



NANOSCALE REINFORCED POLYMER DERIVED CERAMIC MATRIX COATINGS

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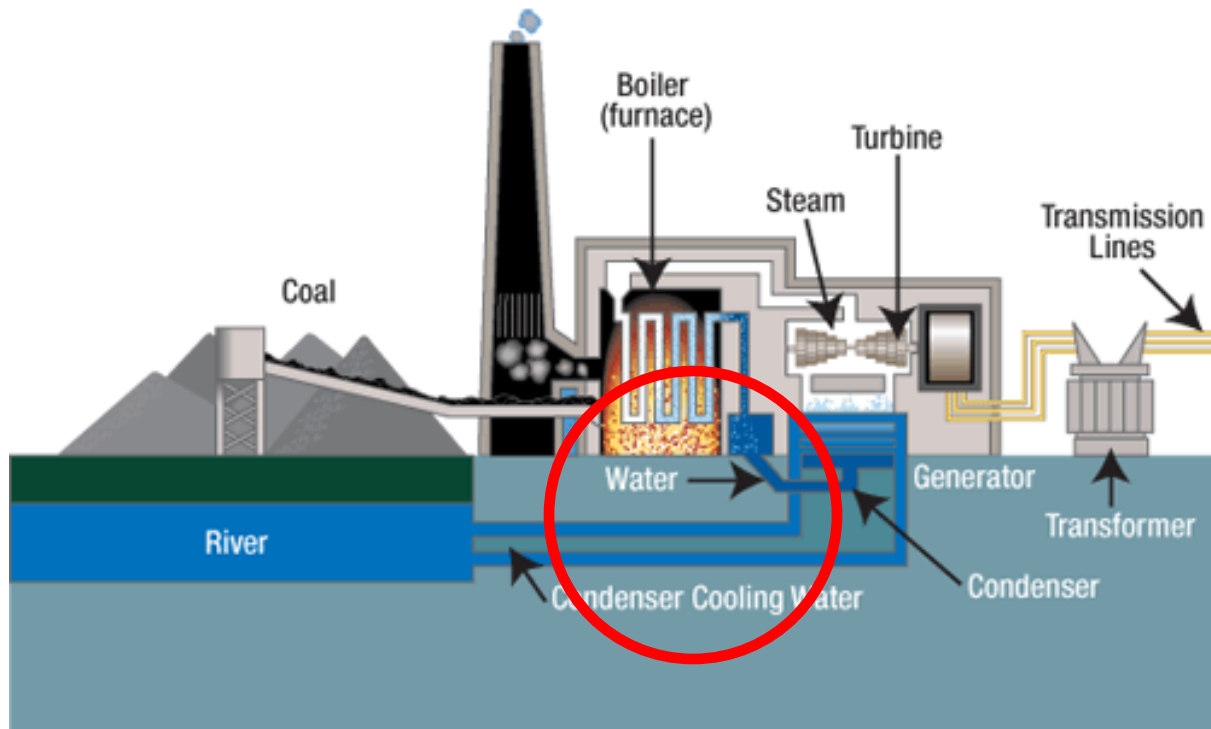
**Department of Materials Science and Engineering
University of Washington
Seattle, WA, USA**

**University Coal Research Contractors Review Conference
Pittsburgh, PA**

June 6, 2007



MOTIVATION



An illustration of coal fired power plant [www.tva.gov/power/coalart.htm]

Technology trends

- Ultrasupercritical coal fired power plant: **higher temperatures and pressures**-the next generation
- Oxy-fuel combustion
- **Advantages**: increase in thermal efficiency of the plant; decrease the emission of SO_x , NO_x , etc., easier to sequester CO_2
- **Disadvantages** : increased corrosion rates of various alloys
- **3 types** of corrosion for boiler parts are of concern:
 - fireside corrosion
 - coal-ash corrosion
 - steamside oxidation

PROJECT STATUS

Project Origin

One possible solution: corrosion-, erosion-, oxidation-resistant coatings

Project Goal

Develop a new class of nanoscale reinforced ceramic coatings for high temperature (600-1000 °C) corrosion and oxidation protection of metallic components in a coal-fired environment.

Our Approach

- Nanostructured composite ceramic coatings
- Easy and inexpensive coating process
- Non-line of sight (for complex shapes)
- Using high yield pre-ceramic polymers

Other Approaches

- Pack cementation
- Electrospark deposition
- Vapor phase (PVD, CVD, Ion implantation etc.)

Project funded by DoE Office of Fossil Energy, National Energy Technology Labs, August 2005 – August 2008

KEY ISSUES BEING ADDRESSED

Processing of Nanoscale Reinforced Polymer Derived Composite Ceramics

- Selection of polymer, fillers and particle size of fillers
- Thermodynamics and kinetics of phase evolution and reactions
- Control of shrinkage during polymer to ceramic conversion
- Mechanistic understanding of the evolution of the phases and microstructure

Understanding and Optimization of the Coating Process

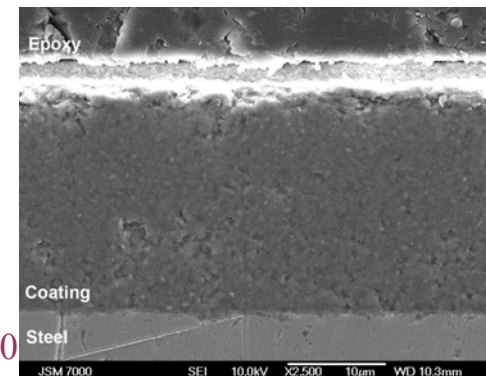
- Dispersion of nanoscale fillers in the polymer
- Control of slurry rheology and its effect on coatings
- Mechanics of constrained pyrolysis of the coating
- Optimized processing strategies for crack free coatings

Performance of the Coatings

- Mechanical properties of the coating and the interface
- Thermomechanical performance under thermal cycling
- Performance under selected corrosion conditions

Key Accomplishment

Have produced high quality coatings with good understanding and control of the process



SPECIFIC OBJECTIVES AND THEIR STATUS

Selection of Material System

- Selection of polymer, fillers and particle size of fillers (completed)
- Densification and microstructure development during polymer to ceramic conversion (completed)
- Evaluation of thermal stability and corrosion response (ongoing)

Processing of Coatings Including Optimization of Slurry Rheology

- Optimization of slurry viscosity for different systems (completed)
- Development of the dip-coating process (completed)
- Densification and microstructure development in the coatings (ongoing)

Characterization of the Coatings

- Mechanical properties of the coating and the interface (year 3)
- Thermomechanical performance under thermal cycling (year 3)
- Performance under selected corrosion and oxidation conditions (year 3)

OUTLINE

I. Background on polymer derived ceramics (processing, thermal conversion, role of fillers)

II. Results

- material selection
- green state processing of coatings
- coating microstructure

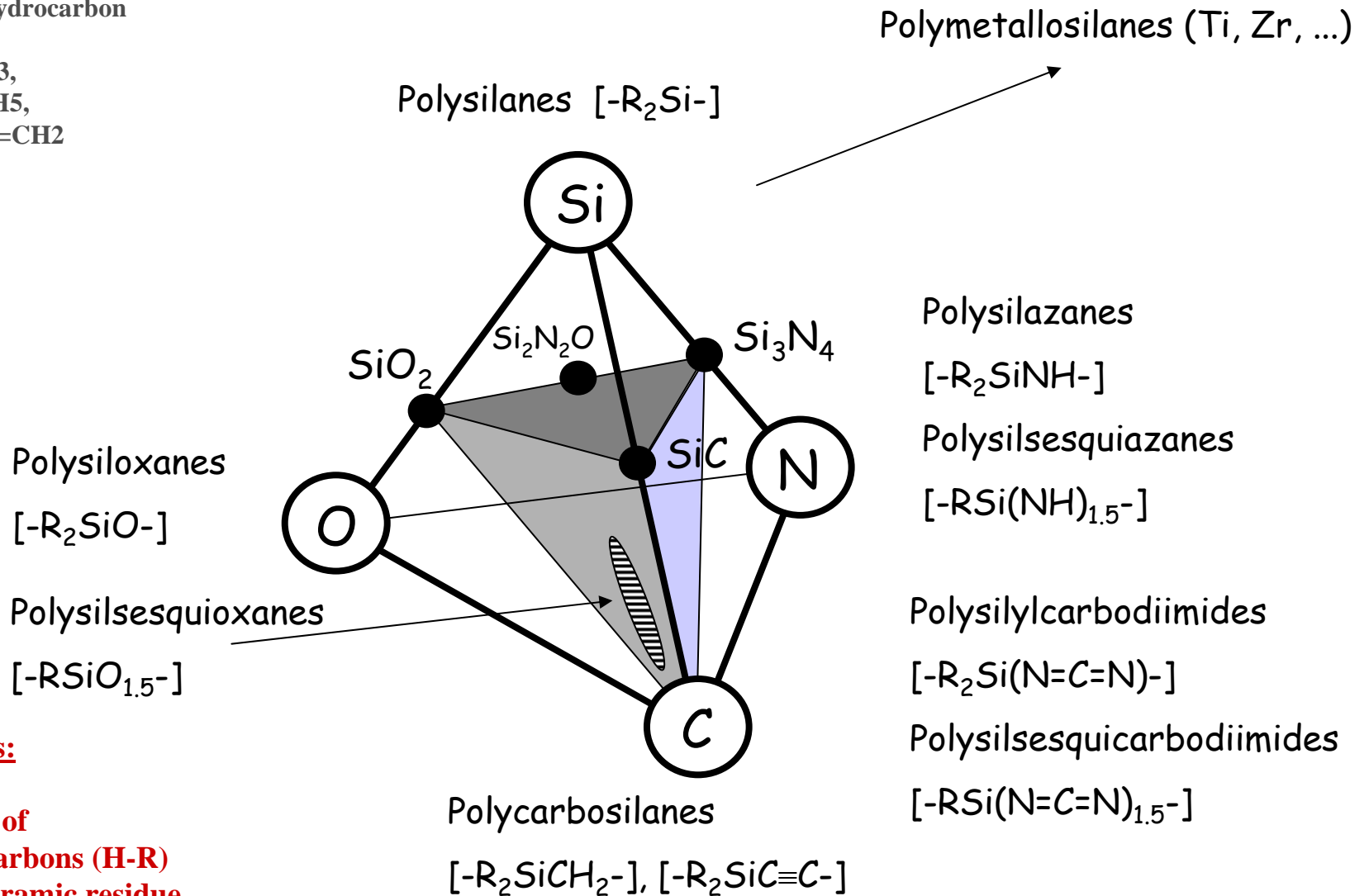
III. Conclusions and planned research

Pioneering work by Prof. Yajima in the 70s which led to the development of Nicalon SiC fibers

