FINITE ELEMENT ANALYSIS OF CHEMICAL REACTION KINETICS AND TRANSPORT PHENOMENA OF A SOLID STATE COMBUSTION SYNTHESIS

Venkata V. K. Doddapaneni and Sidney Lin*

Dan F. Smith Department of Chemical Engineering

Lamar University, Beaumont, TX 77710, USA

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Nitride Materials

- Aluminum Nitride, Silicon Nitride, Boron Nitride, Zirconium Nitride, Tantalum Nitride
- Outstanding thermal, optical, and mechanical properties at high temperatures
- Solar and automotive industries and LED applications
- Our focus is silicon nitride because of its applications as a heat sink in LED

Figures are taken from “THE STORY OF SILICON NITRIDE” a brief narrative by Amedica Corporation.

Conventional Methods for Si_3N_4 Synthesis

- Carbothermal Reduction

$$3SiO_{2\,(s)} + 6C_{(s)} + 2N_{2\,(v)} \underset{\Delta}{\rightarrow} Si_3N_{4\,(s)} + 6CO_{(v)}$$

- Direct Nitridation

$$3Si_{(s)} + 2N_{2(v)} \rightarrow Si_3N_{4(s)}$$

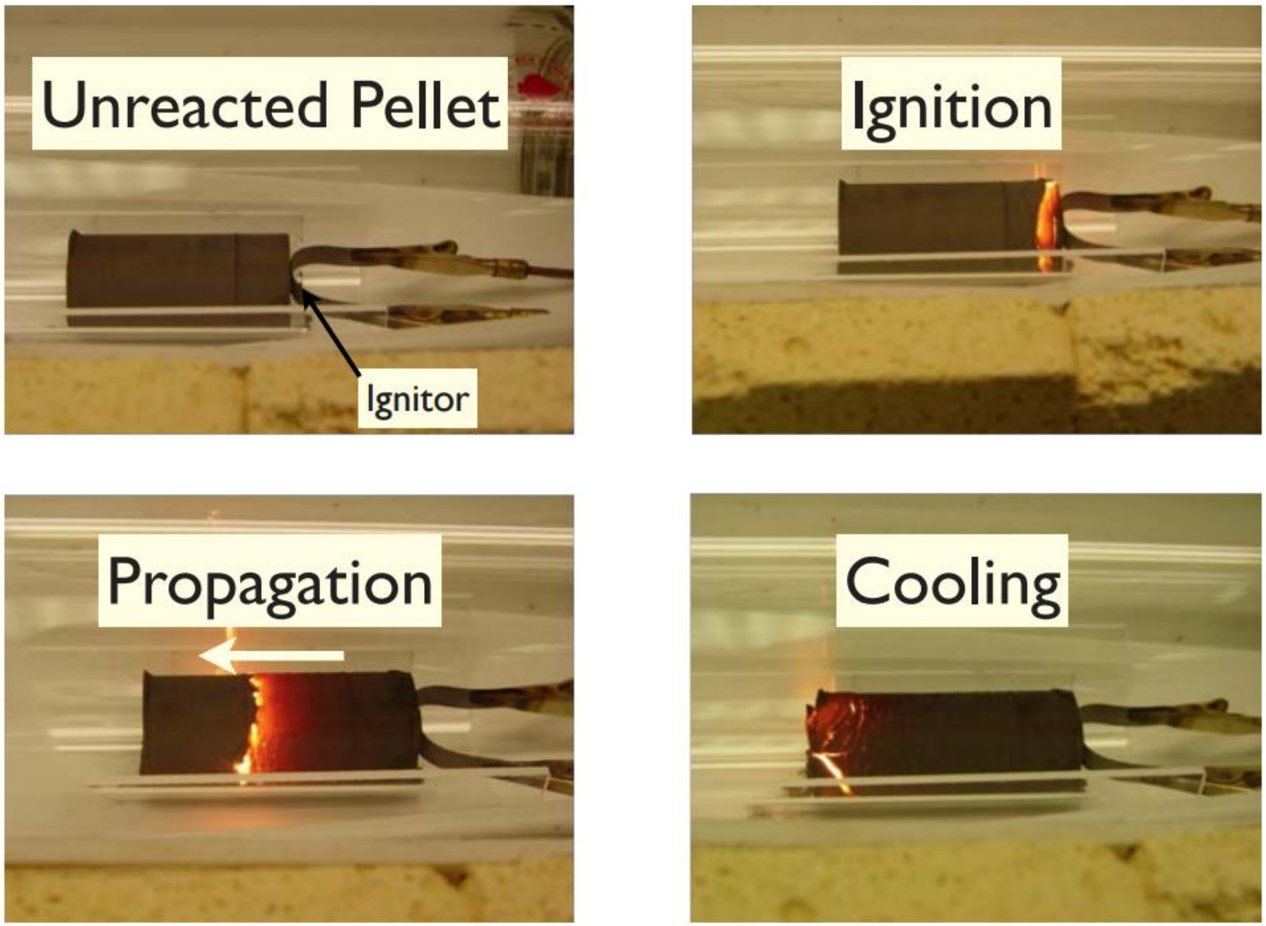
- Diimide Decomposition

$$SiCl_{4\,(s)} + 6NH_{3\,(v)} \rightarrow Si(NH)_{2\,(s)} + 4NH_4Cl_{(s)}$$

$$3Si(NH)_{2\,(s)} \overset{N_2}{\rightarrow} Si_3N_{4\,(s)} + N_{2(g)} + 3H_{2(g)}$$

