Korean J. Chem. Eng., **19**(3), 400-405 (2002)

Observations on Combustion Front Propagation in Self-Propagating High-Temperature Synthesis Process Producing Refractory Ceramics

Chang-Ho Park, Tae-Sung Kang* and Sang Hwan Kim*,†

Department of Chemical Engineering, Kyunghee University, 1 Seochun-ri, Kiheung-eup, Yongin 449-701, Korea
*Department of Chemical Engineering, Konkuk University, 1 Hwayang-dong, Kwangjin-ku, Seoul 143-701, Korea
(*Received 30 July 2001 • accepted 29 October 2001*)

Abstract−High-temperature refractory ceramics can be produced in the combustion regime by using self-propagating, high-temperature synthesis (SHS) processes. The numerical simulation of the SHS process in a simplified diffusion-reaction system is investigated. The SHS process is simplified by the one- and two-dimensional pseudo-homogeneous environment. The stiff equations of the SHS process are solved by using finite difference methods on two-dimensional adaptive meshes. Travelling waves with constant patterns are observed for adiabatic and nonadiabatic systems. For higher values of heat of reaction and activation energy, the combustion front starts to oscillate. Single and complex oscillating waves are detected. In oscillating combustion fronts, the temperature can overshoot the adiabatic temperature to result in the complete conversion of solid reactants. In two dimensional systems, travelling, fingering, and rotating waves are detected in the combustion synthesis process.

Key words: Self-Propagating High-Temperature Process, Combustion Front, Travelling Waves, Oscillating Waves, Rotating Waves

INTRODUCTION

Combustion synthesis is potentially an energy-efficient process for producing refractory ceramics, ceramic composites, and intermetallics. Conventional methods for producing refractory ceramic materials involve heating the solid metal in a furnace for several hours at high temperatures, although the product quality is often affected adversely by incomplete conversion of solid reactant. However, thermal effects generated due to the extreme exothermicity and high activation energy of the synthesis reaction, can be utilized to run the reaction in the self-sustaining regime. Once ignited, a sharp combustion front is formed that propagates through the reactant in the form of a combustion wave. As the combustion wave advances, the reactant is converted to the product. The advantages of combustion synthesis include very low energy consumption, short synthesis time, and high purity of the product. In the production of refractory ceramic materials by combustion synthesis process, the synthesis and densification steps may be combined into one operation. Since the reaction takes place in the combustion regime rather than the kinetic regime, it is difficult to control and predict. The only way to understand these systems is to gain an insight into their dynamics. Since there are a large number of system parameters that govern the behavior of the systems, experiments alone cannot be used to understand these systems. Numerical modeling provides an important alternative to study these systems and to understand the mass and heat transfer characteristics of the systems.

The combustion process between the solid metal and the gaseous nitrogen in one- and two-dimensional systems is referred to as filtration combustion, which has been studied since 1975 [Merzhanov and Borovinskaya, 1975; Aldushin and Kasparyan, 1981]. Most of these studies were analytical in nature and helped define the basic regimes for combustion synthesis and establish the effects of system parameters on front propagation and final conversion to the product.

The stability analysis for filtration combustion was presented early in the 1980's [Aldushin and Kasparyan, 1981]. However, there are no numerical calculations for two-dimensional models to confirm the predictions made from simplified analytical models. For the majority of combustion synthesis processes, many people try to eliminate or at least to suppress the instability effects because they impair the reaction control and lead to the nonuniform product and the incomplete conversion of the reactant. This study aims at simulating the one- and two-dimensional models for the combustion synthesis process and understanding the stability of combustion fronts and the behavior of travelling, oscillating, fingering, rotating and erratic waves during its process under the wide range of operating conditions.