SILICON BASED PRECURSORS FOR CERAMICS

R:
hydrogen
or hydrocarbon

-CH₃,
-C₆H₅,
-CH=CH₂
-



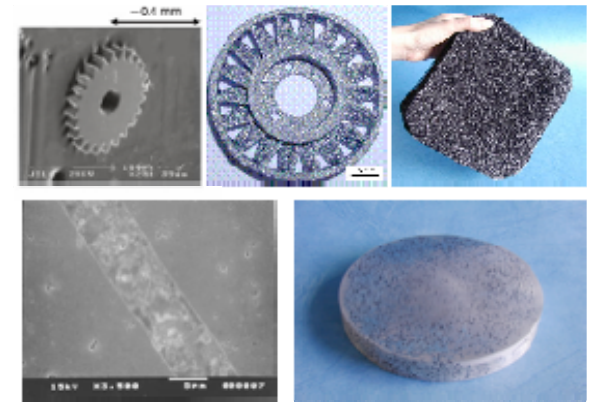
Pyrolysis:

- release of hydrocarbons (H-R)
- solid ceramic residue

POLYMER DERIVED CERAMICS

- **Advantages over traditional methods:**

- Liquid form with low crosslinking temperature
 - use polymer processing techniques
 - Dip or spin coating, spraying, painting
 - Injection molding, pressure curing, etc.
- Relatively low pyrolysis temperatures
- High purity reactants
- Will combine with reactive atmospheres
- Tailorable composition, microstructure and properties
- Unusual nanostructures: amorphous and nano-domains



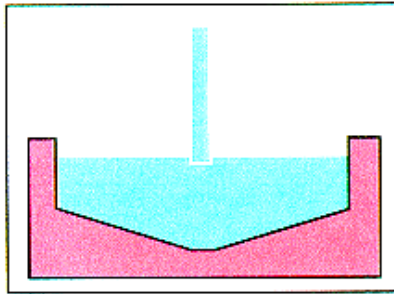
- **Limitations**

- Shrinkage of polymer upon pyrolysis can be up to 50%
- Pore formation on pyrolysis
- Defects and cracks in coatings

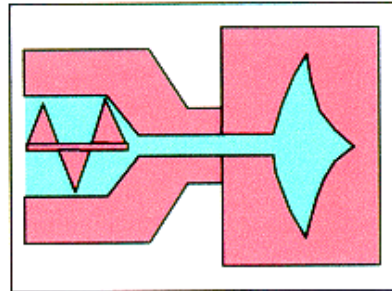
1. MEMS
2. Near net shape part
3. Porous ceramics (foams & filters)
4. Ceramic joint
5. PDC reinforced metals

PLASTIC SHAPING WITH PRECERAMIC POLYMERS

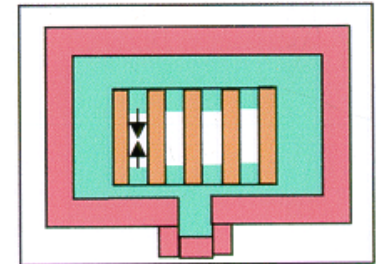
Casting



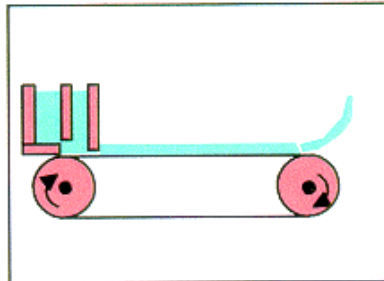
Injection Molding



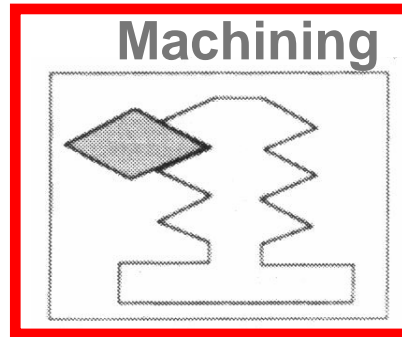
Impregnation



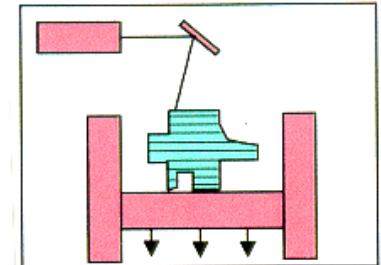
Tape Casting



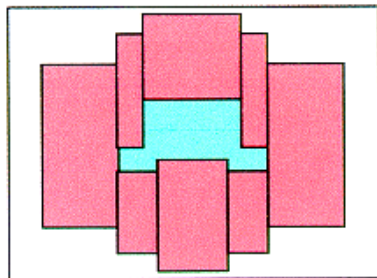
Machining



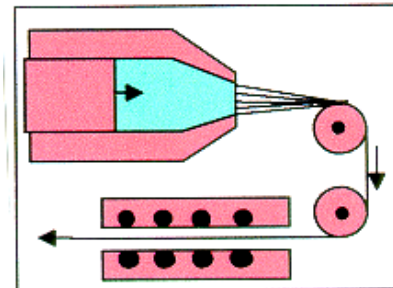
Rapid Prototyping



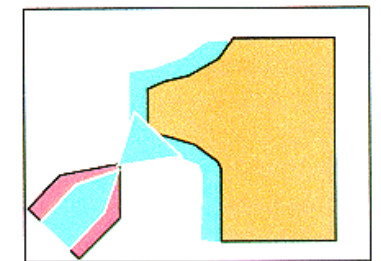
Pressing



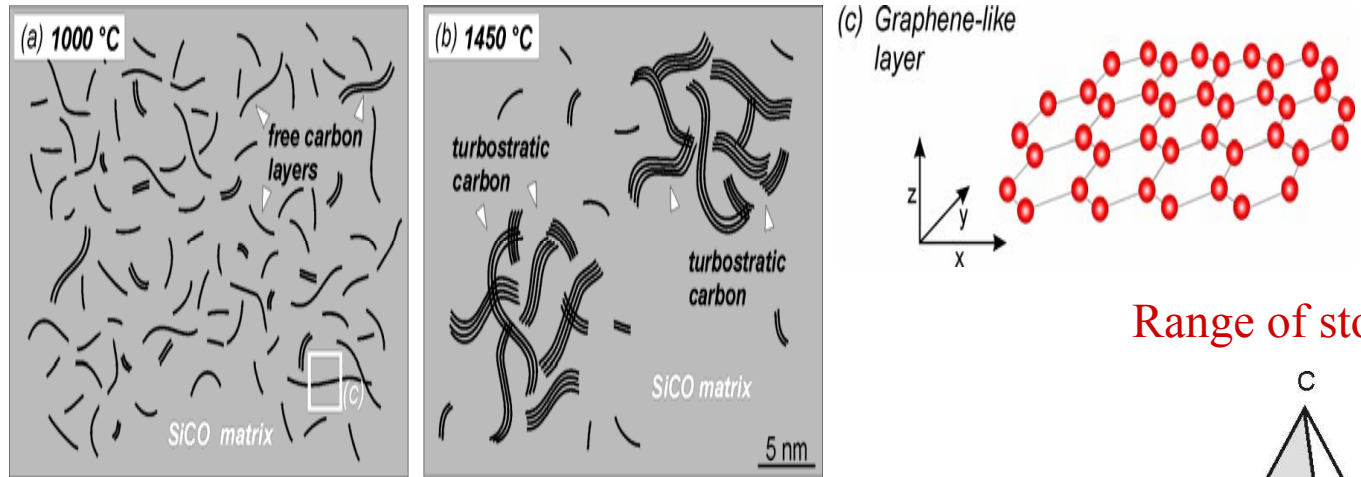
Fiber Drawing



Coating



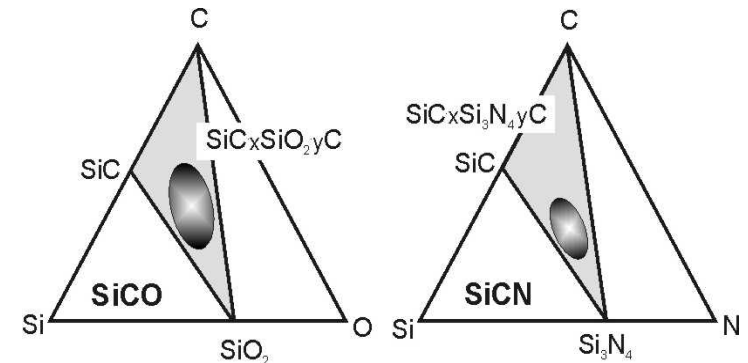
UNIQUE NANOSTRUCTURES



From Yigal Blum (SRI)

- ❖ Evolution of free carbon in polymer derived ceramics
- ❖ Free carbon clusters in single graphene-like sheets (Raman Spectroscopy)
- ❖ Volume fraction of graphene can be controlled

