Nanoscale Reinforced, Polymer Derived Ceramic Matrix Coatings for Coal-fired Environments

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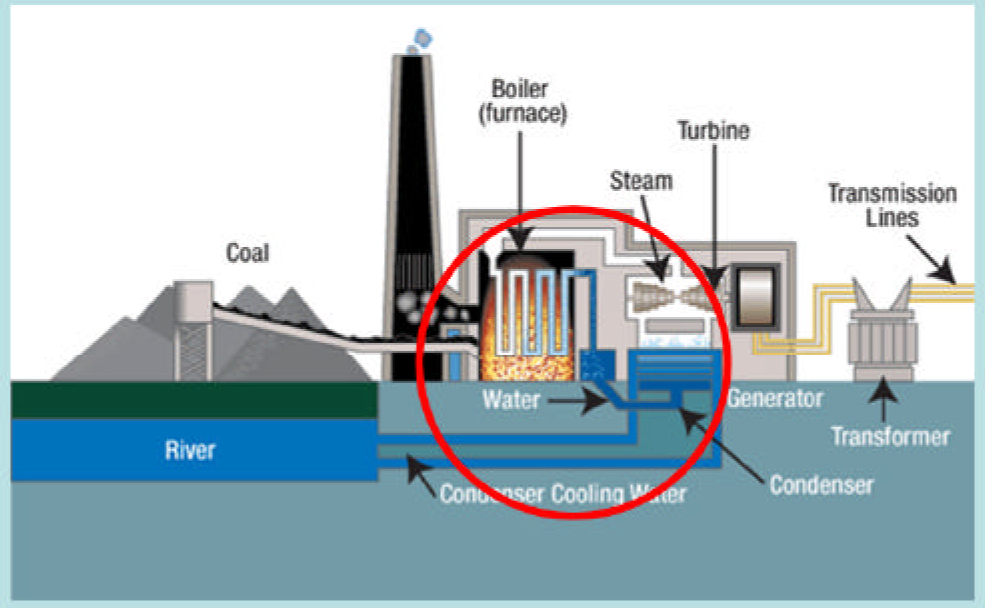
Motivation



Technology trends

- Ultrasupercritical coal fired power plant: higher temperatures (650C) and pressures (34.5 MPa)--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

Introduction

Project goal:

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

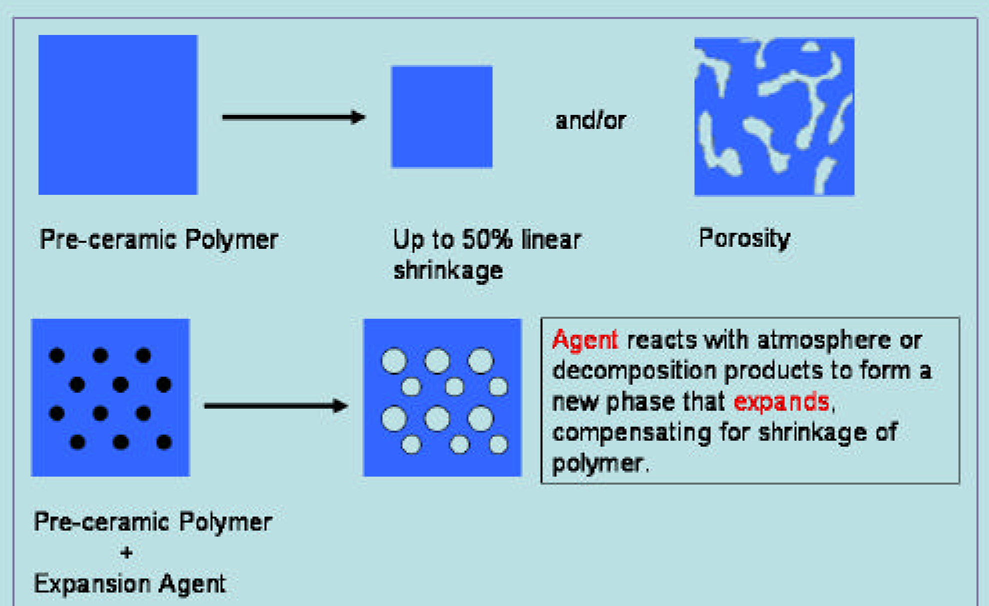
Our approach:

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

Key issues 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 poymer to ceramic conversion
  - 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 therrmal cycling
  - Performance under selected corrosion conditions