MODEL FORMULATION

The model employed for the simulation of combustion synthesis process describes the filtration combustion as depicted in Fig. 1. The reaction is ignited by a short-term energy source such as the resistively heated tungsten wire or graphite. Once ignited, the reaction continues on its own in the form of a steep combustion front which separates unreacted solid from the product. The front propagates down the length of the cylindrical solid reactant. The flow is driven by the pressure gradient imposed by the consumption of the nitrogen at the front and the pressure of the environment around the solid reactant. Inside the system, the reaction between the particles of solid reactant S(s) and the pure nitrogen G(g) results in the gasless solid product P(s) occurs in the following manner.

$$S(s)+G(g)\rightarrow P(s) \quad (1)$$

†To whom correspondence should be addressed.
E-mail: sanghkim@konkuk.ac.kr

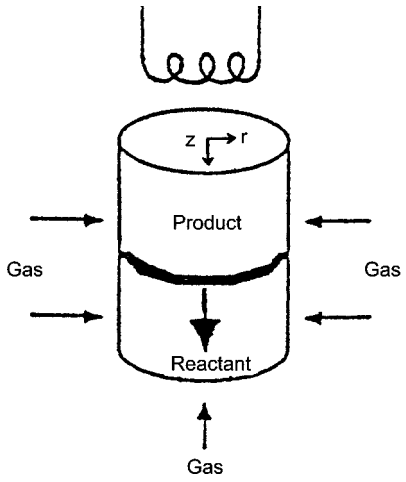

Fig. 1. Schematic of combustion synthesis between solid metal and gaseous nitrogen in the high-pressurized batch system.

Modeling of combustion synthesis process involves the transport of mass and energy and their generation or consumption. To make the model solvable by current techniques of numerical analysis, several simplification assumptions are made as follows:

(1) The system comprised of solid particles and gaseous nitrogen is considered to be pseudohomogeneous. This implies that the temperature and concentration of solid particles and their surrounding area are taken to be identical, and the heat and mass balances can be taken by the whole system instead of solid and gas separately.
(2) Melting, radiation, and pressure drop in the system are not considered.
(3) The physical properties of solid particles and gas are assumed constant.

The governing equations describing the filtration combustion in the porous cylindrical body are written in the following way.

Energy balance

$$\rho C_p\frac{\partial T}{\partial t}=\lambda\left(\frac{\partial^2 T}{\partial z^2}+\frac{\partial^2 T}{\partial r^2}+\frac{1}{r}\frac{\partial T}{\partial r}+\frac{1}{r^2}\frac{\partial^2 T}{\partial\theta^2}\right)+k_0\exp\left(-\frac{E}{RT}\right)(-\Delta H)c_s-\frac{2h}{R}(T-T_i) \tag{2}$$

Mass balance

$$(1-\varepsilon)\frac{\partial c_s}{\partial t}=-k_0\exp\left(-\frac{E}{RT}\right)c_s \tag{3}$$

Initial and boundary conditions can be written as follows:

$$t=0,\ 0\le z<\infty,\ 0\le\theta\le 2\pi,\ 0\le r\le R:\ T=T_i,\ c_s=c_{si} \tag{4}$$

$$z=0,\ t>0,\ 0\le\theta\le 2\pi,\ 0\le r\le R:\ T=T_0,\ c_s=c_{so} \tag{5}$$

$$z=\infty,\ t>0,\ 0\le\theta\le 2\pi,\ 0\le r\le R:\ T=T_i,\ c_s=c_{si} \tag{6}$$

$$r=R,\ t>0,\ 0\le\theta\le 2\pi,\ 0<z<\infty:\ -\lambda\frac{\partial T}{\partial r}=h(T-T_i),\ \frac{\partial c_s}{\partial r}=0 \tag{7}$$

The term ρC_p represents the contribution of pseudohomogeneous-phase heat capacity consisting of the heat capacities of solid reactant and gaseous nitrogen. The whole variables and parameters appearing in this paper are described in the nomenclature. To render the equations dimensionless, the following scaling relations are used for the independent and dependent variables in the following way:

$$\tau=\frac{t}{t^*},\ t^*=\frac{\rho C_p RT_*^2\exp(E/RT_*)}{Ek_0(-\Delta H)c_{si}}$$
$$Z=\frac{z}{z^*}=z\sqrt{\frac{\rho C_p}{\lambda t^*}},\ \Phi=\frac{\theta}{2\pi},\ \xi=\frac{r}{R}$$
$$C_s=\frac{c_s}{c_{si}},\ \Theta=\frac{E}{RT_*}\frac{T-T_*}{T_*},\ \gamma=\frac{\rho C_p RT_*^2}{c_{si}E(-\Delta H)}$$
$$\beta=\frac{RT_*}{E},\ B_i=\frac{hR}{\lambda},\ \alpha=\frac{2ht_*}{\rho C_p R},\ \delta=\frac{4\lambda t_*}{\rho C_p\pi^2 R^2} \tag{8}$$

