 37.5% Y ₂ O ₃)	1950°C, 1 hr, Ar	She ⁴⁴
	564	10 vol% (3 AlN : 2 Y ₂ O ₃)	GPS in 0.3-MPa N ₂ , 1980°C, 30 min	Keppeler ⁴⁷
		10 vol% (60 mol% AlN + 40 mol% Y ₂ O ₃)	GPS in 10-MPa N ₂ , 1950°C, 60 min	Rixecker ³⁵
Fracture toughness [MPa m ^{0.5}]	4.1	7.5% Al ₃ BC ₃	2050°C, 2 hr, Ar	S.H. Lee ⁴⁰
	8.3	6% Al ₂ O ₃ + 4% Y ₂ O ₃	2000°C, 5 hr	S.K. Lee ⁸⁸
	6.5	10 vol% (60 mol% AlN + 40 mol% Y ₂ O ₃)	GPS in 10-MPa N ₂ , 1980°C, 60 min	Rixecker ³⁶
Vickers hardness [GPa]	22.0	7.5% Al ₃ BC ₃	2000°C, 2 hr, Ar	S.H. Lee ⁴⁰
	26	10% (42 Al ₂ O ₃ : 44 Y ₂ O ₃ : 14 MgO)	1950°C, 2 hr, Ar, SiC mould powder	Gubernat ⁴⁵
	15.1	5% AlN + 5% Y ₂ O ₃	1950°C, 2 hr, Ar	Onbattuvelli ⁴²
Thermal conductivity [W m ⁻¹ K ⁻¹]	235	0.25% Al ₂ O ₃	HP, 2000°C, 5 hr, 49 MPa, Ar	Kinoshita ⁷⁷
	234	1 vol% (1 mol Y ₂ O ₃ : 1 mol Sc ₂ O ₃)	HP, 2050°C, 6 hr, 40 MPa, N ₂	Y.-W. Kim ⁸¹
	85	3 vol% (4 mol YAG : 1 mol AlN)	GPS in 0.1-MPa Ar, 1970°C, 30 min + GPS in 10-MPa Ar, 10 min	Sigl ⁷⁸

5.8 Summary

- Additives that form YAG, YAM or YAP at SiC grain boundaries were very reliable densification aids. YAG reduced the bulk thermal conductivity of SiC.

- Powder treatments such as sol-gel that more uniformly distribute additives on SiC particles were a very effective way to improve microstructural homogeneity and consistency.
- Nitride additives consistently yielded the best densification of SiC, mostly due to LPS enabled by Y-Al-O phases. These same phases enabled LPS in many oxide additive systems as well.
- Carbide additives required the highest temperatures to densify, but also the lowest additive contents. The reason for both is that SSS was the usual mechanism for densification by carbide additives.
- The additives increased the self-diffusion in SiC, reactively wetted the passivated SiC grains, and enabled LPS or SSS and pressureless densification.
- The toughness was enhanced by partial $\beta \rightarrow \alpha$ transformation, which was aided by α -SiC seeds or annealing.
- MAT showed no advantages for SiC, but might improve with further study.
- N₂ enhanced or suppressed SiC sintering, depending on additives. N₂ supplanted cover mix during sintering when nitride additives were used.
- Carbon as an additive came from several sources in addition to added powder, including residual free carbon from the Acheson process, organic binder and phenolic resin.
- No one additive group or sintering process resulted in all the best properties, but 99% densification, 600-MPa bending strength, 500-MPa strength at 1500°C, 4-MPa m^{0.5} toughness, 22-GPa hardness, 80-W m⁻¹ K⁻¹ thermal conductivity or high corrosion resistance in SiC were achievable by multiple methods of pressureless sintering.

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CHAPTER 6

6 The Effects of Sintering Additives on the Properties of Silicon Carbide, Part II: Pressure-Assisted Sintering

Abstract

Silicon carbide is the most important and versatile non-oxide ceramic. SiC is useful for its strength, even at high temperature, hardness, corrosion and abrasion resistance, reflectance and many other properties. SiC is difficult to fabricate, but the obstacles can be mitigated with sintering additives. The additives enhance densification, lower the sintering temperature or time, enable fabrication techniques, or improve the properties of SiC. Misused additives can have the opposite effect, especially a reduction in properties. This paper reviews the many additives used with pressure-assisted SiC, and assesses their efficacy. The first paper reviews the effects of additives on pressureless-sintered SiC.

Boris Badenov: “Ah, it’s good to be back on campus!”

Natasha Fatale: “Boris, you went to college? Penn State?”

Boris: “No, state pen.” — television’s *The Rocky and Bullwinkle Show*.

6.1 Introduction

The first paper in this set reviewed the additives, properties and processes used to fabricate silicon carbide ceramics, and a body of papers on SiC sintered without external pressure. This second paper continues with a review of papers on SiC sintered with external pressure, including hot pressing (HP), hot isostatic pressing (HIP) and spark plasma sintering (SPS). SiC without additives can be densified by pressure-assisted sintering, and many of these are compared to SiC with additives.

The purpose of this paper is to compile, examine and summarize the many sintering additives that have been investigated since the 1970s to densify, with pressure assistance, sintered SiC. The selection and processing of additives to facilitate the densification of a ceramic is an important aspect of grain boundary engineering.

A list of abbreviations and acronyms used in this paper is given in the pretext of this thesis. In the text and tables, the additive compositions expressed as percentages are in mass%, unless otherwise specified. The properties such as strength and toughness are at room temperature, unless otherwise specified. The densities are expressed as percent of ideal density.

6.2 Processing of SiC

6.2.1 Hot Pressing

Uniaxial hot pressing (HP), or pressure sintering, combines mechanical energy with thermal energy to achieve densification in a powder compact.¹ Ceramic compacts are compressed between dies during sintering. The particles are also subjected to shear stresses in uniaxial compression. The dies must withstand high stresses at high temperatures, while being inert to the powders and gases present. Several compacts can be compressed simultaneously in series, but uniform cross-section shape and area are

required. Graphite dies are commonly used with SiC powders, but must be protected from oxygen by an inert gas, reducing gas or vacuum. Compacts are usually separated from the dies by foil inserts or loose powders. The degree of densification can be estimated in real-time by the movement of the cylinder that compresses the dies on the compacts.

Hot pressing is characterized by three stages. Particles are rearranged into closer packing in the first stage. Viscous and plastic flow occur in the second stage. Mass transport by diffusion happens in the third stage. Creep may be a factor, also. The heat is usually supplied by electric resistance heating elements, but can also come from a gas flame, induction coil, microwave magnetron or other sources.

Hot pressing enables lower temperatures, shorter times and coarser powders compared to pressureless sintering; densification with little or no additive; near-zero porosity; and densification of powders that are difficult to sinter. The disadvantages of hot pressing include expensive tooling that wears out quickly, limited shapes, preferred orientation and slow production rates. Near-net shape forming is usually an objective of the die design, to minimize post-sinter machining.

6.2.2 Hot Isostatic Pressing

Hot isostatic pressing (HIP) is a special case of hot pressing where the pressure is uniform in all directions.² A green powder compact is sealed in an evacuated borosilicate glass envelope in which the glass transition temperature (T_g) is just below the sintering temperature. Metal envelopes that creep just below the sintering temperature may also be used. The envelope may be lined with a separation powder such as BN, or foil, to prevent reaction with the SiC. The envelope may be applied as a powder coating, to be consolidated upon heating. The semi-fluid glass or metal is omnidirectionally compressed by argon at 100-320 MPa inside a high-pressure furnace. HIP permits complex shapes of varying cross-section shapes and sizes that cannot be formed by uniaxial hot pressing. The HIP temperature is often as much as 300K below pressureless sintering.

Alternatively, the envelope can be eschewed if the compact is first pressureless-sintered to closed porosity, in a process called cladless HIP or sinter HIP. At lower

pressures, sinter HIP becomes similar to gas pressure sintering (GPS), except that GPS begins with a green body.

6.2.3 Spark Plasma Sintering

Spark plasma sintering (SPS) originated with resistance sintering circa 1906.³ Plasma pressure compaction (P²C®, a trademark of Materials Modification Inc., Fairfax, VA, USA), a version of SPS, was invented by Yoo et al.⁴ in 1999, as a means of rapidly bonding and densifying powder compacts. SPS passes an electric current as high as 20 kA through a powder compact between uniaxial compression dies in two steps. The dies are part of the current path, especially when the powder has low electrical conductivity. Pulsed current and high shear in the first step cause electrical discharge plasma and agglomerate-breaking abrasion that evaporate surface oxides and contaminants, and rearrange the particles. The shear stresses may be enhanced by a rotating die. High pressure and steady current in the second step cause resistance heating and neck formation at contact points between particles. The second step is similar to hot pressing, except the thermal energy comes from electrical resistance within the compact rather than an external heating element. One advantage of SPS is that it does in minutes what takes conventional sintering hours to complete. The pressure reduces the need for binders and additives, and minimizes porosity as it does in hot pressing and HIP. The speed of the process concentrates the heat on the particle surfaces and reduces the likelihood of grain growth.^{5,6}

SPS is essentially the same as plasma pressure consolidation, plasma pressure compaction, P²C, plasma activated sintering, field-assisted sintering technique (FAST)⁷, pulsed electric current sintering (PECS) and instrumented pulse electrodischarge consolidation.⁸ The multiple names are due in part to the controversy over the actual presence of plasma, which has not been verified.⁹ Bothara et al.^{10,11,12}, Guillard et al.¹³, S.H. Lee et al.¹⁴, Hotta and Hojo⁹, J.S. Lee et al.^{15,16}, Lara et al.¹⁷ and Lomello et al.¹⁸ used SPS to densify SiC.

6.2.4 Gas Pressure Sintering

Gas pressure sintering (GPS), also known as overpressure, is somewhat of a hybrid of pressureless and pressure-assisted sintering. In GPS, the dies are removed from the compact before sintering, as they are in pressureless sintering. At the same time, the external hydrostatic gas pressure in GPS can be comparable to the pressure of HP, HIP or SPS.

In this thesis, the distinction between pressureless and pressure-assisted sintering or between families of additives is somewhat arbitrary, and certainly not sharply delineated.

6.3 Pressure-Assisted SiC

The additives are somewhat arbitrarily divided into four major groups: (1.) no additives; (2.) carbon, boron, carbide, silicide and metal additives, or simply carbide additives; (3.) oxide additives; and (4.) nitride additives. In Figures 6.1 – 6.10, the oxide additives are divided into two subsets, one with rare earth oxide additives and one without, to illustrate the advantages and disadvantages of rare earth oxides as opposed to the more conventional oxide additives dominated by Al_2O_3 , Y_2O_3 and MgO . The nitride additive systems usually contain oxides as well.

6.3.1 No Additives

SiC was considered notoriously difficult to sinter from the time of Acheson until the 1970s, due largely to the oxide layer on the surface of fine SiC particles and the slow diffusion associated with directional covalent Si-C bonding.¹⁹ Even nanoscale pure SiC cannot be fully densified without some combination of additives, applied pressure and temperatures above $\sim 2000^\circ\text{C}$.²⁰⁵⁰ Hot pressed, HIP and SPS SiC compositions without additives are summarized in Table 6.1.

Nadeau²¹ demonstrated the sensitivity of the density of hot pressed SiC without additives to compaction pressure. The green density was 90% under a cold pressure of 30 kbar (3 GPa), which increased to 98% at 1500°C . The green densification was attributed to

particle crushing and sliding. Self-bonding of the SiC, indicated by an order-of-magnitude decrease in electrical resistivity, was complete after 60 min at 2500°C.

Bind and Biggers¹⁹ were unable to densify hot-pressed SiC without additives, at 1950°C and 3000 lb/in² (20.7 MPa) for 15 min in vacuum. They were more successful with B₄C, B and Al₂O₃ additives, described in subsequent sections.

Guillard et al.¹³ observed different densities and microstructures in SPS without additives, depending on when the pressure was applied. In the first case, designated SPS-1 in Table 6.1, 75 MPa was applied at the maximum temperature. In the second case, designated SPS-2 in Table 6.1, the same pressure was applied at 1000°C and maintained throughout the remainder of the sintering cycle. The former yielded better densification and grain size control than the latter.

Liu et al.²² achieved impressive mechanical properties with β -SiC powder, synthesized by SHS and densified by SPS in N₂. The density was 99%, the hardness was >22 GPa, the bending strength was 715 MPa, and the toughness was >8 MPa·m^{0.5}. Details of the mechanical test methods were not specified.

Mao-lin et al.²³ hot pressed nano β -SiC without additives at high pressures, in a comparison described below under Oxide Additives in §6.3.3

Lara et al.¹⁷ varied the SPS temperature, pressure and holding time to determine their effects on density and grain size of β -SiC without additives, in a vacuum. The 30-nm SiC powder, synthesized by plasma-enhanced CVD, was de-agglomerated to a crystallite size of 10 nm in a centrifugal ball mill. A maximum 98% density was achieved at 2100°C and 70 MPa for 30 min, but the grain size grew from 30 nm to 2.4 μ m. Uncontrolled grain growth was observed in some fully dense nanostructures. High pressure, 150 MPa, was needed to maintain nanoscale grain size. Sintering temperatures $\geq 1800^\circ\text{C}$ were needed for densities $\geq 90\%$.

Lomello et al.¹⁸ synthesized 17-nm β -SiC by laser pyrolysis of silane (SiH₄) and acetylene (C₂H₂). The powder was de-agglomerated by either magnetic stirring ("MS" in Table 2) or ball milling ("BM") of an aqueous dispersion, and densified by SPS at 1700-1900°C and 73 MPa for 5 min at the sintering temperature in a 1-Pa vacuum. Full

densification, $\geq 96\%$, was reached at about 1800°C for SiC of both de-agglomeration methods. At 1900°C , the MS-SiC grain size was 240 nm, while the BM-SiC had grown to 2 μm due to the surface-activation effect of ball milling. The BM-SiC was slightly harder (~ 25 GPa) under a 10-daN load, and tougher ($5\text{--}6\text{ MPa}\cdot\text{m}^{0.5}$) than the MS-SiC. Surface oxidation of both powder types was problematic. Control of oxygen content was considered to be the key to improvement of mechanical properties of nano-SiC.

Table 6.1: Sintering parameters and properties of hot pressed silicon carbide without additives.

No.	SiC Powder	Hot Pressing Conditions	Density	End Note
			% ρ_{ideal}	Year
1	240-grit Norton Crystalon SiC	2500°C , 50 kbar (5 GPa)	99.5	21 Nadeau 1973
	1000-grit Carborundum SiC		99.5	
	Synthesized SiC		99.5	
	Crushed SiC crystals		99.5	
2	$<1\text{-}\mu\text{m } \beta$	1950°C , 3000 lb/in ² (20.7 MPa), 15 min, vacuum	73	19 Bind 1976
3	0.5- μm	SPS-1, 1750°C , 5 min, Ar	77	13 Guillard 2007
		SPS-1, 1780°C , 1 min, Ar	78	
		SPS-1, 1780°C , 5 min, Ar	76	
		SPS-1, 1780°C , 10 min, Ar	88	
		SPS-1, 1850°C , 1 min, Ar	73	
		SPS-1, 1850°C , 5 min, Ar	92	
		SPS-2, 1750°C , 1 min, Ar	69	
		SPS-2, 1750°C , 5 min, Ar	69	
		SPS-2, 1750°C , 10 min, Ar	71	
		SPS-2, 1780°C , 1 min, Ar	72	
		SPS-2, 1780°C , 5 min, Ar	70	
		SPS-2, 1780°C , 10 min, Ar	73	
		SPS-2, 1850°C , 1 min, Ar	76	
		SPS-2, 1850°C , 5 min, Ar	75	
		SPS-2, 1850°C , 10 min, Ar	80	
4	SHS 500-nm α	SPS, 1650°C , N ₂	94	22 Liu 2009
	SHS 120-nm β		99	
5	20-nm β	1100°C , 30 min, 4.5 GPa	91	23 Mao-lin 2010
		1200°C , 30 min, 4.0 GPa	92	
		1200°C , 30 min, 4.25 GPa	93	
		1200°C , 30 min, 4.4 GPa	93	

No.	SiC Powder	Hot Pressing Conditions	Density	End Note
			% ρ_{ideal}	Year
		1200°C, 20 min, 4.5 GPa	94	
		1200°C, 25 min, 4.5 GPa	95	
		1200°C, 30 min, 4.5 GPa	93-95	
		1200°C, 35 min, 4.5 GPa	96	
		1300°C, 30 min, 4.5 GPa	95	
6	30-nm PECVD β	SPS, 1650°C, 5 min, 150 MPa	78.0	17 Lara 2012
		SPS, 1800°C, 10 min, 70 MPa	80.0	
		SPS, 1800°C, 5 min, 100 MPa	87.9	
		SPS, 1800°C, 10 min, 100 MPa	87.9	
		SPS, 1800°C, 5 min, 150 MPa	90.0	
		SPS, 1850°C, 30 min, 70 MPa	85.1	
		SPS, 1875°C, 30 min, 70 MPa	85.4	
		SPS, 1900°C, 15 min, 70 MPa	86.6	
		SPS, 1900°C, 30 min, 70 MPa	87.3	
		SPS, 1900°C, 5 min, 100 MPa	90.7	
		SPS, 1900°C, 15 min, 100 MPa	92.0	
		SPS, 1900°C, 5 min, 150 MPa	91.0	
		SPS, 1950°C, 30 min, 70 MPa	88.7	
		SPS, 1950°C, 10 min, 100 MPa	91.6	
		SPS, 1950°C, 5 min, 150 MPa	91	
		SPS, 1950°C, 7 min, 150 MPa	94.0	
		SPS, 2000°C, 30 min, 70 MPa	89.2	
		SPS, 2050°C, 30 min, 70 MPa	93.4	
		SPS, 2075°C, 30 min, 70 MPa	93.2	
		SPS, 2100°C, 30 min, 70 MPa	98.0	
		SPS, 2100°C, 5 min, 100 MPa	91.0	
		SPS, 2100°C, 5 min, 150 MPa	92.0	
		SPS, 2150°C, 3 min, 100 MPa	90.0	
		SPS, 2200°C, 0 min, 100 MPa	89.0	
		SPS, 2200°C, 0 min, 100 MPa	90.0	
		SPS, 2200°C, 3 min, 100 MPa	94.3	
		SPS, 2200°C, 3 min, 150 MPa	94.0	
7	16.6-nm β	Magnetically stirred, SPS, 1700°C, 5 min, 73 MPa, vacuum	86	18 Lomello 2012
		Ball-milled, SPS, 1700°C, 5 min, 73 MPa, vacuum	85	
		Magnetically stirred, SPS, 1750°C, 5 min, 73 MPa, vacuum	91	
		Ball-milled, SPS, 1750°C, 5 min, 73 MPa, vacuum	91	
		Magnetically stirred, SPS, 1800°C, 5 min, 73 MPa, vacuum	94	
		Ball-milled, SPS, 1800°C, 5 min, 73 MPa, vacuum	95	
		Magnetically stirred, SPS, 1850°C, 5 min, 73 MPa, vacuum	95	
		Ball-milled, SPS, 1850°C, 5 min, 73 MPa, vacuum	95	
		Magnetically stirred, SPS, 1900°C, 5 min, 73 MPa, vacuum	96	
		Ball-milled, SPS, 1900°C, 5 min, 73 MPa, vacuum	96	

6.3.2 Carbon, Boron, Metal, Carbide and Silicide Additives

Bind and Biggers¹⁹ hot-pressed β -SiC with 1% B₄C or 0.6% B additive, at 3000 lb/in² (20.7 MPa) and various temperatures and times in vacuum, in Table 6.2. The submicron SiC powder was synthesized from a gas-phase reaction. SiC + 1% B₄C was nearly 100% dense after 3 min at 1950°C. A geometrical model for the sintering of two spheres, with paraboloids corresponding to the chemical potentials during sintering and hot pressing, was derived for SiC with additives. The difficulty in sintering SiC was attributed to the granulometry of its powder, rather than thermodynamic limits.

Prochazka's²⁴ landmark 1976 paper was an investigation of various forms of boron and carbon, adding up to about 1%, as additives to hot-pressed β -SiC. Densification above 92% was achieved with several compositions at 2040°C, including 0.50% C + 0.24% B, $\geq 0.5\%$ amorphous boron, 1.0% crystalline boron, $\geq 0.4\%$ B from B₄C, and $\geq 0.25\%$ C from polymethylphenylene + 0.36% B. LiBH₄ and boric acid (H₃BO₃) additives, both contributing 1.0% B, did not result in full densification, nor did $\geq 0.25\%$ C from 190-m²/gm carbon black + 0.36% B. Transformation of β -SiC to α -SiC, mostly the 6H polytype, was observed in several cases, and the tabular 6H crystals had a tendency toward exaggerated grain growth. The mechanism of boron's contribution to sintering was its lowering of the grain boundary to surface energy ratio, γ_{gb}/γ_{sv} , by segregating to the grain boundaries. The mechanism of carbon was its reaction with and removal of SiO₂ and Si from the SiC particle surfaces to increase γ_{sv} above ~ 1800 erg/cm² at 2000°C.

In a series of papers, MoberlyChan et al.^{25,26} hot pressed β -SiC with Al, B and C, which they termed ABC-SiC, and compared its mechanical properties to a commercial SiC. The carbon source was a wax binder, half of which evaporated during heat-up. The Al additive stabilized the 4H rather than 6H polytype in the $\beta \rightarrow \alpha$ transformation. The ABC-SiC had more than thrice the toughness (9 MPa·m^{0.5}) of the commercial SiC and greater strength (650 MPa), too, owing to crack bridging, a large aspect ratio of the 4H grains and interlocking α -SiC plates. The structures and compositions of the grain boundary regions were studied extensively via TEM and other instruments. The additives crystallized as

epitaxially-oriented ternary precipitates, e.g., $\text{Al}_8\text{B}_4\text{C}_7$ and Al_4CO_4 , at isolated triple points to increase toughness and strength. A weak ~ 1 -nm amorphous layer was observed between the SiC grains and precipitates, which enhanced toughening by directing fractures onto a longer intergranular path instead of a shorter transgranular path.

Shinoda et al.²⁷ synthesized 30-nm β -SiC particles from a gas-phase reaction. The powder, with 3.5% free carbon, was HIP at 980 MPa and 1600°C for 1 hr with and without 1% amorphous boron as the additive. Both compositions were 97.1% dense, but the B-doped particles grew to 200 nm, while the undoped grain size remained near 30 nm. The flow stresses, i.e., ease of HIP, of the B-doped SiC were one-third lower at 1700 and 1800°C than the undoped SiC but about the same at 1600°C. A second B-doped specimen was hot pressed at 40 MPa and 1900°C, with a final grain size of 0.8 μm . The flow stresses of the B-doped 200-nm SiC were one-third lower than the 0.8- μm SiC. The conclusion was that both boron segregation near the grain boundaries and grain refinement led to improved densification of SiC by HIP.

Ray et al.²⁸ investigated SiC hot pressed with C, B_4C and Al additives in many of their 26 compositions. The three no-nitride results are summarized in Table 6.2, and the other 23 below under Nitride Additives and Table 6.4. Al, B and C reduced the onset temperature of densification and increased the diffusion of dopants in SiC, whereas nitrides had the opposite effect. The authors were able to control the amounts of polytypes, grain size and shape, grain boundary chemistry, toughness, hardness and corrosion resistance through the choice of additives. Composition B, with 1% C + 0.25% B_4C , was the hardest at $\text{HV} = 26.9 \pm 1.0$ GPa. Composition A, with 1.65% Al, was the toughest at $K_{\text{Ic}} = 4.7 \pm 0.3$ $\text{MPa m}^{0.5}$. Composition E, with 2% Al + 1% C + 0.25% B_4C , had the most grain growth with a grain size of 7.8 ± 1.0 μm . All three were more than 50% 6H polytype, and all were estimated to be more than 99% dense.

Ternary compound additives of Al, B and C suppressed grain growth in SPS and PS α -SiC, in a paper by S.H. Lee et al.¹⁴ Al_3BC_3 and $\text{Al}_8\text{B}_4\text{C}_7$ densified SiC as well as conventional Al-B-C additives, but did not oxidize when exposed to air. LPS was the sintering mechanism, and the liquid crystallized upon cooling. Grain growth suppression and a

crack-deflection toughening effect by Al_3BC_3 were observed. The hardness, spanning 21–26 GPa, was independent of the additive content.

J.S. Lee et al.¹⁵ densified β -SiC with 10% Al_4SiC_4 by hot pressing at 60 MPa and 1700°C in a vacuum. The SiC began to consolidate as a result of the Al_4SiC_4 decomposing to SiC, C and Al vapor at 1450°C. Some of the Al dissolved near the SiC grain boundaries and functioned as a diffusion activator, while the carbon reduced the SiO_2 on the SiC grains. Densification was also achieved with 8% Al_4C_3 , but with more porosity even though it had an equivalent Al content.

In a second paper, J.S. Lee et al.¹⁶ densified 30-nm β -SiC with 10% Al_4SiC_4 by SPS at 120 MPa and 1450–1500°C for 30 min in a vacuum. The SiC transformed completely from cubic to hexagonal ($\beta \rightarrow \alpha$) above 1550°C, with a grain size of about 70 nm. Lattice diffusion and LPS were not important in the densification of SiC with Al_4SiC_4 . Grain-boundary diffusion by Al-based segregants was believed to be the major densification mechanism.

Noviyanto and Yoon²⁹, in a paper detailed below under Oxide Additives in §6.3.3, also attempted to hot press 52-nm β -SiC with 5% Si, B_4C , Cr_3C_2 , TiC, VC, WC, FeSi, Mg_2Si , WSi_2 , Al + Fe, Fe + Si and Si + C, at 20 MPa and 1750°C for 2 hr. Densification of the non-oxide additives ranged from about 49 to 75% of ideal density.

Table 6.2: Additives of carbon, carbides, boron, silicon and metals; sintering parameters and properties of hot pressed silicon carbide.

No.	SiC Powder	Additive Composition	Hot Pressing Conditions	Density	End Note
		mass%		% ρ_{ideal}	
1	<1- μm β	1% B_4C	1750°C, 21 MPa, 12 min, vacuum	88	19 Bind 1976
			1800°C, 21 MPa, 12 min, vacuum	90	
			1850°C, 21 MPa, 7 min, vacuum	95	
			1950°C, 21 MPa, 3 min, vacuum	100	
		0.6% B	1850°C, 21 MPa, 15 min, vacuum	88	
			1900°C, 21 MPa, 15 min, vacuum	93	

No.	SiC Powder	Additive Composition	Hot Pressing Conditions	Density	End Note
		mass%		% ρ_{ideal}	Year
			2100°C, 21 MPa, 15 min, vacuum	98	
2	β (3C)	0.50% C + 0.00% B	2040°C	57	24 Prochazka 1976
		0.50% C + 0.06% B		60	
		0.50% C + 0.12% B		69	
		0.50% C + 0.24% B		93	
		0.50% C + 0.36% B		96	
		0.5% B (amorphous)		94	
		1.0% B (amorphous)		96	
		1.0% B (crystalline)		95	
		0.4% B (as B ₄ C)		94	
		0.8% B (as B ₄ C)		95	
		1.0% B (as LiBH ₄)		89	
		1.0% B (as H ₃ BO ₃)		63	
		0.00% C + 0.36% B		62	
		0.12% C + 0.36% B		81	
		0.25% C + 0.36% B		96	
		0.50% C + 0.36% B		96	
		0.80% C + 0.36% B		96	
		0.25% C + 0.36% B		83	
		0.75% C + 0.36% B		87	
		1.50% C + 0.36% B		86	
3	β (3C)	1-3% Al + 0.6% B + 4% C	1600°C, 50 MPa	99	25 Moberly-Chan 1998
4	β (3C)	3% Al + 1% B + 2% C	1650°C, 50 MPa	98	26 Moberly-Chan 1998
5	30-nm β	1% B + 3.5% C	HIP, 1600°C, 980 MPa, 1 hr	97.1	27 Shinoda 1999
		3.5% C		97.1	
		1% B + 3.5% C	1900°C, 40 MPa, 1 hr	-	
6	0.55- μ m α	(A.) 1.65% Al	2100°C, 1 hr, 28 MPa, Ar	>99	28 Ray 2008
		(B.) 1% C + 0.25% B ₄ C		>99	
		(E.) 2% Al + 1% C + 0.25% B ₄ C		>99	
7	0.55- μ m α (6H)	3% Al ₃ BC ₃	SPS, 1500°C, 10 min, 40 MPa, 1900°C, 3 min	97	14 S.H. Lee 2009
		5% Al ₃ BC ₃		98	
		7.5% Al ₃ BC ₃		98	
		10% Al ₃ BC ₃		98	
		10% Al ₃ BC ₃	SPS, 1900°C, 40 MPa, 3 min	96	
		10% (3 mol% Al + 1 mol% B + 3 mol% C)	SPS, 1500°C, 10 min, 40 MPa, 1900°C, 3 min	97	
		10% (3 mol% Al + 1 mol% B + 3 mol% C)	SPS, 1900°C, 40 MPa, 3 min	97	
		1% Al ₈ B ₄ C ₇	SPS, 1500°C, 10 min, 40 MPa, 1900°C, 3 min	96	
		1% Al ₈ B ₄ C ₇	SPS, 1900°C, 40 MPa, 3 min	96	
8	30-nm β	10% Al ₄ SiC ₄		99.42	15

No.	SiC Powder	Additive Composition	Hot Pressing Conditions	Density	End Note
		mass%		% ρ_{ideal}	Year
		2% Al ₄ SiC ₄	1700°C, 2 hr, 60 MPa, vacuum, furnace-cooled	80.89	J.S. Lee 2009
		7.82% (Al ₄ C ₃)		96.77	
		11.08% (Al ₂ O ₃)		87.18	
9	30-nm β	2% Al ₄ SiC ₄	SPS, 1500°C, 30 min, 120 MPa, vacuum	66.32	16 J.S. Lee 2011
		10% Al ₄ SiC ₄	SPS, 1400°C, 30 min, 120 MPa, vacuum	75	
			SPS, 1450°C, 30 min, 120 MPa, vacuum	95	
			SPS, 1500°C, 30 min, 120 MPa, vacuum	98	
			SPS, 1550°C, 30 min, 120 MPa, vacuum	99	
			SPS, 1600°C, 30 min, 120 MPa, vacuum	99	
			SPS, 1650°C, 30 min, 120 MPa, vacuum	99	
10	52-nm β	5% Si	1750°C, 2 hr, 20 MPa, Ar	57.78	29 Noviyanto 2012
		5% B ₄ C		75.35	
		5% Cr ₃ C ₂		51.45	
		5% TiC		59.73	
		5% VC		49.07	
		5% WC		57.21	
		5% FeSi		61.20	
		5% Mg ₂ Si		66.10	
		5% WSi ₂		61.28	
		5% (40% Al + 60% Fe)		60.04	
		5% (66% Fe + 34% Si)		59.03	
		5% (97% Si + 3% C)		57.35	

6.3.3 Oxide Additives

Bind and Biggers¹⁹ hot-pressed submicron β -SiC with 2% Al₂O₃ additive, at 3000 lb/in² (20.7 MPa) and various temperatures and times in vacuum, in comparison to boron and B₄C additives described above under Carbide Additives. Nearly 99.9% density was achieved after 2 min at 2030°C. The Al₂O₃ reacted with the SiO₂ to form a liquid phase at the SiC particle interfaces above 1820°C, removing the diffusion barrier and making γ_{gb}/γ_{sv} more favorable. All the Oxide results are given in Table 6.3.

Foster and Thompson³⁰ investigated MgO as a sintering aid for hot pressed α -SiC, with and without Al₂O₃ and Y₂O₃. The MgO reacted with surface SiO₂ on the SiC particles to form a liquid phase that promoted densification by particle rearrangement, dissolution

and re-precipitation of SiC. Hot pressing with 6% MgO at 1900°C yielded 95% density. A 6% addition of 0.72 MgO + 0.28 Al₂O₃ at 1850°C, 0.85 MgO + 0.15 Y₂O₃ at 1850°C, or 0.67 MgO + 0.16 Al₂O₃ + 0.17 Y₂O₃ at 1800°C yielded 93%, 95% and 99% density, respectively. Some other binary and ternary additive ratios were also successful, by stabilization of the MgO and enhancement of the solution–re-precipitation liquid-phase process. BN + MgO packing powder was used in some cases to minimize MgO evaporation. MgAl₂O₄ spinel formed in some of the MgO–Al₂O₃ additives, and remained solid during sintering. Spinel, YAG and Y₄Si₂O₇N₂ were detected in many of the ternary-additive compositions. Pressureless sintering of compositions with 9% of various combinations of all three additives at 1750–2000°C did not yield any fully dense results due to volatilization.

Huang et al.³¹ compared hydrated nitrate salts of Al, Mg and Y to their oxide counterparts as SiC additives. A 9% addition of a blend of the three salts resulted in better than 97% density, when hot pressed with 0.5-μm SiC powder at 1800°C. The final equiaxed grain size was <1 μm, and toughness-enhancing crystalline YAG was present. The SiC with oxide additives had slightly lower density, but a more homogeneous distribution of Al, Mg and Y.

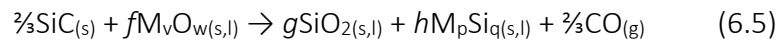
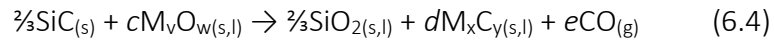
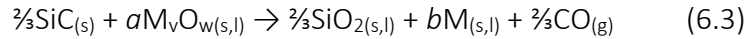
Zhou et al.³² tailored the microstructure of β-SiC with Y₂O₃ and La₂O₃ to optimize the thermal conductivity. The two oxides were maintained at a 1:1 molar ratio in each of four compositions in Table 6.3. All compositions were hot pressed at 40 MPa and 2000°C for 2 hr in Ar. A second set was subsequently annealed at 1900°C for 4 hr in Ar. The secondary phases were Y₂Si₂O₇, Y₂SiO₅ and La₂SiO₅. The density and thermal conductivity exceeded 94% and 200 W·m⁻¹·K⁻¹, respectively, after annealing, when the SiC contained at least 0.5 mol% of each additive. The additives improved the thermal conductivity by gettering the oxygen from the SiC surfaces and lattices, and increasing the contiguity of the SiC grains.

Can et al.³³ examined the intergranular phases and densification paths of α-SiC sintered with 10% Y₂O₃ + Al₂O₃ in various ratios, by hot pressing in Table 6.3 and GPS in Chapter 5 of this thesis. Silica-rich glass and Y₂Si₂O₇ or Y₂SiO₅ were detected at the grain boundaries in most of the hot pressed specimens, while YAG, YAM or YAP was detected in

most of the GPS specimens. Evaporation of SiO₂ was strong in GPS at 1500-1800°C, which prevented the two yttrium silicate phases from precipitating and slowed the densification rate compared to HP.

Mao-lin et al.²³ hot pressed nano β-SiC with and without 4% γ-Al₂O₃ additive at high pressures comparable to those used by Nadeau²¹. At a pressure of 4.0-4.5 GPa, the SiC with additive was densified at 1200°C in as little as 15 min. The pure SiC had a lower density, 96% of ideal compared to ~100%, but similar microstructure and hardness under a 1.96-N load.

Noviyanto and Yoon²⁹ synthesized 52-nm β-SiC by plasma CVD. The SiC was hot pressed at 1750°C and 20 MPa for 2 hr in Ar, with a variety of oxide additives, for nuclear applications. All compositions contained 5% additives. The goal, as a complement to Negita's paper³⁴, was to evaluate the thermodynamic possibility of reduction of oxide additives to metals or silicides, as well as reactions that oxidize SiC and form a metal carbide, in the range of 1700-1800°C. The silica passivation layer on the SiC particles was measured by transmission electron microscope (TEM) on the order of 1.7 nm thick. The three SiC decompositions considered were Reactions 6.3, 6.4 and 6.5:



Fe₂O₃, TiO₂ and WO₃ additives resulted in carbide or silicide precipitates as expected in Reactions 6.4 and 6.5, and densified to <62% of ideal density. The Al₂O₃, MgO and Y₂O₃ additives remained as oxides in the sintered SiC. The MgO reacted with the SiO₂ to form MgSiO₃, but the SiC was only 76% dense. SiC sintered with mixed oxides additives of 5% Al₂O₃ + V₂O₅, Cr₂O₃ + V₂O₅, Fe₂O₃ + V₂O₅, TiO₂ + V₂O₅, FeO + V₂O₅ + SiO₂ and TiO₂ + V₂O₅ + SiO₂ were all <65% dense. SiC with Al₂O₃, Al₂O₃ + MgO, Al₂O₃ + Y₂O₃, and Al₂O₃ + MgO + Y₂O₃ all densified to >96%.

