Finite Element Analysis of Chemical Reaction Kinetics and Transport Phenomena of a Solid State Combustion Synthesis

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Abstract

A 3D unsteady state chemical reaction system was modeled using COMSOL Multiphysics 5.2a. In this work, the Chemical Engineering Module was integrated to calculate physical, chemical, thermodynamic and transport phenomena properties. The developed time dependent three-dimensional model was used to study the synthesis of silicon nitride via $3\ Si + 2\ NaN_3 + 0.2\ Si_3N_4 \rightarrow 1.2\ Si_3N_4 + 2\ Na + N_2$. An eight step reaction mechanism was used to calculate instantaneous local reaction rates and composition.

Introduction

Self-propagating High-temperature Synthesis (SHS) was developed by Merzhanov et al. in the late 1960s[1,2]. It is a self-sustained highly exothermic reaction with theoretical adiabatic temperatures can reach 3,000 K. In this process external heat is only required to initiate the reaction. The reaction wave then moves through the reactant mixtures converting reactants to products. Different materials such as oxides, nitrides, hydrides, and phosphides have been successfully synthesized using this method[3]. Because of the process's high reaction temperature, fast heating/cooling and reaction rate the development of a mathematical simulation is crucial for a safe large scale manufacture.

Experimental Set-up

Self-propagating High-temperature Synthesis (SHS), **an economical, energy saving process has been used to prepare advanced ceramics including oxides, nitrides, carbides, oxynitrides, and composites in our lab. The solid state combustion synthesis is demonstrated in Figure 1.**
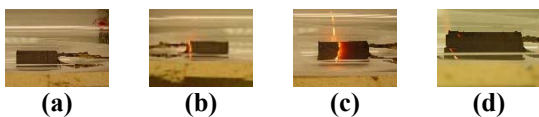

Figure 1. Demonstration of an SHS process in air and at room temperature; (a) reactant pellet before reaction, (b) at ignition, (c) during propagation, (d) while cooling.

When SHS is used to prepare silicon nitride (Si_3N_4) the product purity (chemical compositions and phases) can be controlled by changing the reaction time and reaction temperature. Figure 2 is an example of the silicon nitride (Si_3N_4)/silicon carbide (SiC) composites when different reaction pressure were applied.
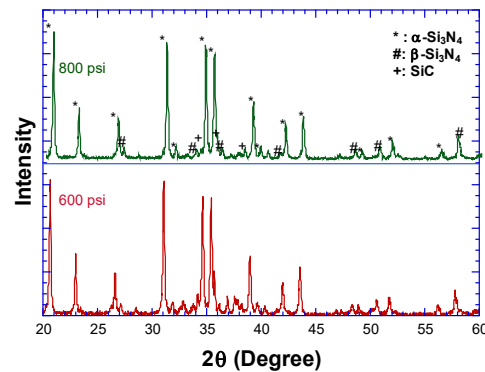

Figure 2. XRD patters of the silicon nitride/silicon carbide composite synthesized by SHS.

Theory and Governing Equations

Figure 3 shows the eight step chemical reaction mechanism is used in this work.
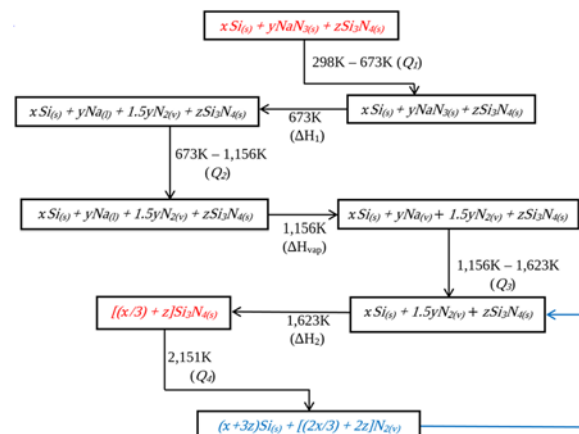

Figure 3. The proposed reaction mechanism of SHS of silicon nitride.

It consists of silicon nitridation, sodium azide decomposition, sodium vaporization and silicon nitride decomposition at high temperatures

In this mathematical model the local temperature and composition vary with time. Therefore, the instantaneous reaction rates, heat generation rates and thermodynamic properties also change with time as shown in the Figure 4.
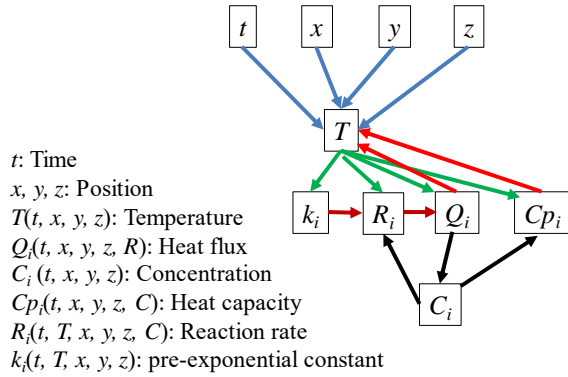

t: Time
x, y, z: Position
$T(t, x, y, z)$: Temperature
$Q_i(t, x, y, z, R)$: Heat flux
$C_i(t, x, y, z)$: Concentration
$Cp_i(t, x, y, z, C)$: Heat capacity
$R_i(t, T, x, y, z, C)$: Reaction rate
$k_i(t, T, x, y, z)$: pre-exponential constant

Figure 4. The relationship among the model variables.

