The Material Response of PICA-NuSil™ to a Hypersonic Flow Environment

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™NuSil (CV-1144-0) is a product of Avantor Sciences

Key Concepts

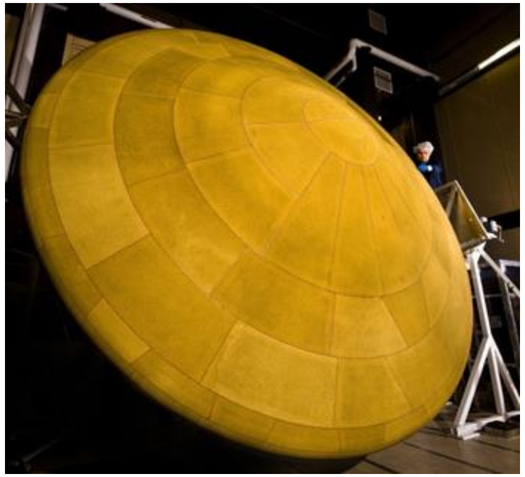
1) What is PICA – NuSil?

2) Does NuSil have an impact on the material response of PICA during arc-jet testing?

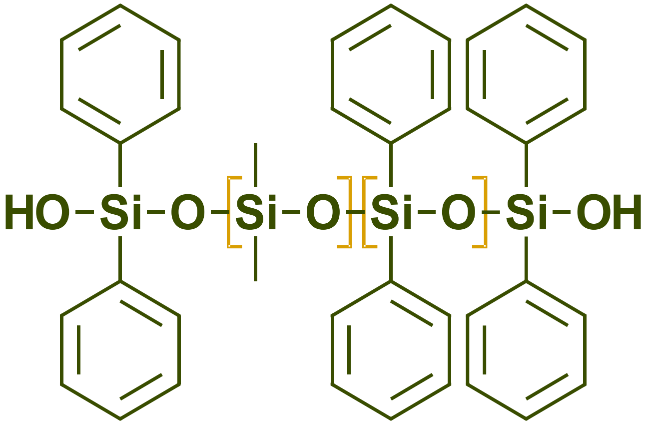
3) What is the ablation mechanism for PICA – NuSil?

What is PICA – NuSil?

PICA

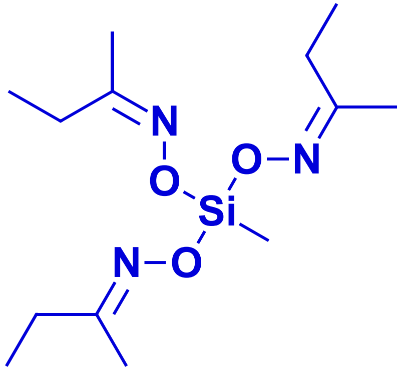


Siloxane Copolymer Backbone



m = 0.95 ; n = 0.05

Oxime Crosslinking Agent

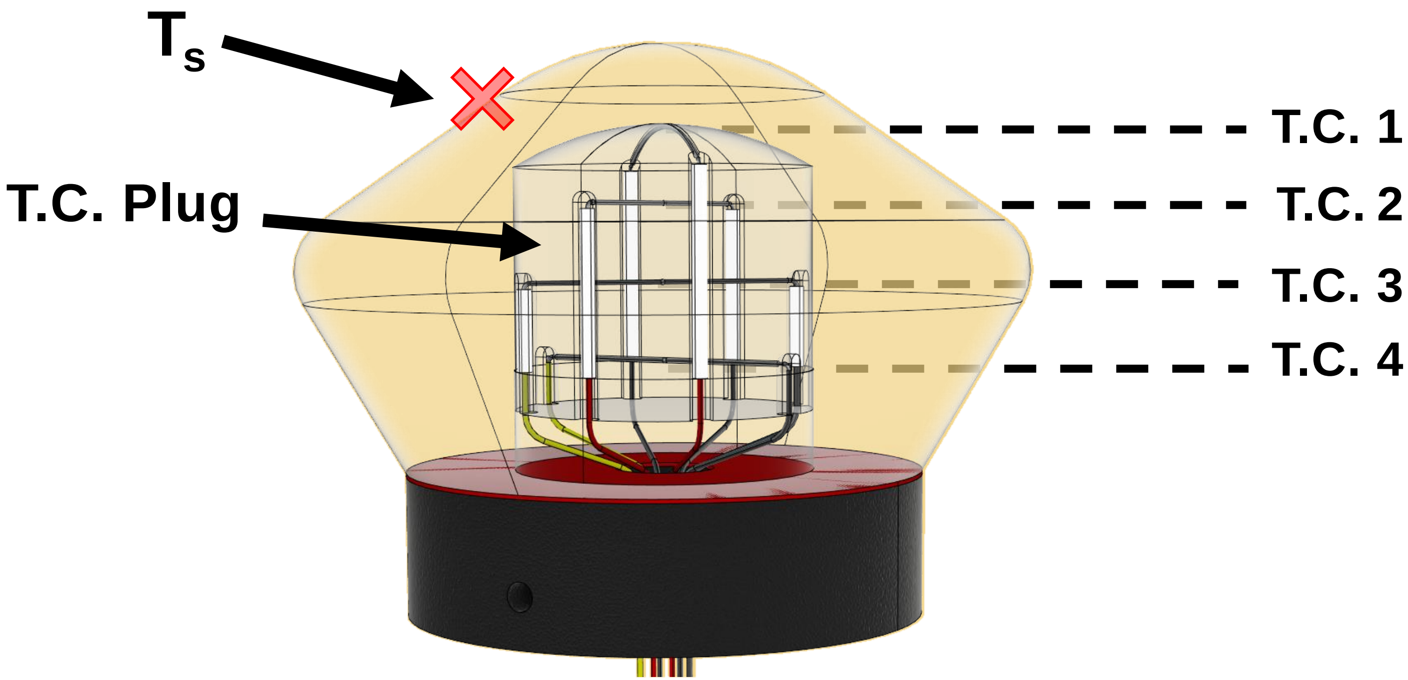


MEKO

- **The phenolic phase of PICA is friable.**
- **A thin coating of NuSil (CV-1144-0) is applied to the surface of flight hardware to mitigate particulate shedding during pre-flight activities.**
- **Does NuSil have an impact on the performance of PICA during arc-jet testing?**

PICA – NuSil / Test Model Architecture

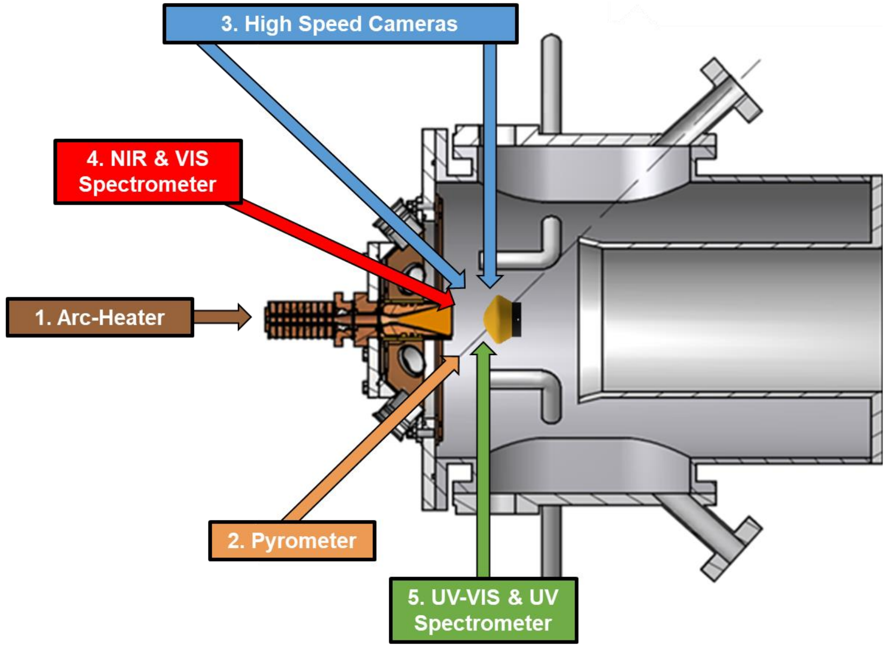
- **Sphere-cone geometry was chosen to observe the formation of a viscous melt layer.**
- **Each model was instrumented with a thermocouple plug to measure the in-depth temperature response.**
- **Two R-type thermocouples and two K-type thermocouples spaced ~ 5 mm apart.**
- **8 sphere-cone models were masked and coated with NuSil.**
- **Average areal density of NuSil coating ~ 10.0 ± 1.0 mg cm^{-2} (PICA-N).**
- **One model coated with twice the areal density ~ 19 mg cm^{-2} (PICA-N′).**



HyMETS / Test Conditions

- A two-color pyrometer was used to measure the surface temperature.
- High-speed cameras were used to observe salient phenomena and measure recession rates.
- A suite of emission spectrometers were used to analyze species in the post-shock region.

