

# Processing and Properties of $\text{Si}_3\text{N}_4$ Matrix Composites Coatings and Joints from Filled Pre-Ceramic Polymer Systems

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# Outline

- **Background and Motivation**
- **Processing**
  - Selection of suitable preceramic polymer
  - Selection of suitable reactive fillers (elemental and binary)
  - Effects of processing parameters (temperature, atmosphere) on conversion
  - Processing of composites
- **Coatings**
  - Effects of processing parameters on coating integrity
  - Mechanical property determination (interfacial fracture energy)
- **Joints**
  - Effects of processing parameters on joint integrity
  - Mechanical property determination (ambient and elevated temperature strength, effect of high temperature annealing on joint properties and interfacial fracture energy)
- **Conclusions**



# Polymer Derived Ceramic Coatings

## Advantages:

- Processing ease (spin coat or dip coat)
- Low processing temperatures
- Amorphous and nano-structures
- Tailorable composition, microstructure and properties

## Limitations:

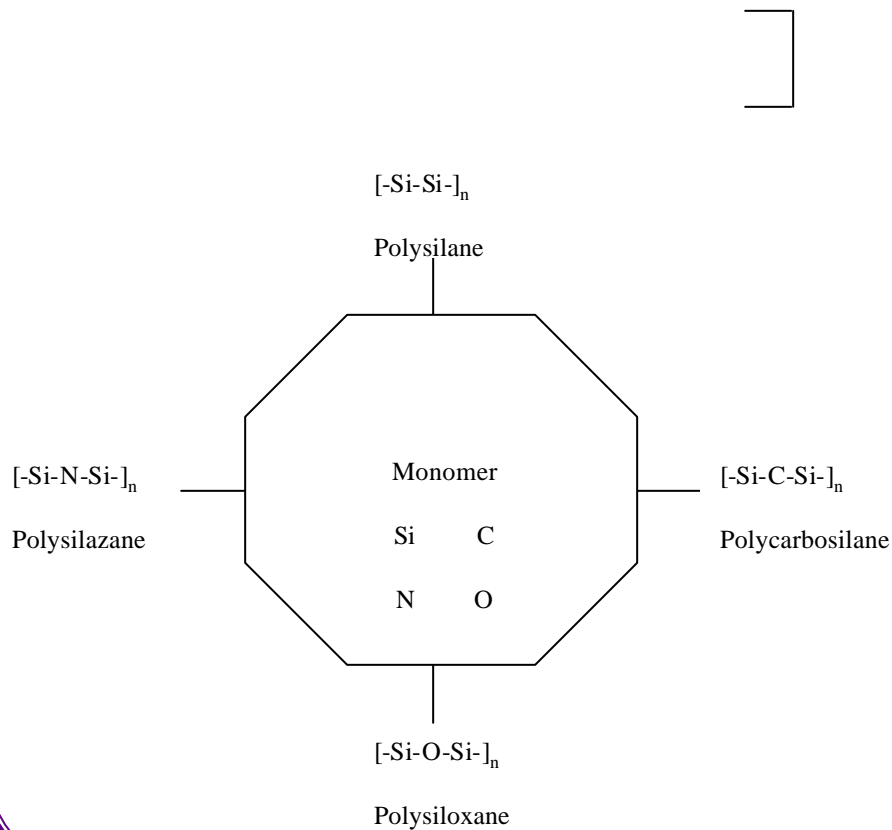
- High porosity
- Large shrinkage
- Defects and cracks in coatings and joints (due to constrained densification)



# Si Based Pre-Ceramic Polymers

low processing temperature

- Processing of ceramic fibers
- Infiltration of fiber preforms



polysilazanes

- precursor to  $Si_3N_4$
- instability in air

polysilane

- crystalline solids
- some are insoluble
- low ceramic yield

polycarbosilanes

- precursor to SiC
- most developed

polysiloxanes

- high  $O_2$  content
- leads to  $SiO_2$  formation



# Polymer Derived Ceramics

**Suitable polymer needs high ceramic yield (a):**

$$a = \frac{m_p - m_g}{m_p}$$

$m_p$  is mass of starting polymer  
 $m_g$  is gas evolved during pyrolysis

- need a ~ 80%
- cage or ring structures

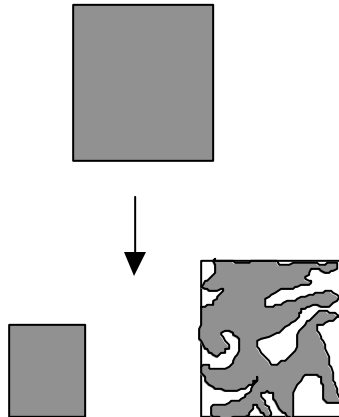
## Disadvantages

- Very high volume shrinkage or porosity
  - Limited to low dimension products (e.g. fibers)
- Difficulty in handling some systems (unstable in air)
- Leads to the use of reactive filler particles which expand during reaction  
Active Filler Controlled Pyrolysis (AFCOP)
- Possible to design systems with near zero shrinkage

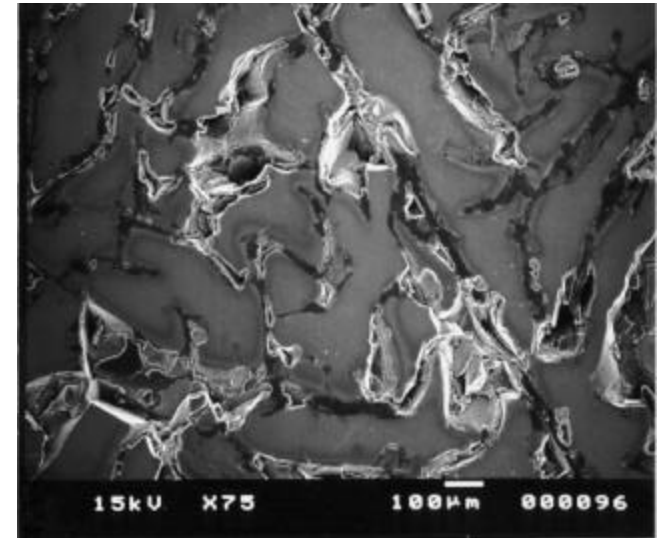


# Principles of AFCOP Pyrolysis\*

## Polymer Pyrolysis

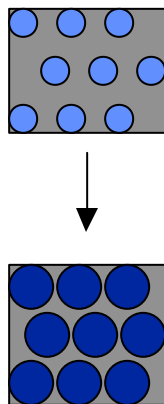


- get large volume change
- shrinkage and porosity



Pyrolysis product (Ar atmosphere)

## AFCOP Pyrolysis



metal + filler network

- near net shape process
- react with decomposition products to form new phases
- use reactive atmosphere to form new phases
- filler particle size is critical

\*Greil et al



# Goals of Research

The goal of the research was to investigate the use of filled preceramic polymers to form composite ceramic coatings and joints.

## Specific Objectives

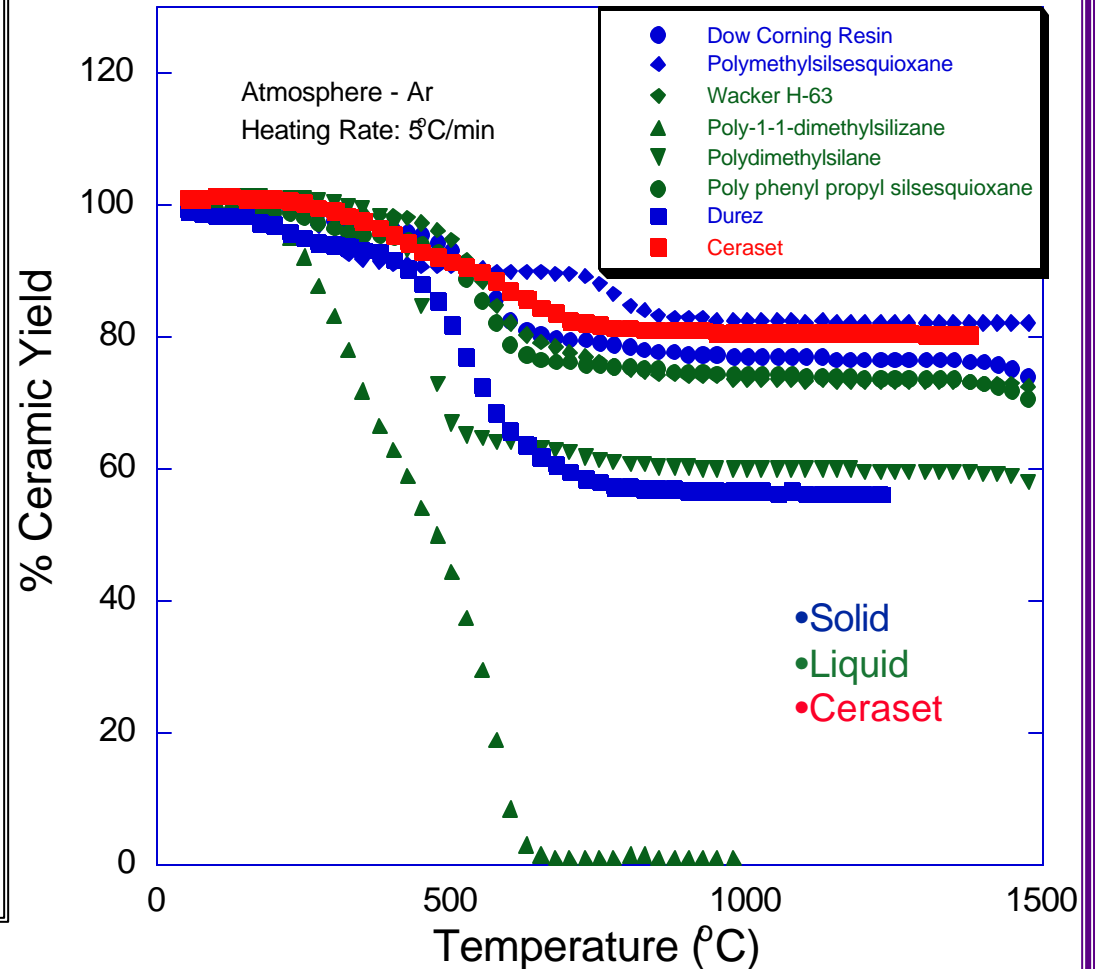
- **Determine most suitable preceramic polymer system**
- **Determine most suitable filler materials**
- **Investigate effect of processing parameters on microstructure**
- **Characterize phase evolution**
- **Develop composite systems with low shrinkage & porosity**
- **Characterize properties of composites**
- **Processing of coatings and joints**
- **Characterize microstructure & properties of coatings & joints**



# Selection of Pre-Ceramic Polymer

## Criteria for suitable pre-ceramic polymer

- High ceramic yield
- Physical state of polymer (solid or liquid) a liquid system is preferred
- Viscosity – optimized to prevent sedimentation yet have ease of processing
- Pyrolysis products – depends on application
- Oxygen content present after pyrolysis – controls high temperature props.
- Cure Time – shorter cure times are desirable