Zhan et al.³⁵ retarded the β→α transformation and grain growth in Al₂O₃-Y₂O₃-CaO doped β-SiC by applying uniaxial pressure during annealing. A starting powder of 87% 90-nm β-SiC + 3% α-SiC + 7% Al₂O₃ + 2% Y₂O₃ + CaCO₃ was hot pressed at 25 MPa at 1750°C

for 40 min in argon. The CaCO_3 decomposed to 1% CaO during sintering. Two sets of specimens were annealed 4 hr at 1900°C in 0.1-MPa Ar. One set was hot pressed at 25 MPa during annealing, while the other set was unconstrained. About one-fourth of the β -SiC that was in compression during annealing transformed to one or more polytypes of α -SiC, while more than half transformed in the unconstrained specimens. The annealing under pressure retarded the $\beta \rightarrow \alpha$ transformation by decreasing the dissolution rate of the SiC at α - β interface, segregating Y to the grain boundaries, and reducing the overall mass transport rate.

Table 6.3: Oxides additives, sintering parameters and properties of hot pressed silicon carbide.

No.	SiC Powder	Additive Composition	Hot Pressing Conditions	Density	End Note
		mass%		% ρ_{ideal}	Year
1	<1- μm β	2% Al_2O_3	1900°C, 21 MPa, 6 min, vacuum	97.6	19 Bind 1976
			1950°C, 21 MPa, 5 min, vacuum	98.3	
			2030°C, 21 MPa, 2 min, vacuum	99.85	
2	α (6H)	6% MgO	1750°C, 30 min, 29 MPa, BN cover mix	76	30 Foster 1999
		6% MgO	1800°C, 30 min, 29 MPa, BN	78	
		6% MgO	1850°C, 30 min, 29 MPa, BN	90	
		6% MgO	1900°C, 30 min, 29 MPa, BN + MgO pack	95	
		10% MgO	1900°C, 30 min, 29 MPa, BN	91	
		6% (92 mol% MgO + 8 mol% Al_2O_3)	1750°C, 30 min, 29 MPa	84	
		6% (88 mol% MgO + 12 mol% Al_2O_3)	1750°C, 30 min, 29 MPa	88	
		6% (72 mol% MgO + 28 mol% Al_2O_3)	1750°C, 30 min, 29 MPa	82	
		6% (50 mol% MgO + 50 mol% Al_2O_3)	1750°C, 30 min, 29 MPa	76	
		6% (88 mol% MgO + 12 mol% Al_2O_3)	1850°C, 30 min, 29 MPa	93	
		6% (72 mol% MgO + 28 mol% Al_2O_3)	1850°C, 30 min, 29 MPa	93	
		6% (92 mol% MgO + 8 mol% Y_2O_3)	1750°C, 30 min, 29 MPa	85	
		6% (85 mol% MgO + 15 mol% Y_2O_3)	1750°C, 30 min, 29 MPa	85	
		6% (68 mol% MgO + 32 mol% Y_2O_3)	1750°C, 30 min, 29 MPa	82	
		6% (56 mol% MgO + 44 mol% Y_2O_3)	1750°C, 30 min, 29 MPa	80	
		6% (85 mol% MgO + 15 mol% Y_2O_3)	1850°C, 30 min, 29 MPa	95	
		6% (68 mol% MgO + 32 mol% Y_2O_3)	1850°C, 30 min, 29 MPa	93	
		9% (68 mol% MgO + 32 mol% Y_2O_3)	1750°C, 30 min, 29 MPa	90	

No.	SiC Powder	Additive Composition	Hot Pressing Conditions	Density	End Note
		mass%		% ρ_{ideal}	Year
		9% (42 mol% MgO : 50 Al ₂ O ₃ : 8 Y ₂ O ₃)	1710°C, 30 min, 29 MPa	79	
		9% (56 mol% MgO : 17 Al ₂ O ₃ : 27 Y ₂ O ₃)	1710°C, 30 min, 29 MPa	84	
		9% (64 mol% MgO : 25 Al ₂ O ₃ : 11 Y ₂ O ₃)	1710°C, 30 min, 29 MPa	86	
		9% (76 mol% MgO : 10 Al ₂ O ₃ : 13 Y ₂ O ₃)	1710°C, 30 min, 29 MPa	86	
		9% (84 mol% MgO : 11 Al ₂ O ₃ : 5 Y ₂ O ₃)	1710°C, 30 min, 29 MPa	84	
		9% (37 mol% MgO : 20 Al ₂ O ₃ : 43 Y ₂ O ₃)	1750°C, 30 min, 29 MPa	86	
		9% (37mol% MgO : 43 Al ₂ O ₃ : 20 Y ₂ O ₃)	1750°C, 30 min, 29 MPa	87	
		9% (42 mol% MgO : 50 Al ₂ O ₃ : 8 Y ₂ O ₃)	1750°C, 30 min, 29 MPa	86	
		9% (56 mol% MgO : 8 Al ₂ O ₃ : 36 Y ₂ O ₃)	1750°C, 30 min, 29 MPa	88	
		9% (56 mol% MgO : 17 Al ₂ O ₃ : 27 Y ₂ O ₃)	1750°C, 30 min, 29 MPa	90	
		9% (56 mol% MgO : 36 Al ₂ O ₃ : 8 Y ₂ O ₃)	1750°C, 30 min, 29 MPa	90	
		9% (64 mol% MgO : 25 Al ₂ O ₃ : 11 Y ₂ O ₃)	1750°C, 30 min, 29 MPa	94	
		9% (64 mol% MgO : 25 Al ₂ O ₃ : 11 Y ₂ O ₃)	1750°C, 30 min, 29 MPa	92	
		9% (67 mol% MgO : 16 Al ₂ O ₃ : 17 Y ₂ O ₃)	1750°C, 30 min, 29 MPa	92	
		9% (67 mol% MgO : 16 Al ₂ O ₃ : 17 Y ₂ O ₃)	1750°C, 30 min, 29 MPa	93	
		9% (69 mol% MgO : 8 Al ₂ O ₃ : 23 Y ₂ O ₃)	1750°C, 30 min, 29 MPa	93	
		9% (71 mol% MgO : 25 Al ₂ O ₃ : 4 Y ₂ O ₃)	1750°C, 30 min, 29 MPa	91	
		9% (76 mol% MgO : 3 Al ₂ O ₃ : 21 Y ₂ O ₃)	1750°C, 30 min, 29 MPa	90	
		9% (77 mol% MgO : 10 Al ₂ O ₃ : 13 Y ₂ O ₃)	1750°C, 30 min, 29 MPa	92	
		9% (77 mol% MgO : 10 Al ₂ O ₃ : 13 Y ₂ O ₃)	1750°C, 30 min, 29 MPa	91	
		9% (77 mol% MgO : 16 Al ₂ O ₃ : 7 Y ₂ O ₃)	1750°C, 30 min, 29 MPa	93	
		9% (84 mol% MgO : 5 Al ₂ O ₃ : 11 Y ₂ O ₃)	1750°C, 30 min, 29 MPa	93	
		9% (84 mol% MgO : 11 Al ₂ O ₃ : 5 Y ₂ O ₃)	1750°C, 30 min, 29 MPa	89	
		9% (37 mol% MgO : 43 Al ₂ O ₃ : 20 Y ₂ O ₃)	1850°C, 30 min, 29 MPa	97	

No.	SiC Powder	Additive Composition	Hot Pressing Conditions	Density	End Note
		mass%		% ρ_{ideal}	Year
		9% (64 mol% MgO : 25 Al ₂ O ₃ : 11 Y ₂ O ₃)	1850°C, 30 min, 29 MPa	99	
		9% (76 mol% MgO : 10 Al ₂ O ₃ : 13 Y ₂ O ₃)	1850°C, 30 min, 29 MPa	99	
		9% (67 mol% MgO : 16 Al ₂ O ₃ : 17 Y ₂ O ₃)	1750°C, 5 min, 29 MPa	79	
		9% (67 mol% MgO : 16 Al ₂ O ₃ : 17 Y ₂ O ₃)	1750°C, 15 min, 29 MPa	88	
		9% (67 mol% MgO : 16 Al ₂ O ₃ : 17 Y ₂ O ₃)	1750°C, 30 min, 29 MPa	93	
		9% (67 mol% MgO : 16 Al ₂ O ₃ : 17 Y ₂ O ₃)	1750°C, 45 min, 29 MPa	93	
		9% (67 mol% MgO : 16 Al ₂ O ₃ : 17 Y ₂ O ₃)	1750°C, 90 min, 29 MPa	95	
		3% (67 mol% MgO : 16 Al ₂ O ₃ : 17 Y ₂ O ₃)	1750°C, 30 min, 29 MPa, BN	80	
		6% (67 mol% MgO : 16 Al ₂ O ₃ : 17 Y ₂ O ₃)	1750°C, 30 min, 29 MPa, BN	90	
		6% (67 mol% MgO : 16 Al ₂ O ₃ : 17 Y ₂ O ₃)	1800°C, 30 min, 29 MPa, BN	93	
		9% (67 mol% MgO : 16 Al ₂ O ₃ : 17 Y ₂ O ₃)	1750°C, 30 min, 29 MPa, BN	93	
		9% (67 mol% MgO : 16 Al ₂ O ₃ : 17 Y ₂ O ₃)	1800°C, 30 min, 29 MPa, BN	98	
		3% (67 mol% MgO : 16 Al ₂ O ₃ : 17 Y ₂ O ₃)	1800°C, 30 min, 29 MPa, BN+M+A+Y	98	
		6% (67 mol% MgO : 16 Al ₂ O ₃ : 17 Y ₂ O ₃)	1800°C, 30 min, 29 MPa, BN+M+A+Y	99	
		9% (67 mol% MgO : 16 Al ₂ O ₃ : 17 Y ₂ O ₃)	1800°C, 30 min, 29 MPa, BN+M+A+Y	98	
3	0.27- μ m β	85.6% β -SiC + 0.9% α -SiC + 13.5% Y ₃ Al ₅ O ₁₂	1800°C, 1 hr, 25 MPa, Ar	97.5	36 Kim 2001
4	90-nm β	7% Al ₂ O ₃ + 2% Y ₂ O ₃ + 1% CaO + 2.7% α -SiC	1750°, 40 min, 25 MPa, Ar. Annealed 1900°C, 4 hr, 25 MPa.	>95	35 Zhan 2002
			1750°, 40 min, 25 MPa, Ar. Annealed 1900°C, 4 hr, no pressure.	>95	
5	0.5- μ m β	9% (67 mol% MgO + 16% Al ₂ O ₃ + 17% Y ₂ O ₃)	1800°C, 30 min, 25 MPa, Ar	97.7	31 Huang 2003
		9% (MgO + Al ₂ O ₃ + Y ₂ O ₃) + 5 vol% 70-nm SiC		>95	
		9% (MgO + Al ₂ O ₃ + Y ₂ O ₃) + 10 vol% 70-nm SiC		96.5	
		9% (MgO + Al ₂ O ₃ + Y ₂ O ₃) + 15 vol% 70-nm SiC		>96	
		9% (67 mol% Mg(NO ₃) ₂ (H ₂ O) ₆ + 16% Al(NO ₃) ₃ (H ₂ O) ₉ + 17% Y(NO ₃) ₃ (H ₂ O) ₆)		98.1	

No.	SiC Powder	Additive Composition	Hot Pressing Conditions	Density	End Note
		mass%		% ρ_{ideal}	Year
		9% (67 mol% $Mg(NO_3)_2(H_2O)_6$ + 16% $Al(NO_3)_3(H_2O)_9$ + 17% $Y(NO_3)_3(H_2O)_6$ + 10 vol% 70-nm SiC		97.3	
		6% (67 mol% $Mg(NO_3)_2(H_2O)_6$ + 16% $Al(NO_3)_3(H_2O)_9$ + 17% $Y(NO_3)_3(H_2O)_6$ + 10 vol% 70-nm SiC		~92	
		3% (67 mol% $Mg(NO_3)_2(H_2O)_6$ + 16% $Al(NO_3)_3(H_2O)_9$ + 17% $Y(NO_3)_3(H_2O)_6$ + 10 vol% 70-nm SiC		86.8	
6	0.30- μm β	99.5 mol% SiC + 0.25% La_2O_3 + 0.25% Y_2O_3	2000°, 2 hr, 40 MPa, Ar	83.9	32 Zhou 2004
		99.0 mol% SiC + 0.50% La_2O_3 + 0.50% Y_2O_3		96.8	
		98.64 mol% SiC + 0.68% La_2O_3 + 0.68% Y_2O_3		96.9	
		98.0 mol% SiC + 1.0% La_2O_3 + 1.0% Y_2O_3		97.1	
		99.5 mol% SiC + 0.25% La_2O_3 + 0.25% Y_2O_3	2000°, 2 hr, 40 MPa, Ar. Annealed 1900°C, 4 hr, Ar.	83.8	
		99.0 mol% SiC + 0.50% La_2O_3 + 0.50% Y_2O_3		95.3	
		98.64 mol% SiC + 0.68% La_2O_3 + 0.68% Y_2O_3		95.1	
		98.0 mol% SiC + 1.0% La_2O_3 + 1.0% Y_2O_3		94.1	
7	α	10% (4 mol Al_2O_3 + 1 mol Y_2O_3)	1975°C, 30 min, 30 MPa, Ar	99	33 Can 2006
		10% (5 mol Al_2O_3 + 3 mol Y_2O_3)		99	
		10% (1 mol Al_2O_3 + 1 mol Y_2O_3)		99	
		10% (1 mol Al_2O_3 + 2 mol Y_2O_3)		99	
		10% (1 mol Al_2O_3 + 4 mol Y_2O_3)		99	
8	40-nm β	10 vol% Y_2O_3	SPS, 1900°C, 600 min, N_2	96	9 Hotta 2010
		2% Al_2O_3		99	
9	20-nm β	4% $\gamma-Al_2O_3$	1000°C, 30 min, 4.5 GPa	94	23 Mao-lin 2010
			1100°C, 30 min, 4.5 GPa	96	
			1200°C, 30 min, 4.0 GPa	96	
			1200°C, 30 min, 4.25 GPa	98	
			1200°C, 30 min, 4.4 GPa	98	
			1200°C, 15 min, 4.5 GPa	96	
			1200°C, 20 min, 4.5 GPa	97	
			1200°C, 25 min, 4.5 GPa	98	
			1200°C, 30 min, 4.5 GPa	98	
			1200°C, 35 min, 4.5 GPa	99	
			1300°C, 30 min, 4.5 GPa	>99	
10	52-nm β	5% Al_2O_3	1750°C, 2 hr, 20 MPa, Ar	98.7	29 Noviyanto 2012
		5% Fe_2O_3		61.3	
		5% MgO		76.1	
		5% TiO_2		61.5	

No.	SiC Powder	Additive Composition	Hot Pressing Conditions	Density	End Note
		mass%		% ρ_{ideal}	Year
		5% WO ₃		60.1	
		5% Y ₂ O ₃		90.3	
		5% eutectic MgO + Al ₂ O ₃		96.8	
		5% eutectic TiO ₂ + Al ₂ O ₃		75.9	
		5% eutectic Al ₂ O ₃ + Y ₂ O ₃		96.1	
		5% eutectic Fe ₂ O ₃ + WO ₃		55.4	
		5% eutectic Fe ₂ O ₃ + Y ₂ O ₃		55.8	
		5% eutectic MgO + Y ₂ O ₃		86.7	
		5% B ₂ O ₃		65.66	
		5% (81% Al ₂ O ₃ + 19% V ₂ O ₅)		65.21	
		5% (72.6% Cr ₂ O ₃ + 27.4% V ₂ O ₅)		59.08	
		5% (78% Fe ₂ O ₃ + 22% V ₂ O ₅)		58.04	
		5% (38% TiO ₂ + 62% V ₂ O ₅)		56.81	
		5% (64% Al ₂ O ₃ + 26% MgO + 10% Y ₂ O ₃)		96.53	
		5% (32% FeO + 25% V ₂ O ₅ + 43% SiO ₂)		55.92	
		5% (22% TiO ₂ + 60% V ₂ O ₅ + 18% SiO ₂)		59.73	

6.3.4 Nitride Additives

Kim et al.³⁶ compared the intergranular glass and fracture mode of 2.7% AlN + 16.9% Er₂O₃ to Y₃Al₅O₁₂ sintering aids in β -SiC, hot pressed and annealed. A 6–9 Å wide grain-boundary glass was detected by TEM in both compositions, and both largely transformed to α -SiC. The strength and toughness of the Al-Er doped SiC were 600 MPa and 6.1 MPa·m^{0.5}, and 550 and 6.2 for the Al-Y. The strength of the former at 1600°C was 93% of its room-temperature value, attributed to the refractoriness of its intergranular glass.

Balog et al.³⁷ did a hardness traverse across SiC grains that had been hot pressed with rare earth oxides and AlN in Table 6.4. Y₂O₃, Yb₂O₃ and Sm₂O₃ in various combinations adding up to 10% were mixed with both α - and β -SiC, densified to >99% by LPS and annealed. The SiC grains were harder, when measured with a nanoscale Berkovich indenter and AFM, in the core than in the rim, due to dissolution of AlN in the rim. The Vickers hardness increased after annealing due to the evaporation of oxide phases on the grain boundaries. The authors applied a 3.5-mN load to a Berkovich indenter and measured the hardness across individual grains. ISE affected the Berkovich indentations,

leading to the optimum 3.5-mN load. The nearly-pure SiC core of the grains was slightly harder (32-35 GPa) than the grain boundary regions (29-33 GPa), which were solid solutions of AlN in SiC. By comparison, the Vickers hardness spanning several grains was 20–26 GPa.

Bothara et al.^{10,11,12} derived a master sintering curve for SPS nano-scale α -SiC + AlN + Y₂O₃ in three papers. Greater than 99.5% density and submicron grain size were achieved in as little as 5 min at 1700°C. The logarithm of resistivity decreased linearly with grain size. A master sintering curve of density vs. sintering work was derived from three compaction pressures and three heating rates.

Nitrogen in the form of AlN or Si₃N₄ retarded sintering of SiC, compared to boron, carbon and aluminum, in Ray's et al.²⁸ 26-composition investigation. Oxygen also had a deleterious effect on sintering when Al₂O₃ additive was compared to Al. Small additions of Al, B and C shifted the onset of densification to lower temperatures, as mentioned above in §6.3.2. The diffusion rate was enhanced by additions of B₄C, C and Al, but slowed by N. Small additions of Y₂O₃ to SiC densified with Al resulted in more intergranular fracture and higher toughness. The corrosion resistance of SiC to hot acid and a hot basic solution decreased when an Al- and O-rich grain-boundary phase was present. Grain size, aspect ratio of grains, density, toughness, intergranular fracture fraction, Vickers hardness (9.8-N load for both scales), Knoop hardness, oxygen content, nitrogen content and polytype content were reported. All 26 compositions reached 99% density from hot pressing at 2100°C for 1 hr in argon. The toughness range, measured by single-edge pre-cracked beam, was 2.4–5.6 MPa·m^{0.5}. The Vickers hardness was 21.2–27.0 GPa, the Knoop hardness 17.4–20.5 GPa, the grain size 1.1–11.2 μ m, the aspect ratio 2.2–6.4, the intergranular fracture 8.2–88.6%, and the 6H phase content 5.4–82.2% for the 23 compositions with nitride additives.

Hotta and Hojo⁹ varied the ratio of AlN to Y₂O₃ in nano β -SiC, SPS with 10% additives. The density increased and the grain size decreased with increasing amounts of AlN. N₂ was used to stabilize the AlN during sintering. One composition with 10% AlN only,

no Y_2O_3 , did not densify. The flexural strength was as high as 1000 MPa and the toughness of all compositions was about $2.5 \text{ MPa}\cdot\text{m}^{0.5}$.

Table 6.4: Nitride + oxides additives, sintering parameters and properties of hot pressed silicon carbide.

No.	SiC Powder	Additive Composition	Hot Pressing Conditions	Density	End Note
		mass%		% ρ_{ideal}	Year
1	0.27- μm β	79.6% β -SiC + 0.8% α -SiC + 2.7% AlN + 16.9% Er_2O_3	1900°C, 1 hr, 25 MPa, N_2	98.9	36 Kim 2001
2	β	2% α + 10% Y_2O_3 + 3% AlN	1850°C, 1 hr, 30 MPa, Ar + N_2 , annealed 10 hr @ 1850°C in Ar + N_2 .	> 99	37 Balog 2005
		2% α + 4.60% Y_2O_3 + 5.40% Yb_2O_3 + 3% AlN		> 99	
		2% α + 3.93% Y_2O_3 + 6.07% Sm_2O_3 + 3% AlN		> 99	
		2% α + 5.30% Yb_2O_3 + 4.70% Sm_2O_3 + 3% AlN		> 99	
	α	2% β + 10% Y_2O_3 + 3% AlN		> 99	
		2% β + 4.60% Y_2O_3 + 5.40% Yb_2O_3 + 3% AlN		> 99	
		2% β + 3.93% Y_2O_3 + 6.07% Sm_2O_3 + 3% AlN		> 99	
		2% β + 5.30% Yb_2O_3 + 4.70% Sm_2O_3 + 3% AlN		> 99	
3	100-nm α	AlN + Y_2O_3 (ratio unspecified)	SPS, 1700°C, 300 s, 20-30 MPa, vacuum	>99.5	11 Bothara 2007
			SPS, 1700°C, 900 s, 20-30 MPa, vacuum	>99.5	
			SPS, 1700°C, 3600 s, 20-30 MPa, vacuum	>99.5	
			SPS, 1850°C, 300 s, 20-30 MPa, vacuum	>99.5	
			SPS, 1850°C, 900 s, 20-30 MPa, vacuum	>99.5	
			SPS, 1850°C, 3600 s, 20-30 MPa, vacuum	>99.5	
4	100-nm α	AlN + Y_2O_3 (ratio unspecified)	SPS, 1700°C, 3600 s, 0.33 K/s, 10 MPa, vacuum	>99.5	12 Bothara 2007
			SPS, 1700°C, 3600 s, 1.0 K/s, 10 MPa, vacuum	>99.5	
			SPS, 1700°C, 3600 s, 1.67 K/s, 10 MPa, vacuum	>99.5	
			SPS, 1700°C, 3600 s, 0.33 K/s, 30 MPa, vacuum	>99.5	

No.	SiC Powder	Additive Composition	Hot Pressing Conditions	Density	End Note
		mass%		% ρ_{ideal}	Year
			SPS, 1700°C, 3600 s, 1.0 K/s, 30 MPa, vacuum	>99.5	
			SPS, 1700°C, 3600 s, 1.67 K/s, 30 MPa, vacuum	>99.5	
			SPS, 1700°C, 3600 s, 0.33 K/s, 50 MPa, vacuum	>99.5	
			SPS, 1700°C, 3600 s, 1.0 K/s, 50 MPa, vacuum	>99.5	
			SPS, 1700°C, 3600 s, 1.67 K/s, 50 MPa, vacuum	>99.5	
5	0.55- μm α	(C.) 2.5% AlN	2100°C, 1 hr, 28 MPa, Ar	> 99	28 Ray 2008
		(D.) 5% AlN		> 99	
		(F.) 2% Al + 1% AlN + 1% C + 0.25% B ₄ C		> 99	
		(G.) 2.5% AlN + 0.5% B ₄ C		> 99	
		(H.) 2% Al + 0.5% AlN + 1% C + 0.25% B ₄ C		> 99	
		(I.) 2% Al + 1.5% AlN + 1% C + 0.25% B ₄ C		> 99	
		(J.) 1% Al + 1.5% AlN + 1% C + 0.25% B ₄ C		> 99	
		(K.) 2.5% Al + 1.5% AlN + 1% C + 0.25% B ₄ C		> 99	
		(L.) 3% Al + 1.5% AlN + 1% C + 0.25% B ₄ C		> 99	
		(M.) 2% Al + 0.5% AlN + 1% C + 0.25% B ₄ C + 0.5% Y ₂ O ₃		> 99	
		(N.) 2% Al + 0.5% AlN + 1% C		> 99	
		(O.) 2% Al + 0.5% AlN + 1% C + 0.25% Y ₂ O ₃		> 99	
		(P.) 2% Al + 0.5% AlN + 1% C + 0.25% Y ₂ O ₃		> 99	
		(Q.) 2% Al + 1% AlN + 1% C + 0.25% B ₄ C + 0.25% Y ₂ O ₃		> 99	
		(R.) 2% Al + 1% AlN + 1% C + 0.25% B ₄ C + 0.5% Y ₂ O ₃		> 99	
		(S.) 2% Al + 1% AlN + 1% C + 0.5% Y ₂ O ₃		> 99	
		(T.) 2% Al + 0.5% AlN + 0.25% B ₄ C + 0.5% Y ₂ O ₃		> 99	
		(U.) 2% Al + 1% AlN + 0.25% B ₄ C + 0.5% Y ₂ O ₃		> 99	
		(V.) 2% Al + 1% AlN + 0.5% C + 0.25% B ₄ C + 0.5% Y ₂ O ₃		> 99	
		(W.) 1% AlN + 1% C + 0.25% B ₄ C + 0.5% Y ₂ O ₃ + 3.78% Al ₂ O ₃		> 99	

No.	SiC Powder	Additive Composition	Hot Pressing Conditions	Density	End Note
		mass%		% ρ_{ideal}	Year
6	40-nm β	(X.) 4.5% Al + 1.33% C + 0.25% B ₄ C + 1.28% Si ₃ N ₄	SPS, 1900°C, 600 s, 30 MPa, N ₂	> 99	9 Hotta 2010
		(Y.) 2% Al + 1% AlN + 0.5% C + 0.25% Y ₂ O ₃		> 99	
		(Z.) 2% Al + 0.5% AlN + 0.5% C + 0.25% B ₄ C + 0.25% Y ₂ O ₃		> 99	
		10 vol% (10 mol% AlN + 90 mol% Y ₂ O ₃)		95	
		10 vol% (30 mol% AlN + 70 mol% Y ₂ O ₃)		97	
		10 vol% (50 mol% AlN + 50 mol% Y ₂ O ₃)		98	
		10 vol% (70 mol% AlN + 30 mol% Y ₂ O ₃)		99	
		10 vol% (90 mol% AlN + 10 mol% Y ₂ O ₃)		> 99	
		10 vol% AlN		88	

6.4 Discussion

The few compositions containing rare earth (lanthanide series) oxide additives are distinguished from the more conventional oxide additives in Figures 6.1 – 6.10. The C-B-carbide family of additives is referred to simply as carbides in this section and in the legends of Figures 6.1 – 6.10.

Oxide additives tended to yield the highest densities at the lowest sintering temperatures, in Figure 6.1. One oxide densified as low as 1000°C in 30 min, but under 4.5 GPa pressure. Under more moderate pressures, most of the oxides needed at least 1750°C to densify to closed porosity. At the same time, a number of oxides sintered at higher temperatures were inadequately dense, due to the non-optimum type or amount of additives. The SiC compositions without additives densified as low as 1200°C in 30 min, but also under 4.5 GPa pressure. Most of the no-additive compositions needed at least 1850°C to densify to closed porosity under pressure. The nitride additives generally required 1700°C and usually higher for densification. The carbide additives resulted in both high densities at lower temperatures and low densities at higher temperatures, indicating that these additives behave less predictably than the others. The few rare earth

oxide additives generally provided high densities. Figure 6.1 contains nearly 300 data points and represents a large swath of SiC ceramics, all sintered under pressure. Many of the points overlap, such as the 26 compositions from Ray et al.²⁸ that were all at least 99% dense at the same sintering temperature.

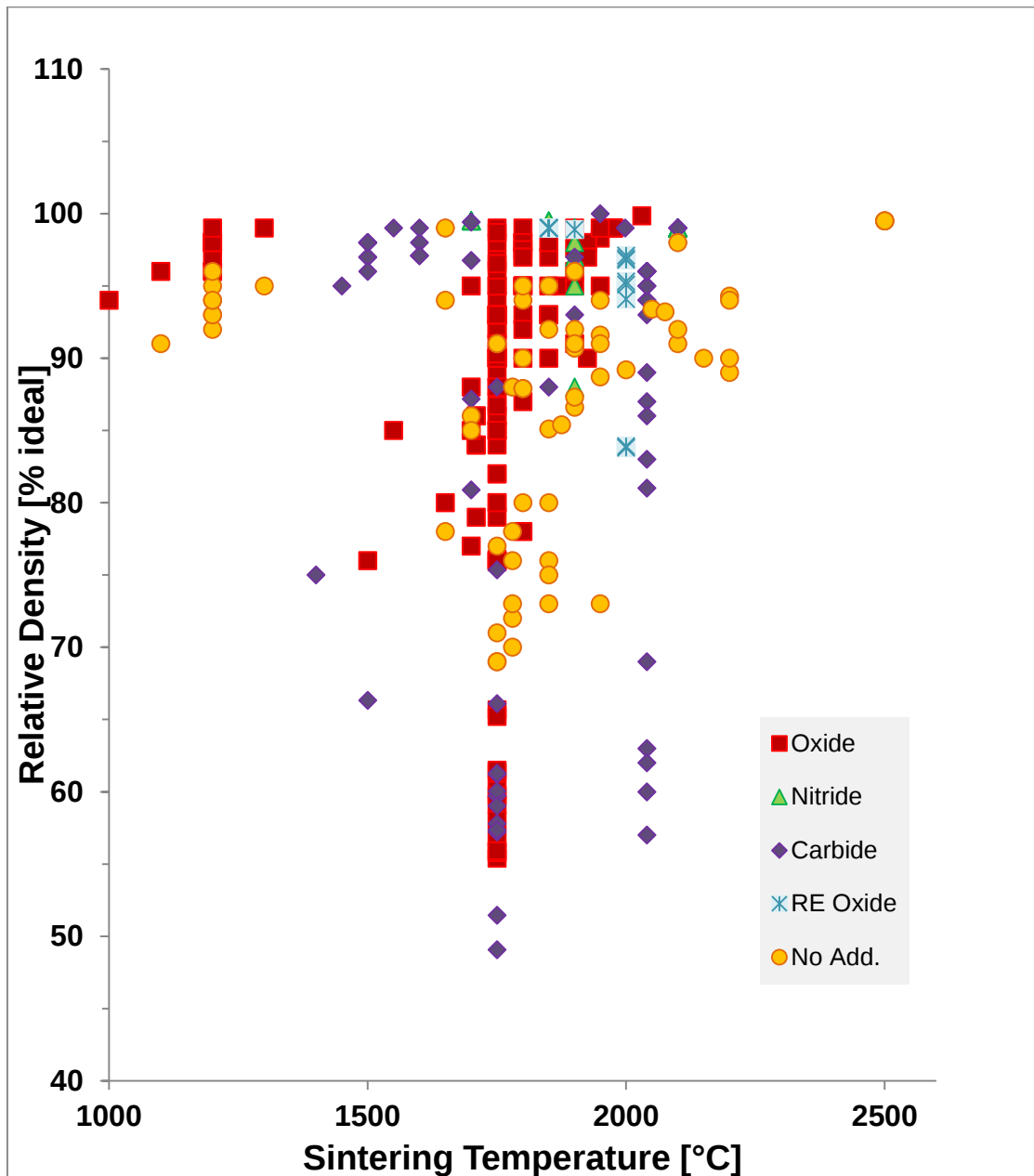


Figure 6.1: Map of relative density as a function of sintering temperature and additive family from the data in Tables 6.1–6.4.

More total additives did not necessarily yield better densification, in Figure 6.2. The carbide group generally densified with the lowest amount of additives, about 2%, among the additive families. Several low-oxide and low-nitride compositions also densified very well, but most needed about 5% additives.

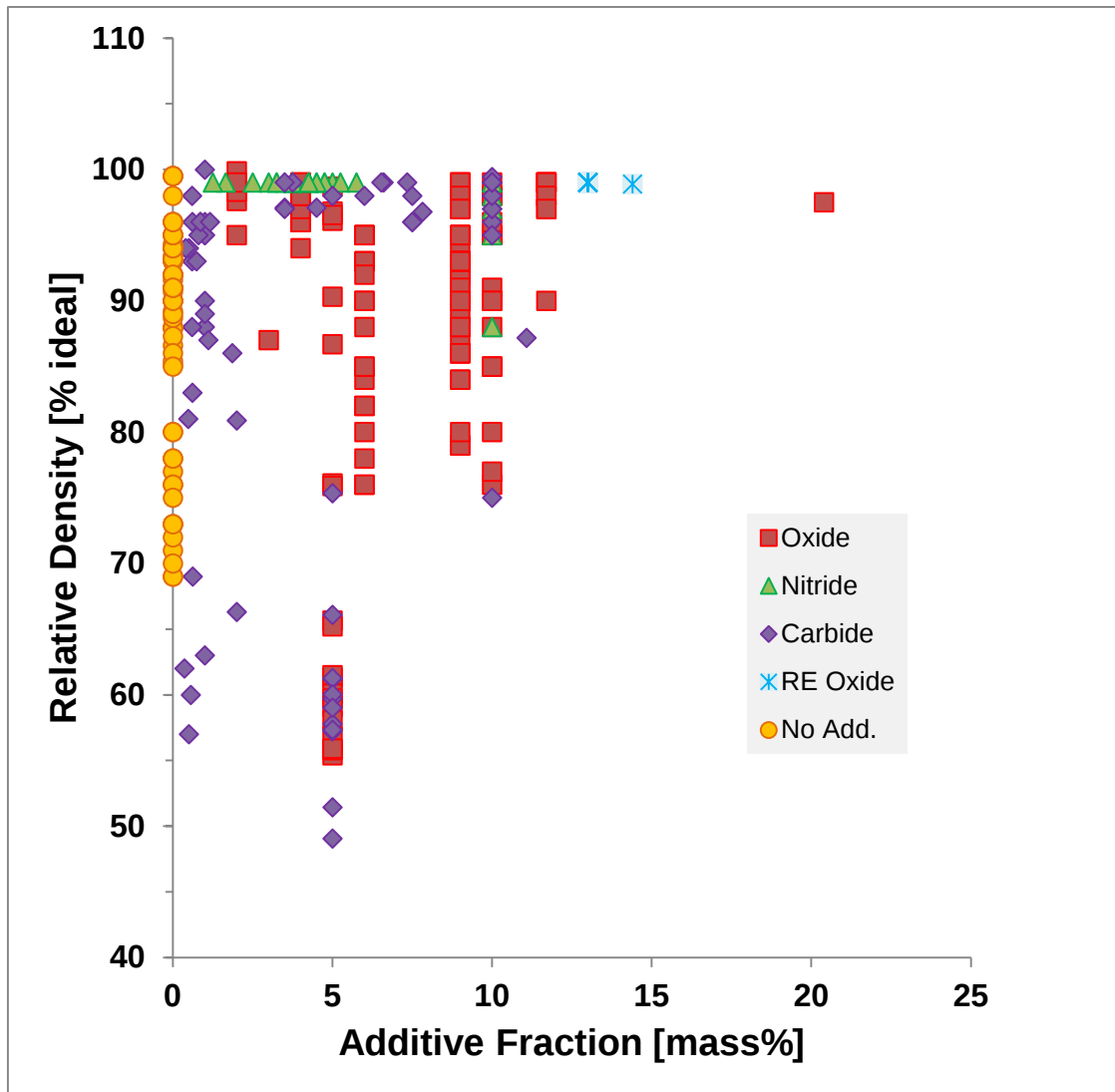


Figure 6.2: Map of relative density as a function of additive fraction and additive family from the data in Tables 6.1–6.4.

The pressure during HP, HIP and SPS had little bearing on the density when $P \leq 100$ MPa in Figure 6.3. The pressure axis was plotted in logarithmic form to accommodate the wide range of pressures. In several cases, $P > 10$ MPa was not enough to overcome the factors that retarded densification, and the compacts were significantly less than 92% of ideal density after pressure-assisted sintering. Most of the carbide, oxide and nitride compositions needed 10–20 MPa, and the no-additive compositions upwards of 100 MPa,

to achieve full densification. GPS proved adequate for several compositions from Part I to densify, including three of the four points in Figure 6.3 to the left of 1 MPa.

