Thermochemical Instabilities at High Temperature Ceramic Surfaces

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Ultra-High Temperature Ceramics: Materials for Extreme Environment Applications VI
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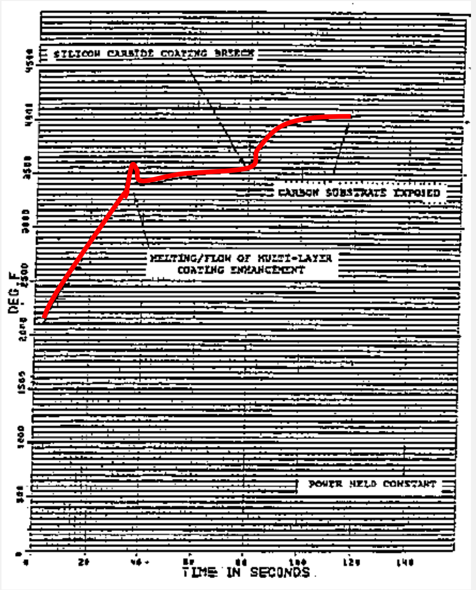
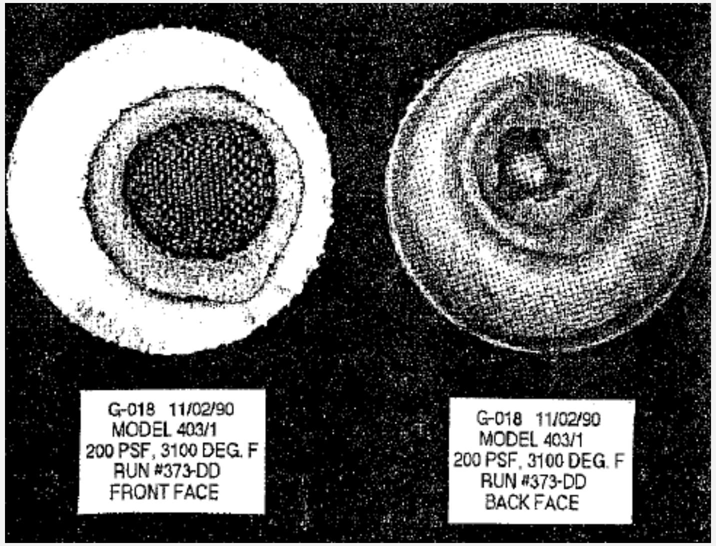
High temperature surface instability during air plasma testing of Si_3N_4 in the CHESS Plasmatron X facility

Outline

- Highlights from the literature
- Mini-story 1: C/SiC Passive/Active Oxidation and Temperature Jump
- Mini-story 2: PICA-NuSil Response to Hypersonic Entry Flow

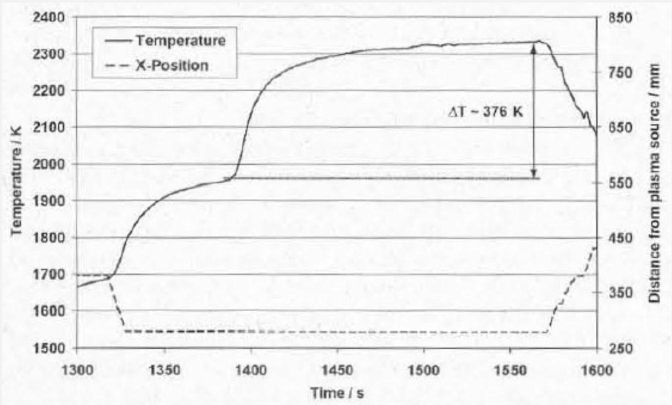
Surface Temperature Instabilities in the Literature





Lacombe and Lacoste, *High Temp High Press*, 3 (1994) 285-296

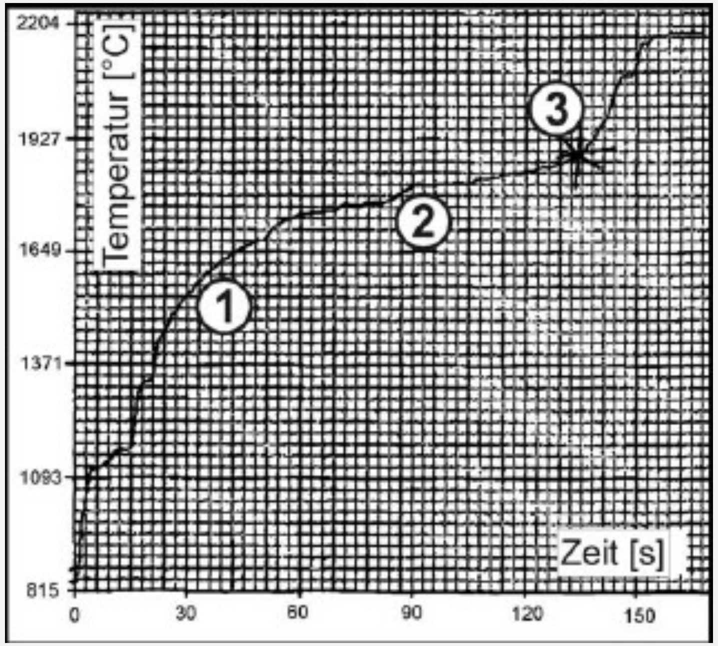
Transition between passive and active oxidation regime



Herdrich et al., J Spacecraft Rockets, 42 (2005) 817-824

Increased catalytic recombination efficiency of SiC vs SiO_2

Hald, *Aero Sci Tech*, 7 (2003) 551-559

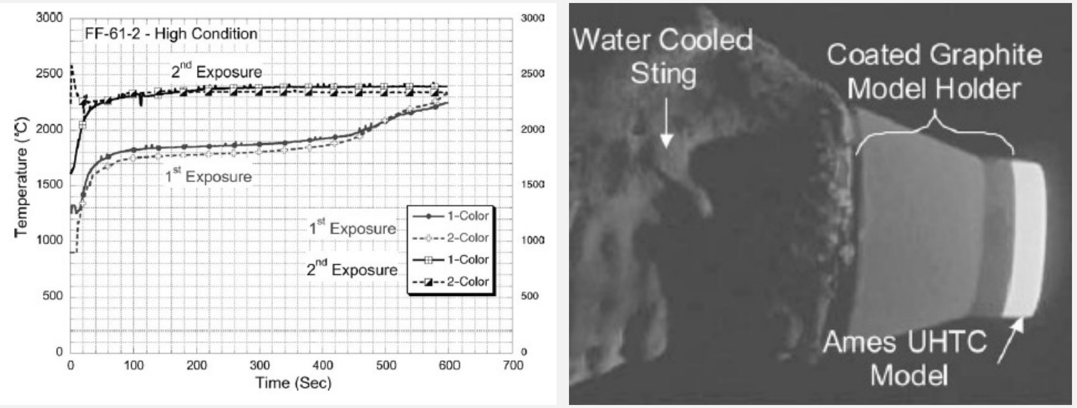


Catalytic recombination reactions involving nitrogen:

$$\mathrm{SiC} + \mathrm{N} \rightarrow \mathrm{SiN}$$
$$\mathrm{SiN} + \mathrm{N} \rightarrow \mathrm{Si} + \mathrm{N_2}$$

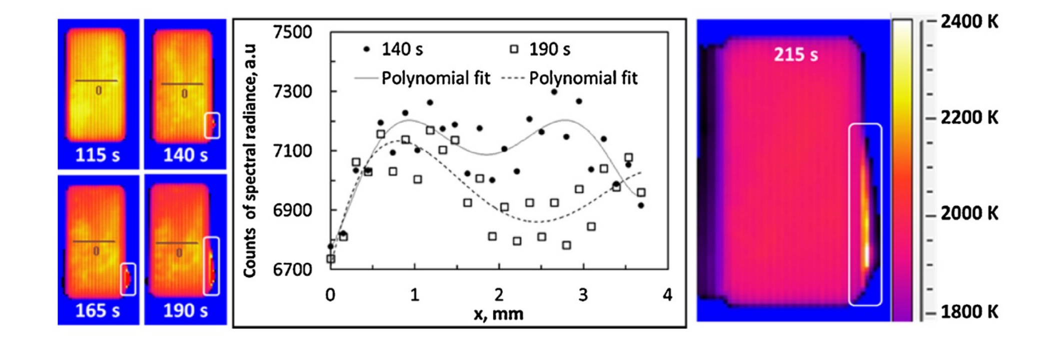
Surface Temperature Instabilities in the Literature, contd.

Gasch et al., *J Mater Sci*, 39 (2004) 5925 -5937



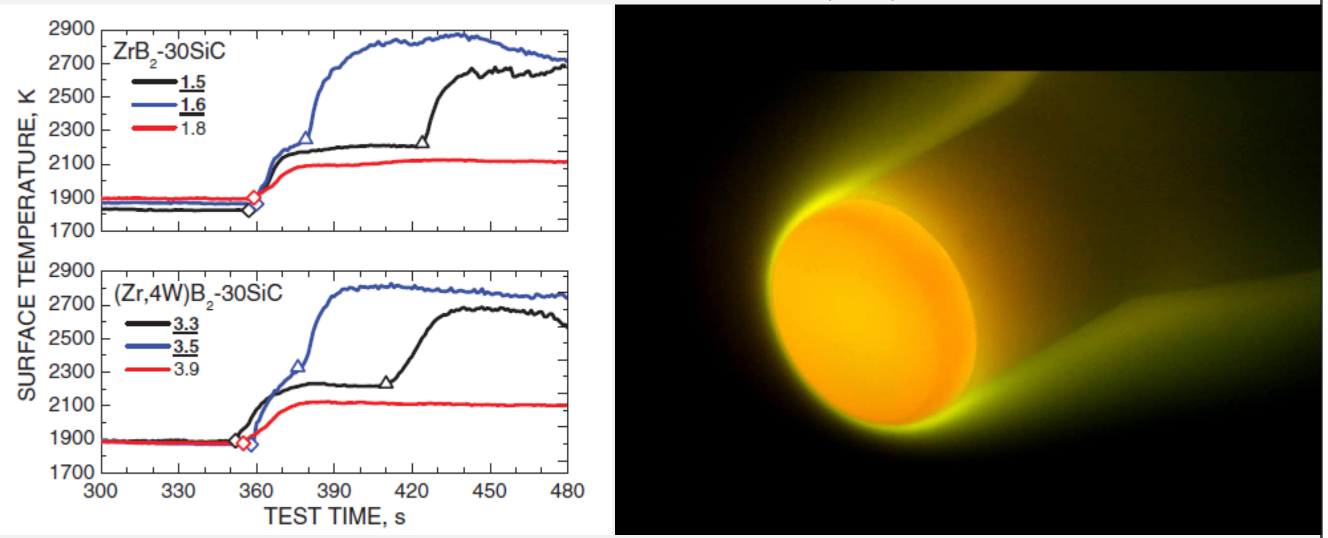
Increased temperatures attributed to the presence of a thick porous HfO_2 layer, which changes in catalycity, emittance and conductivity

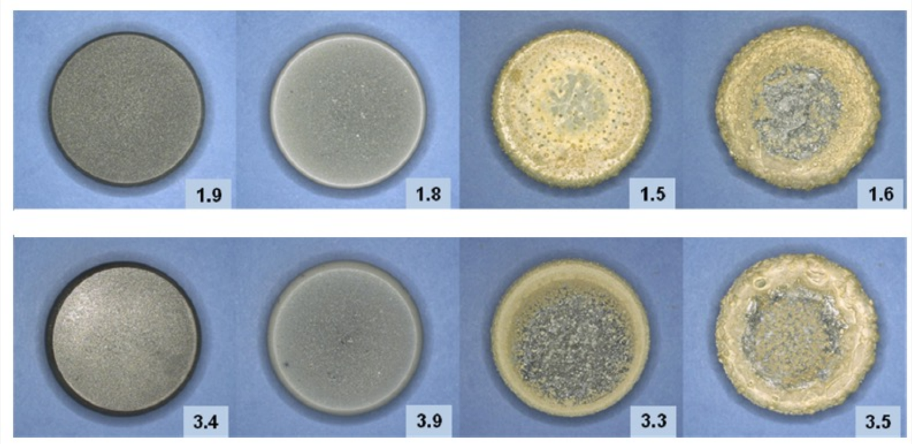
Monteverde et al., *J Europ Ceram Soc*, 37 (2017) 2325-2341