The parameters γ and β are defined as the dimensionless heat of reaction and activation energy, respectively. Low γ and β values represent a system with high heat of reaction and high activation energy and vice versa. The system temperature is made dimensionless by using the adiabatic temperature T_* as the reference value. Thus, the dimensionless temperature values Θ are typically negative when the temperature of the system is lower than the adiabatic temperature T_*. The parameter α describes the dimensionless heat transfer coefficient between the system and the surroundings. Therefore, $\alpha=0$ implies the adiabatic operation of combustion systems, while $\alpha\neq 0$ denotes the nonadiabatic combustion system. Table 1 gives the values of some of the dimensionless parameters for transition metal nitrides [Toth, 1971; Dankekar et al., 1990, 1991; Dimitriou et al., 1989; Agrafiotis et al., 1987].

Table 1. Physical values of parameters γ and β

Parameter range	Physical value range
$0.015\le\gamma\le 0.065$	$170\le(-\Delta H)\le 740$ KJ/mole
$0.010\le\beta\le 0.245$	$80\le E\le 370$ KJ/mole

Substituting into the dimensional equations results in the following dimensionless equations governing the filtration combustion process.

$$\frac{\partial\Theta}{\partial\tau}=\frac{\partial^2\Theta}{\partial Z^2}+\delta\left\{4\pi^2\left(\frac{1}{\xi}\frac{\partial\Theta}{\partial\xi}+\frac{\partial^2\Theta}{\partial\xi^2}\right)+\frac{1}{\xi^2}\frac{\partial^2\Theta}{\partial\Phi^2}\right\}+C_s\exp\left(\frac{\Theta}{1+\beta\Theta}\right)-\alpha(\Theta-\Theta_i) \tag{9}$$

$$(1-\varepsilon)\frac{\partial C_s}{\partial\tau}=-\gamma C_s\exp\left(\frac{\Theta}{1+\beta\Theta}\right) \tag{10}$$

Initial and boundary conditions are:

$$\tau=0,\ 0\le Z<\infty,\ 0\le\Phi\le 1,\ 0\le\xi\le 1:\ \Theta=\Theta_i,\ C_s=1 \tag{11}$$

$$Z=0,\ \tau>0,\ 0\le\Phi\le 1,\ 0\le\xi\le 1:\ \Theta=\Theta_0,\ C_s=1 \tag{12}$$

$$Z=\infty,\ \tau>0,\ 0\le\Phi\le 1,\ 0\le\xi\le 1:\ \Theta=\Theta_i,\ C_s=1 \tag{13}$$

$$\xi=1,\ \tau>0,\ 0\le\Phi\le 1,\ 0<Z<\infty:\ \frac{\partial\Theta}{\partial\xi}=B_i(\Theta-\Theta_i),\ \frac{\partial C_s}{\partial\xi}=0 \tag{14}$$

1. One-Dimensional Model

We assume that the system is angularly symmetrical and the importance of radial gradients is marginal. Furthermore, it is supposed

that the internal structure is perfectly accessible for the gaseous nitrogen. Then, Eqs. (9)-(14) reduce to the simplified one-dimensional model in the following way.

$$\frac{\partial\Theta}{\partial\tau}=\frac{\partial^2\Theta}{\partial Z^2}+C_s\exp\left(\frac{\Theta}{1+\beta\Theta}\right)-\alpha(\Theta-\Theta_i) \quad (15)$$

$$(1-\varepsilon)\frac{\partial C_s}{\partial\tau}=-\gamma C_s\exp\left(\frac{\Theta}{1+\beta\Theta}\right) \quad (16)$$