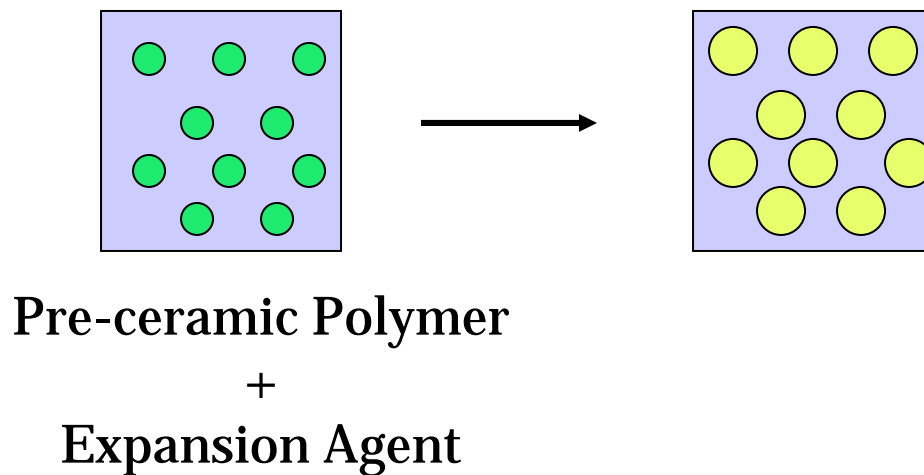
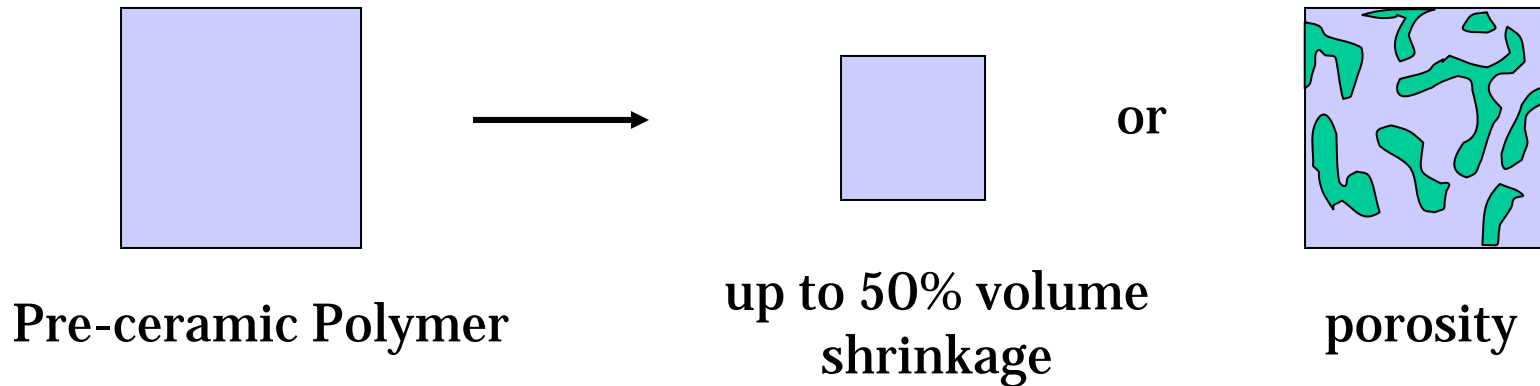
Range of stoichiometries possible



Structure between polymer and ceramic: Need different characterization techniques (IR spectroscopy, Raman spectroscopy, small angle X-ray scattering etc.)

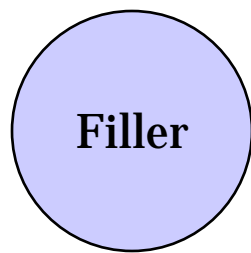
ACTIVE FILLER CONTROLLED PYROLYSIS

(Griel, Erlangen)



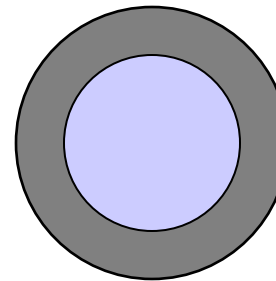
Agent reacts with atmosphere/decomposition products to form a new phase that expands, compensating for shrinkage of polymer

CONVERSION OF EXPANSION AGENT

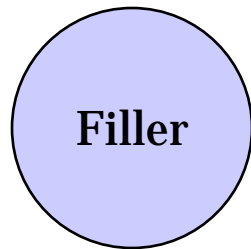


React with matrix or
pyrolysis byproduct

$$\frac{\Delta V}{V_0} \approx 0$$

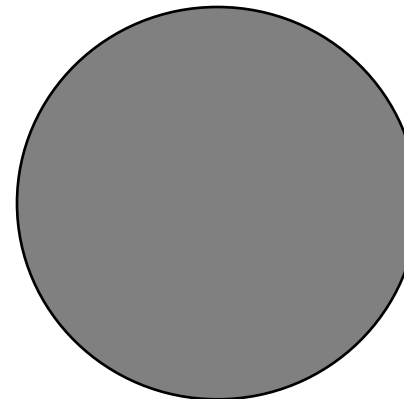


Incomplete
reaction of
expansion agent



React with
reactive gas

$$\frac{\Delta V}{V_0} > 0$$



Complete
conversion

- Preferred reaction is with gas
 - higher volume change
 - faster kinetics

$\frac{\Delta V}{V_0}$ - Specific volume change of filler

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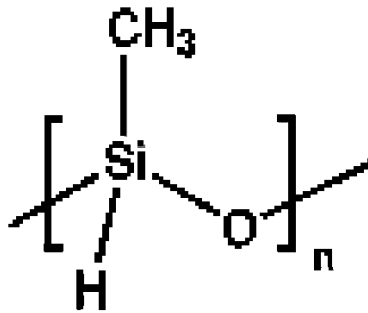
SELECTION OF THE POLYMER

Criteria for selection of a pre-ceramic polymer:

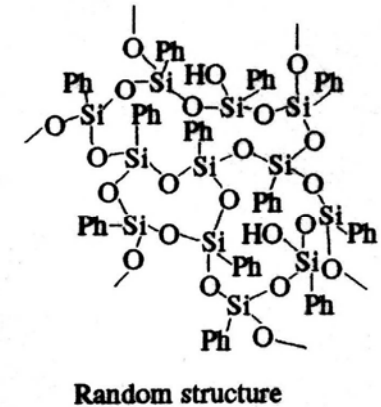
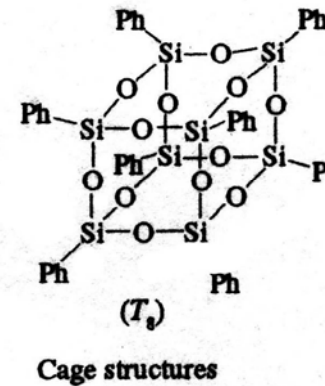
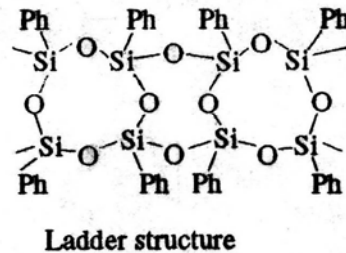
- High ceramic yield on pyrolysis
- Relatively low pyrolysis temperature (limited by metallic substrates)
- Polymer must be soluble or liquid
- Phase formed upon pyrolysis- will depend on ability to react with atmosphere
- Pyrolysis byproducts (their composition and morphology)

POLYMERS INVESTIGATED (Oxycarbides)

Hydromethylsiloxane



Phenylsilsesquioxane

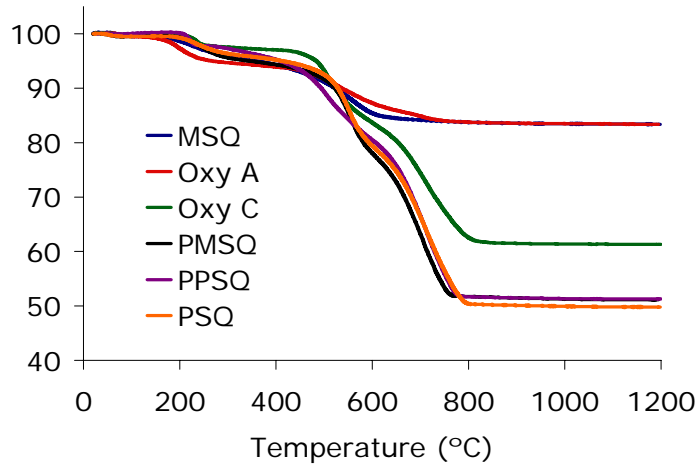


Polymers Studied:

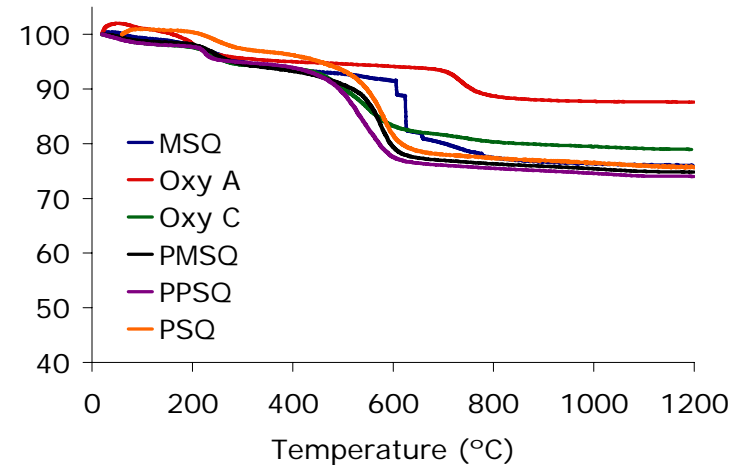
- Methylsilsesquioxane (MSQ)
- Phenylsilsesquioxane (PSQ)
- Phenylmethylsilsesquioxane (PMSQ)
- Phenylpropylsilsesquioxane (PPSQ)
- Oxycarbide A (OxyA) (Starfire Corp.)
- Oxycarbide C (OxyC) (Starfire Corp.)
- Poly(hydromethylsiloxane) (PHMS)