Ceraset (polyureasilazane) meets all criteria

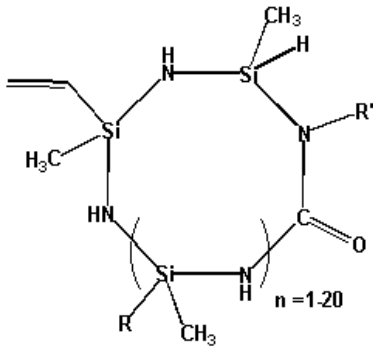




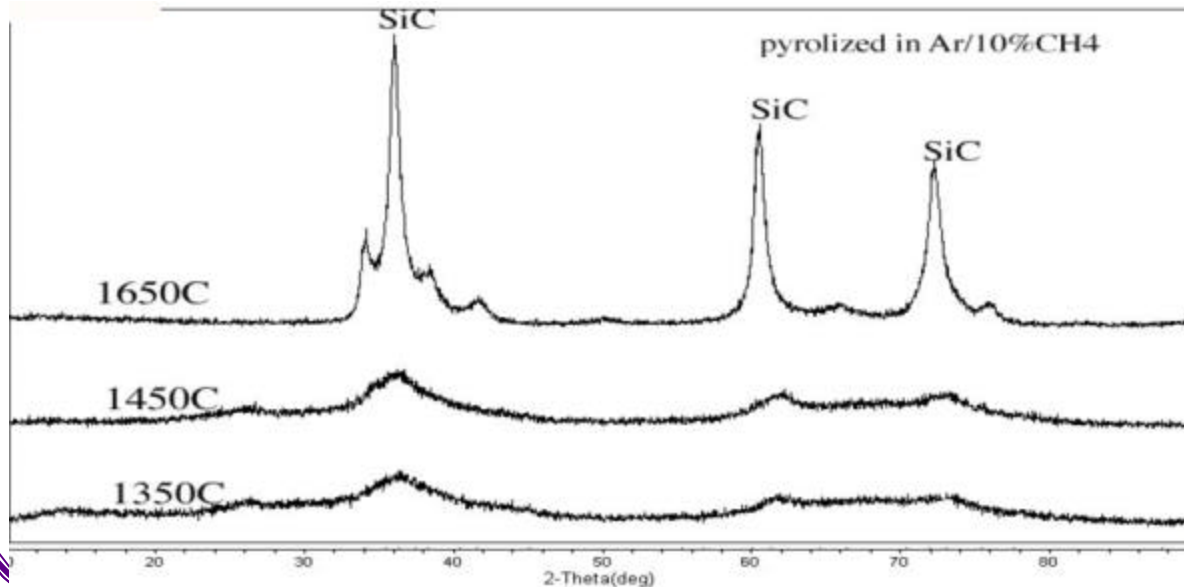
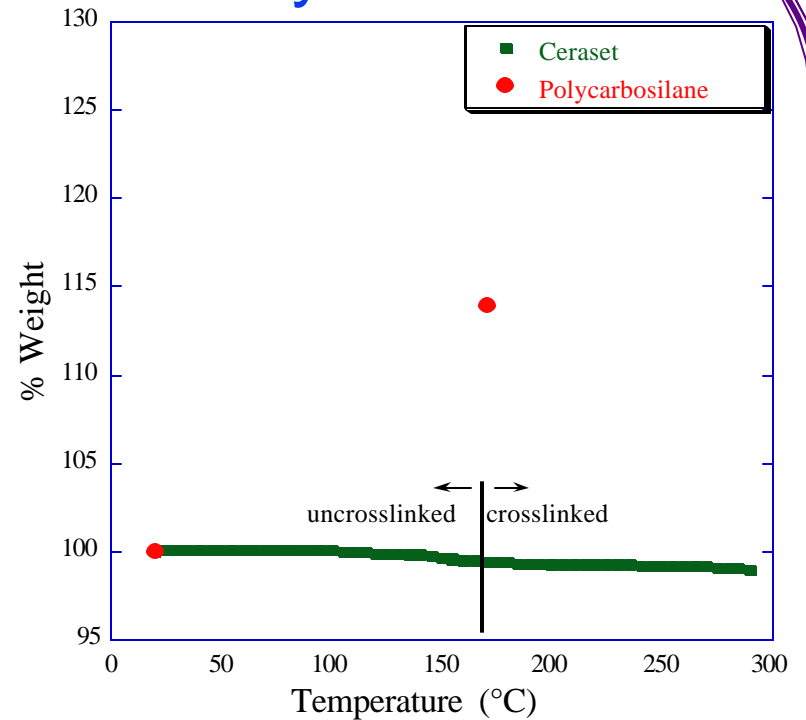
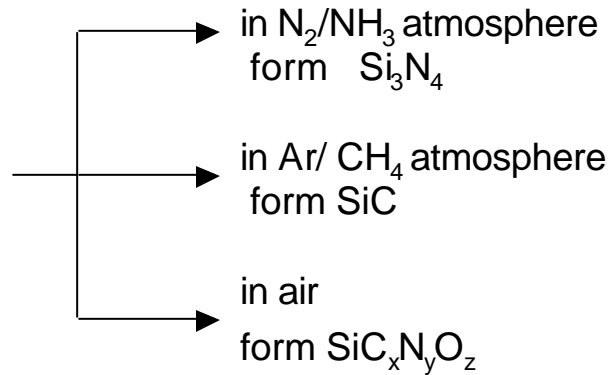
# Selection of Pre-Ceramic Polymer

## Ceraset<sup>SN</sup> - polyureasilizane

- low viscosity thermoset liquid polymer
- low oxygen content even after crosslinking



R = H, CH=CH<sub>2</sub>



PCS gains ~ 12% weight during crosslinking at 170°C

Amorphous or nanocrystalline at lower pyrolysis temperatures

Crystalline at higher processing temperatures

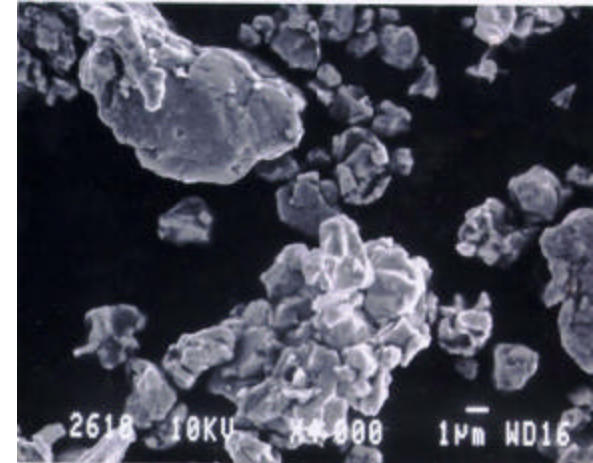


# Criteria for Selection of Reactive Filler Particles

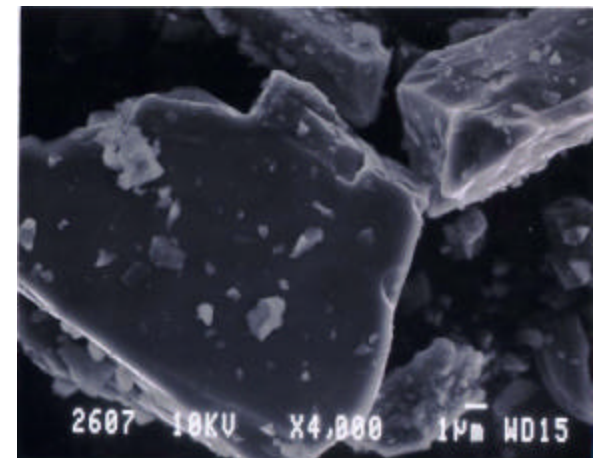
## Criteria for suitable filler materials

- Filler volume expansion observed during reaction
- Density of filler
- Filler particle size
- Filler surface area
- Presence of oxide layer on filler
- Thermodynamically stable phases formed on reaction (atmosphere)
  
- Elemental fillers - transition metals
  - > Ta, Ti, Nb, Cr, Mo, Si, W, V, B, Zr....
  - > needed high  $V_f$  (45%) to compensate for polymer shrinkage for near net shape
- Binary fillers ( $V_f \sim 35\%$ )
  - >  $TiB_2$ ,  $TiSi_2$ ,  $CrB_2$ ,  $ZrSi_2$ ,  $NbB_2$ ,  $ZrB_2$ ,

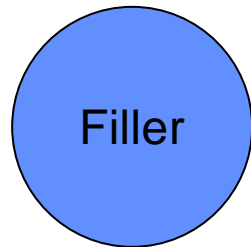
Cr powder



Si powder



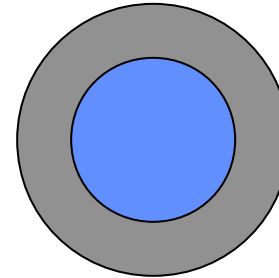
# Mechanisms of Conversion of Reactive Fillers



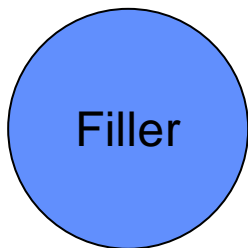
Filler

React with matrix  
or pyrolysis product →

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



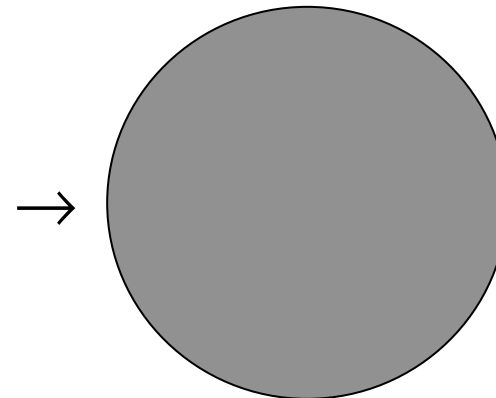
Get incomplete  
reaction of filler



Filler

React with  
reactive gas →

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



Get complete  
filler conversion

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

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



# Criteria for Selection of Reactive Filler Particles

The specific volume change of filler after reaction is:

$$\frac{\Delta V}{V_o} = kb - 1$$

Where:

