Oxidation Kinetics and Strength Degradation of Carbon Fibers in a Cracked Ceramic Matrix Composite

Michael C. Halbig, Army Research Laboratory, Cleveland, OH

Ceramic matrix composites (CMCs) are proposed for use in various high temperature structural applications. Proposed applications for C/SiC materials include leading edges, control surfaces, nozzles, thrusters, inserted blades, cooled panel heat exchangers and combustion chambers, and friction materials for brakes. Two primary benefits of using C/SiC are low weight and high temperature capability compared to other materials. Lighter weight can lead to benefits of increased thrust (performance) and/or increased payload. Higher temperature capability is important for meeting high thermal loads due to combustion gas temperatures in propulsion applications and due to reentry and hypersonic flight conditions in airframe applications. The use of high temperature CMC materials that require little or no cooling can allow for more flexible and simpler designs which can lead to smaller overall vehicle designs and weight savings. Despite the benefits of using C/SiC in certain types of applications, one of the barriers to its use is the degradation of the carbon fiber reinforcement, particularly in oxidizing environments. This leads to strength reduction and potential component failure. For single use or short mission applications in oxidizing environments, the oxidation of the carbon fibers may not be a factor. However, in reusable or long term applications, oxidation protection schemes may be necessary.

The oxidation kinetics of carbon fibers in complex composite systems are not well understood. Many studies involve thermogravimetric analysis (TGA) in which weight loss of the composite is monitored over time. These types of studies provide valuable information, however the oxidation of the composites in unstressed and stressed states can be very different, primarily, due to the presence of pre-existing cracks. The pre-existing cracks are an as-received property of C/SiC. The microcracks form during cool down after high temperature processing due to the coefficient of thermal expansion mismatch between the carbon fiber and the silicon carbide matrix. In an unstressed state at elevated temperatures, the formation of silica and the closing of cracks near the processing temperature can seal the cracks and protect the interior of the composite from the outside oxidizing environment. However in many real application conditions, stresses present can prevent cracks from sealing due to wide crack openings and the relatively slow rate of silica growth. Therefore, fibers are more prone to oxidation when the composite is under stress.

Experimental results and oxidation modeling will be presented to discuss carbon fiber susceptibility to oxidation, the oxidation kinetics regimes, and composite strength degradation and failure due to oxidation. Thermogravimetric analysis (TGA) was used to study the oxidation rates of carbon fiber and of a pyro-carbon interphase. The analysis was used to separately obtain activation energies for the carbon constituents within a C/SiC composite. TGA was also conducted on C/SiC composite material to study carbon oxidation and crack closure as a function of temperature. In order to more closely match application conditions, C/SiC tensile coupons were also tested under stressed oxidation conditions. The stressed oxidation tests show that C/SiC is much more susceptible to oxidation when the material is under an applied load where the cracks are open and allow for oxygen ingress. The results help correlate carbon oxidation with composite strength reduction and failure. Also since the test conditions allow for easy oxygen ingress, the oxidation kinetics of carbon within a C/SiC composite can be studied without the added variable of crack closure.

The results from the experimental analysis were used to provide input for the development of a finite difference model that allows for further analysis of the oxidation kinetics of carbon fibers in a cracked ceramic matrix. Oxygen concentrations and carbon consumption within a cross-section of the composite can be calculated over time during the oxidation process. The effects of such important variables as temperature, diffusion coefficient, reaction rate constant, geometry, and environment can be investigated with the model. The reduction in carbon can be used to predict the composite strength reduction and failure.

As seen from oxidation studies, microstructural analysis, and model development, the oxidation of carbon occurs in two primary regimes, i.e., the diffusion-controlled regime and the reaction-controlled regime. In the reaction-controlled regime, there was a strong temperature dependence. In this regime, component lives were longer and strains to failure were lower in stressed oxidation tests and weight loss rates were lower in TGA tests compared to the trends for the other regime. Microstructural analysis of polished cross-sections tested under stress suggests and the model confirms that the material becomes saturated in oxygen. Due to the relatively slow oxygen/carbon reactions and the high oxygen concentration within the composite, oxidation occurred throughout the material. In the diffusion-controlled regime, there was less of a temperature dependence. In this regime, component lives were shorter and strains to failure were higher in stressed oxidation tests and weight loss rates were higher in TGA tests. Microstructural analysis of polished cross-sections tested under stress suggests and the model confirms that there was a sharp gradient in oxygen concentration from the edge up to the moving reaction front of oxidizing carbon with very low oxygen concentrations on the interior side of the reaction front. A shrinking core of the carbon fiber reinforcement was seen from the outer perimeter inward as oxidation progressed.

From a better understating of carbon fiber oxidation, ways to protect the fiber can be determined for different application conditions, such as environment, temperature, stress, and duration. The carbon fibers can be protected through several different approaches that target oxidation inhibition at either the fiber, interphase, matrix, external coating or a combination of these. Oxidation inhibited C/SiC materials were evaluated in TGA and stressed oxidation conditions. The inhibiting approaches consisted of boron-containing particulates in the matrix and/or a CBS (carbon-boron-silicon) external coating. The results show that the approaches were effective in prolonging life and retaining strength even when the C/SiC materials were under stress in a high temperature, oxidizing environment. The purpose of these oxidation inhibitors is to form glasses and solid oxides that seal cracks. However the methods were only effective in sealing cracks at the stress of 10 ksi and not at the higher stress of 25 ksi.

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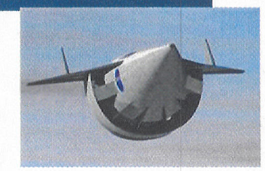
Tensile Test – SoRI

Oxidation Model Development and Theory – J. Cawley and A. Eckel

Outline

- Introduction - GRC Research in CMCs
  - C/SiC Cracks/Oxidation Pathways
  - Oxidation Kinetics
- Oxidation Studies of Carbon Constituents and C/SiC Composites
- Strength Reduction and Lifetime Tests of C/SiC Composites
- Modeling the Oxidation of Carbon Fibers in a Cracked Ceramic Matrix Composite
- Evaluation of Oxidation Inhibited C/SiC Composite Materials

NASA GRC's Role in Ceramic Material and Component Development



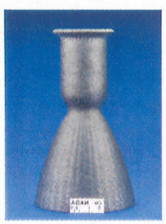
TRL	General NASA Definitions
9	Actual system "flight proven" on operational flight
8	Actual system completed and "flight qualified" through test and demonstration
7	System prototype demonstrated in flight environment
6	System/Subsystem model or prototype demonstrated/validated in a relevant environment
5	Component and/or breadboard verification in a relevant environment
4	Component and/or breadboard test in a laboratory environment
3	Analytical and experimental critical function, or characteristic proof-of-concept
2	Technology concept and/or application formulated (candidate selected)
1	Basic principles observed and reported

System Test and Operations

System/Subsystem Development

Technology Demonstration

Technology Development

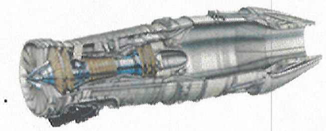


Research to Prove Feasibility

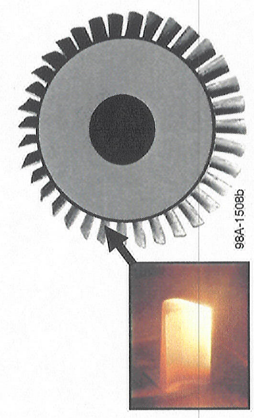
Basic Technology Research

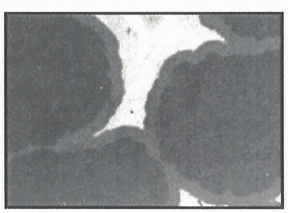
System/Subsystem Development

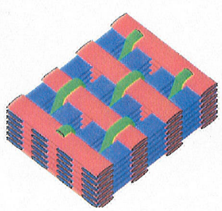
Industry Role

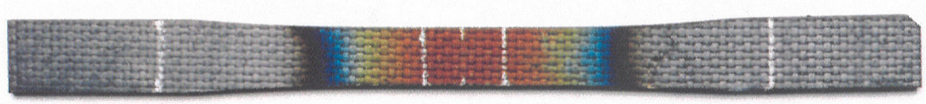


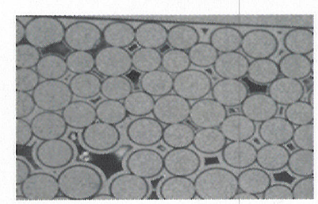
Government Role



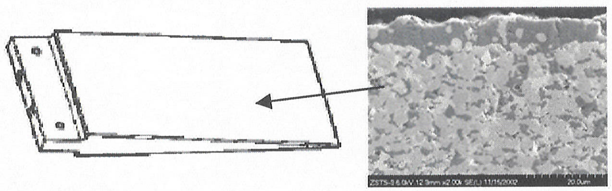
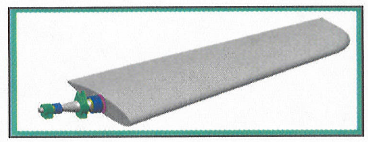
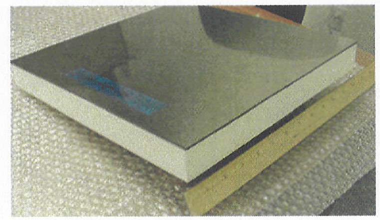
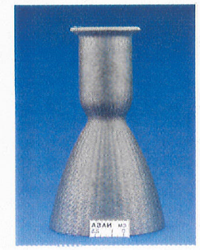
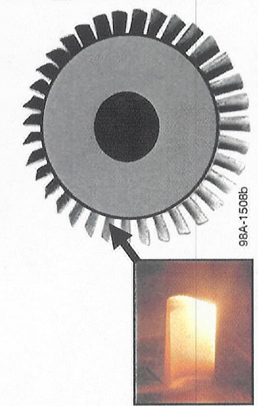








Potential Applications for CMC Components in Aerospace

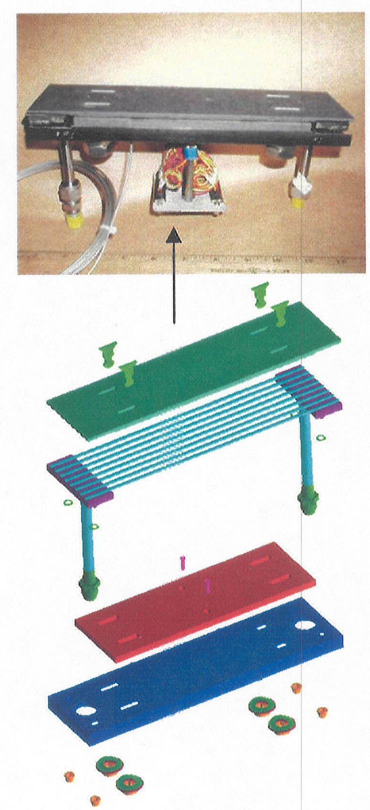
AIRFRAME

Leading Edges: Blunt, sharp, and cooled leading edges, nose and nose skirt

Hot Structures: Control surfaces, elevons, ruddervators, flaperons, body flaps, integrated panels

Acreage Surfaces: Windward TPS panels

Seals: TPS seals, control surface seals, penetration seals



PROPULSION

Turbomachinery Components: Inserted blades, blisks, stators and rotors, gas path ducting, tip seals, and housings

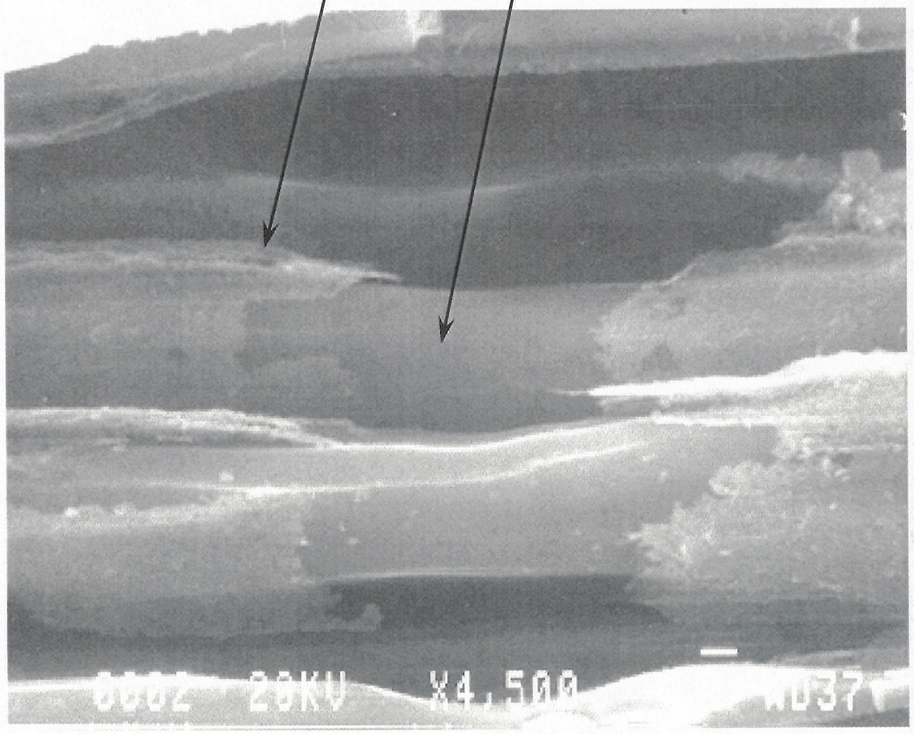
Actively-cooled Components: Cooled panel heat exchangers and combustion chambers (hot gas flow path), nozzles (ramps, bells, extensions), and manifolds

Uncooled Thin Wall Structures: Nozzles (radiation cooled), combustion chambers, manifolds, thrust cells, and ducts