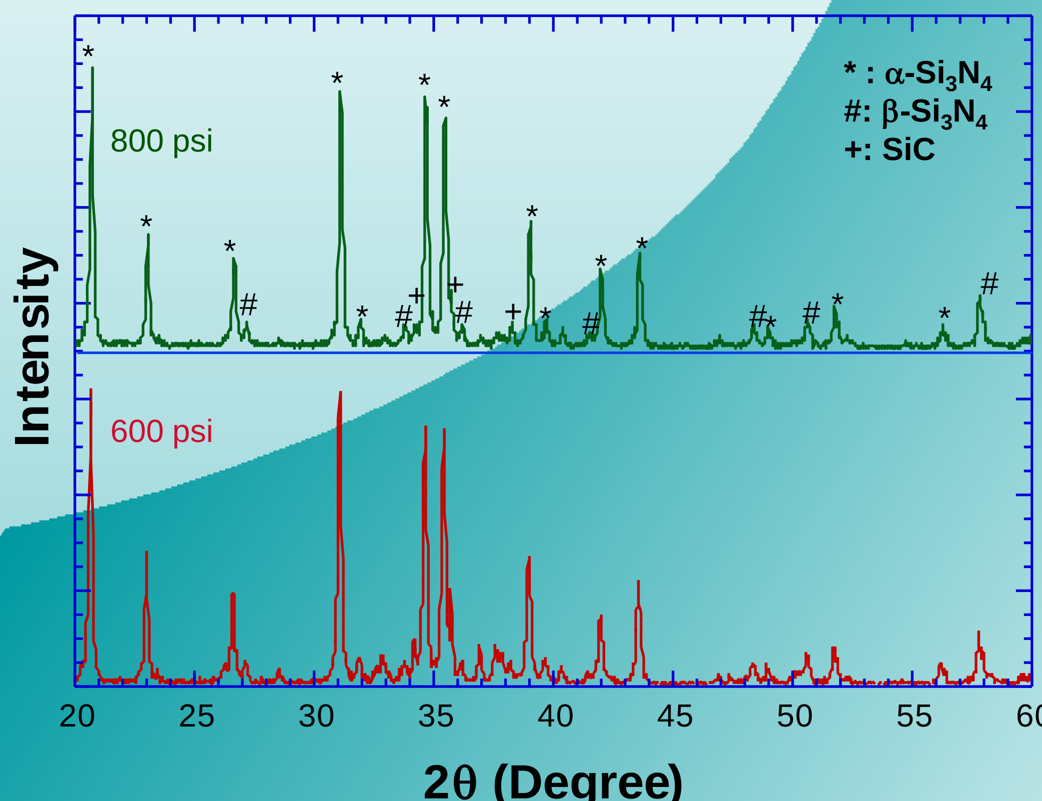
- Expensive and time consuming

Self-propagating High-temperature Synthesis



Self-propagating High-temperature Synthesis (SHS)

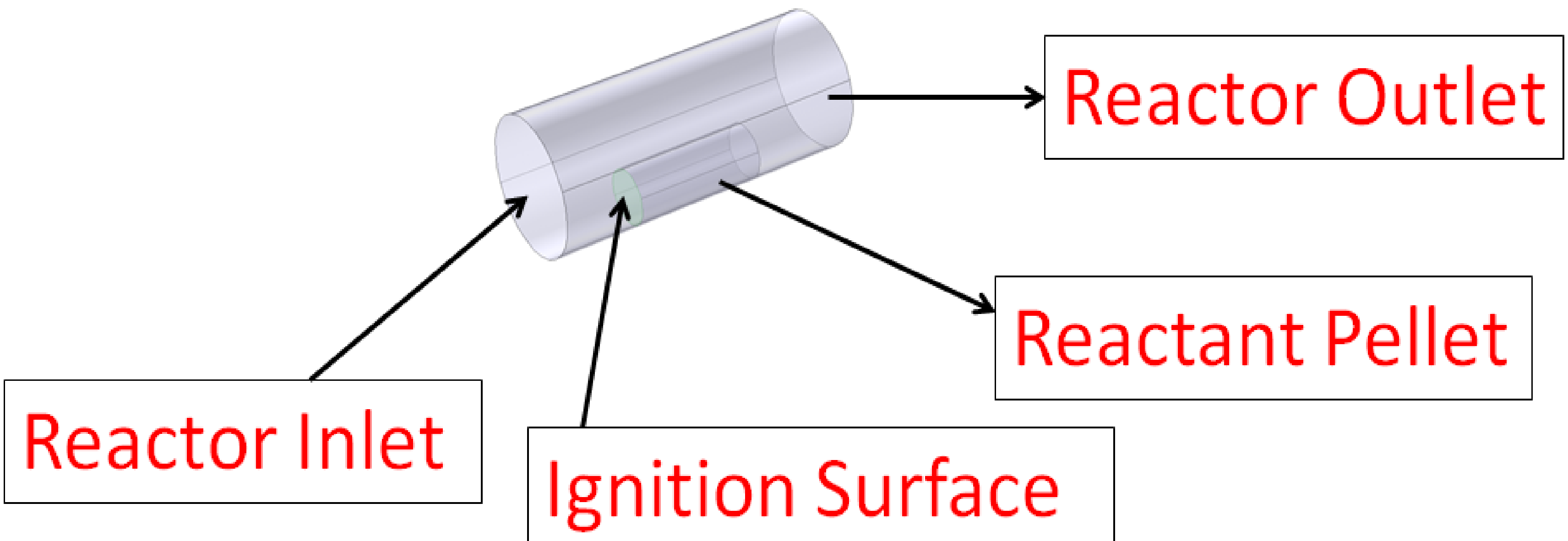
SHS of 3 Si + 2 NaN_3 + 0.25 Si_3N_4 + 0.5 SiC for Si_3N_4 /SiC Composite