$$k = \frac{\text{mass of reaction product}}{\text{mass of unreacted filler}}$$

$$b = \frac{\text{density of filler}}{\text{density of reaction product}}$$

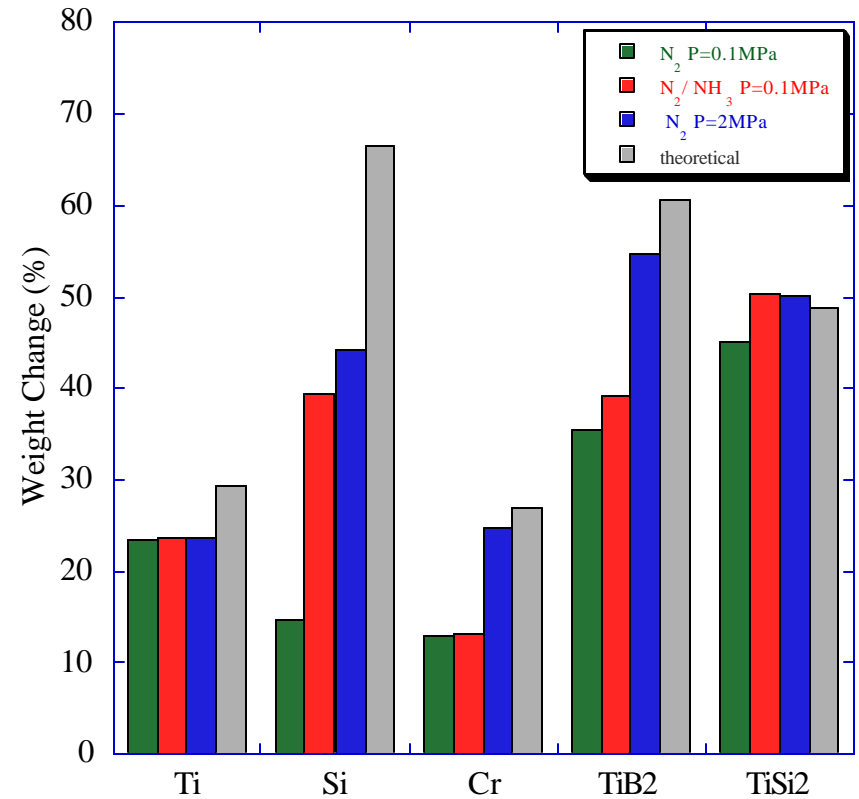
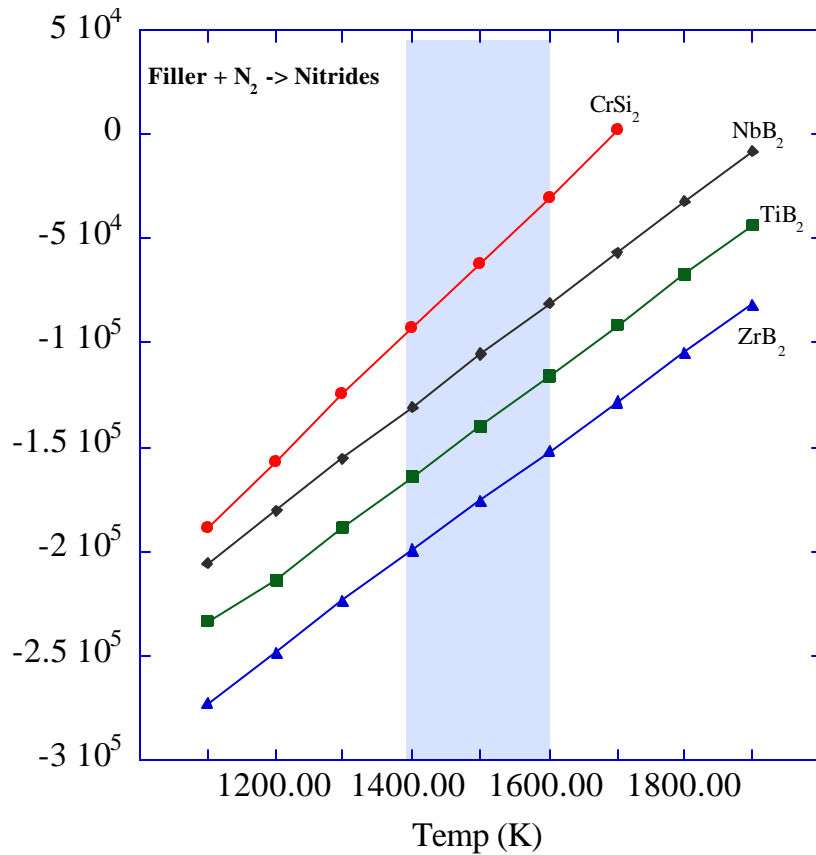
$\kappa\beta = 1$  for inert filler

Need  $\kappa\beta > 1$  for volume expansion of filler

Filler	Car bu riza tion (gaseo us rea ction)		Nit rid ation (gaseo us rea ction)	
	$\kappa\beta$	New Pha se	$\kappa\beta$	New Pha se
Ti	1.14	TiC	1.08	TiN
Cr	1.25	Cr <sub>3</sub> C <sub>2</sub>	1.50	CrN
Si	1.07	SiC	1.13	Si <sub>3</sub> N <sub>4</sub>
TiB <sub>2</sub>	1.12	TiC, B <sub>4</sub> C	2.14	TiN, BN
TiSi <sub>2</sub>	1.47	TiC, SiC	1.53	TiN, Si <sub>3</sub> N <sub>4</sub>



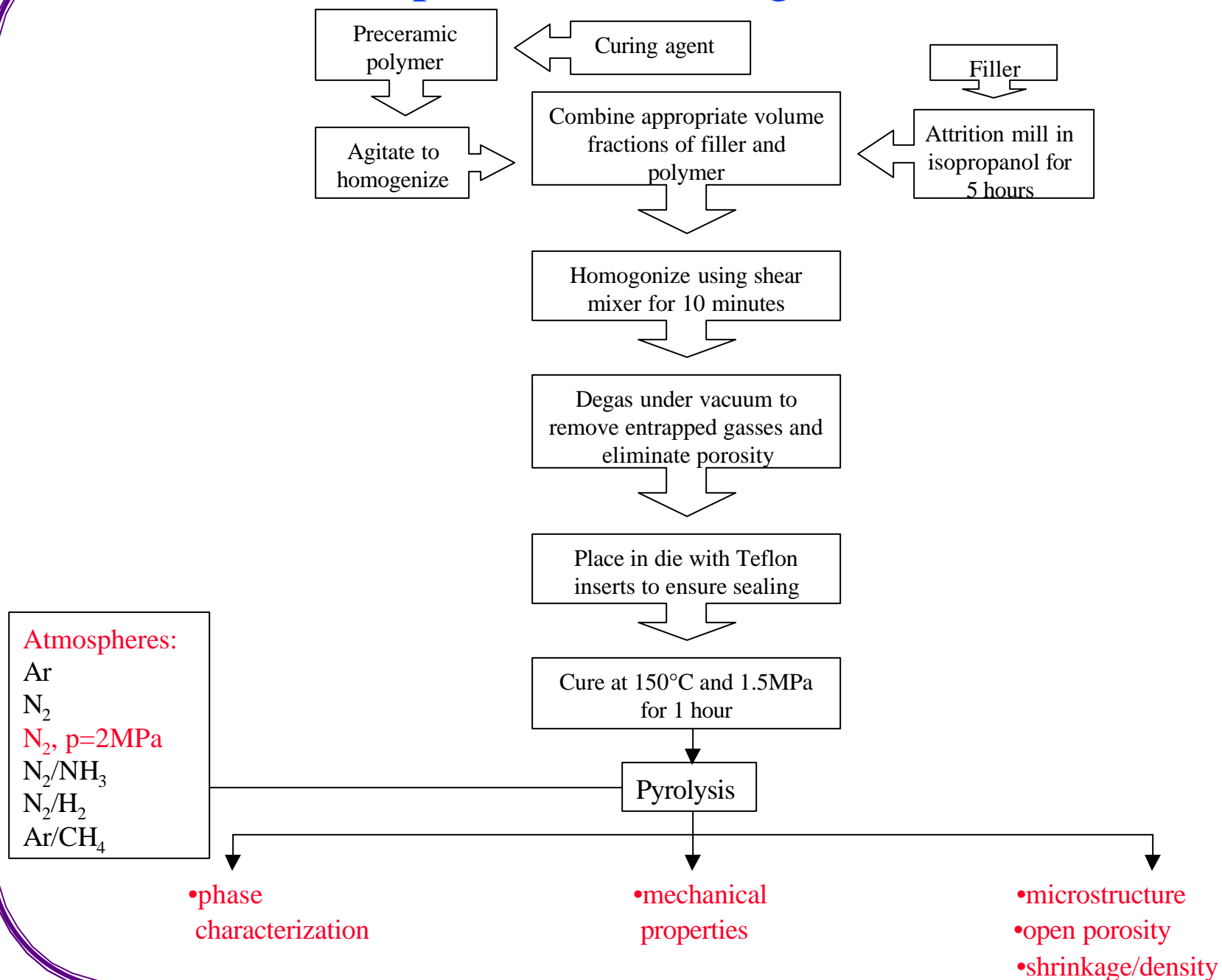
# Effect of Nitridding Atmosphere on Filler Reaction (no polymer in the system, $T=1400^{\circ}\text{C}$ )



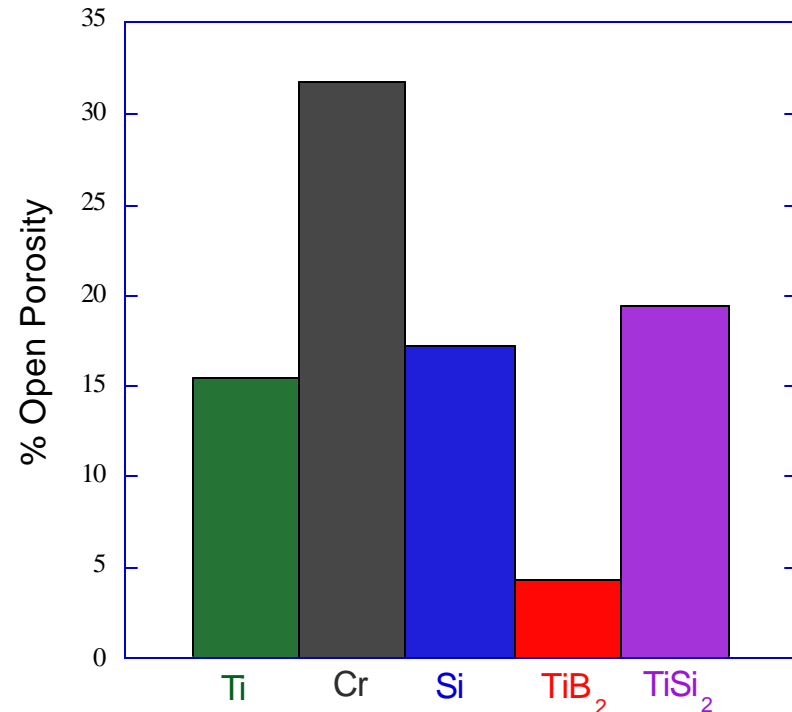
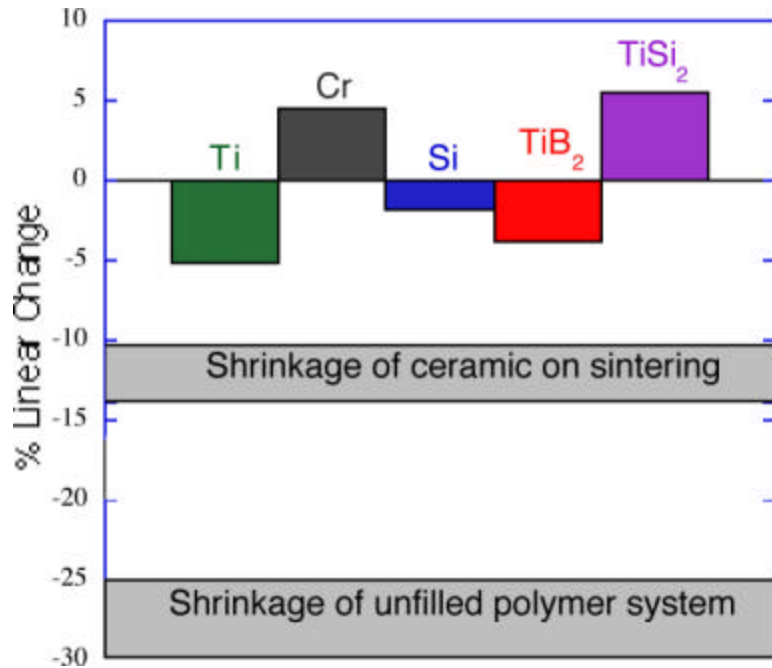
- Thermodynamically favorable for fillers to form corresponding nitrides
- All fillers transform to some degree
- High pressure  $\text{N}_2$  atmosphere most reactive



# Bulk Composite Processing/Characterization



## Effect of Filler on Shrinkage & Porosity for Polymer/Filler System (processing temperature 1400°C in N<sub>2</sub>, p=2MPa)