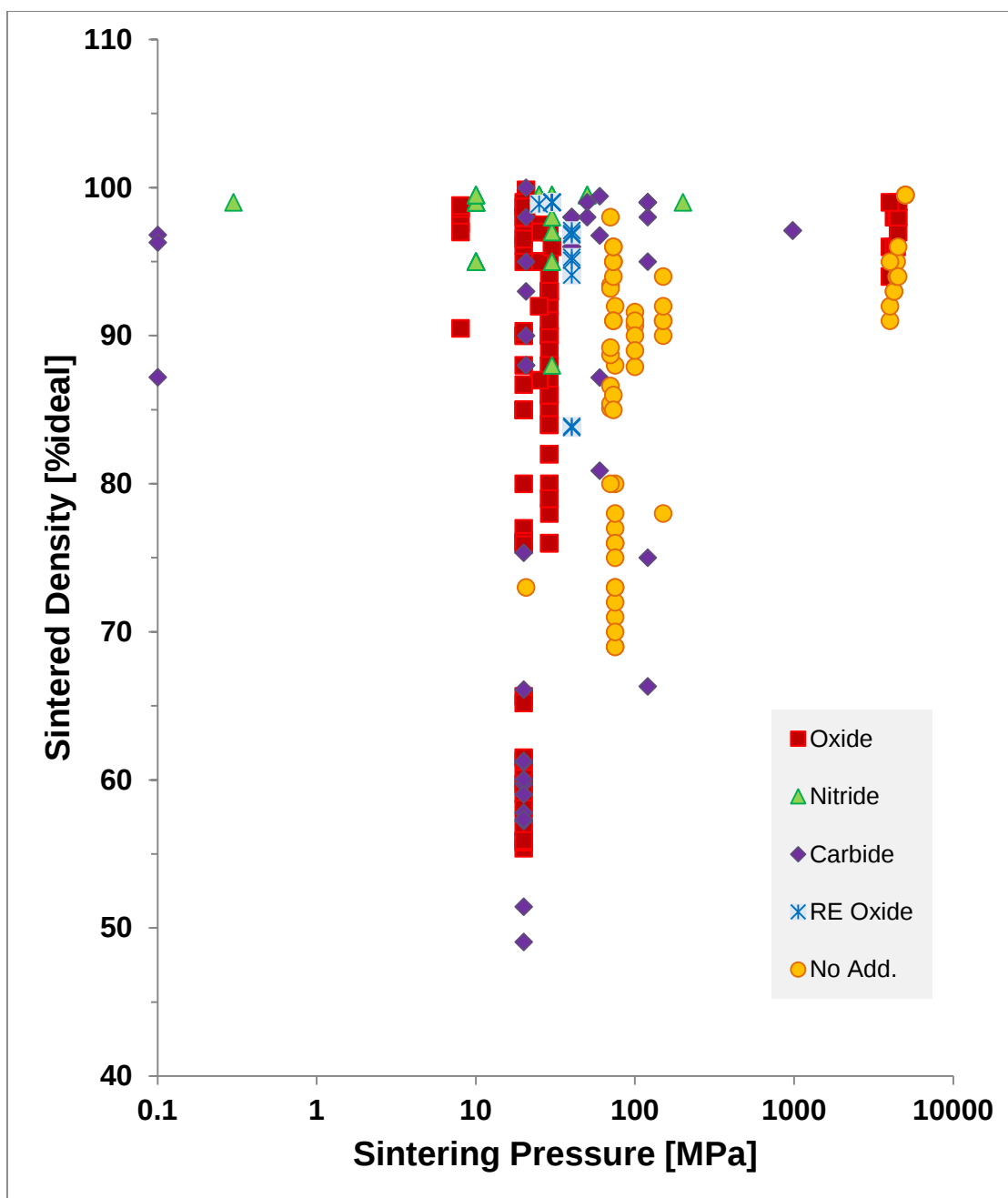


Figure 6.3: Map of relative density as a function of sintering pressure and additive family from the data in Tables 6.1–6.4.

Only about half of the papers cited in this two-part review provided hardness, toughness or strength data. For that reason, the mechanical properties data of the pressureless sintered SiC specimens from Chapter 5 of this thesis were pooled with the pressure-assisted data. Figures 6.4–6.10 contain data from Chapter 5 as well as the citations in the tables in this paper.

The grain growth as a function of sintering temperature was highly variable for SiC without additives in Figure 6.4. The grain growth was calculated as the ratio of the grain size after sintering, G_2 , to the initial SiC particle size, G_1 , for compositions of 92% density or greater. The no-additive compositions ranged from a factor of four ($G_2/G_1 \approx 4$) to nearly two orders of magnitude, increasing with temperature but not in a pattern that suggested a simple mathematical relationship. The oxide, nitride and carbide additives were mostly effective as grain-growth controllers up to 2100°C, compared to compositions without additives. In Table 6.5, the outlier at 2050°C and a growth factor of 154 was neglected in the carbide calculations, giving the carbides a slight edge over the oxides and nitrides for grain growth control. All the compositions have very large standard deviations, indicating that grain growth mechanisms are not necessarily well understood in SiC.

Table 6.5: Statistical summary of property values in the papers cited in Tables 6.1–6.4 and Figure 6.5–6.7.

Property	$\bar{x}$ & s	Oxide	Nitride	Carbide	RE Oxide	No Additives	All Compositions
Grain growth	Mean G_2/G_1	7.69	8.26	6.94	-	33.1	13.6
	Std. Dev.	8.70	6.09	8.12	-	27.8	21.5
Hardness	Mean HV	22.3	20.7	23.1	25.5	22.9	22.1
	Std. Dev.	4.78	4.54	2.27	1.60	5.41	4.57
Fracture toughness	Mean K_{Ic}	5.73	3.57	4.24	6.10	4.88	4.57
	Std. Dev.	1.24	1.23	1.51	-	1.38	1.60
Strength	Mean MOR	528	699	608	588	659	581
	Std. Dev.	115	196	112	-	79	153

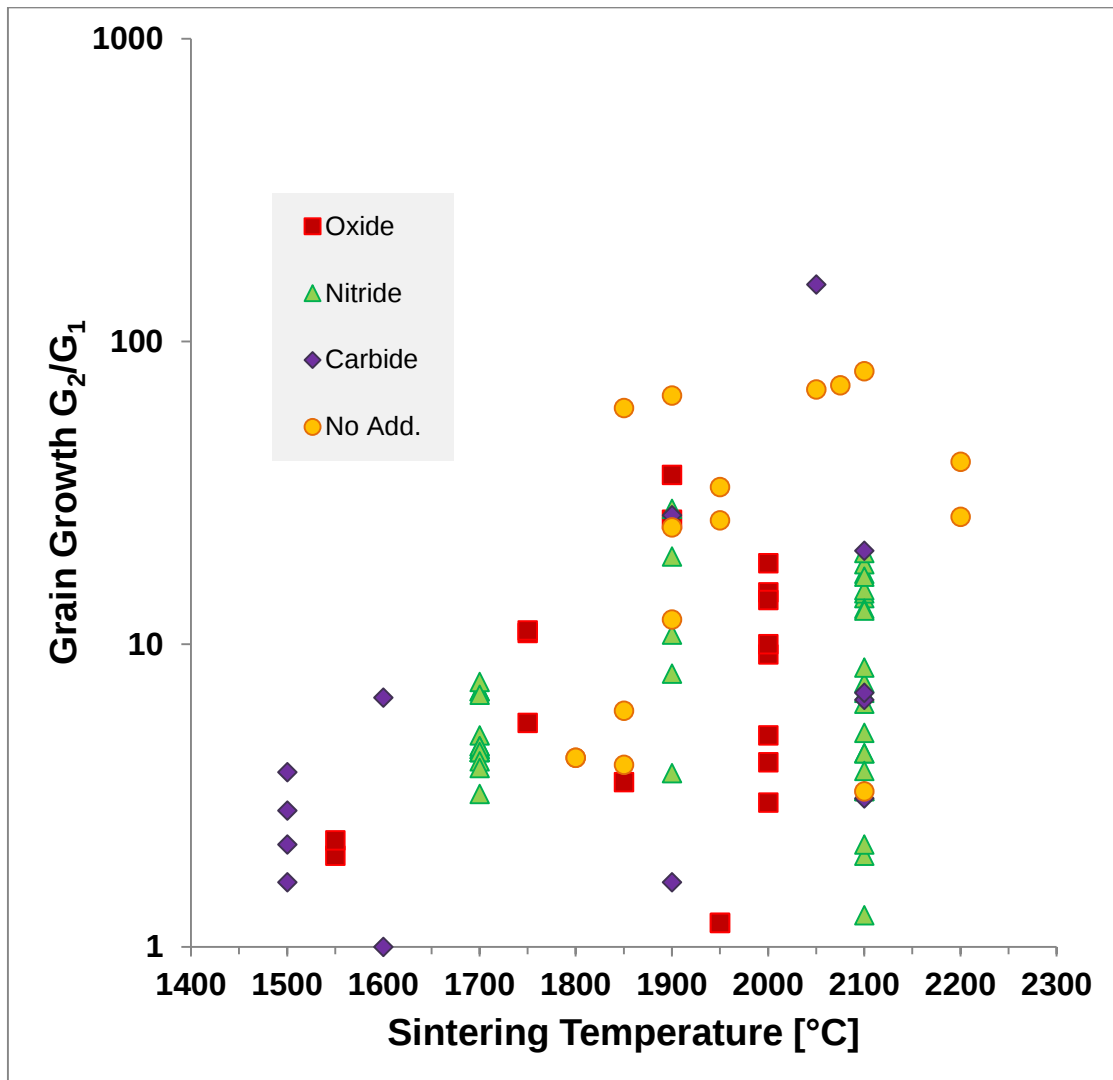


Figure 6.4: Map of grain growth as a function of sintering temperature. The grain growth parameter is the ratio of the grain size after sintering to the initial SiC particle size.

SiC without additives had some of the highest Vickers hardnesses at the lowest sintering temperatures in Figure 6.5, as much as 38 GPa at 1200°C in one case, as did some of the oxide additives, 34 GPa at 1300°C in another case. The pressureless sintered oxides also yielded some of the lowest hardnesses at the higher temperatures, 16 GPa at 2000°C in a third case. The rare earth oxide additives gave the highest mean hardness at nearly 26 GPa, and the nitride additives gave the lowest at 21 GPa, in Table 6.5. The hardnesses were measured under a range of indenter forces, implying that some may have been

biased by ISE. The mean HV for all compositions was 22.1 GPa, with a standard deviation of 4.57 GPa.

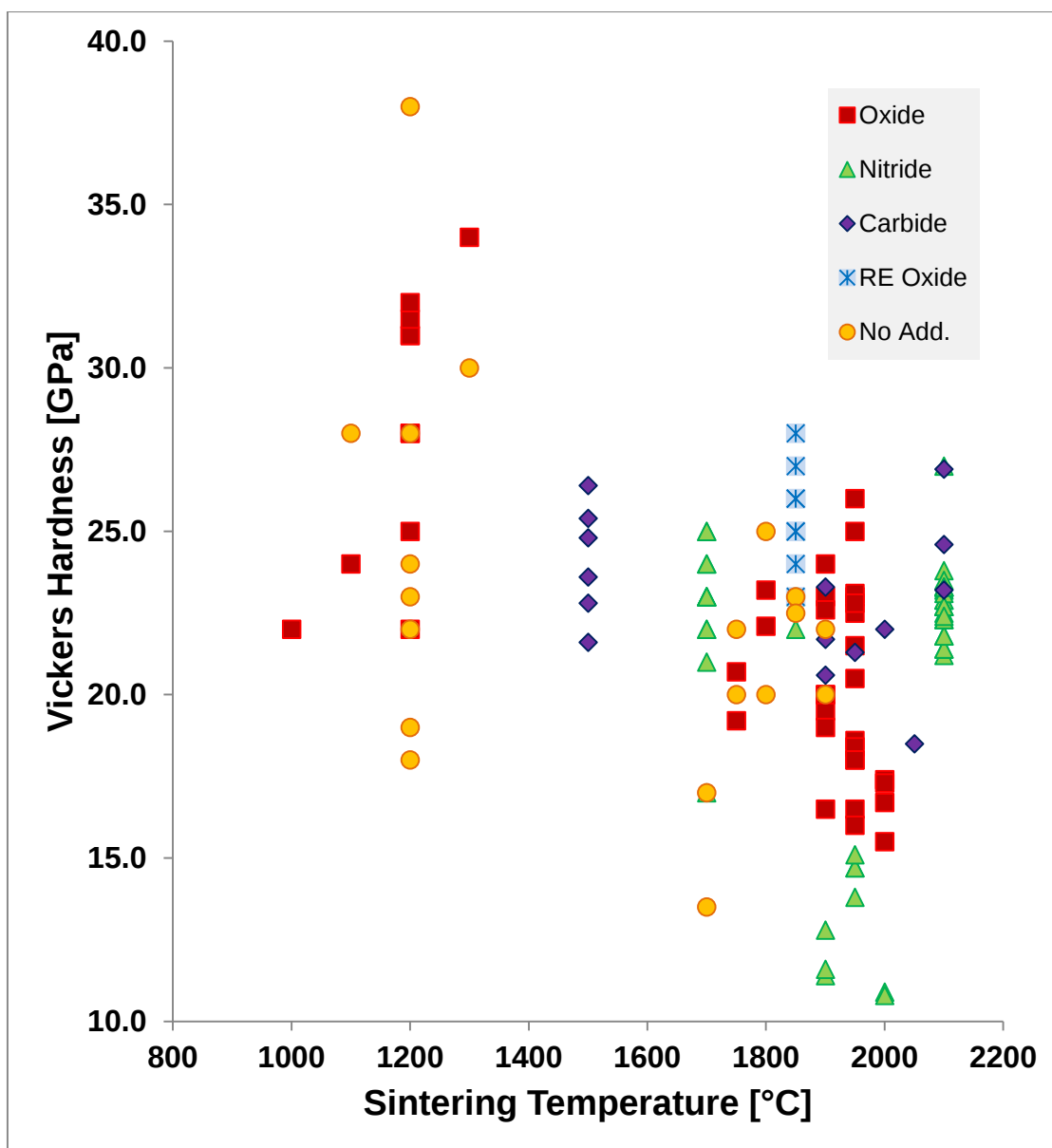


Figure 6.5: Map of Vickers hardness as a function of sintering temperature and additive family, from the data in Tables 6.1–6.4 and Chapter 5. The mean HV = 22.1 GPa.

The oxide additives resulted in the highest fracture toughness measurements at the lowest sintering temperatures, 6.2 MPa m^{0.5} at 1800°C in one case, in Figure 6.6. The

nitrides had the lowest mean toughness, at $3.6 \text{ MPa m}^{0.5}$, in Table 6.5. The carbide additives also had a tendency for lower toughness, even at higher temperatures, as suggested by She and Ueno³⁸. SiC without additives had the second highest mean toughness, $4.9 \text{ MPa m}^{0.5}$, after $5.7 \text{ MPa m}^{0.5}$ for the oxides. Figure 6.6 contains data derived from both notched beam and Vickers indentation methods. The mean toughness for all compositions was $4.57 \text{ MPa m}^{0.5}$, with a standard deviation of $1.60 \text{ MPa m}^{0.5}$.

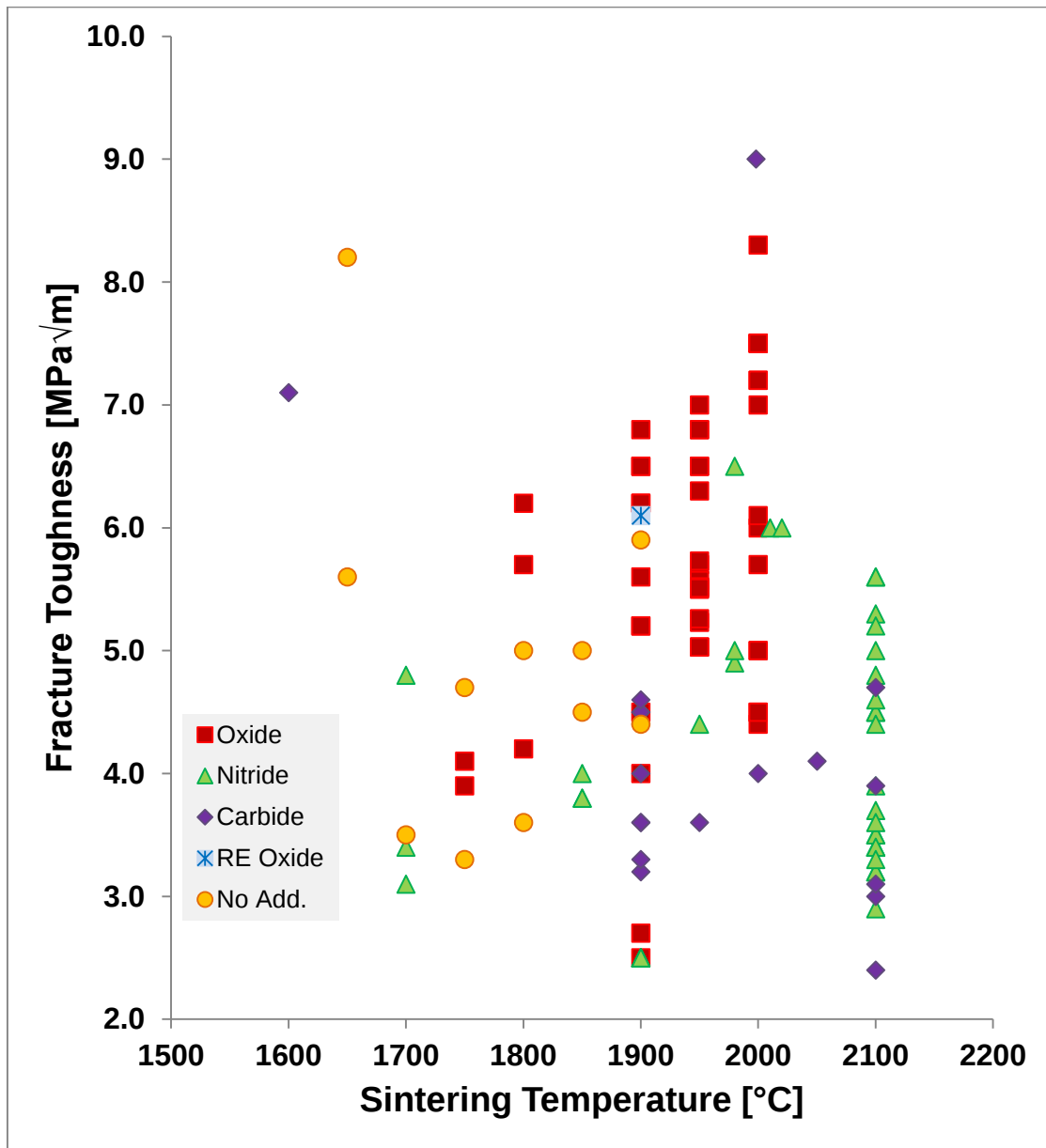


Figure 6.6: Map of fracture toughness as a function of sintering temperature and additive family, from the data in Tables 6.1–6.4 and Chapter 5. The mean $K_{Ic} = 4.57 \text{ MPa}\cdot\text{m}^{0.5}$.

Nitride additives produced the highest strengths in Figure 6.7 and Table 6.5, at 699 MPa and at mostly intermediate sintering temperatures. The data pool is much smaller than that of Figures 6.1–6.3, and includes both 3-pt and 4-pt bending results. The oxides were the weakest of the additives at 528 MPa. Not enough data were available from the other three additive families to draw any meaningful conclusions about their effectiveness

as SiC strengtheners compared to nitrides and oxides. The mean bending strength for all compositions was 581 MPa, with a standard deviation of 153 MPa.

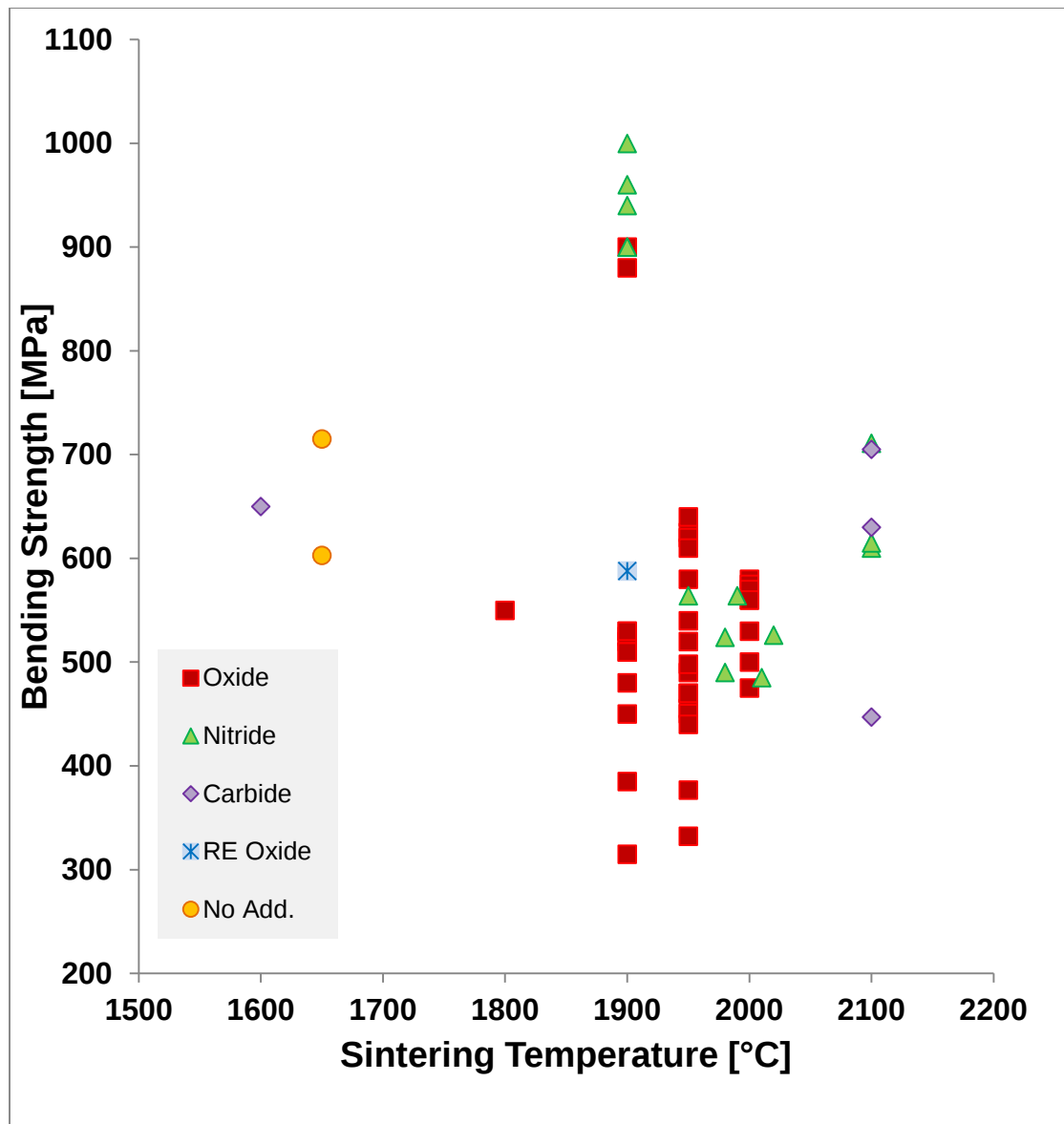


Figure 6.7: Map of bending strength as a function of sintering temperature and additive family, from the data in Tables 6.1–6.4 and Chapter 5. The mean MOR = 581 MPa.

The papers from Tables 6.1–6.4 and Chapter 5 that have both toughness and grain size data are plotted in Figure 6.8. The toughness of SiC with oxide or nitride additives increased slightly with grain size, while the toughness of SiC with metal or carbide additives

has little or no dependence on the grain size. Lomello et al.¹⁸ reported an increase in toughness with grain size.

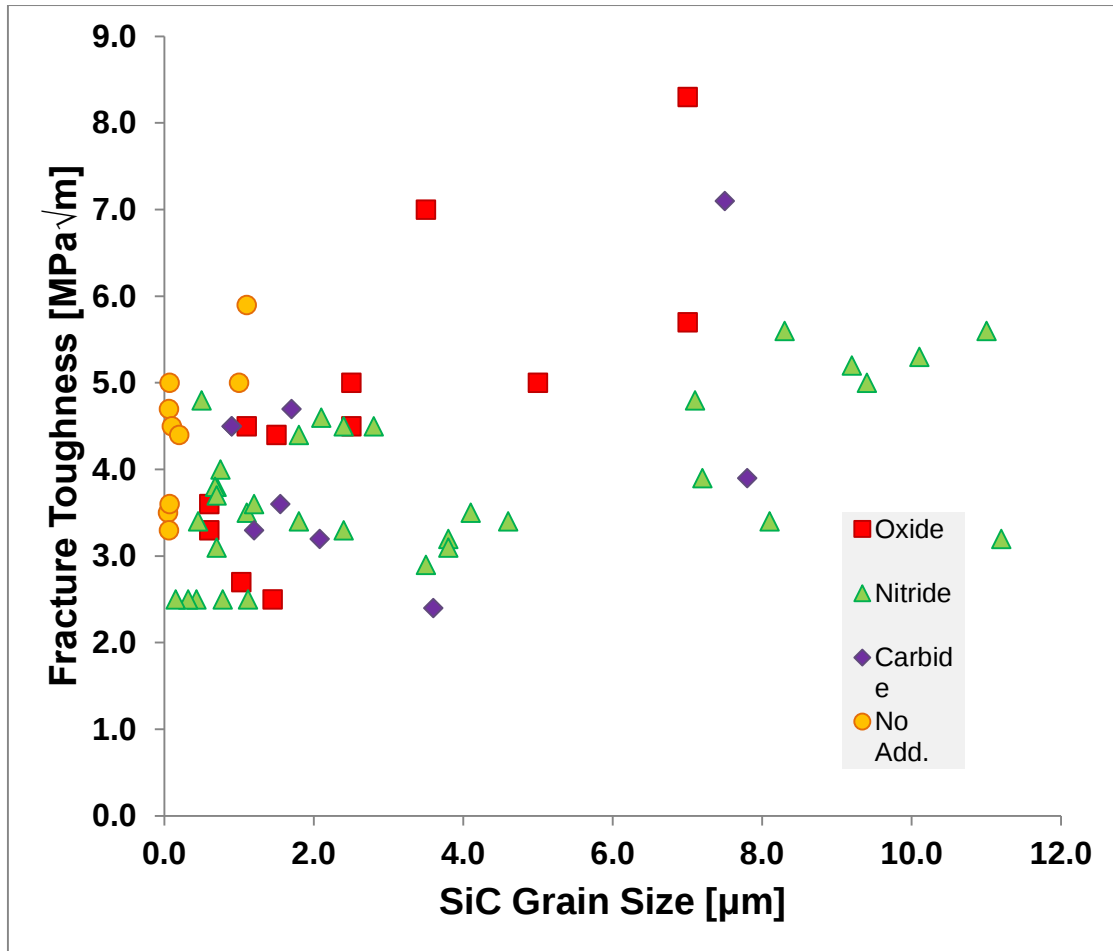


Figure 6.8: Map of fracture toughness as a function of grain size and additive family, from the data in Tables 6.1–6.4 and Chapter 5.

The few papers from Tables 6.1–6.6 and Chapter 5 that have both strength and grain size data are plotted in Figure 6.9. The x-axis is actually the reciprocal square root of grain size, to linearize the Hall-Petch equation, where the y-intercept $\sigma_i = 631$ MPa and slope $B = 166$ MPa·μm^{0.5}. The numerous processing variables and limited data do not strongly support a linear relationship, as the coefficient of determination $R^2 = 0.381$. In

general, the strength declines with grain size, but is also a function of other variables such as porosity and second-phase content not shown in Figure 6.9.

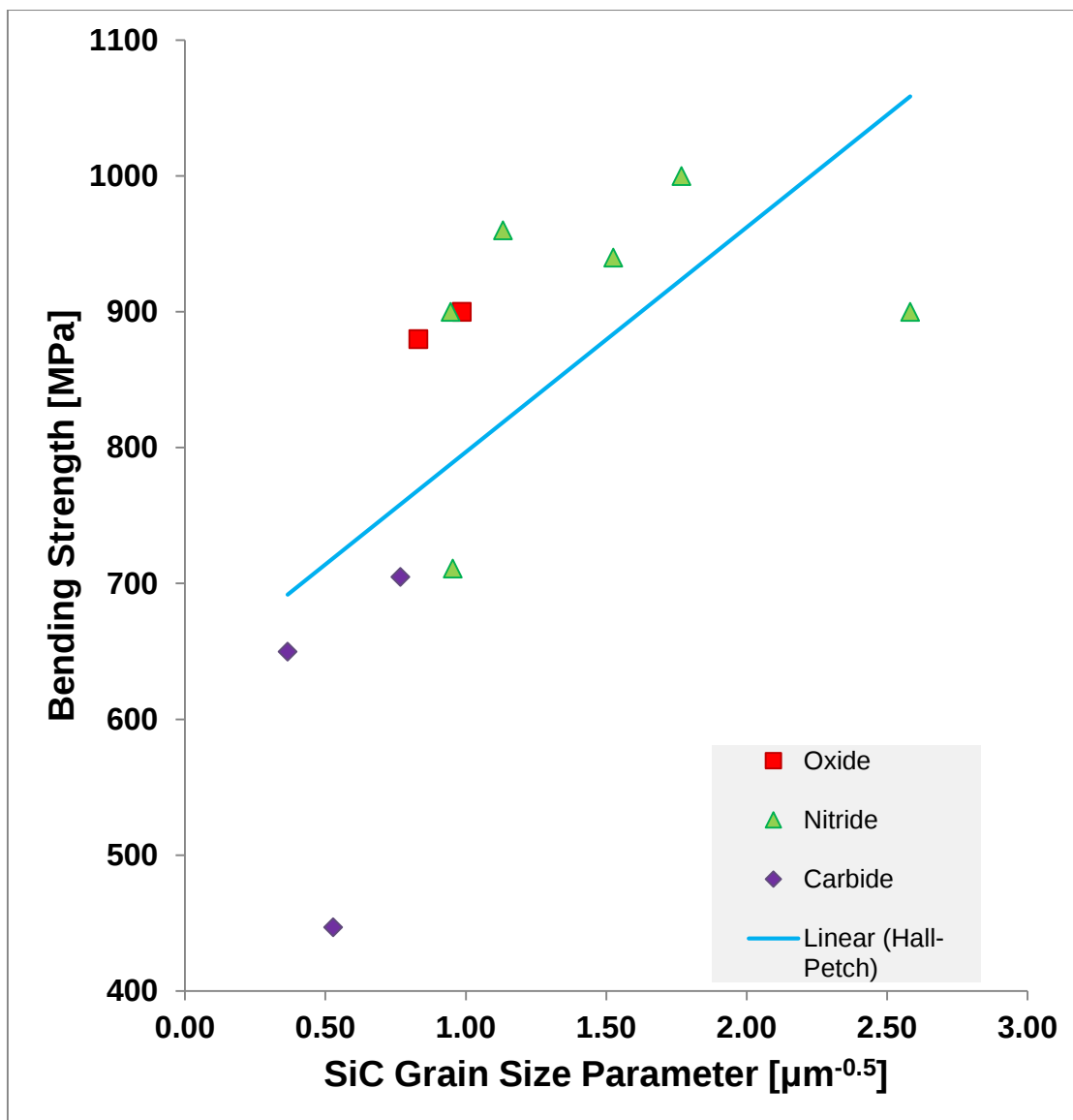


Figure 6.9: Hall-Petch diagram of bending strength as a linear function of the reciprocal square root of grain size, from the data in Tables 6.1–6.4 and Chapter 5.

Similar to Fig. 6.9, the Vickers hardness data are plotted as a function of the reciprocal square root of grain size in Figure 6.10. The y-intercept is 23.9 GPa and the slope is $-0.97 \text{ GPa} \cdot \mu\text{m}^{0.5}$. The goodness of fit of the Hall-Petch line is even more tenuous than

for strength, as the coefficient of determination $R^2 = 0.232$. Lomello et al.¹⁷ were unable to draw a strong correlation between grain size and hardness, as reflected by the no-additive points on the right side of Figure 6.9. As with strength, the hardness is apparently more dependent upon indenter force and other variables than on grain size.

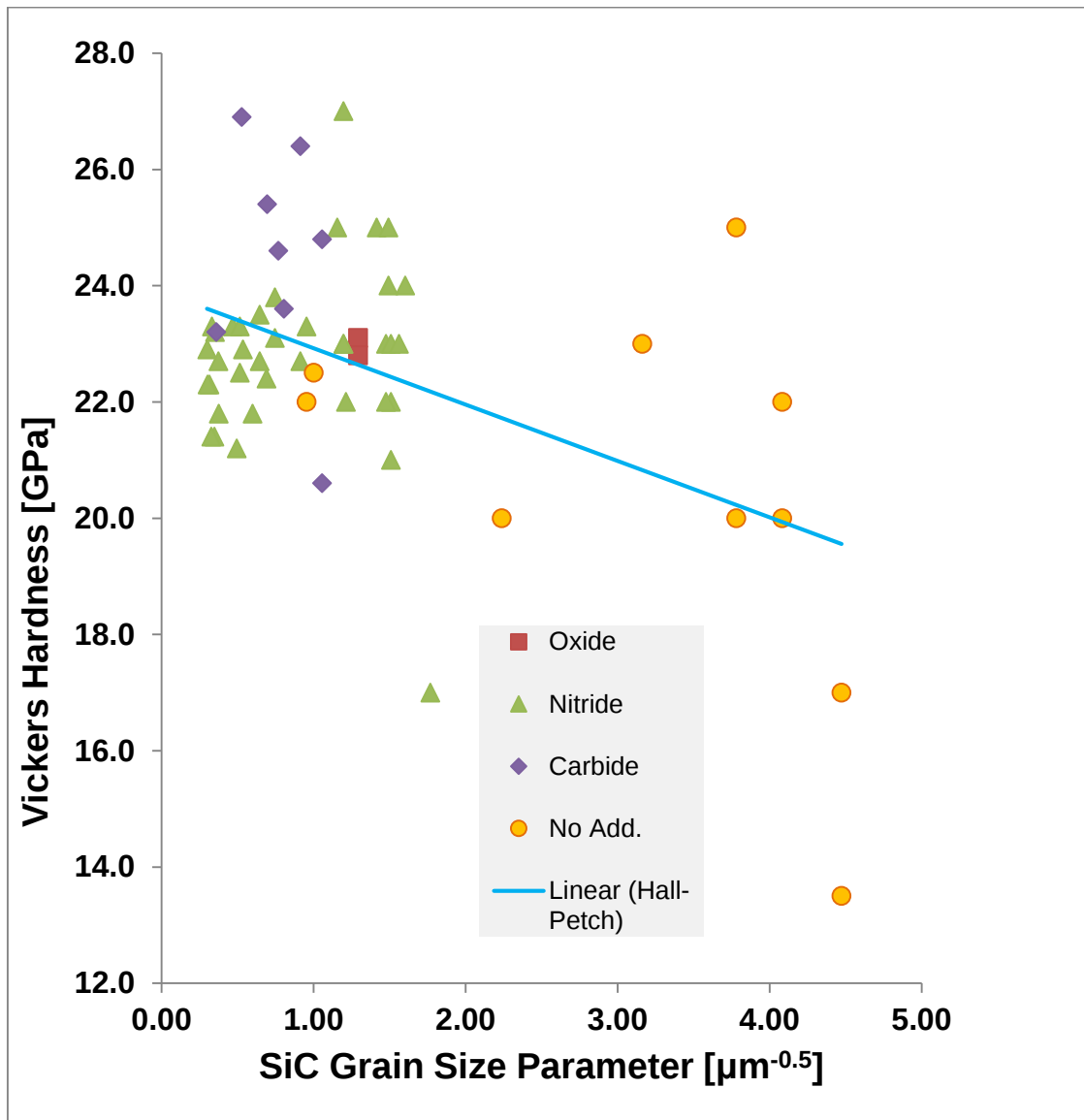


Figure 6.10: Hall-Petch diagram of Vickers hardness as a linear function of the reciprocal square root of grain size, from the data in Tables 6.1–6.4 and Chapter 5.

The value of one on the x-axis in Figures 6.9 and 6.10 somewhat arbitrarily divides microparticles to the left of unity from nanoparticles on the right. The higher costs of SiC nanoparticles are not clearly justified by gains in strength or hardness.

Selections from the best properties from each additive group are given in Table 6.7. Several other composition-process combinations in addition to those given in Table 6.6 yield approximately 100% densification, for example. In each citation in Table 6.6, the results were somewhat dependent upon the measurement method, such as 3-pt vs. 4-pt bending for strength, indentation vs. fracture mechanics for toughness, and ISE for hardness. The grain size control values are the lowest values from Figure 6.4. The citations in Table 6.7 were also selected for their high density, typically >95%, and low additive amounts.

Table 6.6: Summary of selected property values in the papers cited in Tables 6.4–6.4.

