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A numerical study of the effect of heterogeneities in composition on micropyretic synthesis

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Abstract Micropyretic synthesis is a technique whereby a material is synthesized by the propagation of a combustion front across a powder. Composition variations in reactants and diluent are common during micropyretic synthesis when powders are mixed and the conventional modeling treatments thus far have only considered uniform systems. Composition variations are thought to result in the local variations of such thermophysical/chemical parameters for the reactant as density, heat capacity, and thermal conductivity; the result is changes in the combustion temperature, propagation velocity, and propagation pattern of a combustion front. This study investigates the impact of composition variations during micropyretic synthesis with Ni + Al. Correlations of variations in the reactants and diluent with the propagation velocity and combustion temperature are both studied by a numerical simulation.

Nomenclature

C_p	heat capacity of product (general form), kJ/kg/K
E	activation energy, kJ/kg
$\text{Hetero}_{\text{diluent}}$	heterogeneity in diluent, %
$\text{Hetero}_{\text{react}}$	heterogeneity in reactants, %
K_0	pre-exponential constant, (s^{-1} for zero order reaction)
Q	heat of reaction, kJ/kg
P	porosity, %
R	gas constant, kJ/kg/K
$R_{\text{yield},j}$	reaction yield at node j, %
T	temperature, K
T_0	initial temperature, K
$V_{i,j}$	volume fraction of component i at node j, %
V_i^0	original (homogeneous) volume fraction of component i, %
$X_{i,j}$	molar fraction of component i at node j, %
X_i^0	original (homogeneous) molar fraction of component i, %
z	dimensional coordinate, m
d	diameter of the specimen, m
$f_R(j)$	random number at node j
h	surface heat transfer coefficient, J/m^2/K/s
t	time, s
ρ	density, kg/m^3
κ	thermal conductivity (general form), kJ/m/K/s
η	fraction reacted

Introduction

Many exothermic non-catalytic solid–solid or solid–gas reactions, after being ignited locally, can release enough heat so as to sustain the self-propagating combustion front throughout the specimen without additional energy [1–5]. Since the 1970's, this kind of exothermic reaction has been used in the process of

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synthesizing refractory compounds in the former Soviet Union [6–8]. This novel technique, so-called micropyretic synthesis or combustion synthesis, has been intensively studied for process implication [9–12]. This technique employs exothermic reaction processing, which circumvents difficulties associated with conventional methods of time and energy-intensive sintering processing. The advantages of micropyretic synthesis also include the rapid net shape processing and clean products. In addition, the micropyretic-synthesized products have been reported to possess the better mechanical and physical properties [3].

Several numerical and analytical models of micropyretic synthesis in a composite system have been well developed [13–19]. Lakshmikantha and Sekhar firstly explored the numerical model that includes the effects of dilution and porosity, and melting of each constituent of the reactants and products [13, 14]. The analytical modeling of the propagation of the combustion front in solid–solid reaction systems is also reported [15]. The analytical model gives 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 the micropyretic synthesis [16]. These numerical and analytical analyses provide the better understanding of the reaction sequence during micropyretic synthesis reactions.

Composition variations (or heterogeneity) in reactants and diluent are common during micropyretic synthesis when powders are mixed, and this directly leads to the variations of the thermophysical/chemical parameters of the unreacted compacts. Since micropyretic synthesis is sustained by the sequences of the local chemical reactions, the propagation manner is strongly depending on the parameters of each portion of the reactants. Thus, the variation of thermophysical/chemical parameters of reactants caused by heterogeneities in composition is thought to significantly change the processing parameters, such as combustion temperature and propagation velocity; and further affect the product properties. In this study, a numerical simulation is used to characterize the effect of heterogeneities in composition on micropyretic synthesis with Ni + Al. Firstly, the effects of heterogeneities in reactants and diluent on the propagation velocity and combustion temperature are investigated. The influence of the variation of each individual reactant parameter caused by heterogeneities in composition on the propagation velocity is also carried out.