POLYMER TO CERAMIC CONVERSION (oxycarbides)

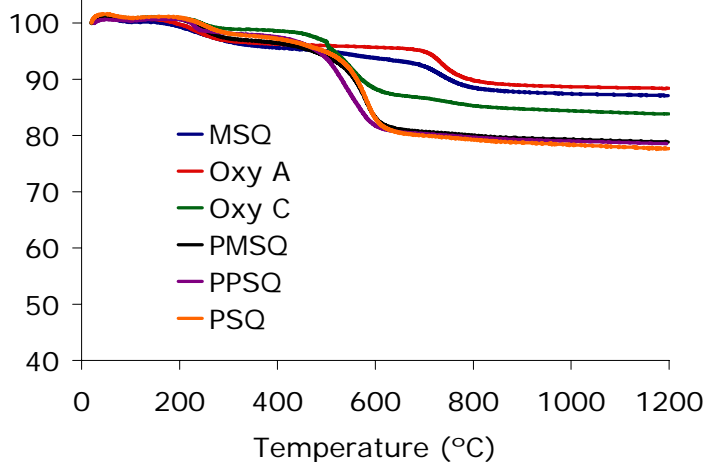
TGA of Polymers in **Air**



TGA of Polymers in **Helium**



TGA of Polymers in **Nitrogen**



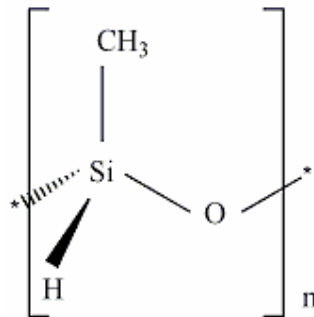
Ceramic Yield:

$$\alpha^P = \frac{\text{mass}_{\text{pyrolyzed ceramic}}}{\text{mass}_{\text{polymer precursor}}}$$

SELECTED POLYMER

Poly(hydromethylsiloxane) (PHMS)

- High ceramic yield: >85%
- Complete conversion to ceramic at temperatures < 800 °C
- Liquid form: viscosity ~1.0 cP, ideal for coating processing
- Stable under ambient conditions
- Rapid crosslinking: @150 °C in humid air
- Inexpensive



Hydrolysis-Condensation-Pyrolysis



Hydrolysis:

- Hydrogen is replaced by -OH group in presence of water and Ru catalyst at 150°C

Condensation:

- -OH groups combine to complete Si-O-Si bond giving off water

Pyrolysis:

- Carbon groups are removed as temperature increases to form a 3-D amorphous random network consisting of Si-O bonds and <5% of residual carbon bonded to Si. Reaction is completed by 650°C.

SELECTION OF EXPANSION AGENT: DETERMINATION OF VOLUME CHANGE

The volume change of the expansion agent upon reaction is given by the equation:

$$\frac{\Delta V}{V_o} = \alpha^{EA} \beta^{EA} - 1$$

Where:

$$\alpha^{EA} = \frac{\text{mass of reaction product}}{\text{mass of expansion agent}}$$

$$\beta^{EA} = \frac{\text{density of expansion agent}}{\text{density of reaction product}}$$

$$\alpha^{EA} \beta^{EA} = 1 \rightarrow \text{no reaction (inert agent)}$$

$$\alpha^{EA} \beta^{EA} > 1 \rightarrow \text{volume expansion due to reaction}$$

SELECTED EXPANSION AGENTS

- Binary metal alloys and intermetallics
- Need $\alpha^{EA} \beta^{EA} > 1$ on oxidation
- Selected expansion agents are:

	APS (μm)*	Oxide	$\frac{\alpha^{EA} \beta^{EA}}{A}$	Theo. WG (%)**	Expe. WG (%) (before/after)	Oxidation Temp. (C)	Atm.
TiSi ₂	~0.3	TiO ₂ + 2SiO ₂	2.58	92.3	~36/~56	800	Air
CrSi ₂	~100/0.8	0.5Cr ₂ O ₃ + 2SiO ₂	2.82	81.3	~2/~52	1000	O ₂
ZrSi ₂	0.9±0.1	ZrO ₂ + 2SiO ₂	2.26	65.1	~50	1000	O ₂
TiAl ₃	~44/0.8	1.5Al ₂ O ₃ + TiO ₂	1.52	80.7	~14/~57	900	Air
TiAl	~44/0.8	0.5Al ₂ O ₃ + TiO ₂	1.62	74.8	~62	900	O ₂
Ti ₃ Al	< 10	0.5Al ₂ O ₃ + 3TiO ₂	1.69	70.3	~75	900	Air

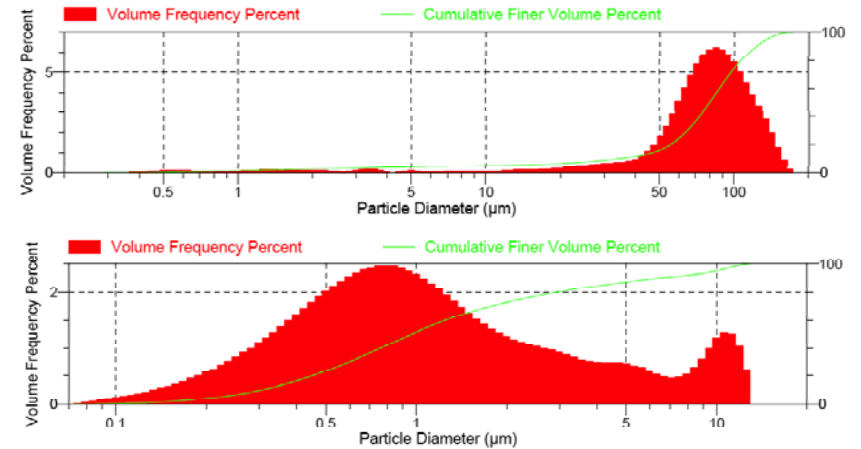
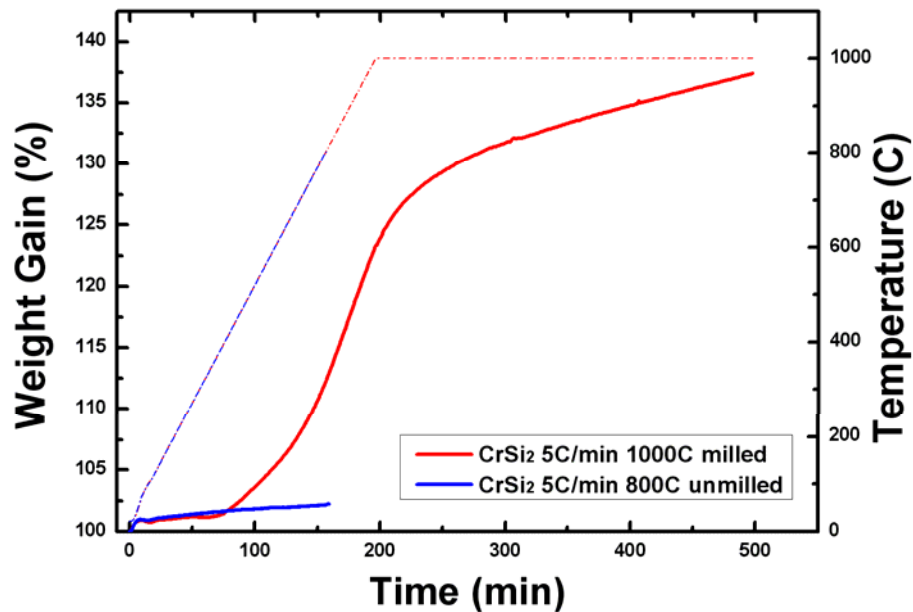
*Average Particle Size in micrometer; **Weight Gain in percentage, "before/after" refers to as received and attrition milled powders

Additional Inert fillers:

SiC, Al₂O₃, SiO₂, Cr₂O₃ nanoparticles (APS ~50 nm)

EXPANSION AGENTS: DISILICIDES

- Thermogravimetric analysis: study on the oxidation kinetics of fillers
- Example: CrSi_2
- Conditions: 1C/min or 5C/min, 800~1000C, air/oxygen atmosphere

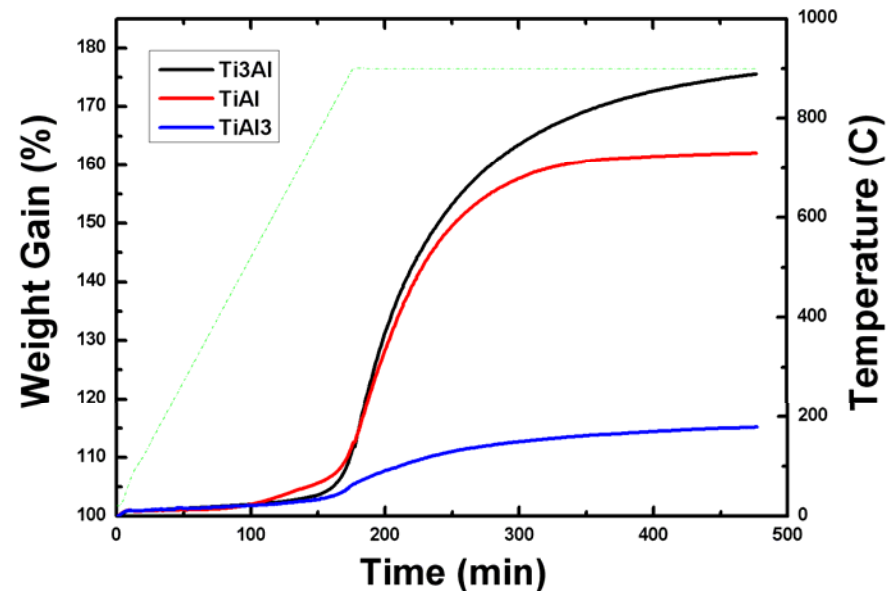


article size distribution of CrSi_2 before and after milling, showing 80 μm and 0.8 μm size in diameter