"Jumps-of-radiance" and "waves of radiance" in SiC-ZrB_2

Marschall et al., *J Thermo Heat Trans*, 26 (2012) 559-572



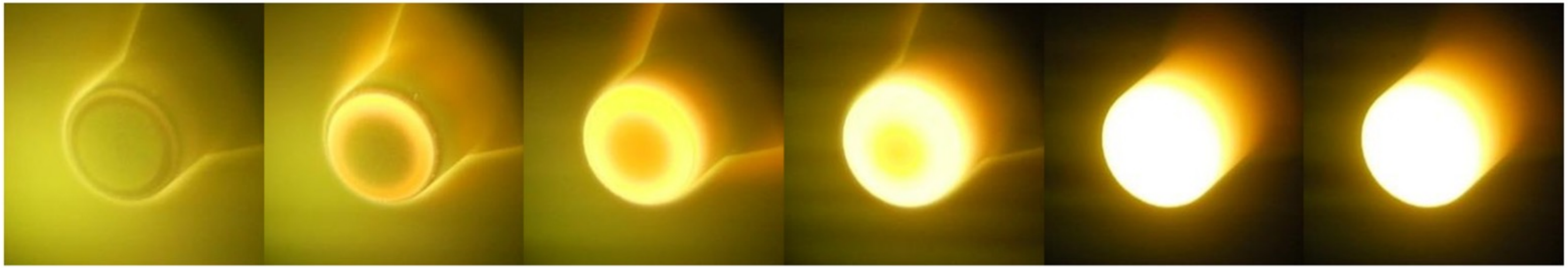


Transition in surface chemistry involving Si-rich compounds

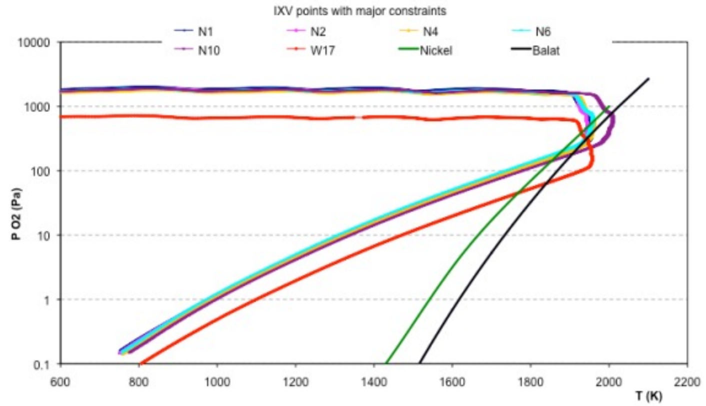
C/SiC Passive/Active Oxidation and Temperature Jump

with B. Helber[1], O. Chazot[1], K Nickel[2], M. Balat-Pichelin[3]

[1]von Karman Institute for Fluid Dynamics, Belgium
[2]Technical University Tuebingen, Germany
[3]PROMES CNRS, France



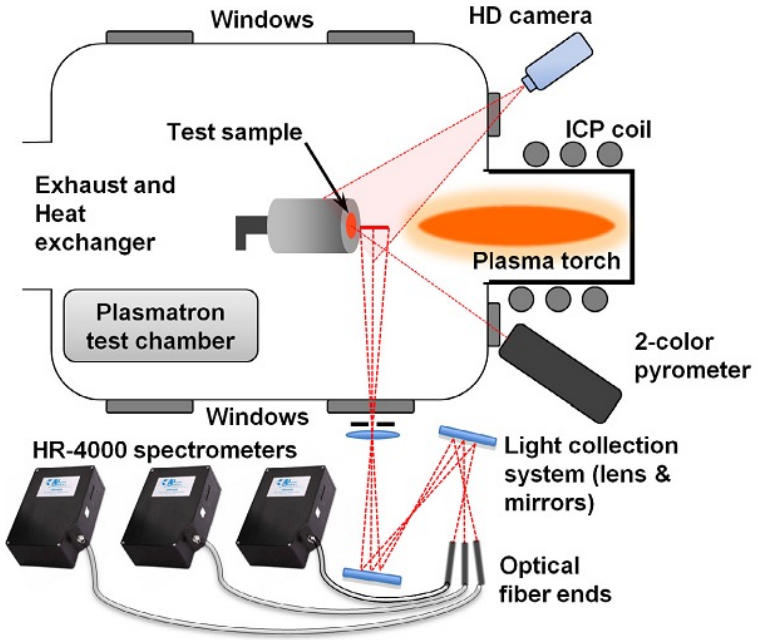
VKI Plasmatron Experiments on C/SiC

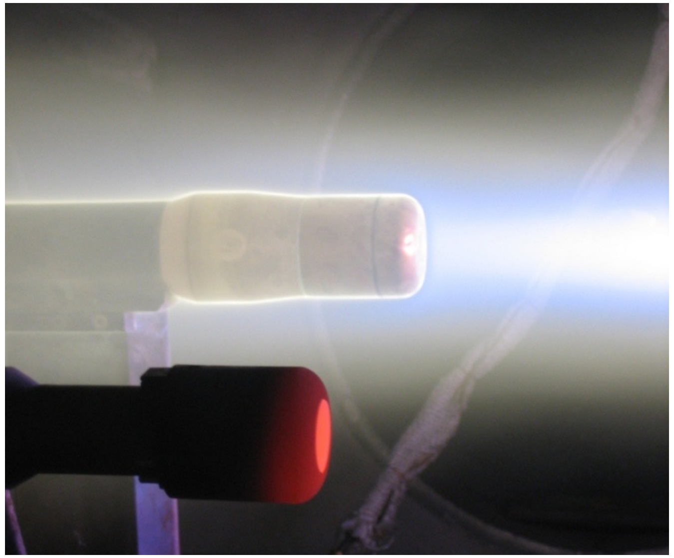


HER C/SiC

MTA C/SiC

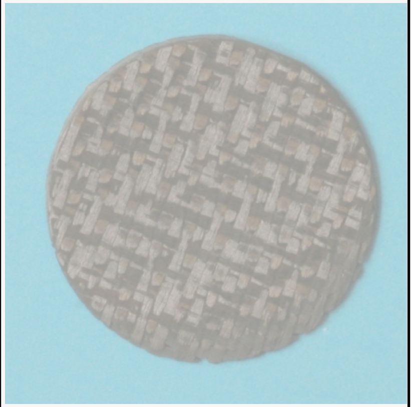
Panerai F, et al. *Aero Sci Tech*, (2014)
Panerai F, et al. *Carbon* 71 (2014) 102-119
Balat-Pichelin M, et al. *J Eur Ceram Soc*, (2014)
Panerai F, Chazot O. *Mater Chem Phys* 134 (2012) 597-607

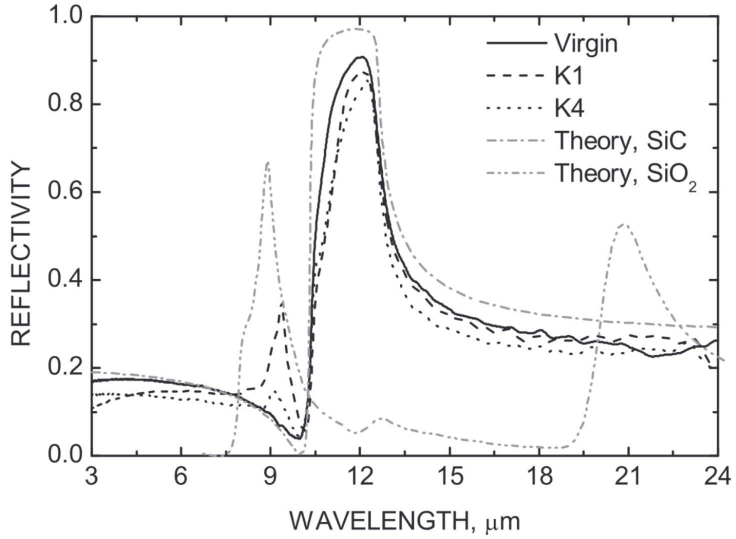


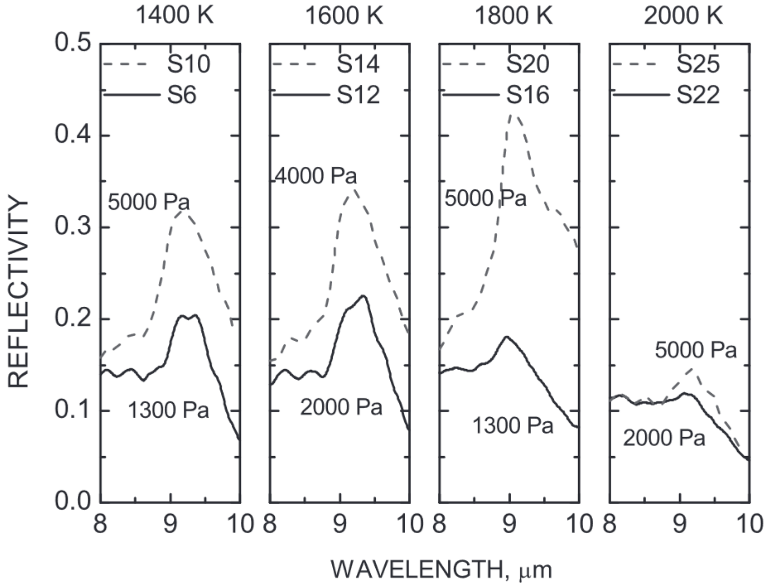


- 1.2 MW Plasmatron, air plasma
- Heat-flux: 9 - 100 W/cm^2
- Pressure: 1000 - 10000 Pa

C/SiC Passive-Active Oxidation

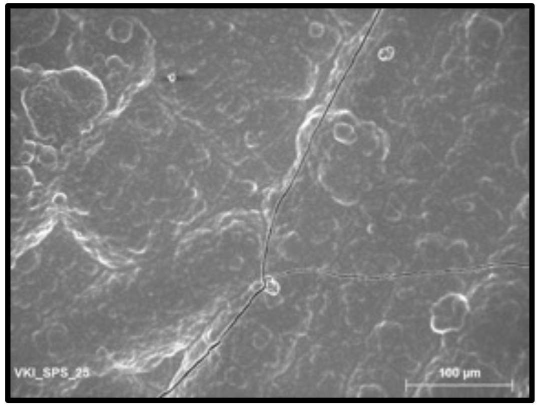
Virgin	*Passive Ox.*	*Active Ox.*	*T Jump*
			
	1942 K, 5000 Pa, 10 min	2090 K, 5000 Pa, 10 min	2141 → 2734 K, 5000 Pa, 2 min
			
	1956 K, 5000 Pa, 10 min	2019 K, 5000 Pa, 10 min	2064 → 2734 K, 5000 Pa, 2 min



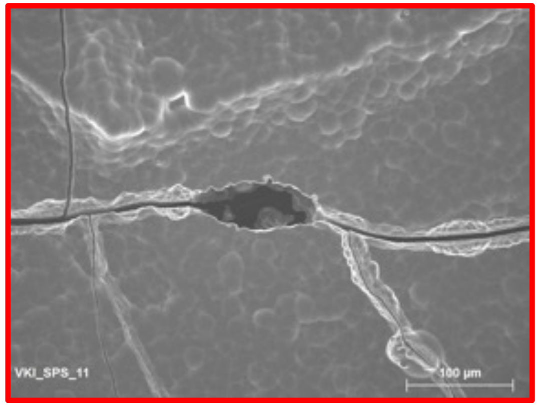


C/SiC Passive-Active Oxidation and Temperature Jump Instability

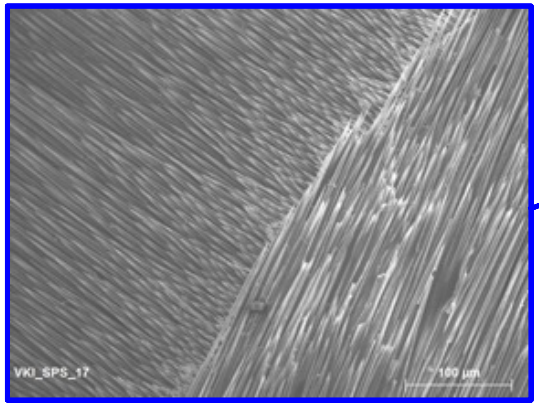
Passive Ox.