Cracks Acting As Oxygen Diffusion Paths

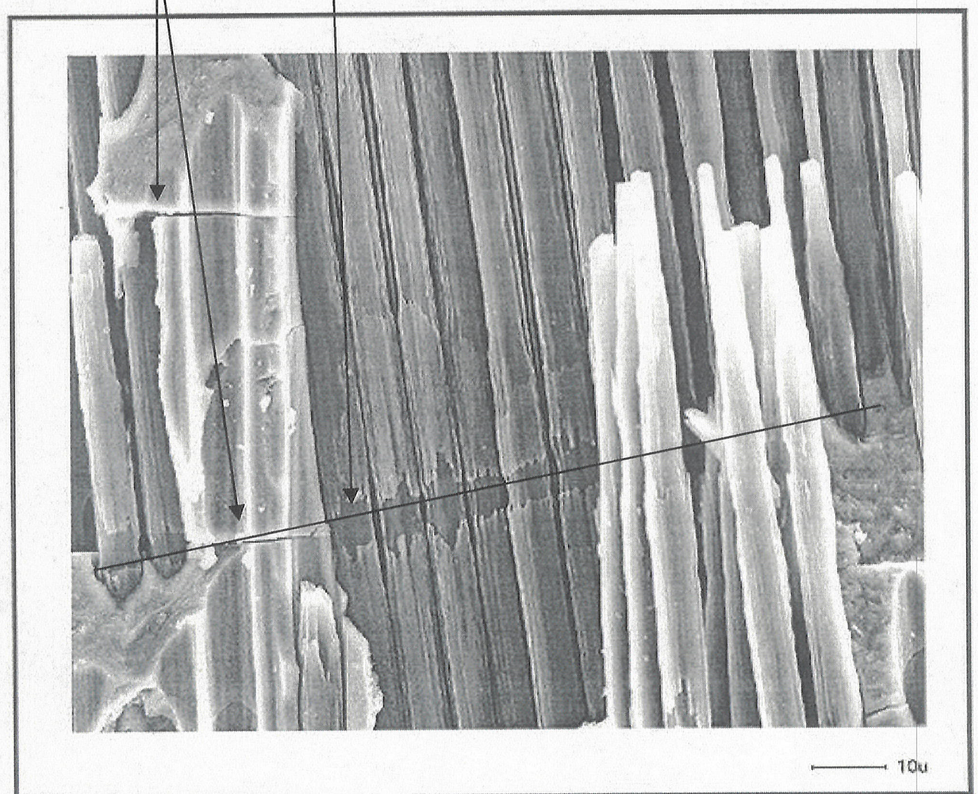
Pyro-Carbon Interphase

Carbon Fiber



SiC Matrix Cracks

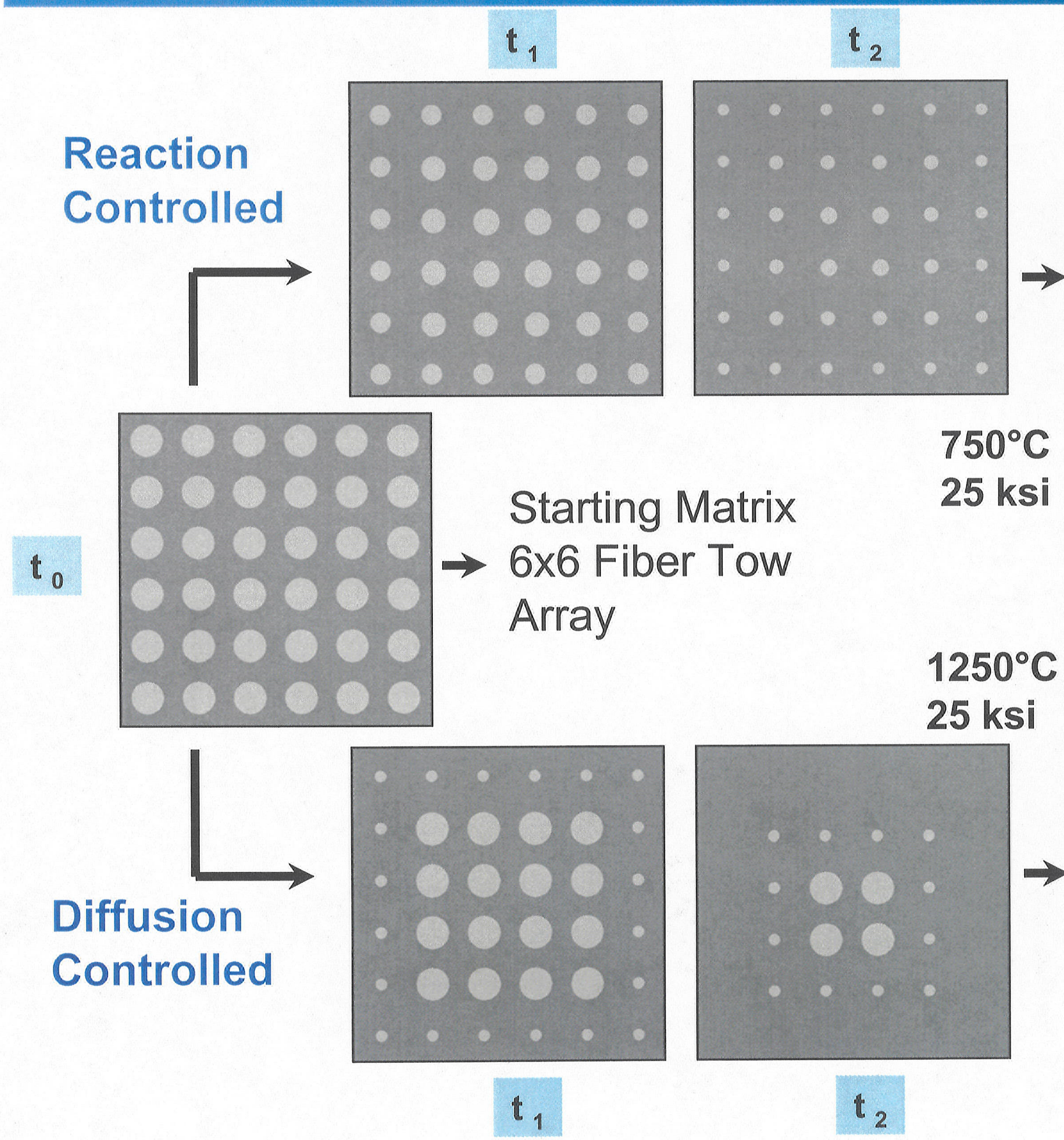
Oxygen Diffusion Path



550ºC (1022ºF), 25 ksi (172MPa)
Fracture surface

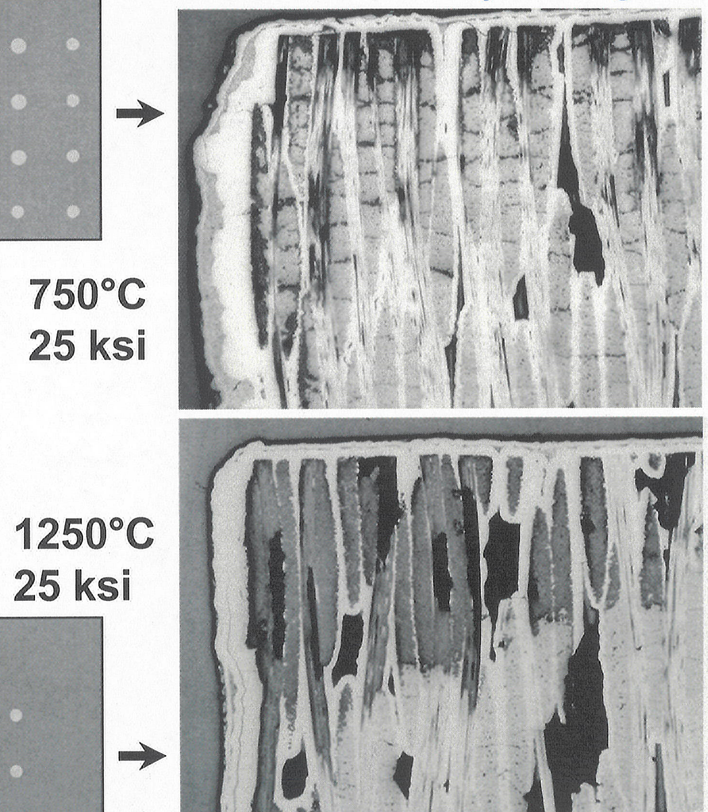
1454ºC (2650ºF), 10 ksi (69MPa)
Fracture surface

Oxidation Kinetics Regimes



Low Temperature Regime

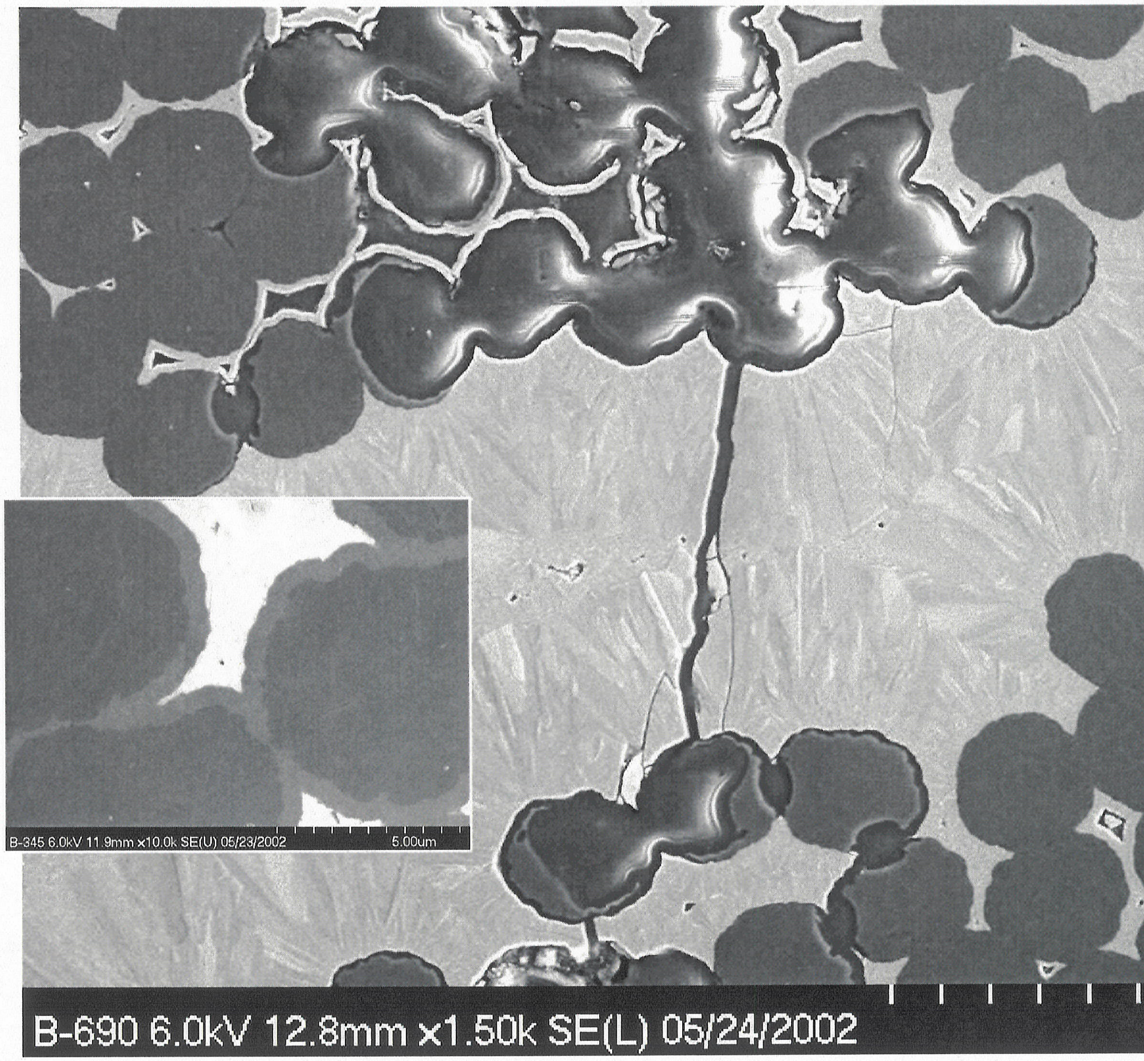
- Controlled by C/O_2 reactions
- Entire section saturated in O_2
- Similar reactivity throughout

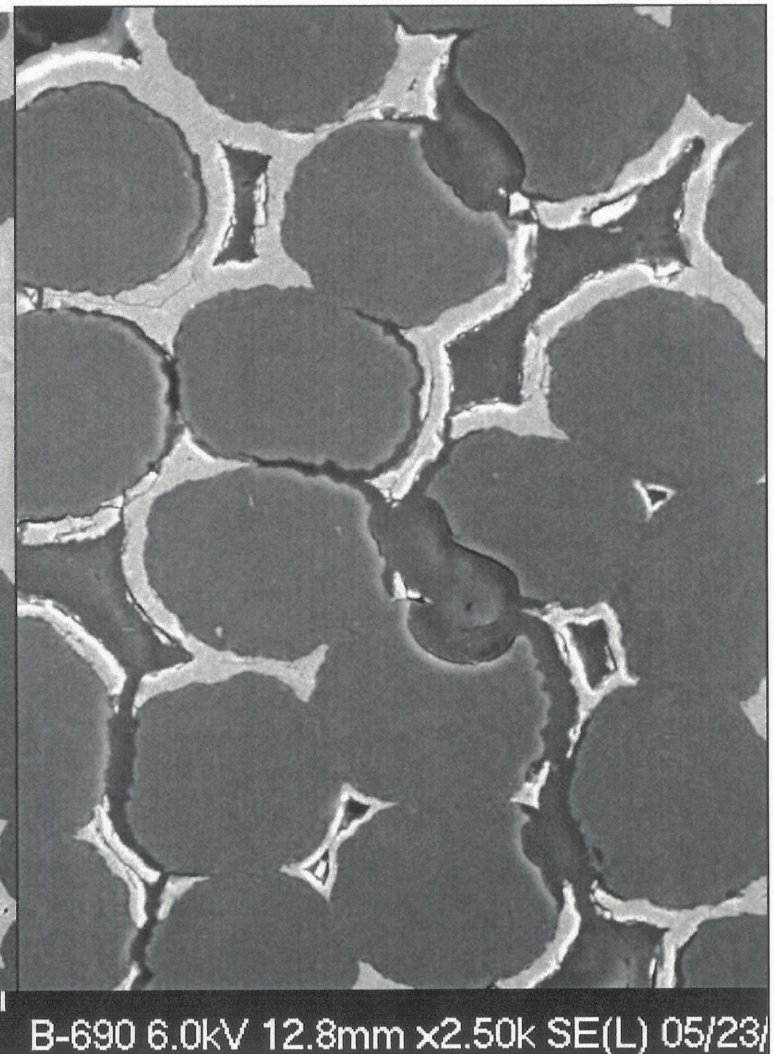


High Temperature Regime

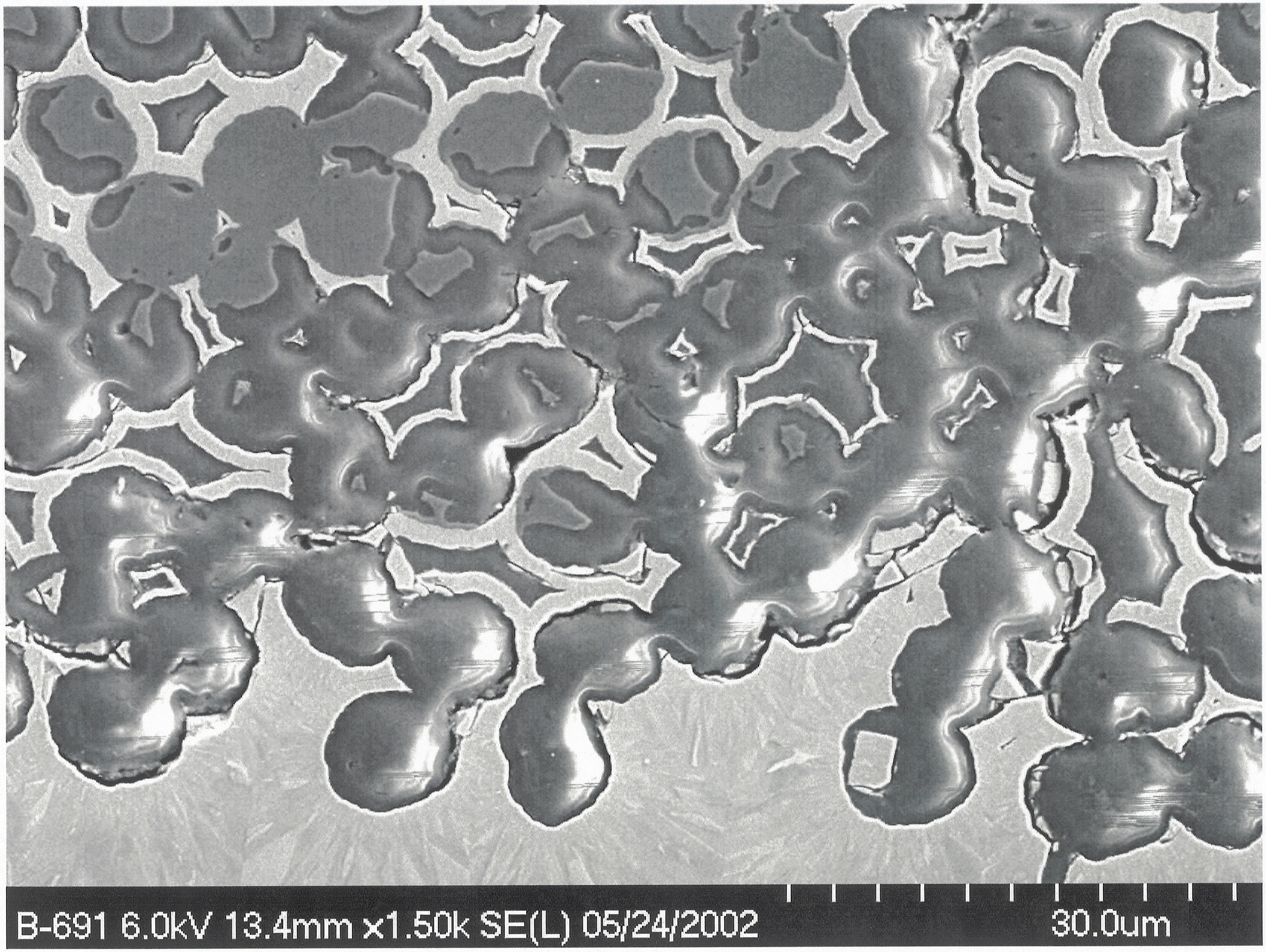
- Controlled by oxygen supply
- Large gradient in O_2 conc.
- Moving reaction front, shrinking core

Oxidation of Carbon Constituents at 800ºC in Oxygen – Failure under a stress of 20 ksi (polished cross-section)



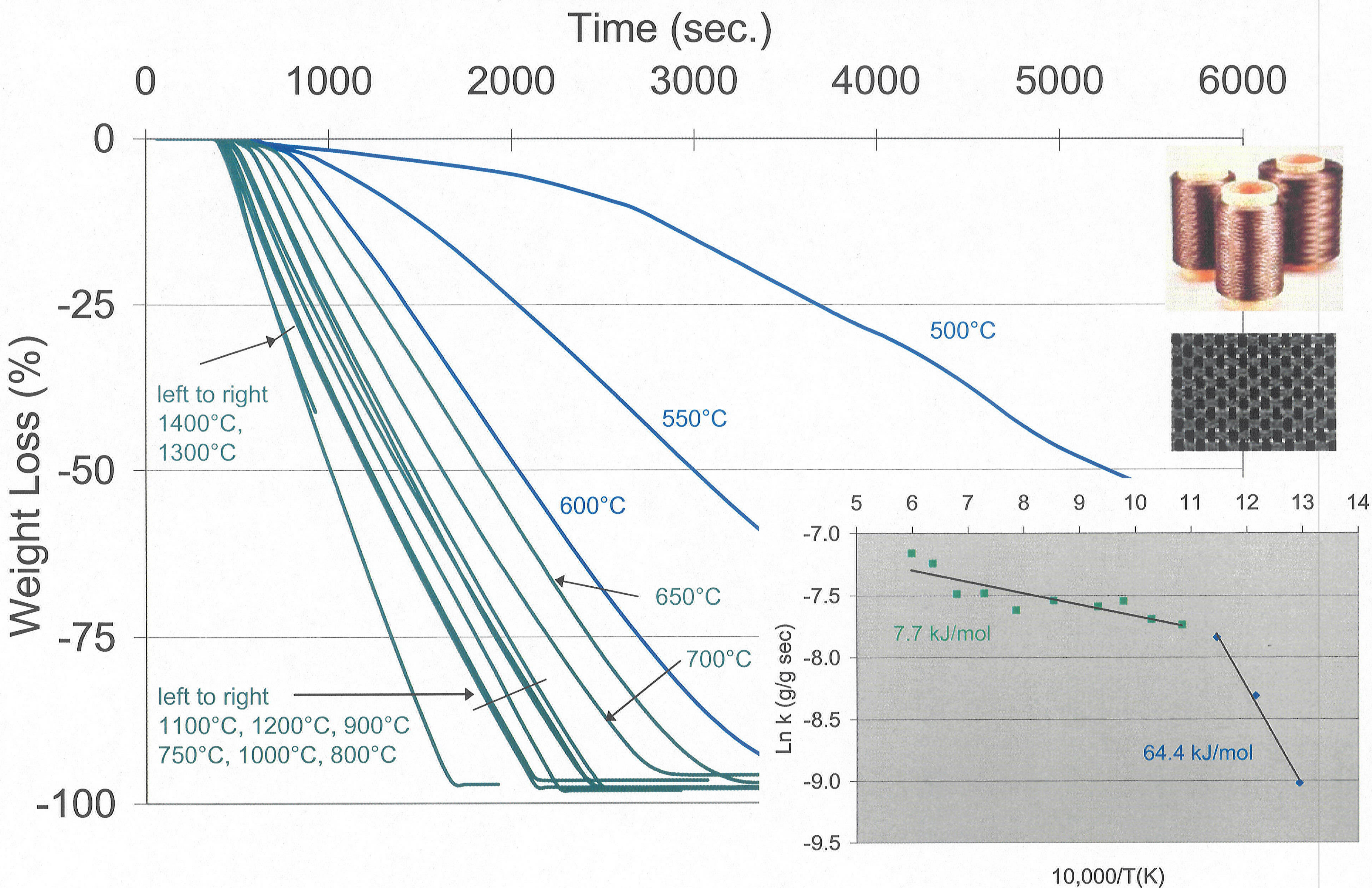


Oxidation of Carbon Constituents at 1200ºC in Oxygen – Failure under a stress of 20 ksi (polished cross-section)



