

## Numerical modeling of a self-propagating high-temperature synthesis process of the TiC system

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A self-propagating high-temperature synthesis process of the TiC reactive system was numerically simulated to investigate the effect of porosity and diluent on the SHS reaction and its activating mechanism by an implicit difference method (IDM) and a Gauss-Seidel iteration procedure. The new features of the model include a consideration of the melting of each constituent of the reactants and product and the inclusion of considerations involving dilution and porosity. The results show that as the porosity is varied, there is not a significant effect on the combustion temperature and mode of the combustion front, and the nature of the combustion front is steady and uniform because of the lower activation energy in this system. As the reactant porosity values are decreased, the combustion velocity first increases because of an increase in the thermal conductivity. The combustion velocity, after reaching a maximum, decreases with a further decrease in the porosity because of the high value of the thermal conductivity of the reactants. To study the effect of the diluent, the product itself is considered as the diluent. The effect of adding the diluent to the initial reactants is to decrease the combustion temperature and the combustion velocity.

**Key words:** Self-propagating high-temperature synthesis, Combustion temperature, Propagation velocity, TiC system.

### Introduction

Self-propagating high-temperature synthesis (SHS), also called combustion synthesis or micropyretic synthesis, is an attractive technique for the synthesis of advanced materials such as ceramics, intermetallics, composites, and superconductors. This technique employs exothermic reaction processing, which circumvents difficulties associated with conventional methods of time and energy-intensive sintering processing [1-3]. The advantages of self-propagating high-temperature synthesis also include rapid net shape processing and clean products. In addition, the synthesized products have been reported to possess better mechanical and physical properties [4].

Several numerical and analytical models of self-propagating high-temperature synthesis have been well developed. Many articles have dealt with the numerical modeling of combustion synthesis without considering the effect of melting of any constituent. Margolis *et al.* [5] have reported that the melting of reactants plays a significant role in the nonsteady, nonplanar modes of combustion and investigated the effect of melting on the bifurcation phenomenon. Lakshmikantha and coworkers [6, 7] first explored a numerical model that includes the effects of dilution and porosity, and melting of each constituent of the

reactants and products. An analytical modeling of the propagation of the combustion front in solid-solid reaction systems has also been reported [8]. The analytical model has given good results when compared with the experimentally-determined numbers and the numerically-calculated values. In addition, a dynamic modeling of the gas and solid reaction has also been carried out to illustrate the effects of various parameters on self-propagating high-temperature synthesis [9]. Due to the limits in thermodynamics and kinetics, the SHS processes of many systems are difficult to enact, restricting the development of SHS to a certain extent. Munir and coworkers [10, 11] developed a model that investigates the effect of electric fields on self-propagating high-temperature synthesis reactions. Modeling studies showed that the effect of the field is primarily thermal, with Joule heating imparted to the system in a distribution which is dependent on the electrical conductivities of the participating phases. These numerical and analytical analyses provided a better understanding of the reaction sequence during SHS reactions.

Although there are many reports on the Ti-C system, little work has been carried out on modeling the combustion wave and the influence of processing parameters on it. Kottke and Niiler [12] developed a model that studied the thermal conductivity effects on SHS by finite-difference heat flow calculations. Advani *et al.* [13] has revealed that material and process parameters have a significant influence on SHS reaction propagation kinetics. Zuccaro *et al.* [14] studied the synthesis of TiC nanosized aggregates during a self-propagating high-temperature synthesis process.

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The overall model describes the transient of the basic mechanisms governing the SHS process in a two-dimensional micrometer size system. At each time step, the continuum (micrometer scale) model computes the current temperature field according to the prescribed boundary conditions. Huque and Azad [15] investigated the effects of thermal conductivity on the steady state propagation speed during the self-propagating high-temperature synthesis of Ti+C green compacts. Lakshmikantha *et al.* [6] explored the effect of the heat of reaction, the activation energy, the frequency factor, thermal conductivity, and initial temperature on the combustion velocity and combustion temperature.

The porosity is known to influence the mechanical properties of a product [4]. The effect of porosity/density on the propagation is to change both the combustion temperature and the combustion velocity. It has been very well established from a number of experimental results [16-19] that the porosity or the relative density has a significant effect on the nature of the propagation of the combustion front. Experiments on TiB<sub>2</sub> [17], NiAl [16], TiC [20], and various other compounds [17] have indicated that with a decrease in the porosity, the propagation rate first increases and then decreases. Experiments on Me-Boron (Me = Ti, Hf, Zr) [19] systems have shown that as the porosity of reactants is increased, the period of oscillations also increase. Hence, it is necessary to consider the influence of porosity in the numerical modeling. It has often been implicitly assumed in the literature [21] that the physical nature of the product formed has little effect on the nature of the combustion front. This is not always the case. Hence, a consideration of both the reactants and products, including the effect of porosity in both phases, is a necessity in the numerical calculations. In this study, a numerical simulation is used to characterize the effects of porosity and diluent on the self-propagating high-temperature synthesis with Ti+C. The results generated in the study can be used to illustrate the effects of porosity and diluent on the propagation velocity and the combustion temperature during self-propagating high-temperature synthesis.