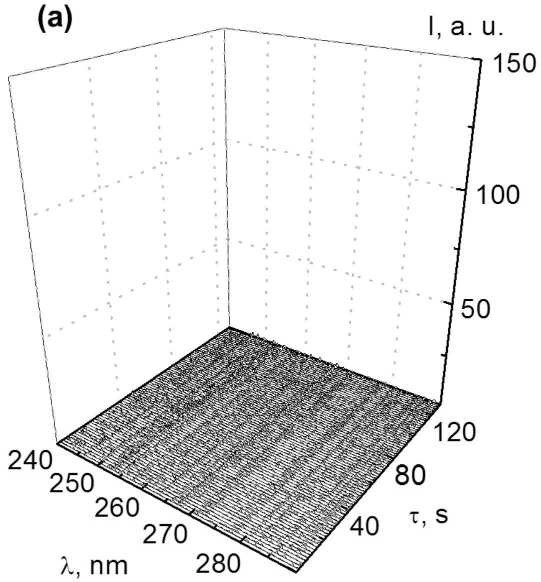


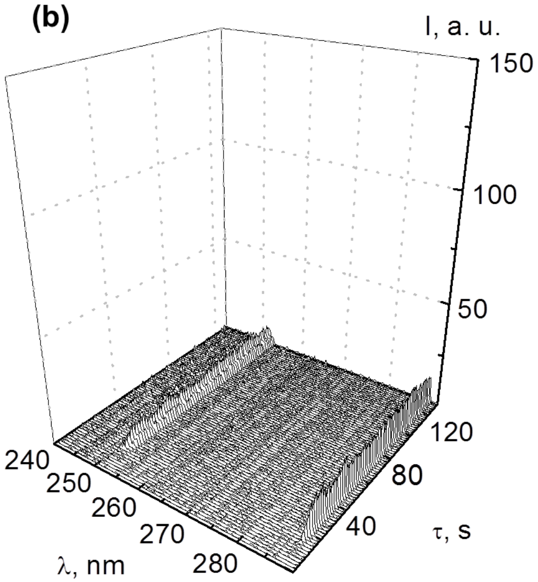
Active Ox.

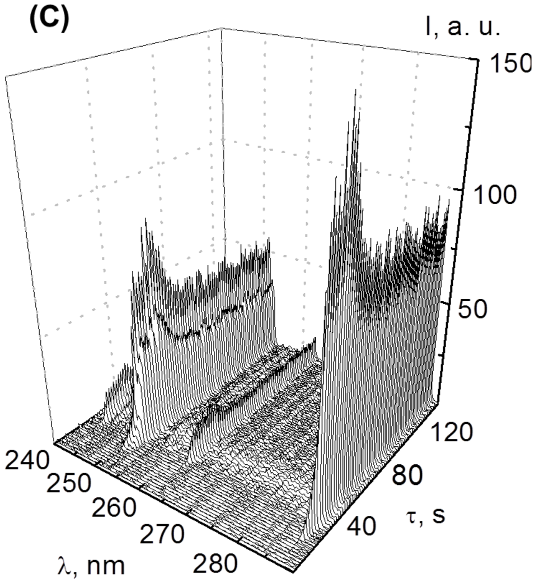


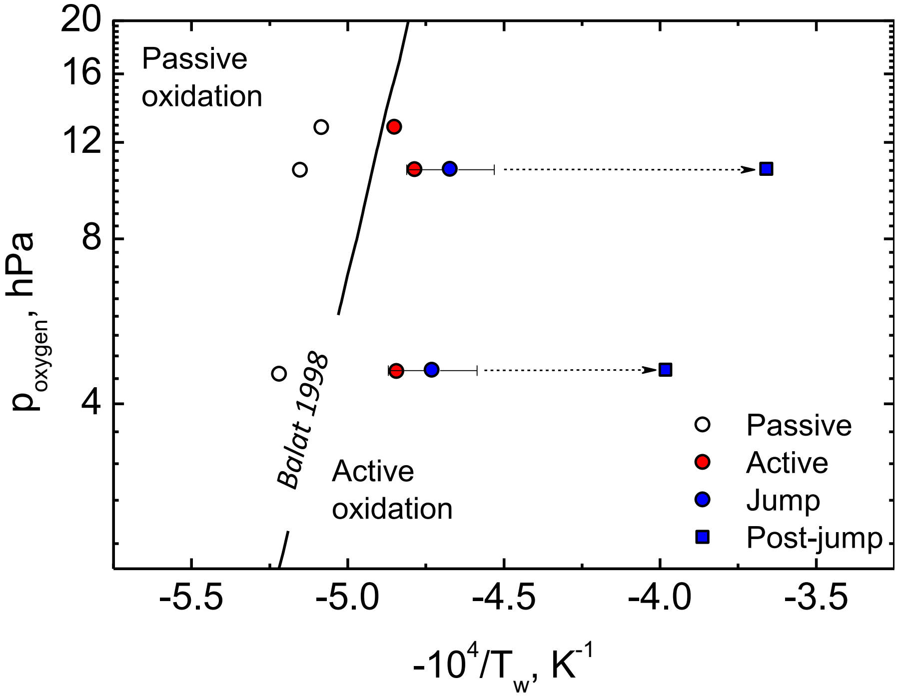
T Jump





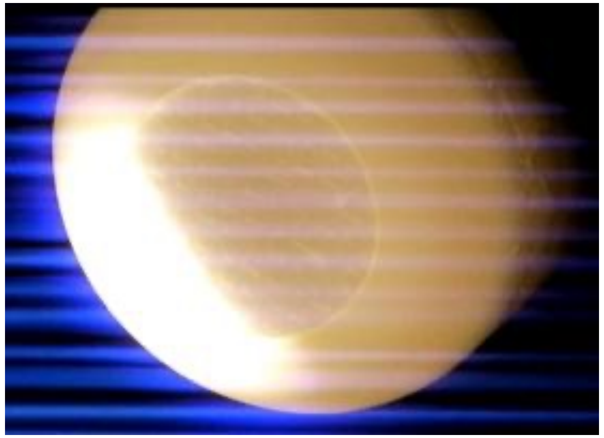


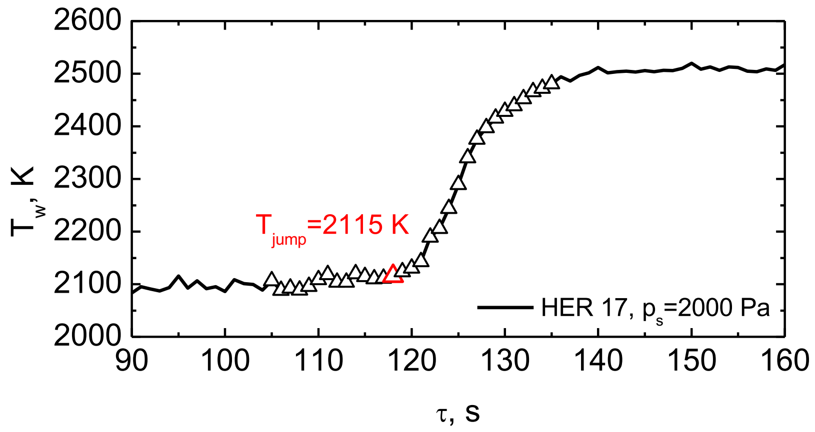




Discussion on the SiC response and Surface Instability

- At low T and high p_{O2}: $SiC_{(s)} + 3O_{(g)} \rightarrow SiO_{2(s)} + CO_{(g)}$
- At low T and high p_{O2} : $SiC_{(s)} + 3O_{(g)} \rightarrow SiO_{2(s)} + CO_{(g)}$
- At the jump instability, increased exothermicity in the chemistry of β-SiC surface
- Two leading contributions:
  - SiC sublimation (~2100 K) accelerates the decomposition of the coating
  - Oxidation ($C + O \rightarrow CO$) and nitridation ($C + N \rightarrow CN$) of the substrate



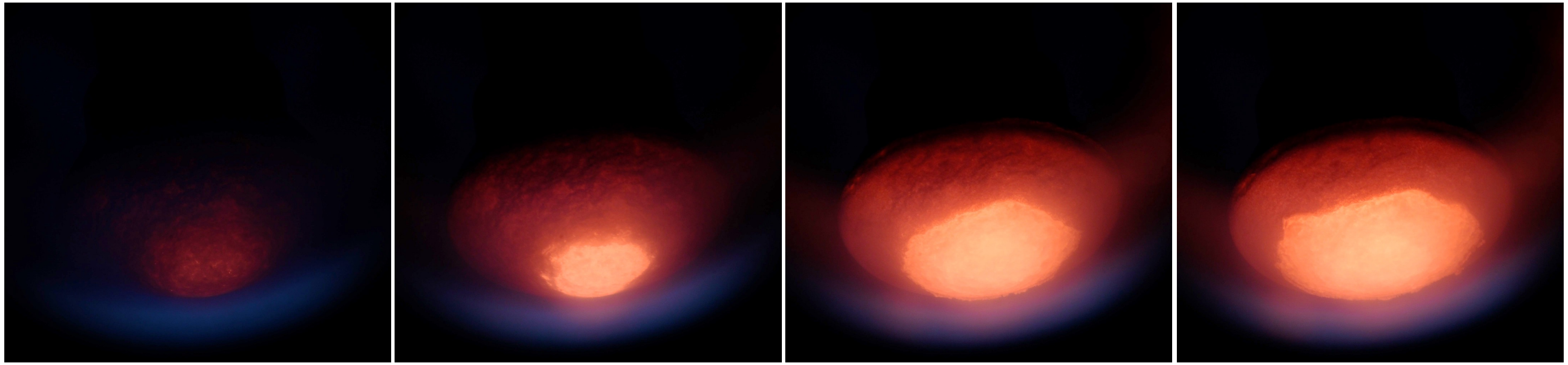


- Contributor to the surface heating after jump:
  - Oxidation and nitridation
  - Active oxidation of the SiC matrix
  - Si-N catalytic cycles and increased SiC react

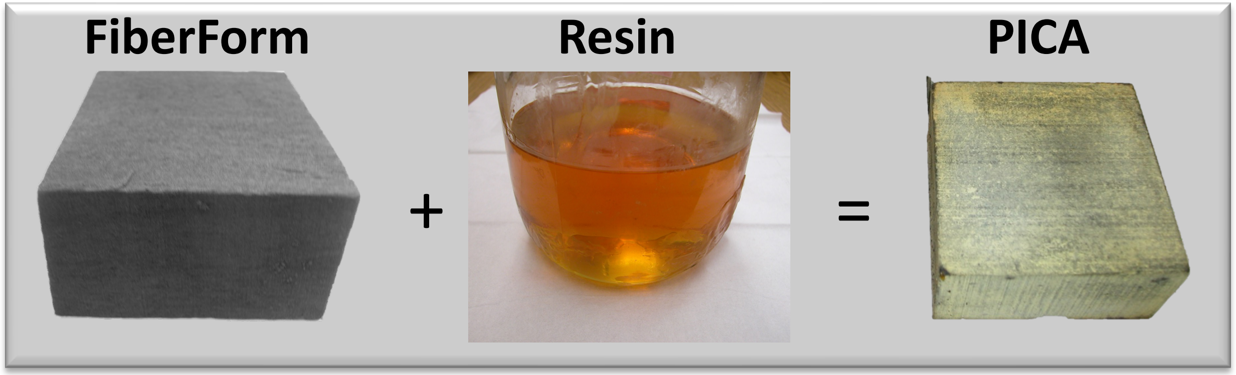
PICA-NuSil Response to Hypersonic Entry Flow

with B. Bessire[1], J. Meurisse[2], N Mansour[2]