Attrition milling significantly enhances conversion kinetics due to reduction in particle size and removal of oxide surface layer

EXPANSION AGENTS: ALUMINIDES

- Thermogravimetric analysis: study on the oxidation kinetics of fillers
- Ti-Al alloy with atomic ratio: 1:1, 1:3, 3:1
- Conditions: 1C/min or 5C/min, 900C, air atmosphere



Comparison of three aluminides @5C/min and in air

Ti-Al becomes more oxidation resistant when Al content increases
@ ~70 at.%, continuous layer of passivating Al_2O_3 can form

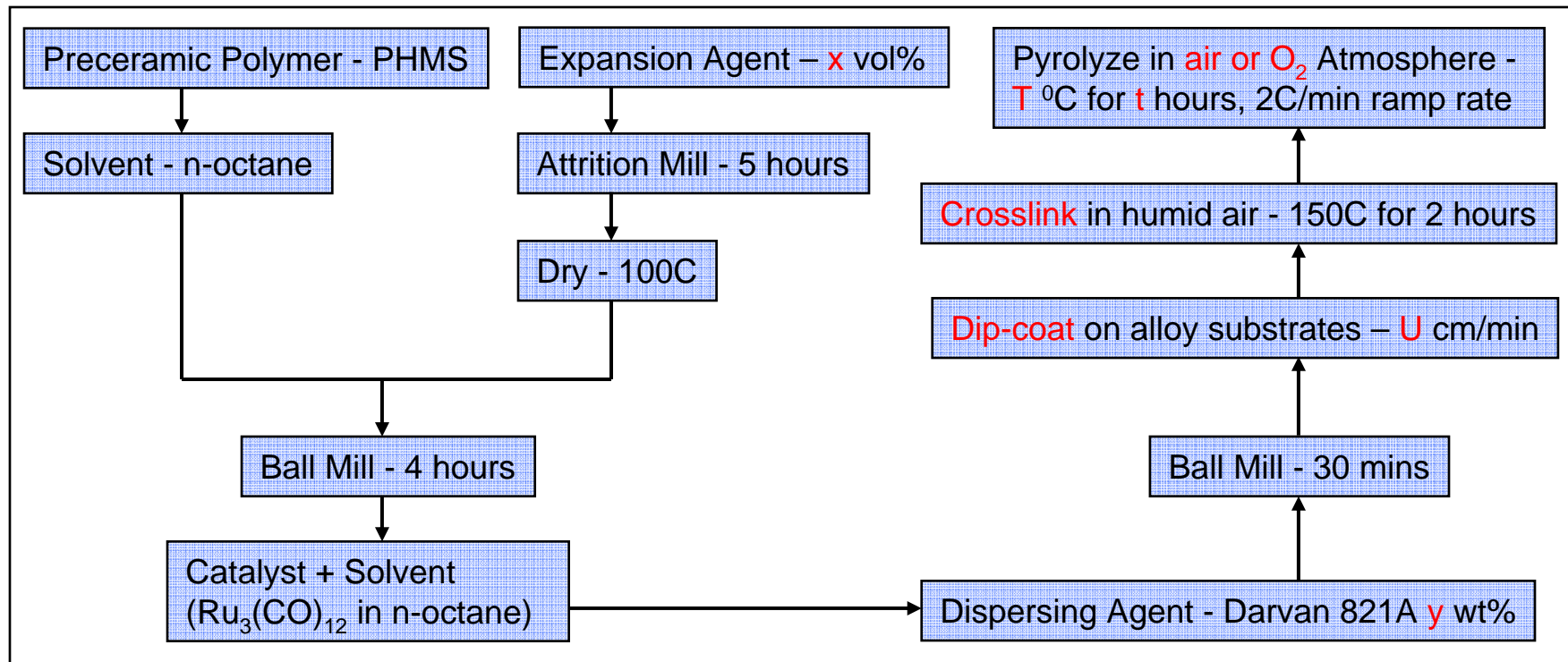
SELECTED SUBSTRATES

Substrates (alloys):

- [Fe-based] Super 304 H: austenitic stainless steel
 - Superheater and reheater tubing
 - Fireside corrosion, oxidation resistance; creep strength
- [Ni-based] Inconel 617: advanced nickel alloy
 - Coal-fired boiler tubing
 - High Cr content enables to serve in highly corrosive environment over 650C

	C	Cr	Ni	Mn	Si	Mo	Fe	Other 1	Other 2
Super 304H	0.10	18-20	8-10.5	2.0	0.75	-	Bal.	S-0.03	N-0.1
Inconel 617	0.08	21.6	53.6	0.1	0.1	9.5	0.9	Co-12.5	Al-1.2

PROCESSING OF COATINGS



Flow chart of the processing procedure of ceramic matrix coatings

CRITICAL COATING THICKNESS

From analytical models, based on stresses generated due to constrained pyrolysis, we have determined a critical coating thickness, t_c , such that

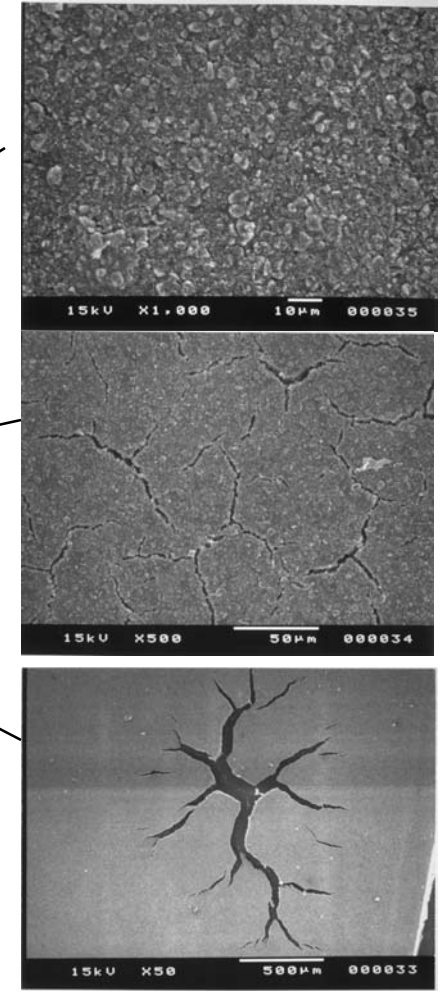
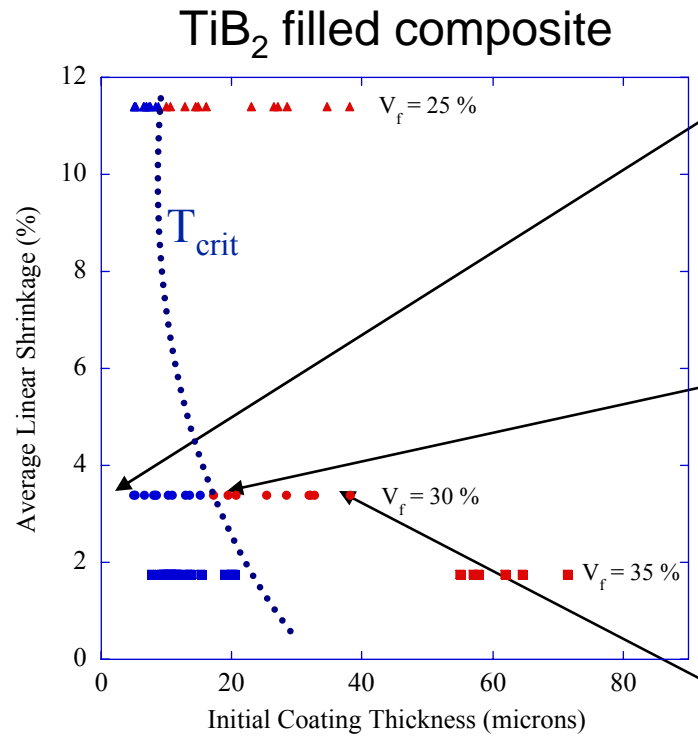
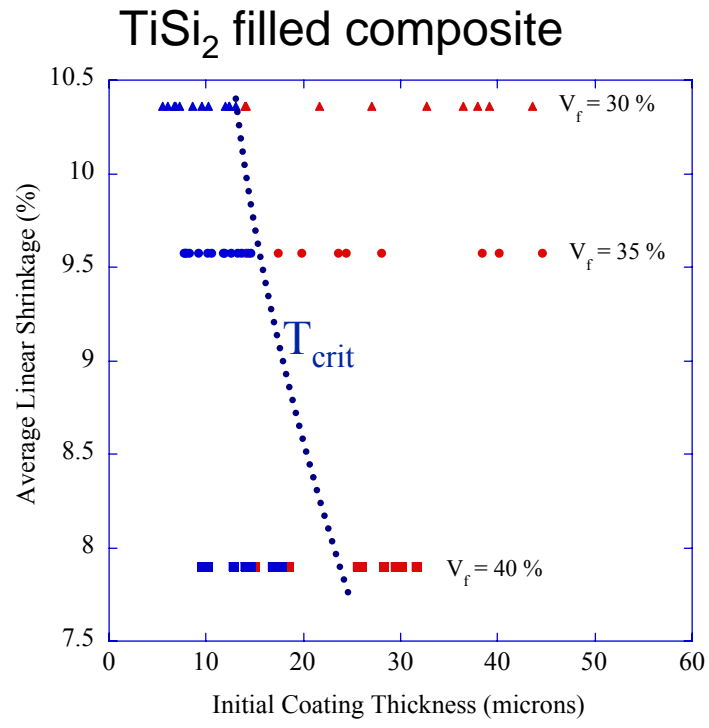
if $t < t_c \rightarrow$ no cracking of film

t_c depends on shrinkage rate

In these composite systems

- Shrinkage rate controlled by filler volume fraction (V_f)
- Expect that as $t \uparrow$ get cracking (at a specific V_f)
- Expect that $t_c \uparrow$ as filler $V_f \uparrow$ (because shrinkage rate \downarrow)