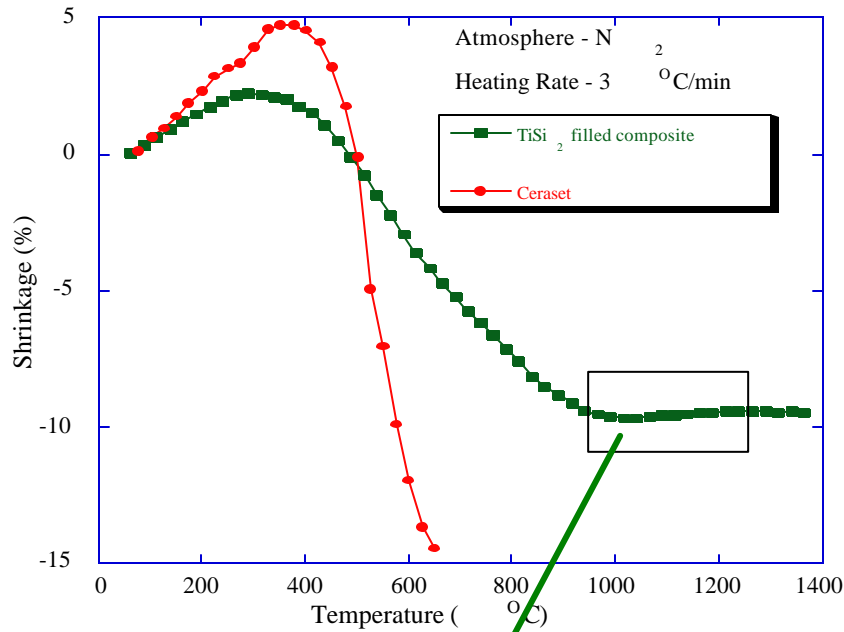


- All systems show improvement over unfilled polymer
- Intermetallic fillers more desirable
  - lower shrinkage
  - lower porosity

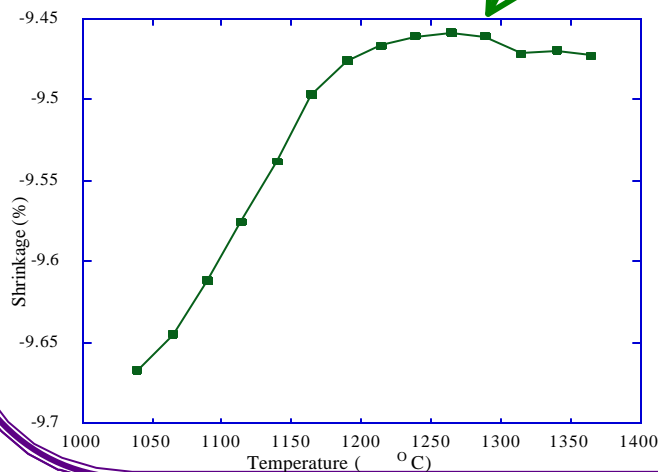
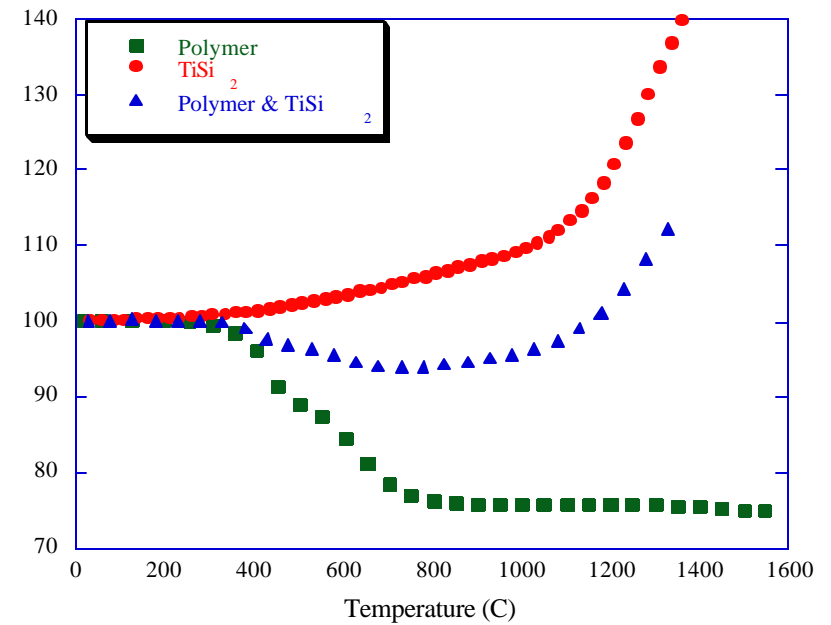


# Dimensional Changes Associated with Filler Reaction (TiSi<sub>2</sub> filled system pyrolyzed in N<sub>2</sub>)

Dimensional Change vs Temperature



Weight Change vs Temperature



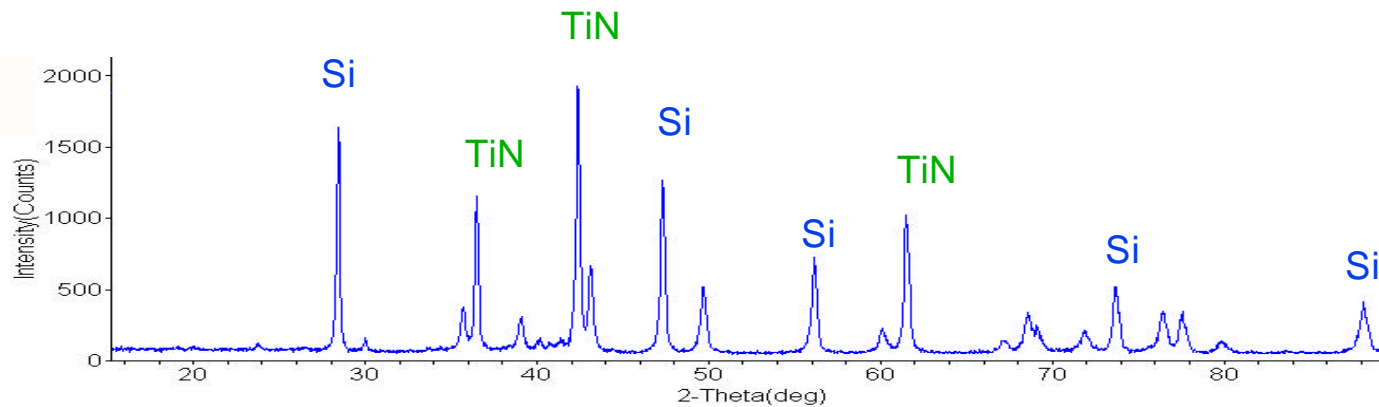
- Weight gain corresponds to sample expansion, however:  
- filler reaction is faster in high pressure nitrogen atmosphere



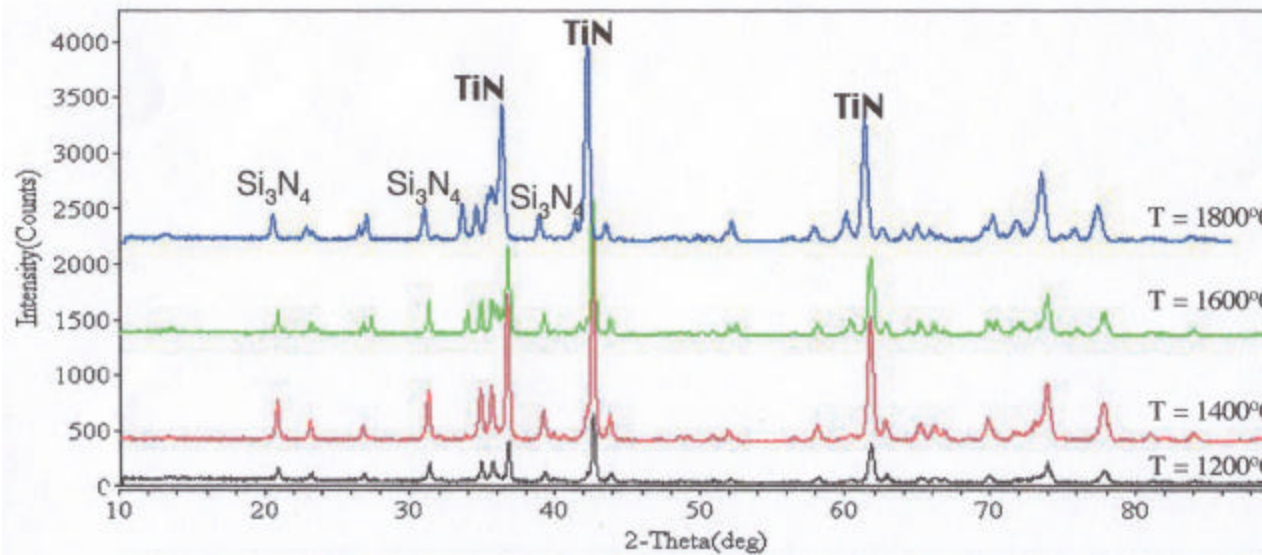


# Crystalline Phases formed in Binary Filled Composites

(Effect of atmosphere on  $\text{TiSi}_2$  filled composite conversion)



Atm:  $\text{N}_2/10\% \text{NH}_3$   
T = 1400°C

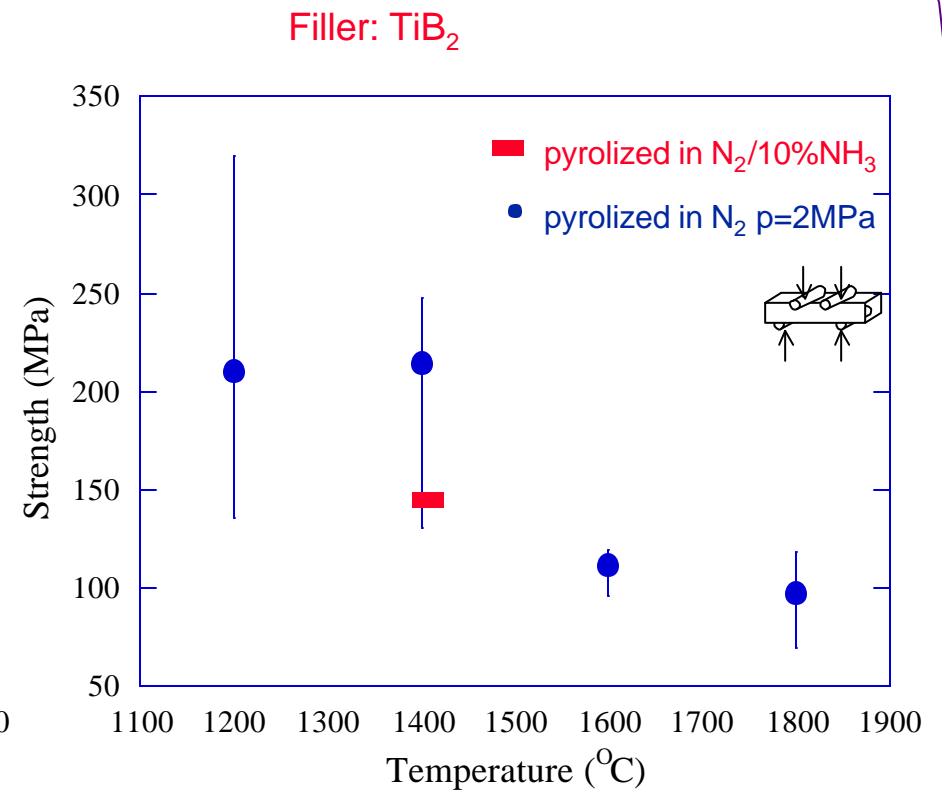
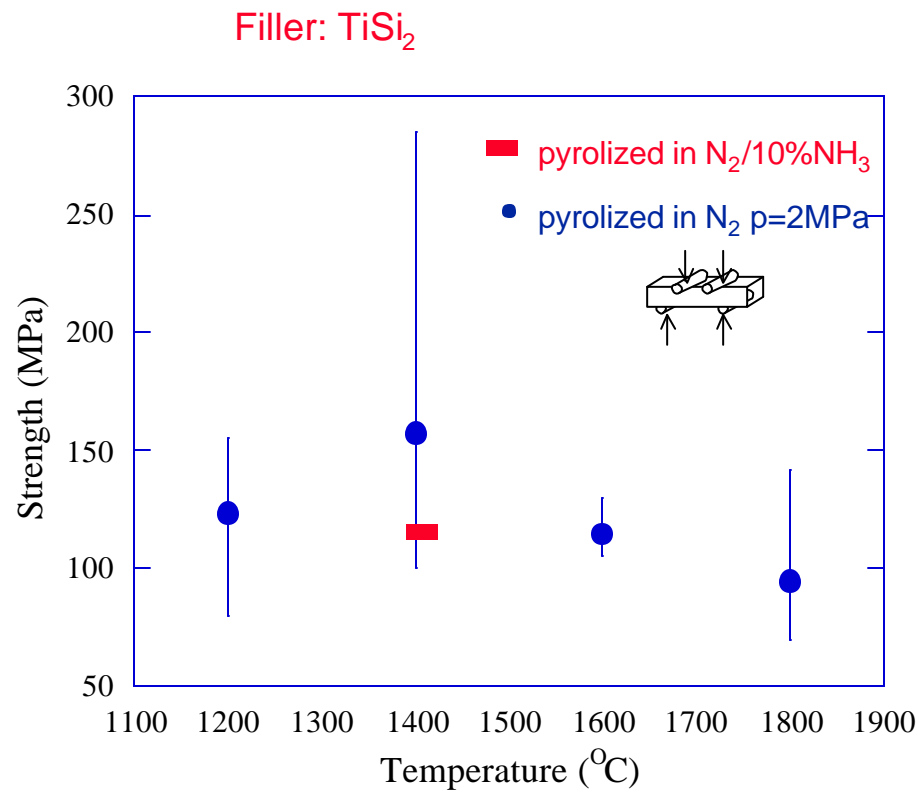