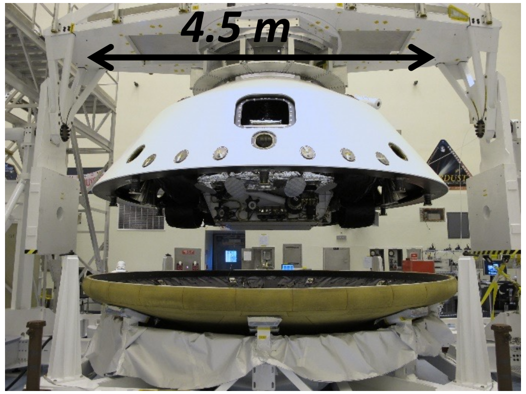
[1]NASA Ames Research Center, USA
[2]Analytical Mechanics Associates, USA



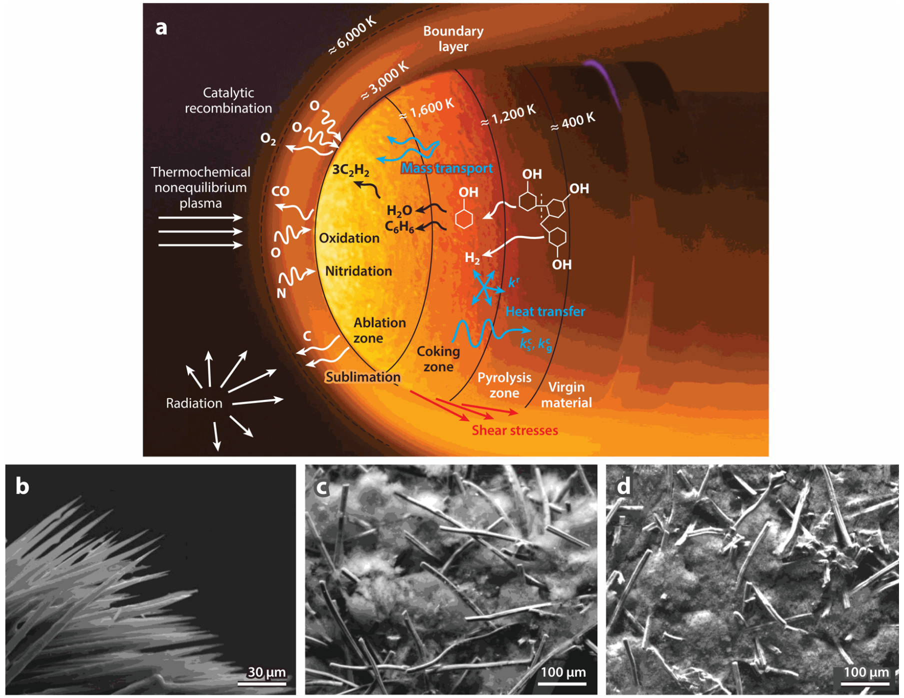
Phenolic Impregnated Carbon Ablator + NuSil^{TM}



Stackpoole et al., *AIAA 2008-1202*

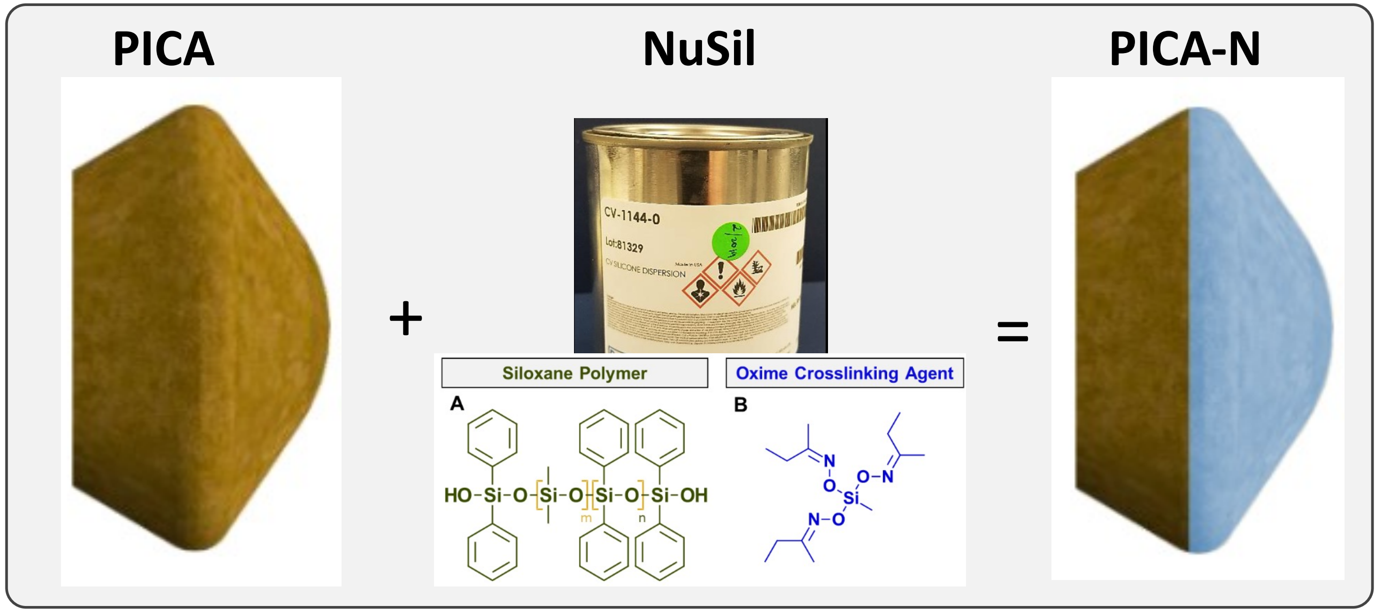


Credit: NASA



Mansour NN, et al 2024
Annu. Rev. Fluid Mech. 56:549–75

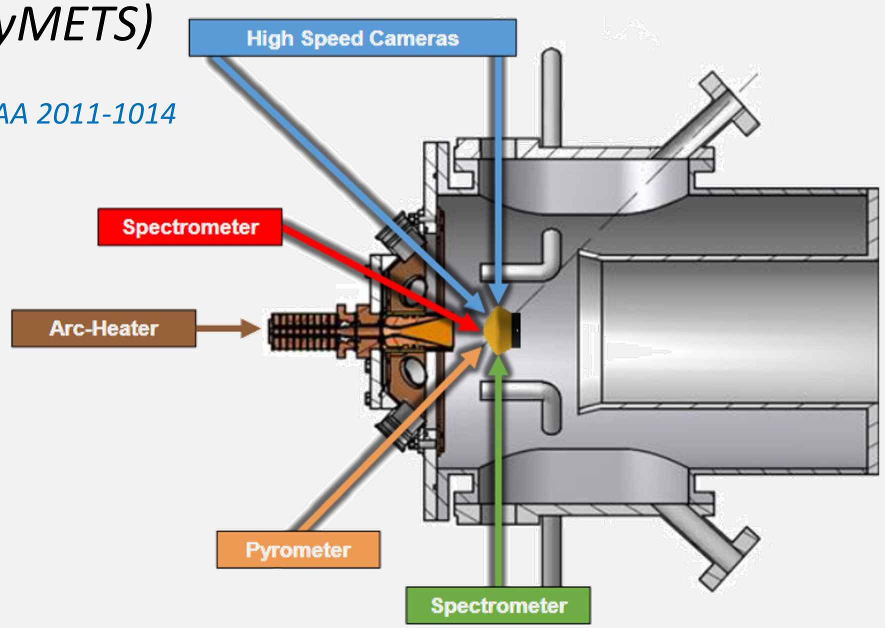
Mansour NN, et al. *Annu Rev Fluid Mech* (2024) 549-75

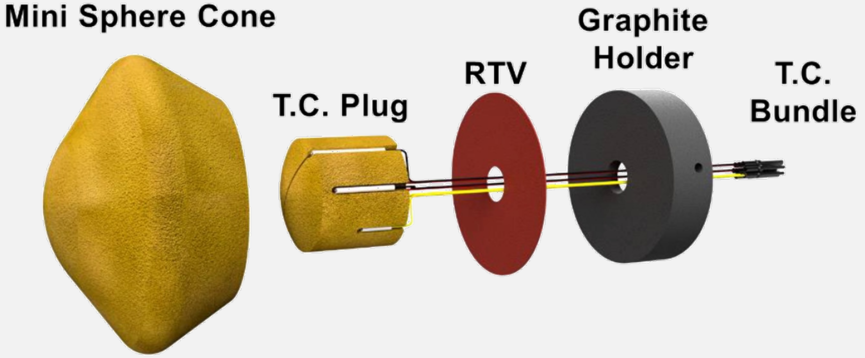


Plasma Wind Tunnels for PICA-NuSil Testing

NASA LaRC Hypersonic Materials Environmental Test System (HyMETS)

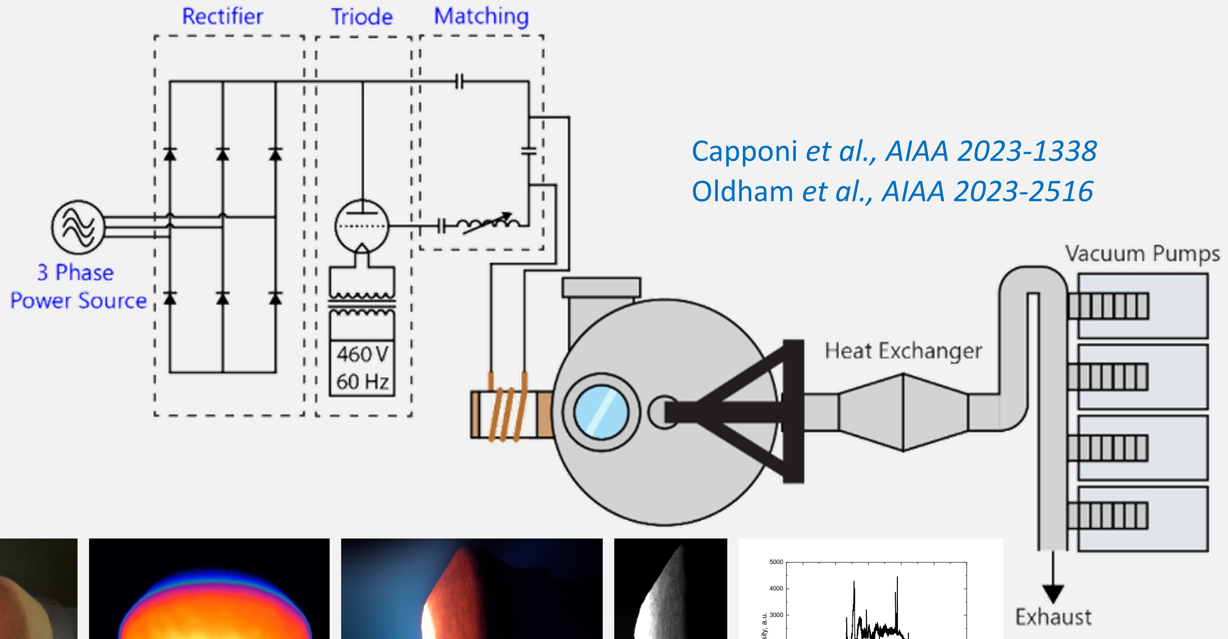
Splinter *et al.*, *AIAA 2011-1014*

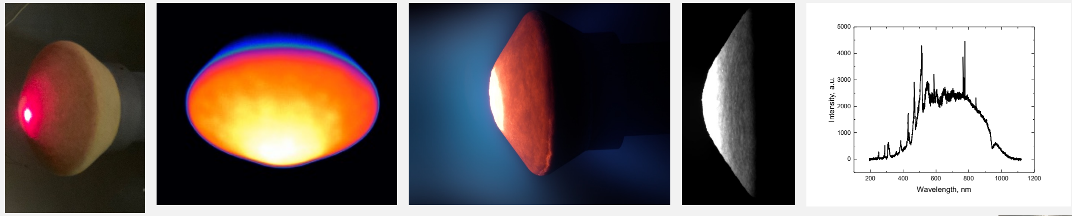


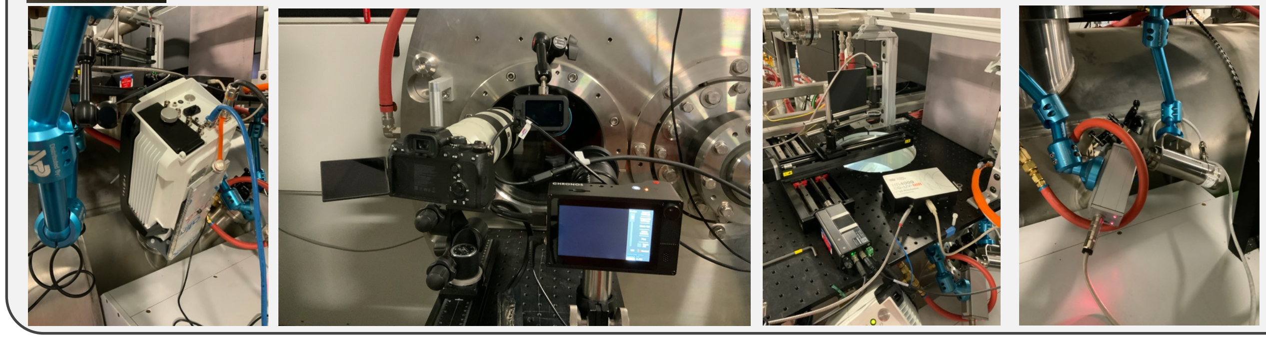


CHESS Plasmatron X

Capponi *et al.*, *AIAA 2023-1338*
Oldham *et al.*, *AIAA 2023-2516*







Plasma Wind Tunnels for PICA-NuSil Testing

NASA LaRC Hypersonic Materials Environmental Test System (HyMETS)