CRITICAL COATING THICKNESS



In these composite coatings $\rightarrow t < t_c \rightarrow$ no cracking of film

- shrinkage rate controlled by filler volume fraction (V_f)
- as $t \uparrow$ get cracking (at a specific V_f)

- *A critical coating thickness exists below which defect free coatings are obtainable
- Initial filler volume fraction controls critical coating thickness

REQUIRED VOLUME FRACTION OF EXPANSION AGENT FOR ZERO SHRINKAGE

Knowing the shrinkage of the polymer and the volume expansion of the filler, the required volume fraction for zero shrinkage of the composite can be calculated

$$V_T = V_T^* \left[\left\{ 1 - \frac{V_T^*}{\varepsilon^P} \left[1 - (\alpha^{EA} \beta^{EA}) \right]^{\frac{1}{3}} \right\}^{-1} \right]$$

V_T^* : critical loading volume fraction
 ε^P : linear shrinkage of the polymer

Filler	Filler Density	Filler Mass	Oxides/Products	Oxide Density	Oxide Mass	$\frac{EA}{EA}$	Volume Fraction	VF Used
TiSi ₂	4.02	104.04	TiO ₂ +2SiO ₂	3.00	200.04	2.577	0.2768	0.30
CrSi ₂	4.91	108.17	0.5Cr ₂ O ₃ +2SiO ₂	3.16	196.17	2.819	0.2636	
ZrSi ₂	4.88	147.40	ZrO ₂ +2SiO ₂	3.56	243.40	2.264	0.2975	
TiAl ₃	3.4	128.81	TiO ₂ +1.5Al ₂ O ₃	4.05	232.81	1.518	0.3775	0.40
TiAl	3.8	74.85	TiO ₂ +0.5Al ₂ O ₃	4.10	130.85	1.620	0.3625	
Ti ₃ Al	4.1	170.58	3TiO ₂ +0.5Al ₂ O ₃	4.14	290.58	1.687	0.3536	

In reality, more filler may be required than predicted, mainly due to incomplete oxidation

CONTROL OF COATING THICKNESS (h)

- Dip-coating: Landau-Levich equation for Newtonian fluids
- Nature of slurries: **non-Newtonian** fluid with **shear-thinning** behavior
- Theoretical basis for controlling the green state coating thickness (h_0) which determines the fired coating thickness (h)

- For our processing window:

$$h_0 = 0.944 \left(\frac{\mu U}{\sigma} \right)^{\frac{1}{6}} \left(\frac{\mu U}{\rho g} \right)^{\frac{1}{2}}$$

h_0 : film thickness
 μ : **apparent viscosity**
 U : withdrawal speed
 σ : surface tension
 ρ : dip-coating slurry density
 g : gravity

- **Optimize viscosity, surface tension and withdrawal speed to get desired thickness**
- Optimized parameters for the processing of TiSi₂-filled coatings:

	Density of the Slurry (g/cc)	Volume Ratio*	Viscosity (cP)	Withdrawal Speed (cm/min)	Film Thickness (μm)
TiSi ₂	1.38±0.02	3:5	15.4	50	~18

* Volume Ratio--(filler powder + PHMS) : n-octane

SHEAR THINNING: APPARENT VISCOSITY

$$(\mu_{app})$$

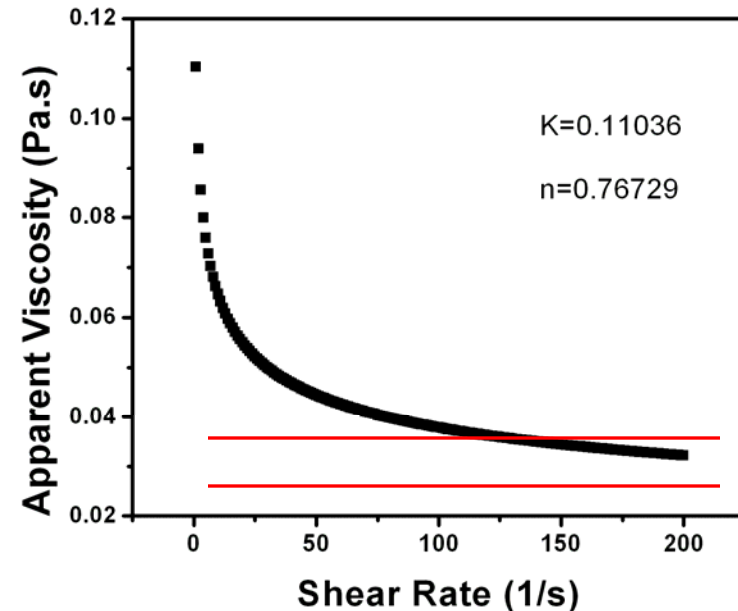
$$\mu_{app} = K \cdot \dot{\gamma}^{n-1}$$

$$h_0 = 0.944 \left(\frac{\mu U}{\sigma} \right)^{\frac{1}{6}} \left(\frac{\mu U}{\rho g} \right)^{\frac{1}{2}}$$

- Withdrawal speed, U , range: 30-100 cm/min
- Correlation between U and shear rate, $\dot{\gamma}$.

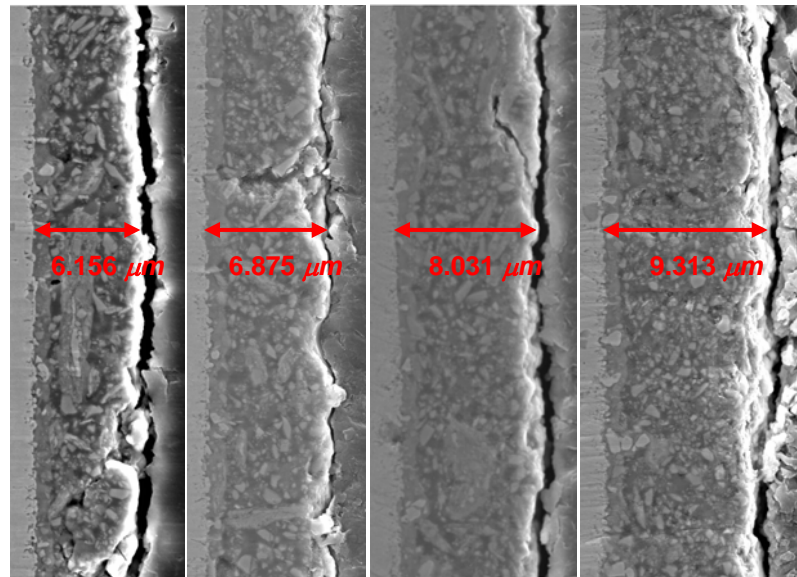
$$\dot{\gamma} = \frac{\partial v_x}{\partial y} = \frac{U - 0}{m \cdot h_0} = \frac{U}{m \cdot h_0}$$

- Assume $h_0 = 20E-6$ m; $1 \leq m \leq 3$
- When $m = 2$,
 $125 \leq \dot{\gamma} \leq 417 \text{ s}^{-1}$, $25 \leq \mu \leq 35 \text{ cP}$
- Near-Newtonian behavior
- Therefore, the average value of apparent viscosity, μ for any specific system can be calculated, and this value is valid throughout the withdrawal speed range investigated.



EFFECT OF WITHDRAWAL SPEED ON FINAL COATING THICKNESS

Example: 30 vol% CrSi₂-filled PHMS coating on Inconel 617, pyrolyzed at 800C in air

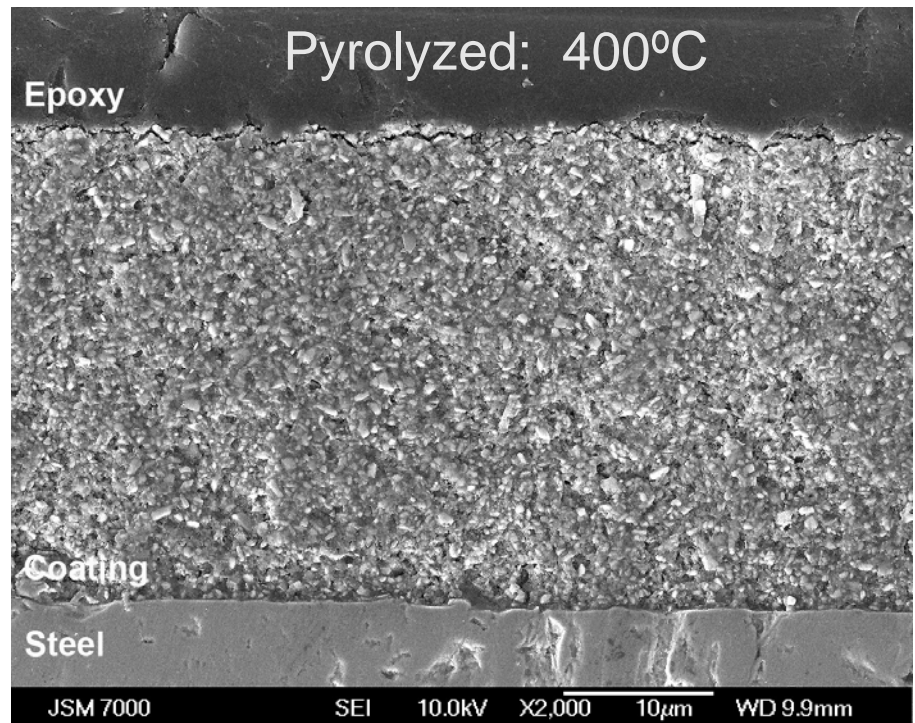
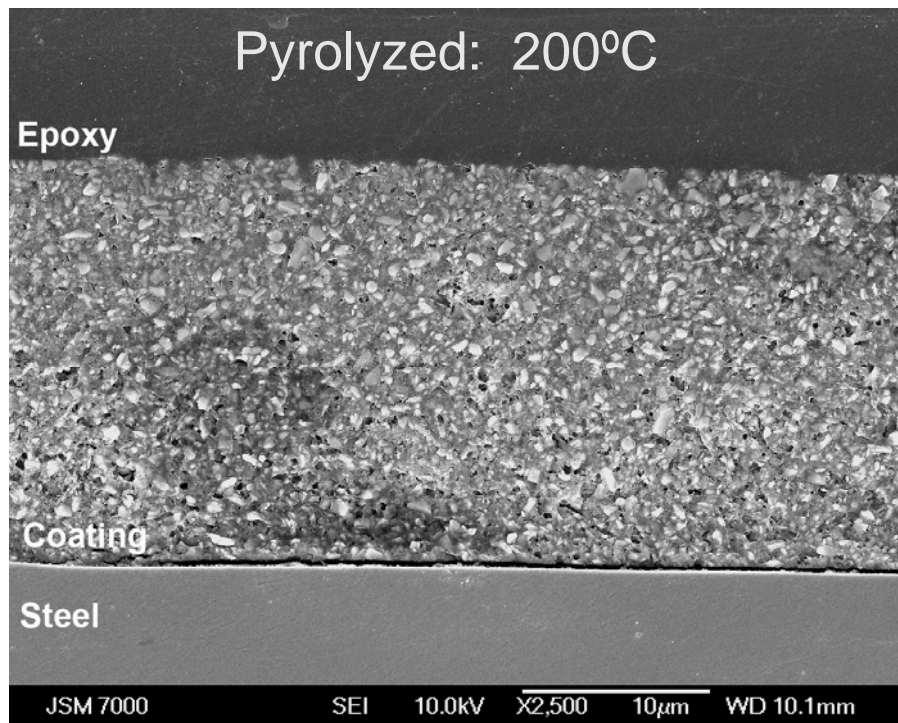