Atm:  $\text{N}_2$ , p=2MPa

- Get complete conversion of filled  $\text{TiSi}_2$  system in high pressure  $\text{N}_2$  atmosphere at pyrolysis temperatures as low as 1200°C



# Strength Data for TiSi<sub>2</sub> and TiB<sub>2</sub> Bulk Composite Systems

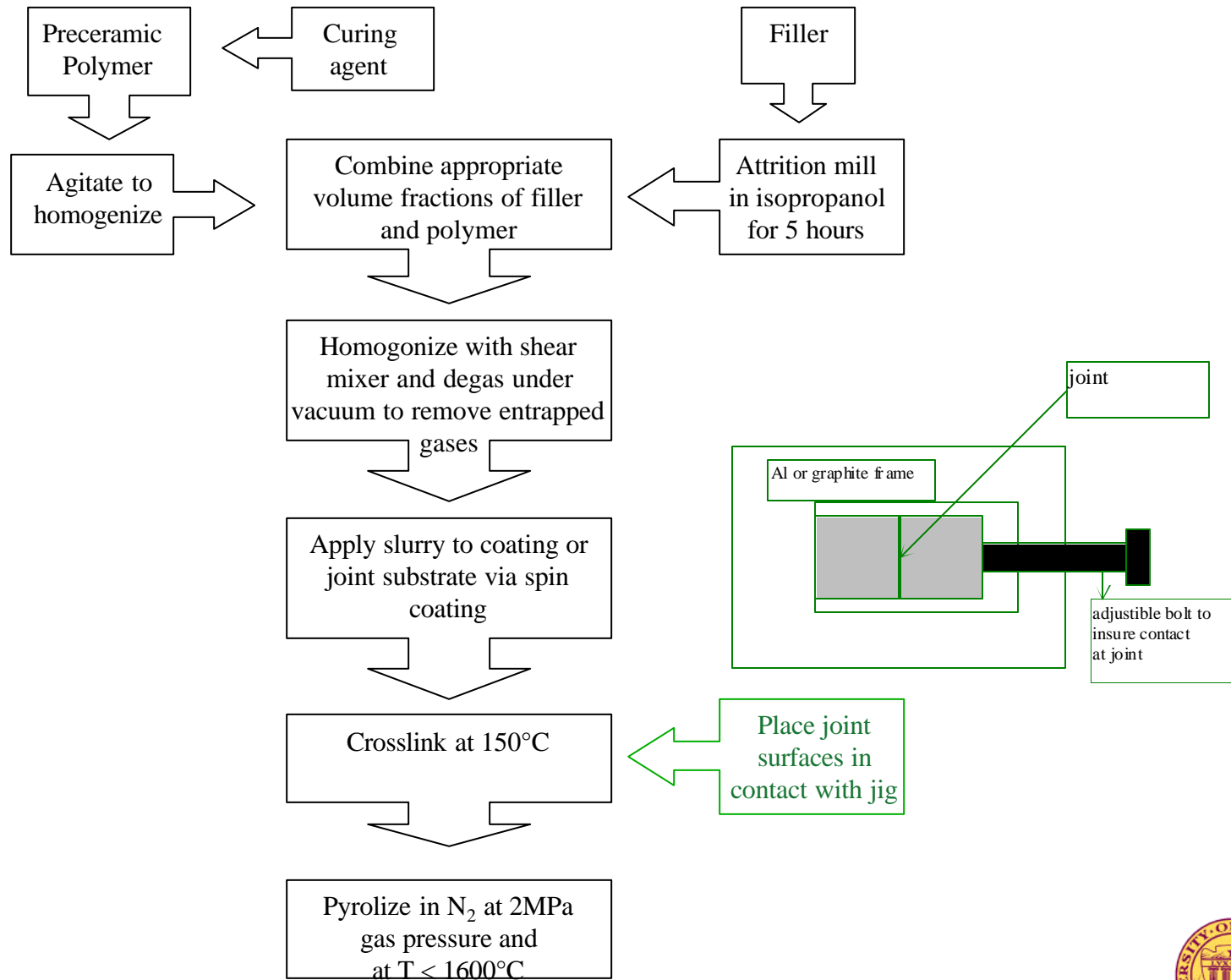


Initial composites formed at lower temperatures were significantly larger than those formed at higher temperatures (cause of large strength variability)

- Strength loss at 1600°C -> due to crystallization of Si<sub>3</sub>N<sub>4</sub>
- N<sub>2</sub> p=2MPa atmosphere leads to higher strength samples



# Processing of Coatings & Joints



# Critical Coating Thickness

In sintering systems  $\rightarrow$  critical coating thickness,  $t_c$

$t < t_c \rightarrow$  no cracking of film

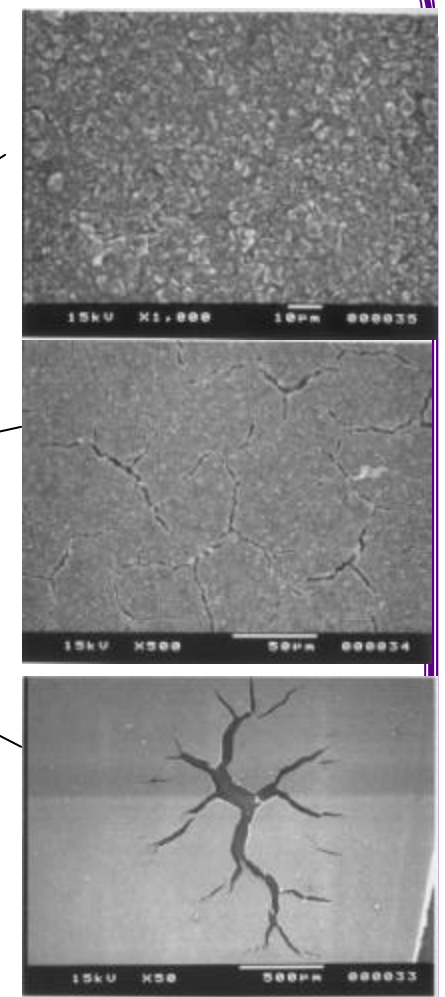
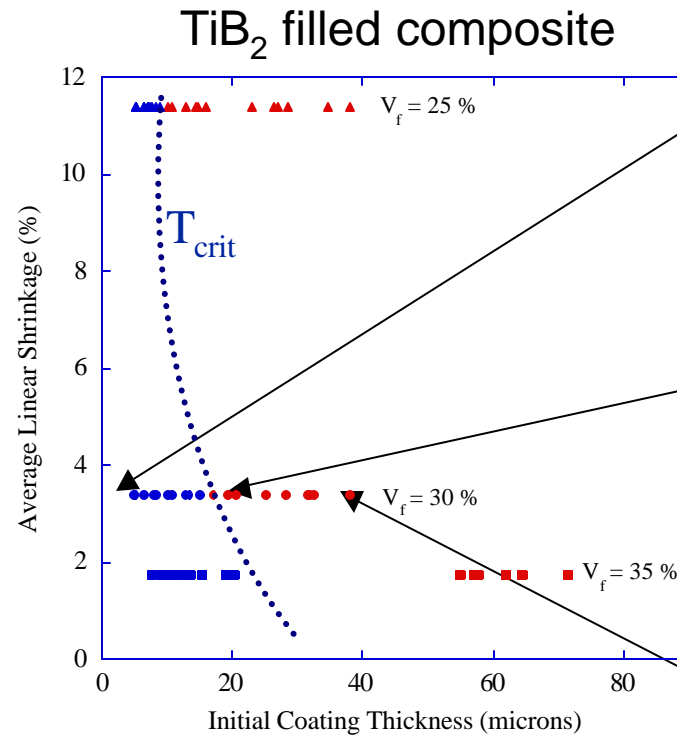
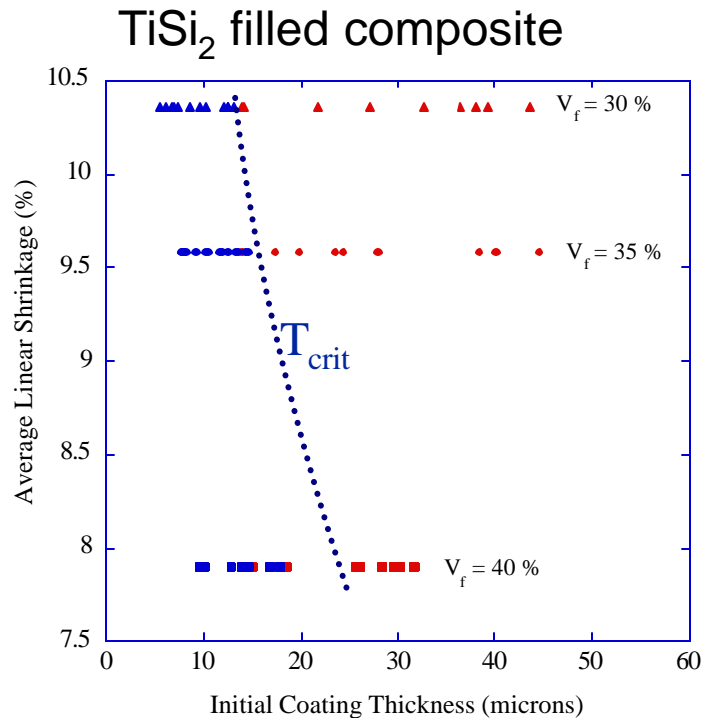
$t_c$  depends on shrinkage rate

In these composite systems  $\rightarrow$  expect similar result

- 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  $\downarrow$ )



# Processing of Coatings



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

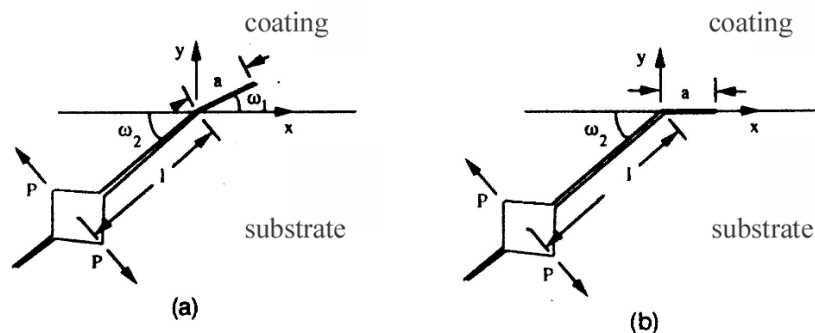
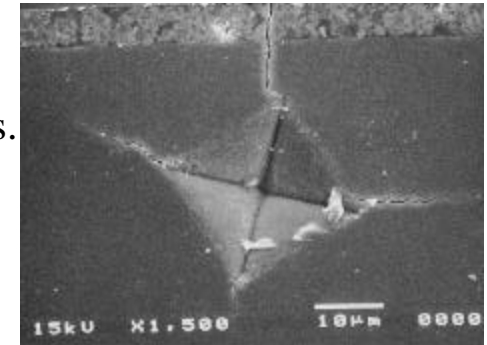
- shrinkage rate controlled by filler volume fraction ( $V_f$ )
- as  $t \uparrow$  get cracking (at a specific  $V_f$ )