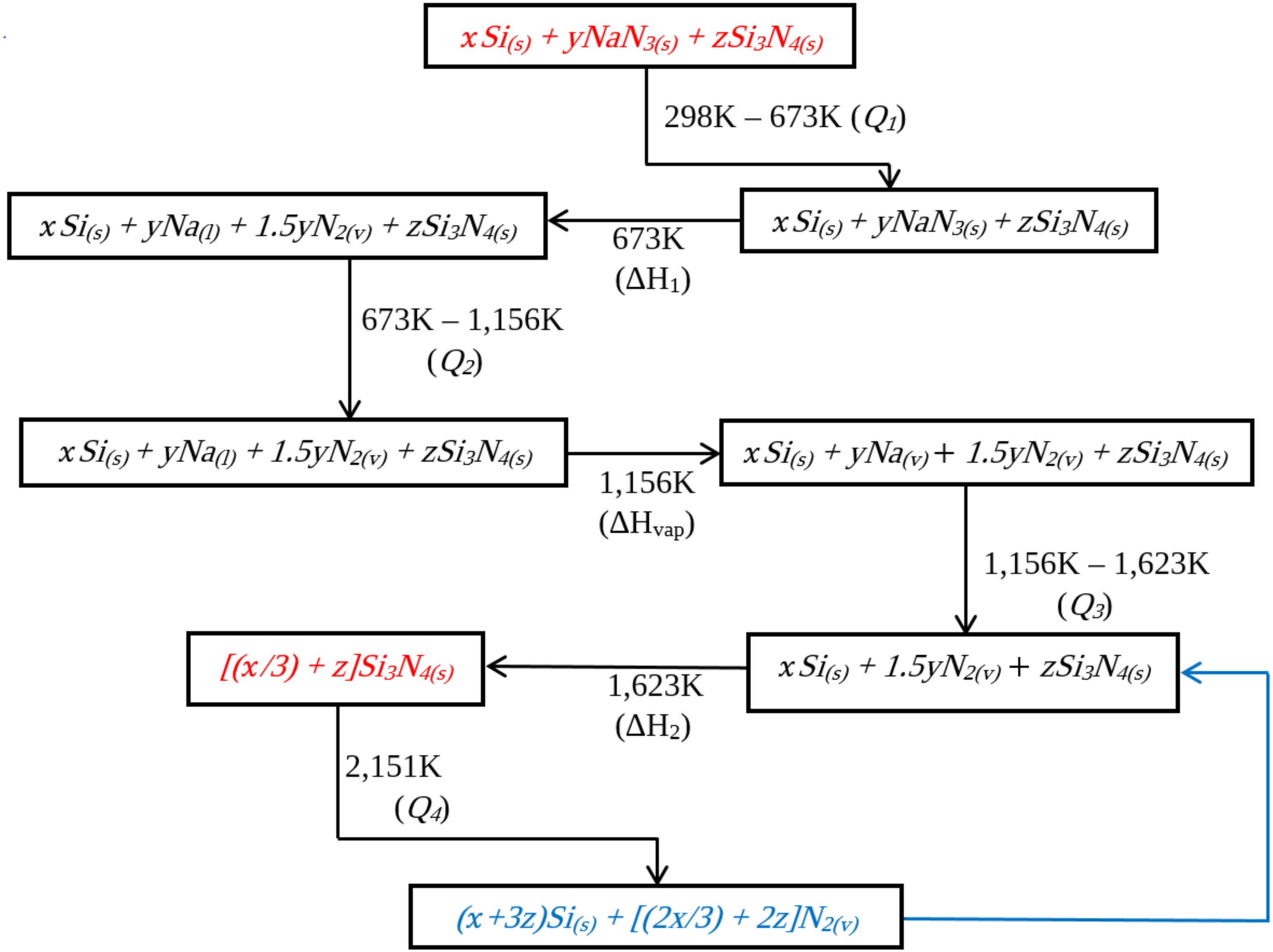
Reactor and Reactant Pellet

Dimensions of the Reactor and Reactant Pellet:

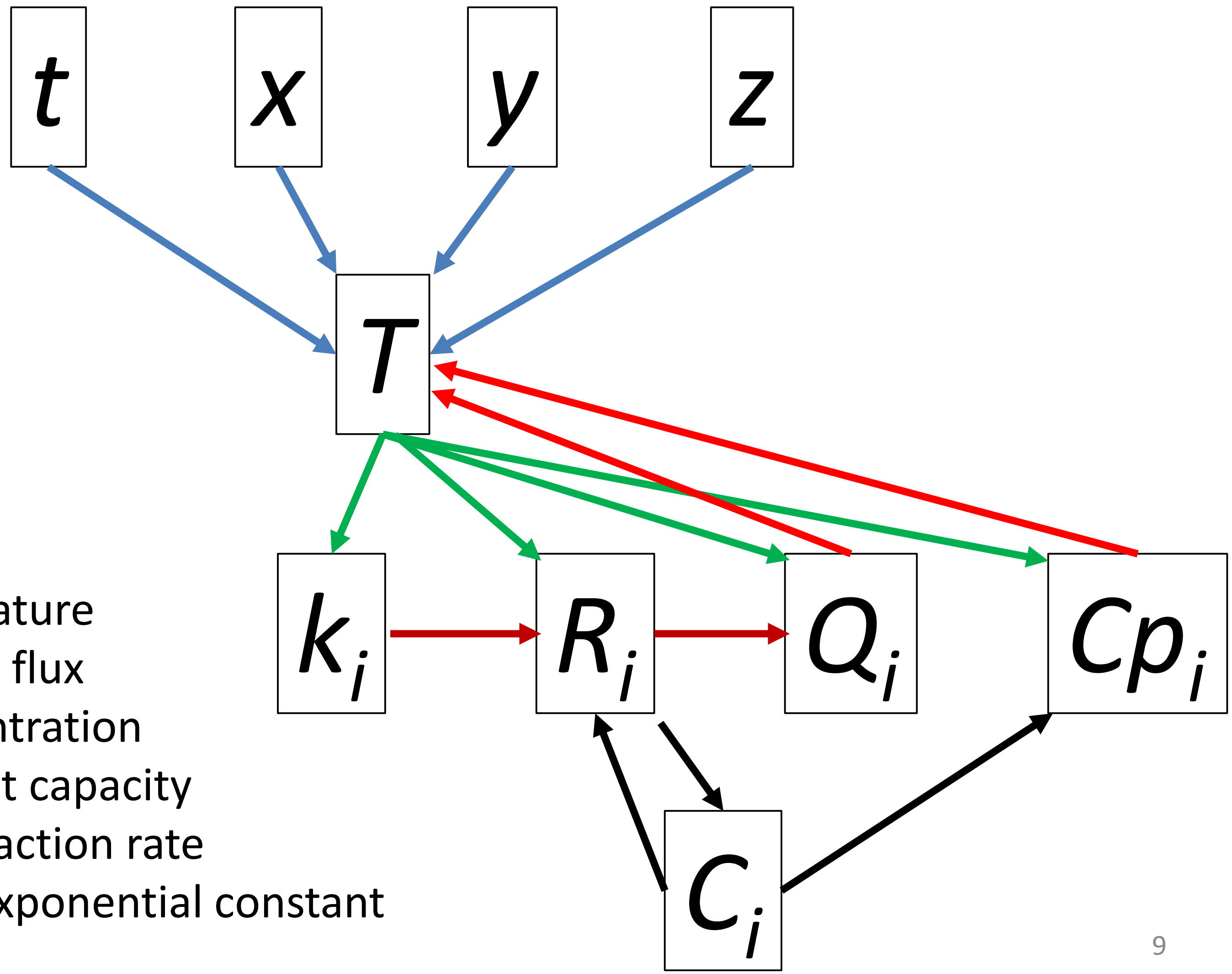
	Reactor	Pellet
Length	304.8 mm	127.0 mm
Diameter	127.0 mm	25.4 mm