The initial and boundary conditions are represented as follows:

$$\tau=0,\ 0\le Z<\infty,\ 0\le\Phi\le1,\ 0\le\xi\le1:\ \Theta=\Theta_i,\ C_s=1 \quad (17)$$

$$Z=0,\ \tau>0,\ 0\le\Phi\le1,\ 0\le\xi\le1:\ \Theta=\Theta_0 \quad (18)$$

$$Z=\infty,\ \tau>0,\ 0\le\Phi\le1,\ 0\le\xi\le1:\ \Theta=\Theta_i \quad (19)$$

2. Two-Dimensional Model

The system is strongly nonlinear, so that the occurrence of an angular temperature gradient cannot be neglected. For this condition Eqs. (9)-(14) reduces to Eqs. (20)-(26) as follows. The second term in Eq. (10) represents the heat conduction in the azimuth-angular direction.

$$\frac{\partial\Theta}{\partial\tau}=\frac{\partial^2\Theta}{\partial Z^2}+\delta\frac{\partial^2\Theta}{\partial\Phi^2}+C_s\exp\left(\frac{\Theta}{1+\beta\Theta}\right)-\alpha(\Theta-\Theta_i) \quad (20)$$

$$(1-\varepsilon)\frac{\partial C_s}{\partial\tau}=-\gamma C_s\exp\left(\frac{\Theta}{1+\beta\Theta}\right) \quad (21)$$

Initial and boundary conditions are

$$\tau=0,\ 0\le Z<\infty,\ 0\le\Phi\le1,\ 0\le\xi\le1:\ \Theta=\Theta_i,\ C_s=1 \quad (22)$$

$$Z=0,\ \tau>0,\ 0\le\Phi\le1,\ 0\le\xi\le1:\ \Theta=\Theta_0 \quad (23)$$

$$Z=\infty,\ \tau>0,\ 0\le\Phi\le1,\ 0\le\xi\le1,\ \Theta=\Theta_i \quad (24)$$

$$\Phi=\Phi \text{ and } \Phi=\Phi+1,\ \tau>0,\ 0<Z<\infty,\ 0\le\xi\le1:\ \Theta(\Phi)=\Theta(\Phi+1),\ C_s(\Phi)=C_s(\Phi+1) \quad (25)$$

Eq. (25) is subject to so-called periodic boundary conditions. Periodic boundary conditions result from the assumptions that the accessible structure is near the surface and represents a thin annular space which can be unfolded.

RESULTS FROM NUMERICAL SIMULATION

The set of equations describing filtration combustion are highly coupled and nonlinear partial differential equations. They exhibit steep spatial gradients in temperature and concentration. An intricate formulation involving finite difference approximation on two-dimensional adaptive grids is used. Details of the adaptive mesh algorithm are available in the literature [Park, 1983].

Travelling waves of constant pattern profiles with constant velocity, propagate through the adiabatic system as shown in Fig. 2. After a short transient heat-up period the concentration and temperature profiles develop, and the combustion front of a constant shape occurs and moves with constant velocity. The reaction front is stable locally and globally. In addition, only one reaction front can exist. According to Shkadinskii's stability analysis for an adiabatic system and a first-order reaction, the numerically calculated neutral stability line is given by $\Delta=9.1\gamma-2.5\beta$ [Shkadinskii, 1971].

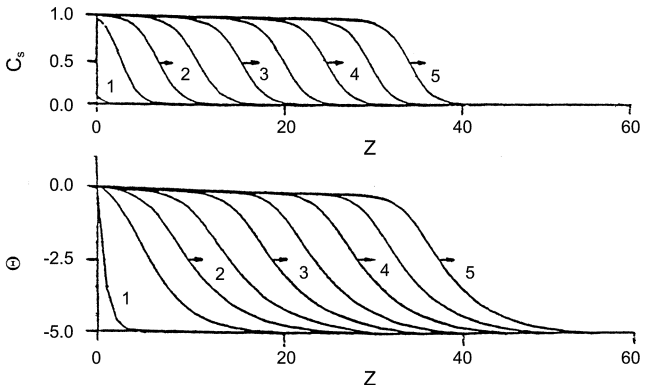

Fig. 2. Travelling waves with constant patterns in one-dimensional adiabatic system.
$\alpha=0.0$, $\beta=0.1$, $\gamma=0.2$, $\Theta_i=-5.0$, $\Theta_0=0.0$, $\varepsilon=0.5$