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



# Indentation technique to estimate interfacial fracture energy

- Substrate is indented at proximity to the interface at different angles of attack.
- Applied indent load (1kg) is sufficient to cause cracking from the indent edges.
- These cracks grow toward the interface at different angles of attack and will deflect and grow along the interface or penetrate through the interface depending on the interfacial properties



The ratio of the energy release rate for the crack deflected along the interface ( $G_d$ ) to the maximum energy release rate for the crack growing into the coating ( $G_p^{\max}$ ) is obtained from:

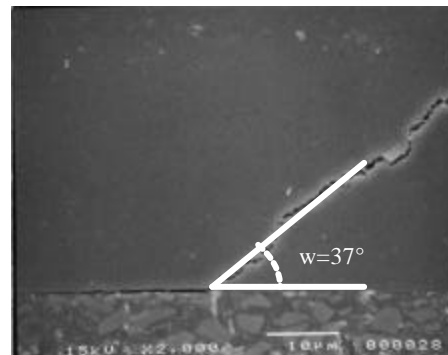
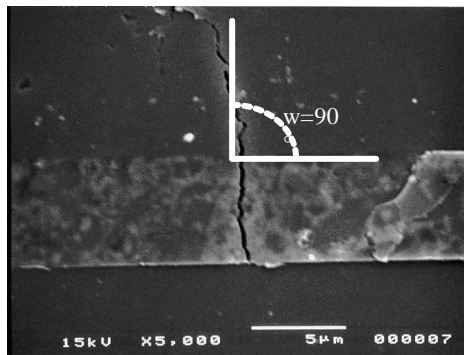
$$\frac{G_d}{G_p^{\max}} = \left( \frac{1}{1-a} \right) \frac{|d|^2}{|c|^2}$$

Where:

$\alpha$  is the Dundars parameter

$G_p^{\max}$  and  $G_d$  are the crack driving forces

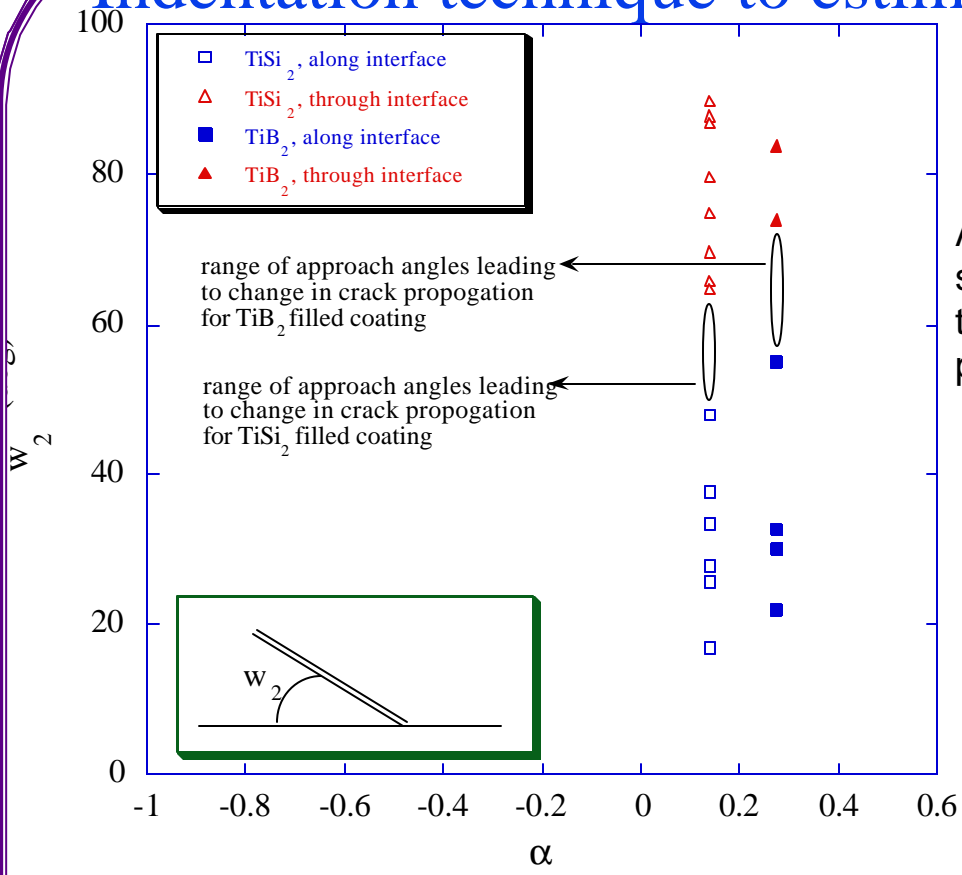
$c$  and  $d$  are complex valued functions (He & Hutchinson)



- Simple approach to estimate interfacial energy of coatings



# Indentation technique to estimate interfacial fracture energy



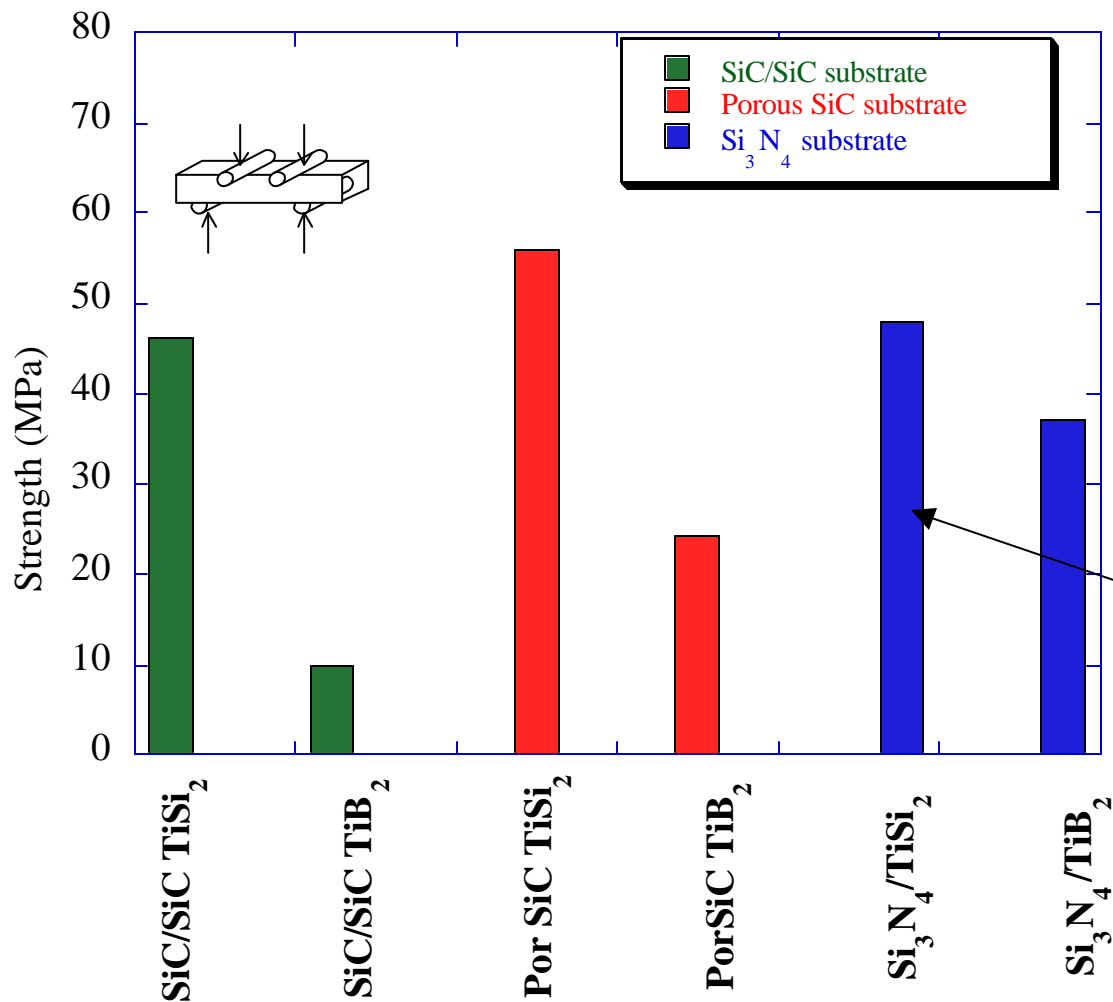
Angle of approach ( $\omega$ ) vs  $\alpha$  for both coating/substrate systems showing the approach angle range at which the crack changes from growing through the interface to propagating along the interface

- Interfacial fracture energy for  $\text{TiB}_2$  filled system estimated between 24 and 31  $\text{J/m}^2$
- Interfacial fracture energy for  $\text{TiSi}_2$  filled system estimated between 26 and 34  $\text{J/m}^2$

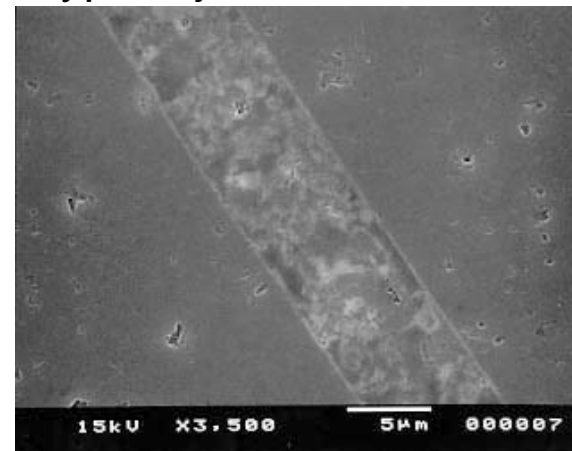
Initial joint composition By volume	Final joint composition By volume	$G^d/G^p_{\max}$	$G^p_{\max}$ estimate $\text{J/m}^2$	$G^d$ $\text{J/m}^2$
35% $\text{TiB}_2$ + 65% Polymer	55.11% BN 25.14% TiN 19.74% $\text{Si}_3\text{N}_4$ (pyrol product)	0.64 to 0.81	37	24 – 31
40% $\text{TiSi}_2$ + 60% Polymer	63.2% $\text{Si}_3\text{N}_4$ 17.19% TiN 19.61% $\text{Si}_3\text{N}_4$ (pyrol product)	0.6 to 0.78	44	26 – 34