Reaction Mechanism



Reaction Mechanism



t: Time

x, y, z: Position

$T(t, x, y, z)$: Temperature

$Q_i(t, x, y, z, R)$: Heat flux

$C_i\ (t, x, y, z)$: Concentration

$Cp_i(t, x, y, z, C)$: Heat capacity

$R_i(t, T, x, y, z, C)$: Reaction rate

$k_i(t, T, x, y, z)$: pre-exponential constant

Momentum Transfer

❑ Steady State Navier-Stokes Equation and Continuity Equation:

$$\rho \boldsymbol{u} . \nabla \boldsymbol{u} = -\nabla p + \nabla . (\mu(\nabla \boldsymbol{u}) + (\nabla \boldsymbol{u})') - \frac{2}{3}\mu\big((\nabla . \boldsymbol{u})\boldsymbol{I}\big)$$

$$\nabla . (\rho u) = 0$$

where

ρ is the density of nitrogen, [kg/m^3]

$\boldsymbol{u}$ is the velocity of nitrogen, [m/s]

p is the nitrogen pressure, [Pa]

μ is the viscosity of nitrogen, [Pa-s]

$\boldsymbol{I}$ is the identity matrix

Momentum Transfer (Contd..)

- **Boundary Conditions**

- At the reactor inlet : u_{in} = 0.00001 [m/s]

- At the reactor outlet: P = atmospheric pressure (10135[Pa])

- Interface between nitrogen gas and the pellet and reactor walls : no slip condition (u = 0 [m/s])

Heat Transfer in Nitrogen

$$\rho Cp\left(\frac{\partial T}{\partial t} + \boldsymbol{u}.\nabla T\right) = \nabla.(k\nabla T)$$

- **Initial Condition**
  - Initial temperature of the nitrogen gas is 25°C

- **Boundary Conditions**
  - At the inlet: Temperature of nitrogen gas is 25°C
  - At the outlet: Convection dominated boundary condition
  - Convective heat transfer to the nitrogen gas from the pellet surface:

$$-\boldsymbol{n}.(-k\nabla T_p) = h \times \left(T_p - T_f\right)$$

Heat Transfer inside Reactant Pellet

$$\rho Cp\left(\frac{\partial T}{\partial t}\right) = \nabla.(k\nabla T) + Q$$

❑ Initial Condition

- Initial temperature of the reactant pellet is 25°C

❑ Boundary Conditions

- At the ignition Surface:

$$-\boldsymbol{n}.\left(-k\nabla T_p\right) = 5\times 10^7\ [W/m^2]\ \text{for 5 sec}$$

- Heat loss from the pellet surface to the surroundings:

$$-\boldsymbol{n}.\left(-k\nabla T_p\right) = -\varepsilon\times\sigma\times\left({T_p}^4 - {T_\infty}^4\right) - h\times\left(T_p - T_f\right)$$

- Heat Source:

$$\boldsymbol{Q} = \Delta\boldsymbol{H_2}\times\frac{\boldsymbol{1}}{\boldsymbol{3}}\left(\frac{-\boldsymbol{dC_{Si}}}{\boldsymbol{dt}}\right) + (\Delta\boldsymbol{H_1})\times\left(\frac{-\boldsymbol{dC_{NaN_3}}}{\boldsymbol{dt}}\right) + \Delta\boldsymbol{H_{vap}}\times(-\boldsymbol{k_{Na}}\times\boldsymbol{C_{Na}})$$

Reaction Kinetics

- **Silicon Nitridation**:

$$3Si_{(s)} + 2N_{2\,(g)} \rightarrow Si_3N_{4\,(s)}$$

$$\frac{-dC_{Si}}{dt} = 3 \times C_{Si} \times k_{Si,o} \times exp\left({}^{-E_{Si}}/_{RT_p}\right)$$

where

- $\frac{-dC_{Si}}{dt}$ is the rate of consumption of silicon nitride, [mol/m^3/s]
- C_{Si} is the concentration of silicon nitride at any time (t), [mol/m^3]
- $k_{Si,o}$ is the pre-exponential factor for formation of silicon nitride, [sec^{-1}]
- $-E_{Si}$ is the activation energy for the formation of silicon nitride, [J/mole]
- R is the gas constant, [8.314 J/mole/K]
- T_p (x, y, z, t) is the temperature of the pellet , [K]

Reaction Kinetics (Contd..)

- **Decomposition of Sodium Azide**:

$$NaN_{3\,(s)} \rightarrow 1.5N_{2\,(v)} + Na_{(l)}$$

$$\frac{-dC_{NaN_3}}{dt} = C_{NaN_3} \times k_{NaN_3,o} \times exp\left({}^{-E_{NaN_3}}/_{RT_p}\right)$$

where

- $\frac{-dC_{NaN3}}{dt}$ is the rate of consumption of sodium azide, [mol/m^3/s]
- C_{NaN3} is the concentration of sodium azide at any time (t), [mol/m^3]
- $k_{NaN_3,o}$ is pre-exponential factor for sodium azide decomposition,[sec^{-1}]
- $-E_{NaN_3}$ is the activation energy for sodium azide decomposition, [J/mole]
- R is the gas constant, [8.314 J/mole/K]
- T_p (x, y, z, t) is the temperature of the pellet, [K]

Reaction Kinetics (Contd..)

- **Vaporization of Sodium:**

$$\boldsymbol{Na_{(l)} \rightarrow Na_{(v)}}$$

$$\frac{dC_{Na}}{dt} = \frac{-dC_{NaN_3}}{dt} \qquad if\ Tp < 1{,}151K$$

$$\frac{dC_{Na}}{dt} = \frac{-dC_{NaN_3}}{dt} + (-k_{Na} \times C_{Na}) \quad if\ Tp \geq 1{,}151K$$

Reaction Kinetics (Contd..)

- **Decomposition of Si_3N_4:**

$$\boldsymbol{Si_3N_{4\,(s)} \rightarrow 3Si_{(s)} + 2N_{2\,(g)}}$$

$$\frac{dC_{Si_3N_4}}{dt} = \frac{1}{3} C_{Si} k_{Si,0} \exp\left(\frac{-E_{Si}}{RT_p}\right) - k_{Si_3N_4} C_{Si_3N_4} \qquad T_p \geq 2{,}151K$$

Reaction Kinetics (Contd..)