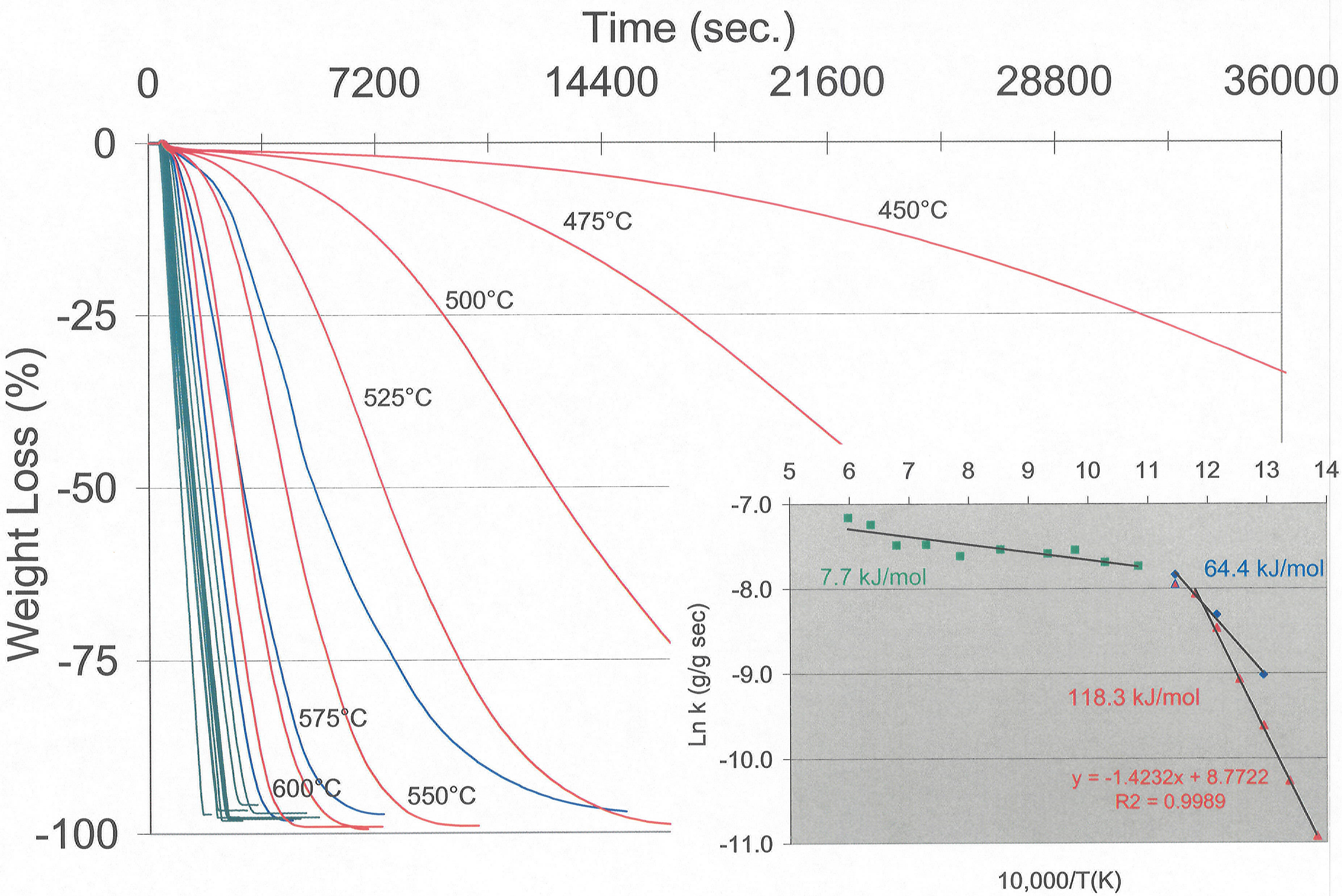
Thermogravimetric Analysis of Uncoated T300 Carbon Fiber

Percent Weight Loss in Oxygen Versus Time



Additional TGA Data of Uncoated T300 Carbon Fiber

Percent Weight Loss Versus Time (oxygen flowing at 100ccm)



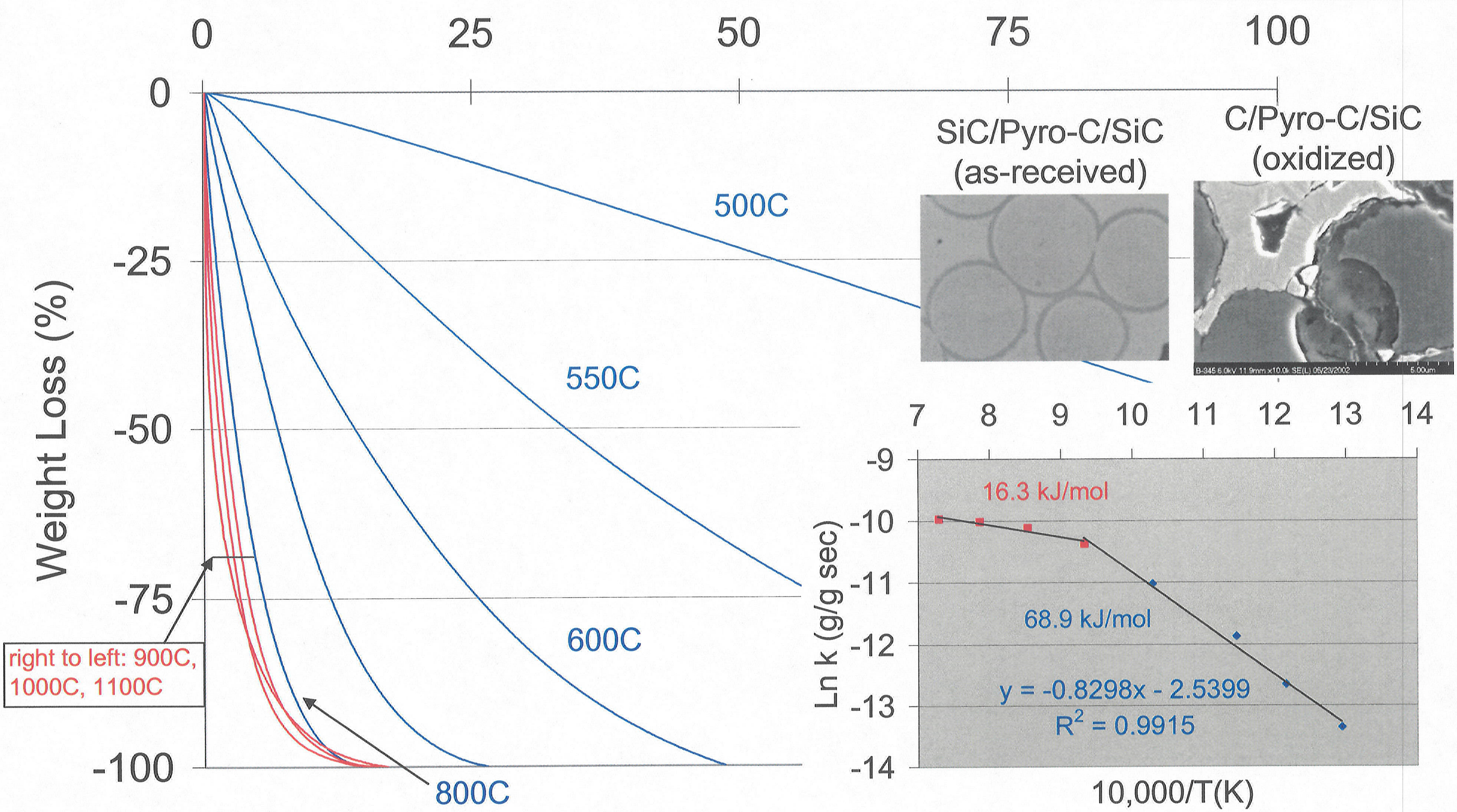
Thermogravimetric Analysis of Pyro-Carbon Interphase

Percent Weight Loss Versus Time (oxygen flowing at 100ccm)

SiC/SiC coupons with machined edges: the pyro-carbon interphase is oxidized in a flowing oxygen environment. The interphase is 3 wt % of the composite (approximately 0.08 grams).

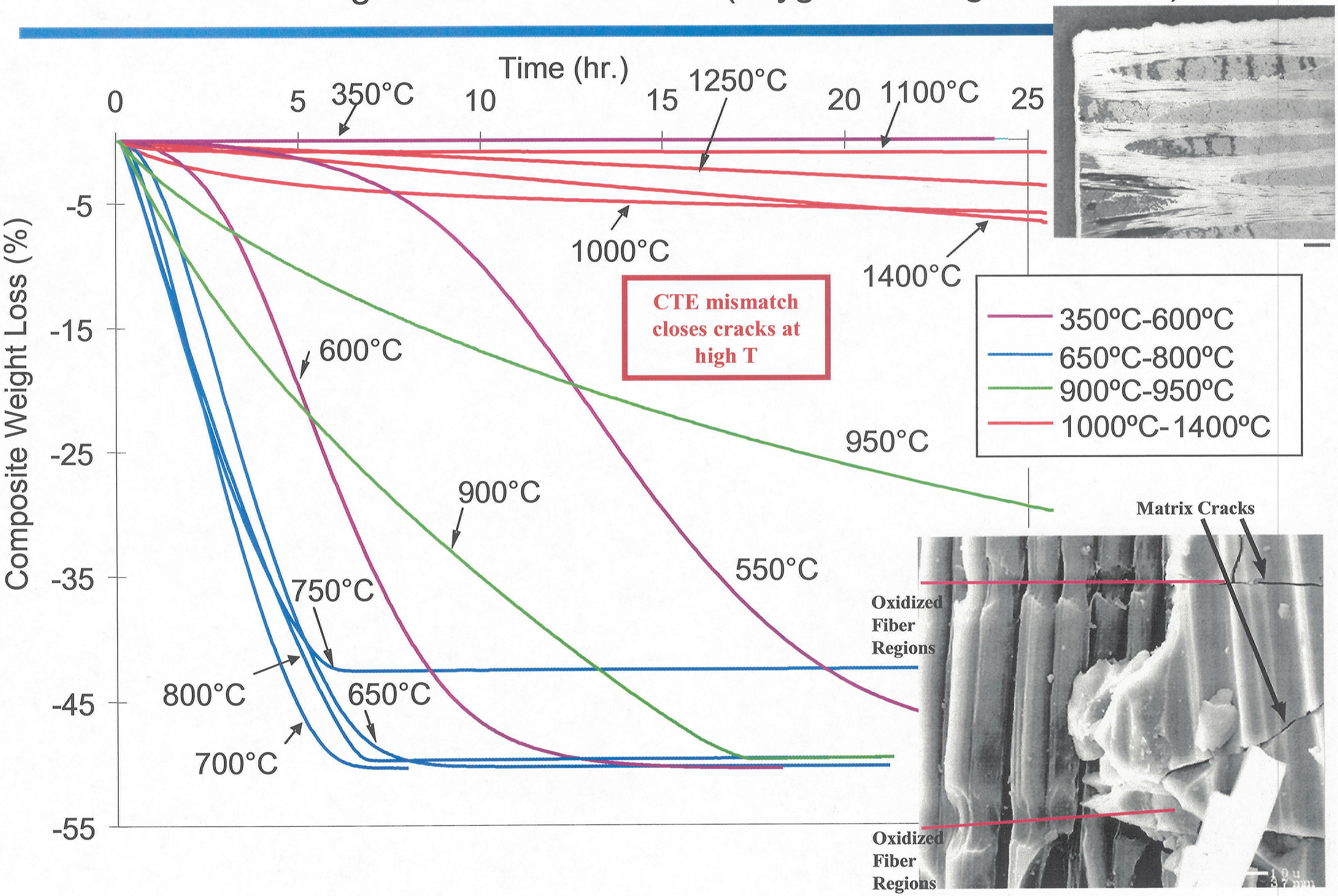
Note: rates are also dependant on the amount of interphase exposed to the environment (i.e. at cracks, voids, and pores)

Time (hr)

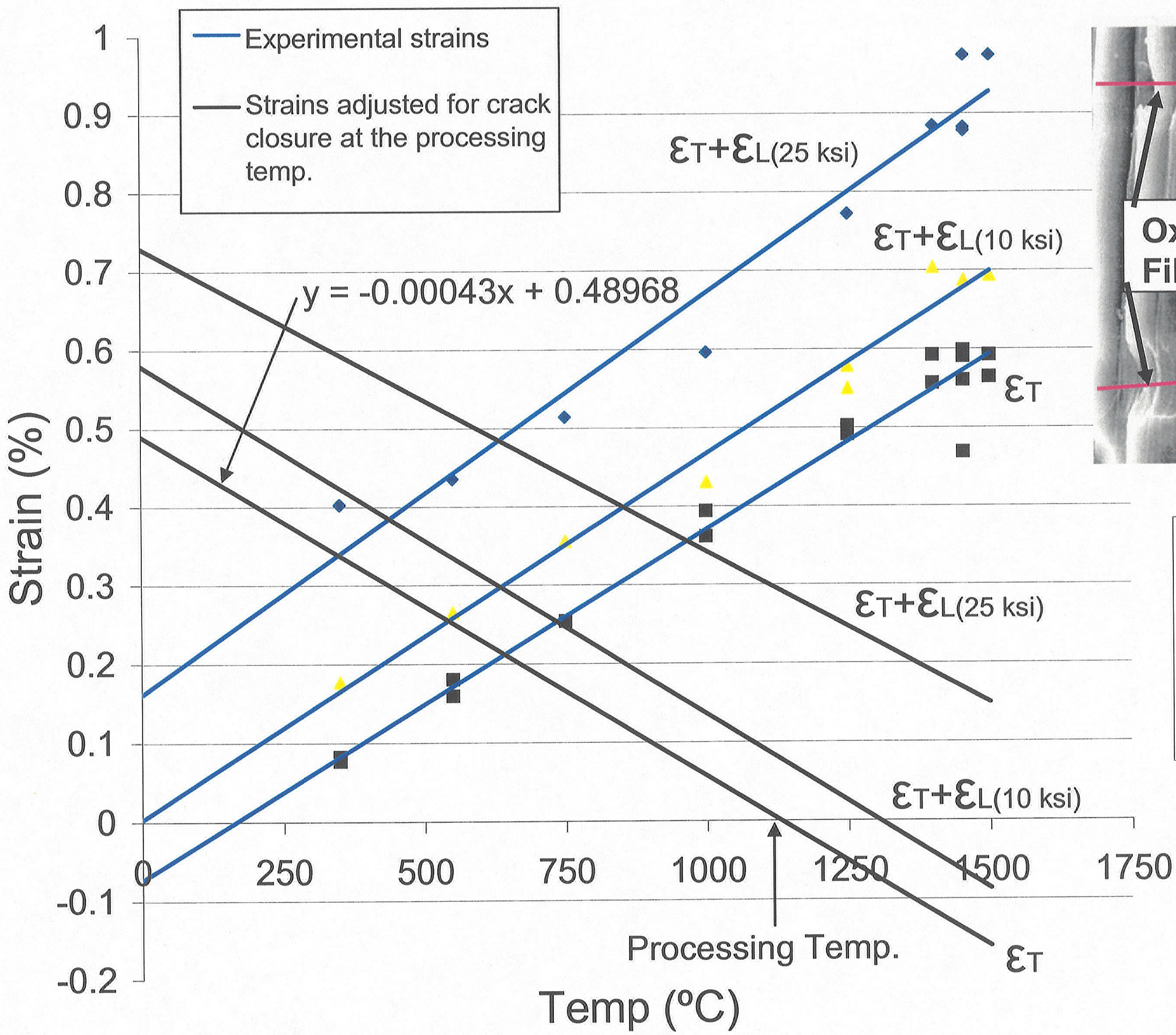


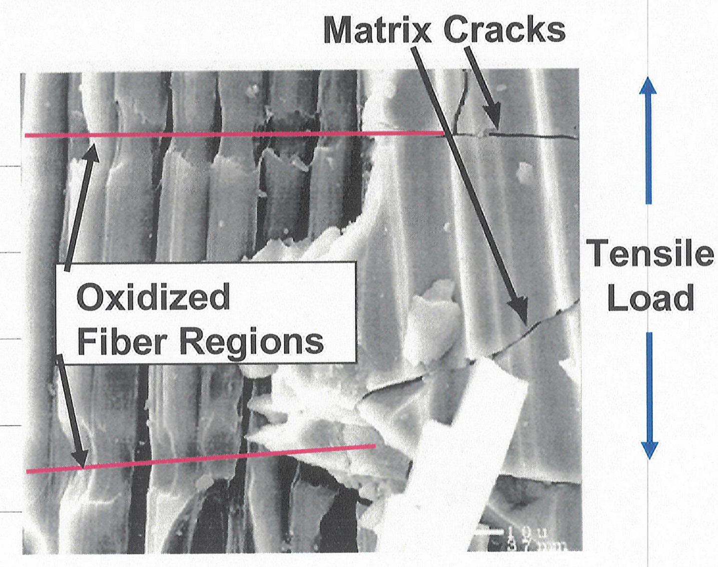
Thermogravimetric Analysis of C/SiC Coupons