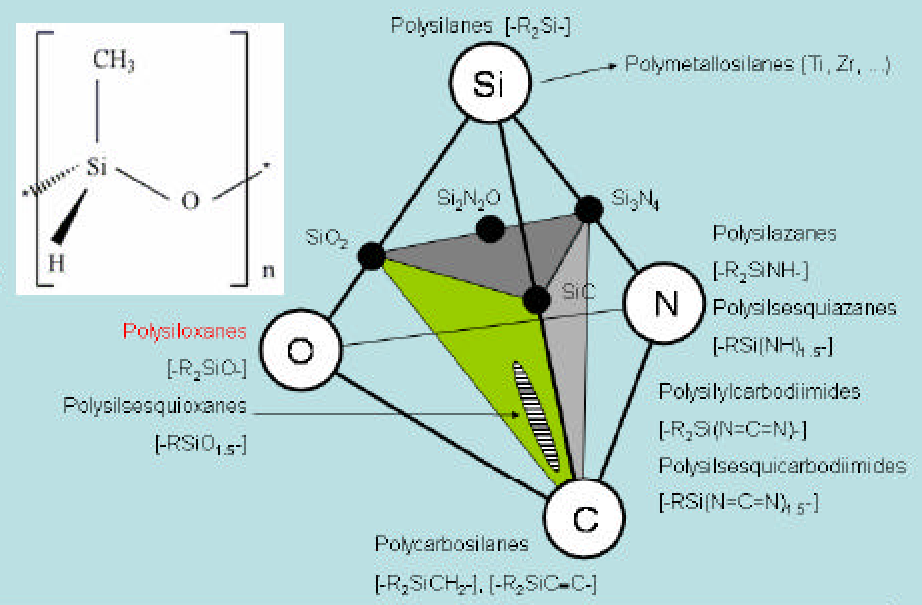
Active Filler Controlled Pyrolysis (AFCOP):



Results

Pre-ceramic polymer:

- Criteria for selection of a preceramic 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)
- Polymer: poly(hydromethylsiloxane) (PHMS)
  - Molecular Formula: (see right)
  - High ceramic yield: >85% when pyrolyzed <800C
  - Liquid form: viscosity ~1.0 cP, ideal for coating processing
  - In-situ crosslinking: @150C in humid air



Expansion agents:

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

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

$\alpha^{EA}\beta^{EA} = 1$	Inert filler
$\alpha^{EA}\beta^{EA} > 1$	Active filler (volume expansion)

Active fillers:

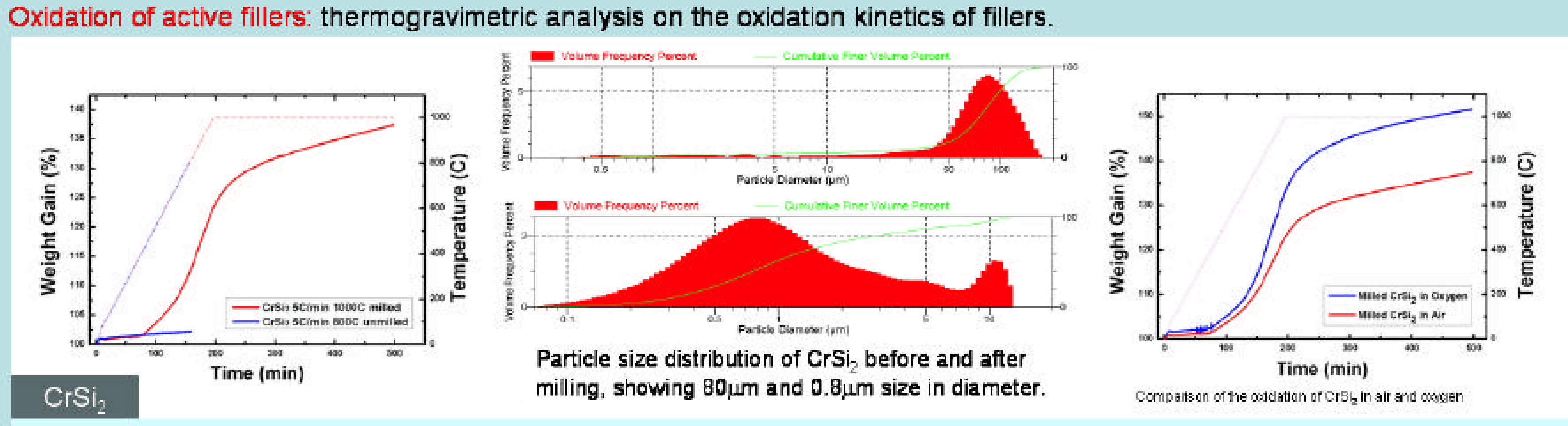
	APS (μm)*		$\alpha^{EA}\beta^{EA}$	Theo. WG (%)**	Expe. WG (%)		Oxidation Temp. (C)	Atm.
	Before	After			Before	After		
$TiSi_2$	--	~0.3	2.58	92.3	~36	~60	800	Air
$CrSi_2$	~100	0.8	2.82	81.3	~2	~52	1000	O_2
$ZrSi_2$	~1	--	2.26	65.1	~50	--	1000	O_2
Ti_3Al	< 10	--	1.69	70.3	~75	--	900	Air
TiAl	~44	0.8	1.62	74.8	--	~62	900	Air
$TiAl_3$	~44	0.8	1.52	80.7	~14	~57	900	O_2