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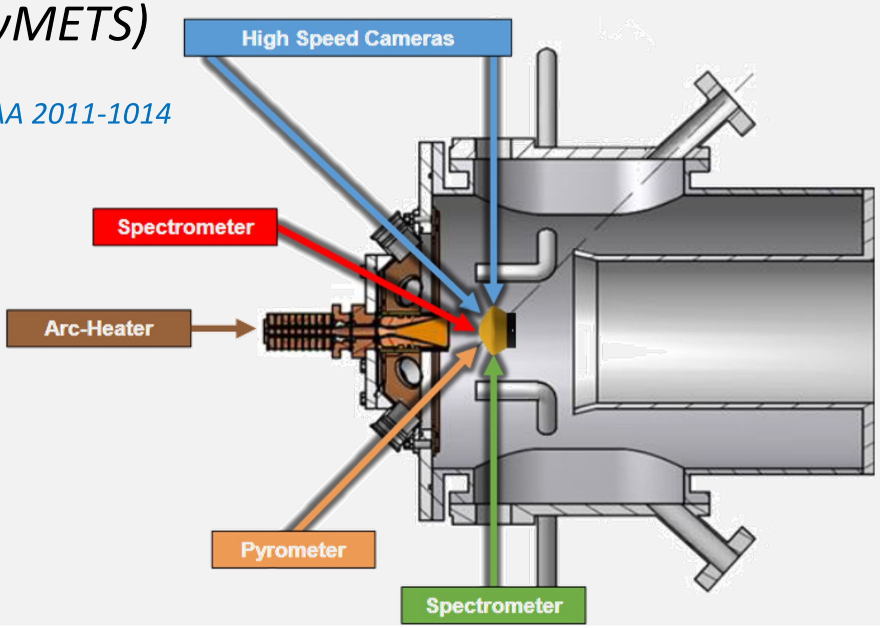
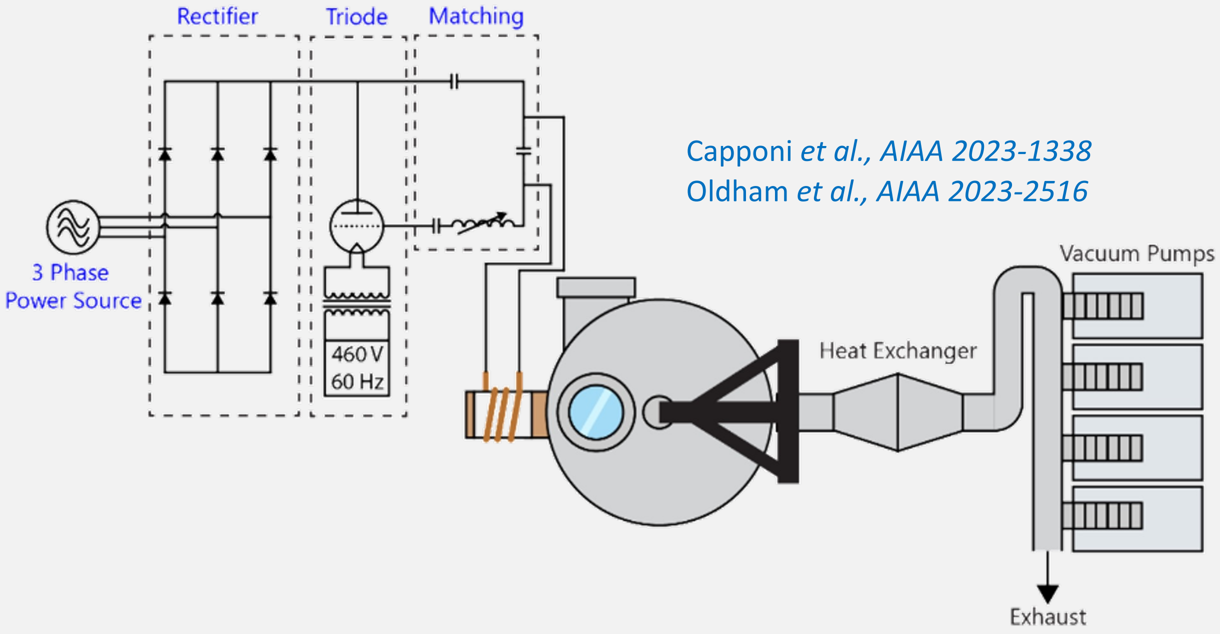


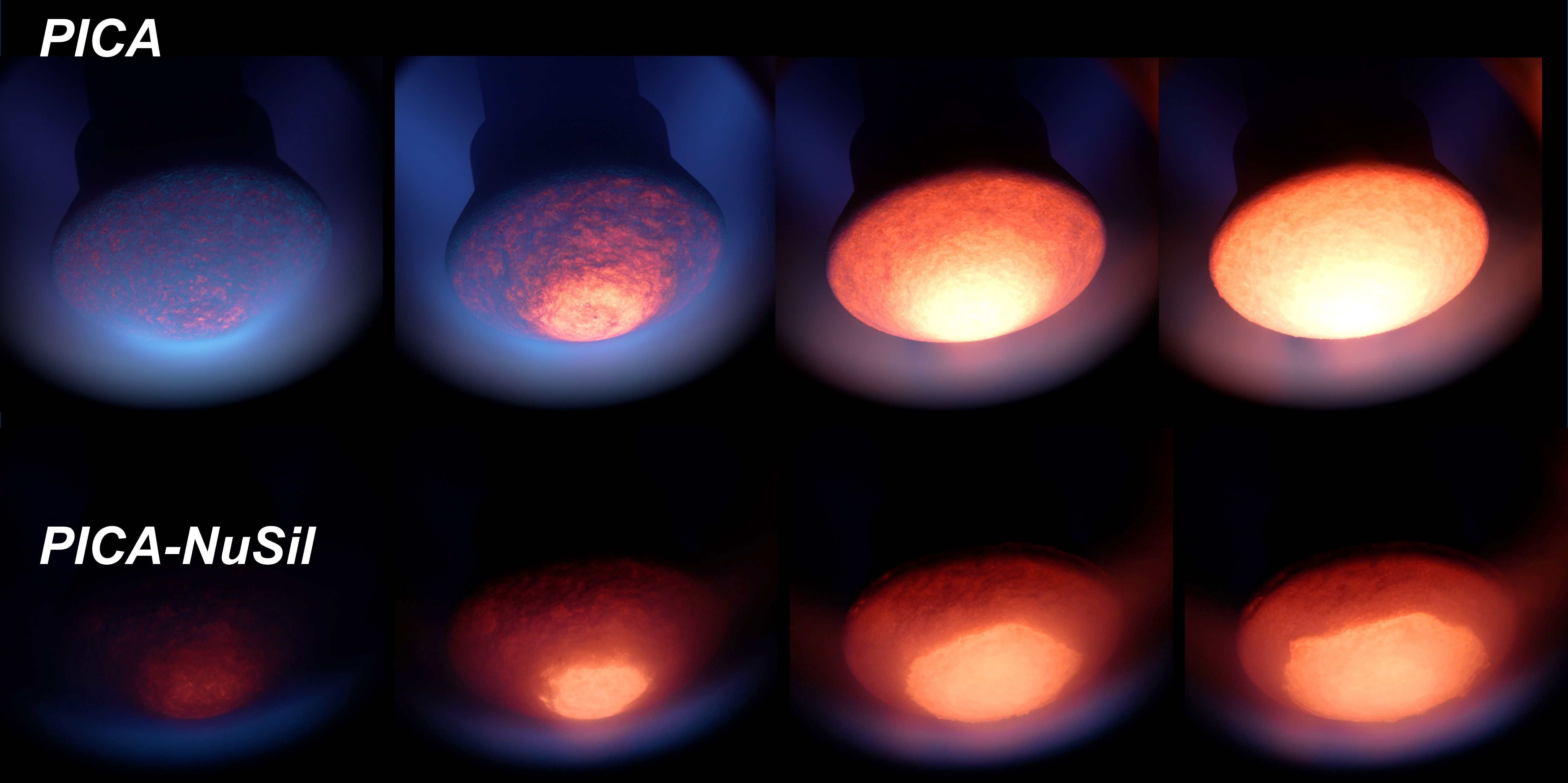
Test Article	Material	Test Condition	Simulated Atmosphere	Heat Flux (W cm^{-2})	Stagnation Pressure (kPa)	Test Length (s)
PS01	PICA-N′	B	Earth	140	5.6	28
PS02	PICA-N	B	Earth	140	5.6	30
PS03	PICA-N	B	Earth	140	5.6	30
PS04	PICA-N	C	Earth	60	4.1	67
PS05	PICA-N	A	Earth	224	6.6	29
PS06	PICA-N	B	N_2	131	5.3	29
PS07	PICA-N	B	Mars	127	5.2	33
PS08	PICA-N	C	Earth	60	3.9	30
PS09	PICA	B	Earth	140	5.6	30
PS10	PICA	B	N_2	130	5.3	30
PS11	PICA	A	Earth	223	6.6	21
PS12	PICA	B	Mars	126	5.3	31

CHESS Plasmatron X

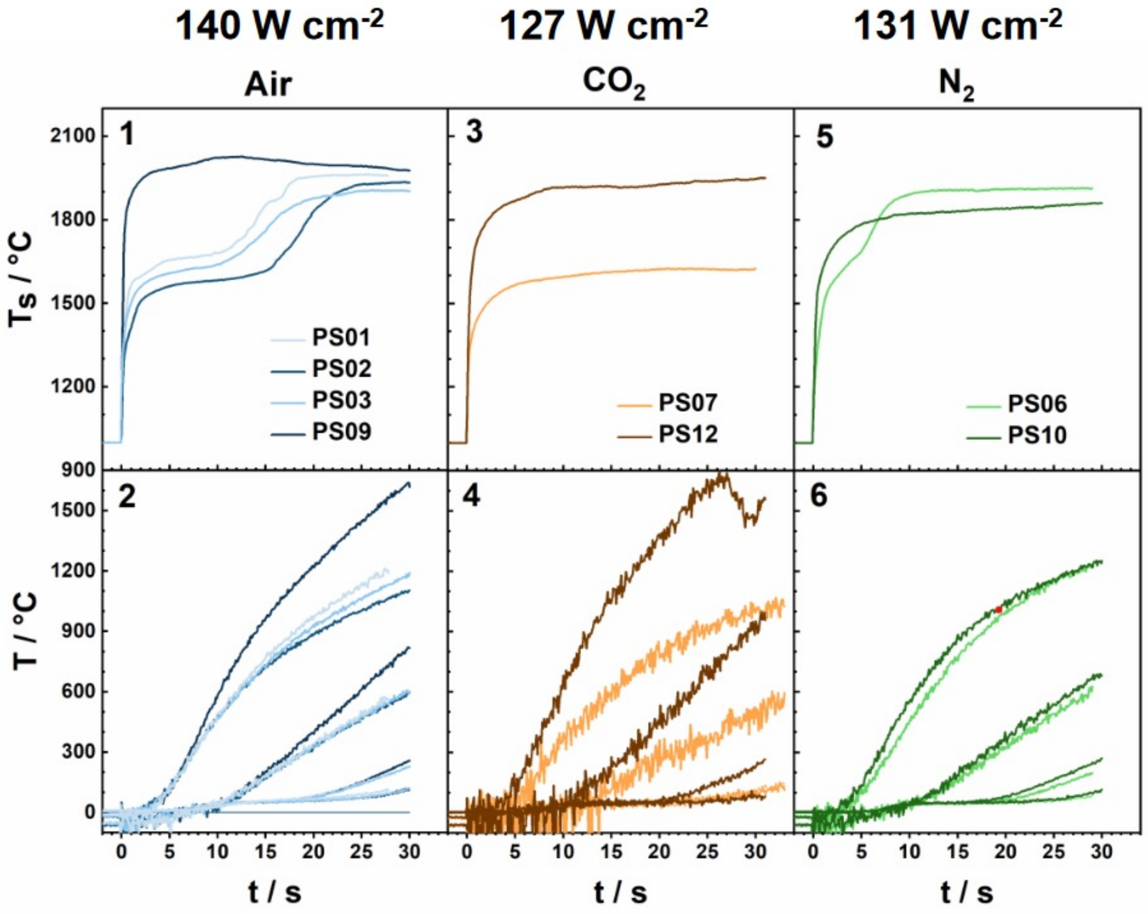
Capponi *et al.*, *AIAA 2023-1338*
Oldham *et al.*, *AIAA 2023-2516*