Percent Weight Loss Versus Time (oxygen flowing at 100ccm)



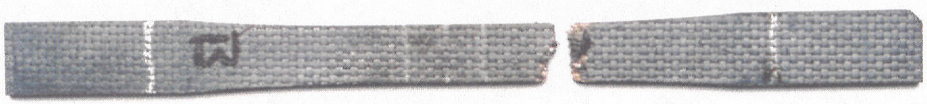
Crack Opening Determined by Thermal and Load Strain



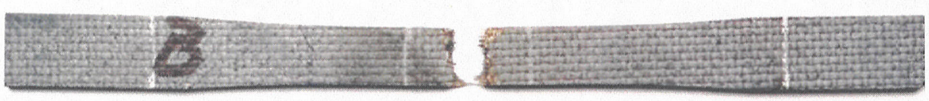


Fractured Test Coupons From Stressed Oxidation Tests in Air

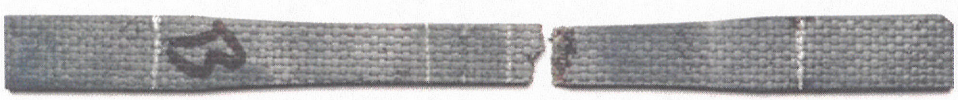
800°C 35 MPa / 69 MPa / 138 MPa
(1498ºF 5 ksi / 10 ksi / 20 ksi)



F6706
800C/5 ksi

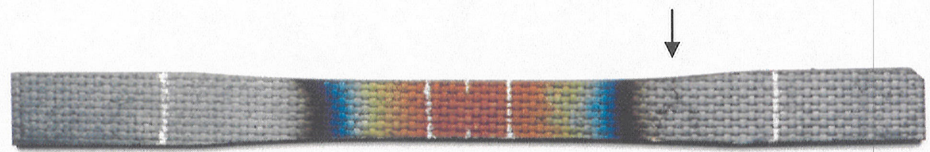


F6704
800C/10 ksi

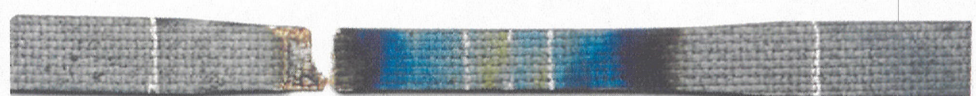


F6702
800C/20 ksi

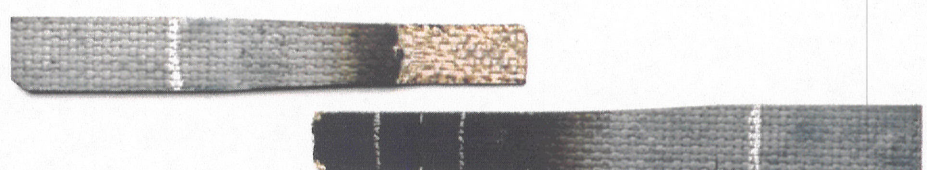
1200°C 35 MPa / 69 MPa / 138 MPa
(2218ºF 5 ksi / 10 ksi / 20 ksi)



F6705
1200C/5 ksi



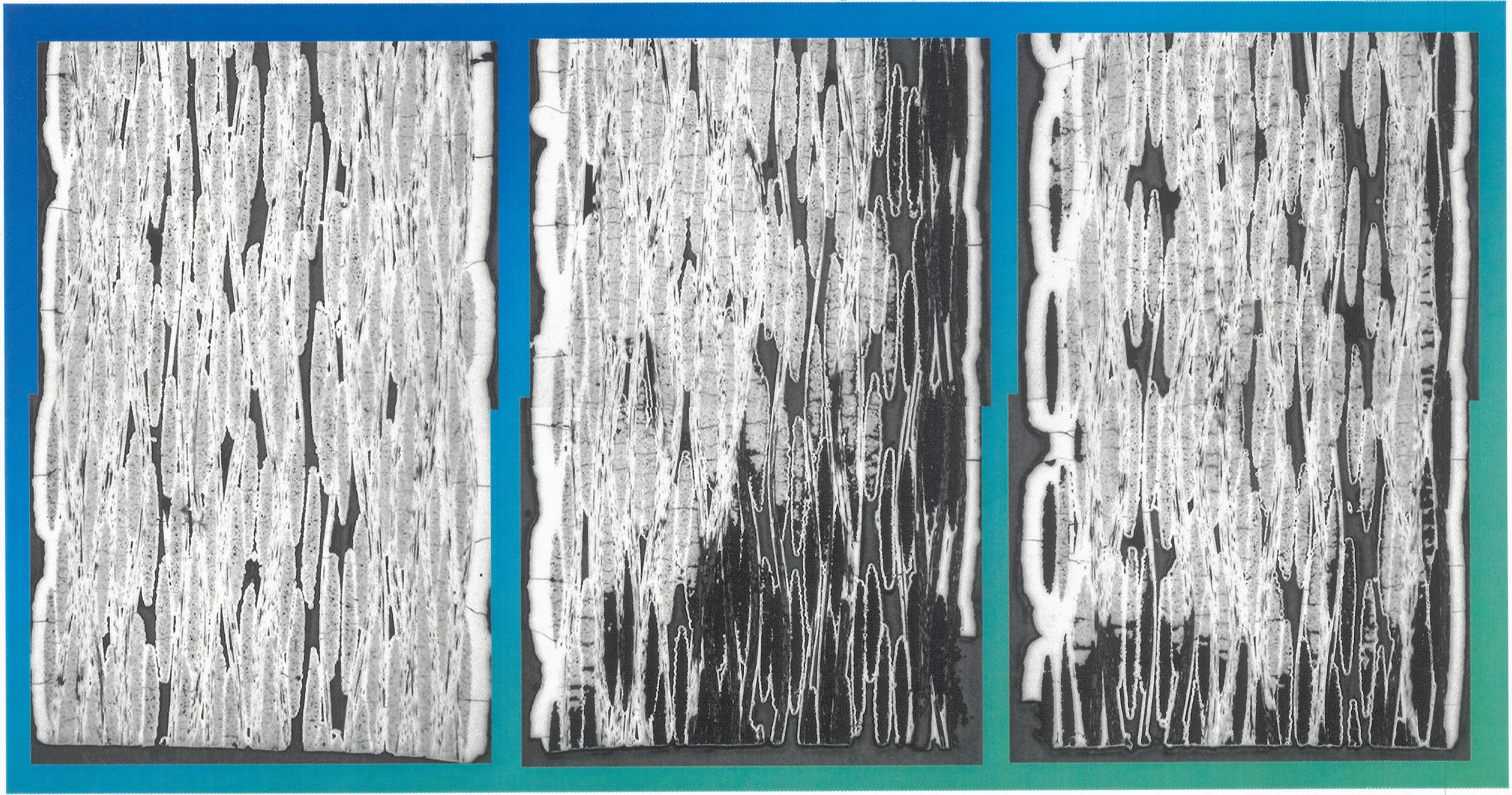
F6703
1200C/10 ksi



F6701
1200C/20 ksi

In Air at 1200°C

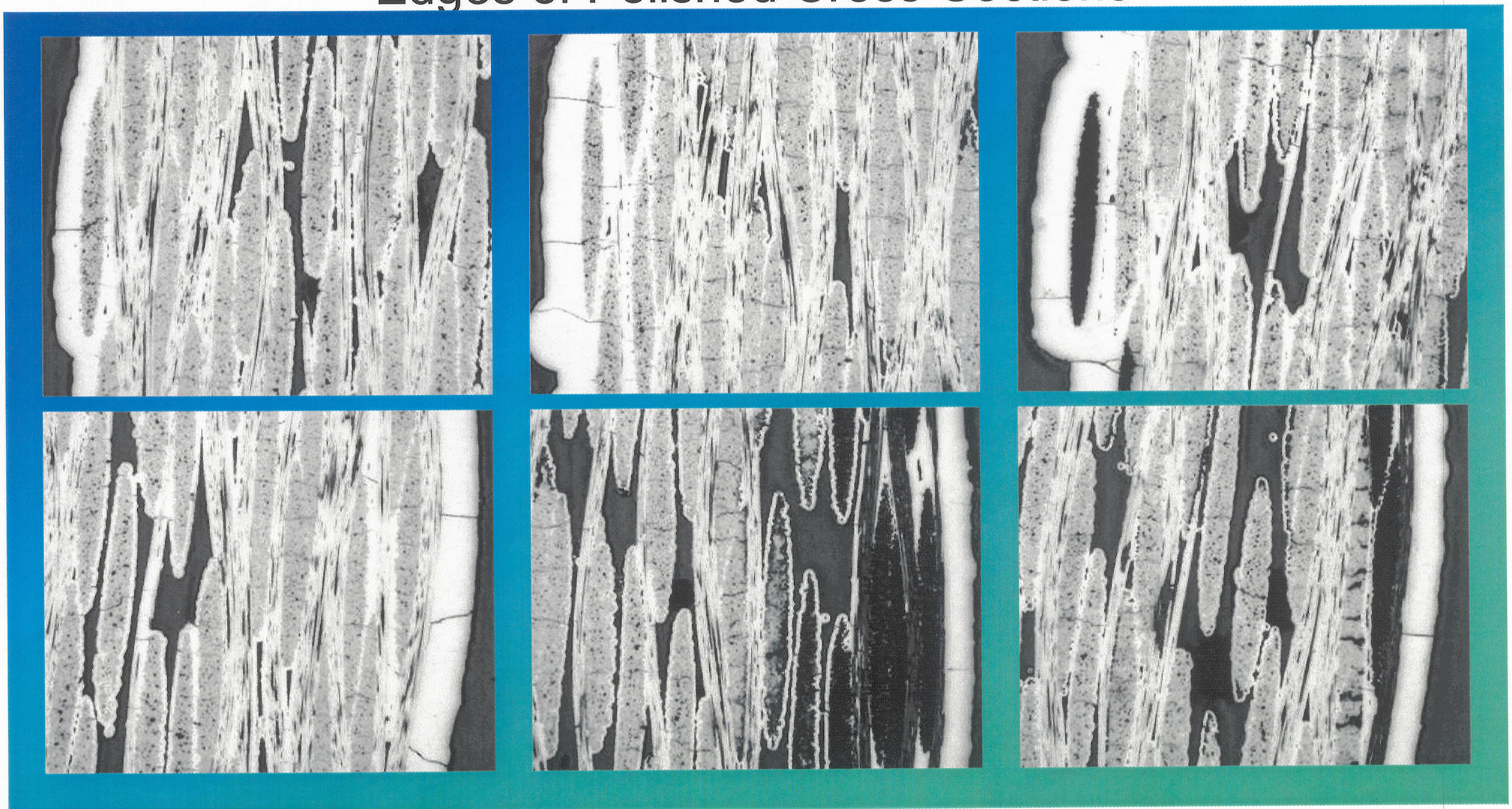
Polished Cross-Section from Gage (section width ~ 0.13")



Stress (MPa):	35	69	138
Time to Failure (hr):	5.07	2.33	0.48
Failure Location:	TG	Thermal Gradient (TG)	Gage

In Air at 1200°C

Edges of Polished Cross-Sections



Stress (MPa):	35	69	138
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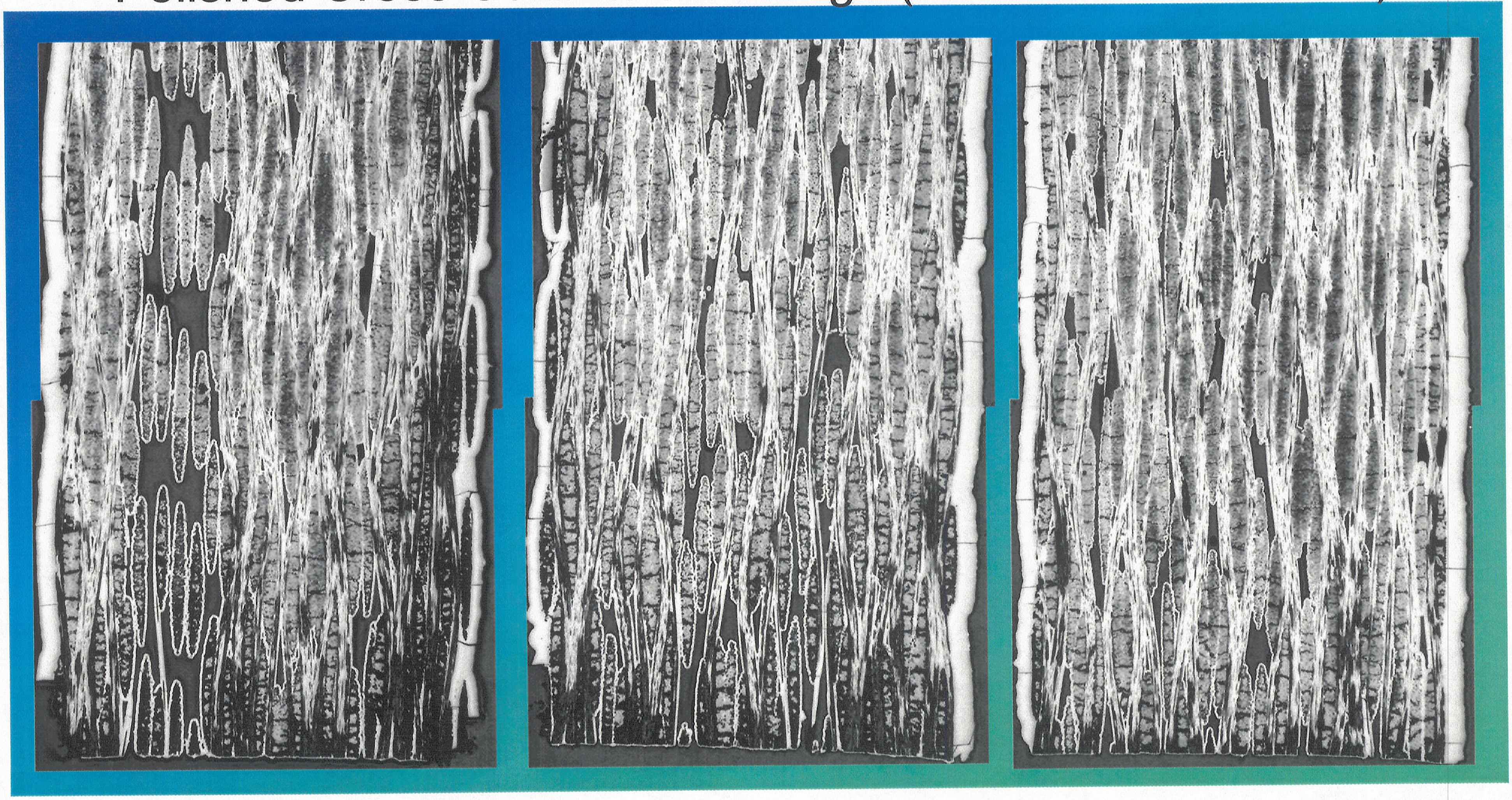
In Air at 800°C