Hypersonic Materials Environmental Test System



Test Conditions

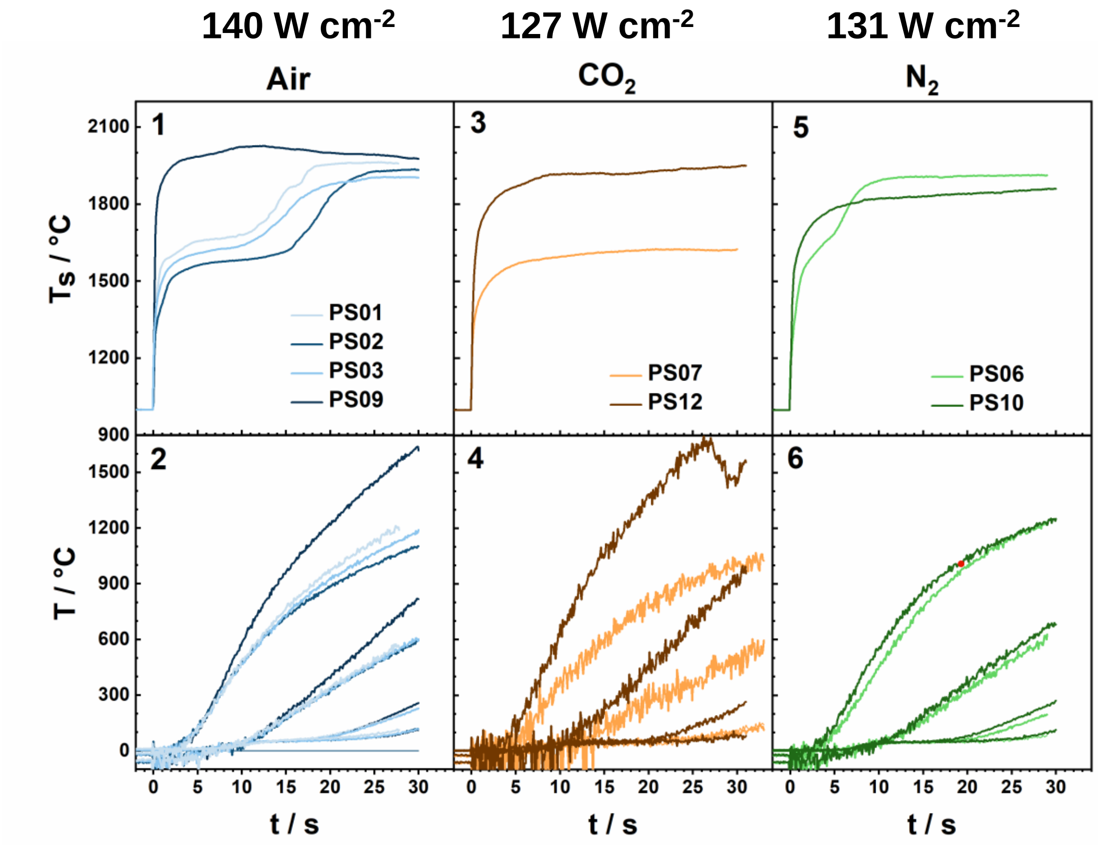
Test Article	Material	Test Condition	Simulated Atmosphere	Heat Flux (W cm^{-2})	Stagnation Pressure (kPa)	Test Length (s)
PS01	PICA-N′	B	Earth	140	5.6	28
PS02	PICA-N	B	Earth	140	5.6	30
PS03	PICA-N	B	Earth	140	5.6	30
PS04	PICA-N	C	Earth	60	4.1	67
PS05	PICA-N	A	Earth	224	6.6	29
PS06	PICA-N	B	N_2	131	5.3	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

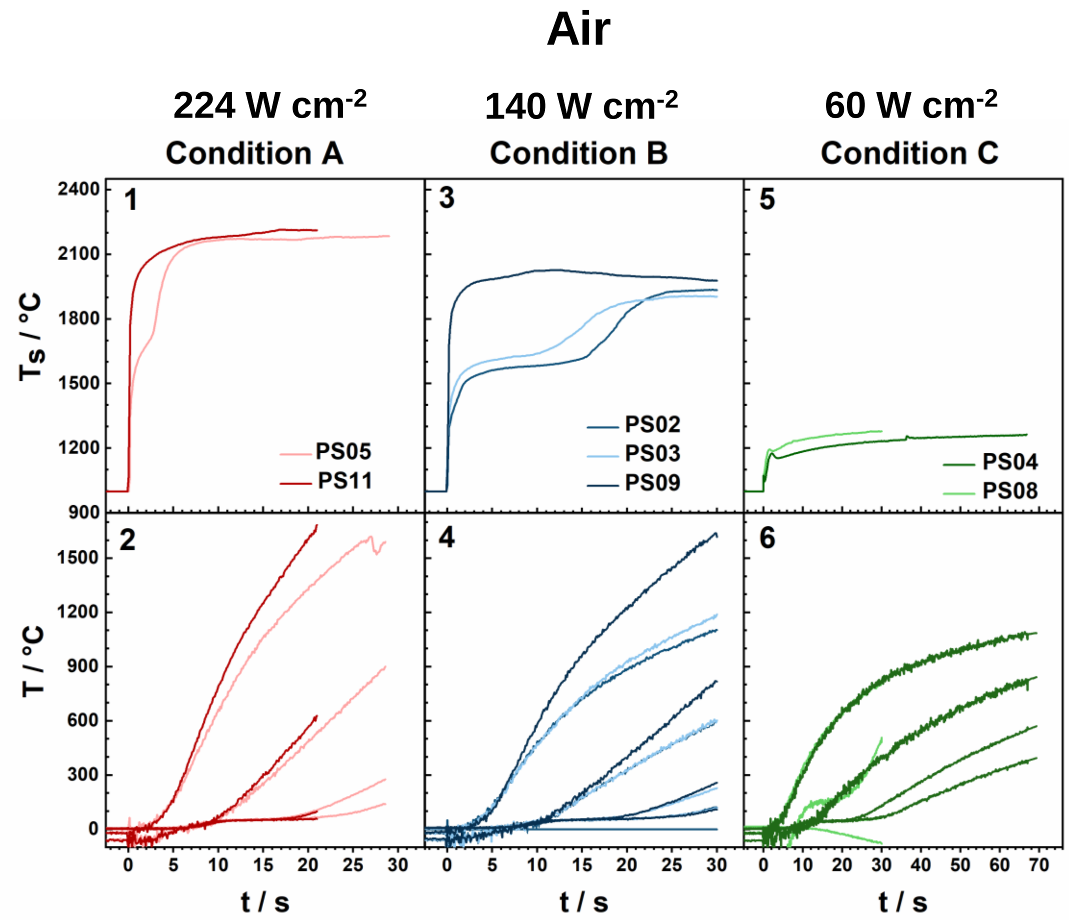
Flow Composition

Flow Composition		
Earth	Mars	Titan
N_2: 75%	CO_2: 85%	N_2: 95%
O_2: 21%	N_2: 10%	Ar: 5%
Ar: 4%	Ar: 5%	

- Data collected in 3 gas flow compositions (e.g., Air, CO_2, N_2).

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.

Post-Test Analysis / Material Response

Panel figures illustrating changes in morphology, surface temperature, and emission.