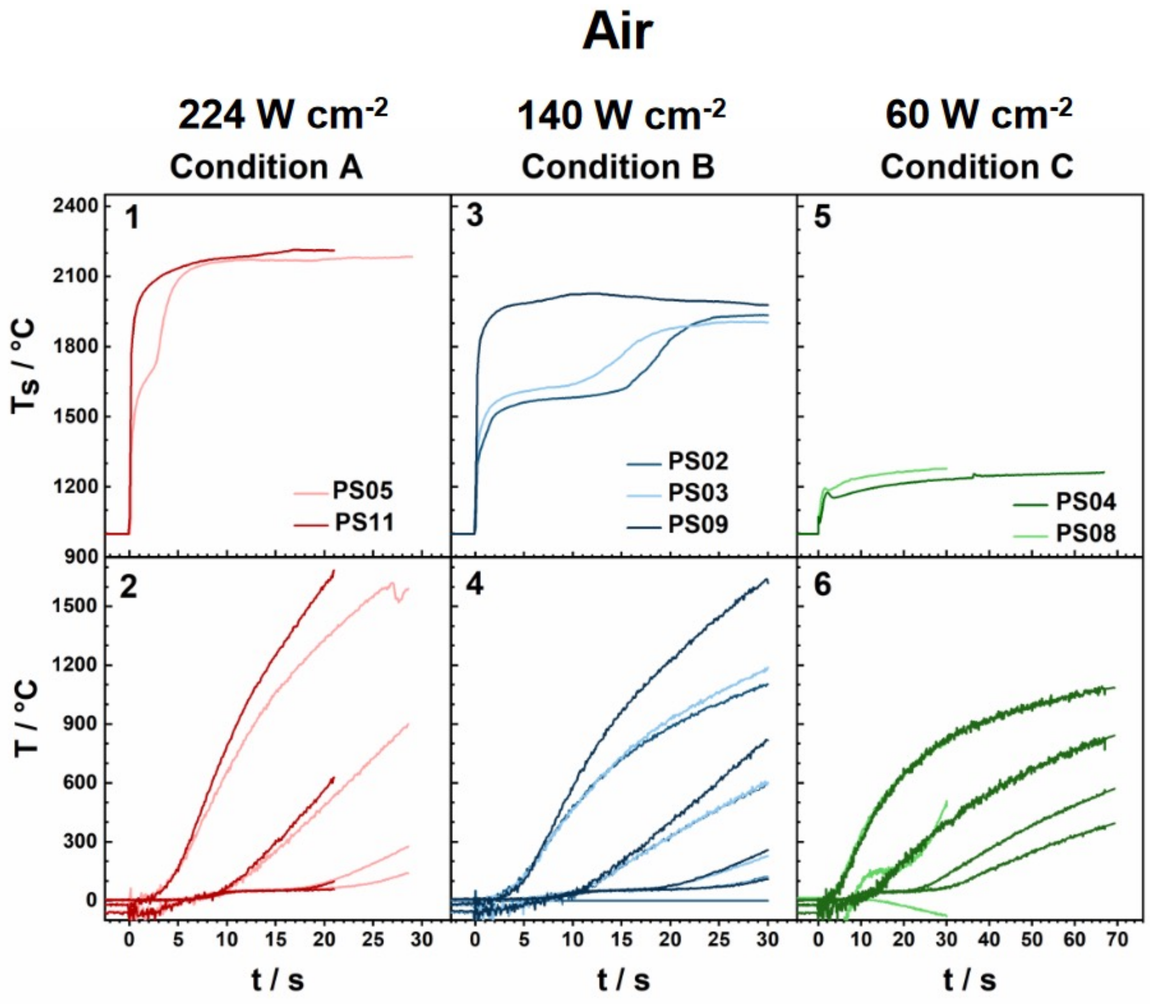


Test ID	Sample ID	P (kW)	p_s (Pa)	p_t (Pa)	$\dot{m}_{CO_2}$ (g/s)	q''_{cw} (W/cm^2)	τ (s)	$\dot{m}_C$ (g/s)
PN1	MS-VI	105	676	1448	6.2	112	60	0.039
PN6	MS-XVIII	105	206	912	5.2	94	32	0.044
PN2	MS-IV	81	104	760	6.5	73	60	0.022
PN3	MS-I	81	114	758	6.5	73	148	0.019
PN4	MS-V	45	203	661	6.5	41	60	0.018
PN5	MS-III	45	199	769	6.5	40	138	0.012
P7	MS-XV	105	203	880	6.5	108	60	0.050
P8	MS-XVI	78	199	832	6.5	75	60	0.041
P9	MS-XVII	45	197	653	6.5	46	60	0.030


PICA
PICA-NuSil

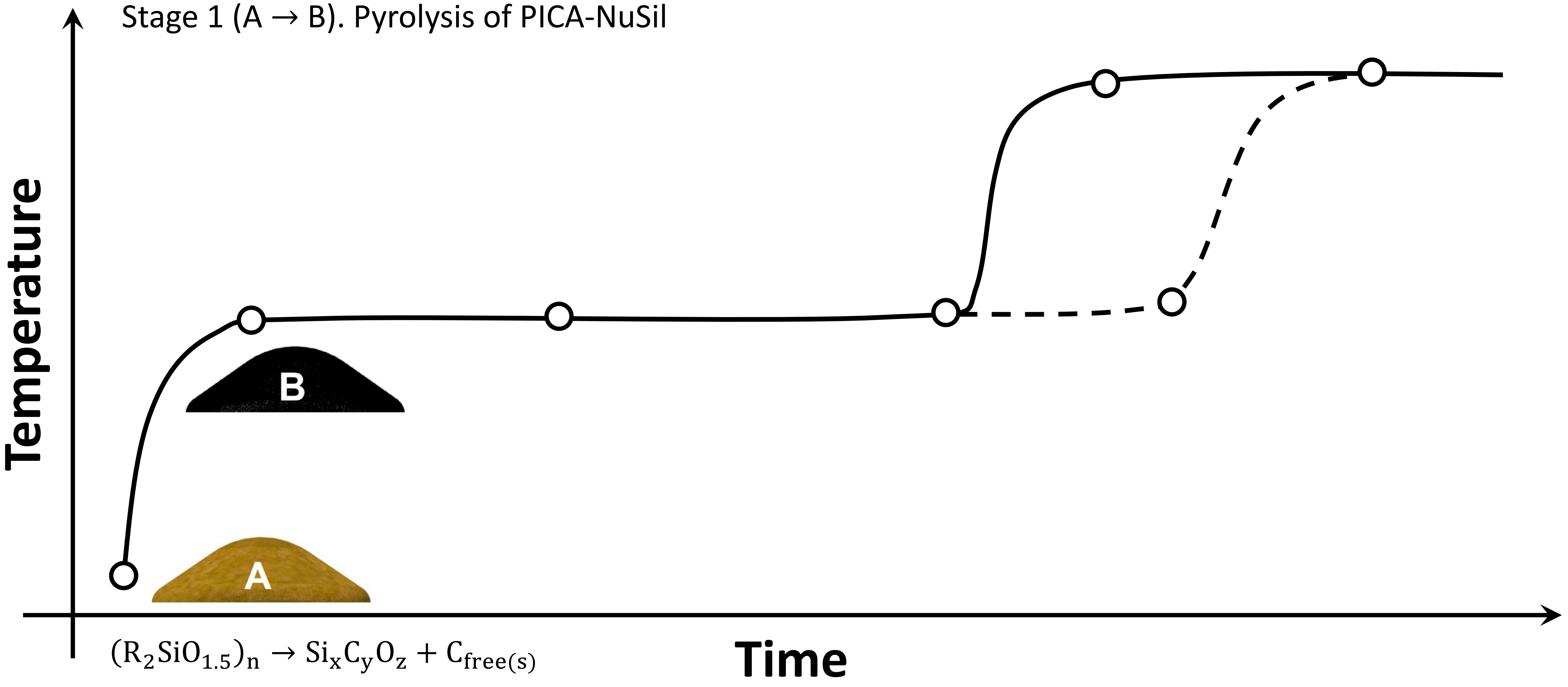
PICA-NuSil Thermal Response





- NuSil lowers the measured surface temperature and in-depth response in oxidizing atmospheres.
- Survival of the coating increases at lower heating rates.

Discussion on PICA-NuSil Ablation Mechanisms



$(R_2SiO_{1.5})_n \rightarrow Si_xC_yO_z + C_{free(s)}$

Discussion on PICA-NuSil Ablation Mechanisms

- **MEKO – Nitrogen (orange trace, A)**

  a) Multistep decomposition process.

  b) Char yield (64 wt.%). > NuSil (10 wt.%)

- **NuSil – Nitrogen**

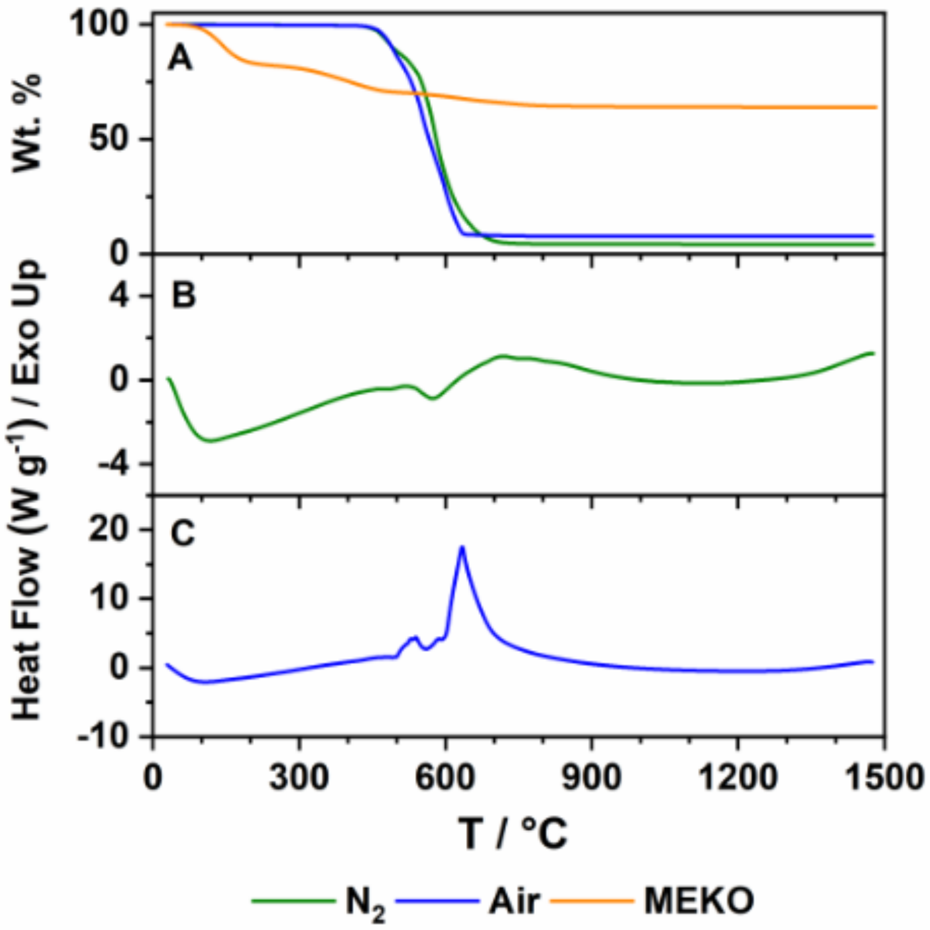
  a) TGA data show significant mass loss at T > 450 ºC (green trace, A).

  b) DSC data indicate that overall process is endothermic (green trace, B).