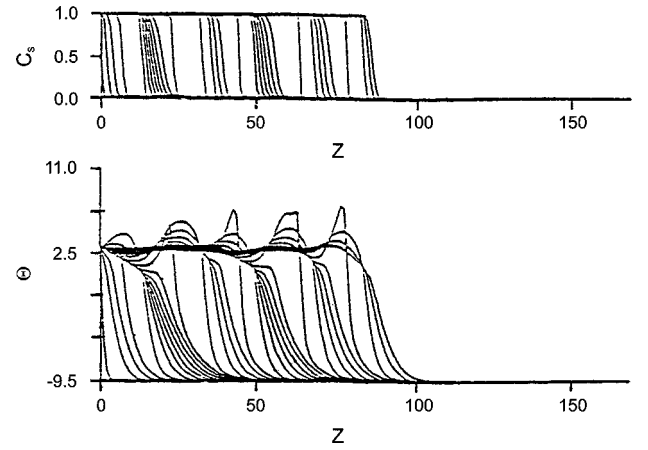

Fig. 3. Oscillating waves in one-dimensional nonadiabatic system.
$\alpha=0.0001$, $\beta=0.03$, $\gamma=0.08$, $\Theta_i=-9.5$, $\Theta_0=3.0$, $\varepsilon=0.5$

For $\Delta<1$, the combustion mode becomes unstable. The calculated value of $\Delta(=1.57)$ for the combustion system shown in Fig. 2 confirms the existence of stable combustion front. For a nonadiabatic system travelling waves with constant patterns are also observed [Munir and Holt, 1987].

For higher values of the parameters γ and β the reaction front starts to oscillate and the velocity of the front depends on the time as shown in Fig. 3. The calculations revealed that multipeak oscillations may exist for higher values of parameters γ and β. The oscillating regimes are observed both for the adiabatic and nonadiabatic combustion. The oscillations have periodic character for the adiabatic and weakly nonadiabatic systems. Oscillations occur because the heat generated by the reaction cannot be transferred from the surface fast enough. In the diffusion-reaction exothermic systems period-doubling bifurcation may occur which ultimately leads to chaotic behavior [Kim and Hlavacek, 1987]. The temperature can overshoot the adiabatic temperature and solid reactants are completely converted. Then the temperature drops below the adiabatic temperature and the fresh unreacted solid is slowly preheated. After the temperature reaches the critical value, the combustion reaction takes place and the temperature of the reaction front again exceeds the adiabatic temperature.

The rise of surface temperature results in a very high reaction

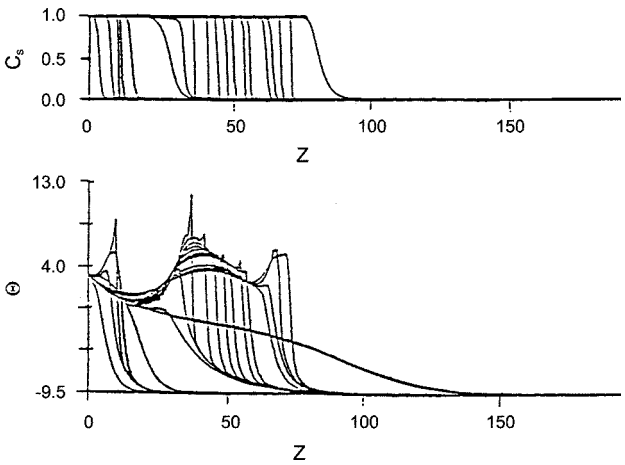

Fig. 4. Complex oscillating waves in one-dimensional nonadiabatic system.
α=0.001, β=0.03, γ=0.08, Le=0.5, Θ_i=−9.5, Θ_0=3.0, ε=0.5

rate. If available reactants are consumed, extinction occurs as shown in Fig. 4. During the period of a slow reaction, heat is conducted to the region with low conversion until the increasing heat generation will start the whole cycle again. The rise of surface temperature is distinctly higher for a nonadiabatic case because the reaction zone is very thin and concentration gradients are steeper than in the adiabatic case. The transient temperature may rise by several hundred degrees above the adiabatic temperature. Such effect can lead to the local melting of the material and finally to a nonuniform product. Extinction occurs for higher values of the heat loss parameter