Panel A)

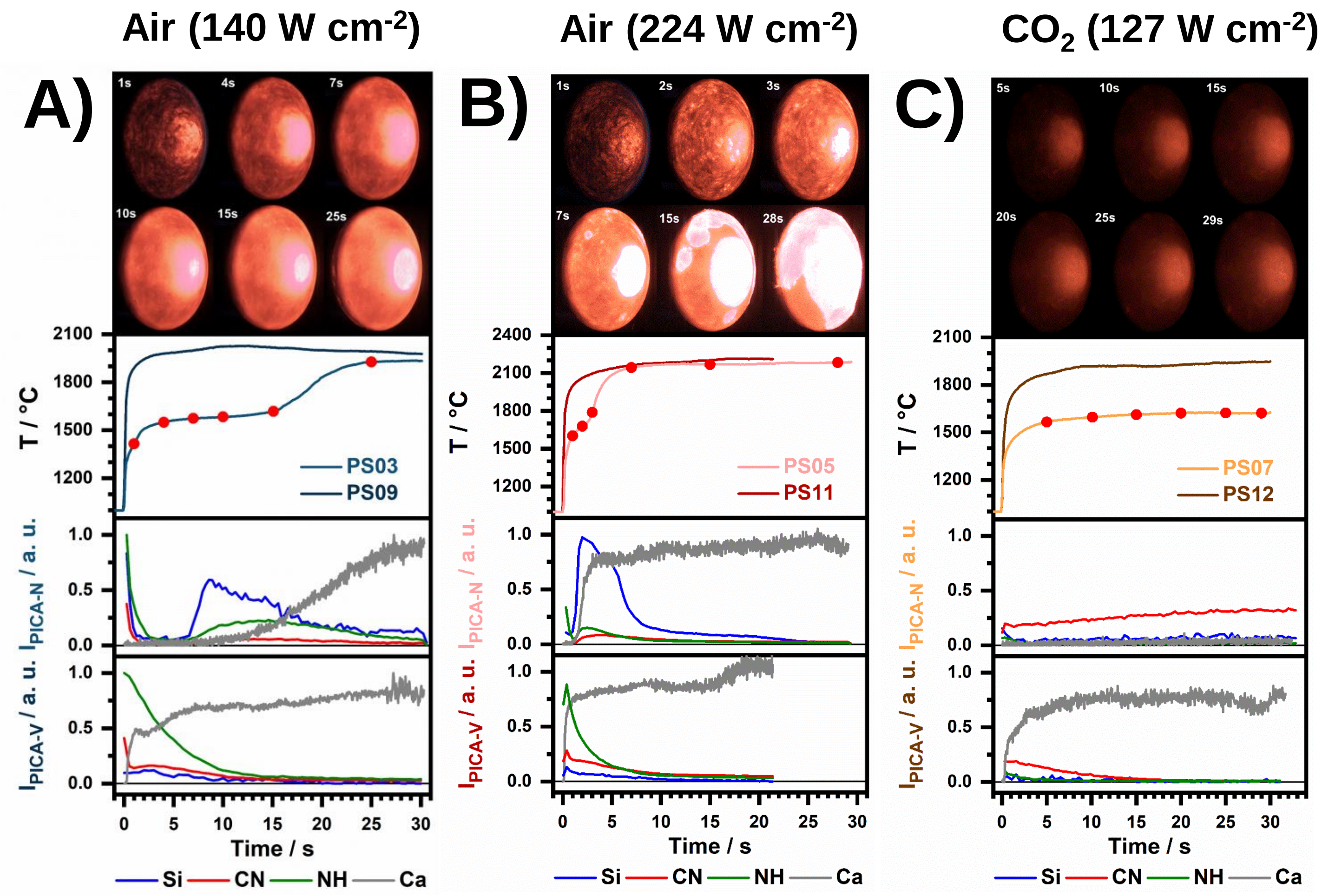
- **Emission signal indicates rapid pyrolysis in the stagnation region.**
- **Pyrolysis is followed by a stagnation in emission signal.**
- **Si emission indicates that NuSil decomposes over the course of 2 seconds.**
- **A rise in Ca emission (t = 11s) indicates that FiberForm has been exposed to the reactive flow.**

Panel B)

- **Similar phenomena observed in panel B but on a compressed timescale.**

Panel C)

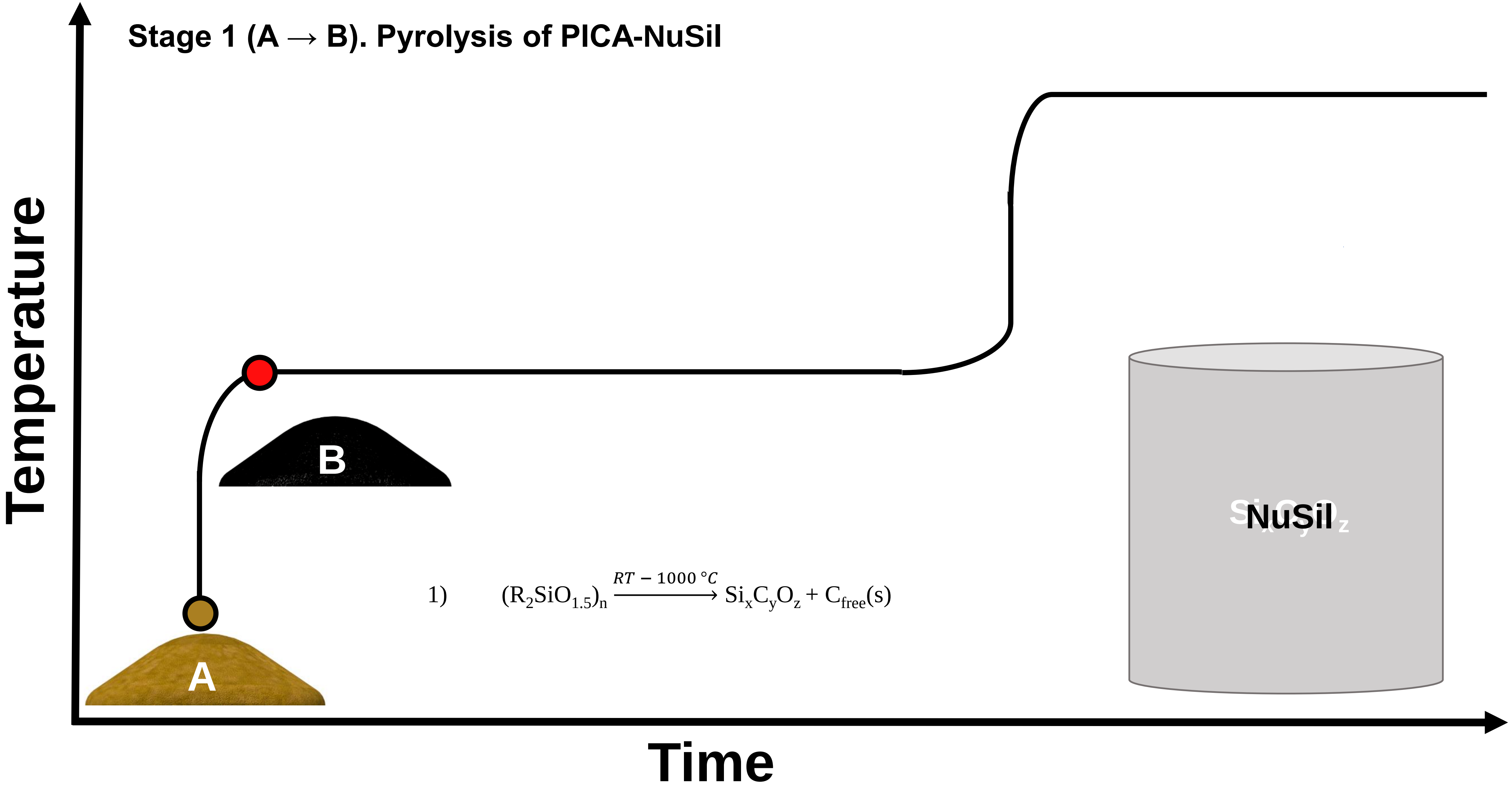
- **Surface temperature and emission data indicate that the coating is relatively stable in CO_2.**



Panel figures showing still images from high-speed video, surface temperature data, and traces of species emitting in the boundary layer (e.g., Si – 251.6 nm, CN – 358.5, & NH – 336.1 nm) and stagnation surface (Ca – 422.7 nm). Panel A) illustrates the ablation process for PS03 and condition B. Panel B) illustrates the ablation process for PS05 and condition A. Panel C) illustrates the ablation process for PS07 and condition B.