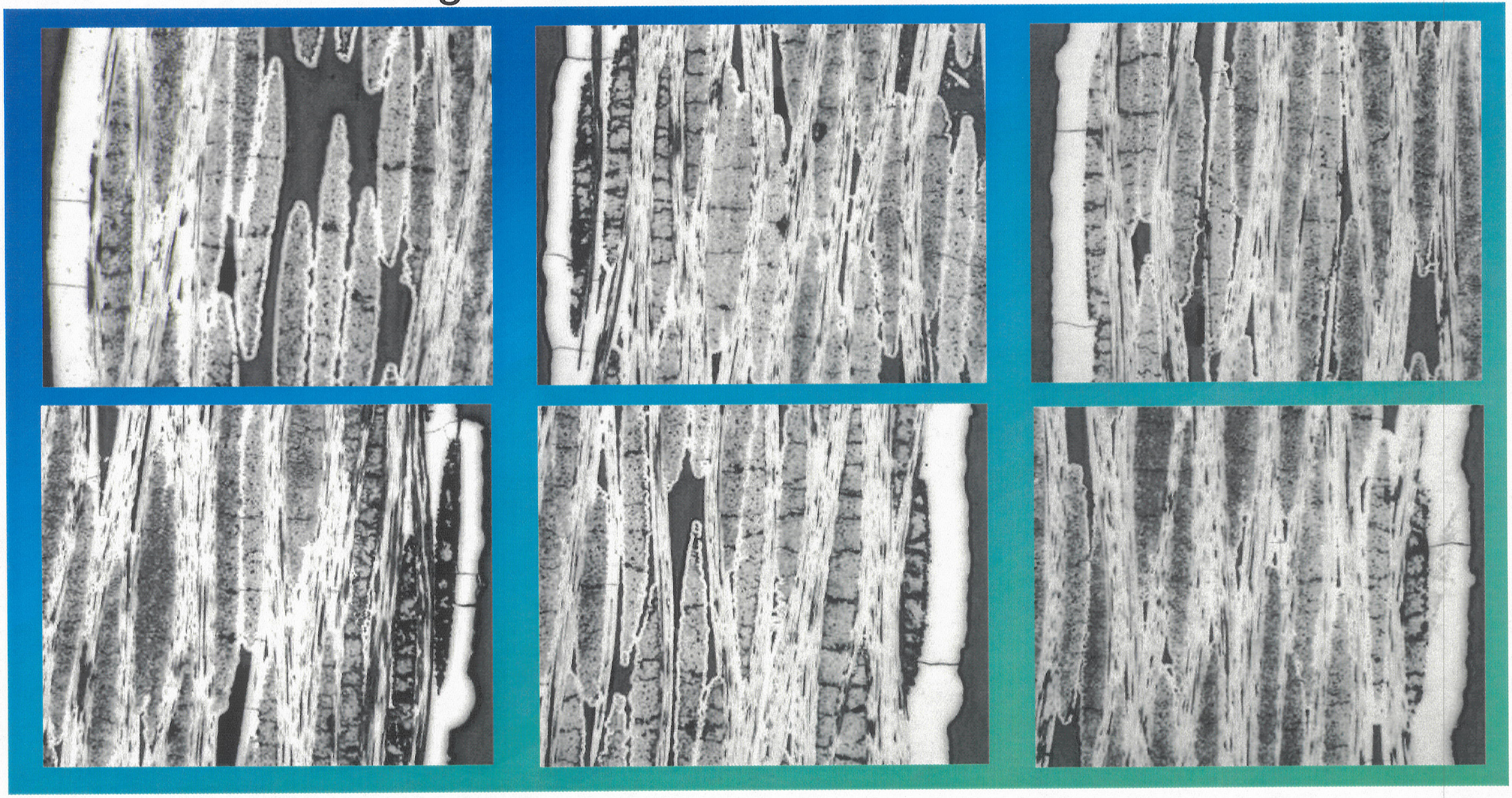
Polished Cross-Section from Gage (section width ~ 0.13")



Stress (MPa):	35	69	138
Time to Failure (hr):	5.70	2.48	0.83
Failure Location:	Gage	Gage	Gage

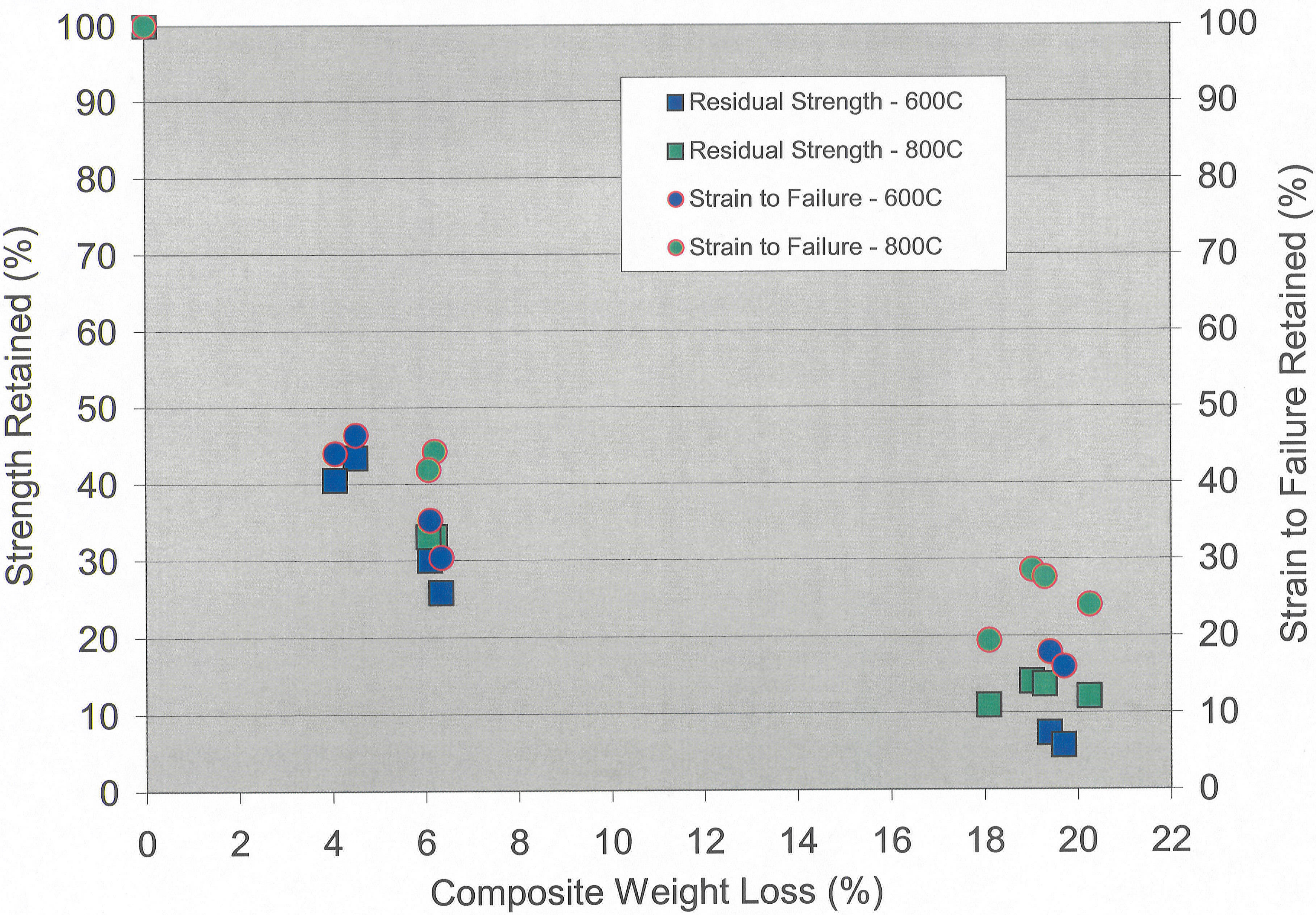
In Air at 800°C

Edges of Polished Cross-Sections



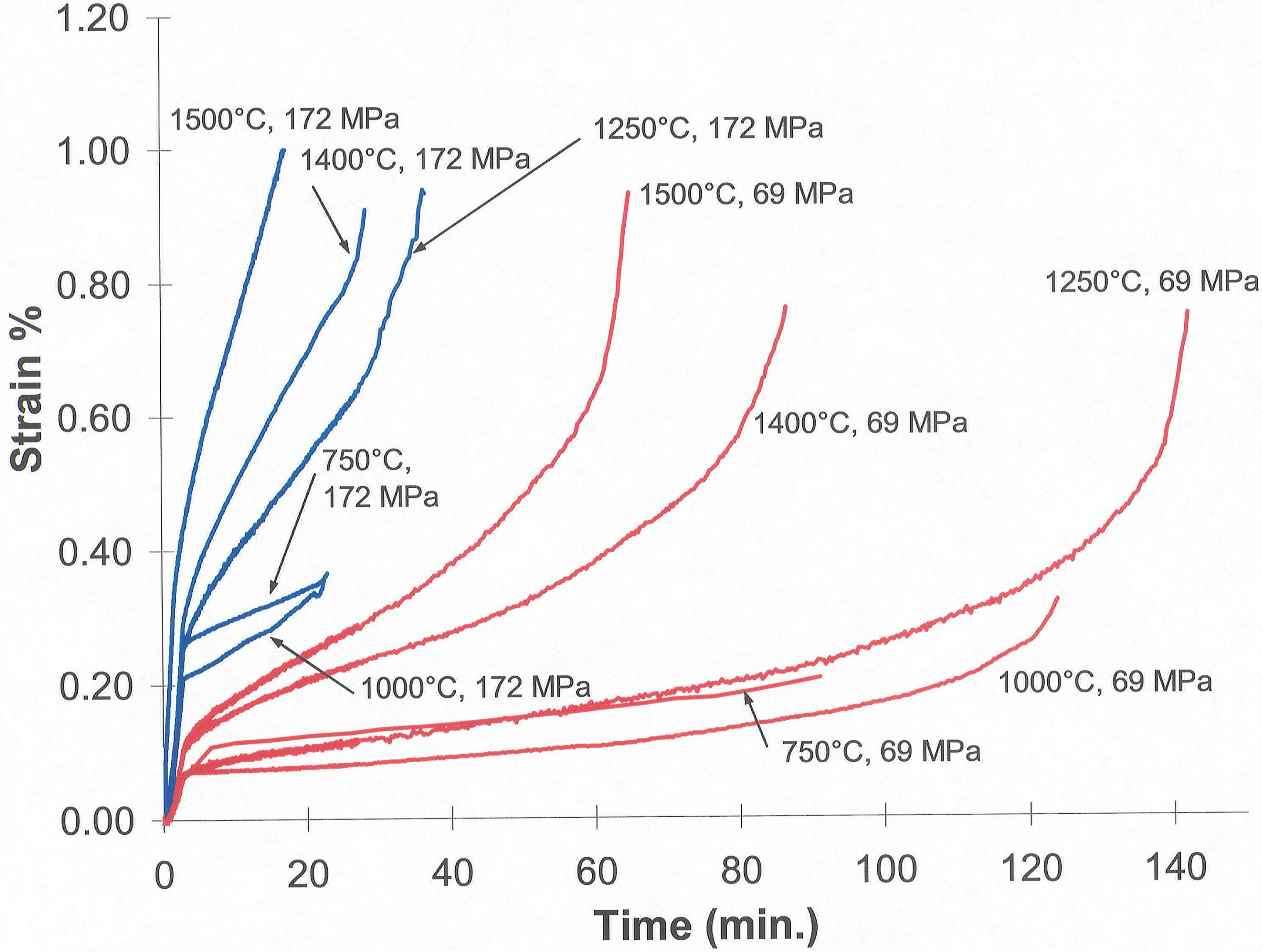
Stress (MPa):	35	69	138
Time to Failure (hr):	5.70	2.48	0.83
Failure Location:	Gage	Gage	Gage

Strength Retained and Strain to Failure After Tensile Coupon Oxidation Exposures



Stressed Oxidation/Creep Rupture of C/SiC in Air

Temperatures from 750ºC-1500ºC, Stresses of 69 and 172 MPa (10 and 25 ksi)



Acknowledgements to David N. Brewer (ARL) and Ralph J. Pawlik (QSS) at NASA GRC for conducting stressed oxidation tests.

C/SiC OXIDATION MODEL

Approach:

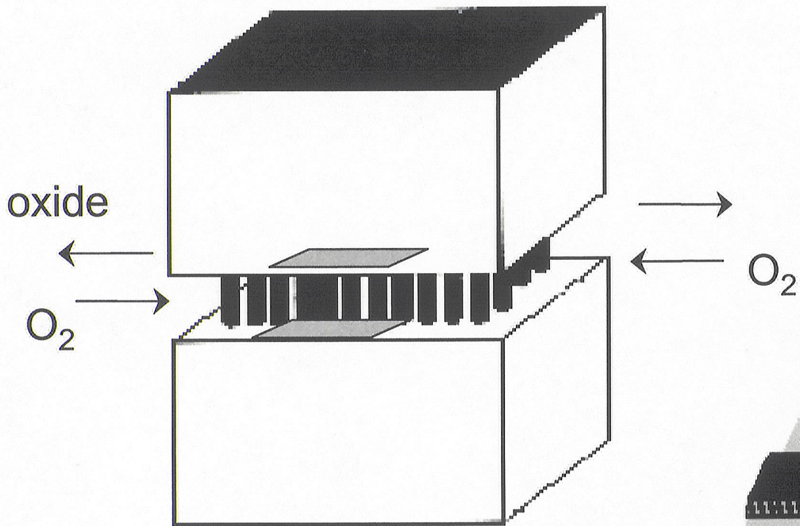
Use a 2-D finite difference model that is physics based to simulate the oxidation of carbon fiber cross-sections in a cracked ceramic matrix composite.

Use theoretically and experimentally based variables in the model to keep track of oxygen concentrations and carbon recession and the time for carbon reactions.

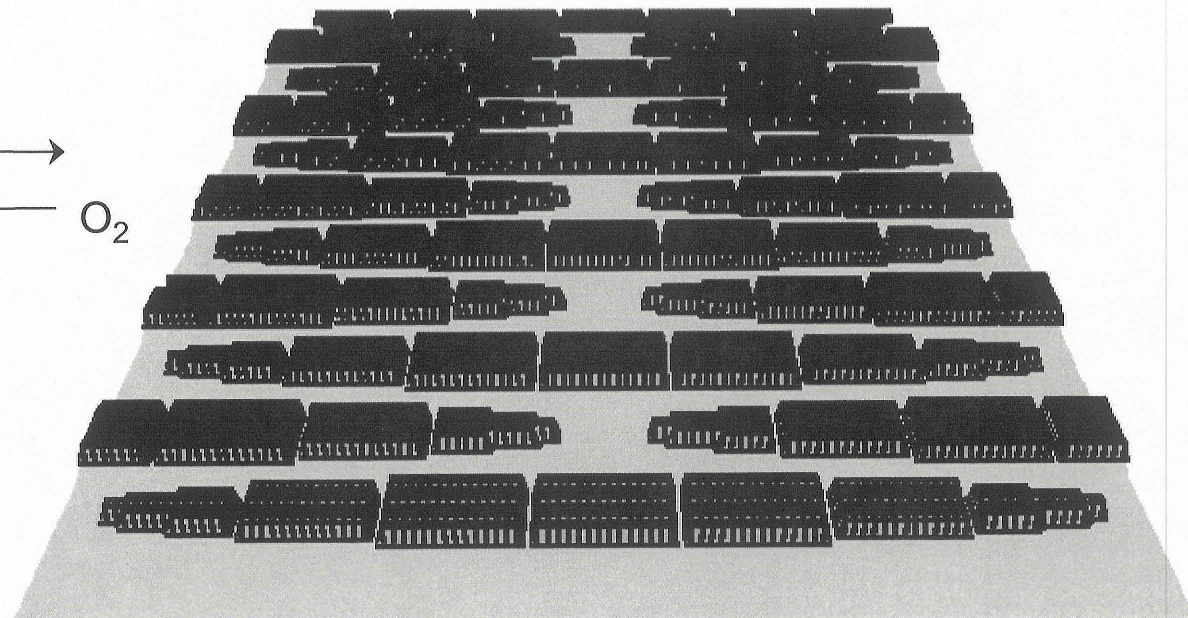
Product:

A model that predicts a composite's strength reduction and/or time to failure based on the oxidation of load bearing fibers for such application variables as environment, temperature, and stress.

CRACKED COMPOSITE AND MODEL REPRESENTATION



Center of the composite



Front edge of the composite

One crack throughout the section is bridged by fiber tows and runs parallel to the gray plane. Also cracks perpendicular to the overall crack run through the individual fiber tows.