Inert fillers:

SiC, Al_2O_3, SiO_2, Cr_2O_3 nanoparticles (APS ~50 nm)

*Average Particle Size in micron;
**Weight Gain in percentage

Oxidation of active fillers: thermogravimetric analysis on the oxidation kinetics of fillers.

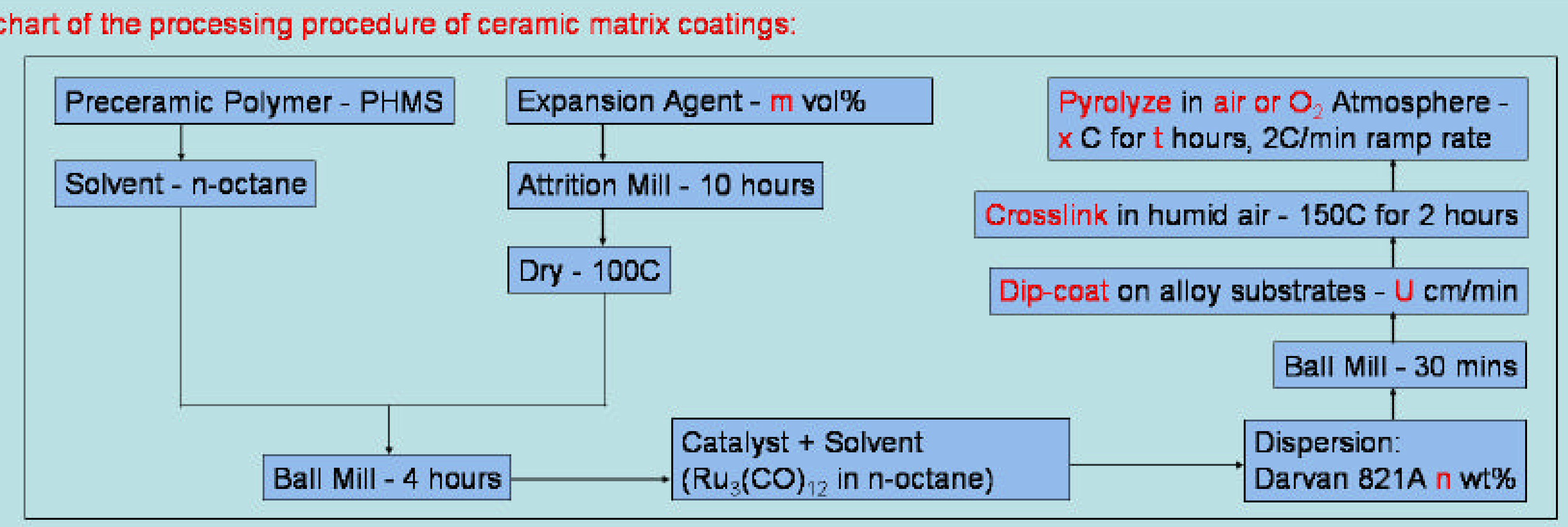


Particle size distribution of $CrSi_2$ before and after milling, showing 80μm and 0.8μm size in diameter.