PICA – NuSil Ablation Mechanism

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



1) $(R_2SiO_{1.5})_n \xrightarrow{RT - 1000\,°C} Si_xC_yO_z + C_{free}(s)$

NuSil / Thermogravimetric Analysis (TGA)

- MEKO – Nitrogen (orange trace, A)

  a) Multistep decomposition process.

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

- NuSil – Nitrogen

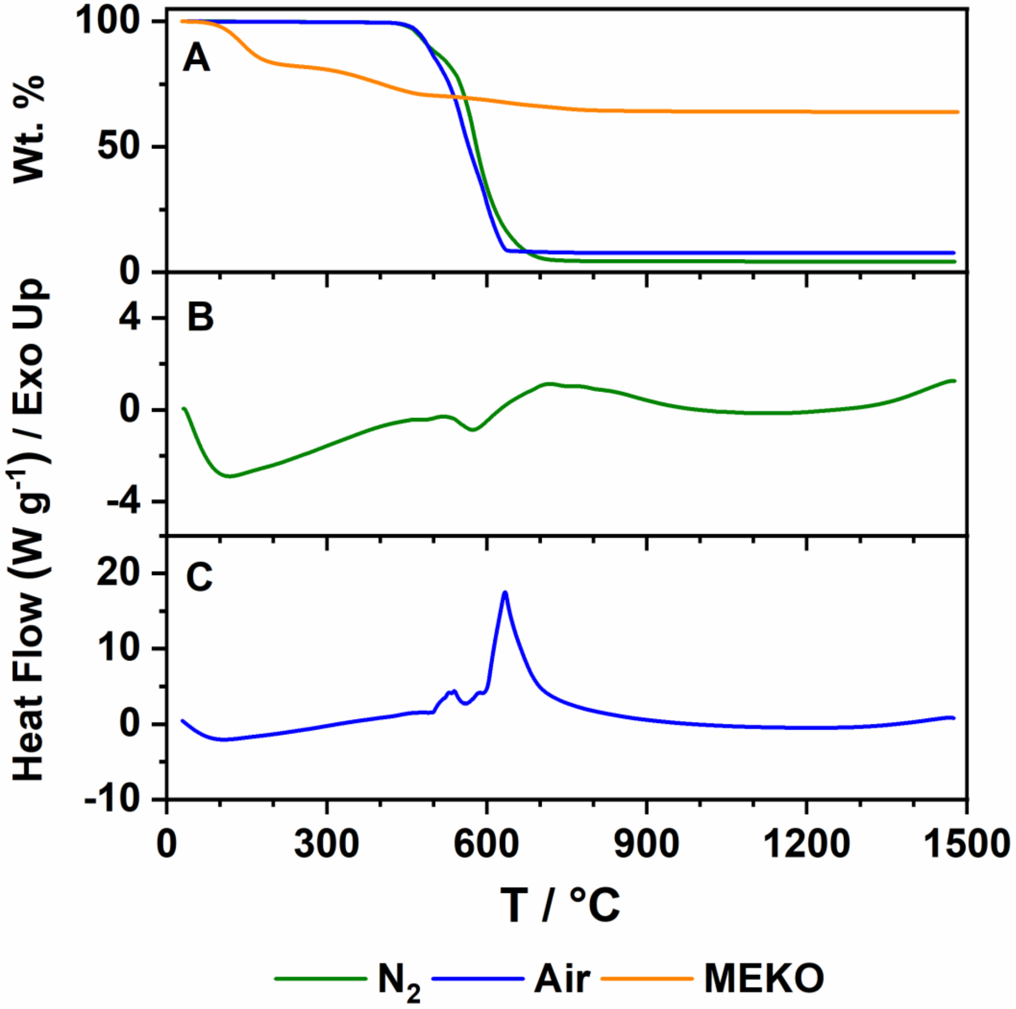
  a) TGA data show significant mass loss at T > 450 ºC (green trace, A).

  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.

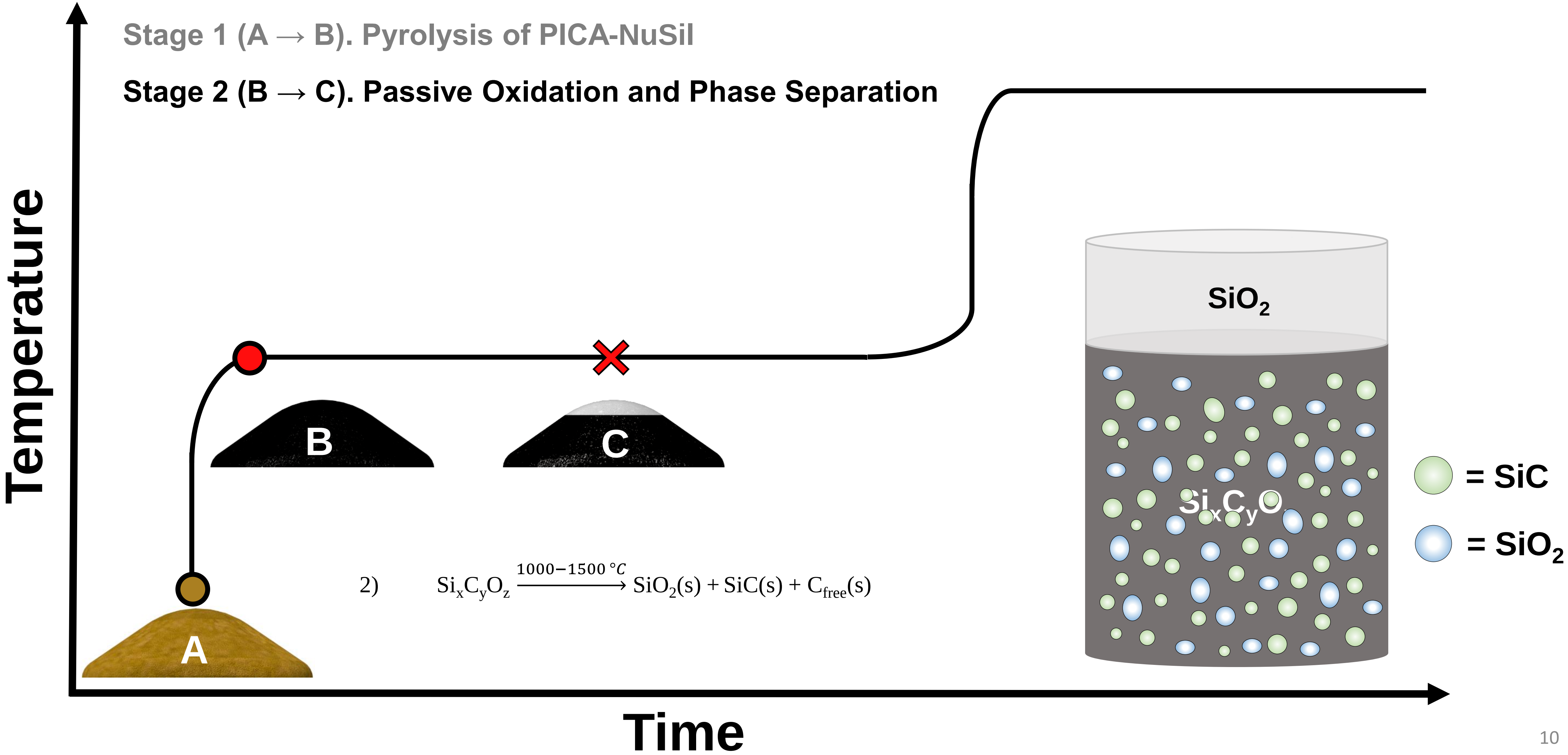


TGA/DSC data were collected on samples of NuSil at a heating rate of 40 ºC min^{-1} between T = ambient - 1475 ºC.