LINEAR-PARABOLIC OXIDATION KINETICS

$$\frac{x}{k_P}^2 + \frac{x}{k_l} = t$$ Linear and Parabolic Contributions

$$k_l = \left(\frac{1}{N}\right)(\chi\, C_T)(K)$$ Linear Rate Constant

$$k_l = \left(\frac{1}{N}\right)\left(\frac{\chi P}{RT}\right)\left\{k_o \exp\left(\frac{-Q}{RT}\right)\right\}$$

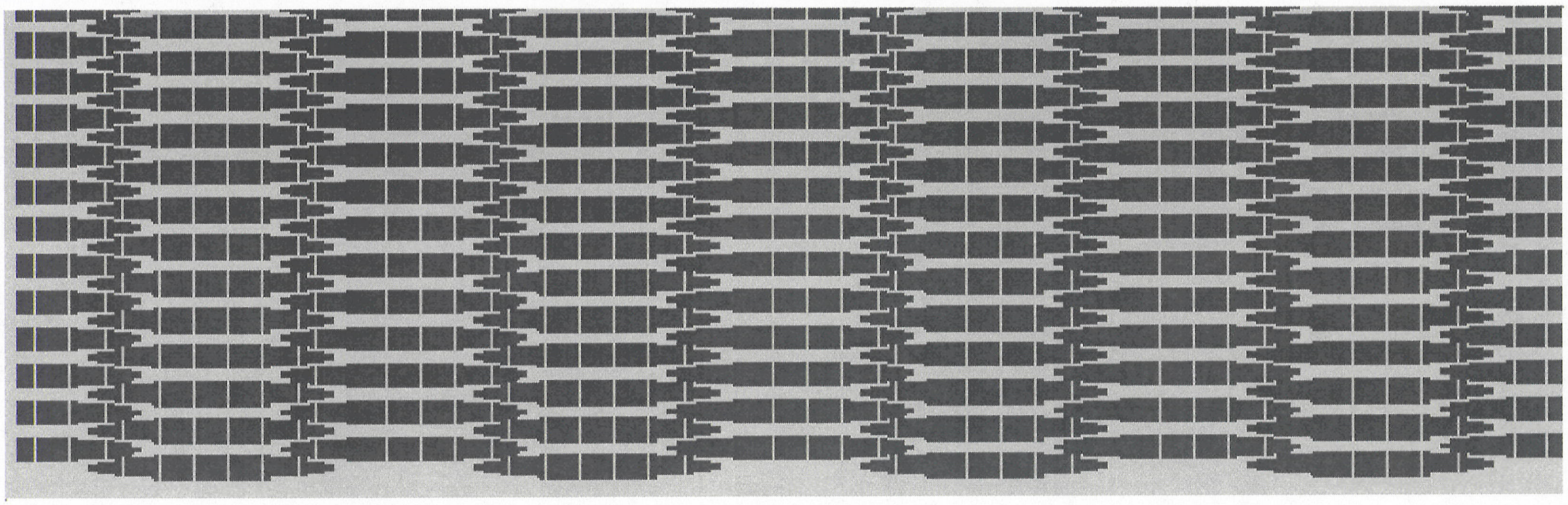
$$k_p = \frac{2\, D\, C_T}{N}$$ Parabolic Rate Constant

$$k_p = \left(\frac{4\, D\, C_T}{N}\right) \ln\left\{\frac{[(1+\chi)(D_k / D)+1]}{[(D_k / D)+1]}\right\}$$ $0_2 + 2C \Rightarrow 2CO$ and Knudsen Diff.

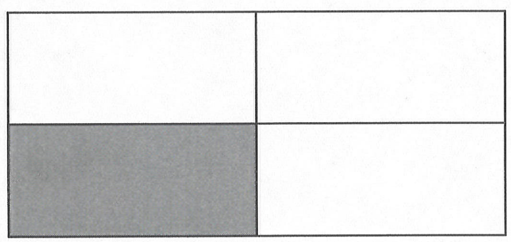
$$D = \frac{5.9543x10^{-24}\,[(1/M_A)+(1/M_B)]^{1/2}\, T^{3/2}}{(P\sigma_{AB}{}^2\Omega_{AB})}$$ Diffusion Coefficient

$$D_k = 8.575 T^{1/2} d$$ Knudsen Diffusion Coefficient

Model Representation



Model ¼ section



D_{eff} = effective diffusion coefficient

ϵ = open void fraction (porosity)

D_{AB} = interdiffusion coefficient

k_t = tortuosity factor

Representation allows for recession at both edges to be modeled.
Use different tortuousity factors for diffusion in the x and y directions.

$$D_{eff} = \frac{\epsilon D_{AB}}{k_t^{2}}$$

Also allows for layout to be easily changed for different specimen geometries (volume and edge effect studies).

Quarter section is 161 x 509 grids, Tow array is 8 x 13, Cracked elliptical tows are 8 x 80 grids.

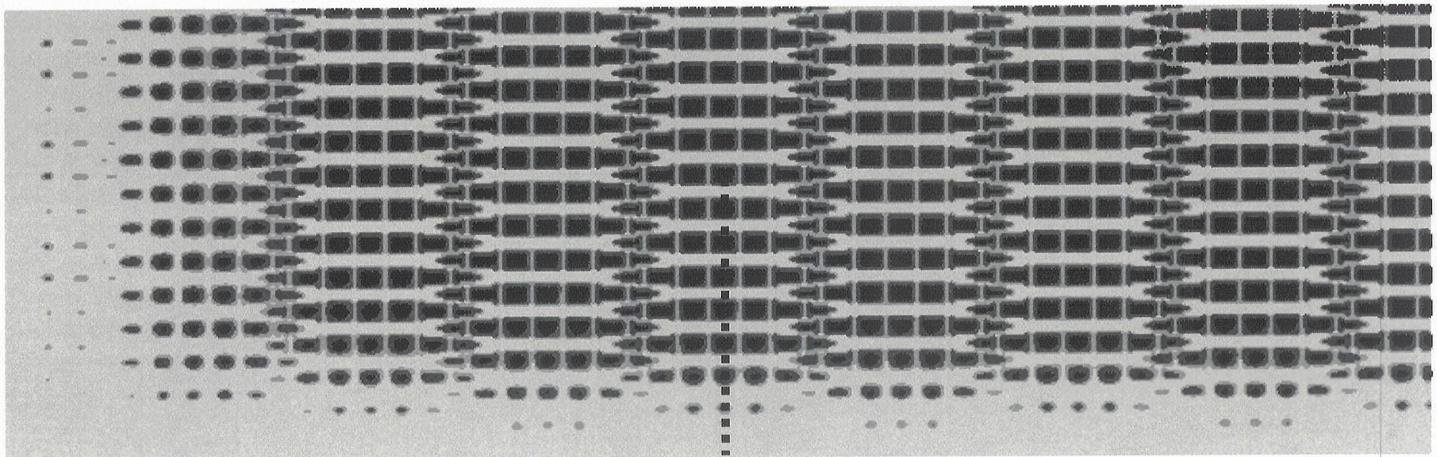
Results from the Oxidation Model - Oxidation Patterns

800ºC

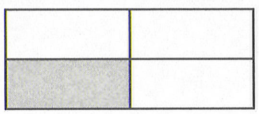
1000 ppm Oxygen

25% Carbon Reacted
Time: 79.1 hr.

39.6% of the carbon grids are flawed.



Modeled Composite Cross-Section

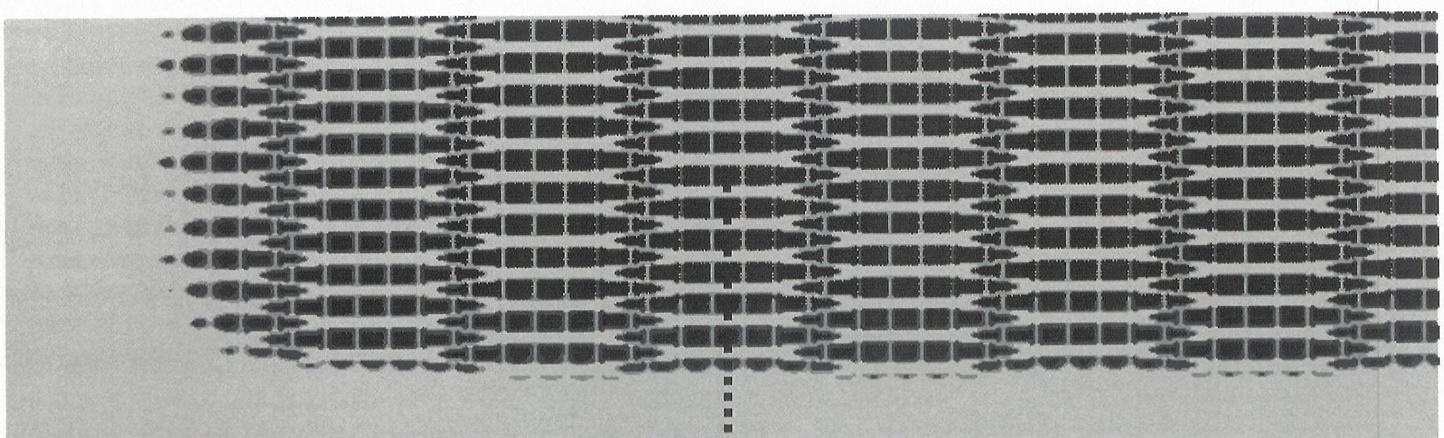


1200ºC

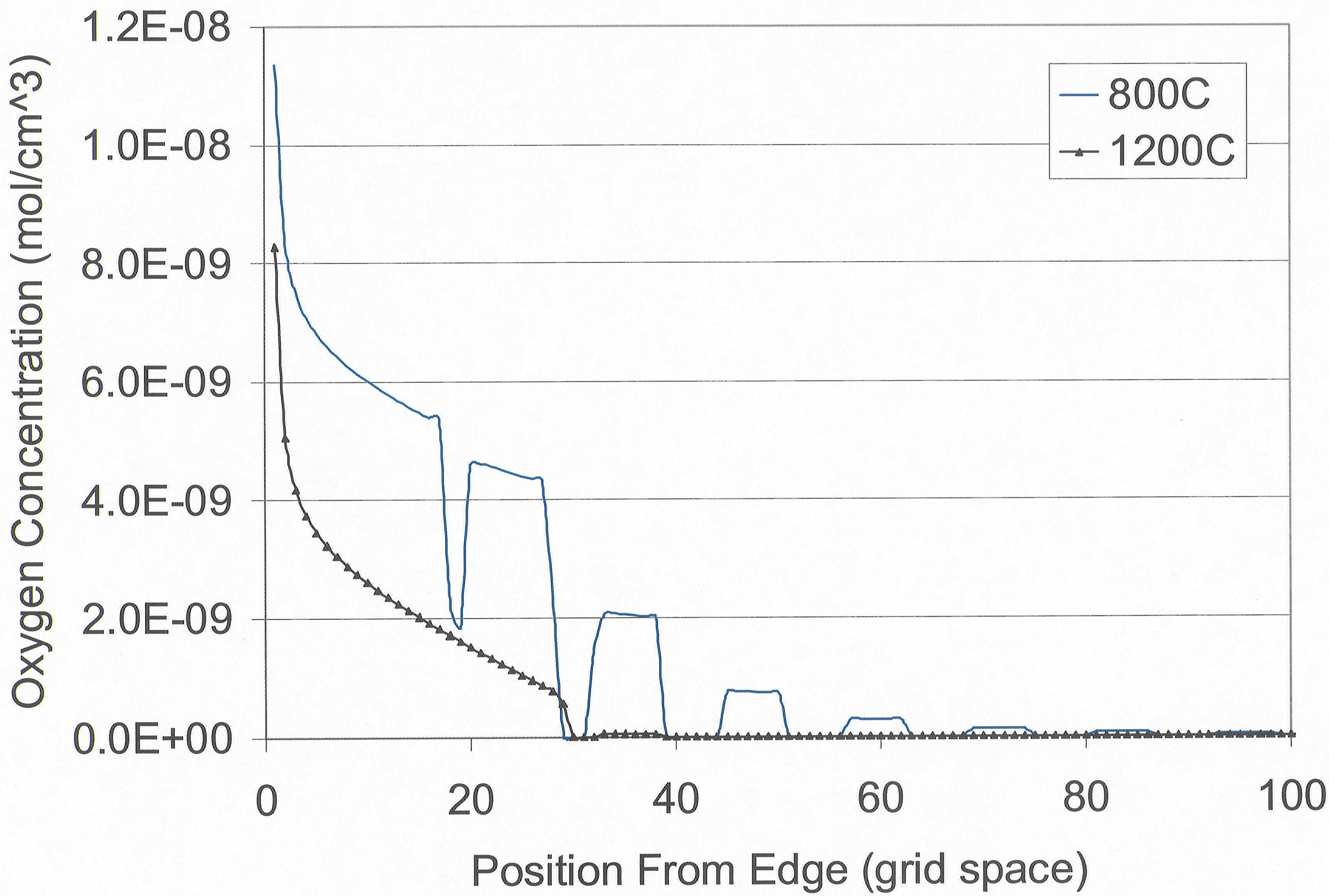
1000 ppm Oxygen

25% Carbon Reacted
Time: 35.6 hr.

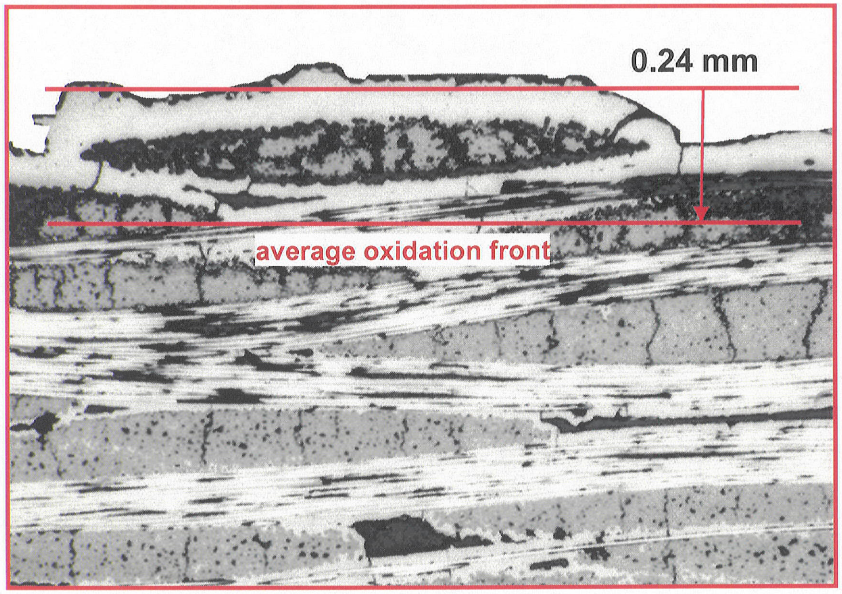
28.9 % of the carbon grids are flawed (at least 5% oxidized).

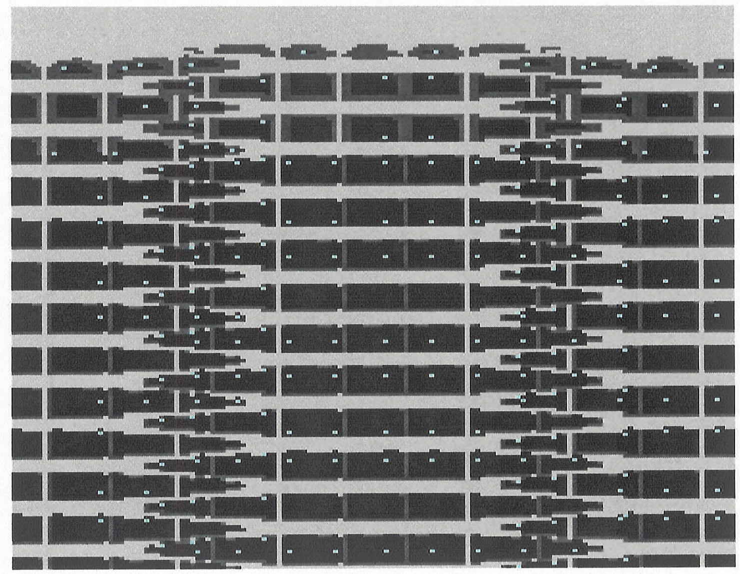


Results from the Oxidation Model - Oxygen Concentrations (at 1000 ppm)



Comparison of the Model to the Microstructure from Experimentation at 1200°C (at 1000 ppm)





9.7 hrs

10.1 hr

8% carbon oxidized

Environmental Durability Task – Oxidation Inhibition of C/SiC

C/SiC Material Descriptions

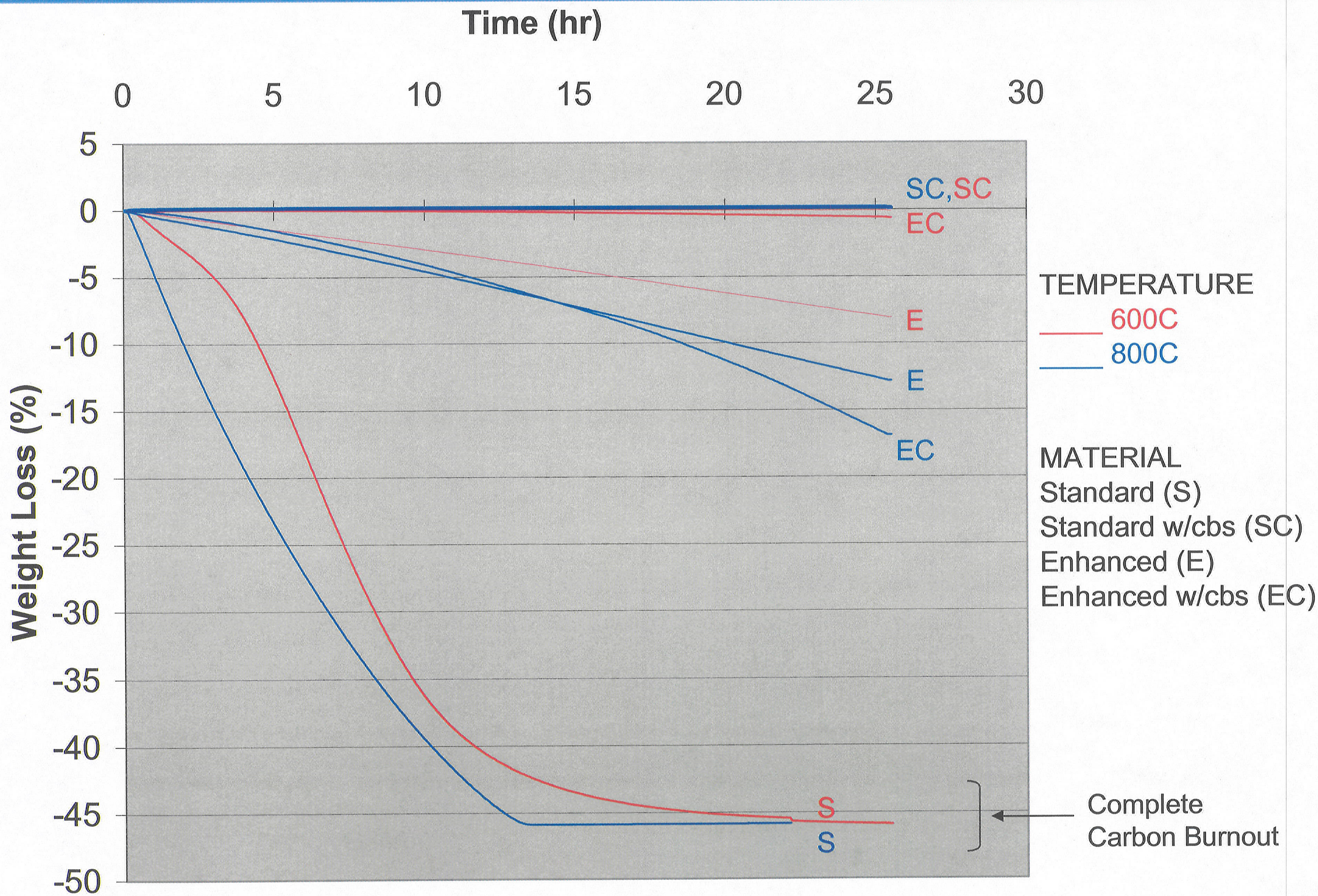
All 4 materials have the following characteristics:

- Manufactured by Honeywell Advanced Composites Inc. (HACI, now General Electric Power System Composites)
- 2D Plain weave fiber architecture
- Pyro-Carbon Alpha-3 interphase coating
- SiC matrix processed through isothermal CVI

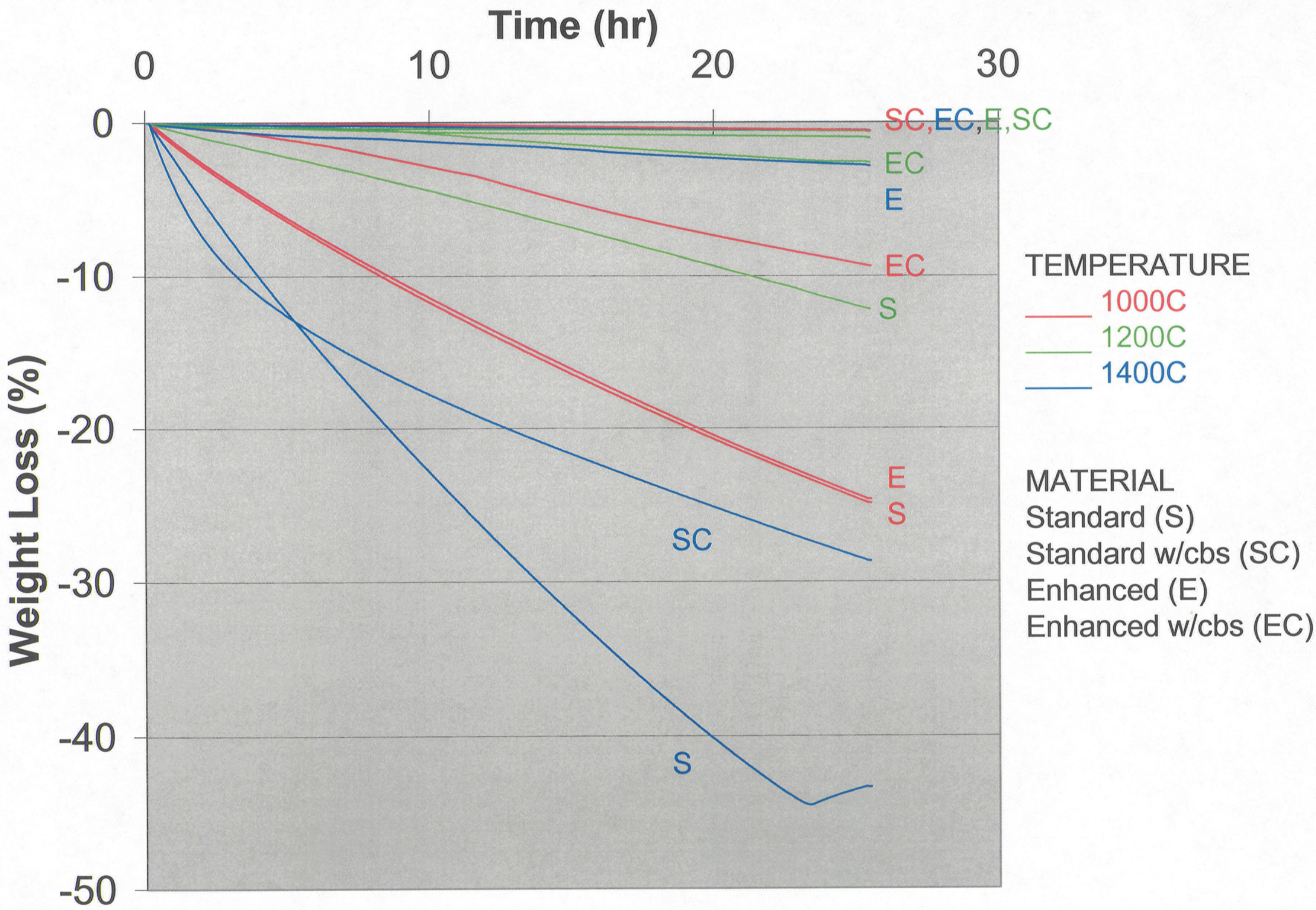
The 4 materials have the following differences:

	Treatment	Inhibitor in Matrix	Coating
standard C/SiC	none	none	SiC
standard C/SiC w/cbs	none	none	SiC, C-B-Si
enhanced C/SiC	1750ºC	yes	SiC
enhanced C/SiC w/cbs	1750ºC	yes	SiC, C-B-Si

TGA of CVI C/SiC Materials in Flowing Oxygen (100ccm) at Temperatures of 600°C and 800°C – out to 25 hr

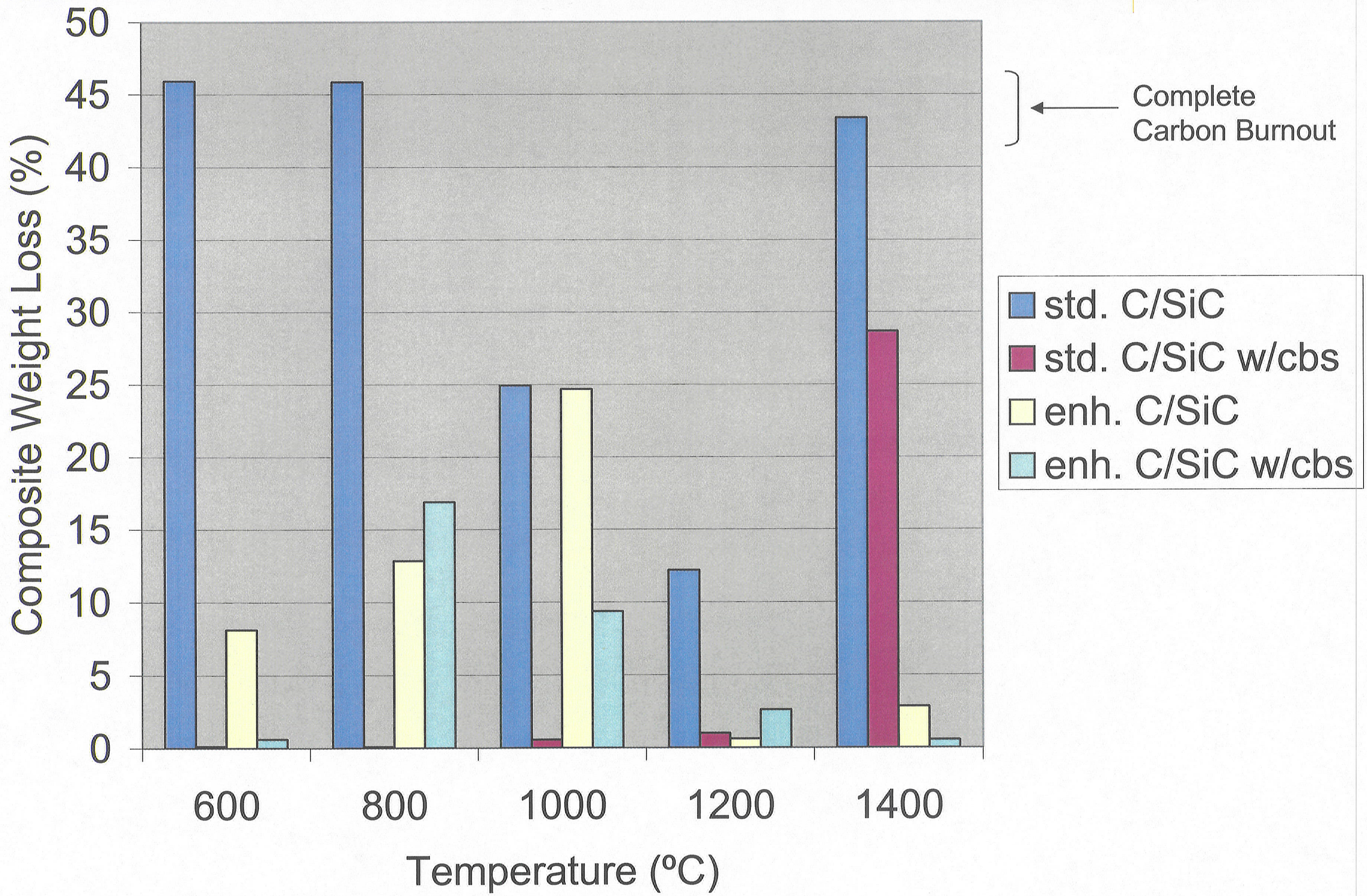


TGA of CVI C/SiC Materials in Flowing Oxygen (100ccm) at Temperatures of 1000°C, 1200°C, and 1400°C – out to 25 hr



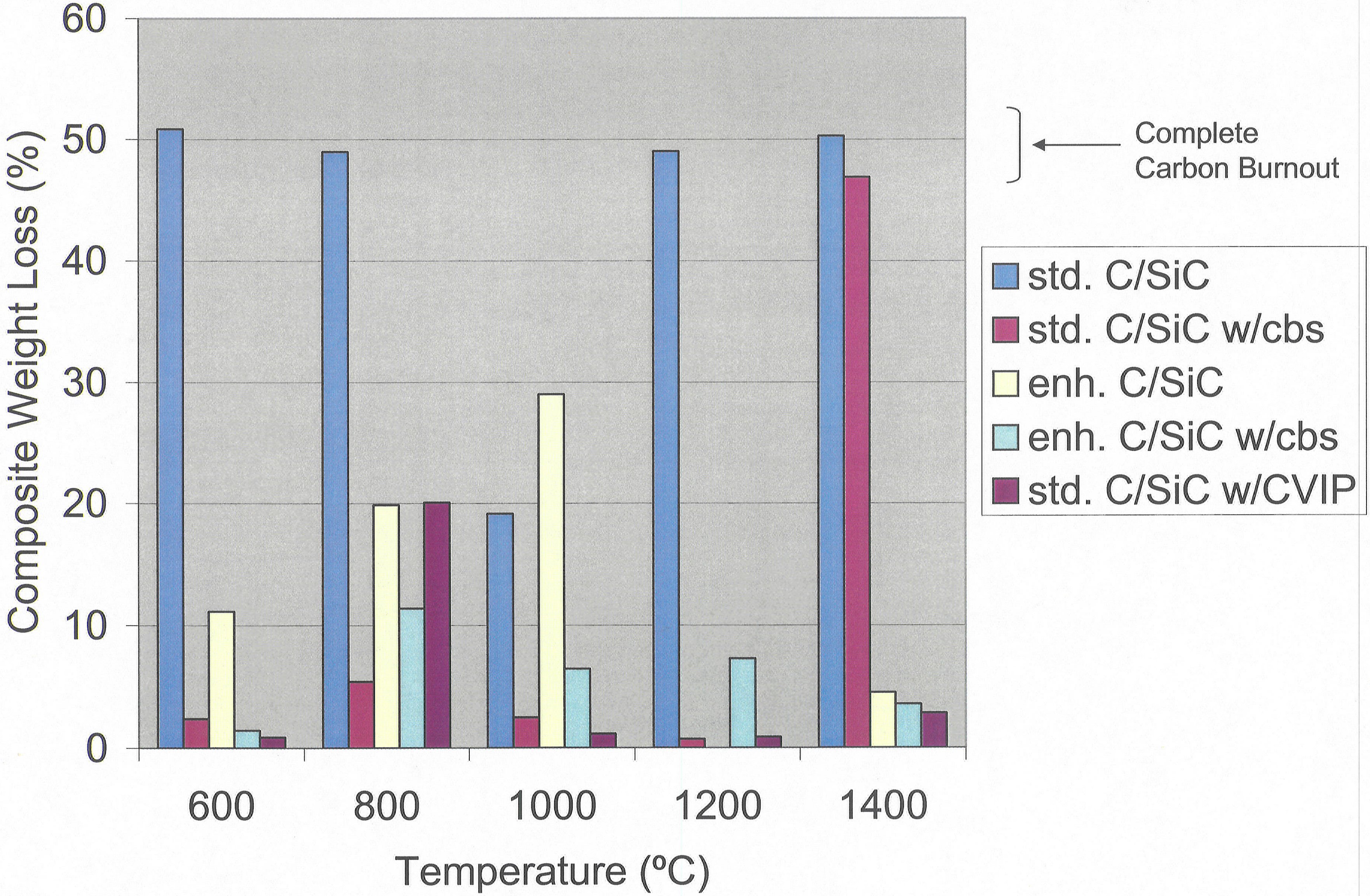
Composite Weight Loss After 25 hr in TGA

(oxygen flowing at 100ccm)