The steady state Navier-Stokes equation and the continuity equation are first used to solve the nitrogen flow profile inside the reactor before the SHS reaction. The steady state velocity profile then is used as the initial value for the unsteady calculation. A constant velocity (0.05 ms⁻¹) of nitrogen gas is used at the reactor inlet and constant pressure (1 atm) boundary condition applied to the outlet of the reactor. The reactor inside wall and the outside surface of the pellet are set to the no slip boundary condition.

$$\rho \frac{\partial u}{\partial t} + \rho u \cdot \nabla u = -\nabla p + \nabla \cdot (\mu(\nabla u) + (\nabla u)') - \frac{2}{3}\mu((\nabla \cdot u)I) + F \quad (1)$$

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho u) = 0 \quad (2)$$

Conduction and convection heat transfers are considered in nitrogen gas which are included in Equation (3).

$$\rho Cp \left(\frac{\partial T_f}{\partial t} + u \cdot \nabla T_f \right) = \nabla \cdot (k \nabla T_f) \quad (3)$$

Equation (4) is used to solve time dependent temperature profile in the reactant pellet.

$$\rho Cp \left(\frac{\partial T_p}{\partial t} \right) = \nabla \cdot (k \nabla T_p) + Q \quad (4)$$

An external heat flux of 5×10^7 W/m² is used at the front end of the reactant pellet for 5 seconds to initiate the reaction.

$$-\boldsymbol{n} \cdot (-k \nabla T_p) = 5 \times 10^7 \ (W/m^2) \quad (5)$$

The heat conducted to the outer surface of the pellet is equal to the radiation and convective heat losses from the pellet outer surface to the surrounding nitrogen gas.

$$-\boldsymbol{n} \cdot (-k \nabla T_p) = -\varepsilon \times \sigma \times (T_p{}^4 - T_\infty{}^4) - h \times (T_p - T_f) \quad (6)$$

The total heat generation rate is calculated by the reaction rates and molar reaction heats of silicon nitridation, sodium azide decomposition and sodium vaporization, respectively.
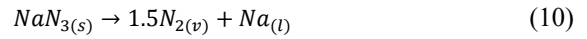
$$Q = \Delta H_{Si_3N_4} \times \frac{1}{3}\left(\frac{-dC_{Si}}{dt}\right) + (\Delta H_{NaN_3}) \times \left(\frac{-dC_{NaN_3}}{dt}\right) + \Delta H_{Na,v} \times (-k_{Na} \times C_{Na}) \quad (7)$$

Kinetic parameters of silicon nitridation are calculated from the data reported by Yin et al.[4]

$$3Si_{(s)} + 2N_{2(g)} \rightarrow Si_3N_{4(s)} \quad (8)$$
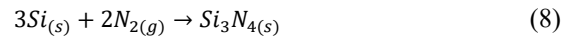
$$\frac{-dC_{Si}}{dt} = 3 \times C_{Si} \times k_{Si,o} \times exp\left(\frac{-E_{Si}}{RT_p}\right) \quad (9)$$

The reported data are used to estimate the activation energy, and pre-exponential factors of decomposition of sodium azide[5].

$$NaN_{3(s)} \rightarrow 1.5 N_{2(v)} + Na_{(l)} \quad (10)$$

$$\frac{-dC_{NaN_3}}{dt} = C_{NaN_3} \times k_{NaN_3,o} \times exp\left(\frac{E_{NaN_3}}{RT_p}\right) \quad (11)$$

Yu et al. studied the evaporation of sodium and potassium in silicate melts[18]. It is concluded that the rate of vaporization of sodium follows the first order kinetics.

$$Na_{(l)} \rightarrow Na_{(v)} \quad (12)$$
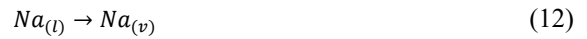
From our previous experiments, it was observed that 90% of sodium evaporates around 50sec when the temperature reaches 1,156 K. Using the above information, the rate constant is estimated to be 0.046 sec⁻¹. The rate of formation of sodium from the sodium azide decomposition and the rate of vaporization of sodium can be calculated using Equations (13) and (14).

$$\frac{dC_{Na}}{dt} = \frac{-dC_{NaN_3}}{dt} \qquad if \ T_p < 1,156 \ K \quad (13)$$

$$\frac{dC_{Na}}{dt} = \frac{-dC_{NaN_3}}{dt} + (-k_{Na} \times C_{Na}) \ if \ T_p > 1,156 \ K \quad (14)$$