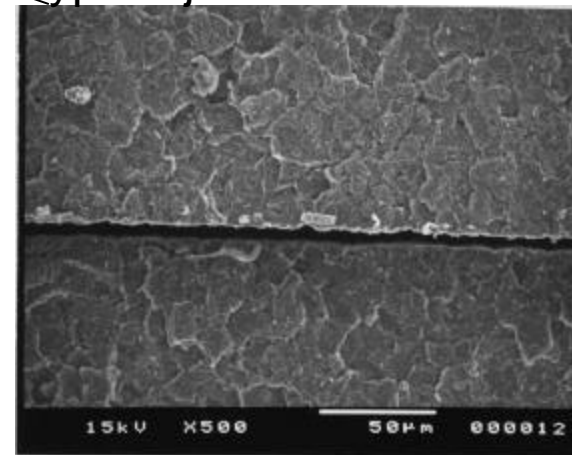
## Room Temperature Joint Strength



Typical joint cross section



Typical joint failure surface

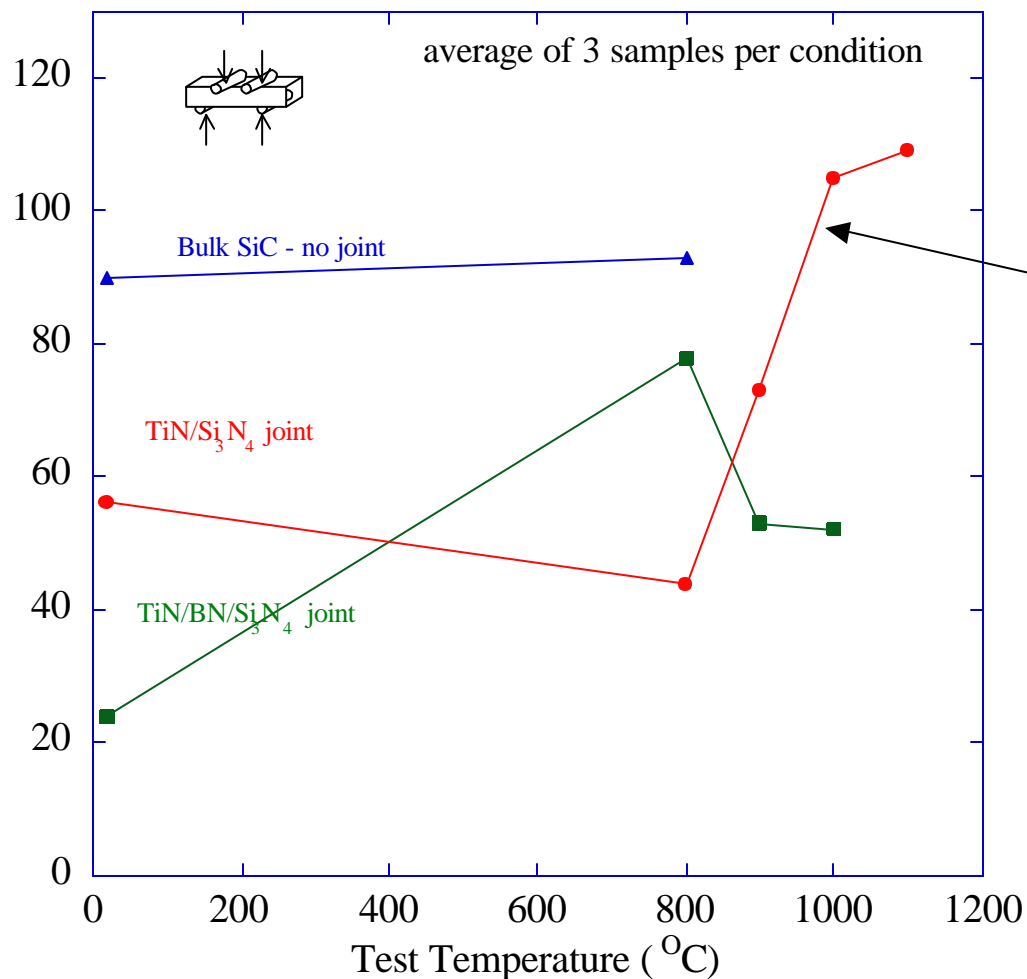


- Obtained promising room temperature joint strengths
- Joints failed in the joint material - not at the interface
- TiSi<sub>2</sub> filled joints lead to higher strengths

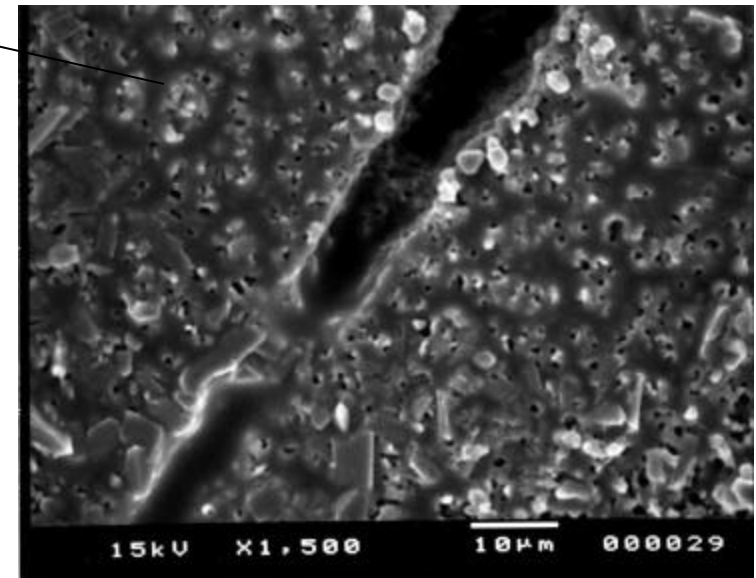




# High Temperature Joint Strength of Siliconized SiC



Samples brought up to test temp and allowed to equilibrate for 1 hr prior to testing

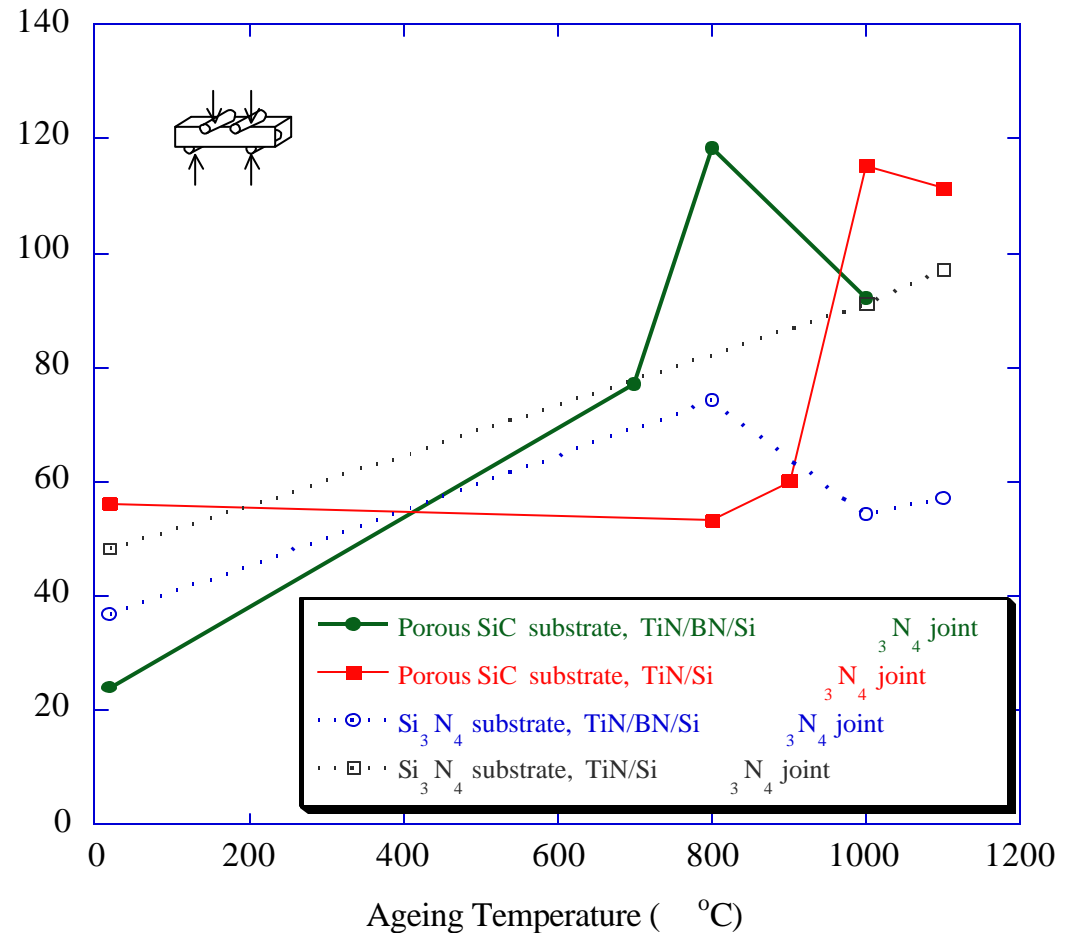


- Elevated temperature leads to an increase in strength (may not fail at joint)
  - possibly due to flaw healing as a result of viscous oxide produce formation
- At  $T > 800^{\circ}\text{C}$  degradation in  $\sigma$  of composite with  $\text{TiB}_2$  starting filler observed
  - due to formation of volatile oxide



# Room Temperature Joint Strength of Samples (Aged between 750°C to 1100°C in air for 24 hours)

Results from elevated temperature strength testing indicate that it may be feasible to improve the strength of the joints by exposing them to a high temperature aging treatment.



- Aging at elevated temps leads to an increase in strength
  - possibly due to flaw healing as a result of viscous oxide produce formation
  - generally failure occurs at the interface and not in the joint material
- At  $T > 800^{\circ}\text{C}$  degradation in  $\sigma$  of composite with  $\text{TiB}_2$  starting filler observed
  - due to formation of volatile oxide



# Effect of Phase Angle on Fracture Toughness

## Monolithic ceramic

- crack grows in Mode I direction

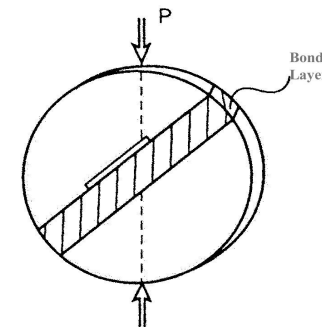
## At interface

- crack confined to interface if interfacial  $K_{IC}$  lower than bulk
- Interfacial toughness ( $G_i$ ) depends on the loading phase angle ( $\phi$ )  
(where  $\phi$  is  $\tan^{-1} K_{II}/K_I$ )
  - $\phi = 0$ : pure mode I loading
  - $\phi = 90$ : pure mode II loading

$G_i$  vs  $\phi$  curve is necessary to characterize a given interface.