- **NuSil – Air**

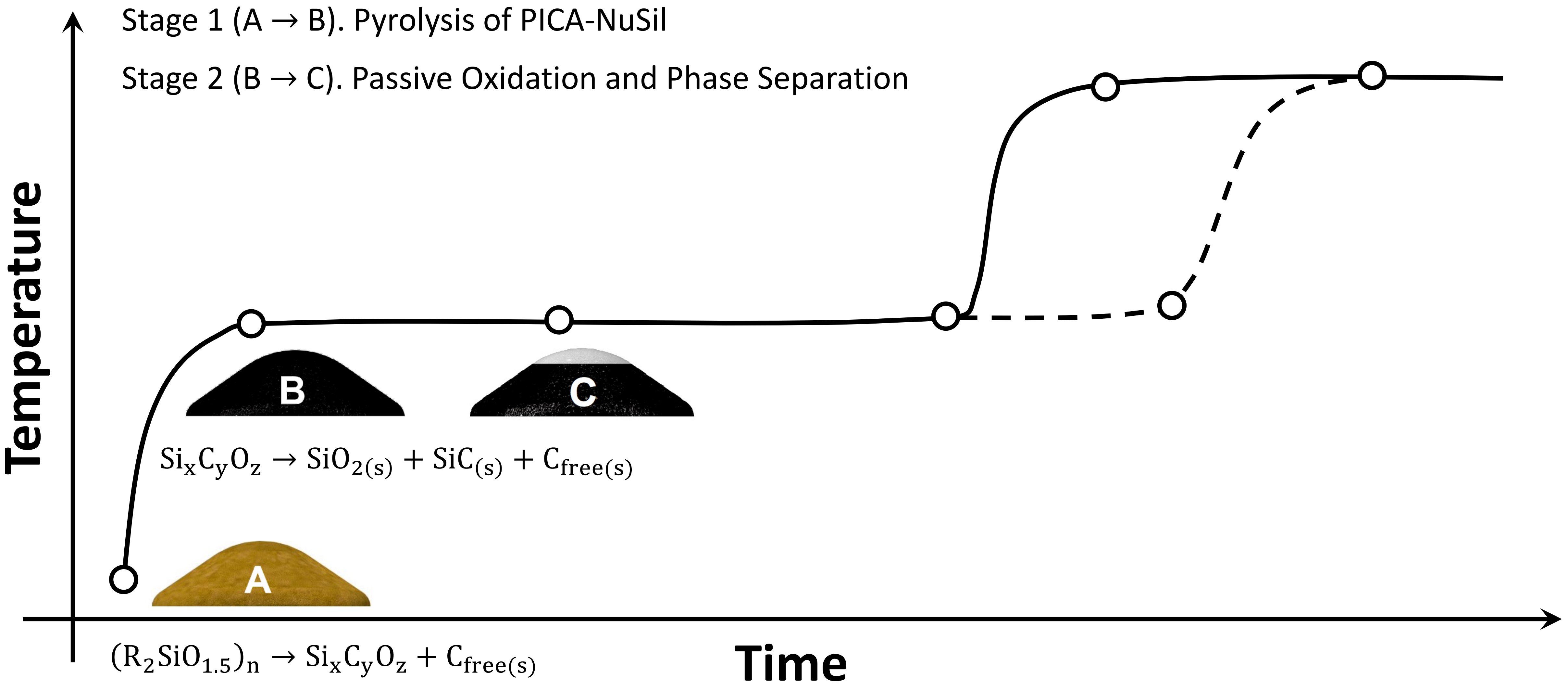
  a) Char yield is comparable to pyrolysis.

  b) DSC data show intense exotherm which is attributed to the oxidation of NuSil.



TGA/DSC data were collected on samples of NuSil at a heating rate of 40 ºC min^{-1} between T = ambient - 1475 ºC.

Discussion on PICA-NuSil Ablation Mechanisms

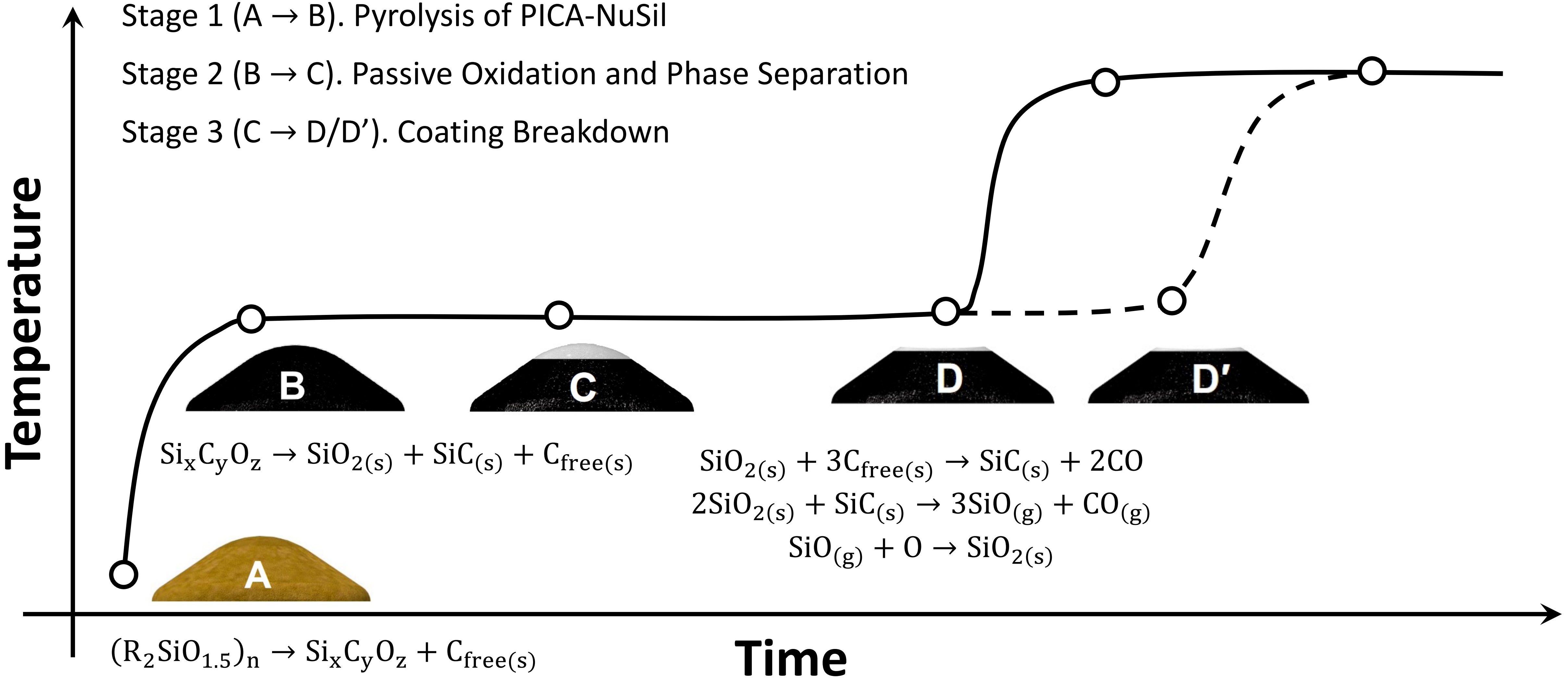


Discussion on PICA-NuSil Ablation Mechanisms

Stage 1 (A → B). Pyrolysis of PICA-NuSil

Stage 2 (B → C). Passive Oxidation and Phase Separation

Stage 3 (C → D/D’). Coating Breakdown



$(R_2SiO_{1.5})_n \rightarrow Si_xC_yO_z + C_{free(s)}$

$Si_xC_yO_z \rightarrow SiO_{2(s)} + SiC_{(s)} + C_{free(s)}$

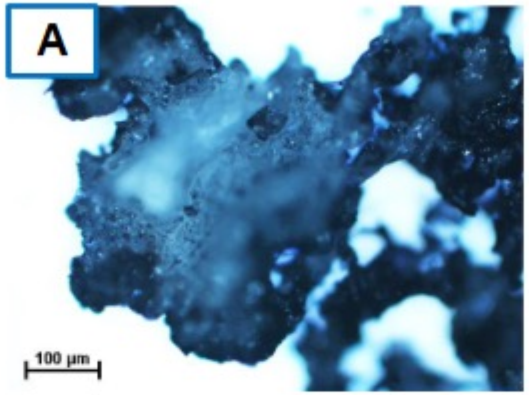
$SiO_{2(s)} + 3C_{free(s)} \rightarrow SiC_{(s)} + 2CO$

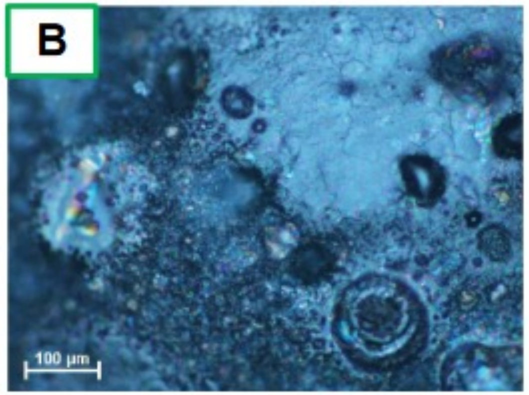
$2SiO_{2(s)} + SiC_{(s)} \rightarrow 3SiO_{(g)} + CO_{(g)}$

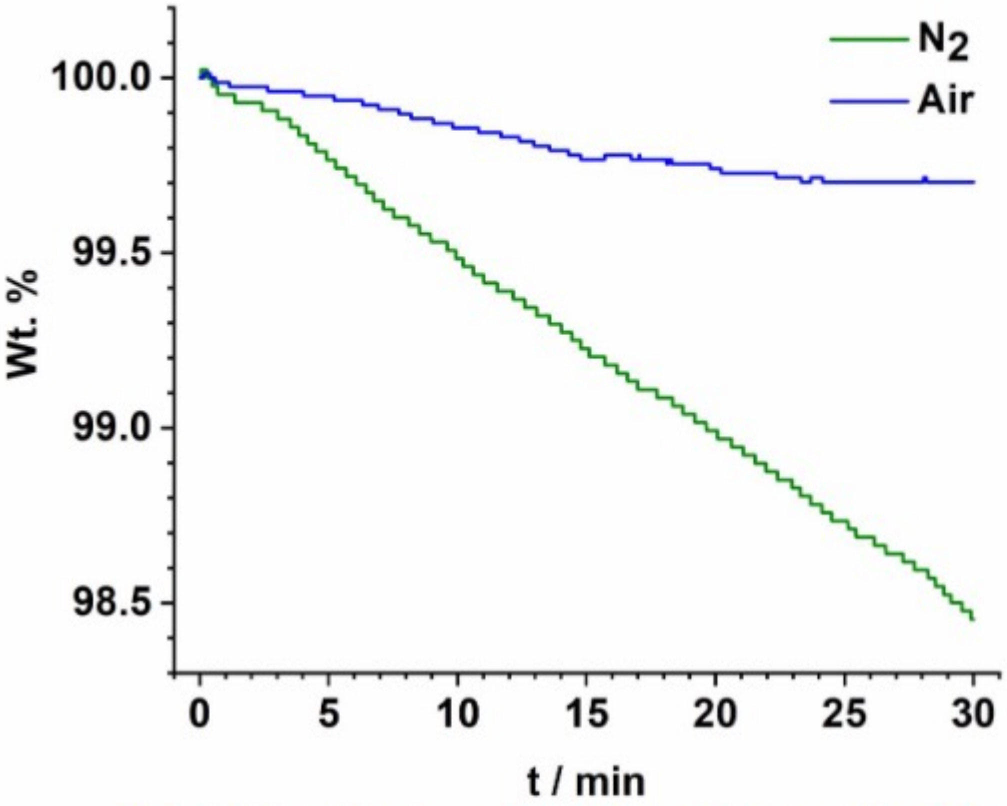
$SiO_{(g)} + O \rightarrow SiO_{2(s)}$

Discussion on PICA-NuSil Ablation Mechanisms

- **Isothermal TGA experiments.**
  - **a) NuSil loses mass at a greater rate in nitrogen than in air.**
- **Microscope images of the post-test resin from TGA experiments performed on NuSil® in (A) air and (B) nitrogen.**
  - **a) Passivating layer of SiO_2 forms at the surface of each material.**