### Numerical Model

We consider a cylindrical sample of radius  $r$  and length  $L$  made of a compacted powder of solid reactants (Fig. 1), the reactions are ignited from the left end, and the combustion front propagates from left to right.

During the passage of a combustion front in the reaction, the energy equation for transient heat conduction, including the source term, containing the heat release due to the

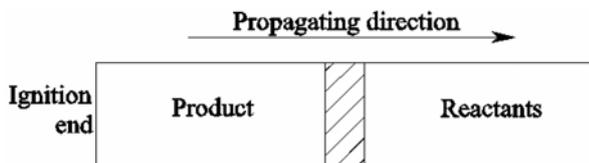


Fig. 1. Schematic representation of the SHS process.

exothermic combustion reaction is given as [6, 22]:

$$\rho \frac{\partial H}{\partial t} = \frac{\partial \left[ \kappa \frac{\partial T}{\partial X^*} \right]}{\partial X^*} - \frac{2h}{r}(T-T_0) + \rho Q(1-M_{FD})\Phi(T, \eta) \quad [1]$$

Each symbol in the equation is explained in the nomenclature. The reaction rate,  $\Phi(T, \eta)$  in Eq. [1] is given as:

$$\Phi(T, \eta) = \frac{\partial \eta}{\partial t} = K_0(1-\eta) \exp\left(-\frac{E}{RT}\right) \quad [2]$$

In this study, a numerical calculation for Eq. [1] was carried out with the assumption of first-order kinetics. In Eq. [1], the energy required to heat the synthesized product from the initial temperature to the adiabatic combustion temperature is shown on the left-hand side. The terms on the right-hand side are the conduction heat transfer term, the surface heat loss parameter, and the heat release due to the exothermic micropyreitic reaction, respectively.

We now define the following dimensionless parameters:

$$\theta = \frac{C_{PU}(T-T_0)}{\Delta H_{SL}}, \quad \phi = \frac{H}{\Delta H_{SL}}, \quad \kappa = \frac{\kappa^*}{\kappa_U}, \quad X = \frac{X^*}{L}, \quad \tau = K_0 t \quad [3]$$

where  $C_{PU}$  is the specific heat of the unreacted reactants, and  $\kappa_U$  is the value of the thermal conductivity of unreacted mixtures with appropriate modification for porosity.

Using the above dimensionless parameters, Eq. [1] may be recast as:

$$\frac{\partial \phi}{\partial \tau} = \gamma \frac{\partial \left[ \kappa \frac{\partial \theta}{\partial X} \right]}{\partial X} - \alpha(\theta - \theta_0) + (1-M_{FD})(1-\eta)v \exp\left[\frac{-N}{1+\beta\theta}\right] \quad [4]$$

Where:

$$\gamma = \frac{K_U}{\rho L^2 C_{PU} K_0}, \quad v = \frac{Q}{\Delta H_{SL}}, \quad N = \frac{E}{RT_0}, \quad \beta = \frac{\Delta H_{SL}}{C_{PU} T_0}, \quad \alpha = \frac{2h}{r \rho K_0 C_{PU}} \quad [5]$$

The above equation is solved simultaneously with the following mass balance equation (first-order reaction):

$$\frac{\partial \eta}{\partial \tau} = (1-\eta) \exp\left[\frac{-N}{1+\beta\theta}\right] \quad [6]$$

The initial and boundary conditions read:

$$\theta(X, 0) = \theta_0, \quad 0 < X \leq 1; \quad \theta(0, \tau) = \theta_{ad};$$

$$\eta(X, 0) = 0, \quad 0 < X \leq 1; \quad \eta(0, \tau) = 1;$$

$$\kappa \frac{\partial \theta}{\partial X} \Big|_{X=1} = Bi^* [\theta_0 - \theta(1, \tau)], \quad Bi = \frac{hL}{\kappa_U} \quad [7]$$