PICA – NuSil / Ablation Mechanism

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

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



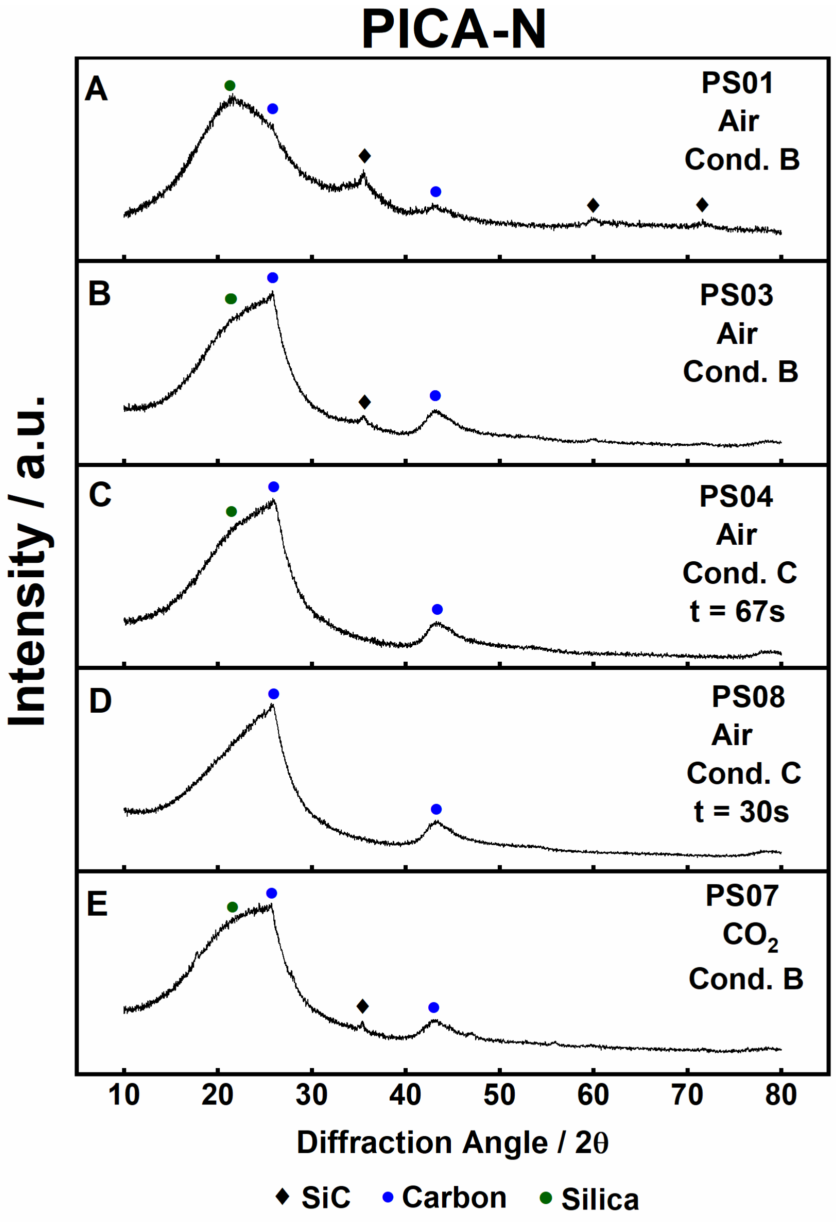
2) $$Si_xC_yO_z \xrightarrow{1000-1500\ ^\circ C} SiO_2(s) + SiC(s) + C_{free}(s)$$

Post-Test Analysis / XRD

- Coatings were collected from the surfaces of models subjected to oxidizing atmospheres.

- Signal for SiC appears in post-test coatings collected from models with a surface temperature T_s > 1500 ºC (e.g., A, B, E).

- Signal for SiC did not appear in coatings collected from models that were subjected to condition C (e.g., T_s < 1300 ºC, 60 W cm^{-2}). Note that this observation remains true even after the length of the test is doubled (e.g., PS04 vs. PS08).

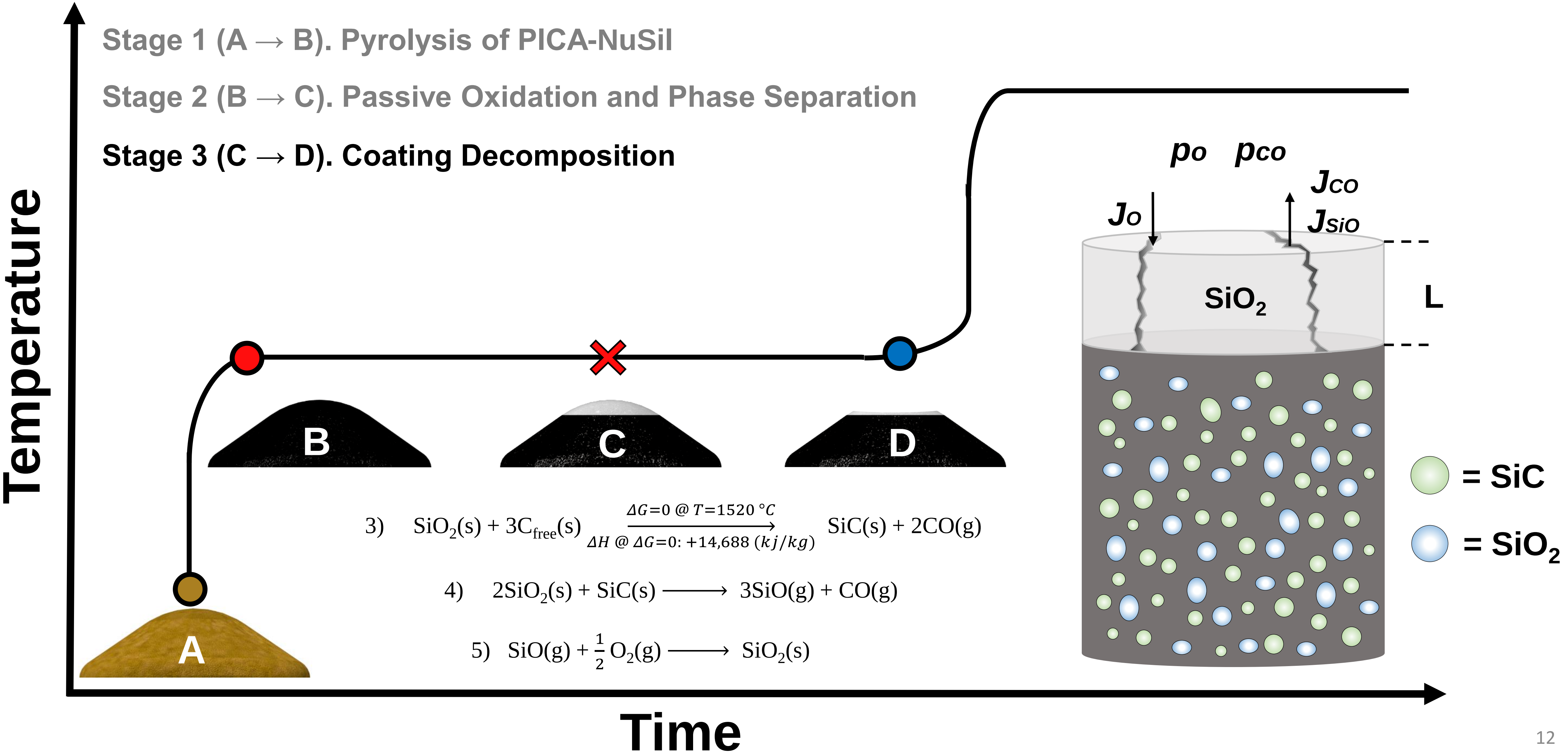


PICA – NuSil / Ablation Mechanism

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

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

Stage 3 (C → D). Coating Decomposition



3) $SiO_2(s) + 3C_{free}(s) \xrightarrow[\Delta H\ @\ \Delta G=0:\ +14{,}688\ (kj/kg)]{\Delta G=0\ @\ T=1520\ °C} SiC(s) + 2CO(g)$