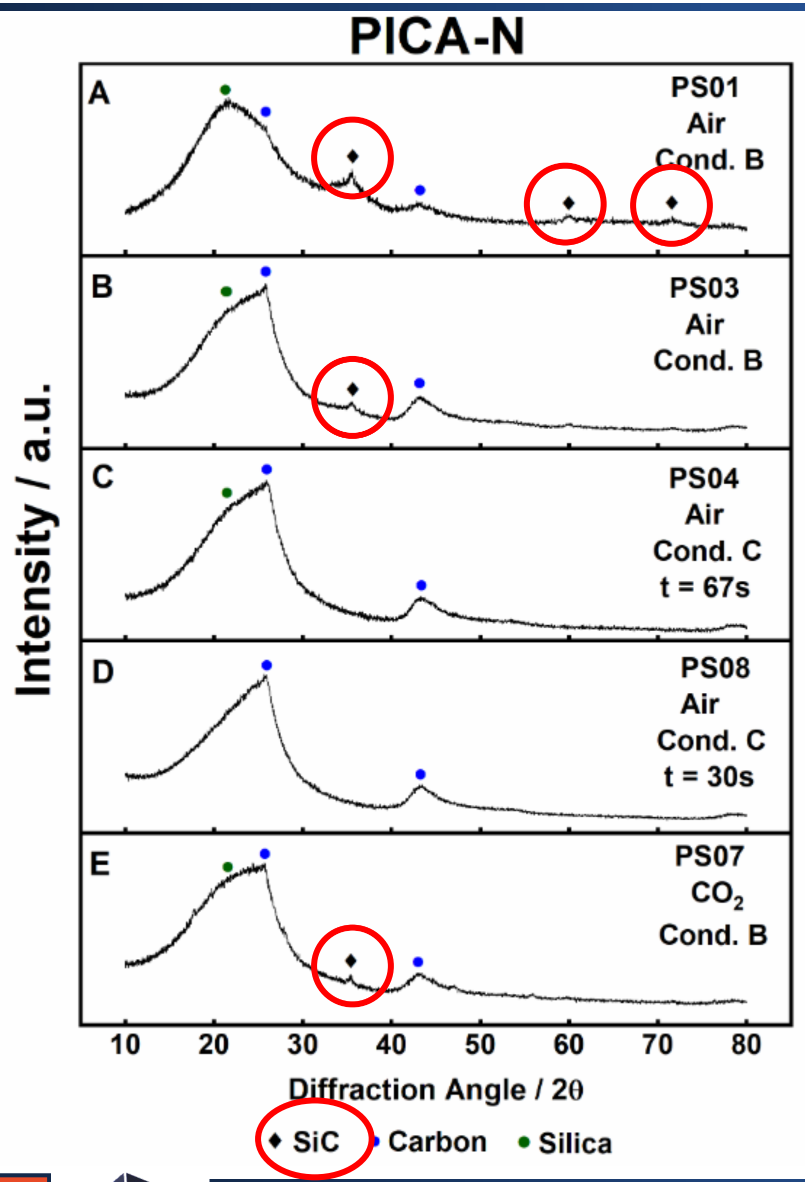




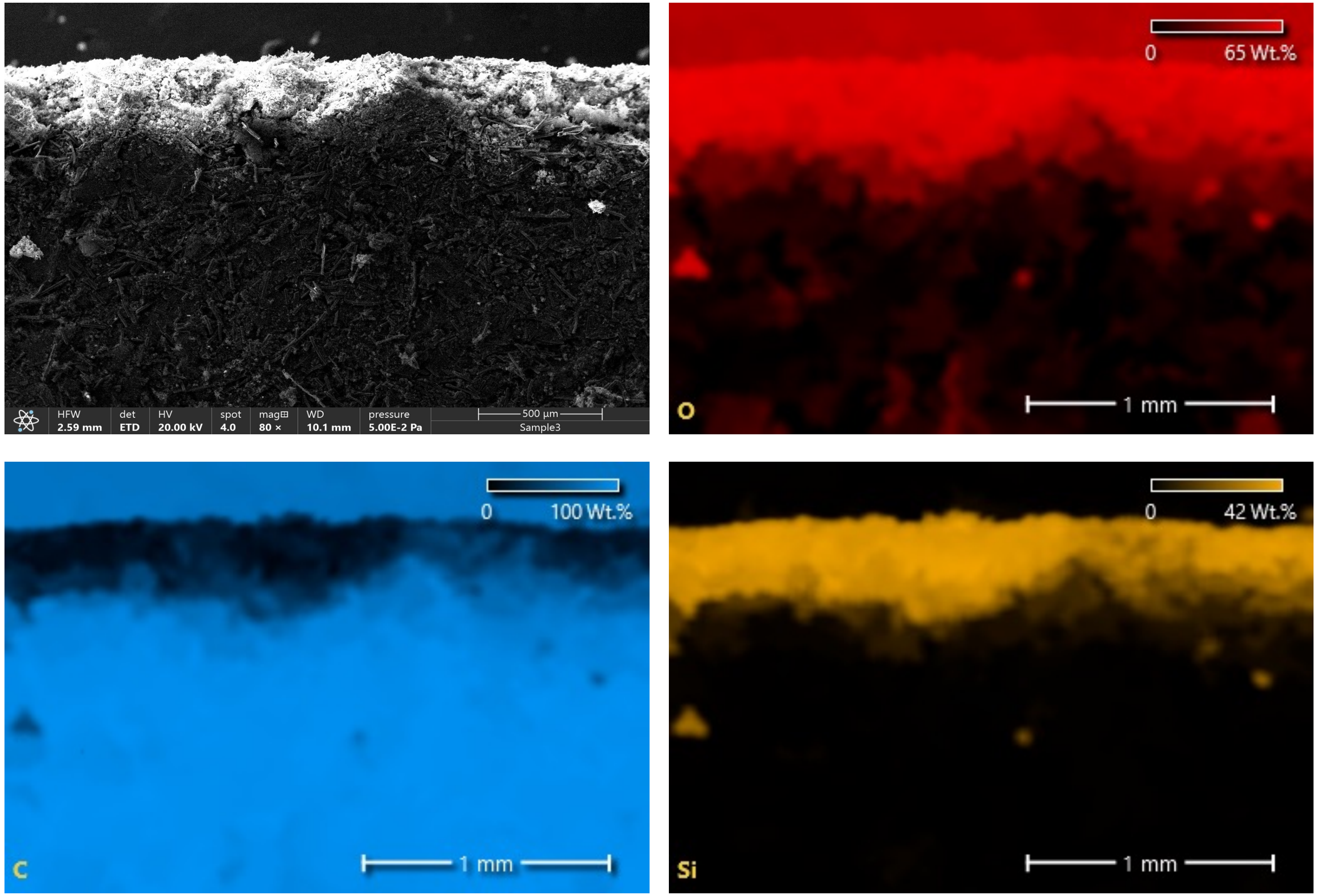


Mass loss rates as a function of time during the isothermal (T = 1475 °C) stage of the TGA experiments.

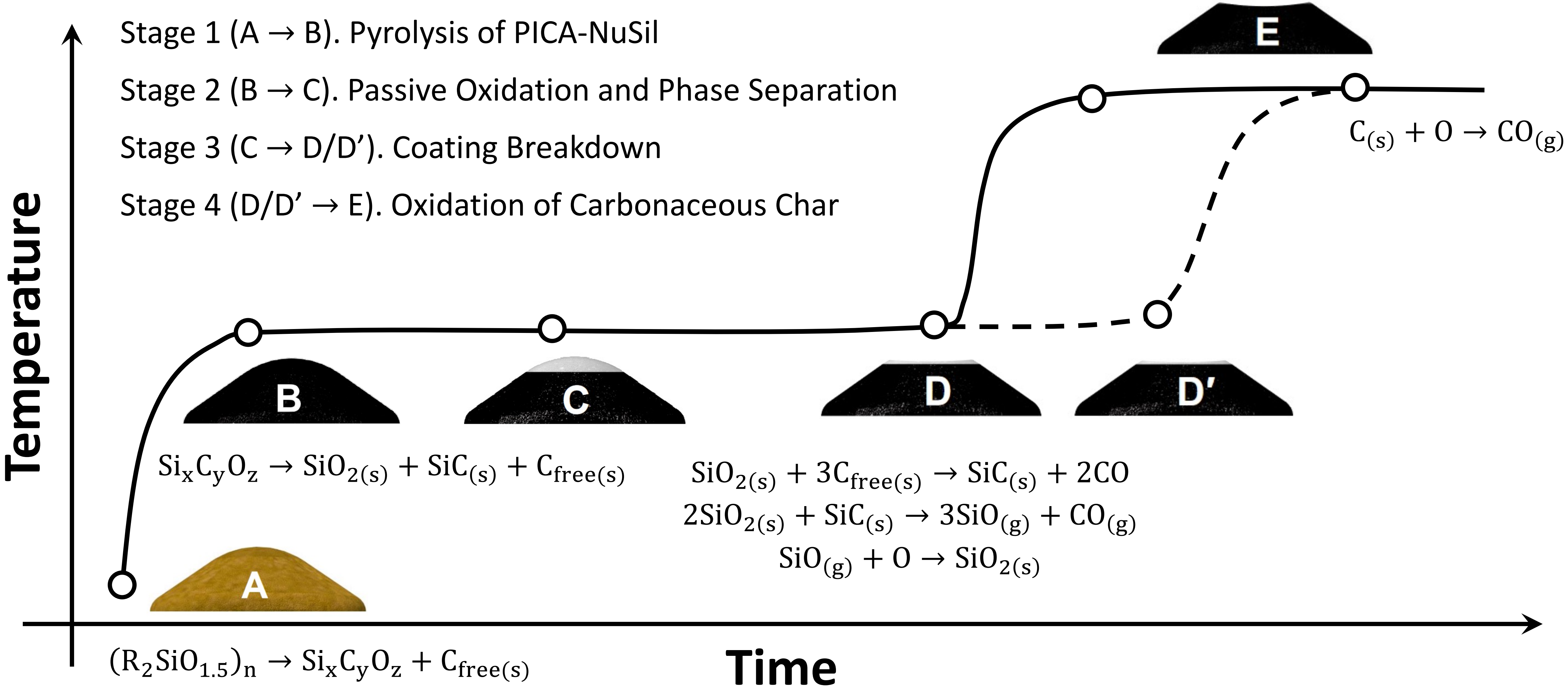
Discussion on PICA-NuSil Ablation Mechanisms



$T_w > 1500°C$



Discussion on PICA-NuSil Ablation Mechanisms



Conclusions

- Active oxidation conditions insufficient to trigger instability
- Sublimation of SiC and Si
- Further exothermicity from O- and N-atom reactions with C, catalytic reactions and properties change (optical and thermal)

- Ablator coating lowers surface temperature and in-depth response in oxidizing conditions (Air & CO2)
- Coating survives longer at lower heating rates and higher partial pressures of O(g) & CO(g)