Objective	Value	Additives	Process	End Note
Density	>99%	none	HP, 2500°C, 5 GPa	Nadeau ²¹
		1% C + 0.25% B ₄ C	HP, 2100°C, 1 hr, 28 MPa, Ar	Ray ²⁸
		6% (67 mol% MgO : 16 Al ₂ O ₃ : 17 Y ₂ O ₃)	HP, 1800°C, 30 min, 29 MPa,	Foster ³⁰
		2% α + 10% Y ₂ O ₃ + 3% AlN	HP, 1850°C, 1 hr, 30 MPa, Ar + N ₂ , annealed 10 hr @ 1850°C in Ar + N ₂ .	Balog ³⁷
Strength [MPa]	715	none	SPS, 1650°C, N ₂	Liu ²²
	705	1.65% Al	HP, 2100°C, 1 hr, 28 MPa, Ar	Ray ²⁸
	900	2% Al ₂ O ₃	SPS, 1900°C, 600 min, N ₂	Hotta ⁹
	1000	10 vol% (70 mol% AlN + 30 mol% Y ₂ O ₃)	SPS, 1900°C, 600 s, 30 MPa, N ₂	Hotta ⁹

Objective	Value	Additives	Process	End Note
Fracture toughness [MPa m ^{0.5}]	8.2	none	SPS, 1650°C, N ₂	Liu ²²
	9	1-3% Al + 0.6% B + 4% C	HP, 1600°C, 50 MPa	MoberlyChan ²⁵
	6.2	85.6% β -SiC + 0.9% α -SiC + 13.5% Y ₃ Al ₅ O ₁₂	HP, 1800°C, 1 hr, 25 MPa, Ar	Kim ³⁶
	6.1	79.6% β -SiC + 0.8% α -SiC + 2.7% AlN + 16.9% Er ₂ O ₃	HP, 1900°C, 1 hr, 25 MPa, N ₂	Kim ³⁶
Vickers hardness [GPa]	38	none	HP, 1200°C, 35 min, 4.5 GPa	Mao-lin ²³
	26.9	1% C + 0.25% B ₄ C	HP, 2100°C, 1 hr, 28 MPa, Ar	Ray ²⁸
	34	4% γ -Al ₂ O ₃	HP, 1300°C, 30 min, 4.5 GPa	Mao-lin ²³
	28	2% α + 5.30% Yb ₂ O ₃ + 4.70% Sm ₂ O ₃ + 3% AlN	HP, 1850°C, 1 hr, 30 MPa, Ar + N ₂ , annealed 10 hr @ 1850°C in Ar + N ₂ .	Balog ³⁷
Grain size control (G ₂ /G ₁)	4	None	SPS, 1850°C, 5 min, Ar	Guillard ¹³
	~1	3.5% C	HIP, 1600°C, 980 MPa, 1 hr	Shinoda ²⁷
	2	9% (67 mol% Mg(NO ₃) ₂ (H ₂ O) ₆ + 16% Al(NO ₃) ₃ (H ₂ O) ₉ + 17% Y(NO ₃) ₃ (H ₂ O) ₆)	HP, 1800°C, 30 min, 25 MPa, Ar	Huang ³¹
	1.2	Colloidal 3.6 vol% (5 mol Al ₂ O ₃ + 3 mol Y ₂ O ₃)	PS, 1950°C, 1 hr, Ar	Ortiz ³⁹
	1.3	5% AlN	HP, 2100°C, 1 hr, 28 MPa, Ar	Ray ²⁸

6.5 Summary

- Oxide additives yield the best densification and toughness of SiC.
- Carbide additives require the highest temperatures and lowest pressures to densify.
- The highest room-temperature strength comes from nitride additives, the lowest from oxides.

- The lowest toughness is yielded by nitride additives. Considerable overlap between the five arbitrarily chosen additive families exists in terms of densification, hardness, strength and toughness.
- The rare earth oxides did not produce any significant improvements in densification or mechanical properties compared to other additives, but may be beneficial for improved thermal conductivity due to the low solubility of lanthanide-series ions in the SiC lattice.
- The toughness is enhanced by partial $\beta \rightarrow \alpha$ transformation, which is aided by α -SiC seeds or annealing.
- SPS is useful for rapid densification of SiC. SHS is promising, but few data are available.
- N_2 can enhance or suppress SiC sintering, depending on additives. N_2 can supplant cover mix during sintering when nitride additives are used.
- The strength of SiC is retained at high temperatures. SiC is promising for creep applications, especially when densified without additives. The trade-off is that SiC without additives is susceptible to uncontrolled grain growth.
- A trade-off exists between strength and toughness, with regard to optimum grain size.
- The strength, hardness and toughness of SiC are only moderately sensitive to grain size. Other variables may be of greater importance to the mechanical properties. This affects the choice of more-expensive nanoparticles over microparticles as a means of strengthening or hardening SiC.
- SiC grain growth may be controlled by high SPS pressure, deagglomeration by magnetic stirring, low boron content, ternary Al-B-C phases, AlN, Al, C and a two-step sintering process. Grain growth generally increases with sintering temperature, but oxide, nitride and carbide additives are effective at preventing uncontrolled grain growth.

- Carbon as an additive has several sources in addition to added graphite or amorphous powder, including residual free carbon from the Acheson process, organic binders and phenolic resin.
- No one additive group or sintering process resulted in all the best properties, but 99% densification, grain growth of a factor less than two, 700-MPa bending strength, 6-MPa m^{0.5} toughness and 26-GPa hardness in SiC can be achieved by multiple methods of pressure-assisted sintering.

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CHAPTER 7

7 Microstructural Development of Green Micro-Machined, Injection-Molded Silicon Carbide

Abstract

Silicon carbide in two particle size distributions with 5% AlN and 5% Y₂O₃ was extruded with a paraffin-polypropylene binder. The extruded feedstock was pelletized and injection-molded into 10-gm bars. The bars were dewaxed by solvent or pyrolysis, green micro-machined (GMM) before or after dewaxing, and sintered at 2000°C for 2 hr in argon at atmospheric pressure. High-temperature x-ray diffraction indicated the beginning of the Al-Y-O precipitates at ~1200°C for both size distributions. Dilatometry quantified the large thermal expansion associated with dewaxing, and the onset of sintering, also at ~1200°C for both size distributions. The monomodal bars withstood the stresses of GMM well, but the waxy swarf had a tendency to adhere to the workpiece and bond to the workpiece during sintering. The bimodal bars were much less resilient to GMM, whether dewaxed before or after GMM, and thermal dewaxing. All bars were at least 95% densified. The effects of particle size distribution at each step were compared.

“Success is the ability to go from one failure to another with no loss of enthusiasm.”
 – Sir Winston Churchill

7.1 Introduction

Powder injection molding (PIM) is promising for silicon carbide fabrication of complex shapes with fine features.^{1,2,3,4} The feature size is limited by the particle size and process parameters such as debinding. PIM SiC is sintered without pressure assistance in contrast to hot pressing, hot isostatic pressing (HIP) or spark-plasma sintering (SPS). The difficulty of sintering SiC without external pressure is mitigated by sintering additives such as carbon, B₄C, Al₂O₃, MgO, AlN and Y₂O₃. Carbon reduces the surface SiO₂ on SiC particles, boron modifies the grain boundary energy, and the others mostly form binary or ternary eutectic liquid phases (fluxes) at high temperatures that enable liquid-phase sintering (LPS).^{5,6,7,8}

Nanoparticles can be used to increase the packing density and solid volume fraction ϕ of the feedstock.⁹ Nanoparticles alone densify easily but tend to agglomerate and shrink excessively, while micro-particles alone avoid the agglomeration and shrinkage but can be difficult to densify. A bimodal distribution of majority SiC micro-particles and minority nanoparticles has been used with favorable results.^{10,11}

Small-scale features can be formed by green micro-machining (GMM), where the green compact is shaped with a high-speed milling bit.^{12,13} GMM can generate defects, and impart residual stresses leading to fractures during and after sintering. The smallest structures that can be formed by PIM are about ten times the particle size.¹⁴ The smallest structures that can be formed by GMM are limited by the particle size, as the fracture is expected to be primarily in the binder. Electrical discharge machining (EDM), ultrasound, lasers, electrochemical etching, plasma etching¹⁵, robocasting¹⁶ and lithography¹⁷ are among the alternatives to GMM.

Dewaxing and debinding studies, that is, removal of the organic components of PIM green bodies, of the two compositions in this paper were reported elsewhere.^{18,19} A thermogravimetric analyzer (TGA) was used to confirm the ceramic : binder ratios. The

effects of solvent debinding versus thermal debinding, both used in this study, on PIM SiC bars were demonstrated elsewhere.¹³ Several other debinding methods are available, but most require specialized equipment.²⁰

The use of argon for sintering could affect the stability of the AlN additive. AlN can decompose to metal vapor and N₂ near the sintering temperature in inert gas or vacuum, but this reaction would be suppressed in an N₂ atmosphere.⁷ At the same time, N₂ retards the densification of SiC.²¹ In Ar, the loss of AlN could result in unreacted yttria or a precipitate such as Y₂Si₂O₇ or Y₂SiO₅ rather than the expected Y-Al oxides.²²

The purpose of this paper is to evaluate GMM of PIM SiC before and after sintering. The effects of GMM, debinding method and particle size distribution on microstructures, phases, hardness, grain size and density are reported.

7.2 Experiment

Two α -SiC thermoplastic feedstocks were prepared and analyzed. All percentages are mass%, except as specified. The first feedstock was monomodal, with $D_{50} = 0.7 \mu\text{m}$ and a solid fraction $\phi = 53 \text{ vol\%}$. The second was bimodal, with 90% of the monomodal powder and 10% of a finer powder with $D_{50} = 20 \text{ nm}$ and a solid fraction $\phi = 54 \text{ vol\%}$. The binder in both cases was 50% paraffin, 35% polypropylene, 10% low-density polyethylene-g-maleic anhydride, LDPE-g-MA, and 5% stearic acid. The polypropylene has a molecular weight of 42,600, and a melting point of 142°C. The LDPE-g-MA served as a bridging agent to help bond the ceramic particles to the polypropylene. The stearic acid acted as a lubricant. Each ceramic powder in the feedstock had 5% 1.1- μm AlN + 5% 40-nm cubic Y₂O₃ as sintering additives. All the ceramic powders and organic binders were commercially available.

The feedstocks were mixed and pelletized in a 27-mm twin-screw counter-rotating extruder (Entek Manufacturing Inc., Lebanon, OR), described elsewhere.^{23,24} The critical and optimum solids loading values were determined by torque rheometry (Intelli-Torque Plasticorder, Brabender GmbH, Duisberg, Germany) in previous papers.^{11,24} The pellets were injected at 32.8 cm³/s into 92 × 23 × 3.1 mm flat “dog bone” tensile bars at $T = 163^\circ\text{C}$

and $P = 41.4$ MPa (monomodal) or 48.3 MPa (bimodal). Segments of green bars of the two particle size distributions were compared by high-temperature X-ray diffraction (HTXRD) (Ultima III, Rigaku Corp., Tokyo, Japan) with Rietveld²⁵ phase analysis, and dilatometry (DIL402C, Netzsch-Gerätebau GmbH, Selb, Germany) under a 30-cN load at ASTM E831²⁶, before any further processing.

The even-numbered green bars in Table 7.1 were machined under the conditions set forth in the next paragraph, with a series of 0.25-mm wide grooves on one face, perpendicular to the long axis. The odd-numbered bars in Table 7.1 were not machined. Some of the bars were thermally dewaxed in a proprietary process before GMM, and some were solvent-dewaxed 4.0 hr in heptane at 60°C after GMM in Table 7.1. All the bars were thermally debound for 2.0 hr at 400°C and 4.0 hr at 500°C in N₂. All the bars were sintered at atmospheric pressure for 2.0 hr at 2000°C in argon, supported in the furnace by graphite foil, and furnace cooled. Thermal dewaxing and debinding of the two feedstocks were described in Chapters 3 and 4.

The GMM setup at Carnegie Mellon University includes an instrumented miniature machine tool (MMT) with a precision three-axis slide with 10-nm resolution, 250 mm/s maximum linear speed and a 25 mm × 50 mm × 50 mm workspace. The MMT is equipped with an ultra-high-speed air bearing/air turbine spindle capable of 160,000-rpm maximum rotational speed. A two-fluted micro-end mill of 254 μ m diameter is attached to the spindle with a 3.125 mm precision collet.²⁷ The end mill has a cobalt-cemented tungsten carbide cutting edge. The effects of PIM SiC and GMM parameters on cutting forces, surface roughness, burr formation and edge retention are the subject of a related but independent study.^{28,29}

Table 7.1: Green processing of specimens.

Set No.	Particle Size Distribution	Dewaxing Method	GMM?
1	Monomodal	Solvent	No
2			Yes
3		Thermal	No
4			Yes
5	Bimodal	Solvent	No
6			Yes
7		Thermal	No
8			Yes

The density was measured by Archimedes' method in water, ASTM C373-14.³⁰ Cross-sections of the bars were ceramographically prepared, and chemically etched in boiling Murakami's etchant for 10 min.³¹ The Knoop hardness was measured via ASTM C1326³² under a 1-kg (9.81 N) load. The grain size was measured via the circular intercept method in ASTM E112.³³

7.3 Results and Discussion

7.3.1 X-Ray Diffraction

Segments of a monomodal green bar were analyzed by HTXRD at room temperature (RT, ~25°C), 400, 500 and 1200°C, and at RT after the 1200°C HTXRD scan, the 1600°C dilatometer scan and full sintering for 2 hr at 2000°C, in Figure 7.1. The first RT scan confirms the presence of the original components. The HTXRD was heated at a rate of 1.0 K/min in low vacuum at $P \approx 70$ mPa, and was intended to simulate the dewaxing, debinding and partial sintering conditions. As expected, the ceramic phase was unchanged after the dewaxing step at 400°C and the debinding step at 500°C. No crystallization in any of the binder components was observed. At 1200°C, the upper limit of the HTXRD, the ceramic microstructure was still virtually unchanged except that the peaks had shifted slightly leftward (greater d-spacing) with thermal expansion. When the HTXRD cooled down to RT, the heating unit was removed (its window has an attenuating effect on X-ray intensity) and the cooled specimen was scanned a fifth time. Three phases were just

beginning to precipitate, $\text{Y}_3\text{Al}_5\text{O}_{12}$ (“YAG,” for yttria-alumina garnet), $\text{Y}_4\text{Al}_2\text{O}_9$ (“YAM,” monoclinic) and YAlO_3 (“YAP,” perovskite).

A different segment from the same bar was heated in a dilatometer in the next section of this paper to 1600°C , cooled back to RT and scanned by XRD as the sixth curve in Figure 7.1. The three precipitate phases were easily detectable after 1600°C , and the Y_2O_3 was entirely consumed, as indicated in Table 7.2. The AlN, although of different lattice dimensions and structure ($4.36 \text{ \AA}$, face-centered cubic), was masked by the dominant 6H SiC ($3.08 \times 15.09 \text{ \AA}$, close-packed hexagonal with a six-layer stacking fault sequence) at its strongest Bragg reflections at all temperatures, and interfered with the Rietveld analysis to the extent that AlN was indistinguishable from SiC at RT and in other cases where AlN was expected, in Table 7.2. The lack of unreacted Y_2O_3 , $\text{Y}_2\text{Si}_2\text{O}_7$ and Y_2SiO_5 indicates the AlN was adequately stable until it reacted with Y_2O_3 somewhere between 1200 and 1600°C . The Al and N that remained after the Y_2O_3 was consumed dissolved in the SiC lattice or evaporated. The additional oxygen in the Y-Al-O phases came from the 2-nm layer of SiO_2 on the surfaces of the SiC particles,³⁴ and a sintering atmosphere of unknown but finite partial pressure of O_2 .

Another bar from Set 1 in Table 7.1 was sintered, cooled to RT and scanned as the seventh and topmost curve in Figure 7.1. The fully densified bar was 95% 6H SiC and the remainder a combination of YAG and YAP in Table 7.2. Some SiO_2 was visible on the as-sintered surface of the bar and detected by the XRD, a clue that the furnace atmosphere was not perfectly oxygen-free.

A bimodal green bar received the same HTXRD treatment in Figure 7.2 and Table 7.2, with nearly identical results, except that no YAG was detected in the fully densified bar from Set 5 in Table 7.1. The nanoparticle addition had an apparently negligible effect on the binder components, precipitated phases and transition temperatures.

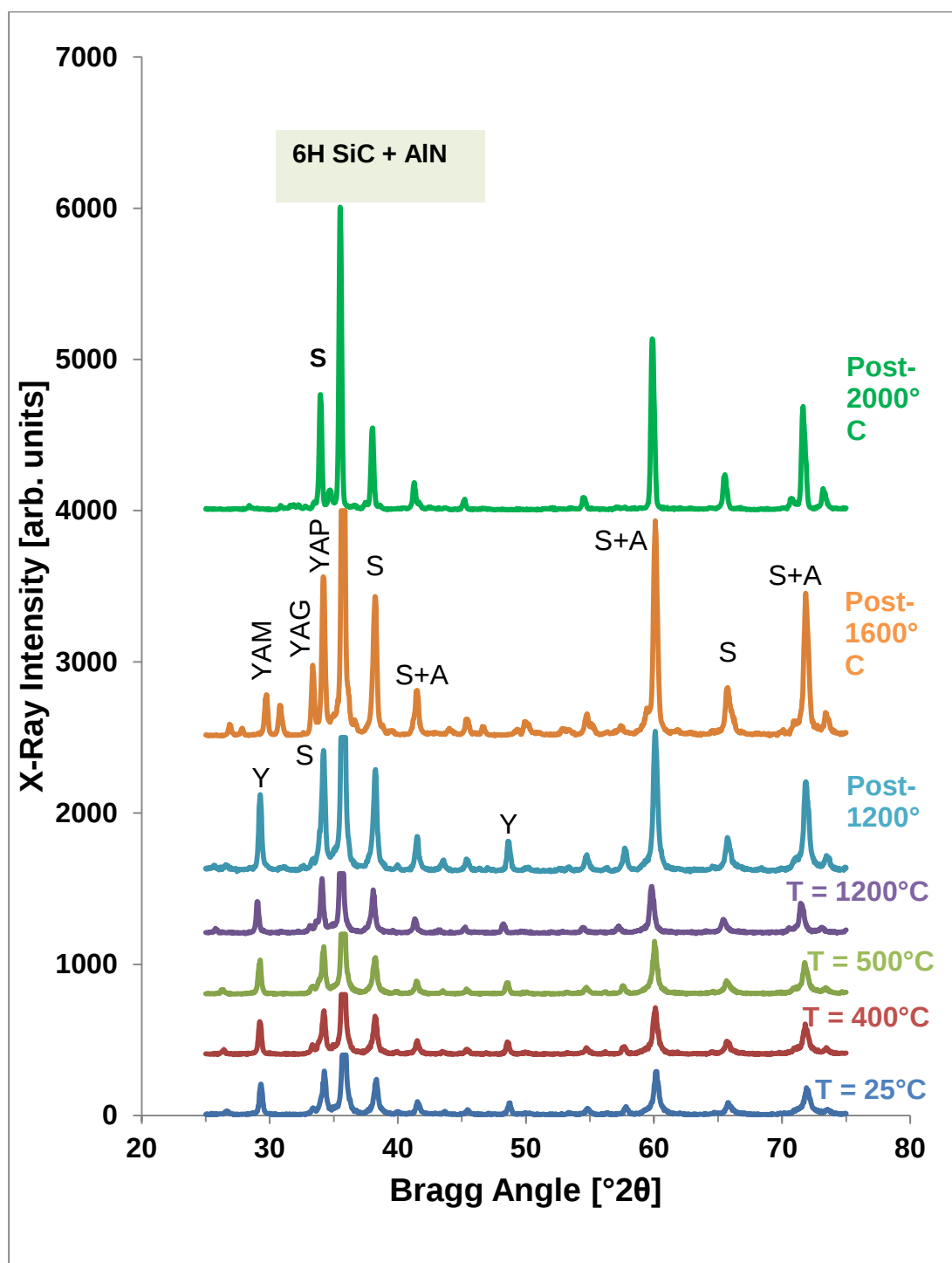


Figure 7.1: High-temperature x-ray diffraction scans of a green monomodal bar. The largest 6H-SiC peak in each of the lower six scans was truncated to magnify the lesser peaks.

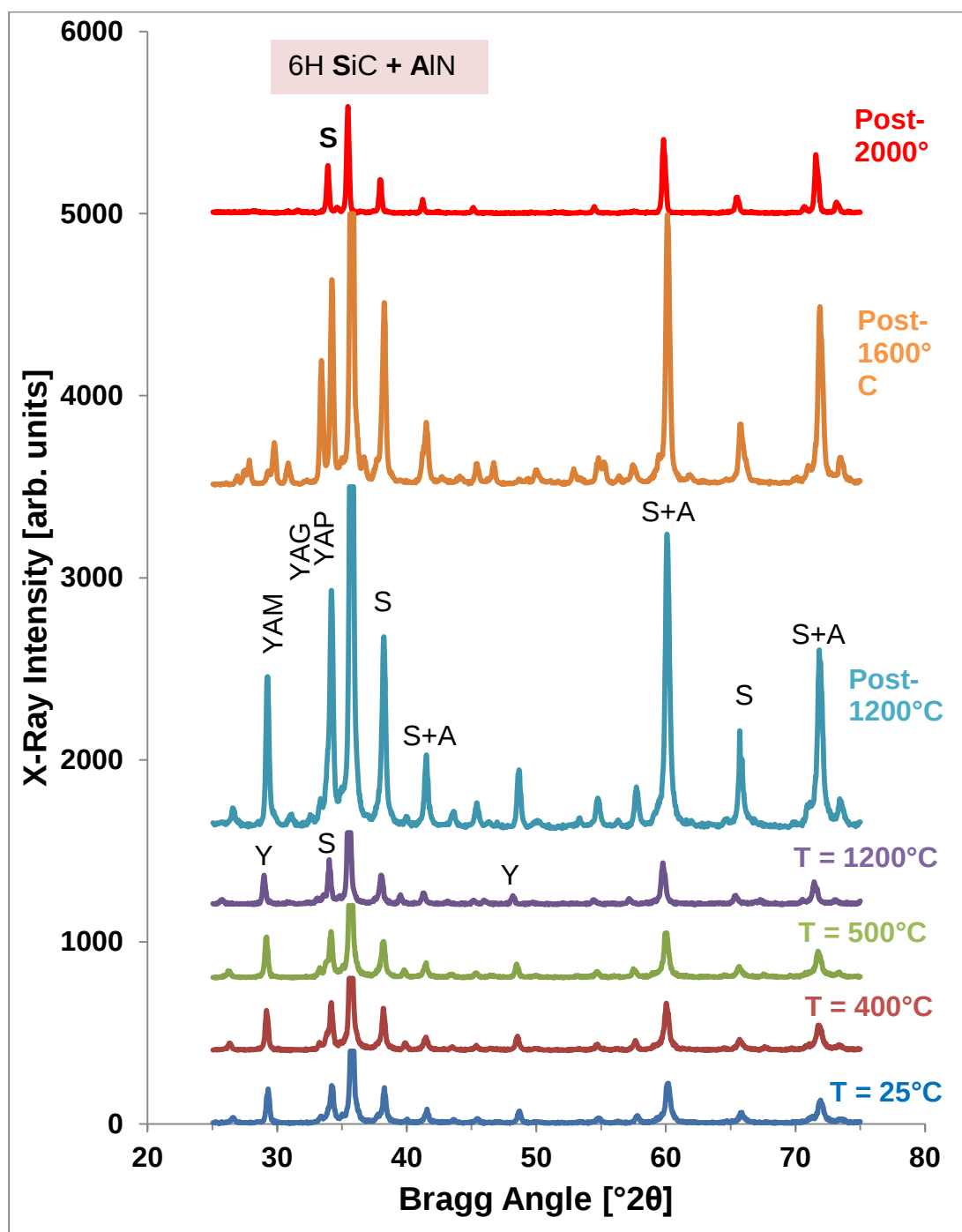


Figure 7.2: High-temperature x-ray diffraction scans of a green bimodal bar. The largest 6H-SiC peak in each of the lower six scans was truncated to magnify the lesser peaks.

Table 7.2: Rietveld phase analysis of feedstocks after thermal treatments.

Rietveld Analysis	Temp	6H SiC	AlN	Y ₂ O ₃	YAG	YAP	YAM	SiO ₂
	°C	mass%	mass%	mass%	mass%	mass%	mass%	mass%
Monomodal	25	97.5		2.5				
	400	94.9		5.1				
	500	90.9	7.4	1.7				
	1200	88.2		1.6	7.7	2.6		
Post-HTXRD	1200@RT	83.3	9.0	4.8	0.2	2.7		
Dilatometer	1600@RT	84.5			4.3	6.7	4.5	
Sintered	2000@RT	94.6			2.7	1.3		1.3
Bimodal	25	98.0		2.0				
	400	97.1		2.9				
	500	96.1		3.9				
	1200	90.1		2.9	1.4	5.6		
Post-HTXRD	1200@RT	79.6	14.4	4.3	0.3	0.5	0.9	
Dilatometer	1600@RT	89.5			6.8	1.0	2.2	0.6
Sintered	2000@RT	92.6				3.8		3.6

7.3.2 Dilatometry

The dilatometer was heated at 1.0 K/min from RT to 400°C, isothermal for 2.0 hr for dewaxing, heated at 2.0 K/min to 500°C, isothermal for 4.0 hr for debinding, heated at 2.0 K/min to 1600°C, cooled at 2.0 K/min to 1000°C to minimize thermal shock, and cooled to RT at 5.0 K/min, all in helium at 75 ml/min STP. The monomodal green bar segment in Figure 7.3 expanded rapidly up to 90°C to the approximate glass transition of the wax, and continued to expand up to 117°C. At that point, viscous flow and expansion in the transverse direction exceeded expansion in the longitudinal direction, and the bar began to shrink in length. The bar shrank to less than its original length up to 273°C, when all its wax had decomposed and evaporated. The polypropylene may have also evaporated at that point, as noted in the slower TGA scans of the monomodal feedstock in Chapter 4.¹⁹ The dewaxed bar began to expand again at the end of the 400°C isothermal hold. The change in length was positive but very small up to and through the 500°C isothermal hold, indicating that the polypropylene was already lost or had a negligible effect on thermal expansion, quite unlike the wax. From 500 to 1200°C, the small expansion of $2.4 \times 10^{-6}/\text{K}$ was comparable to the expansion of fully sintered SiC. The densification began at 1200°C,

increased to the dilatometer's upper limit of 1600°C, and continued briefly even upon cooling.

The bimodal green bar segment in Figure 7.3 expanded rapidly up to 93°C. The transverse expansion and viscous flow began at 96°C. A subtle change in slope at 152°C could be the beginning of the polypropylene decomposition, although it was not seen until nearly 400°C in a TGA scan at 5.0 K/min in Chapter 4.¹⁹ The thermal strain of the green bar reached a minimum at 275°C, before the 400°C isothermal hold, indicating that all the organics had evaporated. The shrinkage was only about half as much at the minimum thermal strain as the monomodal bar, a result of the higher solids loading in the bimodal feedstock. The lattice expansion of $3.3 \times 10^{-6}/\text{K}$ was continuous from 500 to 1183°C, when densification began. The shrinkage of the bimodal bar over the 1600°C partial sintering cycle was 59% as much as that of the monomodal bar.

The XRD and dilatometry results taken together indicated that the densification of SiC and the precipitation of the Y-Al-O phases both began at ~1200°C, and the precipitation reactions were complete by 1600°C. The density results in Table 7.3 indicated that the pressureless densification of SiC was complete after 2.0 hr at 2000°C.

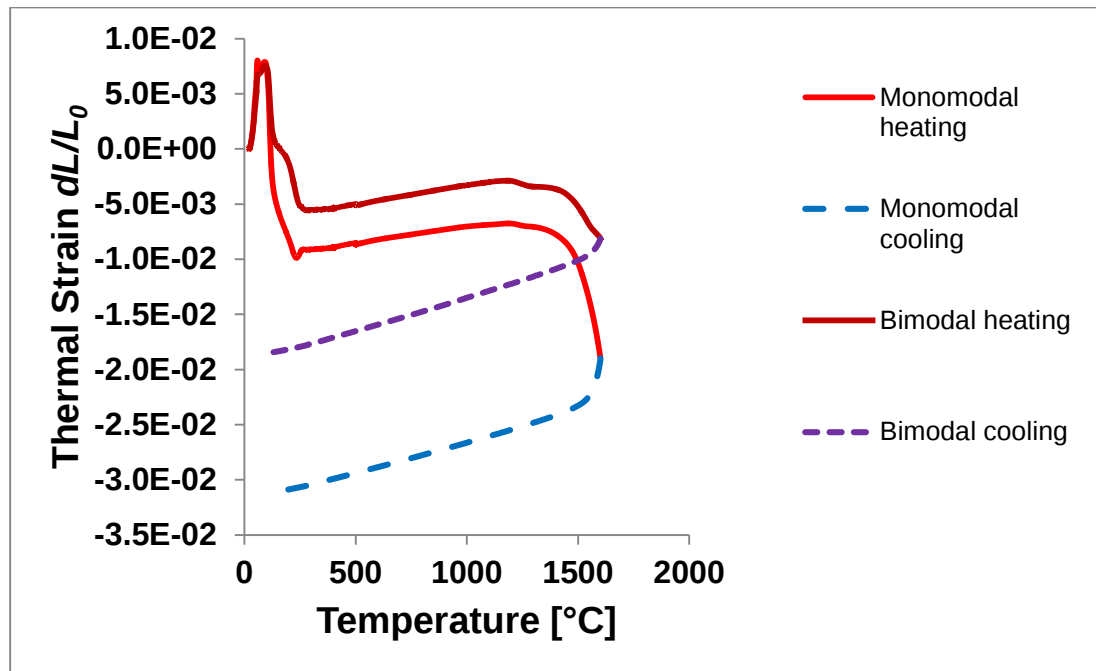


Figure 7.3: Thermal expansion and contraction of green injection moldings.

7.3.3 Green Micro-machining

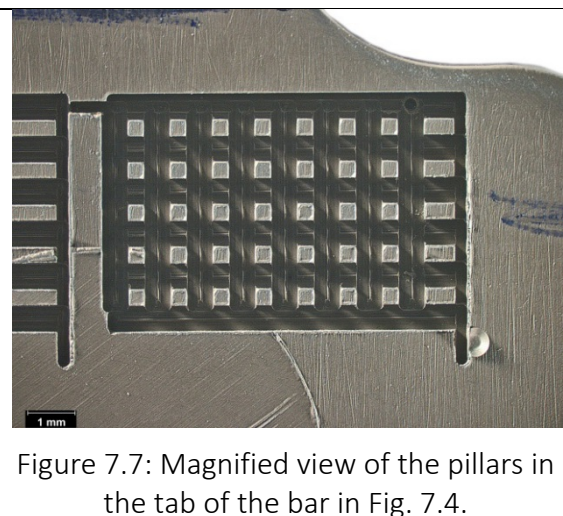
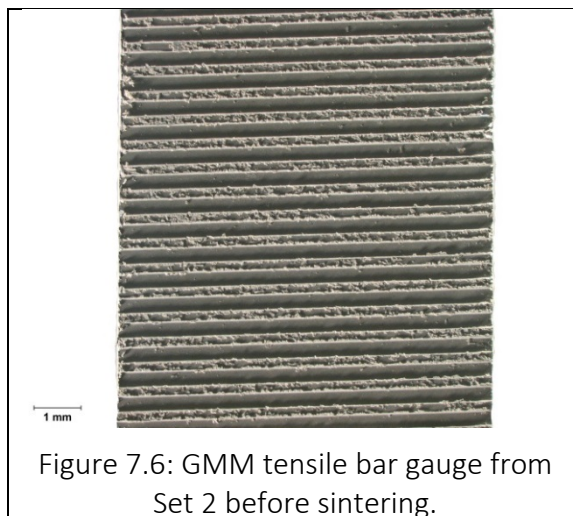
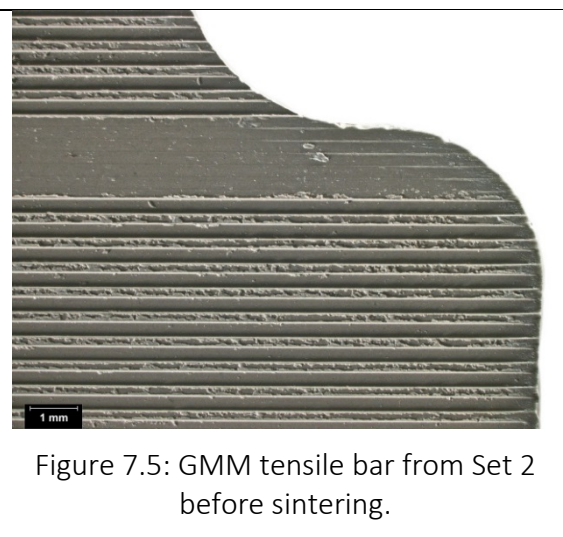
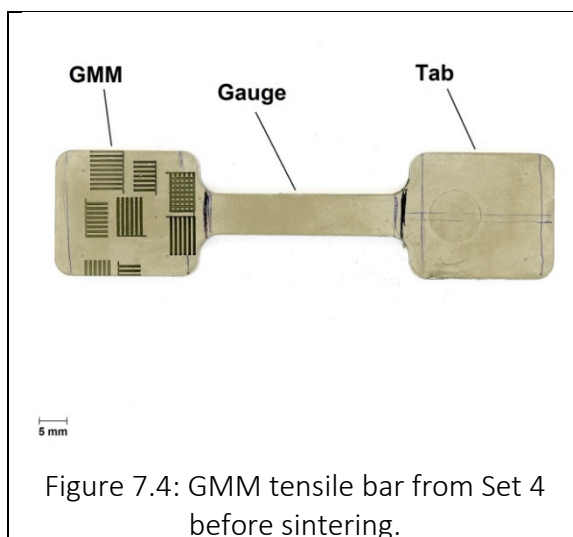
The GMM tensile bar before sintering, from Set 4 in Table 7.1, shown in its entirety in Figure 7.4, was machined with 0.25- and 0.54-mm bits. The damage from GMM was small enough that cross-grooves were possible, creating 0.375-mm pillars. This bar was thermally dewaxed before GMM, and the loss of wax as a lubricant for the tool and strengthener of the green structure was not detrimental.

The 0.25-mm bit made smooth grooves in monomodal Set 2 before sintering, but left waxy swarf attached to the corners of the ridges in the tab in Figure 7.5 and gauge in Figure 7.6. The GMM features in Set 4 in Figures 7.7 and 7.8 retained very little swarf, while the parallel 0.25-mm grooves in Figure 7.9 retained almost as much swarf as the similarly machined bar in Figure 7.5. The dewaxed gauge in Figure 7.10 retained much less swarf than its wax-on counterpart in Figure 7.6.

The bimodal bars in Figure 7.11–7.14 were heavily damaged by GMM, leaving only the two tabs from Sets 6 and 8 as nominally viable. The wax-on bar in Figures 7.11 and 7.12 retained little swarf and showed little GMM damage within the tab. The dewaxed bar

in Figures 7.13 and 7.14 also retained little swarf but had much more GMM damage than the wax-on bimodal bar in Figure 7.11 or the dewaxed monomodal bar in Figures 7.4 and 7.7–7.10.

Some of the surface markings visible in Figures 7.4, 7.5 and 7.7–7.9 came from the PIM mold, rather than as artifacts of GMM.



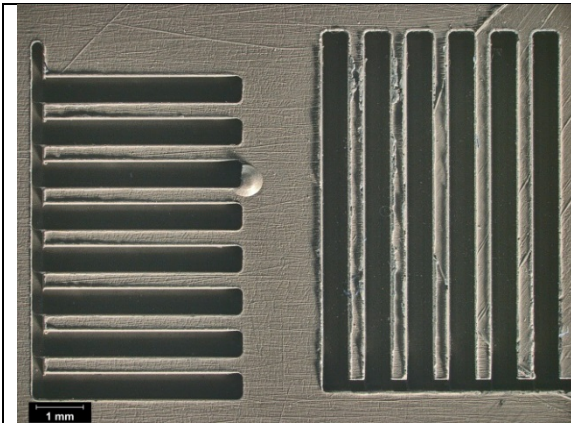


Figure 7.8: Magnified view of the two groove sizes in the tab of the bar in Fig. 7.4.

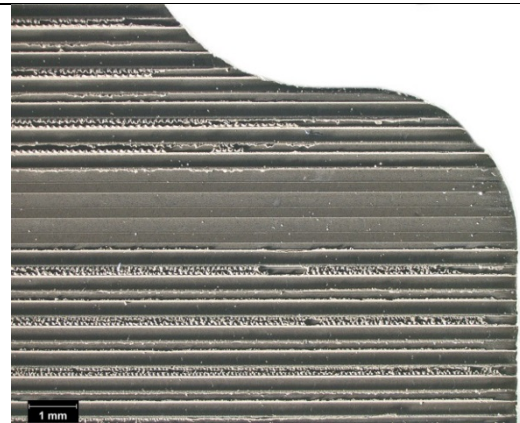


Figure 7.9: GMM tensile bar tab from Set 4 before sintering.