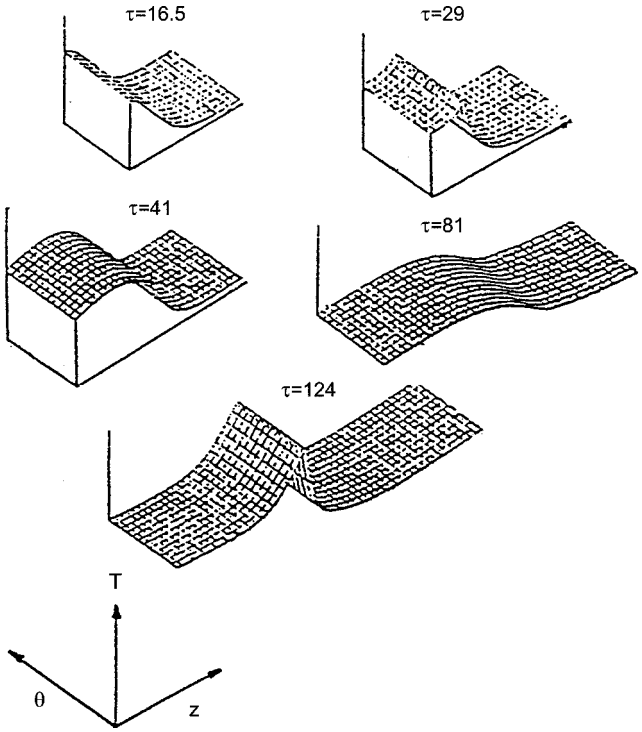

Fig. 5. Piston-like oscillating waves in two-dimensional adiabatic system.
α=0.0, β=0.03, γ=0.08, Θ_i=−9.5, Θ_0=3.0, ε=0.5, δ= 0.001

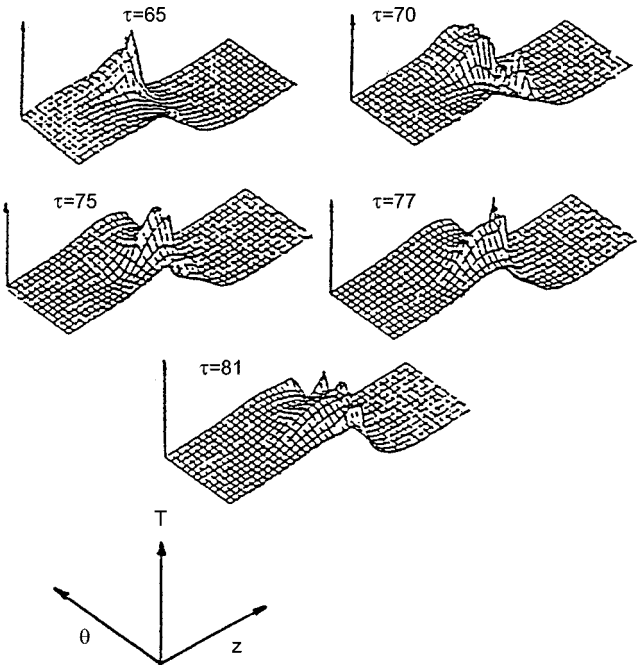

Fig. 6. Fingering waves in two-dimensional adiabatic system.
α= 0.0, β=0.03, γ=0.08, Θ_i=− 9.5, Θ_0=3.0, ε=0.5, δ=0.001

α as shown in Fig. 4. In such a case the material is not completely converted.

In Fig. 5, the oscillating piston wave is presented. The reaction front propagates with oscillating velocity and no angular gradients. If a strong perturbation takes place in the system, two-dimensional instability of surface combustion occurs. The type of resulting reaction front depends on the perturbation imposed. For a symmetrical perturbation, a front results which is symmetrical with respect to this perturbation. On the other hand, for an asymmetrical perturbation an asymmetrical fingering wave occurs as depicted in Fig. 6. For a special type of perturbation a rotating wave can be triggered as shown in Fig. 7. Merzhanov and Borovinskaya experimentally observed rotating waves for combustion of hafnium and zirconium under the environment of gaseous nitrogen. These types of waves are more stable than the piston wave because the piston wave may result in extinction of the combustion. Evidently, for strongly nonlinear situations, multiple propagating fronts may exist. For identical parameter values and initial and boundary conditions, we have calculated piston, fingering, rotating, and erratic waves.