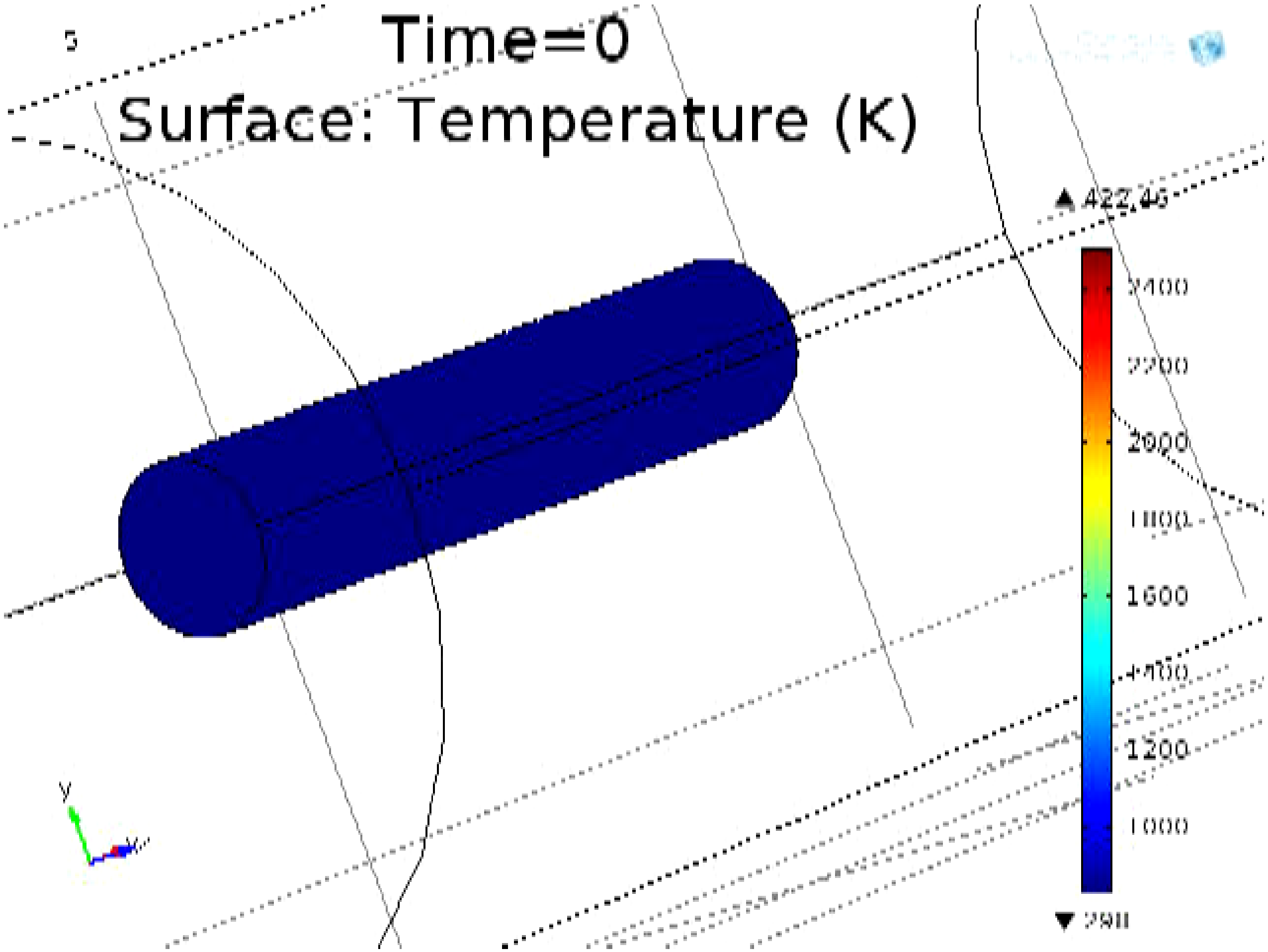
$$\frac{dC_{Si}}{dt} = -C_{Si} k_{Si,0} \exp\left(\frac{-E_{Si}}{RT_p}\right) \qquad T_p < 2{,}151K$$

$$\frac{dC_{Si}}{dt} = -C_{Si} k_{Si,0} \exp\left(\frac{-E_{Si}}{RT_p}\right) + 3k_{Si_3N_4} C_{Si_3N_4} \qquad T_p \geq 2{,}151K$$

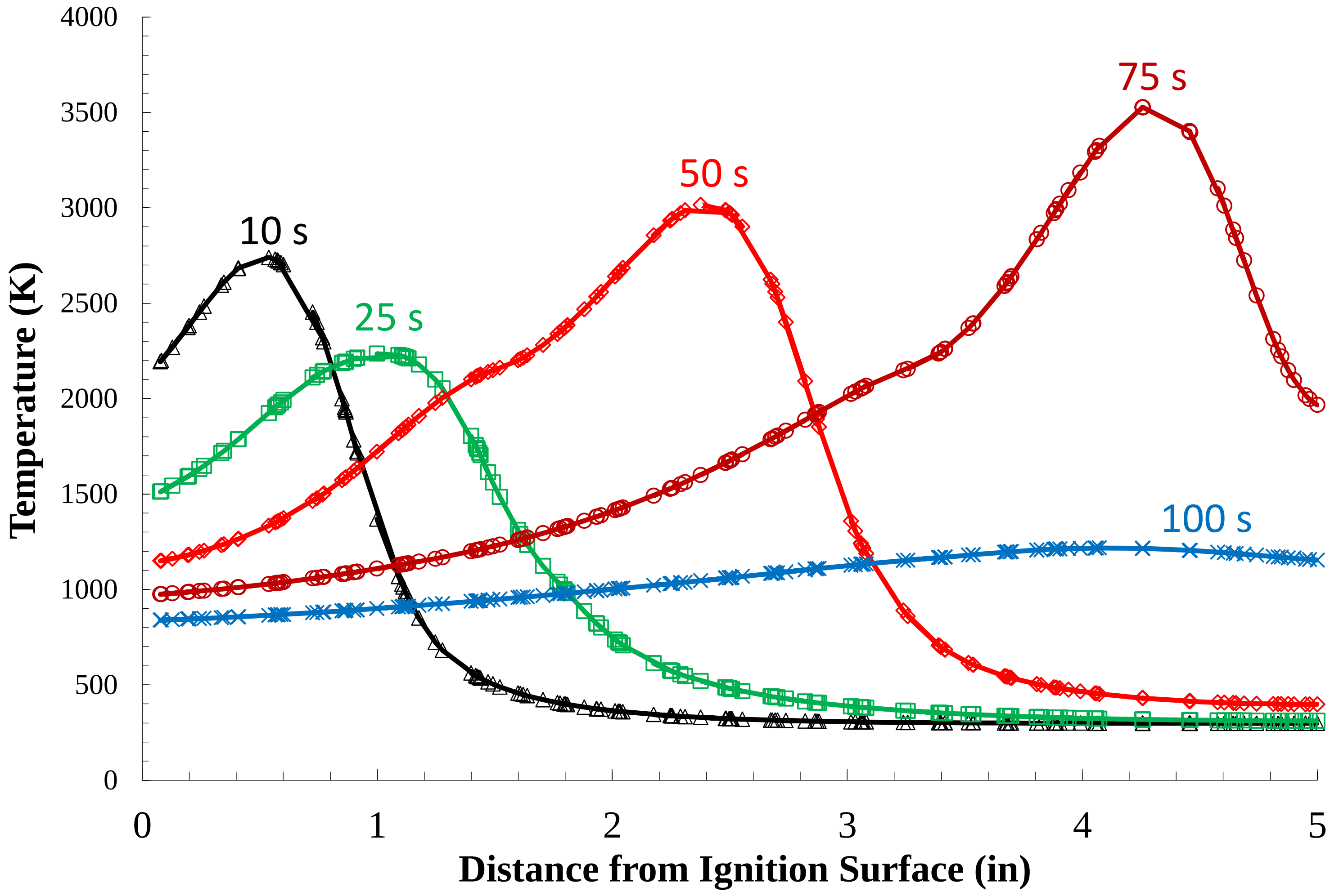
$$\frac{dC_{Si_3N_4}}{dt} = \frac{1}{3} C_{Si} k_{Si,0} \exp\left(\frac{-E_{Si}}{RT_p}\right) \qquad T_p < 2{,}151K$$