A middle-difference approximation and an enthalpy-

**Table 1.** The thermophysical/chemical parameters used in the numerical calculation

Thermophysical/chemical parameters	Ti	C	TiC
Specific heats at 300K/J·kg <sup>-1</sup> ·K <sup>-1</sup>	528 [26]	846 [24]	564 [25]
Specific heats in liquid state/J·kg <sup>-1</sup> ·K <sup>-1</sup>	700 [26]	2200 [24]	1119 [25]
Thermal conductivity at 300K/W·m <sup>-1</sup> ·K <sup>-1</sup>	21.6 [26]	120 [24]	17 [26]
Thermal conductivity in liquid state/W·m <sup>-1</sup> ·K <sup>-1</sup>	11 [26]	25 [24]	13 [24]
Densities at 300K/kg·m <sup>-3</sup>	4500 [26]	1600 [24]	4940 [24]
Densities in liquid state/kg·m <sup>-3</sup>	4110 [26]	1520 [24]	4800 [26]
Melting points/K	1933 [26]	3823 [24]	3373 [24]
Latent heats/J·kg <sup>-1</sup>	0.175E5 [26]	-	0.193E7 [25]

temperature method coupled with a Gauss-Seidel iteration procedure are used to solve the dimensionless equations of the combustion synthesis problems. The total length and radius of the sample taken for the calculation are 1cm and 0.05 cm, respectively. The value of  $K_0$  used in the TiC system was obtained by matching the experimentally- [23] and numerically-obtained velocities at 60% porosity (an equal value for both the product and the reactants). The value of the pre-exponential factor was assumed to remain constant for all values of the porosity at 5.0E4 [24]. The time step used in the problem was 0.004 seconds, depending on the  $K_0$  value of the problem. In the calculation, the adiabatic temperature of TiC was 3373 K [20], and the exothermic heat and the activation energy of combustion synthesized TiC were taken to be 184 kJ·mol<sup>-1</sup> [25] and 124 kJ·mol<sup>-1</sup> [20], respectively. The various thermophysical/chemical parameters, including the thermal conductivity, the density and the heat capacities, are assumed to be independent of temperature, but they are different in each state. The average values of these parameters vary as the reaction proceeds, depending upon the degree of reaction. The parameter values used in the computational calculations are shown in Table 1. In this study, the combustion temperature is defined as the highest reaction temperature during micropyreitic synthesis, and the propagation velocity is the velocity of the propagating combustion front.

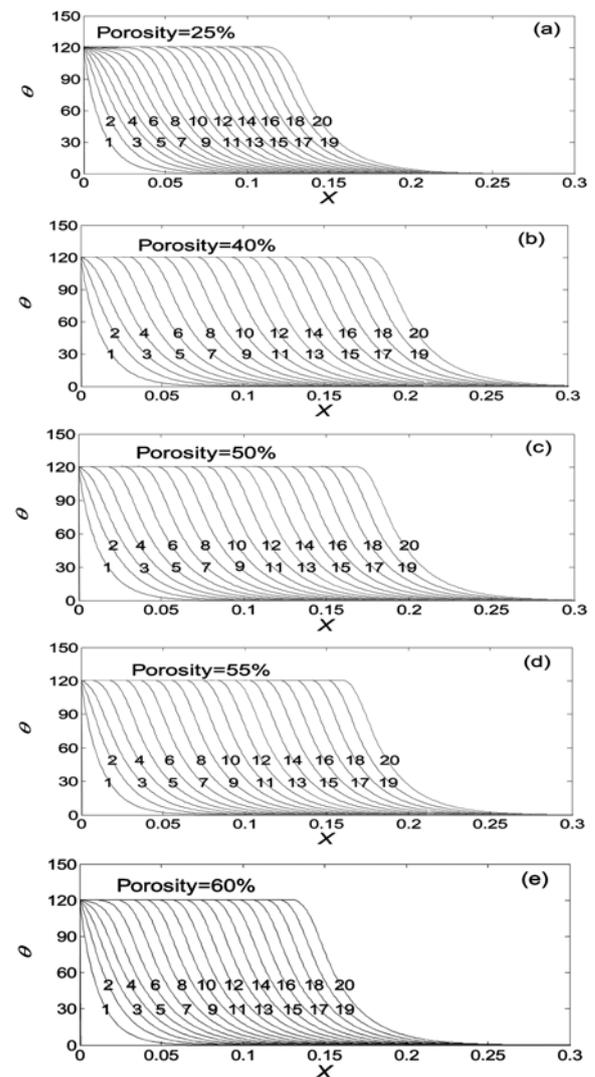
## Results and Discussion

### Influence of porosity on the SHS process

It has been reported that porosity has a dramatic effect on the mechanism properties of the product [4]. The porosity also influences the thermal conductivity and density of the unreacted compact and further changes the temperature and velocity of the combustion front. In many instances, the combustion front may not propagate at all as is found when the thermal conductivity is significantly increased or decreased [6]. Therefore, it is important to consider the influence of porosity in the numerical investigation. For the calculations, the thermal conductivity and density of the reactants and porosity with the porosity can be expressed as thermal conductivity with porosity:

$$\kappa_{\text{porosity}}^* = \kappa_{\text{without porosity}}^* (1 - P)/(1 + P/2) \quad [8]$$