CONCLUSIONS

The dynamic behavior of a solution of highly nonlinear differential equations describing the combustion synthesis producing transition metal nitrides was investigated. Travelling waves with constant pattern profiles are observed for adiabatic and nonadiabatic combustion systems. For higher values of dimensionless heat of reaction γ and dimensionless activation energy β, the reaction front starts to oscillate and the velocity of the front depends on the time. Single as well as multiple oscillations for adiabatic and nonadiabatic systems are detected in the combustion synthesis process. The temperature can overshoot the adiabatic temperature and the solid reac-

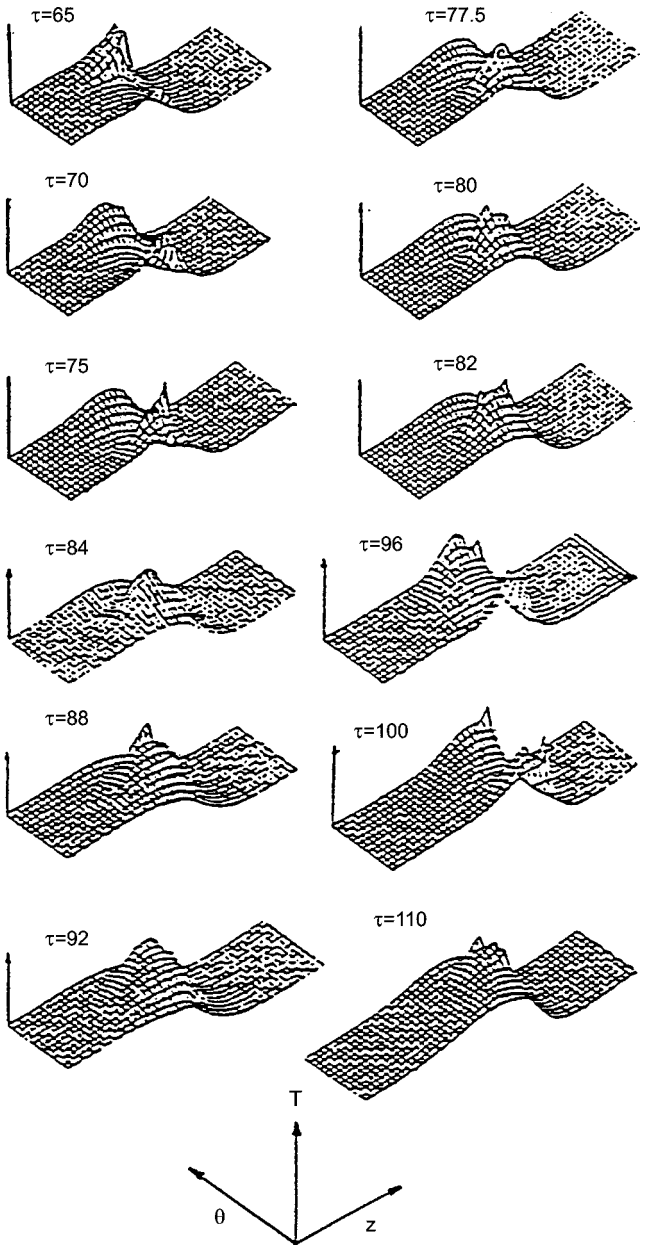

Fig. 7. Rotating waves in two-dimensional adiabatic system.
α= 0.0, β=0.03, γ=0.08, Θ_i=− 9.5, Θ_0=3.0, ε=0.5, δ=0.001

tants are completely converted. Extinction occurs for high values of dimensionless heat loss α (α>0.001) and solid reactants are not completely converted. For two-dimensional system, constant-pattern travelling waves, oscillating waves, fingering waves, and rotating waves are developed depending on the perturbation imposed on the system.