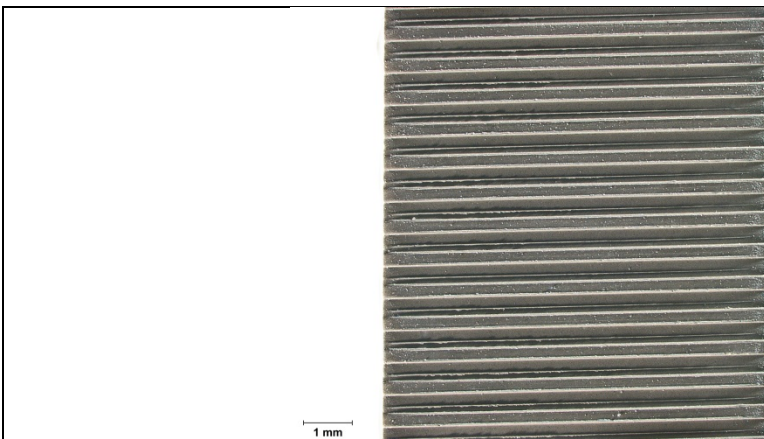
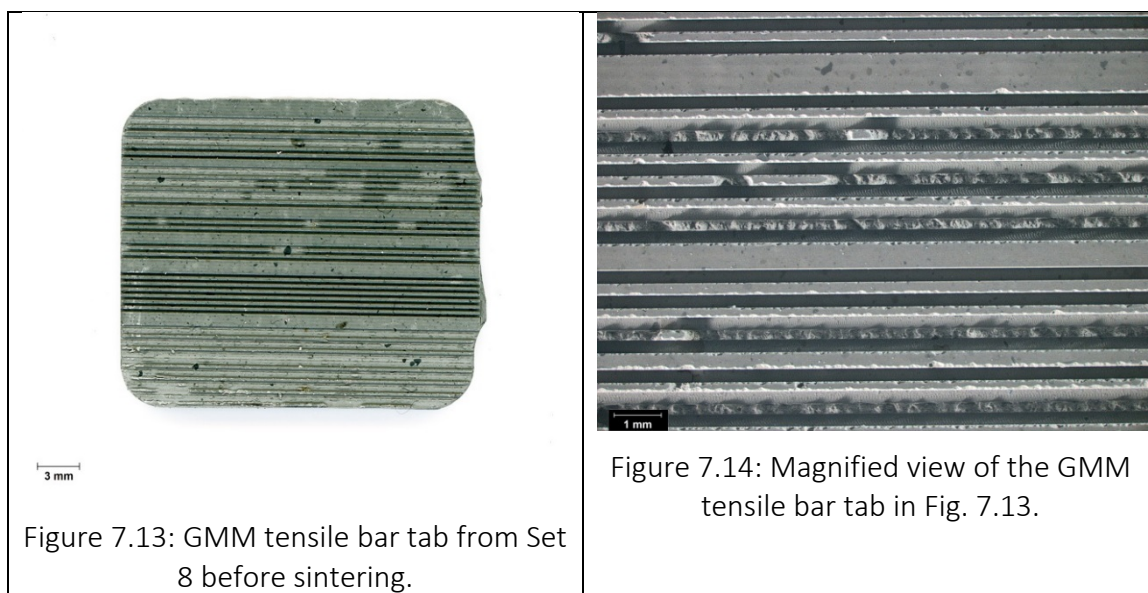
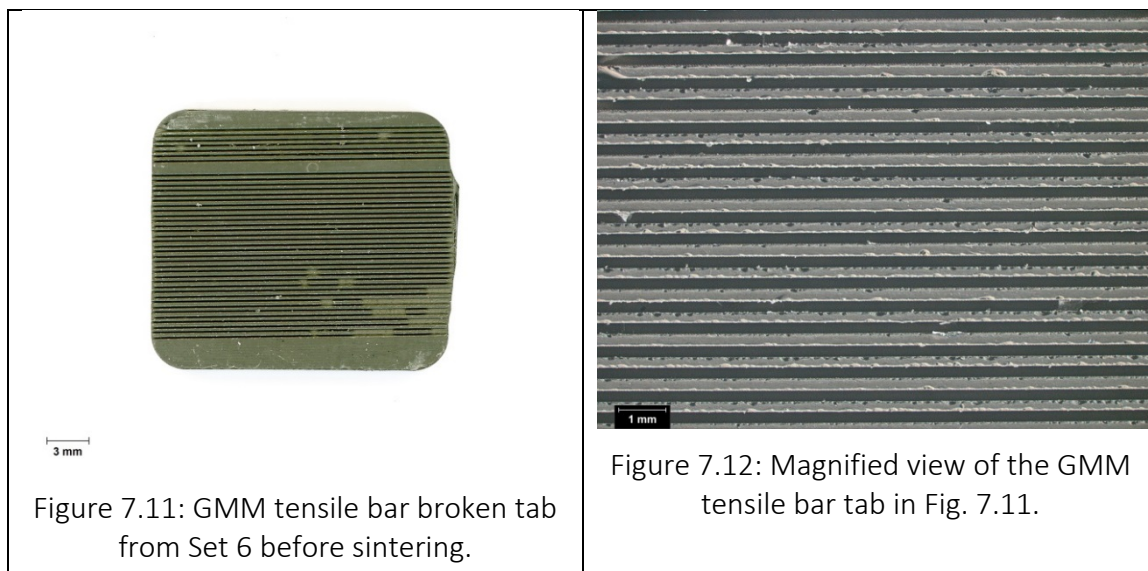


Figure 7.10: GMM tensile bar gauge from Set 4 before sintering.



7.3.4 Sintering

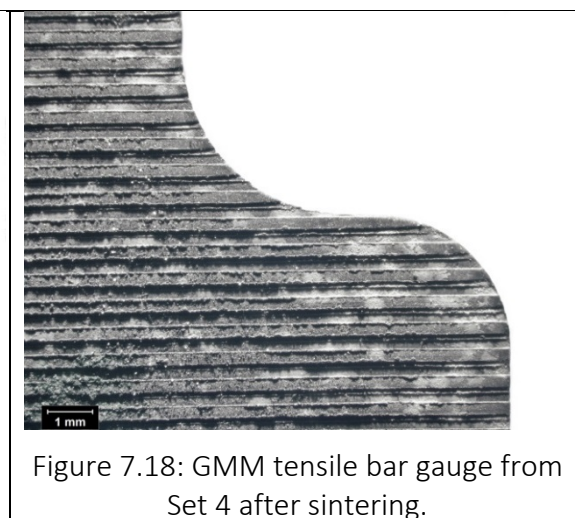
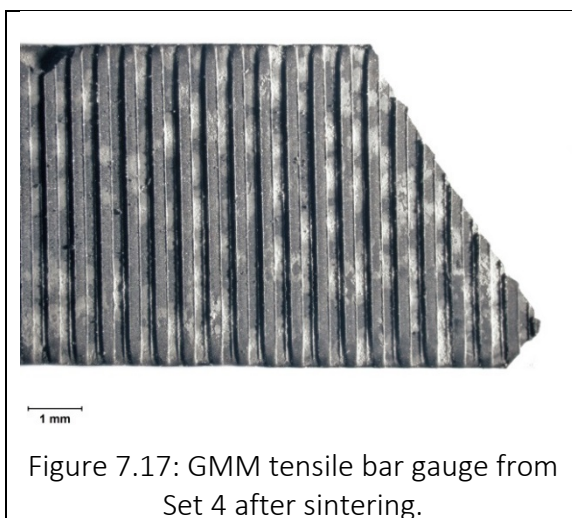
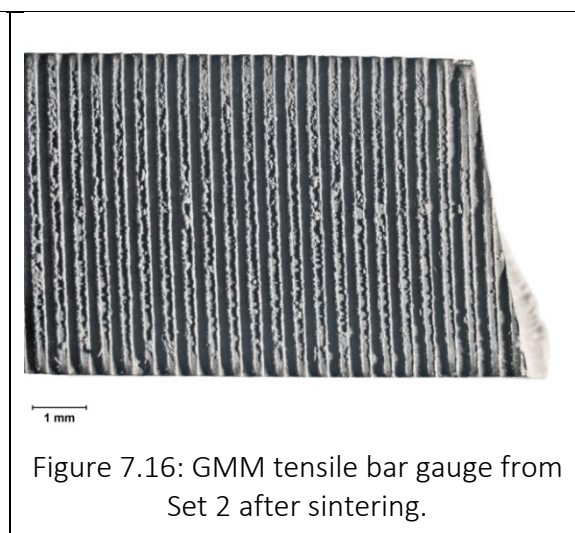
All the whole bars fractured during sintering, even those that did not have GMM grooves as stress-raisers or were solvent-dewaxed, such as the monomodal bar from Set 1 in Figure 7.15. A layer of oxide scale was noted on all the bars, in spite of the inert sintering atmosphere. All the bars shrank about 50 vol% from the as-PIM dimensions in Table 7.3. Some warpage was also noted. All bars were densified to 95% of ideal density or better. The ideal density was estimated as 3.25 gm/cm³ based on the initial phases, with some

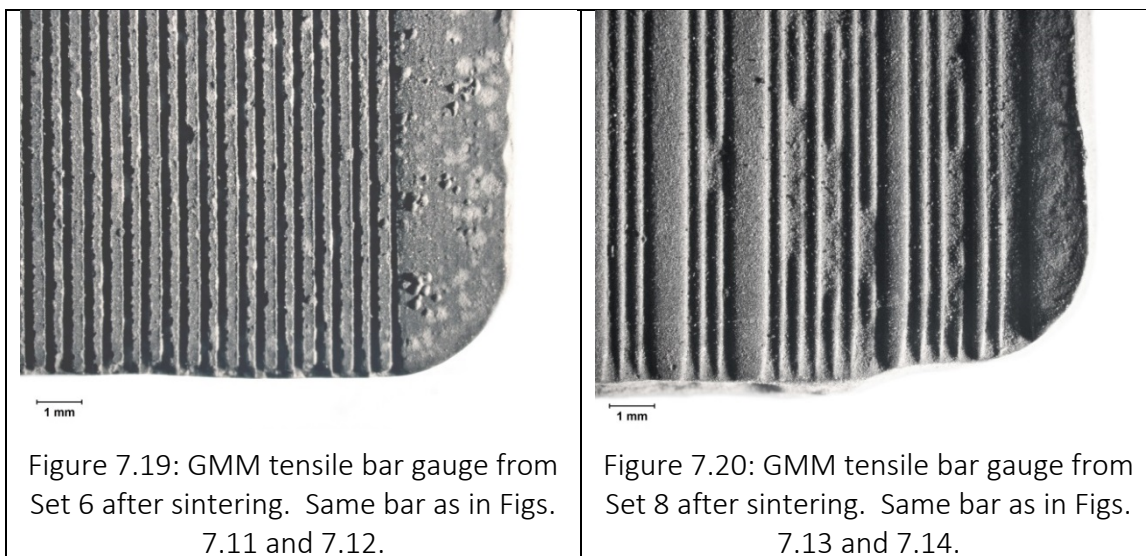
error as a result of the conversion or evaporation of the additives. The shrinkage in the bimodal bars appeared to exceed the monomodal bars in contradiction to the higher bimodal density, but the shrinkage values may be distorted slightly by the warpage. Linear shrinkages of 20% for monomodal and 15% for bimodal were reported for essentially the same two compositions in an earlier study.³⁵

Table 7.3: Density (ρ) and shrinkage of bars in length (L), width (W) and thickness (T) after sintering.

Bar No.	ρ [% ideal]	$\Delta L/L_0$	$\Delta W/W_0$	$\Delta T/T_0$
1	94.9	-0.180	-0.188	-0.154
2	95.2	-0.176	-0.178	-0.196
3	96.1	-0.166	-0.181	-0.205
4	96.6	-	-0.180	-0.221
Monomodal mean	95.7	-0.174	-0.182	-0.194
5	97.0	-0.160	-0.167	-0.196
6	96.8	-	-0.169	-0.147
7	98.3	-0.205	-0.209	-0.215
8	99.2	-	-0.225	-0.311
Bimodal mean	97.8	-0.182	-0.192	-0.217

The sintered monomodal gauge section from Set 2 in Figure 7.16 retained the swarf during sintering, and its fracture crossed at least three planes corresponding to the GMM grooves. The thermal stresses of sintering were not limited to the notch effect of the grooves alone. The swarf-free gauge section from Figure 7.10 yielded smooth although not defect-free grooves and ridges in Figure 7.17. The attached swarf seen on the tab in Figure 7.9 was present on the same set in Figure 7.18, although not as much as in Figure 7.16. The sintered bimodal tab section from Set 6 in Figure 7.19 changed little during sintering, but the GMM features are much rougher than those of the monomodal bars in Figures 7.16–7.18. The GMM features in the tab section from Set 8 in Figure 7.20 appear to be rounded rather than square and sharp-edged as the other three GMM sets are.





7.3.5 Microstructures

7.3.5.1 Knoop Hardness

The Knoop hardness (HK) was about the same, 14–15 GPa, for Sets 1–6 in Table 7.4. The two bimodal, thermally dewaxed bars, Sets 7 and 8, were substantially lower at 9–10 GPa. In all cases, the HK was about the same within ~ 0.1 mm of the machined grooves (“Near GMM”) as it was in the center of the cross-section (“Bulk”). The GMM had no effect on the HK, but the combination of bimodal particles and thermal dewaxing reduced the HK, and by extension, the strength by about one-third. The weakening effect is thought to be due to the partial oxidation of the nano-SiC particles during the dewaxing step that was not fully counterbalanced by either the modest reducing effect of the pyrolysis of the binder or the dissolution of the SiO_2 by the LPS flux.

The HK in this study was similar to that reported by Onbattuvelli et al.³⁵ for similar compositions and processing, and among the lower values of Figure 6.5. The HK, and by extension, the strength, of the SiC bars in this study might be increased by GPS or annealing for, say, 8 hr at 1500°C, to reduce porosity and optimize bonding between grains.

Table 7.4: Knoop hardness and grain size of sintered microstructures.

Bar	Particle Size	Dewaxing Method	Knoop Hardness [GPa]		Grain Size [μm]
			Near GMM	Bulk	
1	Monomodal	Solvent	-	14.6	0.56
2			14.5	14.3	0.52
3		Thermal	-	14.0	0.69
4			13.7	14.4	0.59
5	Bimodal	Solvent	-	14.9	0.70
6			14.2	15.5	0.79
7		Thermal	-	9.59	2.7
8			10.1	9.07	3.0

7.3.5.2 GMM in Cross-Section

As-polished cross-sections of the four GMM bars are shown in Figures 7.21–7.24. The tenacious hold by the swarf onto the substrates is apparent in Figures 7.21 and 7.22, even after post-GMM solvent-dewaxing in Figure 7.21. The rectangular grooves in Figure 7.21 were distorted to more of a dovetail shape during sintering. In Figure 7.23, the bimodal swarf was removed from the substrate solvent-dewaxing after GMM, but the solvent treatment did not alleviate residual stresses enough to prevent fracture in the machined features or the substrate. The apparent rounding of the grooves in Figure 7.20 during sintering in Set 8 was confirmed in Figure 7.24. The rounding suggests premature decomposition of the polypropylene backbone during thermal dewaxing that caused creep in the binder and SiC particle rearrangement in the fine features of the green body. The decomposition of the polypropylene may have been catalyzed by the SiC nanoparticles, in contrast to the kinetics study by thermogravimetric analysis of the feedstock in Chapter 4.¹⁹ The high density of pluck-outs in Figure 7.22 is another manifestation of the grain-bonding weakness detected by the HK test. Knoop indentations are visible just below the GMM grooves in Figures 7.21, 7.23 and 7.24.

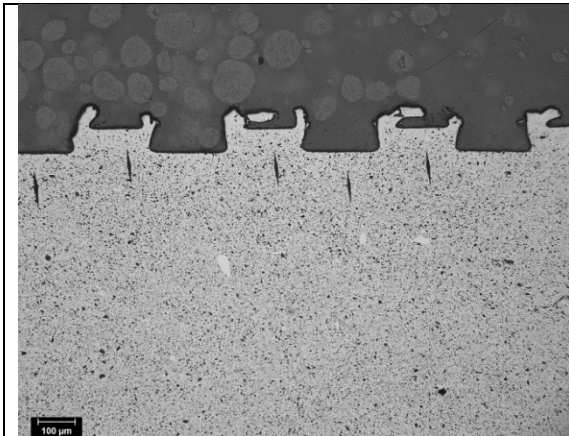


Figure 7.21: Unetched cross-section of the GMM region in a bar from monomodal Set 2.

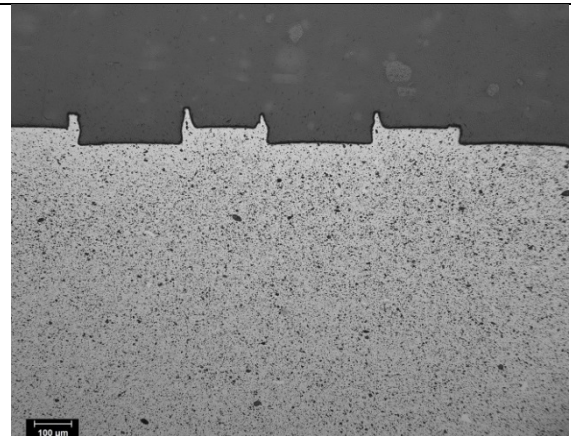


Figure 7.22: Unetched cross-section of the GMM region in a bar from thermally dewaxed monomodal Set 4.

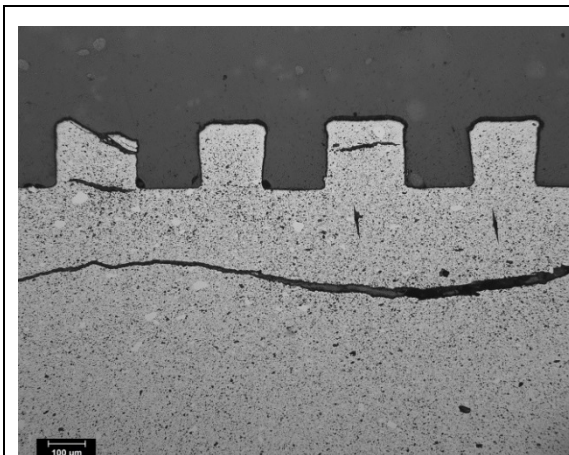


Figure 7.23: Unetched cross-section of the GMM region in bimodal Bar 6.

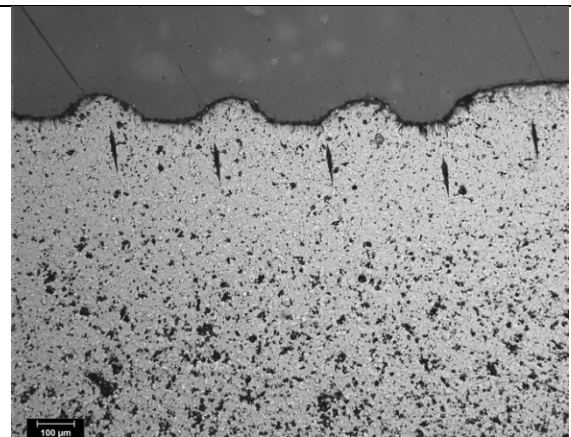


Figure 7.24: Unetched cross-section of the GMM region in thermally dewaxed bimodal Bar 8.

7.3.5.3 Grain Size

The etched microstructures of monomodal bars 1–4 are shown in Figures 7.25–7.28, where the grain size and morphology are very similar and essentially independent of GMM or the dewaxing method. The edges shown in the lower left corner of Figure 7.26 and the lower right corner of Figure 7.28 are the boundaries of GMM features. The grain sizes of Bars 1–4 in Table 7.4 are about the same as the initial mean particle size.

The etched microstructures of bimodal bars 5–8 are shown in Figures 7.29–7.32. The grain size and morphology in Figures 7.29 and 7.30 are very similar to the four monomodal bars in Figures 7.25–7.28 and also independent of GMM or the dewaxing method. The edge shown on the right side of Figure 7.30 is the boundary of a GMM feature, where the microstructure is the same as the interior of the bar and its non-GMM counterpart, Bar 5.

The microstructures of the two bimodal, thermally dewaxed Bars 7 and 8 in Figures 7.31 and 7.32 are quite unlike the other six. These two microstructures have the appearance of fracture surfaces, yet they were polished and etched together with Bars 1–6. The grain size is larger than Bars 1–6 by a factor of five, indicating a lack of grain-growth control by the sintering additives. The Y-Al-O droplets visible on the SiC grains in Figures 7.31 and 7.32 suggest that the additives formed a non-crystallizing liquid that did not wet the SiC grains adequately. Y-Al-O-rich flakes in the lower left corner of Figure 7.32 suggest the liquid phase did partially crystallize. Bars 7 and 8 were fully dense but weakly bonded, resulting in the topography in Figures 7.31 and 7.32, the pluck-outs in Figure 7.24, and the low HK in Table 7.4. The mechanism of the seemingly contradictory full densification but weak bonding is under further investigation by electron probe micro-analysis (EPMA) mapping.

A conjectural explanation of the mechanism in Bars 7 and 8 is that the combination of thermal dewaxing and SiC nanoparticles created an unfavorable environment for the additives. The SiO₂ layer on the SiC nanoparticles and O₂ partial pressure oxidized the AlN to Al₂O₃. The carbon from the pyrolyzed polypropylene reduced the Al₂O₃ to metallic Al. The liberated Al increased the diffusion rate of the SiC and caused grain growth, unlike AlN, which retards grain growth.^{36,37,38} The lower YAG content in the bimodal body in Table 7.2 indicated that more Al was in solution than in the monomodal body after complete sintering. The 6H polytype has a tendency for exaggerated grain growth compared to other polytypes.⁵ The intergranular weakness was caused by the higher (than SiC) thermal expansion of the YAG or Y-Al-O glass on the grain boundaries, resulting in a residual tensile stress at the interface upon cooling.³⁹ Potential preventive measures include N₂

overpressure during thermal dewaxing to stabilize AlN, and annealing the SiC for several hours at $T \geq 1500^{\circ}\text{C}$ after sintering to distribute the additives.⁴⁰

Some oversized SiC grains are visible at the lower magnifications in Figures 7.21-7.24. These oversized grains had no effect on densification or HK, but could be detrimental to bending strength.

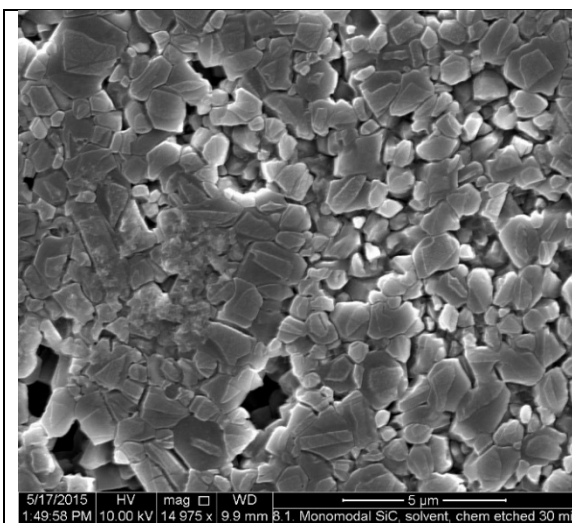


Figure 7.25: Etched cross-section of monomodal Bar 1.

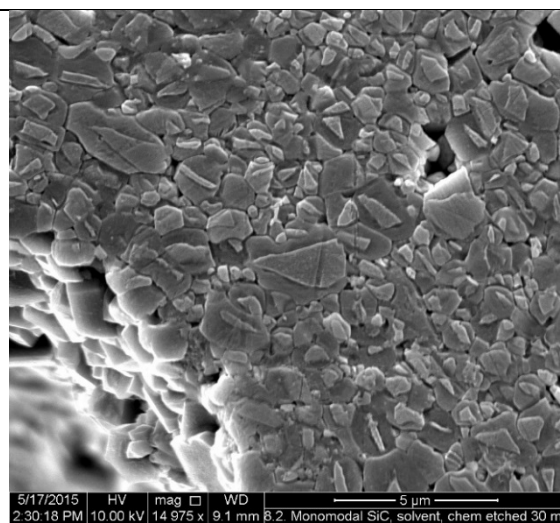


Figure 7.26: Etched cross-section of the GMM region in monomodal Bar 2.

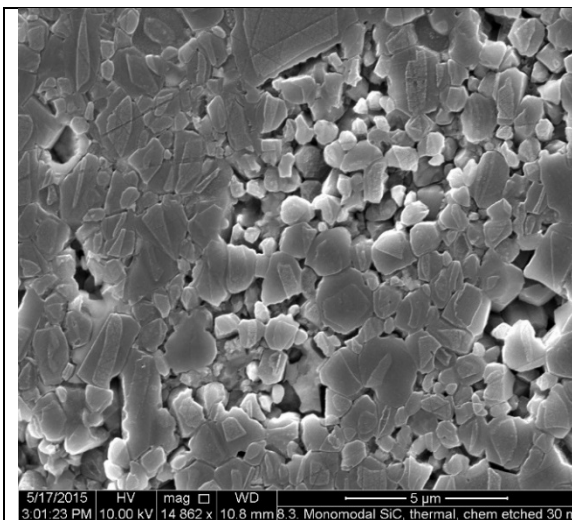


Figure 7.27: Etched cross-section of monomodal Bar 3.

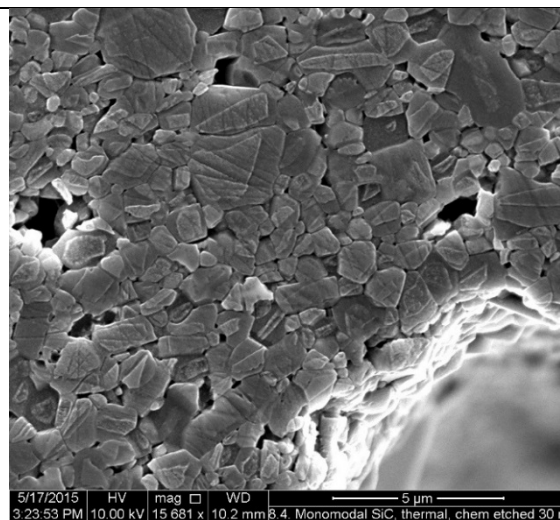


Figure 7.28: Etched cross-section of the GMM region in monomodal Bar 4.

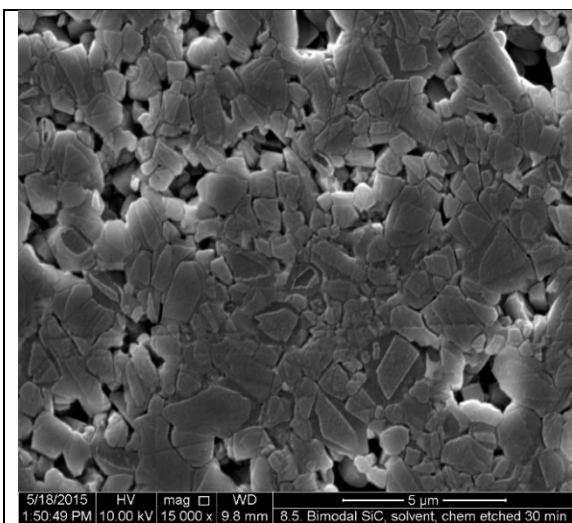


Figure 7.29: Etched cross-section of bimodal Bar 5.

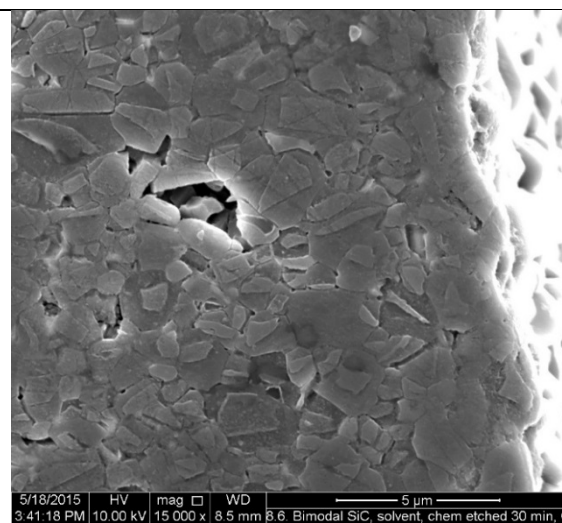


Figure 7.30: Etched cross-section of the GMM region in bimodal Bar 6.

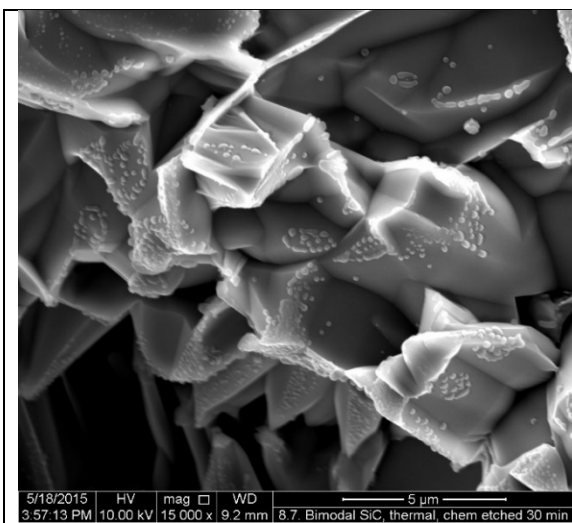


Figure 7.31: Etched cross-section of bimodal Bar 7.

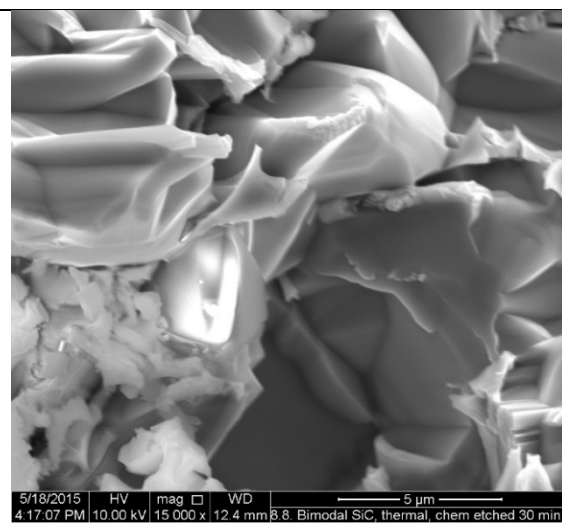


Figure 7.32: Etched cross-section of the GMM region in bimodal Bar 8.

7.4 Conclusions

Monomodal PIM SiC densified with AlN and Y_2O_3 was very compatible with GMM, except that the swarf adhered strongly to the substrate whether the substrate was solvent-dewaxed after GMM or thermally dewaxed before GMM. Thermal dewaxing reduced the amount of adhering swarf and sintering distortion but did not completely eliminate either.

Bimodal PIM SiC densified with AlN and Y₂O₃ was much less compatible with GMM than monomodal, except that swarf adhesion was not a problem. Solvent-dewaxing after GMM resulted in low distortion of the GMM grooves but fractures during sintering. Thermal dewaxing before GMM affected the mechanism of the sintering additives and resulted in severe rounding of the GMM edges and corners, and uncontrolled grain growth and weak bonding between grains during sintering. The mechanism of LPS failure associated with thermal dewaxing that nevertheless resulted in a fully dense microstructure is unclear, and the subject of further investigation.

A dilatometer scan showed equal strain during dewaxing expansion, but twice as much strain in monomodal SiC during debinding. Densification began at about 1200°C in both compositions.

HTXRD did not reveal any crystallization in the binder components during heat-up, but showed the beginnings of precipitation of yttria-alumina compounds at about 1200°C in both compositions. XRD after full sintering verified that all the AlN and Y₂O₃ had been converted to YAG and YAP. The 6H α -SiC was stable throughout the thermal debinding and sintering processes; no other polytypes were detected at any point.

All compositions and treatments were densified to closed porosity by sintering at 2000°C for 2 hr in Ar, with 17–20% shrinkage in each dimension.

Future work may include EPMA mapping of elemental distribution in the microstructures, to assess the differences between Bars 1–6 and 7–8; higher-temperature XRD and dilatometry; and a stress evaluation of the dewaxing methods.

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CHAPTER 8

8 Green Micro-Machining and Sintering of Injection Molded Silicon Carbide

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Abstract

Powder injection molded (PIM) silicon carbide, SiC, is promising for a number of small-scale applications, but the feature size is limited by the particle size and process parameters. Small-scale features can be formed by green micro-machining (GMM), where the green compact is shaped with a high-speed milling bit. GMM can generate defects, and impart residual stresses leading to fractures during and after sintering. Two SiC compositions were mixed, extruded with paraffin-polypropylene binder, pelletized, injection molded as rectangular or tensile bars, micro-machined, dewaxed and sintered. The sintered bars were studied for microstructure development, crack growth, mechanical properties and feature morphology as functions of composition, GMM variables and sintering temperature and time. The volume : surface area ratio and dewaxing method proved critical to the viability of the coupon after sintering.

"Men of few words are the best men." — William Shakespeare, *King Henry V*

8.1 Introduction

Powder injection molded (PIM) silicon carbide, SiC, is promising for a number of small-scale applications, but the feature size is limited by the particle size and process parameters such as debinding. Small-scale features can be formed by green micro-machining (GMM), where the green compact is shaped with a high-speed milling bit. GMM can generate defects, and impart residual stresses leading to fractures during and after sintering. The purpose of this paper is to evaluate GMM PIM SiC before and after sintering.

8.2 Experiment

Two α -SiC thermoplastic feedstocks were prepared and analyzed.^{1, 2} All percentages are mass%, except as specified. The first feedstock was monomodal, with $D_{50} = 0.7 \mu\text{m}$ and a solid fraction $\phi = 53 \text{ vol}\%$. The second was bimodal, with 90% of the monomodal powder and 10% of a finer powder with $D_{50} = 20 \text{ nm}$ and a solid fraction $\phi = 54 \text{ vol}\%$. The binder in both cases was 50% paraffin, 35% polypropylene, 10% low-density polyethylene-g-maleic anhydride (LDPE-g-MA), and 5% stearic acid. The LDPE-g-MA is a bridging agent to help bond the ceramic particles to the polypropylene (PP). The stearic acid acted as a lubricant. Each feedstock had 5% 1.1- μm AlN + 5% 40-nm cubic Y_2O_3 as sintering additives.

The feedstocks were mixed and pelletized in a 27-mm twin-screw counter-rotating extruder, described elsewhere.¹ The critical and optimum solids loading values were determined by torque rheometry in previous papers.^{1,2}

The pellets were injected at $32.8 \text{ cm}^3/\text{s}$ into (a.) 70.25 mm bars with a 7.46 mm $\times$ 13.30 mm rectangular cross-section or (b.) 92 $\times$ 23 $\times$ 3.1 mm flat "dog bone" tensile bars at $T = 163^\circ\text{C}$ and $P = 41.4 \text{ MPa}$ (monomodal) or 48.3 MPa (bimodal). The green bars were machined under the conditions set forth in the next paragraph, with a series of 0.25-mm grooves on one face, perpendicular to the long axis. The GMM bars were thermally debound and sintered at atmospheric pressure under the conditions shown in Table 8.1,

supported in the furnace by graphite foil, and furnace cooled. Some of the bars were solvent-dewaxed before GMM. The density was measured by Archimedes' method in water, ASTM C373-14.³ The Knoop hardness was measured via ASTM C1326⁴ under a 1-kg (9.81 N) load.

The GMM setup at Carnegie Mellon University includes an instrumented miniature machine tool (MMT) with a precision three-axis slide with 10-nm resolution, 250 mm/s maximum linear speed and a 25 mm × 50 mm × 50 mm workspace. The MMT is equipped with an ultra-high-speed air bearing/air turbine spindle capable of 160,000-rpm maximum rotational speed. A two-fluted micro-end mill of 254 μm diameter is attached to the spindle with a 3.125 mm precision collet. The end mill has a cobalt-cemented tungsten carbide cutting edge. The effects of PIM SiC and GMM parameters on cutting forces, surface roughness, burr formation and edge retention are the subject of a related but independent study.^{5,6}

Table 8.1: Thermal debinding and sintering parameters.

Bar #	Step	Heating Rate	Set Point	Isothermal Time	Gas
		K/min	°C	hr	
1-4	Dewaxing	2.0	300	2	N ₂
	Bisque	2.0	500	4	N ₂
	Sintering	2.0	2000	2	Ar
5, 6, 8, 10, 11 & 13	Dewaxing	1.7	500	5	N ₂
	Sintering	1.7	2000	5	Ar
7, 9, 12 & 14	Dewaxing 1	1.7	500	5	N ₂
	Dewaxing 2	1.7	550	1	air
	Sintering	1.7	1900	5	Ar

8.3 Results and Discussion

8.3.1 Debinding

All fourteen bars were thermally dewaxed before they were sintered, in one or more steps, as given in Table 8.2. The first set, rectangular Bars 1–4, were GMM in the green state, before any dewaxing. The wax was removed by thermal evaporation in an N₂ atmosphere at 300°C for 2 hr, to open a network of pores to provide a path for the PP

vapors. The PP was removed by thermal degradation at 500°C for 4 hr in the same operation as the dewaxing. All the rectangular bars had a shape factor ψ , defined as the ratio of volume to surface area, of 2.24. In solvent debinding, the debinding rate varies inversely with ψ .⁷ The shape factor ψ is expected to affect the thermal debinding rate in a similar manner, as it is indicative of the diffusion path length in bars of similar mass.

Table 8.2: Thermal debinding and GMM parameters.* Not green micro-machined.