Withdrawal speed: 30, 50, 75, 100 cm/min.

Thickness increases as withdrawal speed increases

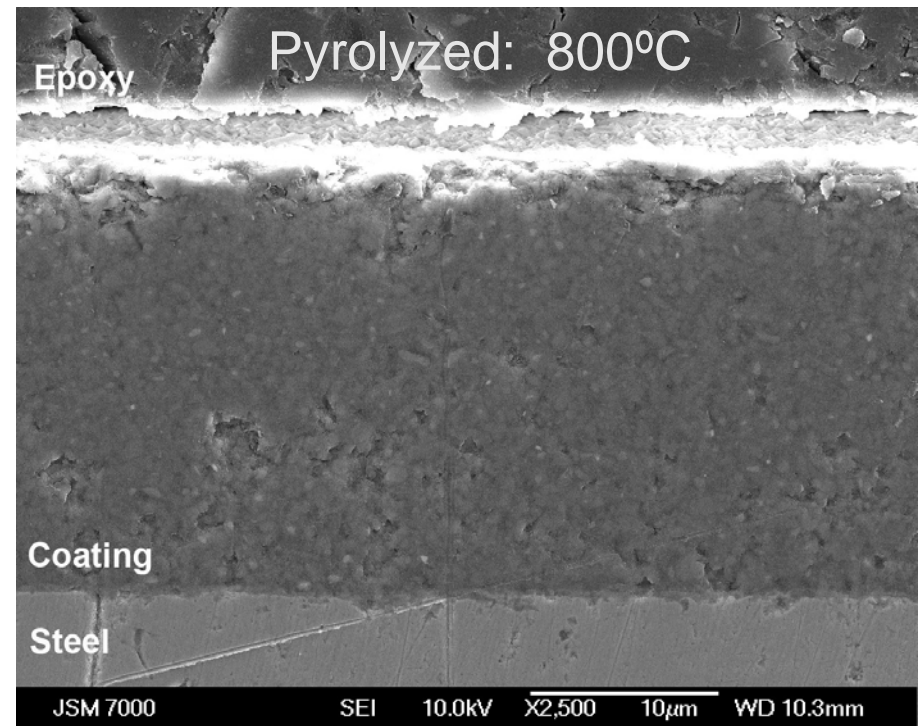
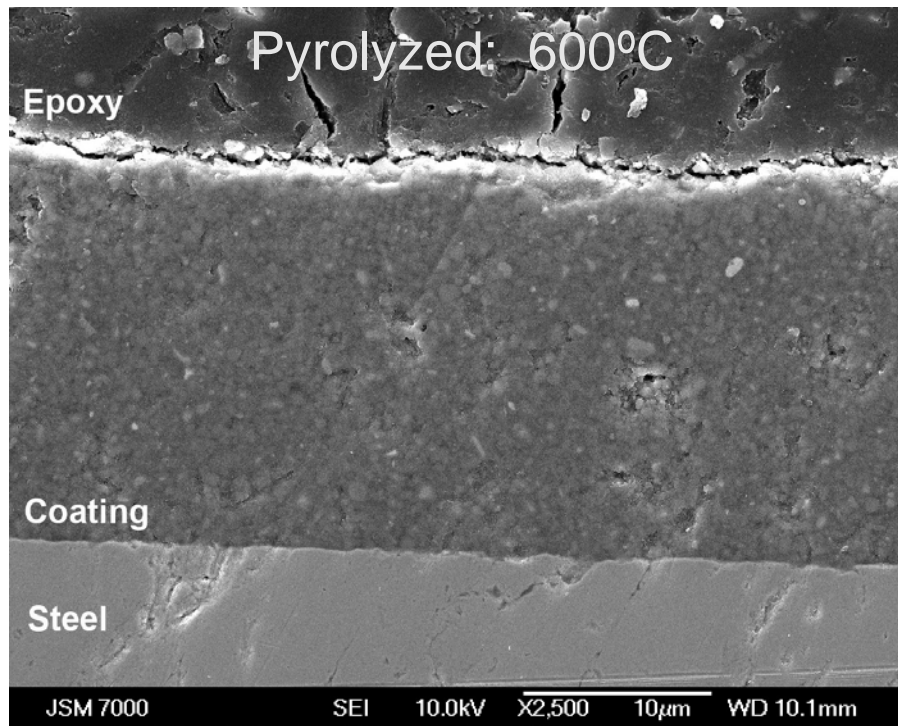
Results will be analyzed using the Landau-Levich model (on-going)

MICROSTRUCTURE EVOLUTION: TiSi₂- FILLED PHMS COATINGS ON STEEL



- Both coatings have **little reaction** of expansion agents
 - 200°C coating has very **poor bonding** to the steel
 - Coatings contain large percentage of **porosity**

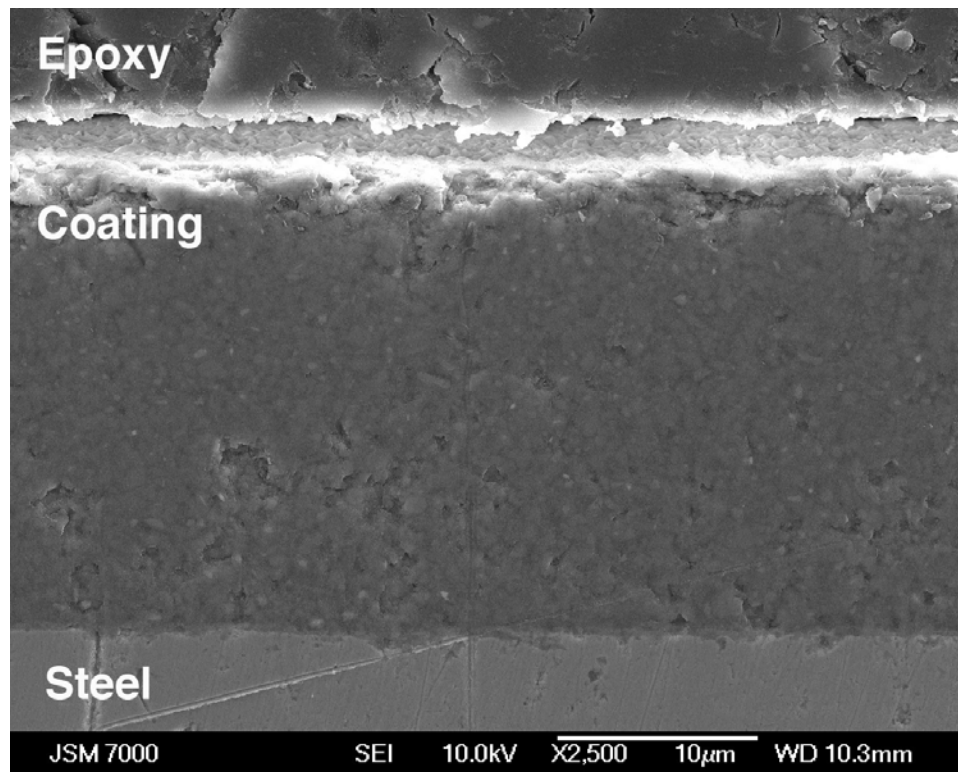
MICROSTRUCTURE EVOLUTION: TiSi_2 - FILLED PHMS COATINGS ON STEEL



- 600°C coating has partial conversion of filler
- 800°C coating has good bonding and full conversion of filler
- Both coatings exhibit reduced porosity