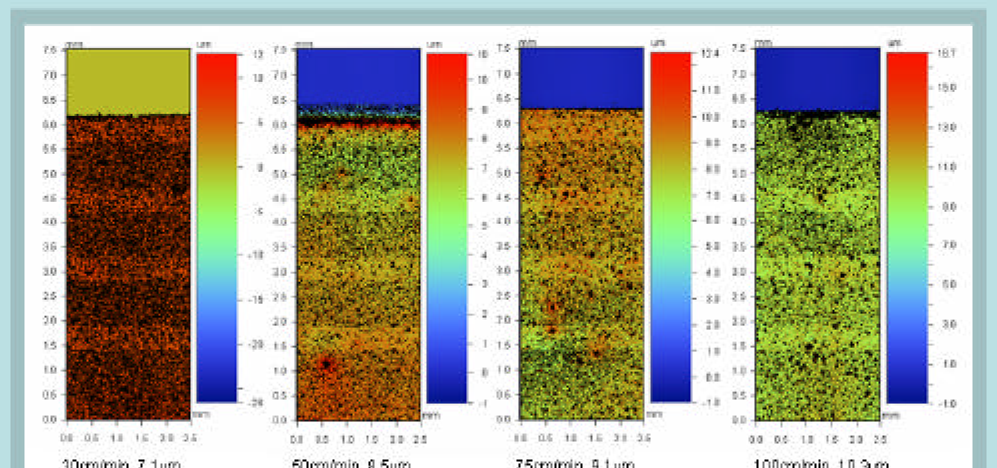
Comparison of the oxidation of $CrSi_2$ in air and oxygen

- Attrition milling significantly enhances conversion kinetics due to reduction in particle size and removal of oxide surface layer.
- Increased oxygen partial pressure can assist filler oxidation to a larger degree under the same condition.

Flow chart of the processing procedure of ceramic matrix coatings:



Film thickness control using Landau-Levich model:



- Laser profiler: 2-D top profile analysis
- 30 vol% $CrSi_2$+PHMS green coating thickness
- Uniform thickness; controlled by withdrawal speed

Landau-Levich model 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.

Results

$ZrSi_2$-filled system

Apparent viscosity of $ZrSi_2$-filled slurry: $\mu_{app} = 0.11036 \cdot \dot{\gamma}^{-0.23271}$

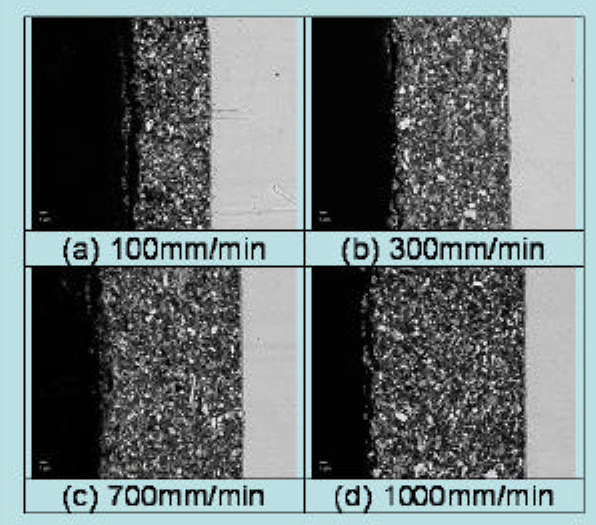
	Density of the Slurry (g/cc)	Volume Ratio (PHMS+filler):n-Octane	Surface Tension (mN/m)	Withdrawal Speed (cm/min)
$ZrSi_2$	1.59±0.02	3:5	35	10-100

Parameters used in Landau-Levich equations.

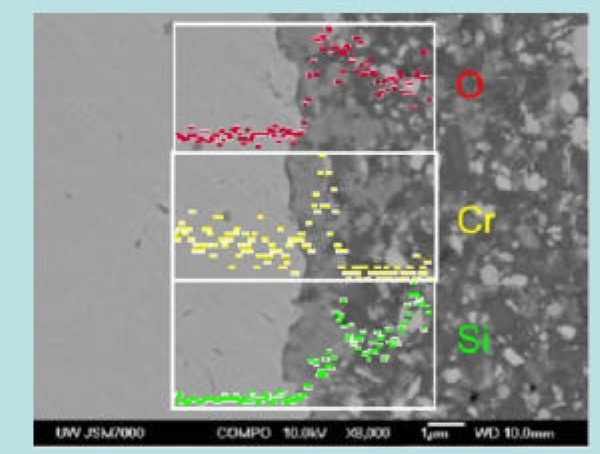
U (mm/min)	100	300	700	1000
γ (s^{-1})	28.9	61.2	108.8	132.7
μ_{app} (Pa.s)	0.0505	0.0424	0.0371	0.0354
h_d (μm, measured)	10.3	14.6	19.1	22.4
h_w (μm, calculated)	28.9	40.9	53.6	62.8
h_{L-L} (μm, predicted)	25.4	47.0	75.6	92.9

$ZrSi_2$-filled coating thicknesses as temperature and withdrawal speed vary.