Density with porosity:



**Fig. 2.** Plots of the combustion front temperature at various times along the length of the specimen. The amounts of porosity are (a) 25%, (b) 40%, (c) 50%, (d) 55%, (e) 60%. The time interval between two consecutive time step is 0.004 s.

$$\rho_{\text{porosity}} = \rho_{\text{without porosity}} (1 - p) \quad [9]$$

where  $P$  is the porosity of the reactants or product. The effect of melting of the reactants, Ti and C and product, TiC, is also included in the calculation procedure.

Fig. 2 shows plots of the dimensionless temperature

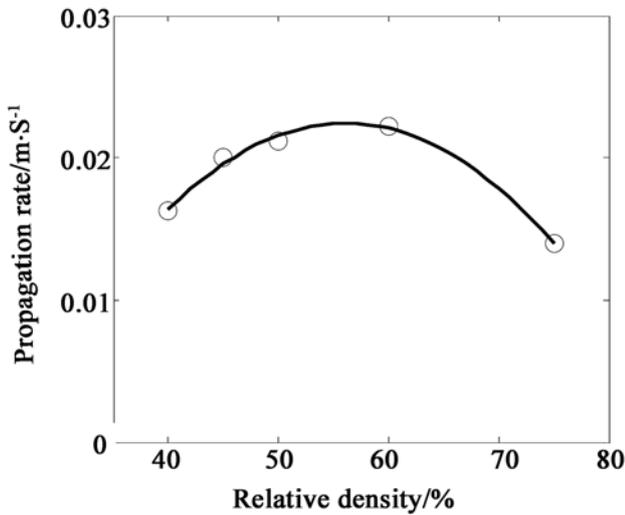


Fig. 3. Dependence of the propagation rate on the relative density of Ti+C mixtures.

profile with the dimensionless distance. The values of reactant porosities used in (a)-(e) are 25, 40, 50, 55 and 60% respectively. The value of the porosity of the product is assumed to be equal to that of the initial reactants in all the cases. The interval time between two consecutive time steps (profiles) is 0.004 s, the numbers in the figure give the propagation sequence (time steps). It is noted from this figure that as the porosity values are increased, the temperature profile is steady and uniform. The experimental results for the TiC system do not indicate any oscillations, probably because of the lower activation energy in the system.

As the porosity is varied, there is a considerable effect on the propagation rate of the combustion front. The effect of the relative density of Ti+C mixtures on the propagation rate is shown in Fig. 3. It is noted that initially the propagation rate slightly increases and then decreases with an increase in the relative density of the mixtures. As the reactant porosity values are decreased, the combustion velocity first increases because of an increase in the thermal conductivity. The combustion velocity, after reaching a maximum, decreases with a further decrease in the porosity because of the high value of thermal conductivity of the reactants. This result agrees with the analytical conclusions by Rice [23].

#### Influence of the diluent on SHS process

The effect of the addition of diluents on the rate of the combustion process has been examined in some studies [27, 28]. The diluents can be divided into two categories depending on their role in the combustion process. (i) Those that do not participate in the combustion reaction and play a role of enthalpy absorbers. These diluents are passive diluents. These are mostly the products of the combustion reaction, for instance, the addition of TiC powder as a diluent to the reactants in the synthesis of TiC. (ii) Diluents that participate in the combustion reaction either by going into solid solution in the product or by generating another