Bar	M/B	Dewaxed before GMM?		Shape factor ψ (V/SA)	Δm in N ₂	Δm in air	Microstructure
		Thermal	Solvent		%	%	
1	Monomodal	N	N	2.24	-	-	dense
2	Bimodal	N	N	2.24	-	-	dense
3	Monomodal	N	N	2.24	-	-	dense
4	Bimodal	N	N	2.24	-	-	dense
5	Monomodal	N	Y	2.24	-6.3		dense
6	Bimodal	N	Y	2.24	-5.9		dense
7	Bimodal	N	Y	2.24	-5.0	-13.6	-
8*	Monomodal	Y	N	1.23	-5.2		dense
9*	Monomodal	Y	N	1.23	-5.9	-9.2	pluck-outs
10	Monomodal	N	N	2.24	-12.4		dense but cracked
11	Monomodal	N	N	2.24	-12.4		dense but cracked
12	Monomodal	N	N	2.24	-13.6	0.3	dense but cracked
13*	Bimodal	Y	N	1.23	-7.5		dense
14*	Bimodal	N	N	1.23	-10.1	0.2	pluck-outs

The second set—rectangular Bars 5–7 and 10–12 and tensile bars 8, 9, 13 and 14—were processed in different furnaces from the first set. Bars 5–7 were partially solvent dewaxed in heptane, before thermal dewaxing in N₂ at 500°C. Bar 7 was further dewaxed in air at 550°C. The mass change in N₂ and air in Table 8.2 is relative to the original (green) mass of the bars. About half the wax was dissolved by the heptane, and most of the remainder was evaporated in the nitrogen furnace in Bars 5–7. The further air dewaxing of Bar 7 apparently removed a significant amount of PP and weakened the bar so much that it disintegrated into numerous fragments during sintering.

Tensile Bars 8, 9 and 13 were partially thermally dewaxed immediately following the PIM. All four were thermally dewaxed in N₂ at 500°C, and Bars 9 and 14 were further dewaxed in air at 550°C. Like Bar 7, the air dewaxing of Bar 9 removed a significant amount of PP and cracked but did not destroy the bar. The air dewaxing of Bar 14 caused a negligible mass change, an indication the wax removal was complete in the previous step, with no additional loss of PP. All the tensile bars had a shape factor ψ of 1.23, indicative of a shorter diffusion path length by a factor of nearly two than the rectangular bars. The difference in ψ between Bars 7 and 9 may have made the difference between shattering and cracking in the air dewaxing step. The particle size distribution, bimodal Bar 7 compared to monomodal Bar 9, may have also been a factor. A slightly slower debinding rate was expected in the bimodal feedstock due to reduced capillary size by the nanoparticles.⁷

Rectangular Bars 10–12, like Bars 1–4, were not dewaxed by solvent or heat before GMM. Virtually all the wax was removed in the nitrogen furnace after GMM at 500°C. Bar 12 were further dewaxed in air at 550°C, but the negligible mass change in Table 8.2 indicates the wax removal was complete in the previous step, with no additional loss of PP.

8.3.2 Sintering and Densification

Bars 1–4 were fully densified in Table 8.3. The ideal density is 3.25–3.27 gm/cm³, by the rule of mixtures, not taking into account the possibility of evaporation or degradation of any of the ceramic constituents. Values closer to 95% were reported for similar but not machined bars in a related paper.⁸

Bimodal rectangular Bar 7, as mentioned under Debinding in §8.3.1, lost much of its PP in the air-dewaxing step and crumbled. No further testing was done on it. Monomodal tensile Bar 9 also lost much of its PP in the air-dewaxing step and cracked but was suitable for further study. Its microstructure appears to be fully densified but is riddled with pluck-outs, that is, weakly bonded grains that were easily fractured along the grain boundaries and removed by the ceramographic abrasives. The pluck-out debris is visible in the as-sintered bar when it is rubbed gently between fingers. Monomodal rectangular

Bar 12 actually gained a small amount of weight in the air-dewaxing step but had essentially the same densified but cracked microstructure as Bars 10 and 11. Bimodal tensile Bar 14 had the same dense but plucked-out microstructure as Bar 9 but a small weight gain similar to Bar 12. The oxygen present in the air-dewaxing step may have weakened the grain boundary regions in Bars 7, 9 and 14, causing the fractures and pluck-outs. The reason for the absence of this effect on Bar 12, except as a slightly lower bulk hardness in Table 8.3, is unclear.

Table 8.3: Properties of GMM SiC.

Specimen	Particle distribution	Densification	Knoop Hardness [GPa]	
		%	Near GMM	Bulk
1	Monomodal	98	9.34	13.2
2	Bimodal	98	10.8	15.4
3	Monomodal	98	15.7	16.9
4	Bimodal	98	16.2	18.5
5	Monomodal		16.9	17.9
6	Bimodal		16.6	17.9
7	Bimodal		-	-
8	Monomodal		-	19.7
9	Monomodal		-	-
10	Monomodal		15.6	17.1
11	Monomodal		18.2	16.0
12	Monomodal		15.2	15.2
13	Bimodal		-	17.8
14	Bimodal		-	-

The remainder of the bars all appeared to be fully densified after sintering. The macroscopically visible cracks in Bars 10–12, at least one order of magnitude larger than the grain size and pore size, were probably caused by too rapid wax expansion and evaporation, or PP decomposition. The microstructures of PIM SiC were clearly very sensitive to the debinding steps.

The use of argon for sintering may have affected the stability of AlN. AlN can decompose to metal vapor and N₂ near the sintering temperature, but this reaction would be suppressed in an N₂ atmosphere.⁹ At the same time, N₂ retards the densification of

SiC.¹⁰ In Ar, the loss of AlN could result in unreacted yttria or a precipitate such as $\text{Y}_2\text{Si}_2\text{O}_7$ or Y_2SiO_5 rather than the expected yttrium aluminum garnet, $\text{Y}_3\text{Al}_5\text{O}_{12}$ or YAG.¹¹

8.3.3 Knoop Hardness

The Knoop hardness results in Table 8.3 indicate a drop in hardness within approximately 0.5 mm (“Near GMM”) of the machined grooves, and values in line with literature values more than 1 mm (“Bulk”) away from the grooves in Bars 1–4. The indentation size effect, if any, was indeterminate but unexpected as the hardness tester was used at its maximum load.¹² The bimodal bars were harder in both areas than the monomodal in Bars 1–4. The source of the differences is unclear, but may be due in part to residual stresses and micro-cracks emanating from the corners of the grooves that weaken the SiC.

The hardness results for Bars 5–14 in Table 8.2 are less consistent than Bars 1–4. Bars 5 and 6 were processed the same way and differ only in particle size distribution, yet have essentially the same hardness in bulk and near the GMM grooves.

Monomodal Bar 8 was harder than bimodal Bar 13, opposite the trend of Bars 1–4. Bars 9 and 14 were too fragile for meaningful hardness measurements. Bars 8, 9, 13 and 14 were not GMM; hence, no *Near GMM* data.

The hardness results for Bars 10–12 in Table II are also less consistent than Bars 1–4. Bar 10 shows the same trend as Bars 1–4, where the bulk is ~10% harder than near the grooves, while Bar 11 is the opposite. Bar 12, ostensibly weakened by grain boundary corrosion, was not as hard as Bars 10 and 11, but the same in bulk as near the grooves. All the hardness results for Bars 5, 6, 8 and 10–13 were consistent with fully densified SiC.

8.3.4 Ceramography and Fractography

All four bars from the first set in Figures 8.1–8.8 were significantly distorted and cracked after being sintered for 2.0 hr at 2000°C. Only Bar 1 was intact, and it had macroscopically visible cracks emanating from the 2-mm molded holes as well as the machined grooves. The fractures in Bars 2 and 3 in Figures 8.5 and 8.6 have multiple origins

in the corners of grooves, while Bar 4 failed across one of the holes where there was no groove. Bar 1 was intact, but several cracks are visible in Figure 8.1, especially near the two holes. The straight-path fractures in Figures 8.7 and 8.8 are consistent with differential thermal expansion caused by temperature gradients during sintering.

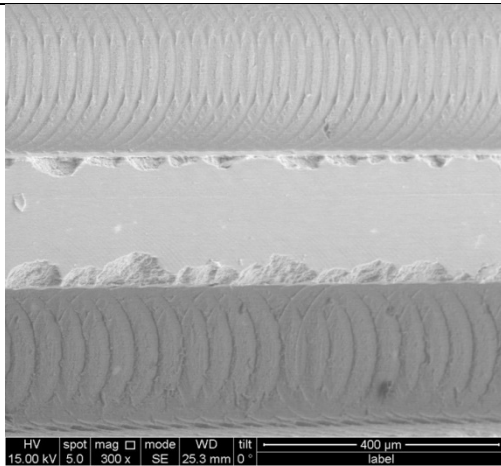


Figure 8.1: Monomodal bar #1 before sintering.

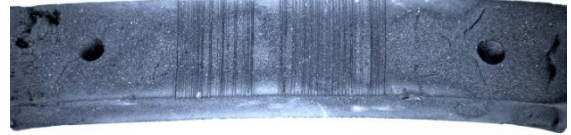


Figure 8.2: Monomodal bar #1 after sintering.

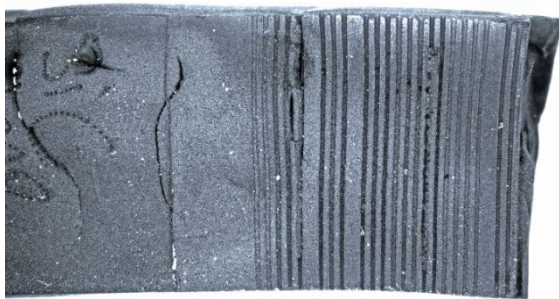


Figure 8.3: Monomodal bar #2 after sintering.

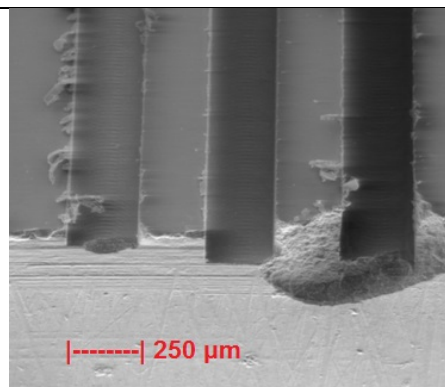


Figure 8.4: Bimodal bar #3 before sintering.

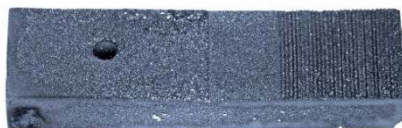


Figure 8.5: Bimodal bar #3 after sintering.

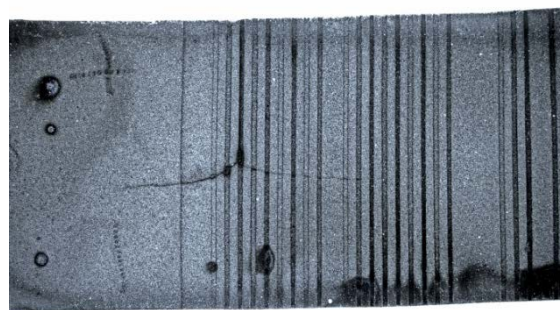


Figure 8.6: Bimodal bar #4 after sintering.



Figure 8.7: Fracture surface of monomodal bar #2, the right end of Fig. 8.2.

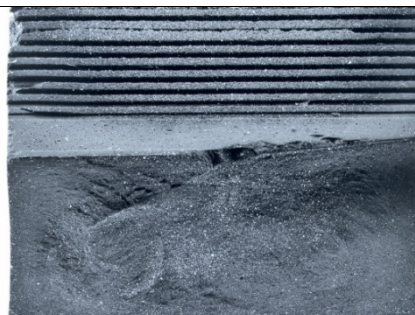
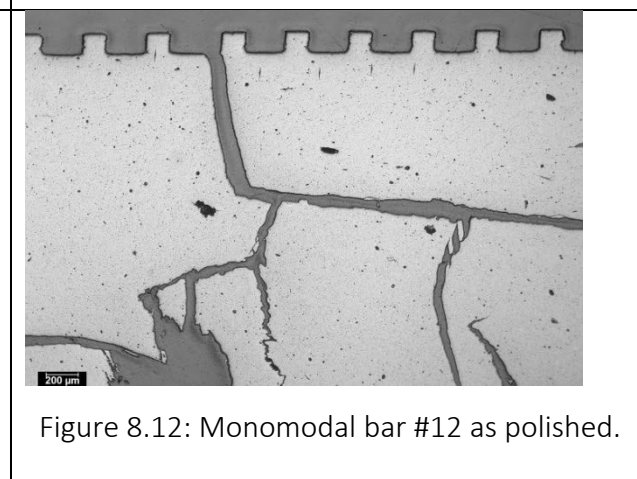
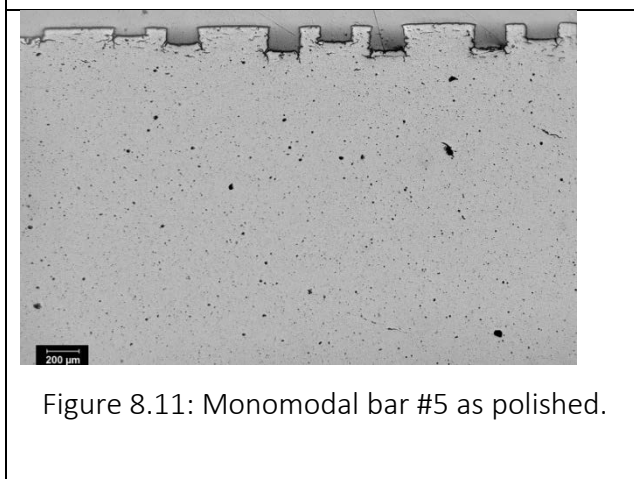
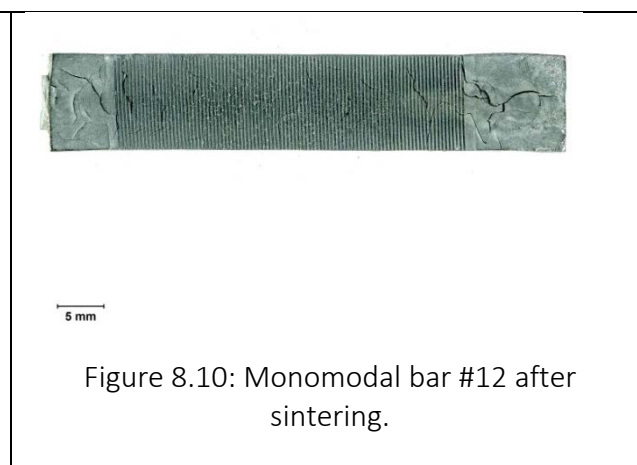
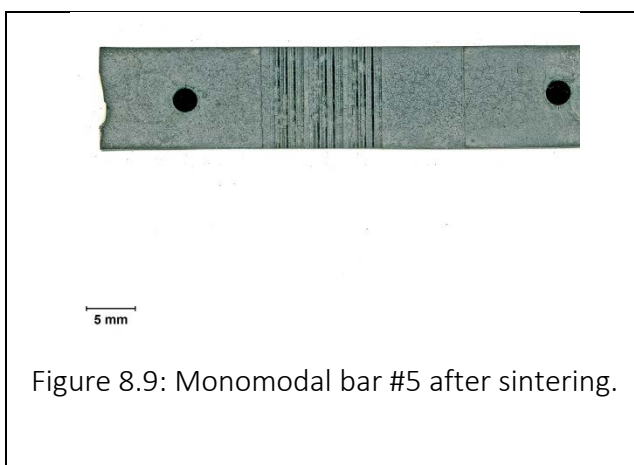


Figure 8.8: Fracture surface of bimodal bar #3, the right end of Fig. 8.3.

Bars 5 and 12 in Figures 8.9–8.12 were largely the same except that the former was solvent dewaxed before GMM and sintering. In Figure 8.9, the as-sintered surface was scaly but without any obvious fractures, even with the grooves and holes as stress concentrators. The ceramographic cross-sections of these two bars in Figures 8.11 and 8.12 confirm the macroscopic observations. The microstructure of Bar 5 is intact, homogenous and dense, but micro-cracks emanate from the corners at the bases of the grooves. The grooves in Figure 8.12 were not cracked, but the stresses associated with dewaxing and sintering were relieved by the macroscopic ruptures that began deep within the bar. The near-GMM Knoop indentations are visible about 100 μm below the central grooves in Figure 8.12. Grooves of three depths are visible in Figure 8.11, at 80, 160 and 240 μm , but the depth of GMM had no apparent effect on post-sinter morphology.



The different particle size distributions had little if any effect on the grain size, porosity or second-phase distribution in Figures 8.13–8.16, for monomodal Bars 8 and 9 and bimodal Bars 13 and 14. The light-colored precipitate was YAG, about 6.5% by volume and 8.7% mass fraction, if all the Y_2O_3 was consumed in the reaction between the two additives. The additional oxygen in the YAG came from reduction of the SiO_2 , about 2 nm thick, on the surfaces of the SiC particles.¹³ The AlN may have been oxidized to some degree in the bars that were dewaxed in air, although oxidation of AlN was not necessarily detrimental to the densification of SiC. The excess nitrogen and aluminum evaporated, dissolved in the SiC lattice, or formed undetected nanoparticles on the SiC grain boundaries.

An estimate of the grain size in Figures 8.14 and 8.16 by the circle-intercept method¹⁴ yielded 7.8 and 6.8 μm for the monomodal and bimodal bars, respectively. The narrowest ridge between two grooves in Figure 8.11 or 8.12 was about 129 μm wide, making the smallest GMM features in this study equivalent to about 16–19 grains after sintering, 184 microparticles before sintering. The smallest features that can be made by PIM are about ten times the particle size, in alumina.¹⁵ Christian and Kenis,¹⁶ using gelcasting, fabricated alumina microdevices where the smallest dimension was 30 times larger than the mean particle size D_p in the range of $0.3 \leq D_p \leq 3.0 \mu m$. The groove corners and sides were slightly rounded and distorted in Figures 8.11 and 8.12. The grooves in Figure 8.11 were narrowed from 254 to about 200 μm by sintering shrinkage, which was 14–15% linear in bimodal SiC and 18–19% in monomodal.⁸ The grooves in Figure 8.11 were the same as their original width, with the shrinkage stress relieved by the dewaxing fractures.

An estimate of the grain size of the stronger-bonded SiC in Figures 8.13 and 8.15 by the circle-intercept method yielded 0.66 and 1.0 μm for the monomodal and bimodal bars, resp. The narrowest ridge between two grooves in Figure 8.11 or 8.12 made the smallest GMM features in this study equivalent to about 130–195 grains after sintering, 184 microparticles before sintering. The microstructures in Figures 8.13 and 8.15 are expected to be more representative of the other bars in this study than those of Figures

8.14 and 8.16. The differences in microstructures were addressed in §7.3.5.3 and are the subject of further study.

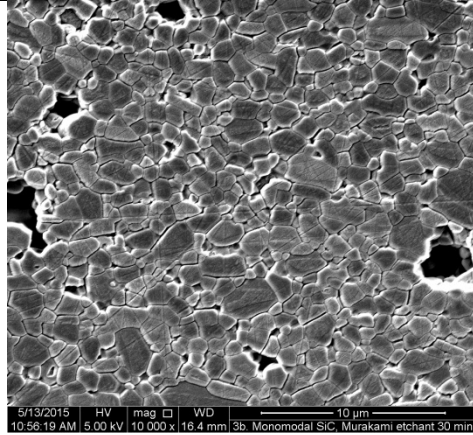


Figure 8.13: Monomodal bar #8 after etching.

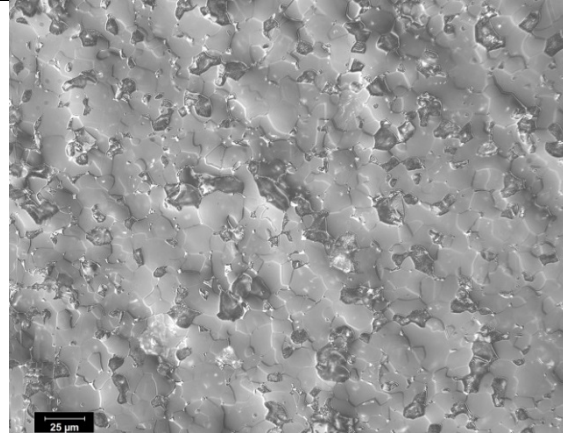


Figure 8.14: Monomodal bar #9 as polished.

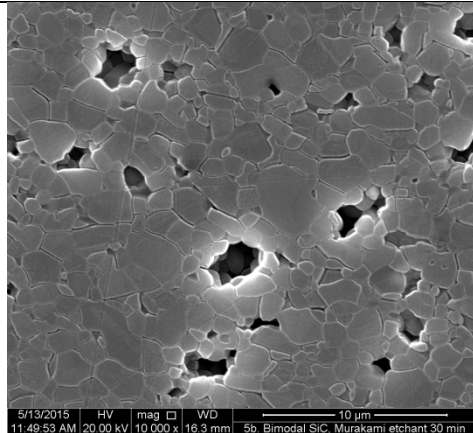


Figure 8.15: Bimodal bar #13 after etching.

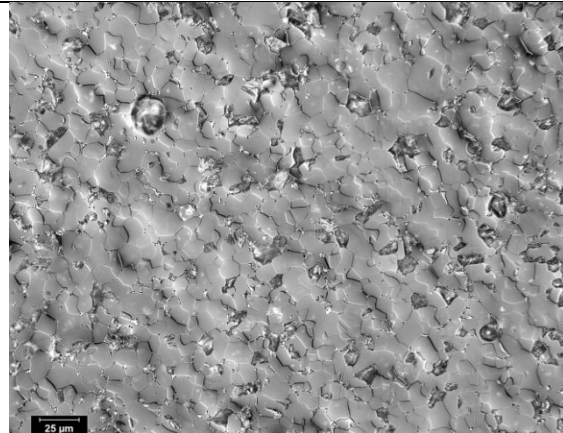


Figure 8.16: Bimodal bar #14 as polished.

8.4 Conclusions

SiC fabricated by PIM and densified with AlN and Y_2O_3 additives was shaped by GMM. Solvent debinding prior to thermal debinding, and a low volume-to-surface ratio, reduced the chance of fractures during sintering. Air dewaxing may have introduced excess oxygen to the SiC grain boundaries, or removed too much polypropylene backbone

before sintering. Thermal debinding alone had a tendency to distort and crack the bars. Two sintering schedules, 2 hr at 2000°C in argon or 5 hr at 1900°C in argon, adequately densified all the bars. The hardness was usually but not always lower near the GMM features than in the bulk. The exceptions to this rule showed stress relief from large debinding fractures in the bulk. Cracking at the corners of the GMM grooves was observed in unfractured bars, but absent in bars with debinding fractures, and also attributed to the stress relief effect of the debinding fractures. Features of a size equivalent to 130–195 sintered SiC grains were created by GMM. Future work includes optimization of the debinding and sintering processes to minimize the residual stresses.

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CHAPTER 9

9 Conclusions and Future Research

“What a long, strange trip it’s been!” – The Grateful Dead, lyric from *Truckin’*

9.1 Conclusions

This dissertation presented a study of thermal processing of powder injection-molded, green micro-machined silicon carbide ceramics with AlN and Y₂O₃ additives, with (bimodal) and without (monomodal) nanoparticles. Monomodal PIM SiC of low (<2) volume : surface area was very tractable to extrusion, PIM, GMM, dewaxing by solvent or heat, sintering, grain size control and densification. Bimodal PIM SiC was less agreeable with GMM and thermal dewaxing. Coupons of higher volume : surface area were difficult to dewax or sinter without distortion and fractures.

9.1.1 Solvent Dewaxing

The bimodal SiC samples in Chapter 3 had slightly lower debinding rates compared to the monomodal SiC samples, due to the combined effect of increased powder content and reduced average particle size via nanoparticle addition. The differences in solvent debinding rates as a result of nanoparticle addition were much smaller than what might be expected from permeability estimates. The activation energy for solvent extraction estimated from diffusion coefficients and the master decomposition curve were in close agreement. No significant difference in activation energy for solvent extraction was observed for bimodal SiC samples compared to monomodal SiC samples, indicating an absence of any major mechanistic changes in solvent debinding as a result of nanoparticle addition. Despite the addition of nanoparticles and the higher solids loading, practical solvent debinding times were still possible without introducing defects in the bimodal samples.

9.1.2 Thermal Dewaxing

The activation energy by the Flynn-Wall model of pyrolysis of paraffin wax from monomodal, 64 ± 12 kJ/mol, and bimodal, 53 ± 7 kJ/mol, SiC injection molding feedstock in Chapter 4 was similar to that of paraffin removed by dissolution in a liquid solvent in Chapter 3.

The activation energy by the F-W method of pyrolysis of polypropylene from monomodal, 103 ± 17 kJ/mol, and bimodal, 109 ± 11 kJ/mol, SiC dewaxed feedstock was comparable to the lower end of ranges reported in other studies. The dependence of the activation energy on wax or polypropylene conversion was examined, but the mathematical relationship was inconsistent. The activation energy by the Kissinger model was similar to the F-W model only near 20% conversion, but was very consistent. The activation energy by the Speyer model was too scattered to be reliable in this study.

The differences between the two feedstocks, although small, were attributed to the additional nanoparticles in the bimodal feedstock. The differences between the dewaxed feedstocks and pure polypropylene were attributed to the particle properties and organic additives in the feedstocks. The differences between these results and those reported by other authors were numerous and included, in addition to the differences within this study, test methods and equipment, sample sizes, heating rates and conversion levels.

9.1.3 Sintering Additives

Additives that form YAG, YAM or YAP at SiC grain boundaries were very reliable densification aids for pressureless-sintered SiC in Chapter 5. Nitride additives consistently yielded the best densification of SiC, mostly due to LPS enabled by Y-Al-O phases. The additives increased the self-diffusion in SiC, reactively wetted the passivated SiC grains, and enabled LPS and pressureless densification. Carbon as an additive came from several sources, including residual free carbon from the Acheson process and organic binder. No one additive group or sintering process resulted in all the best properties, but 99% densification, 600-MPa bending strength, 500-MPa strength at 1500°C, 4-MPa m^{0.5}

toughness, 22-GPa hardness, $80\text{-W m}^{-1}\text{ K}^{-1}$ thermal conductivity or high corrosion resistance in SiC were achievable by multiple methods of pressureless sintering.

For pressure-assisted sintering in Chapter 6, the highest room-temperature strength came from nitride additives, the lowest from oxides. The lowest toughness was yielded by nitride additives. N_2 can enhance or suppress SiC sintering, depending on additives, or supplant cover mix during sintering when nitride additives are used. The strength of SiC is retained at high temperatures, making it promising for creep applications, especially when densified without additives. The trade-off is that SiC without additives is susceptible to uncontrolled grain growth. A trade-off exists between strength and toughness, with regard to optimum grain size. The strength, hardness and toughness of SiC are only moderately sensitive to grain size. Other variables may be of greater importance to the mechanical properties. This affects the choice of more-expensive nanoparticles over microparticles as a means of strengthening or hardening SiC. SiC grain growth may be controlled by AlN or low boron content, among other factors. Grain growth generally increases with sintering temperature, but nitride and other additives are effective at preventing uncontrolled grain growth.

9.1.4 GMM and Sintering of PIM SiC

Monomodal PIM SiC densified with AlN and Y_2O_3 in Chapter 7 was very compatible with GMM, except that the swarf adhered strongly to the substrate whether the substrate was solvent-dewaxed after GMM or thermally dewaxed before GMM. Thermal dewaxing reduced the amount of adhering swarf and sintering distortion but did not completely eliminate either.

Bimodal PIM SiC densified with AlN and Y_2O_3 in Chapter 7 was much less compatible with GMM than monomodal, except that swarf adhesion was not a problem. Solvent-dewaxing after GMM resulted in low distortion of the GMM grooves but fracture propagation during sintering. Thermal dewaxing before GMM resulted in severe rounding of the GMM edges and corners, uncontrolled grain growth and weak bonding between grains during sintering.

A dilatometer scan showed equal strain during dewaxing expansion, but twice as much strain in monomodal SiC during debinding. Densification began at about 1200°C in both compositions.

HTXRD did not reveal any crystallization in the binder components during heat-up, but showed the beginnings of precipitation of yttria-alumina compounds at about 1200°C in both compositions. XRD after full sintering verified that all the AlN and Y₂O₃ had been converted to YAG and YAP.

All compositions and treatments were densified to closed porosity by sintering at 2000°C for 2 hr in Ar, with 17–20% shrinkage in each dimension.

SiC fabricated by PIM and densified with AlN and Y₂O₃ additives was shaped by GMM in Chapter 8. Solvent debinding prior to thermal debinding, and a low volume-to-surface ratio, reduced the chance of fractures during sintering. Air dewaxing may have introduced excess oxygen to the SiC grain boundaries, or removed too much polypropylene backbone before sintering. Thermal debinding alone had a tendency to distort and crack the bars. Two sintering schedules, 2 hr at 2000°C in argon or 5 hr at 1900°C in argon, adequately densified all the bars. The hardness was usually but not always lower near the GMM features than in the bulk. The exceptions to this rule showed stress relief from large debinding fractures in the bulk. Cracking at the corners of the GMM grooves was observed in unfractured bars, but absent in bars with debinding fractures, and also attributed to the stress relief effect of the debinding fractures. Features of a size equivalent to 130–195 sintered SiC grains were created by GMM.

9.2 Future Research

9.2.1 Feedstock Rheology and PIM Forecasting

A sizeable amount of SiC feedstock rheology data, and predictions of feedstock properties with different solids fractions ϕ , were “left on the cutting-room floor,” as they say in the movie business. The theory is that when the viscosity, specific volume, heat capacity, thermal conductivity, mechanical moduli and thermal expansion as functions of

temperature, pressure and shear rate are known for one value of φ , they can be scaled up or down for other values of φ by rules of mixtures, as alluded to briefly in §2.3. A paper on the results of a test of that theory might yet come out of this body of research.

The company that injection-molded the SiC bars in Chapters 7 and 8 provided a report on the injection conditions, in Appendix 2. A second paper comparing those results to a Moldflow® simulation of the process, mentioned in §2.4, might also come out of this body of research.

9.2.2 Solvent Dewaxing

A study or finite-element simulation of the stresses and swelling associated with solvent dewaxing would help explain and optimize some of the shortcomings of the bimodal bars in Chapter 7.

9.2.3 Thermal Dewaxing

Future work in this study might include the evaluation of kinetics parameters at conversion levels higher than 20%, evaluations of the stearic acid and LDPE-g-MA with a possible rule-of-mixtures model for multi-component PIM binder, higher and lower heating rates, and further study of the outlier data. A study or finite-element simulation of the stresses associated with thermal dewaxing would help explain and optimize some of the shortcomings of the bars in Chapters 7 and 8.

The binder system in this study was borrowed from earlier studies. Research on other binder systems and other dewaxing methods might have more favorable outcomes in terms of kinetics, GMM feasibility, microstructures and sintering characteristics.

Thermal dewaxing in air has been done successfully on PIM SiC, and is worthy of further study in the context of kinetics as in Chapter 4 and as an alternative to thermal dewaxing in N₂ in Chapters 7 and 8. Weak bonding of the thermally dewaxed bimodal bars was attributed *a priori* to possible oxidation of the SiC or excess deterioration of the polypropylene backbone in Chapter 7, but these conclusions should be verified by a more in-depth investigation.

9.2.4 GMM and Sintering of PIM SiC

Future work includes optimization of the debinding and sintering processes to minimize the residual stresses. A dilatometer or HTXRD that is capable of say, 2000°C, might reveal something that was not obvious at 1600 or 1200°C, respectively, in Chapter 7. A chemical or mechanical post-GMM process to remove swarf, without damaging the fragile substrate, is needed. A comparison of the distribution of aluminum after sintering in monomodal to bimodal SiC distributions might begin to solve the sintering problems sometimes encountered with thermally dewaxed SiC.

The effect of other additives, namely, graphite and B₄C, on PIM SiC was begun here but did not progress far enough for any sort of fruition. To date, SiC + C + B₄C has been pressureless-sintered but not injection-molded in the literature. One notable difference between that composition and those of this study is that LPS was the sintering mechanism here, while SiC + C + B₄C is densified by solid-state processes. A comparison of PIM SiC + C + B₄C to the compositions in this study would greatly increase the body of knowledge of PIM SiC.

The GMM in this study used only a single tool size and shape. The effect of other GMM feature sizes and shapes on SiC, binders and dewaxing are not necessarily predictable from the results presented here.

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"The devil can cite Scripture for his purpose." — William Shakespeare, *The Merchant of Venice*

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Appendices

“In this house, we OBEY the laws of thermodynamics!” — parental admonition from Homer Simpson

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Appendix 1: Properties of SiC from the Literature

Table A.1: Data for the plots in Chapters 5 and 6. The heading abbreviations include $T_{\text{ sint }}$ = sintering temperature, $P_{\text{ sint }}$ = sintering pressure (0.0 = pressureless sintering), Σ Add. = sum of additives, ρ = density, σ = bending strength, $K_{\text{ Ic }}$ = fracture toughness, HV = Vickers hardness and GS = grain size. In the Add. Fam. (Additive Family) column, NA = no additives, C+B = carbon and boron, Oxid = oxides, REOx = rare earth oxides and Nitrd = nitrides.