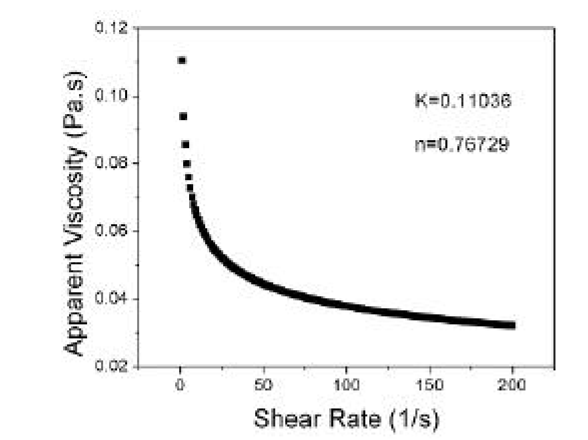
U (mm/min)	100	300	700	1000
150C (cross-linking)	10.3	14.6	19.1	22.4
600C (pyrolysis)	8.1	14.6	16.3	17.1
800C (filler oxidation)	11.5	17.3	21.4	23.7
1000C (shrinkage)	7.8	14.0	16.4	17.8



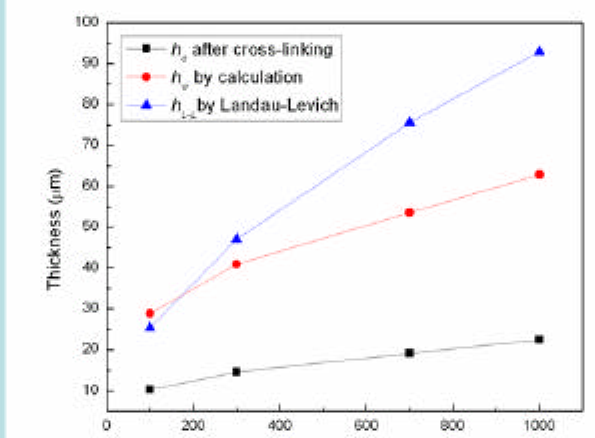
ZrSi2-filled coating system after pyrolysis at 800C.



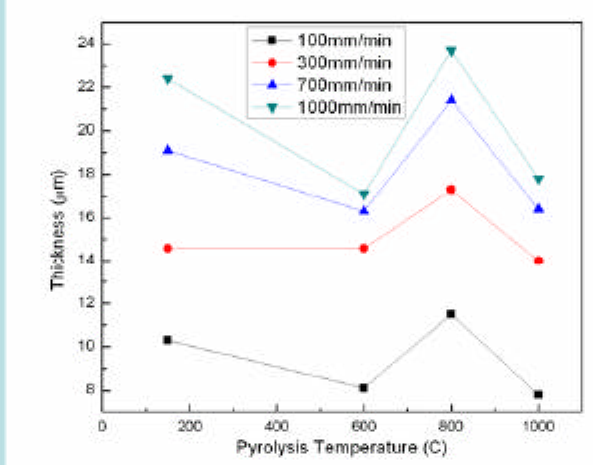
EDS study at the interface of 1000C-pyrolyzed $ZrSi_2$-filled coating. The interface layer is rich in elements like oxygen, chromium and silicon.