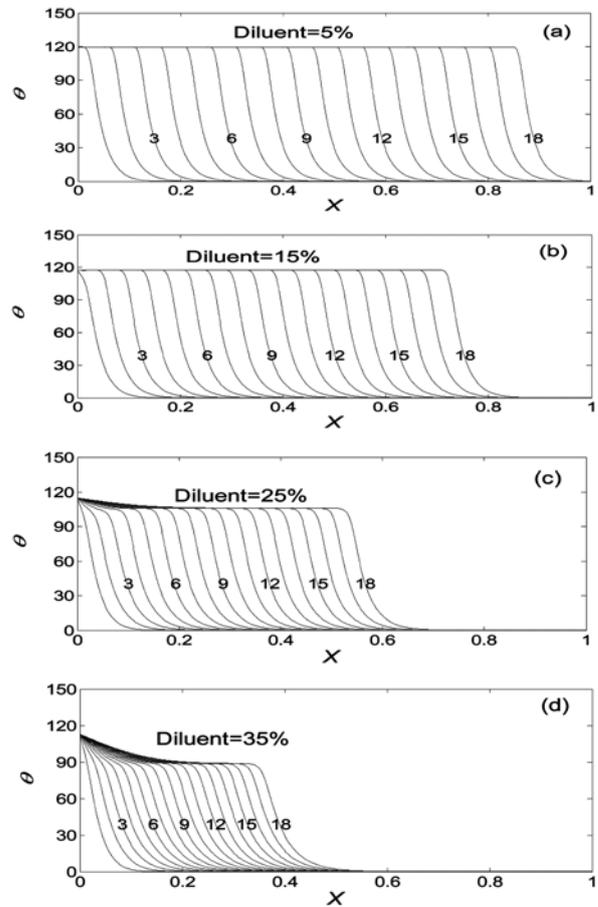


Fig. 4. Plots of the combustion front temperature at various times along the length of specimen. The amounts of the diluent used are (a) 5%, (b) 15%, (c) 25%, (d) 35%. The time interval between two consecutive time steps is 0.02 s.

phase. Such reactants can be referred to as active diluents. The role of active diluents on the process of combustion has not been examined in as much detail as that of passive diluents [16]. For this study of the effect of a diluent, the end product of the combustion reaction, TiC, is also chosen to be the diluent for such calculations. An increase in the amount of the diluent decreases the exothermic energy; hence, the combustion temperature and velocity are expected to decrease with the addition of the diluent. The value of the porosity of the product was assumed to be equal to that of the initial reactants at 40% in all the cases. The interval time between two consecutive time steps (profiles) is 0.02 s. Fig. 4 shows plots of the dimensionless temperature profile with the dimensionless distance. The values of diluent used in (a)-(d) are 5, 15, 25 and 35% respectively. The numerical results also indicate that an increase in the diluent from 5at% to 35at% reduces the combustion temperature and propagation rate.

#### Conclusions

The paper is based on a one-dimensional Fourier heat balance equation. A mathematical model of a self-

propagating high-temperature synthesis process was presented. On the above basis, by a finite difference scheme, the SHS process of the Ti-C reactive system was numerically simulated to investigate the effect of porosity and diluent on the SHS reaction and its activating mechanism.

(1) As the reactant porosity values are varied, there is not a significant effect on the combustion temperature and mode of the combustion front, and the nature of the combustion front is steady and uniform because of the lower activation energy in the system. As the reactant porosity values are decreased from 60% to 25%, the combustion velocity first increases because of an increase in the thermal conductivity. The combustion velocity, after reaching a maximum, decreases with a further decrease in the porosity because of the high value of the thermal conductivity of the reactants. For the study of the effect of a diluent, the product itself is considered as the diluent. The effect of adding the diluent to the initial reactants is to decrease the combustion temperature and the combustion velocity.

(2) For a study of the effect of a diluent, the end product of the combustion reaction, TiC, is chosen to be the diluent for such calculations. The numerical results also indicate that an increase in the diluent from 5at% to 35at% reduces the combustion temperature and propagation rate.

### Nomenclature

$r$	radius of the specimen, m
$E$	activation energy, $\text{kJ}\cdot\text{mol}^{-1}$
$H$	enthalpy, $\text{J}\cdot\text{kg}^{-1}$
$h$	surface heat transfer coefficient, $\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$
$\Delta H_{\text{SL}}$	latent-heat release at the melting point of reactant Ti, $\text{J}\cdot\text{kg}^{-1}$
$K_0$	pre-exponential constant, $\text{s}^{-1}$
$L$	length of the specimen, m
$M_{\text{FD}}$	molar fraction of diluent, %
$P$	porosity, %
$Q$	heat of reaction, $\text{kJ}\cdot\text{mol}^{-1}$
$R$	gas constant, $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
$t$	time, s
$T$	temperature, K
$T_0$	ambient temperature, K
$X^*$	dimensional coordinate, m
$X$	dimensionless coordinate
$\rho$	density, $\text{kg}\cdot\text{m}^{-3}$
$\kappa^*$	thermal conductivity, $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
$\kappa$	dimensionless thermal conductivity
$\theta$	dimensionless temperature
$\theta_0$	dimensionless ambient temperature
$\theta_{\text{ad}}$	dimensionless adiabatic temperature
$\tau$	dimensionless time

$\eta$	dimensionless fraction of reacted product
$\phi$	dimensionless enthalpy
$\Phi$	reaction rate, $\text{s}^{-1}$

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