4) $2SiO_2(s) + SiC(s) \longrightarrow 3SiO(g) + CO(g)$

5) $SiO(g) + \frac{1}{2}O_2(g) \longrightarrow SiO_2(s)$

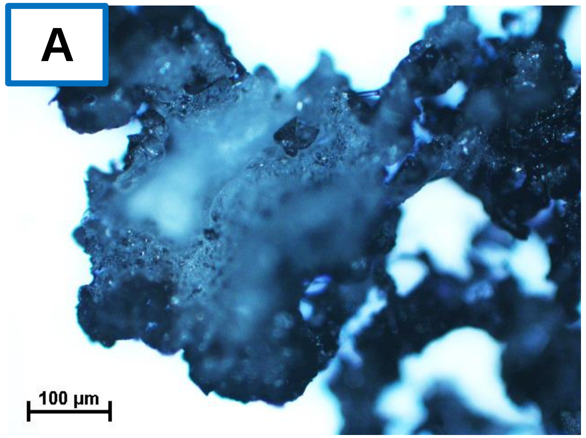
NuSil / Isothermal Analysis (TGA)

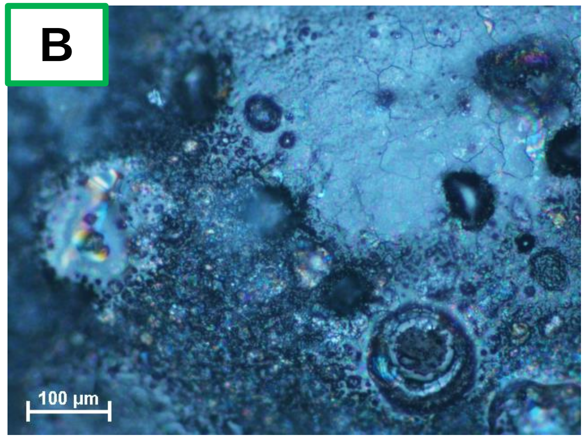
- **Isothermal TGA experiments.**

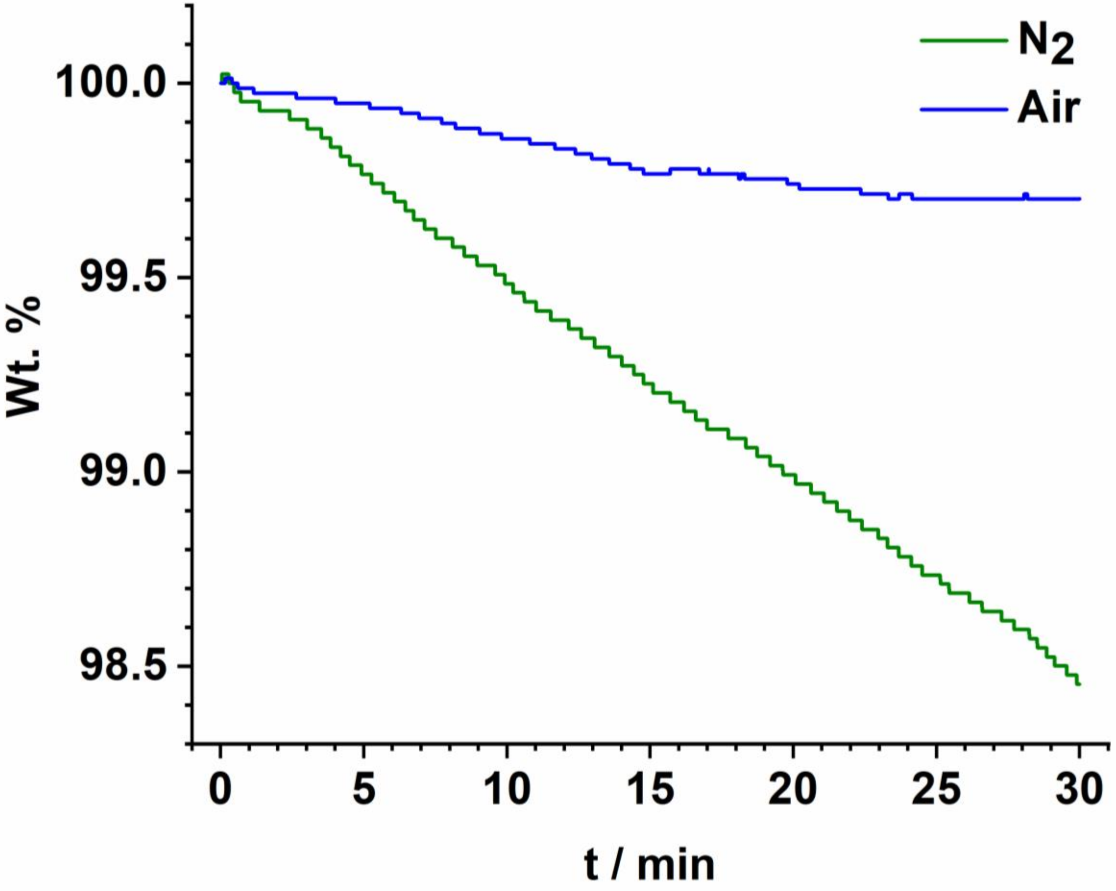
  a) NuSil loses mass at a greater rate in nitrogen than in air.

- **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.