Power law data fitting on $ZrSi_2$-filled slurry

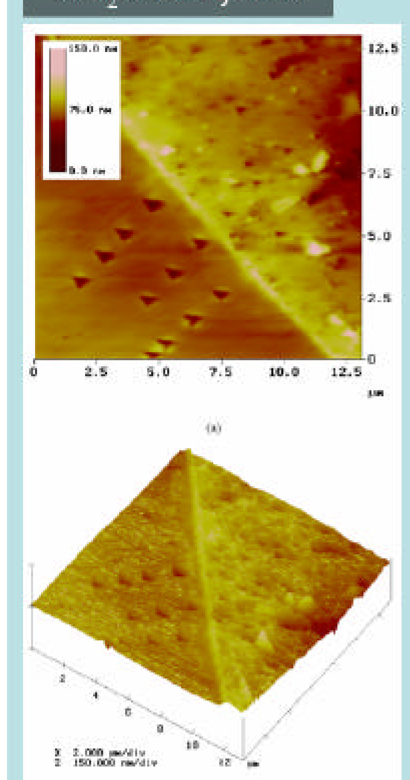


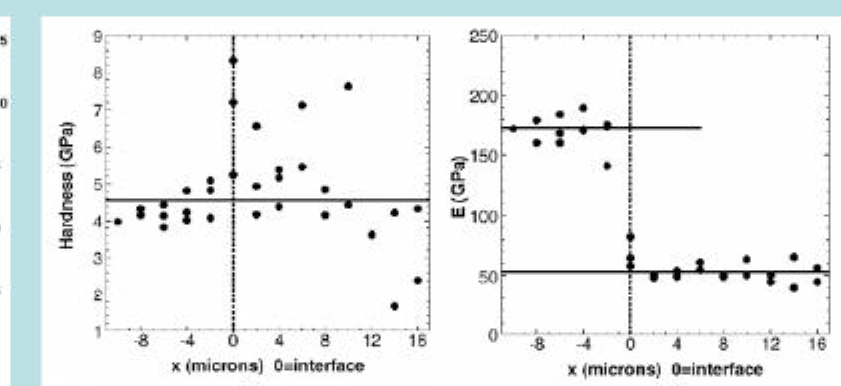
Derived and predicted film thickness comparison by different methods.



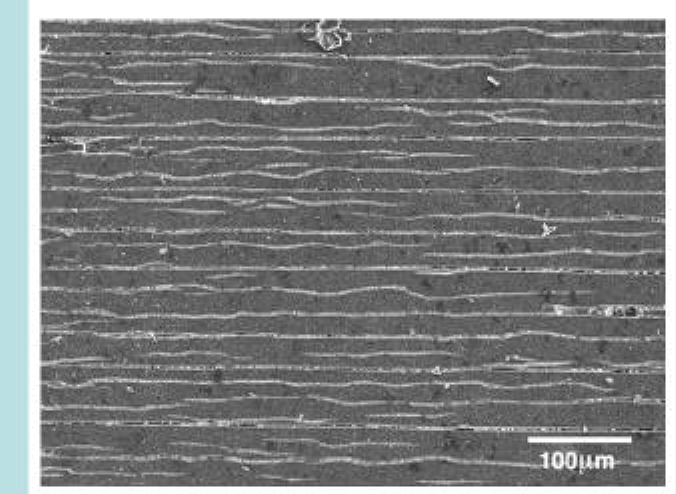
Trend of thickness change as a function of pyrolysis temperature in $ZrSi_2$-filled system.

$TiSi_2$-filled system





Atomic force microscopy (AFM) images of nanoindents across the interface of a $TiSi_2$-filled composite coating pyrolyzed at 800C on a steel substrate: (a) 2D top view, (b) 3D representation. [c] and (d) exhibit the hardness and elastic modulus as a function of position across the steel/coating interface for the sample pyrolyzed at 800C respectively. Negative represents the steel, zero the interface, and positive the coating. Elastic modulus was found out to be 54±8.1 GPa near the interface.



Saturated crack spacing (15% strain) in $TiSi_2$-filled coating on steel. Calculated tensile strength is 1.9 GPa, and the shear strength of the interface is 2.35 GPa.

Summary

Future work

1. Mechanical properties of the coating and the interface; 2. Thermomechanical performance under therrmal cycling; 3. Performance under selected corrosion conditions.

Publication and presentation

1. Kaishi Wang, Rajendra K. Bordia, Film thickness control in a complex non-Newtonian fluid system via Landau-Levich model for Newtonian fluids. (in preparation)
2. Jessica D. Torrey, Rajendra K. Bordia, Mechanical properties of polymer-derived ceramic composite coatings on steel, *Journal of the European Ceramic Society*, Volume 28, Issue 1, , 2008, Pages 253-257.
3. K. Wang, J. Torrey, R. Bordia, "Nanoscale Reinforced, Polymer Derived Ceramic Matrix Coatings", *31st International Cocoa Beach Conference & Exposition on Advanced Ceramics & Composites, American Ceramic Society*, Daytona Beach, Florida, January 2007.
4. R. Bordia, "Nanoscale Reinforced, Polymer Derived Ceramic Matrix Coatings", *University Coal Research Contractors Review Meeting, DoE NETL*, Pittsburgh, PA, June 2007.
5. R. Bordia, "Nanoscale polymer derived ceramic composites", 11 invited seminars presented at various universities and labs, 2006-08.

Acknowledgement

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