TiSi₂-FILLED PHMS COATINGS ON STEEL

Submicron Filler- 30 vol%



Approx. Composition by wt: 40% Si,
25% Ti, <5% C, balance O

Achieved a uniform thickness
of 25-30 μm

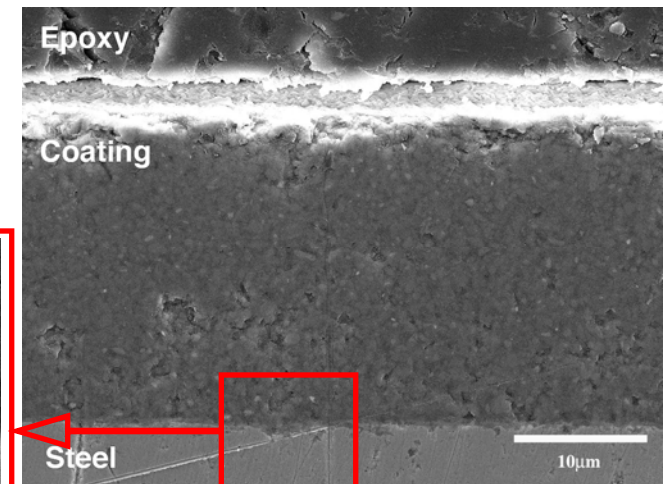
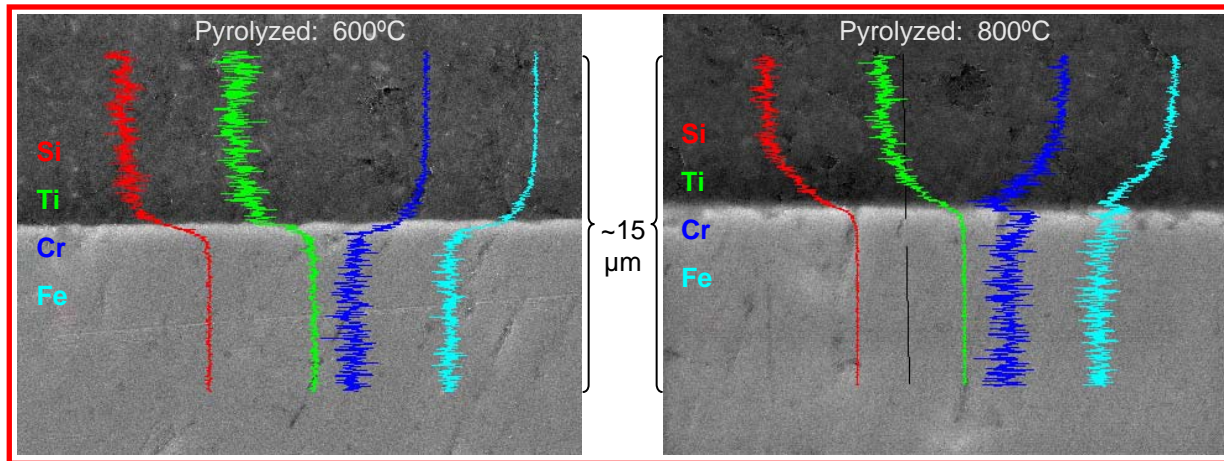
Full conversion of nanoscale
expansion agent

Coating still contains some
porosity

Good bonding seen between
coatings and substrate

INTERFACIAL CHEMISTRY: TiSi_2 -FILLED PHMS COATINGS ON STEEL

- Example: 30 vol% TiSi_2 -filled PHMS coating on steel, pyrolyzed at 800C in air
- Results show:
 - Uniform thickness, very limited porosity
 - Full conversion of the expansion agent
 - Good bonding between coating layer and the substrate

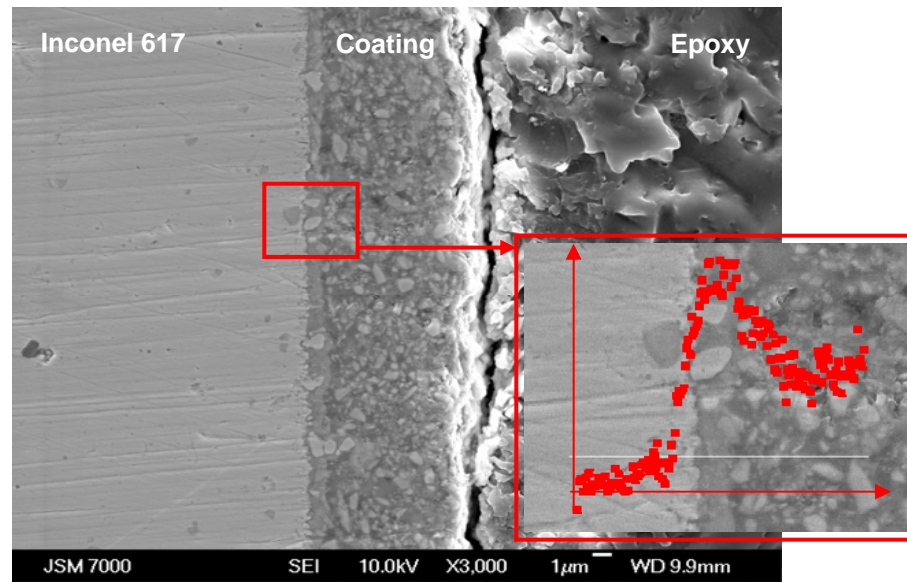


30 vol% TiSi_2 + PHMS, @ 800C in air

EDS analysis at the pyrolyzed interface: abrupt interface (600C), diffusion layer with good bonding (800C)

INTERFACIAL CHEMISTRY: CrSi₂-FILLED PHMS COATINGS ON INCONEL 617

30 vol% CrSi₂-filled PHMS coating on Inconel 617, pyrolyzed at 800C in air



EDS: Oxygen higher in the interfacial region ($\sim 1.5\mu\text{m}$)

In-situ formation of thermally grown bond coat

SUMMARY AND PLANNED RESEARCH

Processing of Nanoscale Reinforced Polymer Derived Composite Ceramics

- Polymer, six active fillers of appropriate particle size and two substrates have been selected
- Thermodynamics and kinetics of phase evolution and reactions has been completed
- Control of shrinkage during polymer to ceramic conversion by controlling the volume fraction and conversion of the fillers
- Mechanistic understanding of the evolution of the phases and microstructure is being developed

Understanding and Optimization of the Coating Process

- Dispersion of nanoscale fillers in the polymer has been accomplished
- Control of slurry rheology and its effect on coatings has been investigated
- Mechanics of constrained pyrolysis of the coating has been analyzed (critical coating thickness)
- Optimized processing strategies for crack free coatings have been developed for the silicide filled systems

Ongoing and Planned Research

- Optimization of the processing for aluminide filled systems
- Mechanical properties of the coating and the interface
- Thermomechanical performance under thermal cycling
- Performance under selected corrosion conditions

POLYMER DERIVED CERAMICS

Processing with polymer derived ceramics offers a great variety of:

- Shaping possibilities
- Novel routes of ceramic processing
- Potential process improvements (e.g. temperature decrease!)
- Specific solutions to desired properties
- Unique nanostructures (between polymer and ceramic)

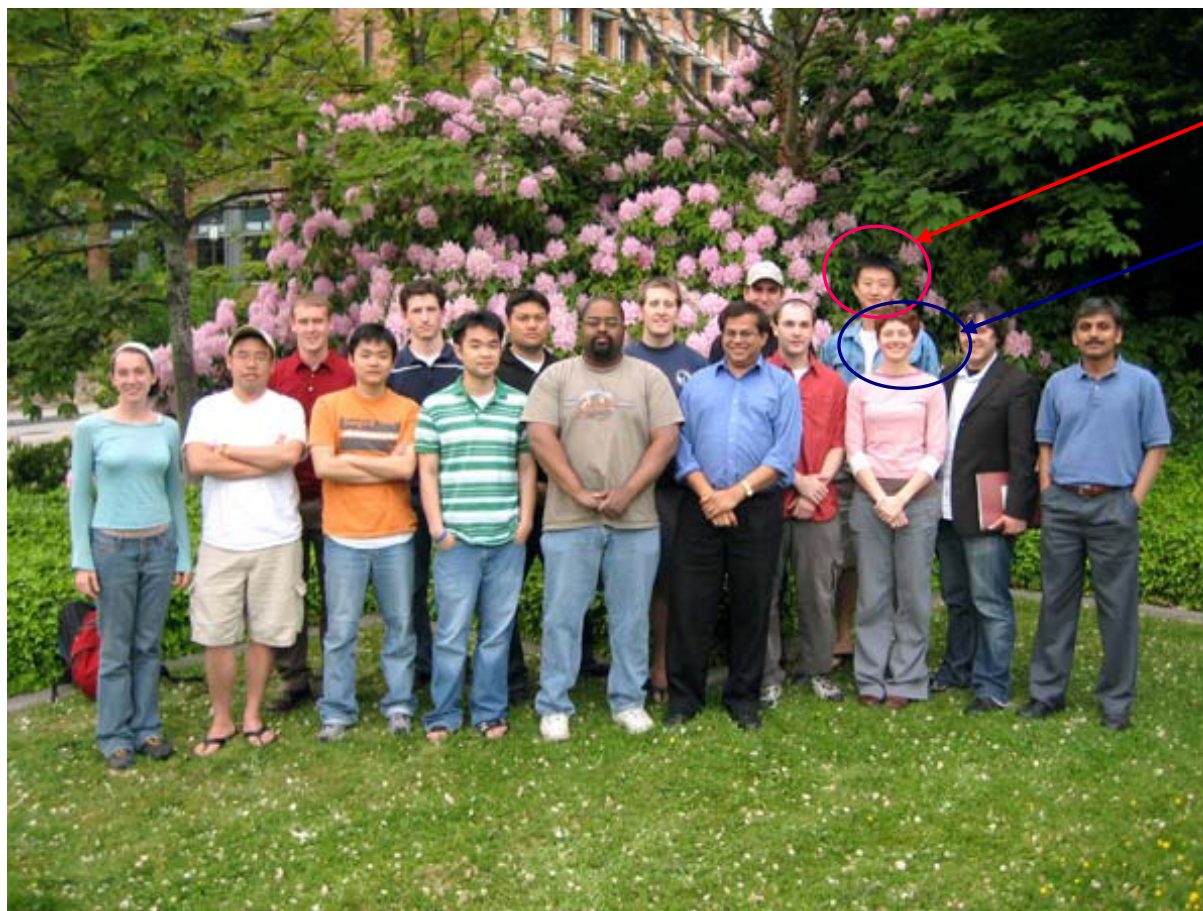
Inexhaustible R&D playground specially for chemists and material scientists and engineers !!!



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Kaishi Wang

Jessica Torrey

Thank you