Paper Year/Journal	$T_{\text{ sint }}$ °C	$P_{\text{ sint }}$ MPa	Σ Add. mass%	Add. Fam.	ρ % $\rho_{\text{ ideal }}$	σ MPa	$K_{\text{ Ic }}$ MPaVm	HV GPa	GS $\mu\text{ m}$
Nadeau 1973 <i>ACerSB</i> 52	2500	5000	0	NA	99.5				
	2500	5000	0	NA	99.5				
	2500	5000	0	NA	99.5				
	2500	5000	0	NA	99.5				
Bind 1976 <i>JAppPhys</i> 47	1950	20.7	0	NA	73				
	1750	20.7	1	C+B	88				
	1800	20.7	1	C+B	90				
	1850	20.7	1	C+B	95				
	1950	20.7	1	C+B	99.99				
	1850	20.7	0.6	C+B	88				
	1900	20.7	0.6	C+B	93				
	2100	20.7	0.6	C+B	98				
	1870	20.7	2	Oxid	95				
	1900	20.7	2	Oxid	97.6				
	1950	20.7	2	Oxid	98.3				
	2030	20.7	2	Oxid	99.85				
Prochazka 1976 <i>SpecCer6</i>	2040	0.0	0.5	C+B	57				
	2040	0.0	0.56	C+B	60				
	2040	0.0	0.62	C+B	69				
	2040	0.0	0.74	C+B	93				
	2040	0.0	0.86	C+B	96				
	2040	0.0	0.5	C+B	94				
	2040	0.0	1	C+B	96				
	2040	0.0	1	C+B	95				
	2040	0.0	0.4	C+B	94				
	2040	0.0	0.8	C+B	95				
	2040	0.0	1	C+B	89				
	2040	0.0	1	C+B	63				
	2040	0.0	0.36	C+B	62				
	2040	0.0	0.48	C+B	81				

Paper Year/Journal	T _{sint} °C	P _{sint} MPa	Σ Add. mass%	Add. Fam.	ρ %ρ _{ideal}	σ MPa	K _{Ic} MPa√m	HV GPa	GS μm
	2040	0.0	0.61	C+B	96				
	2040	0.0	0.86	C+B	96				
	2040	0.0	1.16	C+B	96				
	2040	0.0	0.61	C+B	83				
	2040	0.0	1.11	C+B	87				
	2040	0.0	1.86	C+B	86				
Tanaka 1985 <i>JMatSciL</i> 4	2100	0.0	2.638	C+B	75				
	2100	0.0	2.637	C+B	83				
	2100	0.0	2.6	C+B	74				
	2100	0.0	2.56	C+B	82				
	2100	0.0	2.82	C+B	98	630			
	2100	0.0	2.94	C+B	98				
S.K. Lee 1994 <i>JACerS</i> 77	2000	0.0	10	Oxid	99.1				1.1
	2000	0.0	10	Oxid	99.2				2.50
	2000	0.0	10	Oxid	99.0				4
	2000	0.0	10	Oxid	98.7				5
	2000	0.0	10	Oxid	98.8				1.5
	2000	0.0	10	Oxid	98.8				2.50
	2000	0.0	10	Oxid	99.1				5.00
	2000	0.0	10	Oxid	98.5				7.00
S.K. Lee 1995 <i>JACerS</i> 78	2000			Oxid	99.0		4.5		
	2000			Oxid	99.0		5		
	2000			Oxid	99.0		7		
	2000			Oxid	99.0		8.3		
	2000			Oxid	99.1		4.4		
	2000			Oxid	99.1		4.5		
	2000			Oxid	99.1		5		
	2000			Oxid	99.1		5.7		
	2100			Oxid	98.5		3		
Moberly	1950	50.0	6.6	C+B	99		9		
Moberly	1600	50.0	6	C+B	98	650	7.1		7.5
Foster 1999 <i>JECerS</i> 19	1750	29.0	6.00	Oxid	76				
	1800	29.0	6.00	Oxid	78				
	1850	29.0	6.00	Oxid	90				
	1900	29.0	6.00	Oxid	95				
	1900	29.0	10.00	Oxid	91				
	1750	29.0	6	Oxid	84				
	1750	29.0	6	Oxid	88				
	1750	29.0	6	Oxid	82				

Paper Year/Journal	T _{sint} °C	P _{sint} MPa	Σ Add. mass%	Add. Fam.	ρ %ρ _{ideal}	σ MPa	K _{Ic} MPa√m	HV GPa	GS μm
	1750	29.0	6	Oxid	76				
	1850	29.0	6	Oxid	93				
	1850	29.0	6	Oxid	93				
	1750	29.0	6	Oxid	85				
	1750	29.0	6	Oxid	85				
	1750	29.0	6	Oxid	82				
	1750	29.0	6	Oxid	80				
	1850	29.0	6	Oxid	95				
	1850	29.0	6	Oxid	93				
	1750	29.0	6	Oxid	90				
	1710	29.0	9	Oxid	79				
	1710	29.0	9	Oxid	84				
	1710	29.0	9	Oxid	86				
	1710	29.0	9	Oxid	86				
	1710	29.0	9	Oxid	84				
	1750	29.0	9	Oxid	86				
	1750	29.0	9	Oxid	87				
	1750	29.0	9	Oxid	86				
	1750	29.0	9	Oxid	88				
	1750	29.0	9	Oxid	90				
	1750	29.0	9	Oxid	90				
	1750	29.0	9	Oxid	94				
	1750	29.0	9	Oxid	92				
	1750	29.0	9	Oxid	92				
	1750	29.0	9	Oxid	93				
	1750	29.0	9	Oxid	93				
	1750	29.0	9	Oxid	91				
	1750	29.0	9	Oxid	90				
	1750	29.0	9	Oxid	92				
	1750	29.0	9	Oxid	91				
	1750	29.0	9	Oxid	93				
	1750	29.0	9	Oxid	93				
	1750	29.0	9	Oxid	89				
	1850	29.0	9	Oxid	97				
	1850	29.0	9	Oxid	99				
	1850	29.0	9	Oxid	99				
	1750	29.0	9	Oxid	79				
	1750	29.0	9	Oxid	88				
	1750	29.0	9	Oxid	93				

Paper Year/Journal	T _{sint} °C	P _{sint} MPa	Σ Add. mass%	Add. Fam.	ρ %ρ _{ideal}	σ MPa	K _{Ic} MPa√m	HV GPa	GS μm
	1750	29.0	9	Oxid	93				
	1750	29.0	6	Oxid	95				
	1750	0.0	9	Oxid	80				
	1750	0.0	9	Oxid	90				
	1800	0.0	9	Oxid	93				
	1750	0.0	9	Oxid	93				
	1800	0.0	9	Oxid	98				
	1800	0.0	9	Oxid	98				
	1800	0.0	9	Oxid	99				
	1800	0.0	9	Oxid	98				
She & Ueno 1999 <i>MC&P</i> 59	1850	0.0	10	Oxid	96				
	1850	0.0	10	Oxid	96.8				
	1850	0.0	10	Oxid	95				
	1850	0.0	10	Oxid	93				
	1900	0.0	10	Oxid	98	530	6.8		
	1900	0.0	10	Oxid	98	525	6.5		
	1900	0.0	10	Oxid	97	520	5.6		
	1900	0.0	10	Oxid	95	510	5.2		
	1950	0.0	10	Oxid	98	625	7		
	1950	0.0	10	Oxid	98	620	6.8		
	1950	0.0	10	Oxid	98	580	6.3		
	1950	0.0	10	Oxid	96	540	5.7		
	2000	0.0	10	Oxid	97	580	7.2		
	2000	0.0	10	Oxid	97	575	7.5		
	2000	0.0	10	Oxid	97	560	7.5		
	2000	0.0	10	Oxid	96	530	6		
She & Ueno 1999 <i>MRB</i> 34	1850	0.0	5	Oxid	95				
	1850	0.0	10	Oxid	97				
	1850	0.0	15	Oxid	96				
	1850	0.0	25	Oxid	94				
	1900	0.0	5	Oxid	97	510	6.2	20	
	1900	0.0	10	Oxid	97	530	6.5	19.5	
	1900	0.0	15	Oxid	97	480	6.2	19	
	1900	0.0	25	Oxid	95	450	5.2	16.5	
	1950	0.0	5	Oxid	98	640	6.5	18.6	
	1950	0.0	10	Oxid	98	610	6.8	18.4	
	1950	0.0	15	Oxid	98	520	6.5	18	
	1950	0.0	25	Oxid	95	490	5.5	16.5	
	2000	0.0	5	Oxid	97	570	7.2	17.4	

Paper Year/Journal	T _{sint} °C	P _{sint} MPa	Σ Add. mass%	Add. Fam.	ρ %ρ _{ideal}	σ MPa	K _{Ic} MPa√m	HV GPa	GS μm
	2000	0.0	10	Oxid	97	560	7.5	17.3	
	2000	0.0	15	Oxid	97	500	7.5	16.7	
	2000	0.0	25	Oxid	94	475	6.1	15.5	
Shinoda 1999 <i>JACerS</i> 82	1600	980.0	4.5	C+B	97.1				0.2
	1600	980.0	3.5	C+B	97.1				0.03
	1900	40.0	1	C+B	97.1				0.8
Rixecker 2000 <i>JCPR</i> 1	2030	10.0	10	Nitrd	95				
	2000	200.0	10	Nitrd	99				
	1980	10.0	10	Nitrd	99	490	4.9		
	2010	10.0	10	Nitrd	99		5.9		
	1980	10.0	10	Nitrd	99	485	6.0		
	2020	10.0	7	Nitrd	99		6.5		
	1950	10.0	10	Nitrd	99		5.0		
	2000	10.0	10	Nitrd	99	526	5.6		
	1980	10.0	10	Nitrd	99	564	5.0		
Kim 2001	1800	25.0	20.4	Oxid	97.5	550	6.1		
	1900	25.0	14.4	REOx	98.9	588	6.2		
Datta 2002 <i>BMatSci</i> 25	2000	0.0	1	C+B	62				
	2000	0.0	1.5	C+B	81				
	2000	0.0	2	C+B	89				
	2050	0.0	1	C+B	62				
	2050	0.0	1.5	C+B	81				
	2050	0.0	2	C+B	99				5.7
	2100	0.0	1	C+B	62				
	2100	0.0	1.5	C+B	81				
	2100	0.0	2	C+B	99				
Goldstein 2002	1900	0.0		Oxid	95	315		23	
	1900	0.0		Oxid	98.5	385		24	
Zhan 2002	1750	25.0	10	Oxid	95				0.98
	1750	25.0	10	Oxid	95				1
Huang 2003 <i>Cer Intl</i> 29	1800	25.0	9	Oxid	95				1
	1800	25.0	9	Oxid	95				1
	1800	25.0	9	Oxid	95				1
	1800	25.0	9	Oxid	95				1
	1800	25.0	9	Oxid	97				1
	1800	25.0	9	Oxid	97				1
	1800	25.0	6	Oxid	92				1
	1800	25.0	3	Oxid	87				
Y.I. Lee	1500	20.0	10	Oxid	76				0.035

Paper Year/Journal	T _{sint} °C	P _{sint} MPa	Σ Add. mass%	Add. Fam.	ρ %ρ _{ideal}	σ MPa	K _{IC} MPa√m	HV GPa	GS μm
2003 <i>JACerS</i> 86	1550	20.0	10	Oxid	85				0.040
	1750	20.0	10	Oxid	90				0.050
	1750	20.0	10	Oxid	98				0.110
	1700	20.0	10	Oxid	77				0.030
	1750	20.0	10	Oxid	85				0.035
	1800	20.0	10	Oxid	90				0.045
	1850	20.0	10	Oxid	98				0.070
	1650	20.0	10	Oxid	80				0.030
	1700	20.0	10	Oxid	85				0.035
	1700	20.0	10	Oxid	88				0.035
	1700	20.0	10	Oxid	95				0.040
	1750	20.0	10	Oxid	99				0.045
Zawrah 2004 <i>Cer Intl</i> 30	1750	0.0	10	Oxid	96		4.1	20.7	
	1800	0.0	10	Oxid	97		5.7	23.2	
	1900	0.0	10	Oxid	95		4.5	22.6	
	1750	0.0	12	Oxid	95		3.9	19.2	
	1800	0.0	12	Oxid	96		4.2	22.1	
	1900	0.0	12	Oxid	89		4.0	20	
Zhou 2004 <i>JECerS</i> 24	2000	40.0		REOx	83.9				
	2000	40.0		REOx	96.8				
	2000	40.0		REOx	96.9				
	2000	40.0		REOx	97.1				
	2000	40.0		REOx	83.8				
	2000	40.0		REOx	95.3				
	2000	40.0		REOx	95.1				
	2000	40.0		REOx	94.1				
Balog 2005 <i>JECerS</i> 25	1850	30.0	13	REOx	99			26	
	1850	30.0	13	REOx	99			25	
	1850	30.0	13	REOx	99			26	
	1850	30.0	13	REOx	99			28	
	1850	30.0	13	REOx	99			25	
	1850	30.0	13	REOx	99			24	
	1850	30.0	13	REOx	99			27	
	1850	30.0	13	REOx	99			23	
Can 2006 <i>JECerS</i> 26	1975	30.0	11.7	Oxid	99				
	1975	30.0	11.7	Oxid	99				
	1975	30.0	11.7	Oxid	99				
	1975	30.0	11.7	Oxid	99				
	1975	30.0	11.7	Oxid	99				

Paper Year/Journal	T _{sint} °C	P _{sint} MPa	Σ Add. mass%	Add. Fam.	ρ %ρ _{ideal}	σ MPa	K _{IC} MPa√m	HV GPa	GS μm
	1925	0.0	11.7	Oxid	97				
	1925	0.0	11.7	Oxid	98				
	1925	0.0	11.7	Oxid	98				
	1925	0.0	11.7	Oxid	97				
	1925	0.0	11.7	Oxid	90				
Bothara 2007 <i>NSTI 4</i>	1700	25.0		Nitrd	99.5		4.8	25	0.50
	1700	25.0		Nitrd	99.5		3.4	25	0.45
	1700	25.0		Nitrd	99.5		3.1	23	0.70
	1850	25.0		Nitrd	99.5		3.8	23	0.70
	1850	25.0		Nitrd	99.5		4.0	25	0.75
	1850	25.0		Nitrd	99.5		3.8	22	0.68
Bothara 2007 <i>CPM&PM</i>	1700	10.0		Nitrd	99.5			22	0.44
	1700	10.0		Nitrd	99.5			21	0.44
	1700	10.0		Nitrd	99.5			22	0.46
	1700	30.0		Nitrd	99.5			24	0.45
	1700	30.0		Nitrd	99.5			23	0.46
	1700	30.0		Nitrd	99.5			23	0.44
	1700	50.0		Nitrd	99.5			23	0.41
	1700	50.0		Nitrd	99.5			24	0.39
	1700	50.0		Nitrd	99.5			17	0.32
Gubernat 2007 <i>JECerS 27</i>	1900	0.0	5	Oxid	90				
	1900	0.0	10	Oxid	94				
	1900	0.0	15	Oxid	91				
	1900	0.0	20	Oxid	93				
	1900	0.0	15	Oxid	95				
	1900	0.0	20	Oxid	94				
	1900	0.0	10	Oxid	82				
	1900	0.0	10	Oxid	80				
	1950	0.0	5	Oxid	94				
	1950	0.0	10	Oxid	94				
	1950	0.0	15	Oxid	95				
	1950	0.0	20	Oxid	93				
	1950	0.0	15	Oxid	91				
	1950	0.0	20	Oxid	95				
	1950	0.0	10	Oxid	89				
	1950	0.0	10	Oxid	81				
	1950	0.0	5	Oxid	95				
	1950	0.0	10	Oxid	94				
	1950	0.0	15	Oxid	93				

Paper Year/Journal	T _{sint} °C	P _{sint} MPa	Σ Add. mass%	Add. Fam.	ρ %ρ _{ideal}	σ MPa	K _{Ic} MPa√m	HV GPa	GS μm
	1950	0.0	20	Oxid	92				
	1950	0.0	15	Oxid	93				
	1950	0.0	20	Oxid	93				
	1950	0.0	10	Oxid	77				
	1950	0.0	10	Oxid	81				
	1950	0.0	5	Oxid	94	332.15	5.03	23	
	1950	0.0	10	Oxid	96	455.23	5.57	22.5	
	1950	0.0	15	Oxid	95	470.14	5.23	25	
	1950	0.0	20	Oxid	95	498.22	5.52	20.5	
	1950	0.0	15	Oxid	95	470.19	4.26	21.5	
	1950	0.0	20	Oxid	94	450.34	5.51	16	
	1950	0.0	10	Oxid	96	440.09	5.73	26	
	1950	0.0	10	Oxid	93	376.79	5.03	18	
	2000	0.0	5	Oxid	85				
	2000	0.0	10	Oxid	84				
	2000	0.0	15	Oxid	82				
	2000	0.0	20	Oxid	83				
	2000	0.0	15	Oxid	86				
	2000	0.0	20	Oxid	81				
	2000	0.0	10	Oxid	79				
	2000	0.0	10	Oxid	74				
Guillard 2007 <i>JECerS 27</i>	1750	75.0	0	NA	77				0.5
	1780	75.0	0	NA	78				0.5
	1780	75.0	0	NA	76				0.7
	1780	75.0	0	NA	88				0.8
	1850	75.0	0	NA	73				1.5
	1850	75.0	0	NA	92				2
	1750	75.0	0	NA	69				0.5
	1750	75.0	0	NA	69				0.6
	1750	75.0	0	NA	71				0.7
	1780	75.0	0	NA	72				0.5
	1780	75.0	0	NA	70				0.7
	1780	75.0	0	NA	73				1
	1850	75.0	0	NA	76				1.5
	1850	75.0	0	NA	75				2.5
	1850	75.0	0	NA	80				3
Tatli 2007 <i>JECerS 27</i>	1450	0.0	5	Oxid	87				
	1450	0.0	5	Oxid	88				
	1550	0.0	5	Oxid	96				

Paper Year/Journal	T _{sint} °C	P _{sint} MPa	Σ Add. mass%	Add. Fam.	ρ %ρ _{ideal}	σ MPa	K _{IC} MPaVm	HV GPa	GS μm
	1650	0.0	5	Oxid	94				
	1650	0.0	5	Oxid	96				
	1750	0.0	5	Oxid	65				
	1450	0.0	5	Oxid	64				
	1450	0.0	5	Oxid	62				
	1550	0.0	5	Oxid	63				
	1650	0.0	5	Oxid	62				
	1650	0.0	5	Oxid	63				
	1750	0.0	5	Oxid	64				
Ray 2008 <i>JACerS</i> 91	2100	28.0	1.65	C+B	99	705	4.7	24.6	1.7
	2100	28.0	1.25	C+B	99	447	2.4	26.9	3.6
	2100	28.0	2.5	Nitrd	99	711	3.5	23.2	1.1
	2100	28.0	5	Nitrd	99		3.7	23.3	0.7
	2100	28.0	3.25	C+B	99		3.9	27	7.8
	2100	28.0	4.25	Nitrd	99		3.2	22.9	11.2
	2100	28.0	3	Nitrd	99		3.4	23.8	1.8
	2100	28.0	3.75	Nitrd	99		3.4	23.2	8.1
	2100	28.0	4.75	Nitrd	99		3.5	21.2	4.1
	2100	28.0	3.75	Nitrd	99		2.9	22.9	3.5
	2100	28.0	5.25	Nitrd	99		3.4	23.3	4.6
	2100	28.0	5.75	Nitrd	99		3.2	22.5	3.8
	2100	28.0	4.25	Nitrd	99		5.6	21.4	8.3
	2100	28.0	3.5	Nitrd	99		3.3	23.5	2.4
	2100	28.0	3.75	Nitrd	99		4.5	22.7	2.4
	2100	28.0	3.75	Nitrd	99		4.5	21.8	2.8
	2100	28.0	4.5	Nitrd	99		5	21.4	9.4
	2100	28.0	4.75	Nitrd	99		5.3	22.3	10.1
	2100	28.0	4.5	Nitrd	99		4.4	23.1	1.8
	2100	28.0	3.25	Nitrd	99		3.9	22.7	7.2
	2100	28.0	3.75	Nitrd	99		4.8	21.8	7.1
	2100	28.0	4.25	Nitrd	99		5.6	22.3	11
	2100	28.0	6.53	Oxid	99		3.6	22.7	1.2
	2100	28.0	7.34	Nitrd	99		3.1	23.3	3.8
	2100	28.0	3.75	Nitrd	99		4.6	22.4	2.1
	2100	28.0	3.5	Nitrd	99		5.2	23.3	9.2
S.H. Lee 2009 <i>JECerS</i> 29	1500	40.0	3.5	C+B	97		3.2	25.4	2.08
	1500	40.0	5	C+B	98		3.3	26.4	1.2
	1500	40.0	7.5	C+B	98		3.6	23.6	1.55
	1500	40.0	10	C+B	98		4.5	24.8	0.9

Paper Year/Journal	T _{sint} °C	P _{sint} MPa	Σ Add. mass%	Add. Fam.	ρ %ρ _{ideal}	σ MPa	K _{Ic} MPa√m	HV GPa	GS μm
	1900	40.0	10	C+B	96		4.5	20.6	0.9
	1500	40.0	10	C+B	97		4	22.8	
	1900	40.0	10	C+B	97		3.6	23.3	
	1500	40.0	7.5	C+B	96		3.6	21.6	
	1900	40.0	7.5	C+B	96		4	21.7	
	1950	0.1	7.5	C+B	87.2		4.1	21.3	
	2000	0.1	1	C+B	96.8		4.6	22	
	2050	0.1	1	C+B	96.3		4.4	18.5	
J.S. Lee 2009 <i>JECerS 29</i>	1700	60.0	10	C+B	99.42				
	1700	60.0	2	C+B	80.89				
	1700	60.0	7.82	C+B	96.77				
	1700	60.0	11.08	C+B	87.18				
Y.Q. Liu 2009	1650	-		NA	94	603			
	1650	-		NA	99	715			
Hotta 2010 <i>JECerS 30</i>	1900	30.0	10	Oxid	96	880	2.5		1.45
	1900	30.0	10	Nitrd	95	900	2.5		1.03
	1900	30.0	10	Nitrd	97	960	2.5		1.12
	1900	30.0	10	Nitrd	98	940	2.5		0.78
	1900	30.0	10	Nitrd	99	1000	2.5		0.43
	1900	30.0	10	Nitrd	99	900	2.5		0.32
	1900	30.0	10	Nitrd	88				
	1900	30.0	2	Oxid	99	900	2.7		0.15
Mao-lin 2010 <i>FE&D 85</i>	1000	4000	4	Oxid	94			28	
	1100	4000	4	Oxid	96			18	
	1200	4250	4	Oxid	96			19	
	1200	4250	4	Oxid	98			23	
	1200	4400	4	Oxid	98			22	
	1200	4400	4	Oxid	96			24	
	1200	4500	4	Oxid	97			28	
	1200	4500	4	Oxid	98			38	
	1200	4500	4	Oxid	98			30	
	1200	4500	4	Oxid	99			22	
	1300	4000	4	Oxid	99			24	
	1100	4000	0	NA	91			25	
	1200	4000	0	NA	92			31	
	1200	4250	0	NA	93			31	
	1200	4250	0	NA	93			22	
	1200	4400	0	NA	94			28	
	1200	4400	0	NA	95			28	

Paper Year/Journal	T _{sint} °C	P _{sint} MPa	Σ Add. mass%	Add. Fam.	ρ %ρ _{ideal}	σ MPa	K _{Ic} MPa√m	HV GPa	GS μm
	1200	4500	0	NA	94			31.5	
	1200	4500	0	NA	96			32	
	1300	4000	0	NA	95			34	
J.S. Lee 2011 <i>JACerS</i> 94	1500	120.0	2	C+B	66.32				
	1400	120.0	10	C+B	75				
	1450	120.0	10	C+B	95				
	1500	120.0	10	C+B	98				
	1550	120.0	10	C+B	99				
	1600	120.0	10	C+B	99				
	1650	120.0	10	C+B	99				
Lara 2012 <i>Cer Intl</i> 38	1650	150.0	0	NA	78				-
	1800	70.0	0	NA	80				-
	1800	100.0	0	NA	87.9				0.44
	1800	0.0	0	NA	87.9				0.84
	1800	150.0	0	NA	90				0.105
	1850	70.0	0	NA	85.1				1.07
	1875	70.0	0	NA	85.4				1.38
	1900	70.0	0	NA	86.6				1.49
	1900	0.0	0	NA	87.3				1.67
	1900	100.0	0	NA	90.7				0.67
	1900	0.0	0	NA	92				0.73
	1900	150.0	0	NA	91				0.095
	1950	70.0	0	NA	88.7				1.95
	1950	100.0	0	NA	91.6				0.77
	1950	150.0	0	NA	91				0.091
	1950	0.0	0	NA	94				0.99
	2000	70.0	0	NA	89.2				1.91
	2050	70.0	0	NA	93.4				2.08
	2075	70.0	0	NA	93.2				2.15
	2100	70.0	0	NA	98				2.39
	2100	100.0	0	NA	91				0.97
	2100	150.0	0	NA	92				0.098
	2150	100.0	0	NA	90				0.85
	2200	100.0	0	NA	89				2.2
	2200	0.0	0	NA	90				1.72
	2200	0.0	0	NA	94.3				0.79
	2200	150.0	0	NA	94				1.2
Lomello 2012	1700	73.0	0	NA	86			17	0.05
	1700	73.0	0	NA	85			13.5	0.05

Paper Year/Journal	T _{sint} °C	P _{sint} MPa	Σ Add. mass%	Add. Fam.	ρ %ρ _{ideal}	σ MPa	K _{Ic} MPa√m	HV GPa	GS μm
<i>JECerS 32</i>	1750	73.0	0	NA	91			20	0.06
	1750	73.0	0	NA	91			22	0.06
	1800	73.0	0	NA	94			20	0.07
	1800	73.0	0	NA	95			25	0.07
	1850	73.0	0	NA	95			23	0.1
	1850	73.0	0	NA	95			22.5	1
	1900	73.0	0	NA	96			20	0.2
	1900	73.0	0	NA	96			22	1.1
Noviyanto 2012 CAP	1750	20.0	5	C+B	57.78				
	1750	20.0	5	C+B	75.35				
	1750	20.0	5	C+B	51.45				
	1750	20.0	5	C+B	59.73				
	1750	20.0	5	C+B	49.07				
	1750	20.0	5	C+B	57.21				
	1750	20.0	5	C+B	61.2				
	1750	20.0	5	C+B	66.1				
	1750	20.0	5	C+B	61.28				
	1750	20.0	5	C+B	60.04				
	1750	20.0	5	C+B	59.03				
	1750	20.0	5	C+B	57.35				
	1750	20.0	5	Oxid	98.7				
	1750	20.0	5	Oxid	61.3				
	1750	20.0	5	Oxid	76.1				
	1750	20.0	5	Oxid	61.5				
	1750	20.0	5	Oxid	60.1				
	1750	20.0	5	Oxid	90.3				
	1750	20.0	5	Oxid	96.8				
	1750	20.0	5	Oxid	75.9				
	1750	20.0	5	Oxid	96.1				
	1750	20.0	5	Oxid	55.4				
	1750	20.0	5	Oxid	55.8				
	1750	20.0	5	Oxid	86.7				
	1750	20.0	5	Oxid	65.66				
	1750	20.0	5	Oxid	65.21				
	1750	20.0	5	Oxid	59.08				
	1750	20.0	5	Oxid	58.04				
	1750	20.0	5	Oxid	56.81				
	1750	20.0	5	Oxid	96.53				
	1750	20.0	5	Oxid	55.92				

Paper Year/Journal	T _{sint} °C	P _{sint} MPa	Σ Add. mass%	Add. Fam.	ρ %ρ _{ideal}	σ MPa	K _{Ic} MPaVm	HV GPa	GS μm
	1750	20.0	5	Oxid	59.73				
Ortiz 2012	1950	0.0		Oxid	99			23.1	0.6
	1950	0.0		Oxid	95			22.8	0.6
Onbattuvelli 2012 <i>Cer Intl</i> 38	1850	0.0	10	Nitrd	<90		1.49	3.11	
	1850	0.0	10	Nitrd	<90		1.58	3.21	
	1900	0.0	10	Nitrd	<95		2.47	11.4	
	1900	0.0	10	Nitrd	<95		2.62	11.6	
	1950	0.0	10	Nitrd	96		3.38	14.7	
	1950	0.0	10	Nitrd	96		3.25	14.7	
	2000	0.0	10	Nitrd	95		2.51	9	
	2000	0.0	10	Nitrd	95				
	1800	0.0	10	Nitrd	<90		1.7	3.78	
	1800	0.0	10	Nitrd	<90		1.41	4.11	
	1850	0.0	10	Nitrd	<90		1.88	5.51	
	1850	0.0	10	Nitrd	<90		1.96	5.68	
	1900	0.0	10	Nitrd	<90		2.8	9.44	
	1900	0.0	10	Nitrd	<95		3.07	12.8	
	1950	0.0	10	Nitrd	97		3.18	15.1	
	1950	0.0	10	Nitrd	97		3.16	13.8	
	2000	0.0	10	Nitrd	95		2.44	10.9	
	2000	0.0	10	Nitrd	95		2.4	10.8	

Appendix 2: Powder Injection Molding Data

Table A.2: Powder injection molding data for the bars in Chapters 7 and 8.

	Unit	Monomodal	Bimodal	Unit	Monomodal	Bimodal
Temperature						
Hot Sprue	°F	365	365	°C	185	185
Feed t801	°F	325	325	°C	163	163
Barrel t802	°F	325	325	°C	163	163
Barrel t803	°F	325	325	°C	163	163
Barrel t804	°F	334	334	°C	168	168
Nozzle t805	°F	334	334	°C	168	168
Mold A	°F	75	75	°C	24	24
Mold B	°F	75	75	°C	24	24
Injection						
Inj speed Q301	in ³ /s	2.00	2.00	cm ³ /s	32.8	32.8
Inj speed Q302	in ³ /s	2.00	2.00	cm ³ /s	32.8	32.8
Inj pressure p301	psi	6000	7000	MPa	41.4	48.3
2nd speed v301	in ³ /s	0.70	0.70	cm ³ /s	11.5	11.5
Inj delay t301	s	0.30	0.30			
Hold Pressure						
Sw time t312	s	0.50	0.50			
HP flow Q321	in ³ /s	1.03	1.03	cm ³ /s	16.9	16.9
1st HP	psi	5439	5439	MPa	37.5	37.5
2nd HP	psi	3626	3626	MPa	25.0	25.0
3rd HP	psi	3626	3626	MPa	25.0	25.0
1st HT	s	1.00	1.00			
2nd HT	s	0.7	0.7			
3rd HT	s	0.5	0.5			
Rem cool time t400	s	50	50			

Appendix 3: DataPoint Labs Feedstock Data

Appendix 3.1: Paraffin-Polypropylene Binder Properties

Binder mixture

Test Report

Binder mixture

Client	Valmikanathan Onbattuveli
Company	Oregon State University
Address	Hall 10 Corvallis, OR United States
Sample Received	3/26/2009
Sample Source	Oregon State University
Report Prepared	4/9/2009
Prepared By	
Title	Engineer
Issued By	
Title	Operations Manager

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C-MOLD/Moldflow TestPak™ Results

< 14979.21000.udb

Analysis	Property & T-CODE	Value	Units
Filling & Cooling	Cross/WLF Model (01313):		
	n	0.40120	
	τ^*	7.935E+02 Pa	
	D1	4.293E+23 Pa•s	
	D2	333 K	
	D3	0 K/Pa	
	A1	78.13	
	A2	51.60 K	
	Juncture Loss Constants (01360):		
	C1	Pa ⁴ (1-C2)	
	C2		
	Melt Density (01000)	705 kg/m ³	
	Melt Specific Heat (01100)	2589 J/kg•K	
	Melt Thermal Conductivity (01200)	0.159 W/m•K	
	Transition Temperature (01500)	372 K	
	Specific Heat Table (01101)	See Page 7	
	Thermal Conductivity Table (01201)	See Page 8	
Post-Filling	Two-Domain Tait PVT Model (01004):		
	b5	3.360E+02 K	
	b6	1.465E-07 K/Pa	
	b1m	1.255E-03 m ³ /kg	
	b2m	1.344E-06 m ³ /kg•K	
	b3m	1.256E+08 Pa	
	b4m	5.867E-03 1/K	
	b1s	1.170E-03 m ³ /kg	
	b2s	8.568E-07 m ³ /kg•K	
	b3s	2.396E+08 Pa	
	b4s	4.155E-03 1/K	
	b7	8.458E-05 m ³ /kg	
	b8	6.688E-02 1/K	
	b9	1.387E-08 1/Pa	
Shrink / Warp - Uncorrected Stress	Anisotropic Mechanical Properties (01602)		
	Modulus E ₁ (flow direction)		MPa
	Modulus E ₂ (transverse direction)		MPa
	Poisson's ratio ν_{12}		
	Poisson's ratio ν_{23}		
	Shear Modulus G		MPa
	Anisotropic Thermal Expansion (01702)		
	CLTE α_1 (flow direction)		x 10E-6/°C
	CLTE α_2 (transverse direction)		x 10E-6/°C

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Viscosity



Method	ASTM D 3835: 2008 Determination of Properties of Polymeric Materials by Means of a Capillary Rheometer	
Instrument	Instron 5582 Electromechanical UTM	
Specimen	type	powder
	drying	none
	other preparation	none
Parameters	initial pressure	0 MPa
	barrel diameter	12 mm
	die entry angle	180 °
	die inner diameter	1 mm
	die length	20 mm
	preheating time	6 min
Data Correction		
Precision	temperature	+/- 0.1 °C
	die inner diameter	+/- 0.0069 mm
	die length	+/- 0.025 mm
Uncertainty	per standard	

Polymer rheology characterizes the complex flow behavior of plastics. A capillary rheometer measures viscosity as a function of temperature and shear rate. The Goettfert rheometer utilizes direct measurement of melt pressures through a side mounted pressure transducer.

Data are modeled using empirical or semi-empirical equations.

Notes: This material had totally unstable pressures throughout all testing.

Viscosity Data

140 °C		150 °C		160 °C	
Shear Rate	Viscosity	Shear Rate	Viscosity	Shear Rate	Viscosity
s ⁻¹	Pa·s	s ⁻¹	Pa·s	s ⁻¹	Pa·s
80	46.66	80	25.23	80	7.62
160	38.08	160	22.85	160	5.71
400	28.24	400	12.98	400	4.87
800	19.47	800	8.73	800	1.87
		1600	4.10		

Viscosity Continued

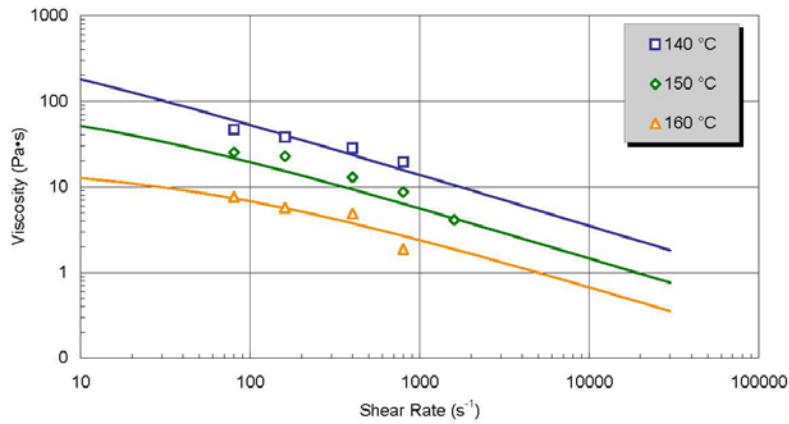
Cross/WLF Model (C-MOLD, Moldflow)

$$\eta(T, \dot{\gamma}) = \frac{\eta_0(T)}{1 + \left(\frac{\eta_0 \dot{\gamma}}{\tau^*} \right)^{1-n}}, \text{ where}$$
$$\eta_0(T) = D_1 \exp \left(- \frac{A_1 (T - D_2)}{A_2 + (T - D_2)} \right)$$

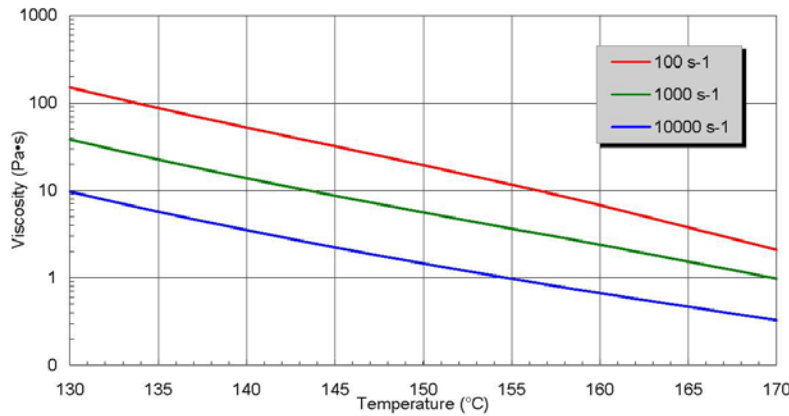
Coefficients (SI units)

n	0.40120
τ^*	793.461
D1	4.29E+23
D2	333
A1	78.13
A2	51.6

Viscosity vs Shear Rate



Viscosity vs Temperature



Specific Heat



Method	Based on ASTM E1269: 2005 Determining Specific Heat Capacity by Differential Scanning Calorimetry	
Instrument	Perkin Elmer DSC7	
Specimen	type drying other preparation	pellets none cut from pellet
Parameters	purge gas purge gas purity purge gas rate cooling rate initial temperature final temperature equilibration times sample weight sample pans	N2 99.99 % 25 ml/min 20 °C/min 180 °C 0 °C 4 min 5.63 mg Al, volatile
Calibration Standards	temperature heat flow specific heat	In, Zn In sapphire

Heat capacity is a thermodynamic quantity and is a measure of the amount of heat retained by the material. The DSC can measure this property over a range of temperatures and in both solid and melt states.

Transition Analysis

extrapolated onset	99 °C
peak	95 °C
extrapolated end	89 °C

0 Digital Data at www.matereality.com

Specific heat measurements are not included in our current scope of accreditation.

Tested By: WL

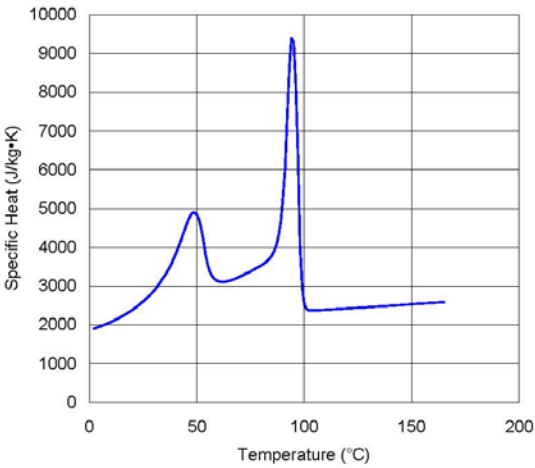
Certified By:

Test Date: 4/2/2009

Specific Heat Continued

Specific Heat Data

Temp °C	Cp J/kg•K
170	2598
134	2473
104	2371
95	9286
79	3505
49	4894
10	2077



Thermal Conductivity

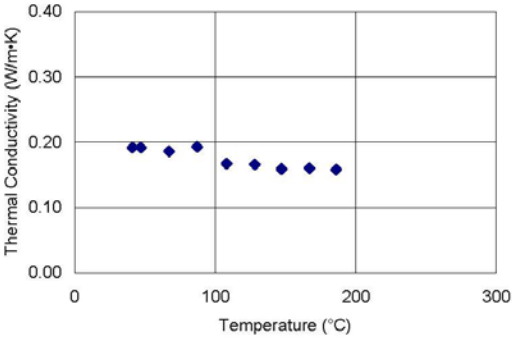


Method	ASTM D 5930: 2001 Thermal Conductivity of Plastics by Means of a Transient Line-Source Technique	
Instrument	Instron 8872 Servohydraulic UTM	
Specimen	type	powder
	drying	none
	other preparation	none
Parameters	calibration material	60,000 cstk PDMS
	probe constant	0.743
	probe length	50 mm
	loading temperature	160 °C
	initial temperature	180 °C
	final temperature	30 °C
	probe voltage	4 V
	acquisition time	45 s
Uncertainty	per standard	

Thermal conductivity is a measure of the rate of heat conduction of the material. It is a critical property for heat transfer calculations. The line-source method measures thermal conductivity in both melt and solid state.

Thermal Conductivity Data

Temp °C	k W/m·K
186	0.158
167	0.160
147	0.159
128	0.166
108	0.167
87	0.193
67	0.186
47	0.192
41	0.192



Tested By: JL
Certified By:
Test Date: 3/31/2009

PVT data are equation-of-state thermodynamic properties that describe the compressibility and volumetric expansion of the material. Dilatometry measures the change in volume of a specimen subjected to different temperatures and pressures.