## Brazil Nut Geometry

(test geometry chosen to obtain  $G_i$  vs  $\phi$  curve)

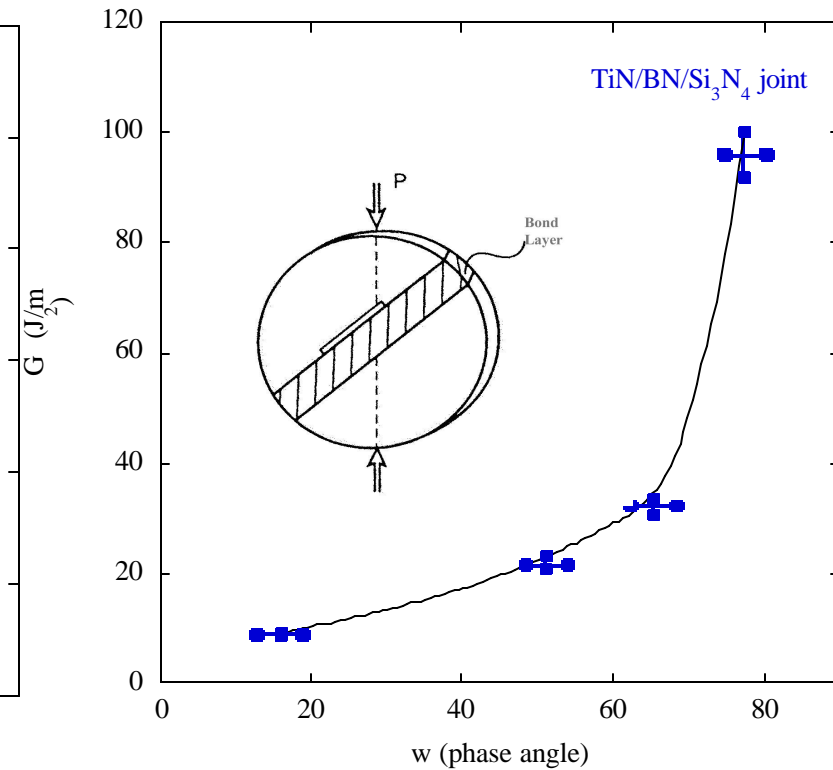
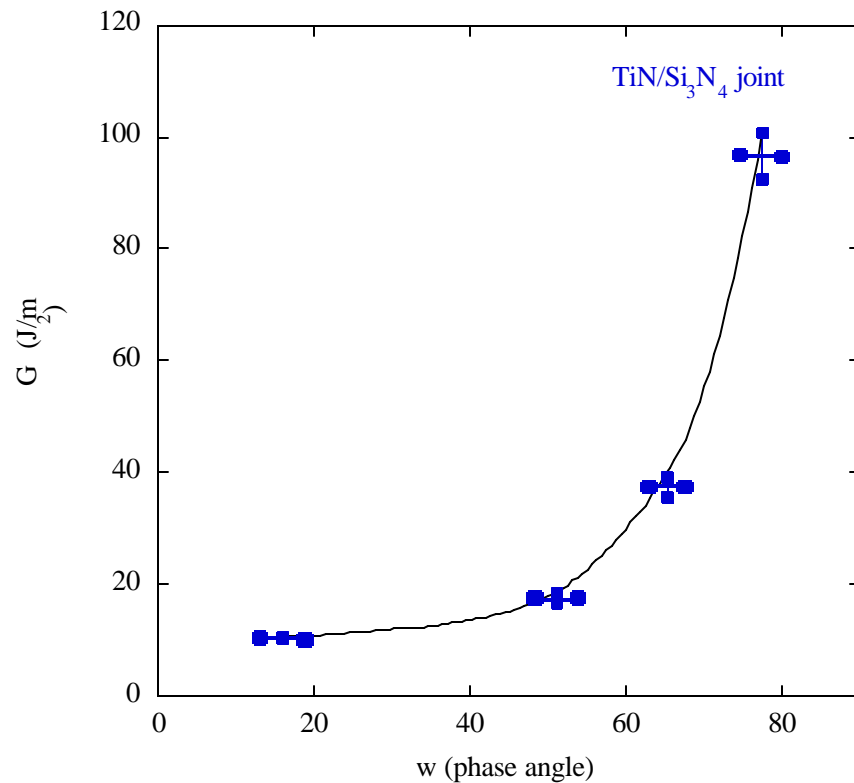


## Most versatile

- the loading phase angle is controlled by the compression angle.
- a large range of phase angles ranging from  $-\pi/2$  to  $\pi/2$  are possible
- also this test geometry is attractive due to the ease of loading of the specimen compared to other geometries



# Effect of Phase Angle on Fracture Toughness



- Interfacial toughness increases with phase angle
- In all cases the samples failed at the interface
- At  $\phi \approx 0$  (Mode I):
  - toughness of joints close to experimentally determined toughness of coatings measured using indentation approach (as expected)



# Effect of Phase Angle on Fracture Resistance

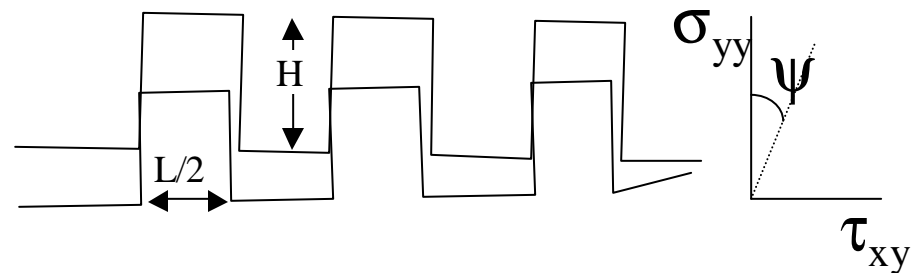
Magnitude of shielding induced by asperities at the interfacial fracture surface is governed by the loading phase angle and a non-dimensional material parameter  $\chi$  (Evans *et al*)

$$c = \frac{EH^2}{LG_o}$$

H is the roughness amplitude,  
L is the roughness wavelength  
E is the youngs modulus.

when  $\chi$  is small or  $\psi$  is zero  
(  $H \ll 0$  or  $L \ll 8$  ) no shielding

as  $\chi$  and  $\psi$  increase  
(  $H > 0$  or  $L \ll 0$  ) shielding effects observed



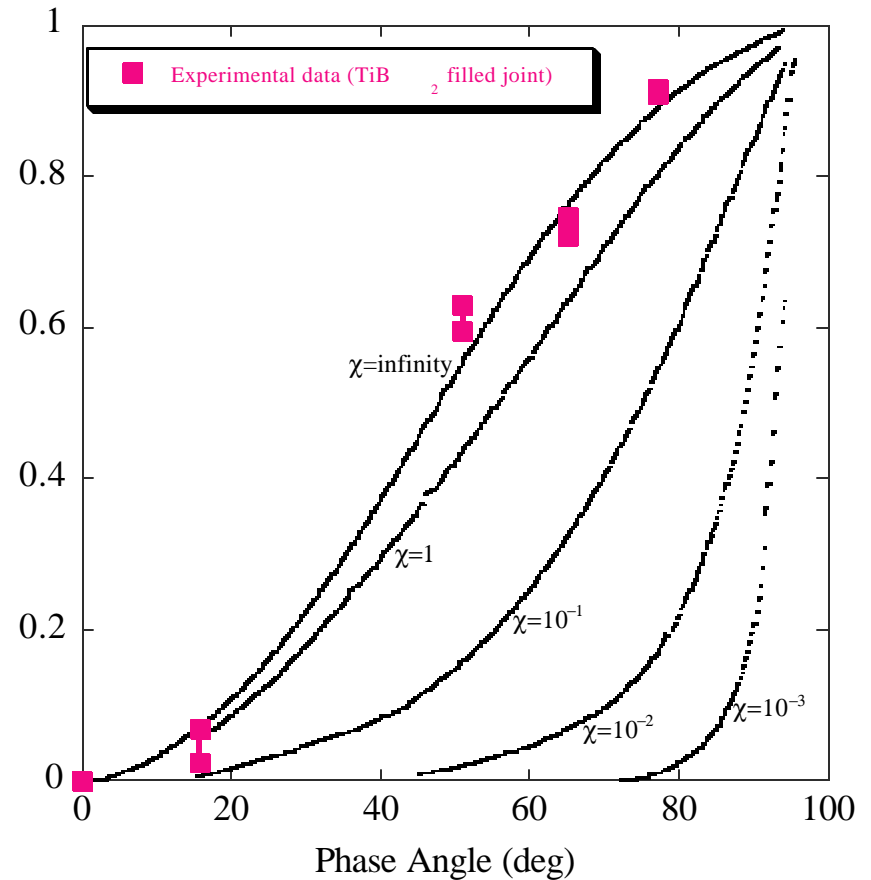
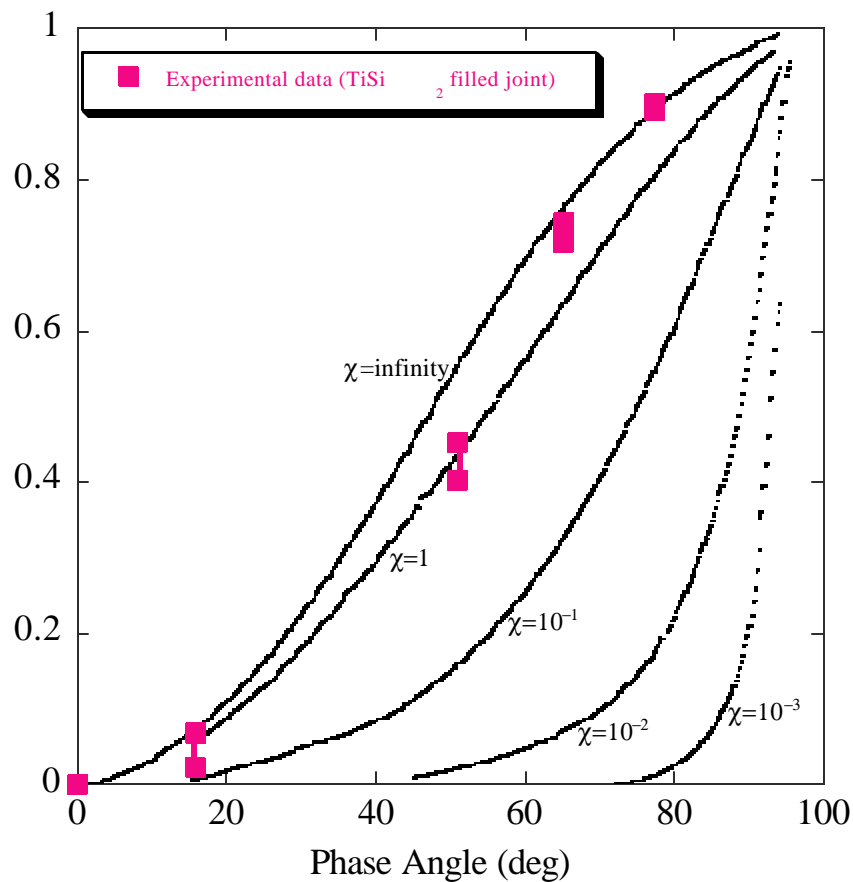
Measure H and L using  
laser profilometry

Joint starting filler composition	H (average) (microns)	$G_o$ J/m <sup>2</sup>	E (GPa)	L (microns)	$\chi = EH/LG_o$ (experimental)
TiSi <sub>2</sub> filled joint	3.5	10	100	300	~ 400
TiB <sub>2</sub> filled joint	3.5	8.5	80	300	~ 380

- Shielding will strongly depend on the interface roughness (i.e. the magnitude of H and L).
- Model attempts to explain what is happening at the microstructural level during fracture.



# Effect of Phase Angle on Fracture Toughness



- Model is in agreement with values of  $c$  obtained experimentally (~400)
- Model explains the role of asperities in controlling the interfacial fracture toughness.

y axis is  $\{G(\Psi) - G(\Psi = 0^0)\} / \{G(\Psi = 90^0) - G(\Psi = 0^0)\}$



# Summary and Conclusions

- Pre-ceramic polymers filled with reactive fillers are a versatile route to ceramic composites, coatings and joints
- Intermetallics are the most promising fillers ( $\text{TiB}_2$ ,  $\text{TiSi}_2$ )
- Optimized processing parameters (heating rate, atmosphere, pyrolysis temp.)
- Can process crack free near net shape bulk composites coatings and joints at lower temperatures and without applied stress with encouraging properties.
- At Temp  $<1400^\circ\text{C}$  pyrolysis product is amorphous (or nanocrystalline)
- Strength degradation at  $T > 1400^\circ\text{C}$  due to polymer product crystallization (or grain growth)
- Joints tested (or aged) at elevated temperatures leads to an increase in strength - possibly due to flaw healing
- Evaluated interfacial toughness of both  $\text{TiB}_2$ ,  $\text{TiSi}_2$  filled joints and coatings
  - Indentation technique used to evaluate interfacial fracture energy in coatings
  - Brazil nut geometry used to evaluate interfacial fracture energy in joints

**Initiated a new project on the development of oxidation and corrosion resistant coatings for metals. In this project we will use filled Polysiloxanes (collaboration with Henager, PNNL)**