PICA – NuSil / Ablation Mechanism

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

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

Stage 3 (C → D). Coating Decomposition

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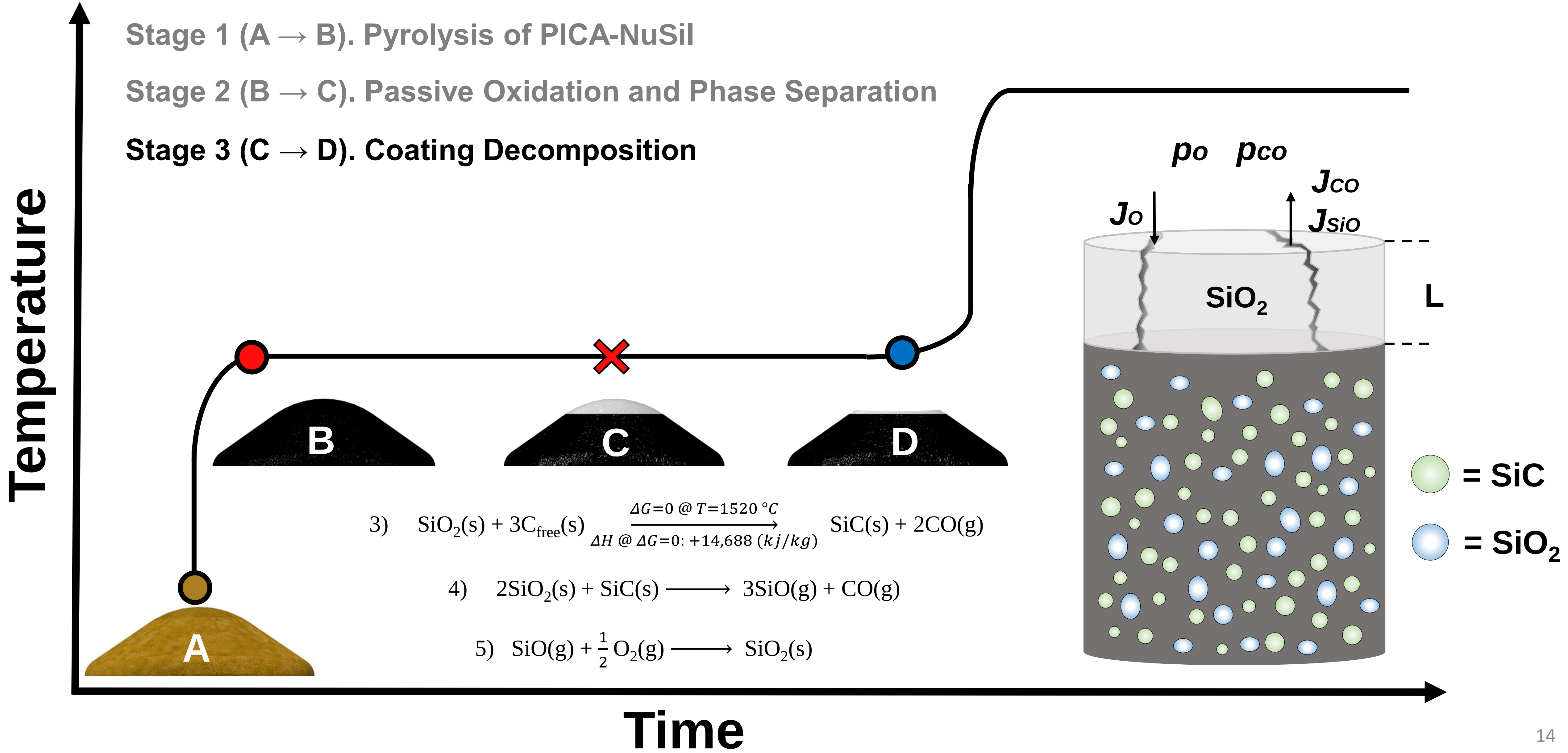
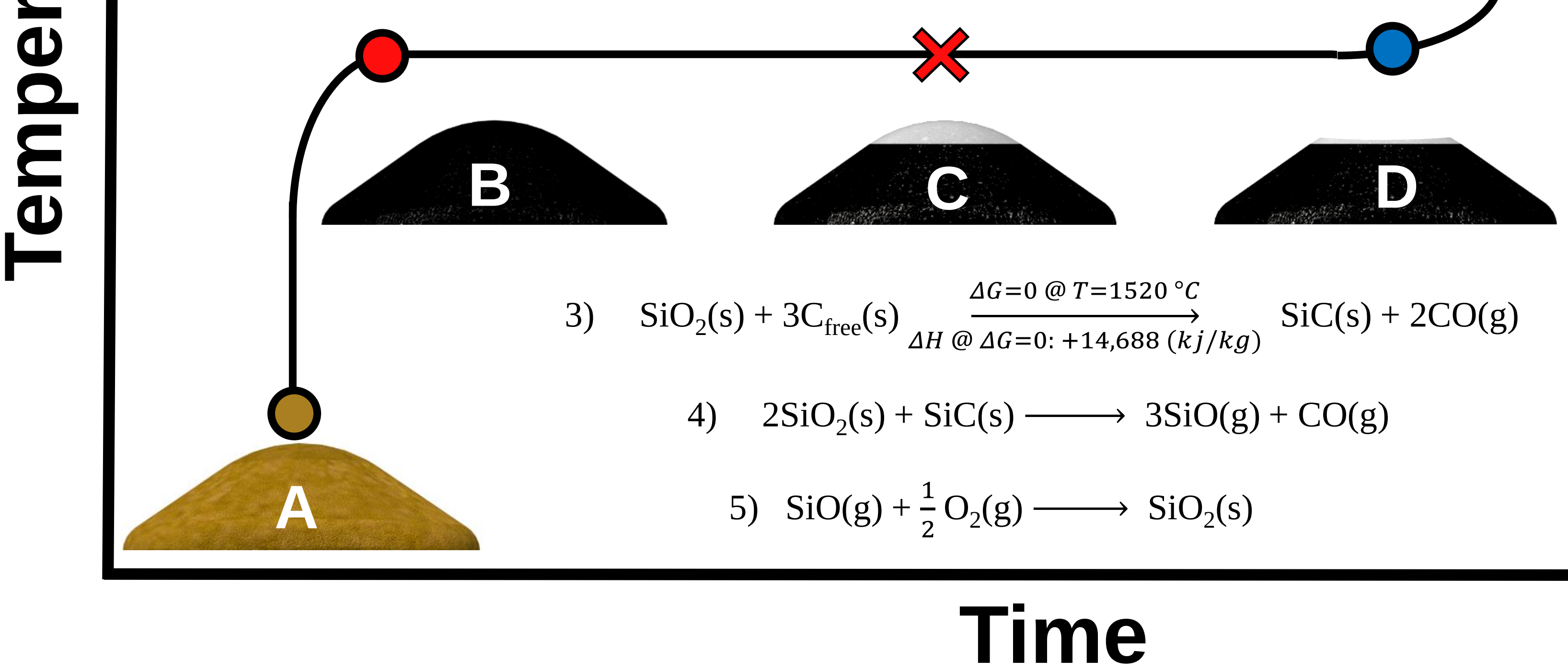


PICA – NuSil / Ablation Mechanism

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

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

Stage 3 (C → D). Coating Breakdown



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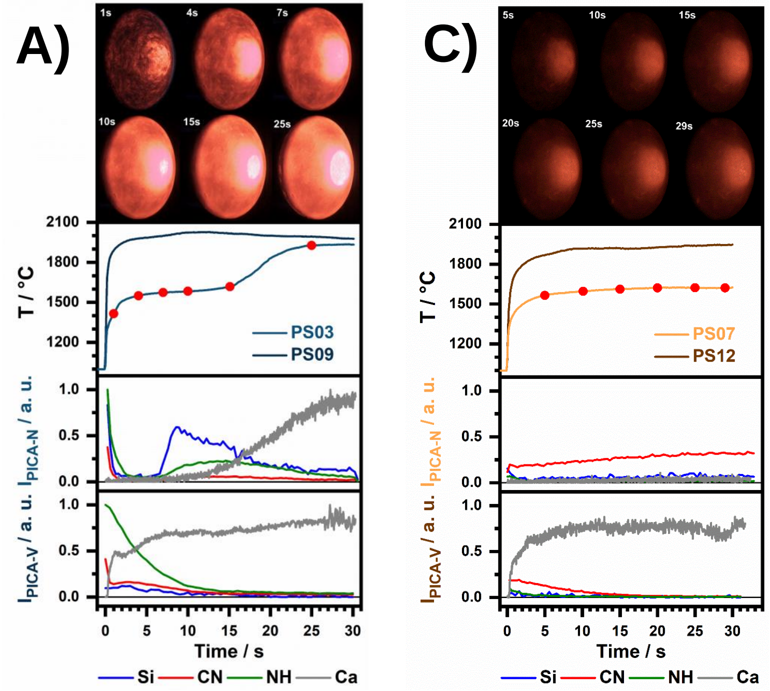