Simulation Results and Discussion

Figure 5 shows the temperature distribution on the centerline at various time. It can be seen from this figure that the combustion front moves from left end of the reaction pellet toward the right end. The velocity of combustion front movement rate is slow initially and reaches a stable faster velocity when it moves further toward the right.
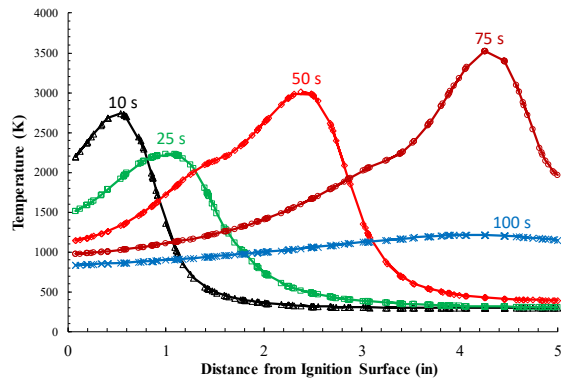

Figure 5. Temperature distribution on centerline.

The temperature histories of 1, 2.5 and 4 inches from the ignition surface are shown in Figure 6. It can be seen that the temperature increases from room temperature to a maximum rapidly and then cools down slowly. The cooling rate changes when the temperature is around 2,151 K which is caused by the silicon nitride decomposition.
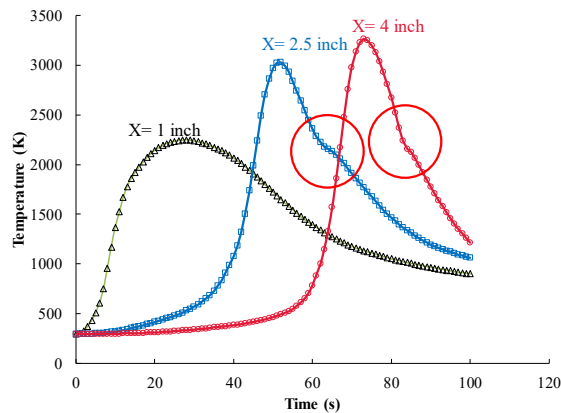

Figure 6. Temperature history on centerline.

Figure 7 shows the concentrations of reactants and product at different times. Slight changes of silicon and silicon nitride concentrations are observed at 85 sec. It is the time silicon nitride decomposes to form silicon.
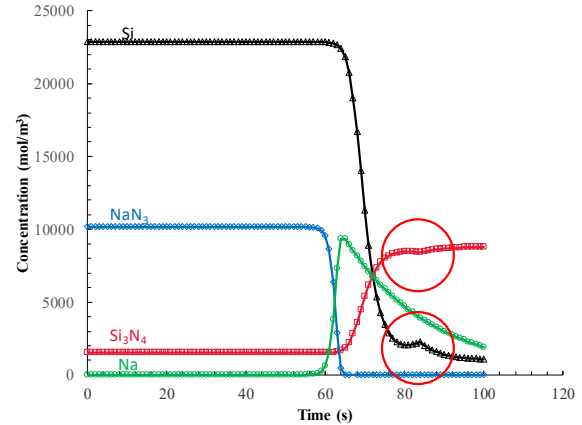

Figure 7. Concentrations history on centerline.

Conclusions

A finite element analysis model of Self-propagating High-temperature Synthesis (SHS) of silicon nitride is successfully developed to investigate the reaction at a normal pressure nitrogen environment (1 atm). It is shown that the velocity of reaction front movement is highest at the midpoint of the pellet and the maximum temperature of the pellet is strongly dependent on the green density and amount of silicon nitride added because of the variation of heat density and thermal conductivity with both green density and silicon nitride diluent.

References

1. G. Xanthopoulou, G. Vekinis, "An Overview of Some Environmental Applications of Self-propagating High-temperature Synthesis", Adv. Environ. Res (Oxford, U. K.), 5, 117-128 (2001).
2. S. Lin, J. Selig, H.T. Lin, H. Wang, "Self-propagating High-temperature Synthesis of Calcium Cobaltate Thermoelectric Powders", J. Alloys Compd., 503, 402-409 (2010).
3. A. Varma, S.R. Alexander, S.X. Alexander, S. Hwang, "Combustion Synthesis of Advanced Materials: Principles and Applications", Adv. Chem. Eng., 24, 79-226 (1998).
4. S.W. Yin, L. Wang, L.G. Tong, F.M. Yang, Y.H. L, "Kinetic Study on the Direct Nitridation of Silicon Powders Diluted with α-Si3N4 at Normal Pressure", International Journal of Minerals, Metallurgy and Materials, 20 (5), 493 (2013).
5. P.W.M. Jacobs, T.A.R. Kureishy, "Kinetics of Thermal Decomposition of Sodium azide", J. Chem. Soc., 4718-4723 (1964).

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