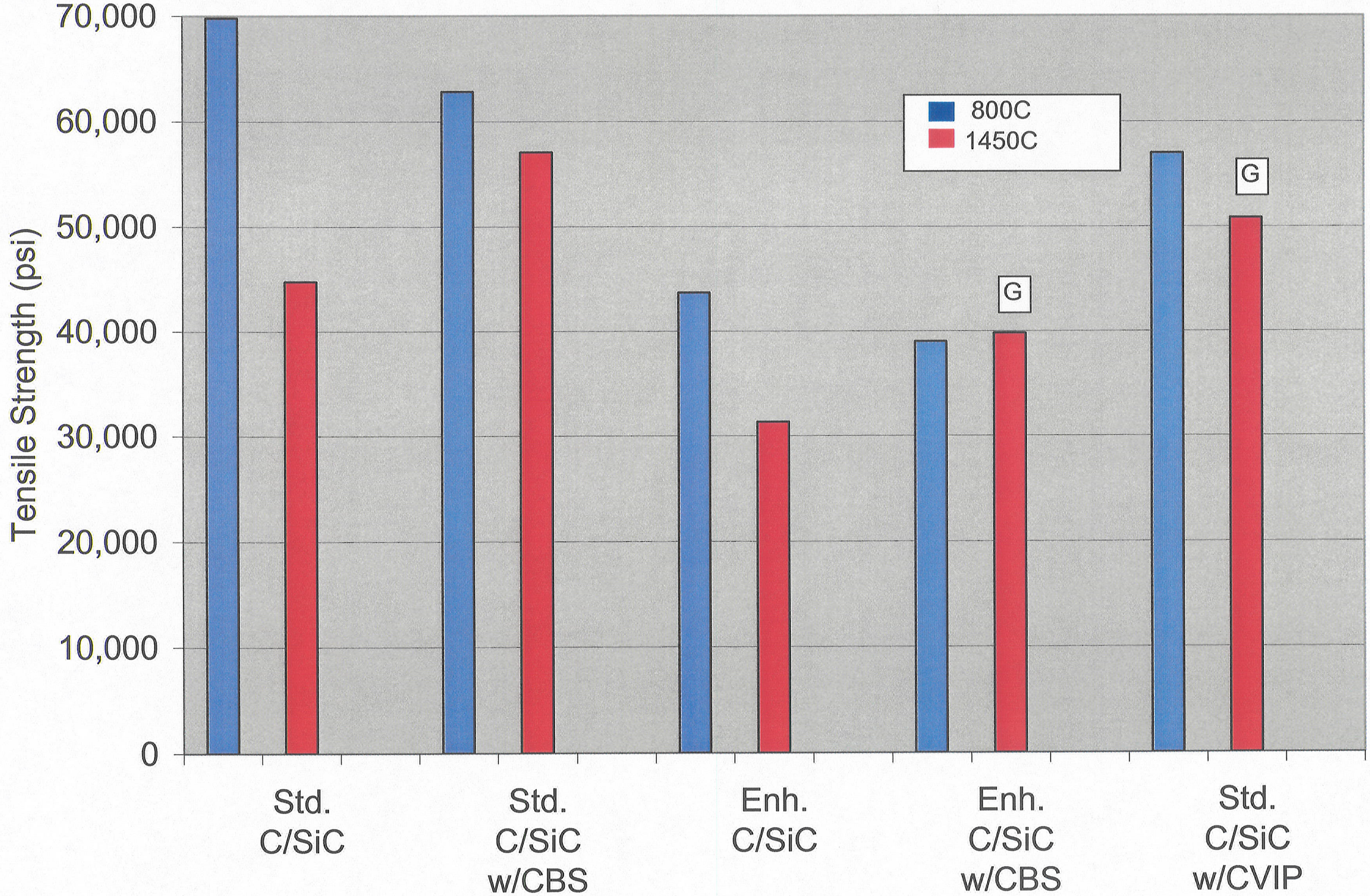


Composite Weight Loss After 50 hr in TGA

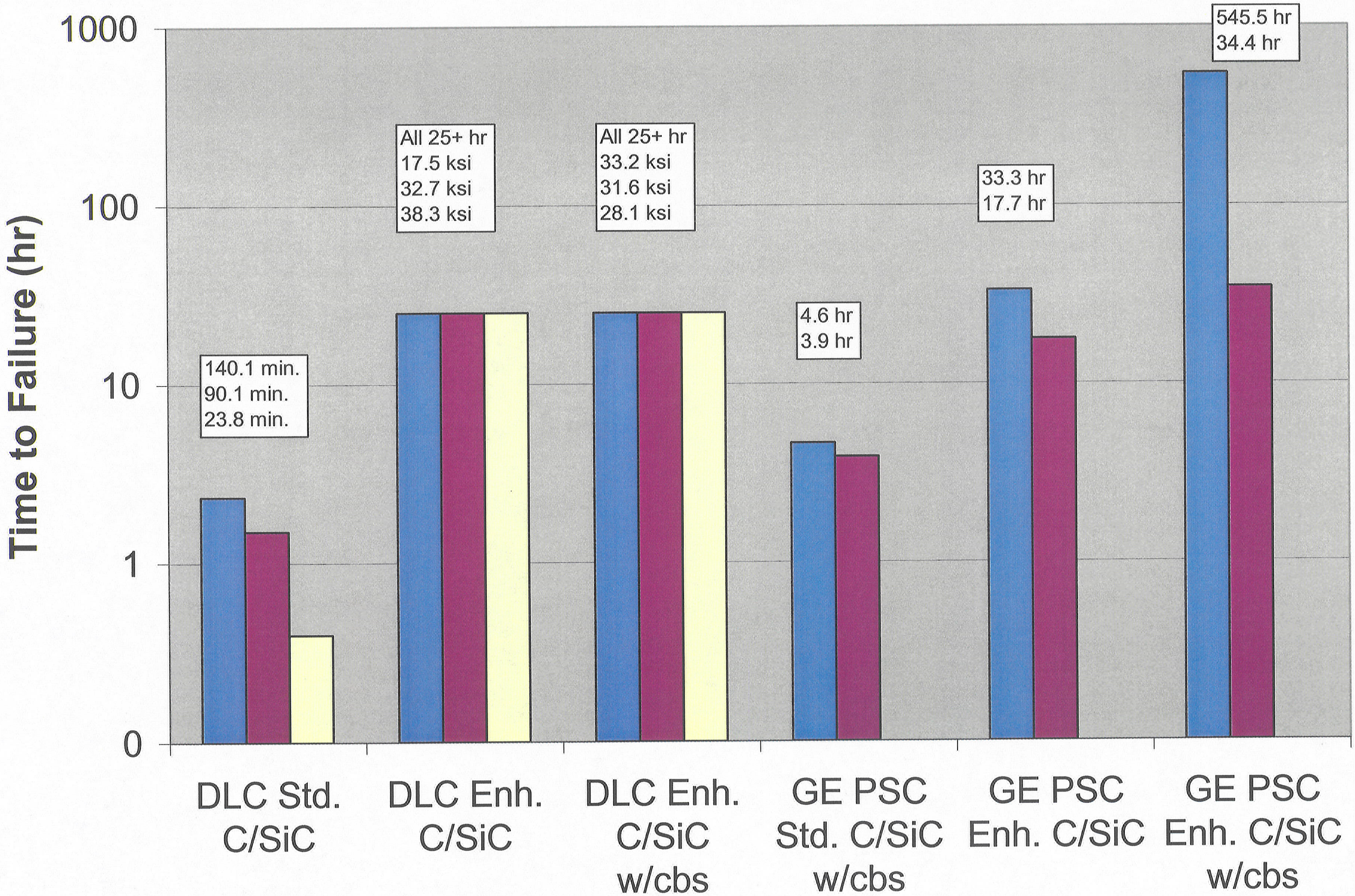
(oxygen flowing at 100ccm)



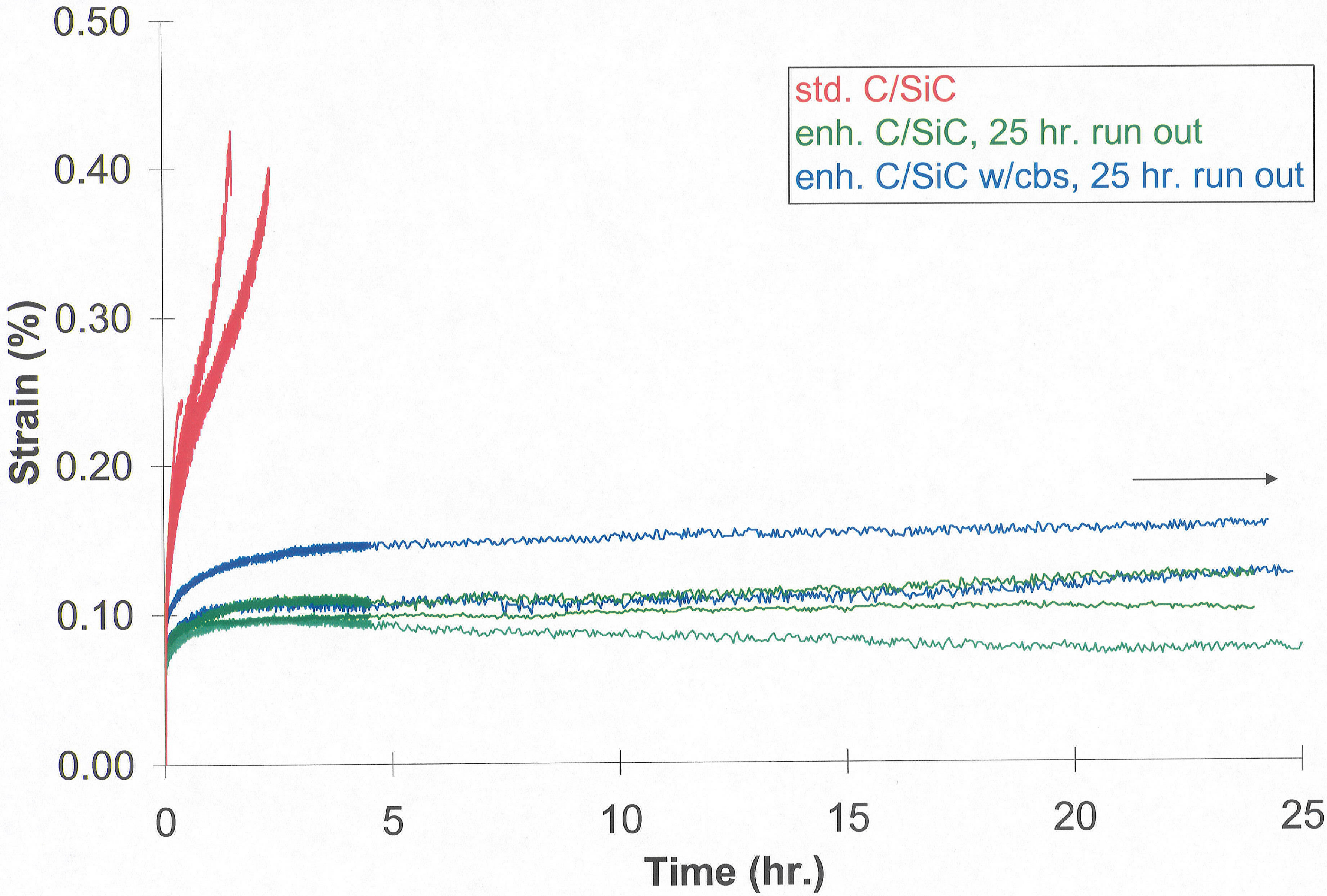
Tensile Strength in Air



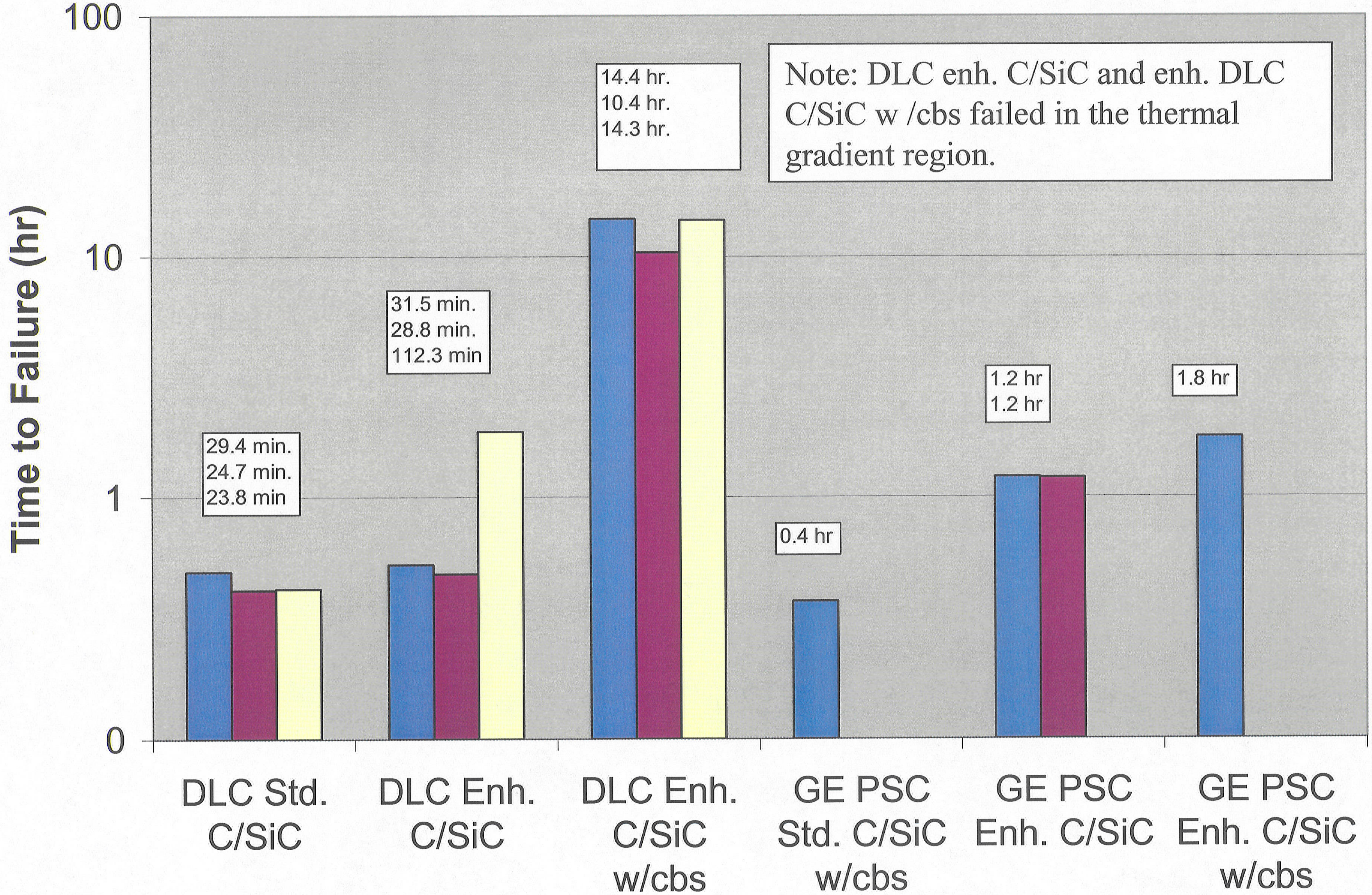
Stressed Oxidation at 1454ºC/10 ksi in Air



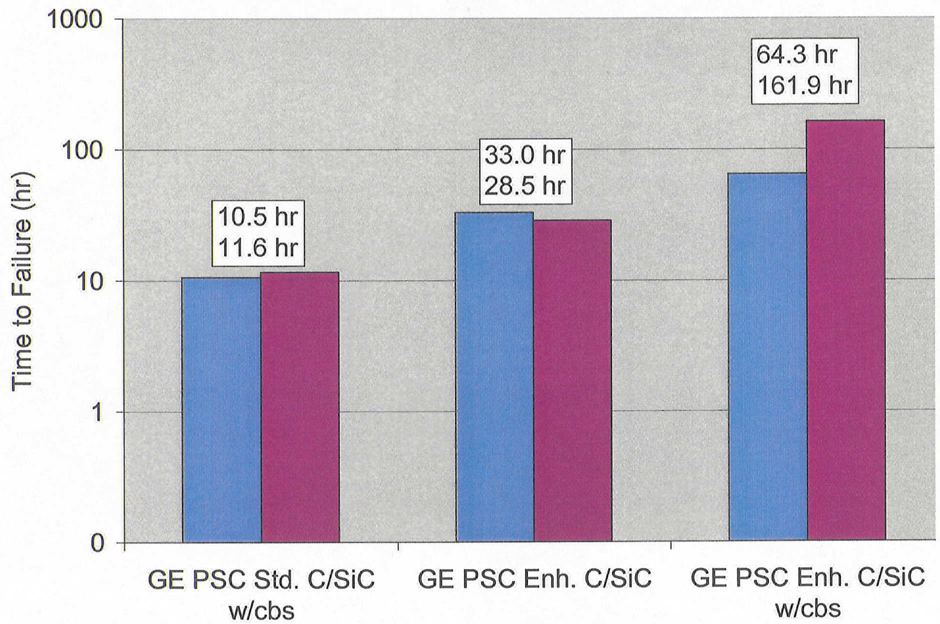
Strain Versus Time for Stressed Oxidation of HACI C/SiC Materials -Tests at 1454ºC/69MPa (2650ºF/10 ksi)



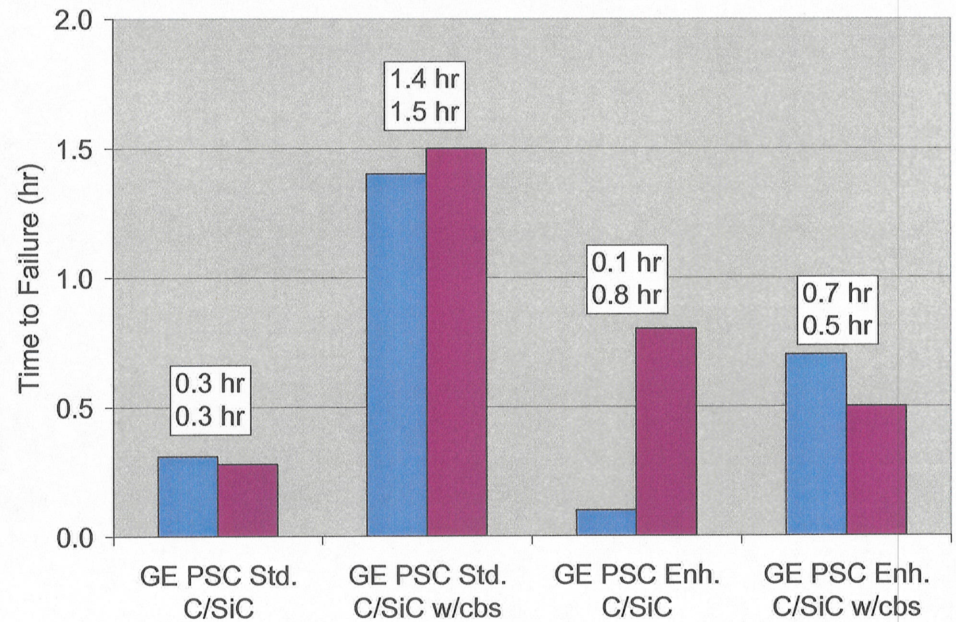
Stressed Oxidation at 1454ºC/25 ksi in Air



Stressed Oxidation at 800ºC in Air



800ºC/10 ksi in Air



800ºC/25 ksi in Air

Summary/Conclusions

Oxidation of the carbon constituents within C/SiC occurs in two primary regimes.

- Reaction controlled regime: lower temperatures, oxygen saturates into the interior, oxidation rate is slower but oxidation is more widespread, embrittlement effect and low strains to failure.
- Diffusion controlled regime: higher temperatures, oxygen and carbon reactions occur quickly, reaction front moves inward, shrinking core, high strains to failure.

The T300 carbon fiber and the pyrolytic carbon interphase have different oxidation rates. In the lower temperature regime, the pyro-C has a slower reaction rates. Resulting activation energies suggest further testing is necessary.

Stress has a significant effect in opening cracks especially at high temperatures.

- In unstressed conditions: crack closure near processing temperature due to CTEs and silica formation. Cracks remain open at low temperatures.
- Under stress at high temperatures and at low temperatures, cracks are open and allow for oxygen ingress. Oxidation patterns according to kinetic regimes are observed.

Summary/Conclusions Continued

The oxidation model is a useful tool for studying the oxidation kinetics, the effect of different variables (temperature, environment, porosity and tortuosity), and edge effects. With additional adjustment of the model (effective diffusion coefficients) to match experimental results, the model can be used to determine oxidation damage over time and determine strength reduction and failure.

Oxidation inhibitors can significantly improve the oxidation resistance of carbon in C/SiC composites at intermediate (800ºC) and high temperatures (1454ºC). However, the approaches investigated in this study were only effective at low stress levels.