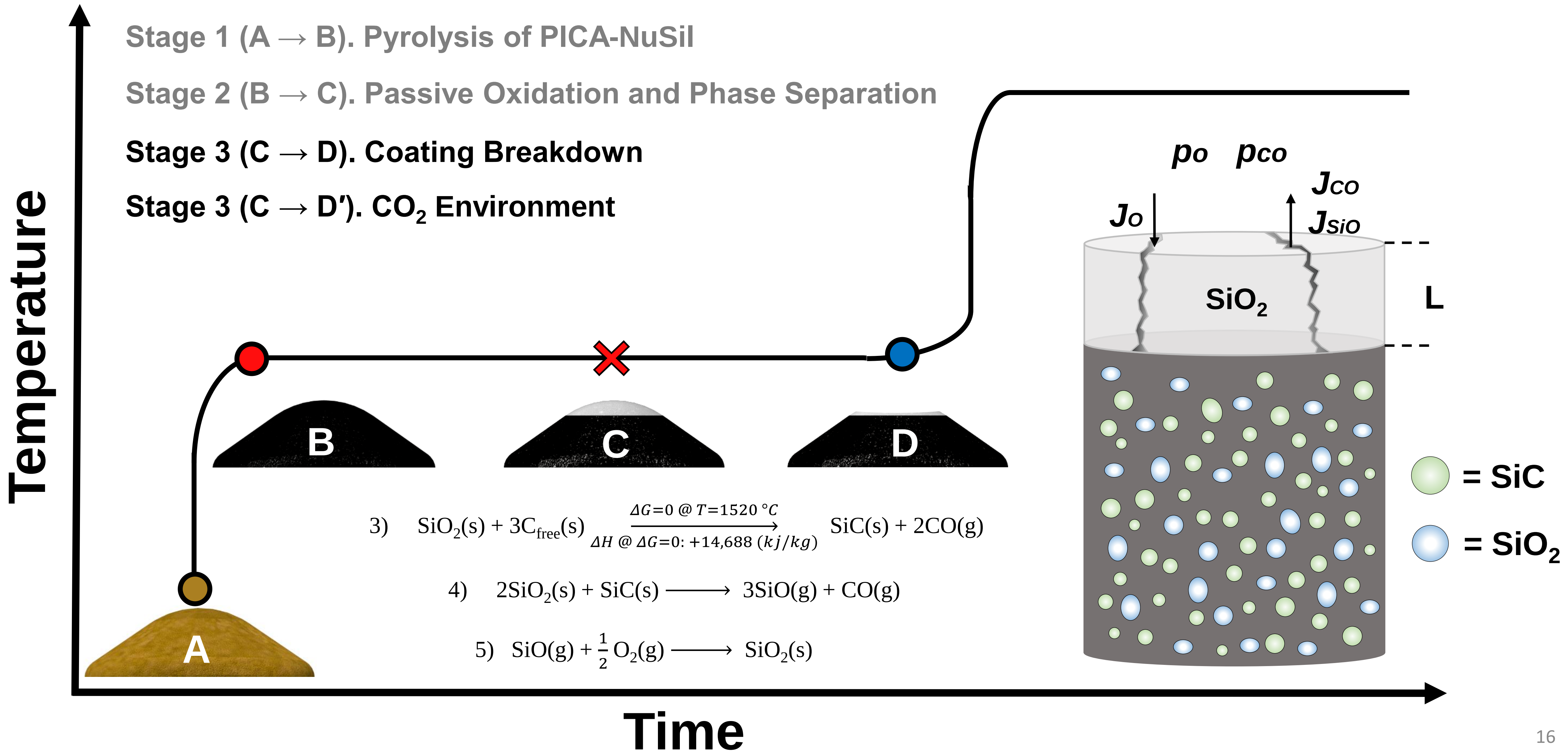
PICA – NuSil / Ablation Mechanism

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

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

Stage 3 (C → D). Coating Breakdown

Stage 3 (C → D′). CO_2 Environment



$$3)\quad SiO_2(s) + 3C_{free}(s) \xrightarrow[\Delta H\ @\ \Delta G=0:\ +14{,}688\ (kj/kg)]{\Delta G=0\ @\ T=1520\ °C} SiC(s) + 2CO(g)$$

$$4)\quad 2SiO_2(s) + SiC(s) \longrightarrow 3SiO(g) + CO(g)$$

$$5)\quad SiO(g) + \frac{1}{2}O_2(g) \longrightarrow SiO_2(s)$$

PICA – NuSil / Ablation Mechanism

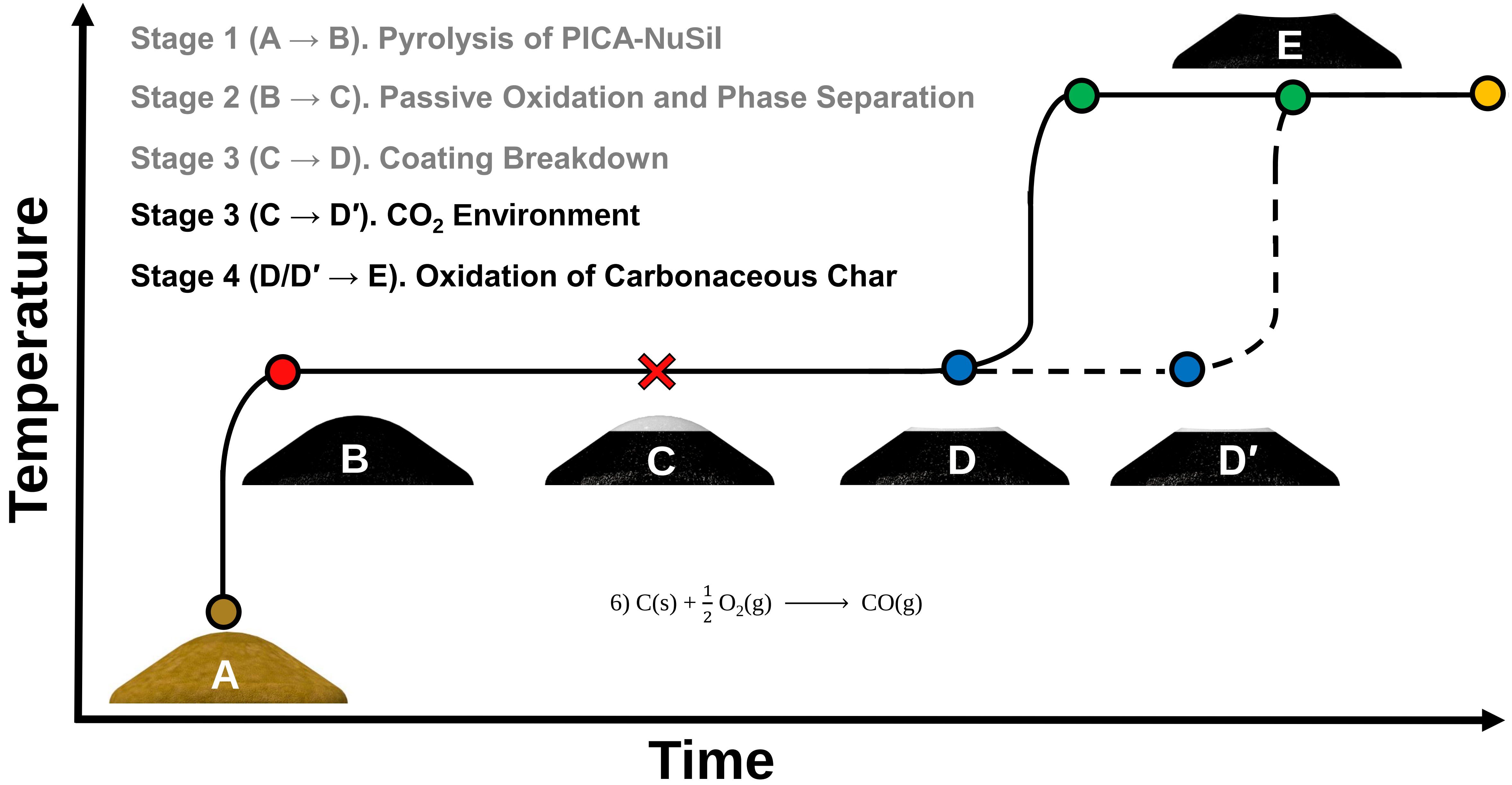
Stage 1 (A → B). Pyrolysis of PICA-NuSil

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

Stage 3 (C → D). Coating Breakdown

Stage 3 (C → D′). CO_2 Environment

Stage 4 (D/D′ → E). Oxidation of Carbonaceous Char



$$6)\ C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g)$$

Conclusions

1) Does NuSil have an impact on the material response of PICA during arc-jet testing?

- NuSil lowers the surface temperature and in-depth response in oxidizing conditions (Air & CO_2).
- NuSil survives longer at lower heating rates and higher partial pressures of $O_{(g)}$ & $CO_{(g)}$.

2) What is the ablation mechanism for PICA – NuSil?

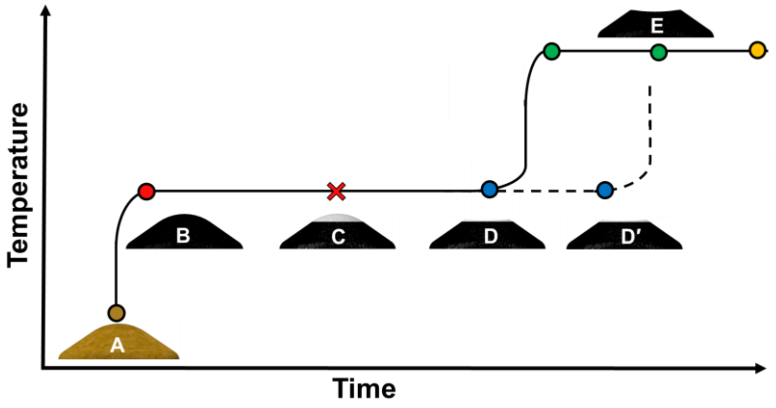
- The ablation mechanism of NuSil consists of four steps:

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

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

Stage 3 (C → D). Coating Breakdown

Stage 4 (D → E). Oxidation of Carbonaceous Char



Surface Temperature Measurements

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