NOMENCLATURE

B_i : Biot number [hR/λ]
c_s : concentration of solid [kg m^{-3}]
C_s : dimensionless concentration of solid [c_s/c_{si}]
C_p : heat capacity [J kg^{-1}K^{-1}]
E : activation energy [J mol^{-1}]
h : heat transfer coefficient [J m^{-1}K^{-1}]
$(-\Delta H)$: heat of reaction [J kg^{-1}]
k_0 : reaction rate constant [s^{-1}]
r : radial length [m]
R : radius [m]
t : time [s]
t^* : scaling time $\left[\frac{\rho C_p RT_*^2 \exp(E/RT_*)}{Ek_0(-\Delta H)c_{si}}\right]$
T : temperature [K]
T_* : reference temperature [K]
z : axial length [m]
Z : dimensionless length $\left[z\sqrt{\frac{\rho C_p}{\lambda t^*}}\right]$

Greek Letters

α : dimensionless heat transfer coefficient $\left[\frac{2ht_*}{\rho C_p R}\right]$
β : dimensionless activation energy $\left[\frac{RT_*}{E}\right]$
γ : dimensionless heat of reaction $\left[\frac{\rho C_p RT_*^2}{c_{si}E(-\Delta H)}\right]$
ε : porosity of system
Δ : stability parameter
θ : angular coordinate [°]
Θ : dimensionless temperature $\left[\frac{E}{RT_*}\frac{T-T_*}{T_*}\right]$
λ : heat conductivity [J m^{-1} K^{-1}]
ξ : dimensionless radial length [r/R]
ρ : density [kg m^{-3}]
τ : dimensionless time [t/t^*]
Φ : dimensionless angular coordinate [$\theta/2\pi$]

Superscript

* : scaling factor

Subscripts

i : initial condition
o : boundary condition

REFERENCES

Agrafiotis, C. C., Puszynski, J. A. and Hlavacek, V., "Experimental Study on the Synthesis of Titanium and Tantalium Nitrides in the Self-Propagating Regime," *J. of Mat. Sci*., **22**, 710 (1987).

Aldushin, A. P. and Kasparyan, S. G., "Stability of Stationary Filtration Combstion Waves," *Fiz. Gor. Vzryva*, **17**, 37 (1981).

Dankekar, H. W., Puszynski, J. A. and Hlavacek, V., "Two-Dimensional Numerical Study of Cross-Flow Filtration Combustion," *AIChE J*., **36**, 1649 (1990).

Dankekar, H. W., Puszynski, J. A. and Hlavacek, V., "Dynamic Modeling and Simulation of Gas-Solid Reactions in Self-Propagating Regime," Ceramics Today-Tomorrow's Ceramics, Elsevier Science, 1207 (1991).

Dimitriou, P., Puszynski, J. A. and Hlavacek, V., "On the Dynamics of Equations Describing Gasless Combustion in Condensed Systems," *Combust. Sci. and Tech*., **68**, 101(1989).

Kim, S. H. and Hlavacek, V., "On the Dynamics of Parabolic Equation

Describing Diffusion, Convection, and Chemical Reaction," *Physica D*, **10**, 413 (1984).
Kim, S. H. and Park, H.-S., "Dissipative Structures of Autocatalytic Reactions in Tubular Flow Reactors," *Korean J. Chem. Eng*., **10**, 226 (1993).
Merzhanov, A. D. and Borovinskaya, I. P., "A New Class of Combustion Process," *Combust. Sci. and Tech.*, **10**, 195 (1975).
Munir, Z. A. and Holt, J. B., "The Combustion Synthesis of Refractory Nitrides," *J. of Mat. Sci*., **22**, 710 (1987).
Park, C.-H., M.S. Thesis, State University of New York at Buffalo (1983).
Shkadinskii, K. G., Khaikin, B. I. and Merzahanov, A. G., "Propagation of a Pulsating Exothermic Reaction Front in the Condensed Phase," *Combust. Explosives and Shock Waves*, **1**, 19 (1971).
Toth, L. E., "Transition Metal Carbides and Nitrides," Academic Press, New York (1971).