$$\frac{dC_{Si_3N_4}}{dt} = \frac{1}{3} C_{Si} k_{Si,0} \exp\left(\frac{-E_{Si}}{RT_p}\right) - k_{Si_3N_4} C_{Si_3N_4} \qquad T_p \geq 2{,}151K$$

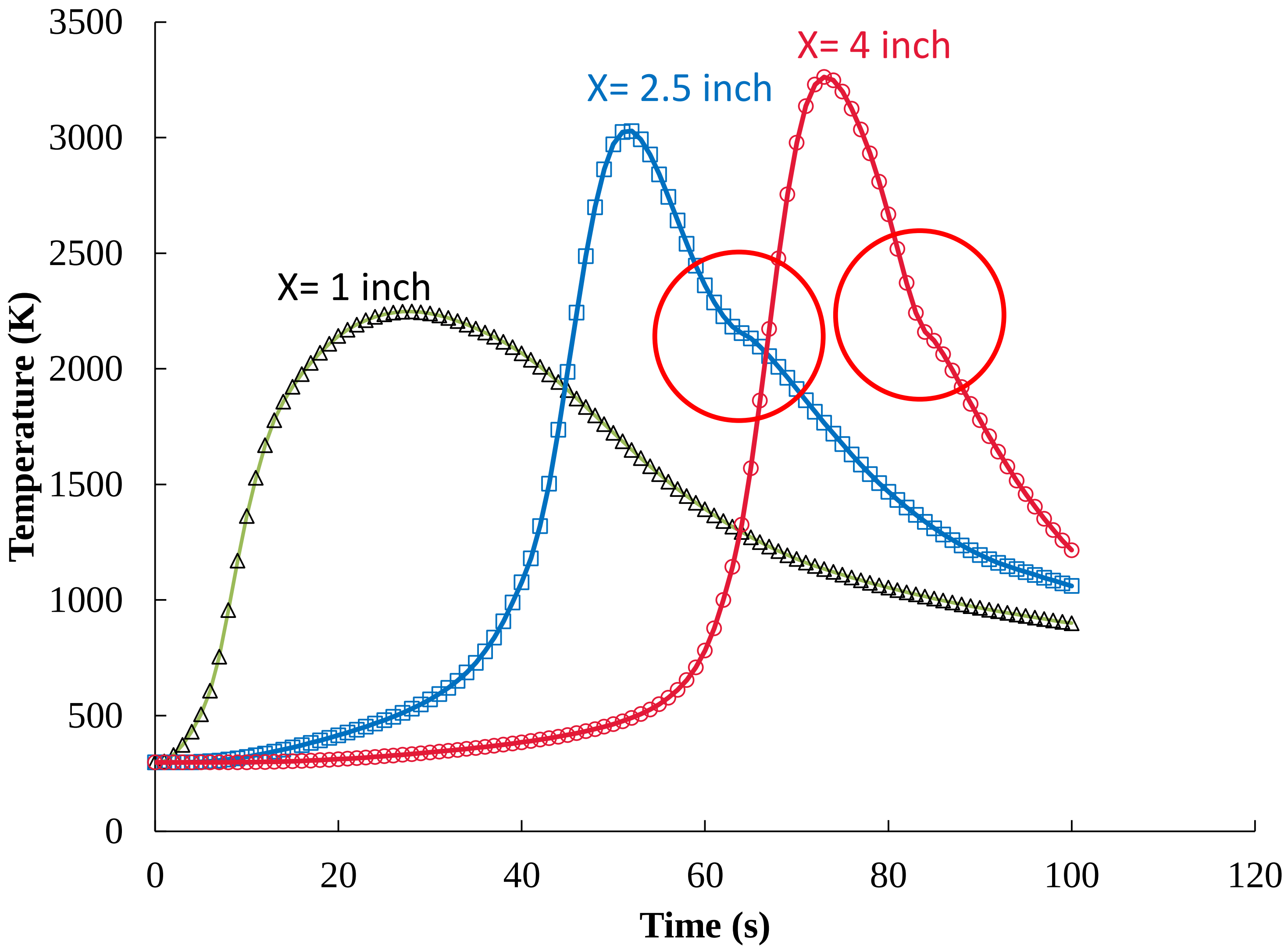
Temperature History



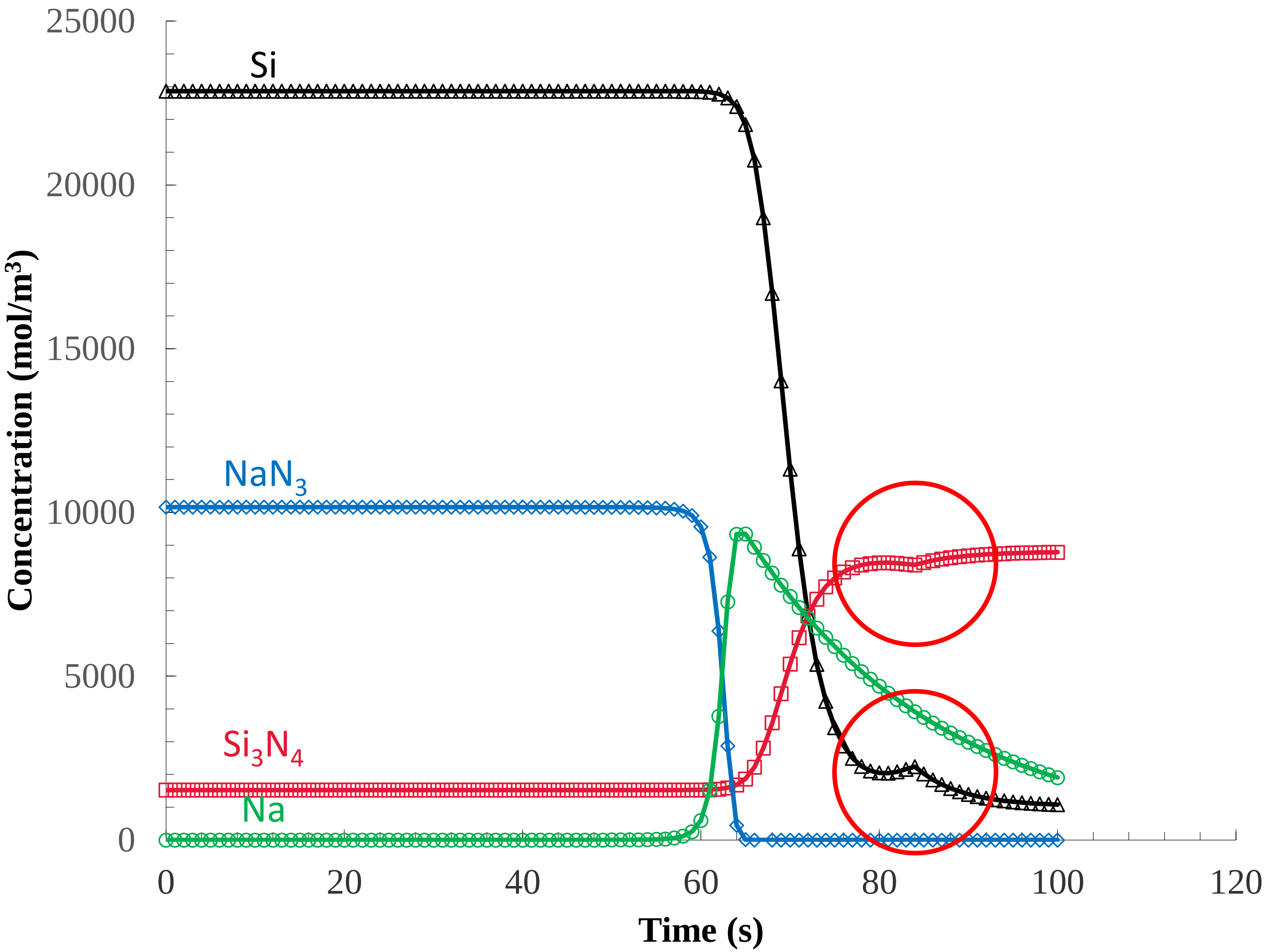
Temperature Distribution on Centerline



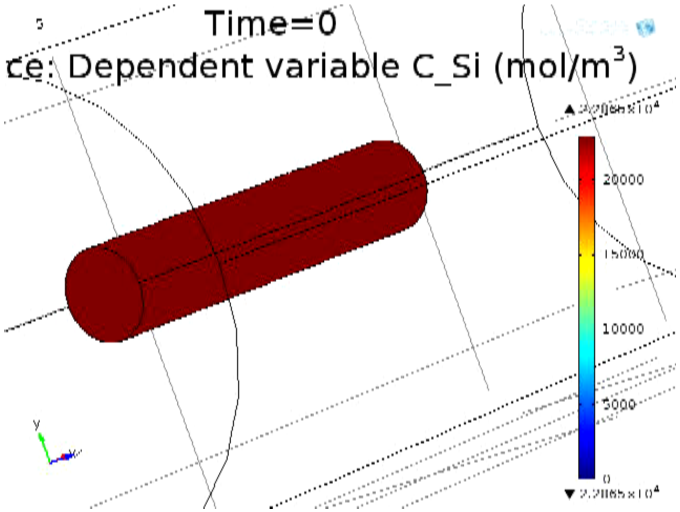
Temperature History on Centerline

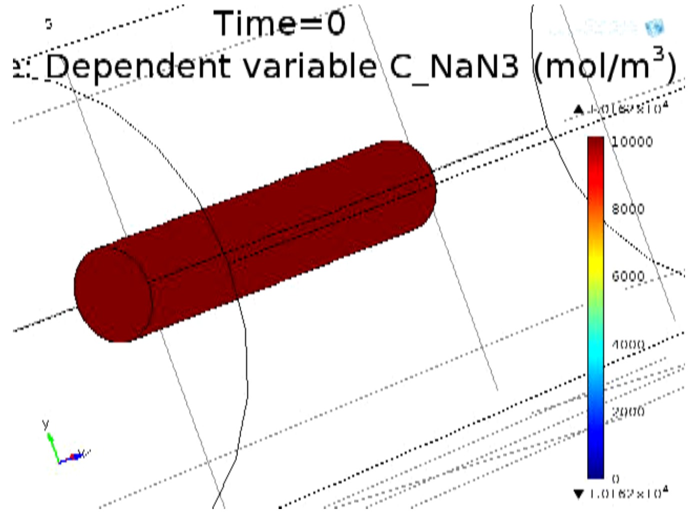


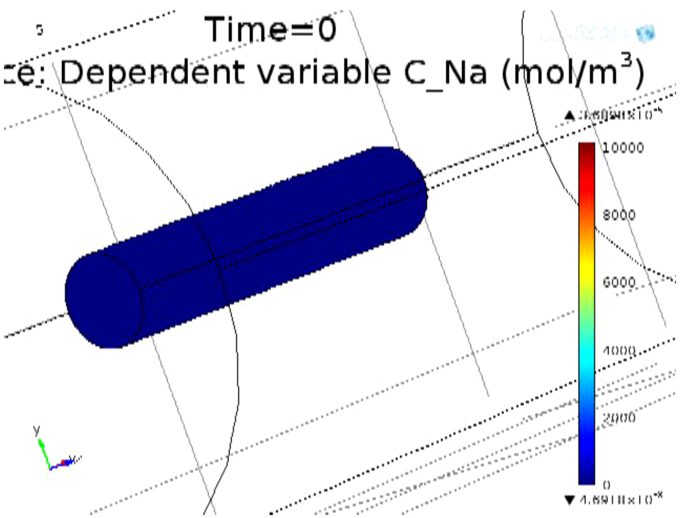