Notes: Specimen was cut from a plug that was manufactured by Datapoint Labs from pellets supplied by client.

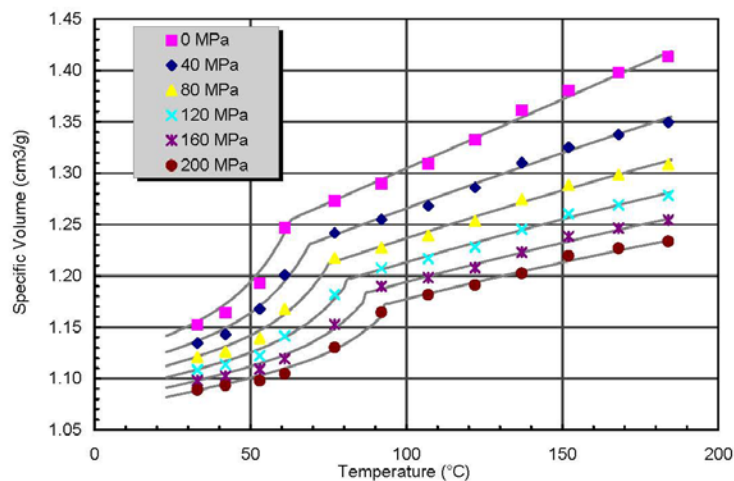
Density 23°C	873 kg/m3
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0 Digital data at www.matereality.com
PVT measurements are not included in our current scope of accreditation.

Tested By: WL
Certified By:
Test Date: 4/7/2009

Pressure-Volume-Temperature Data

Specific Volume cm ³ /g						
Temp °C	Pressure MPa					
	0	40	80	120	160	200
33	1.1521	1.1346	1.1207	1.1084	1.0980	1.0890
42	1.1640	1.1428	1.1261	1.1136	1.1024	1.0934
53	1.1929	1.1678	1.1394	1.1221	1.1090	1.0979
61	1.2467	1.2011	1.1678	1.1415	1.1194	1.1049
77	1.2733	1.2418	1.2174	1.1819	1.1527	1.1301
92	1.2897	1.2549	1.2277	1.2074	1.1898	1.1645
107	1.3088	1.2682	1.2393	1.2169	1.1981	1.1817
122	1.3324	1.2861	1.2534	1.2283	1.2079	1.1911
137	1.3615	1.3101	1.2745	1.2456	1.2229	1.2025
152	1.3805	1.3251	1.2882	1.2607	1.2385	1.2194
168	1.3975	1.3378	1.2983	1.2693	1.2464	1.2270
184	1.4138	1.3497	1.3085	1.2783	1.2542	1.2336

Modified Two-Domain Tait Model (C-MOLD, Moldflow)

Coefficients	
b5	6.30E+01
b6	1.47E-01
b1m	1.255E+00
b2m	1.344E-03
b3m	1.256E+02
b4m	5.867E-03
b1s	1.170E+00
b2s	8.568E-04
b3s	2.396E+02
b4s	4.155E-03
b7	8.46E-02
b8	6.688E-02
b9	1.387E-02

Modified Two-Domain Tait Equation

$$v(T, p) = v_0(T) \left(1 - C \ln \left(1 + \frac{p}{B(T)} \right) \right) + v_t(T, p), T_i(p) = b_5 + b_6 p$$

$$\text{for } T > T_i(p): v_0(T) = b_{1m} + b_{2m}(T - b_5), B(T) = b_{3m} \exp(-b_{4m}(T - b_5)), v_t(T, p) = 0$$

$$\text{for } T < T_i(p): v_0(T) = b_{1s} + b_{2s}(T - b_5), B(T) = b_{3s} \exp(-b_{4s}(T - b_5)), v_t(T, p) = b_7 \exp(b_8(T - b_5) - b_9 p)$$

Model Terms	Units
specific volume, v	cm³/g
pressure, P	MPa
temperature, T	°C

No-Flow Temperature



Method	non-standard	
	Moldflow specification; no-flow temperature defined by extrudate flow < 2 mm/min	
Instrument	Goettfert Capillary Rheometer	
Specimen	type	pellets
	drying	none
	other preparation	none
Parameters	equivalent load	172 kg
	barrel diameter	12 mm
	initial pressure	0 MPa
	test temperature	140 °C
	dwelt time	6 min
	die inner diameter	1 mm
	die length	20 mm
	die entry angle	180 °

The no-flow temperature provides a measure of the solidification temperature of the melt. During the test, a molten specimen is cooled under constant load; the no-flow temperature is one at which flow ceases to occur.

NOTE: No Flow temperature is taken from DSC data.

Results

No-Flow Temperature	47 °C
----------------------------	-------

Tested By: JA

Certified By: BC

Test Date: 4/2/2009

No-Flow temperature measurements are not included in our current scope of accreditation.

Appendix 3.2: Monomodal SiC + Binder Properties

silicon carbide/binder mixture

Test Report

silicon carbide/binder mixture

Client	Valmikanathan Onbattuveli
Company	Oregon State University
Address	Hall Cornallis, OR United States
Sample Received	2/25/2009
Sample Source	Oregon State University
Report Prepared	3/4/2009
Prepared By	
Title	Engineer
Issued By	
Title	Operations Manager

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C-MOLD/Moldflow TestPak™ Results

< 14898.21000.udb

Analysis	Property & T-CODE	Value	Units
Filling & Cooling	Cross/WLF Model (01313):		
	n	0.15861	
	τ^*	2.808E+04 Pa	
	D1	1.741E+18 Pa•s	
	D2	263 K	
	D3	0 K/Pa	
	A1	37.73	
	A2	51.60 K	
	Juncture Loss Constants (01360):		
	C1	Pa ⁴ (1-C2)	
	C2		
	Melt Density (01000)	1852 kg/m ³	
	Melt Specific Heat (01100)	1204 J/kg•K	
	Melt Thermal Conductivity (01200)	2.445 W/m•K	
	Transition Temperature (01500)	325 K	
	Specific Heat Table (01101)	See Page 7	
	Thermal Conductivity Table (01201)	See Page 8	
Post-Filling	Two-Domain Tait PVT Model (01004):		
	b5	3.440E+02 K	
	b6	1.050E-07 K/Pa	
	b1m	5.154E-04 m ³ /kg	
	b2m	3.087E-07 m ³ /kg•K	
	b3m	2.832E+08 Pa	
	b4m	5.235E-03 1/K	
	b1s	5.031E-04 m ³ /kg	
	b2s	1.910E-07 m ³ /kg•K	
	b3s	3.719E+08 Pa	
	b4s	6.730E-03 1/K	
	b7	1.229E-05 m ³ /kg	
	b8	6.162E-02 1/K	
	b9	8.500E-09 1/Pa	
Shrink / Warp - Uncorrected Stress	Anisotropic Mechanical Properties (01602)		
	Modulus E ₁ (flow direction)		MPa
	Modulus E ₂ (transverse direction)		MPa
	Poisson's ratio ν_{12}		
	Poisson's ratio ν_{23}		
	Shear Modulus G		MPa
	Anisotropic Thermal Expansion (01702)		
	CLTE α_1 (flow direction)		x 10E-6/°C
	CLTE α_2 (transverse direction)		x 10E-6/°C

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Viscosity



Method	ASTM D 3835: 2008 Determination of Properties of Polymeric Materials by Means of a Capillary Rheometer	
Instrument	Goettfert Rheograph 2003 Capillary Rheometer	
Specimen	type	pellets
	drying	none
	other preparation	none
Parameters	initial pressure	0 MPa
	barrel diameter	12 mm
	die entry angle	180 °
	die inner diameter	1 mm
	die length	20 mm
	preheating time	6 min
Data Correction	Rabinowitsch	
Precision	temperature	+/- 0.1 °C
	die inner diameter	+/- 0.0069 mm
	die length	+/- 0.025 mm
Uncertainty	per standard	

Polymer rheology characterizes the complex flow behavior of plastics. A capillary rheometer measures viscosity as a function of temperature and shear rate. The Goettfert rheometer utilizes direct measurement of melt pressures through a side mounted pressure transducer.

Data are modeled using empirical or semi-empirical equations.

Viscosity Data

140 °C		150 °C		160 °C	
Shear Rate s ⁻¹	Viscosity Pa·s	Shear Rate s ⁻¹	Viscosity Pa·s	Shear Rate s ⁻¹	Viscosity Pa·s
12	5627.90	12	6145.48	12	6411.75
88	911.47	44	1812.87	50	1705.77
121	632.00	93	1108.54	153	668.29
179	548.99	264	443.35	395	276.60
341	328.09	505	249.02	600	170.98
780	201.27	860	177.42	813	180.97
2071	91.40	2010	93.90	2176	81.10
4174	50.47	4423	47.22	4909	39.44
9683	27.69	12356	21.05		
22438	13.42	57574	4.68		

Viscosity Continued

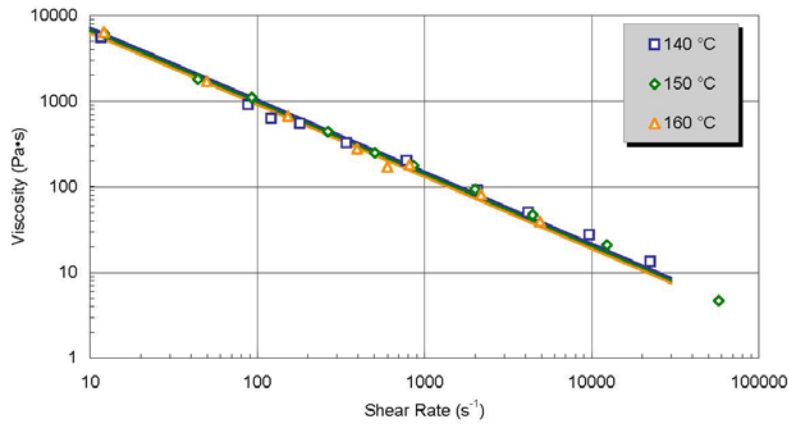
Cross/WLF Model (C-MOLD, Moldflow)

$$\eta(T, \dot{\gamma}) = \frac{\eta_0(T)}{1 + \left(\frac{\eta_0 \dot{\gamma}}{\tau^*}\right)^n}, \text{ where }$$
$$\eta_0(T) = D_1 \exp\left(-\frac{A_1(T - D_2)}{A_2 + (T - D_2)}\right)$$

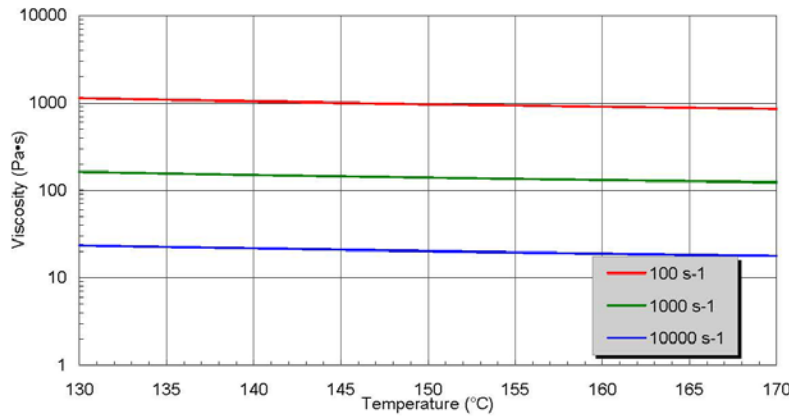
Coefficients (SI units)

n	0.15861
τ^*	28082.455
D1	1.74E+18
D2	263
A1	37.73
A2	51.6

Viscosity vs Shear Rate



Viscosity vs Temperature



Specific Heat



Method	Based on ASTM E1269: 2005 Determining Specific Heat Capacity by Differential Scanning Calorimetry	
Instrument	Perkin Elmer DSC7	
Specimen	type drying other preparation	pellets none cut from pellet
Parameters	purge gas purge gas purity purge gas rate cooling rate initial temperature final temperature equilibration times sample weight sample pans	N2 99.99 % 25 ml/min 20 °C/min 160 °C 20 °C 4 min 9.99 mg Al, volatile
Calibration Standards	temperature heat flow specific heat	In, Zn In sapphire

Heat capacity is a thermodynamic quantity and is a measure of the amount of heat retained by the material. The DSC can measure this property over a range of temperatures and in both solid and melt states.

Notes: Two peaks were observed. Transition analysis temperatures and specific heat data are for larger peak.

Transition Analysis

extrapolated onset	52 °C
peak	46 °C
extrapolated end	33 °C

Tested By: WL

Certified By: BC

Test Date: 3/2/2009

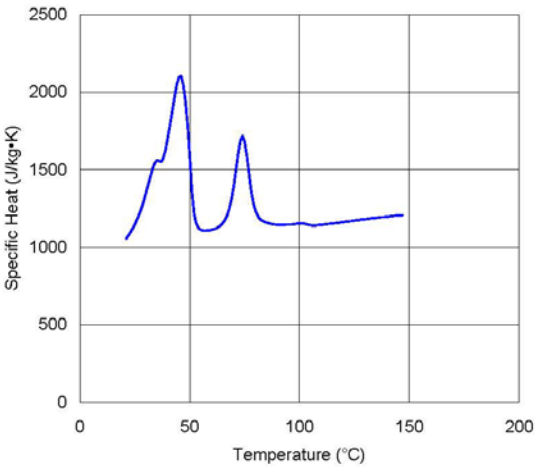
0 Digital Data at www.matereality.com

Specific heat measurements are not included in our current scope of accreditation.

Specific Heat Continued

Specific Heat Data

Temp °C	Cp J/kg•K
150	1200
101	1156
57	1108
46	2105
23	1098
31	1402
30	1350



Thermal Conductivity

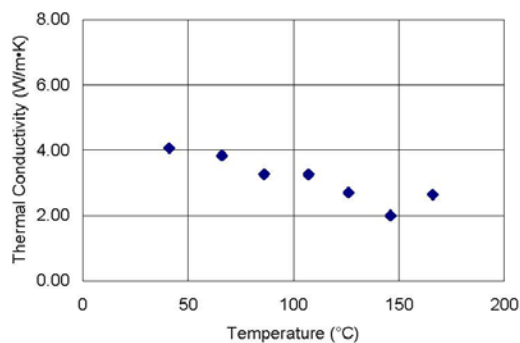


Method	ASTM D 5930: 2001 Thermal Conductivity of Plastics by Means of a Transient Line-Source Technique	
Instrument	K-System II Thermal Conductivity System	
Specimen	type	pellets
	drying	none
	other preparation	none
Parameters	calibration material	60,000 cstk PDMS
	probe constant	0.743
	probe length	50 mm
	loading temperature	140 °C
	initial temperature	160 °C
	final temperature	30 °C
	probe voltage	4 V
	acquisition time	45 s
Uncertainty	per standard	

Thermal conductivity is a measure of the rate of heat conduction of the material. It is a critical property for heat transfer calculations. The line-source method measures thermal conductivity in both melt and solid state.

Thermal Conductivity Data

Temp °C	k W/m·K
166	2.639
146	1.997
126	2.698
107	3.255
86	3.263
66	3.835
41	4.072



PVT data are equation-of-state thermodynamic properties that describe the compressibility and volumetric expansion of the material. Dilatometry measures the change in volume of a specimen subjected to different temperatures and pressures.

Notes: PVT specimen was cut from a plug that was manufactured by Datapoint Labs from pellets supplied by the client.

Initial Solid Density

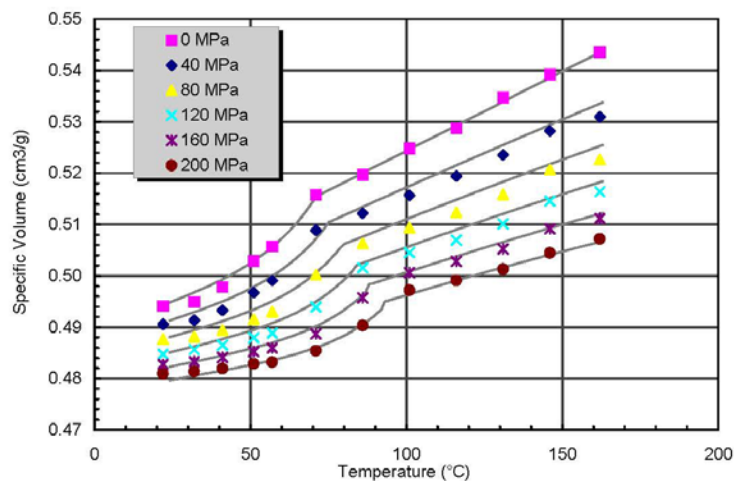
Density 23°C	2027 kg/m3
--------------	------------

0 Digital data at www.matereality.com
PVT measurements are not included in our current scope of accreditation.

Tested By: WL
Certified By: BC
Test Date: 3/3/2009

Pressure-Volume-Temperature Data

Specific Volume cm ³ /g						
Temp °C	Pressure MPa					
	0	40	80	120	160	200
22	0.4941	0.4906	0.4876	0.4847	0.4828	0.4809
32	0.4949	0.4913	0.4881	0.4856	0.4833	0.4814
41	0.4978	0.4933	0.4895	0.4865	0.4841	0.4819
51	0.5029	0.4968	0.4915	0.4880	0.4853	0.4829
57	0.5057	0.4991	0.4930	0.4889	0.4859	0.4832
71	0.5157	0.5089	0.5002	0.4940	0.4887	0.4854
86	0.5197	0.5122	0.5063	0.5016	0.4958	0.4903
101	0.5248	0.5157	0.5094	0.5046	0.5006	0.4972
116	0.5287	0.5194	0.5124	0.5070	0.5028	0.4991
131	0.5347	0.5236	0.5159	0.5102	0.5053	0.5013
146	0.5392	0.5283	0.5207	0.5146	0.5092	0.5045
162	0.5436	0.5310	0.5227	0.5164	0.5112	0.5072

Modified Two-Domain Tait Model (C-MOLD, Moldflow)

Coefficients	
b5	7.10E+01
b6	1.05E-01
b1m	5.154E-01
b2m	3.087E-04
b3m	2.832E+02
b4m	5.235E-03
b1s	5.031E-01
b2s	1.910E-04
b3s	3.719E+02
b4s	6.730E-03
b7	1.23E-02
b8	6.162E-02
b9	8.500E-03

Modified Two-Domain Tait Equation

$$v(T, p) = v_0(T) \left(1 - C \ln \left(1 + \frac{p}{B(T)} \right) \right) + v_t(T, p), T_i(p) = b_5 + b_6 p$$

$$\text{for } T > T_i(p): v_0(T) = b_{1m} + b_{2m}(T - b_5), B(T) = b_{3m} \exp(-b_{4m}(T - b_5)), v_t(T, p) = 0$$

$$\text{for } T < T_i(p): v_0(T) = b_{1s} + b_{2s}(T - b_5), B(T) = b_{3s} \exp(-b_{4s}(T - b_5)), v_t(T, p) = b_7 \exp(b_8(T - b_5) - b_9 p)$$

Model Terms	Units
specific volume, v	cm³/g
pressure, P	MPa
temperature, T	°C

No-Flow Temperature



Method	non-standard	
	Moldflow specification; no-flow temperature defined by extrudate flow < 2 mm/min	
Instrument	Goettfert Capillary Rheometer	
Specimen	type	pellets
	drying	none
	other preparation	none
Parameters	equivalent load	172 kg
	barrel diameter	12 mm
	initial pressure	0 MPa
	test temperature	140 °C
	dwel time	6 min
	die inner diameter	1 mm
	die length	20 mm
	die entry angle	180 °

The no-flow temperature provides a measure of the solidification temperature of the melt. During the test, a molten specimen is cooled under constant load; the no-flow temperature is one at which flow ceases to occur.

Results

No-Flow Temperature	110 °C
----------------------------	--------

No-Flow temperature measurements are not included in our current scope of accreditation.

Tested By: JA

Certified By: BC

Test Date: 2/27/2009

Appendix 3.3: Bimodal SiC + Binder Properties

Silicone Carbide

DatapointLabs Report # 16881: Silicone Carbide

PAGE 1 OF 12

Test Report

Silicone Carbide

Client	Valmikanathan Onbattuveli
Company	Oregon State University
Address	Hall Corvallis, OR United States
Sample Received	6/11/2010
Sample Source	Oregon State University
Report Prepared	6/16/2010
Prepared By	
Title	Engineer
Issued By	
Title	Operations Manager

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C-MOLD/Moldflow TestPak™ Results

16881.21000.udb

Analysis	Property & T-CODE	Value	Units
Filling & Cooling	Cross/WLF Model (01313):		
	n	0.06498	
	τ^*	1.278E+05 Pa	
	D1	1.000E+20 Pa•s	
	D2	263 K	
	D3	0 K/Pa	
	A1	42.69	
	A2	51.60 K	
	Juncture Loss Constants (01360):		
	C1	Pa ⁴ (1-C2)	
	C2		
	Melt Density (01000)	1987 kg/m ³	
	Melt Specific Heat (01100)	1250 J/kg•K	
	Melt Thermal Conductivity (01200)	2.325 W/m•K	
	Transition Temperature (01500)	325 K	
	Specific Heat Table (01101)	See Page 7	
	Thermal Conductivity Table (01201)	See Page 8	
Post-Filling	Two-Domain Tait PVT Model (01004):		
	b5	3.350E+02 K	
	b6	1.600E-07 K/Pa	
	b1m	4.750E-04 m ³ /kg	
	b2m	2.328E-07 m ³ /kg•K	
	b3m	3.190E+08 Pa	
	b4m	4.844E-03 1/K	
	b1s	4.628E-04 m ³ /kg	
	b2s	1.534E-07 m ³ /kg•K	
	b3s	5.000E+08 Pa	
	b4s	1.000E-02 1/K	
	b7	1.220E-05 m ³ /kg	
	b8	9.026E-02 1/K	
	b9	1.590E-08 1/Pa	
Shrink / Warp - Uncorrected Stress	Anisotropic Mechanical Properties (01602)		
	Modulus E ₁ (flow direction)		MPa
	Modulus E ₂ (transverse direction)		MPa
	Poisson's ratio ν_{12}		
	Poisson's ratio ν_{23}		
	Shear Modulus G		MPa
	Anisotropic Thermal Expansion (01702)		
	CLTE α_1 (flow direction)		x 10E-6/°C
	CLTE α_2 (transverse direction)		x 10E-6/°C

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Viscosity



Method	ASTM D 3835: 2008 Determination of Properties of Polymeric Materials by Means of a Capillary Rheometer	
Instrument	Goettfert Rheograph 2003 Capillary Rheometer	
Specimen	type	pellets
	drying	none
	other preparation	none
Parameters	initial pressure	0 MPa
	barrel diameter	12 mm
	die entry angle	180 °C
	die inner diameter	1 mm
	die length	20 mm
	preheating time	6 min
Data Correction		
Precision	temperature	+/- 0.1 °C
	die inner diameter	+/- 0.0069 mm
	die length	+/- 0.025 mm
Uncertainty	per standard	

Polymer rheology characterizes the complex flow behavior of plastics. A capillary rheometer measures viscosity as a function of temperature and shear rate. The Goettfert rheometer utilizes direct measurement of melt pressures through a side mounted pressure transducer.

Data are modeled using empirical or semi-empirical equations.

Notes: Pressures were quite unstable during all testing temperatures.

Viscosity Data

140 °C		160 °C		180 °C	
Shear Rate s ⁻¹	Viscosity Pa·s	Shear Rate s ⁻¹	Viscosity Pa·s	Shear Rate s ⁻¹	Viscosity Pa·s
10	19984.50	10	20715.70	10	16328.80
20	9931.34	20	10388.30	20	8164.42
50	3969.48	50	4177.11	50	3273.29
100	1984.74	100	2064.13	100	1630.54
200	998.48	200	1013.74	200	812.22
500	433.59	500	405.50	500	326.11
1000	233.26	1000	236.92	1000	188.07
2000	116.94	2000	125.80	2000	98.62
5000	59.23	5000	52.03	5000	48.97
10000	29.62	10000	30.53	10000	26.01

☐ Digital data at www.matereality.com

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Test Date: 6/15/2010

Viscosity Continued

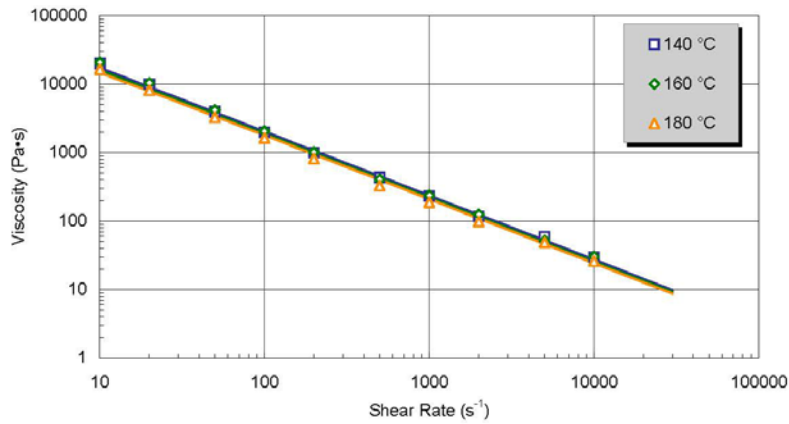
Cross/WLF Model (C-MOLD, Moldflow)

$$\eta(T, \dot{\gamma}) = \frac{\eta_0(T)}{1 + \left(\frac{\eta_0 \dot{\gamma}}{\tau^*} \right)^{1-n}}, \text{ where}$$
$$\eta_0(T) = D_1 \exp \left[- \frac{A_1 (T - D_2)}{A_2 + (T - D_2)} \right]$$

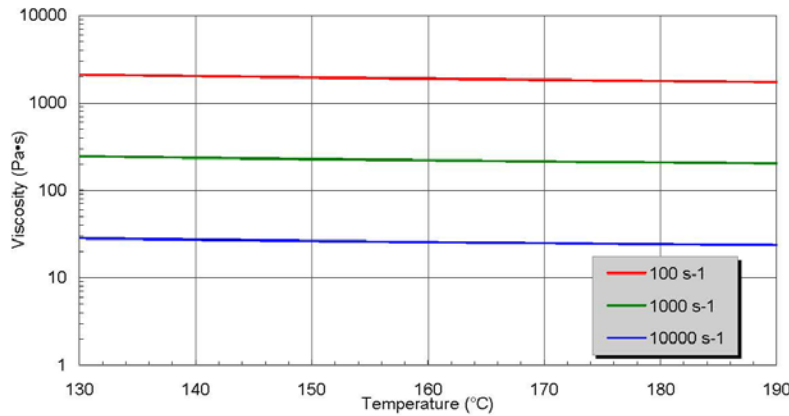
Coefficients (SI units)

n	0.06498
τ^*	127756.7
D1	1E+20
D2	263
A1	42.69
A2	51.6

Viscosity vs Shear Rate



Viscosity vs Temperature



Specific Heat



Method	Based on ASTM E1269: 2005 Determining Specific Heat Capacity by Differential Scanning Calorimetry	
Instrument	Perkin Elmer DSC7	
Specimen	type drying other preparation	pellets none cut from pellet
Parameters	purge gas purge gas purity purge gas rate cooling rate initial temperature final temperature equilibration times sample weight sample pans	N2 99.99 % 25 ml/min 20 °C/min 180 °C -10 °C 4 min 6.43 mg Al, volatile
Calibration Standards	temperature heat flow specific heat	In, Zn In sapphire

Heat capacity is a thermodynamic quantity and is a measure of the amount of heat retained by the material. The DSC can measure this property over a range of temperatures and in both solid and melt states.

Notes: An additional peak was observed in the 60° to 90°C range.

Transition Analysis

extrapolated onset	52 °C
peak	47 °C
extrapolated end	36 °C



Digital Data at www.matereality.com

Specific heat measurements are not included in our current scope of accreditation.

Tested By: WL

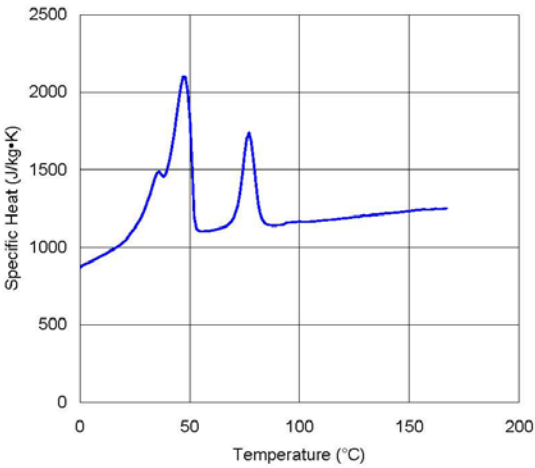
Certified By:

Test Date: 6/14/2010

Specific Heat Continued

Specific Heat Data

Temp °C	Cp J/kg•K
170	1252
111	1174
57	1105
47	2100
28	1149
18	1013
0	871



Thermal Conductivity

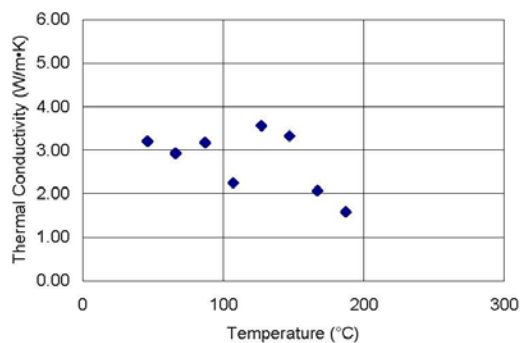


Method	ASTM D 5930: 2001 Thermal Conductivity of Plastics by Means of a Transient Line-Source Technique	
Instrument	K-System II Thermal Conductivity System	
Specimen	type	pellets
	drying	none
	other preparation	none
Parameters	calibration material	60,000 cstk PDMS
	probe constant	0.796
	probe length	50 mm
	loading temperature	180 °C
	initial temperature	180 °C
	final temperature	30 °C
	probe voltage	3.5 V
	acquisition time	45 s
Uncertainty	per standard	

Thermal conductivity is a measure of the rate of heat conduction of the material. It is a critical property for heat transfer calculations. The line-source method measures thermal conductivity in both melt and solid state.

Thermal Conductivity Data

Temp °C	k W/m·K
187	1.579
167	2.070
147	3.327
127	3.568
107	2.252
87	3.176
66	2.926
46	3.210



PVT

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Method	Non-standard. Pressure-specific volume-temperature measurements using high-pressure dilatometry	
	Instrument Gnomix PVT apparatus	
Specimen	type	plaque
	drying	none
	other preparation	cut from plaque
Parameters	solid density method	ASTM D792
	immersion liquid	water
	PVT confining fluid	Mercury
	max temperature	180 °C
	measurement type	isothermal heating scan
	heating rate	approx. 3 °C/min

PVT data are equation-of-state thermodynamic properties that describe the compressibility and volumetric expansion of the material. Dilatometry measures the change in volume of a specimen subjected to different temperatures and pressures.

Initial Solid Density

Density 23°C	2183 kg/m3
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Digital data at www.matereality.com

PVT measurements are not included in our current scope of accreditation.

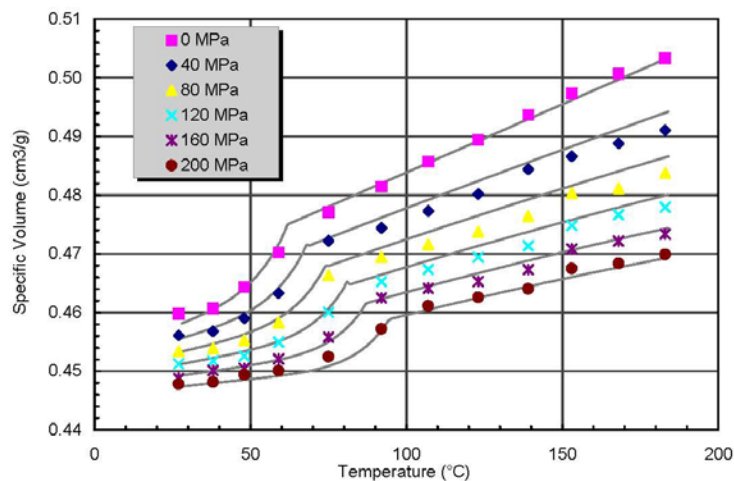
Tested By: WL

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Test Date: 6/15/2010

Pressure-Volume-Temperature Data

Specific Volume cm ³ /g						
Temp °C	Pressure MPa					
	0	40	80	120	160	200
27	0.4598	0.4561	0.4534	0.4512	0.4488	0.4478
38	0.4607	0.4568	0.4539	0.4517	0.4501	0.4482
48	0.4644	0.4590	0.4553	0.4526	0.4505	0.4494
59	0.4703	0.4633	0.4583	0.4549	0.4521	0.4501
75	0.4771	0.4723	0.4663	0.4600	0.4558	0.4525
92	0.4815	0.4745	0.4695	0.4653	0.4625	0.4572
107	0.4857	0.4773	0.4716	0.4674	0.4642	0.4612
123	0.4894	0.4802	0.4738	0.4695	0.4653	0.4626
139	0.4937	0.4844	0.4765	0.4714	0.4673	0.4640
153	0.4973	0.4866	0.4804	0.4749	0.4708	0.4675
168	0.5007	0.4888	0.4812	0.4767	0.4722	0.4684
183	0.5034	0.4911	0.4838	0.4780	0.4734	0.4699

Modified Two-Domain Tait Model (C-MOLD, Moldflow)

Coefficients	
b5	6.20E+01
b6	1.60E-01
b1m	4.750E-01
b2m	2.328E-04
b3m	3.190E+02
b4m	4.844E-03
b1s	4.628E-01
b2s	1.534E-04
b3s	5.000E+02
b4s	1.000E-02
b7	1.22E-02
b8	9.026E-02
b9	1.590E-02

Modified Two-Domain Tait Equation

$$v(T, p) = v_0(T) \left(1 - C \ln \left(1 + \frac{p}{B(T)} \right) \right) + v_t(T, p), T_i(p) = b_5 + b_6 p$$

$$\text{for } T > T_i(p): v_0(T) = b_{1m} + b_{2m}(T - b_5), B(T) = b_{3m} \exp(-b_{4m}(T - b_5)), v_t(T, p) = 0$$

$$\text{for } T < T_i(p): v_0(T) = b_{1s} + b_{2s}(T - b_5), B(T) = b_{3s} \exp(-b_{4s}(T - b_5)), v_t(T, p) = b_7 \exp(b_8(T - b_5) - b_9 p)$$

Model Terms	Units
specific volume, v	cm³/g
pressure, P	MPa
temperature, T	°C

No-Flow Temperature



Method	non-standard	
	Moldflow specification; no-flow temperature defined by extrudate flow < 2 mm/min	
Instrument	Goettfert Capillary Rheometer	
Specimen	type	pellets
	drying	none
	other preparation	none
Parameters	equivalent load	172 kg
	barrel diameter	12 mm
	initial pressure	0 MPa
	test temperature	140 °C
	dwelt time	6 min
	die inner diameter	1 mm
	die length	20 mm
	die entry angle	180 °

The no-flow temperature provides a measure of the solidification temperature of the melt. During the test, a molten specimen is cooled under constant load; the no-flow temperature is one at which flow ceases to occur.

Results

No-Flow Temperature	58 °C
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No-Flow temperature measurements are not included in our current scope of accreditation.

Tested By: JA

Certified By: BC

Test Date: 6/15/2010

About the Author

“He has all the virtues I dislike and none of the vices I admire.” — Sir Winston Churchill

Richard Edward Chinn, P.E., CQE, was born in Pueblo, Colorado, USA, and graduated from Pueblo Central High School. He earned a B.Sc. in Metallurgical Engineering in 1984 and an M.Sc. in Materials Science in 1995, both from the Colorado School of Mines in Golden, CO. Between degrees, he was a materials engineer for Coors Porcelain Company (now CoorsTek, Inc.) and Coors Brewing Company, both in Golden, where he worked in technical ceramics, beer cans, sheet aluminum, plastic film laminates and glass bottles. Chinn had a brief stint with a chromium and manganese smelter in Ohio before he moved to Albany, Oregon, to work for ATI Wah Chang and later an automation contractor. He has been a research materials engineer at the United States Department of Energy in Albany, once the U.S. Bureau of Mines and now the National Energy Technology Laboratory, since 2000.



Chinn is a registered metallurgical Professional Engineer in Colorado and Oregon, and an ASQ Certified Quality Engineer. He is a member of ASM International and the American Ceramic Society, and served as chairman of the Oregon Chapter of ASM in 2006-7. He has written or co-authored papers in a number of journals, and two books. CERAMOGRAPHY (ASM and ACerS, 2002) is a textbook and reference on ceramic microstructures, and LIVE TO RIDE (PivoPub, 2008, under the pen name *Bo Edwards*) is a novel of bicycle touring in Europe.

Richard and his wife Patricia have two daughters, OSU alumna Melissa (B.Sc., Political Science, 2010) and Heidi, and two grandchildren.

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