Concentrations History on Centerline

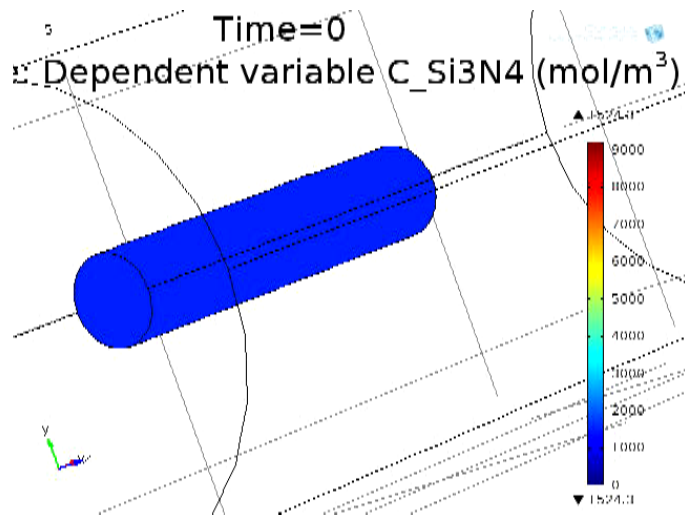


Concentration Histories

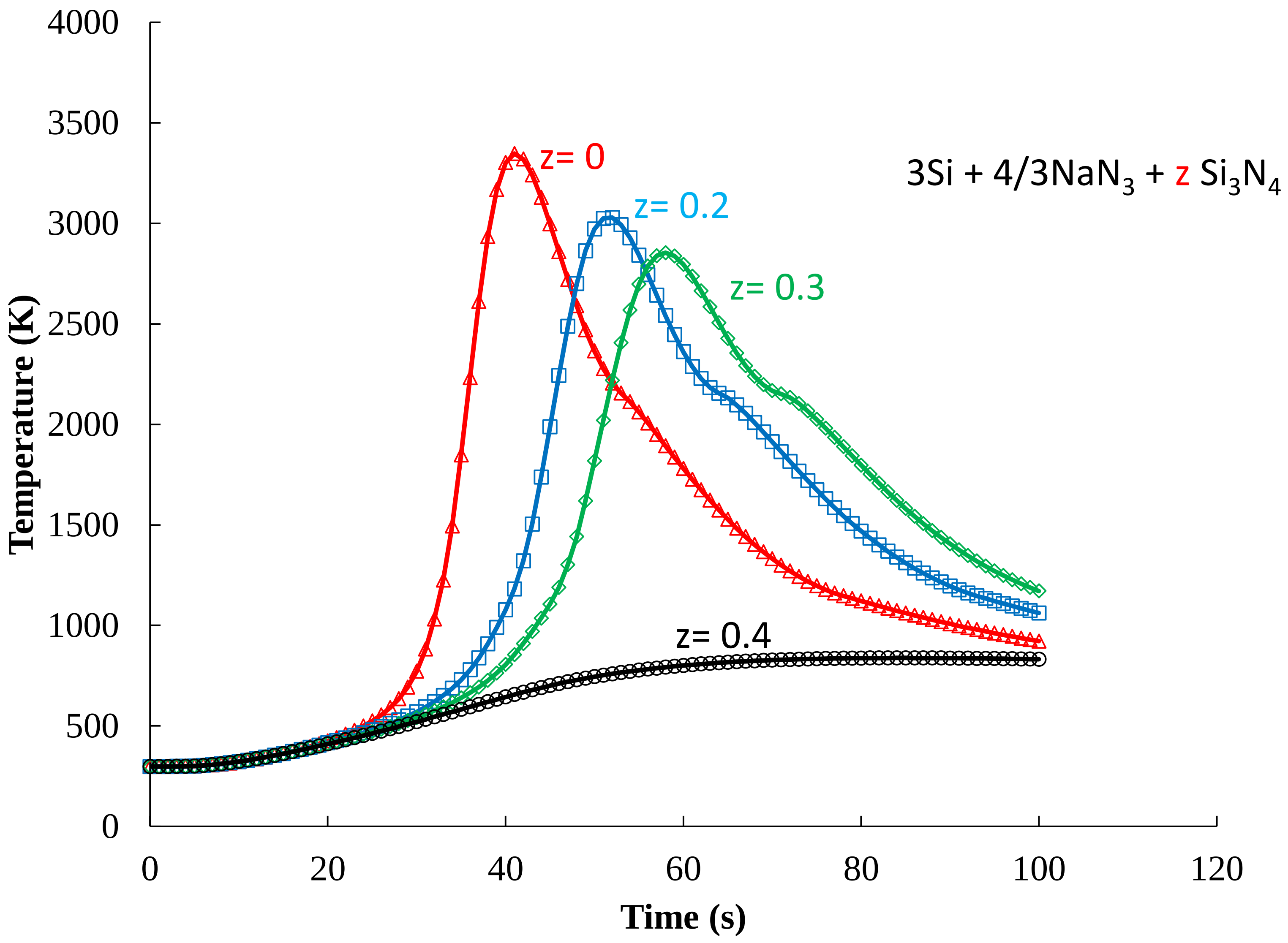








Silicon Nitride Dilution



Conclusions

- A time dependent three-dimensional finite element analysis model is developed to study the SHS of silicon nitride via $3Si + 2\ NaN_3 + 0.2\ Si_3N_4 \rightarrow 1.2\ Si_3N_4 + 2Na + N_2$.

- Momentum transfer, heat transfer, temperature dependent thermodynamic properties and reaction kinetics are integrated in the model.

- Temperature history, reaction rates, reaction conversion, combustion front movement, and the impact of silicon nitride diluent on the SHS process are presented.

Thank You!

Future Work

- Nitrogen diffusion through the porous reaction pellet.
- High temperature thermal conductivity measurement.
- Phase change (α-Si_3N_4 → β-Si_3N_4).
- Pellet porosity change.