Numerical calculation procedure

During the passage of a combustion front in the reaction, the energy equation for transient heat conduction, including the source term, containing heat release due to the exothermic combustion reaction is given as [6, 13, 15]

$$\rho C_p \left(\frac{\partial T}{\partial t}\right) = \kappa \left(\frac{\partial T^2}{\partial^2 z}\right) - \frac{4h(T - T_0)}{d} + \rho Q\left(1 - X^0_{\text{diluent}}\right) K_0(1 - \eta)\exp\left(-\frac{E}{RT}\right) \quad (1)$$

Each symbol in the equation is explained in the nomenclature section.

In this study, a numerical calculation for Eq. 1 was carried out with the assumption of the first order kinetics. In the Eq. 1, the energy required for heating 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 combustion reaction, respectively.

The middle-difference approximation and an enthalpy-temperature method coupled with Guass–Seidel iteration procedure are used to solve the equations of the combustion synthesis problems. In the computational simulation, a one-dimensional sample of 1-cm long is divided into 1201 nodes (regions) to calculate the local temperature using an enthalpy-temperature method. The choice of 1-cm sample length is only for computational purpose, and the simulation results are applicable to practical experimental conditions. Firstly, the proper initial and boundary conditions are used to initialize the temperatures and enthalpies at all nodes. The initial conditions in the simulation are taken as follows: (1) At the ignition node, at time t (0, the temperature is taken to be the adiabatic combustion temperature, ($T = T_c$ and $\eta = 1$). It has been reported that the chosen temperature value at the ignition node would not influence the temperature profiles [13, 15]. (2) At the other nodes, at time $t = 0$, the temperatures are taken to be the same as the substrate temperature, ($T = T_0$ and $\eta = 0$). Depending on the values of the temperature and enthalpy occurred in the reaction, the proper thermophysical/chemical parameters are considered and the limits of the reaction zone are determined for each node in the numerical calculation. At any given time, the fraction reacted and enthalpy of the current iteration are calculated from the previous fraction reacted and enthalpy of the earlier iteration. The range of the enthalpy as well as the molar ratio among each material for each node is thus determined, and the values of temperature, density, and thermal conductivity at each node can be further calculated in appropriate zone.

Since concurrent heterogeneous distributions of reactants and diluent are common when powders are mixed, the effects of heterogeneities in the reactant and diluent are also both considered in this study. Composition at each node is calculated from the random number ($f_R(j)$ at node j) and the assigned heterogeneity (Hetero$_{\mathrm{react}}$ and Hetero$_{\mathrm{diluent}}$) that determines the magnitude of the variation. The sequence of the random numbers (–0.5 to +0.5) generated from the computation is repeatedly used in the specimens with different heterogeneities to compare the magnitude of heterogeneity effect. In this study, the heterogeneities in the reactant (Ni/Al) and diluent (NiAl) are respectively considered in the numerical calculation. The heterogeneities in compositions are calculated to be as

$$\text{NiAl diluent molar fraction at node } j: \quad X_{\mathrm{diluent},j} = X^0_{\mathrm{diluent}}(1 + \mathrm{Hetero}_{\mathrm{diluent}} \cdot f_R(j)) \tag{2a}$$

$$\text{Ni molar fraction at node } j: \quad X_{\mathrm{Ni},j} = \left(1 - X_{\mathrm{diluent},j}\right) \cdot X^0_{\mathrm{Ni}} \cdot (1 + \mathrm{Hetero}_{\mathrm{react}} \cdot f_R(j)) \tag{2b}$$

$$\text{Al molar fraction at node } j: \quad X_{\mathrm{Al},j} = 1 - X_{\mathrm{diluent},j} - X_{\mathrm{Ni},j} \tag{2c}$$

where j = 1,2,...,1201. In order to assure the sum of the compositions for all 1201 nodes equal to the stoichiometric values, the calculated Ni and Al composition of each node is adjusted so that the average value of each composition is equal to the original homogeneous value, i.e., $\frac{1}{n}\sum_{j=1}^{n=1201} X_{\mathrm{Ni},j} = X^0_{\mathrm{Ni}} = 50\,\mathrm{at.\%}$ $\frac{1}{n}\sum_{j=1}^{n=1201} X_{\mathrm{Al},j} = X^0_{\mathrm{Al}} = 50\,\mathrm{at.\%}$. In addition, the effects of porosity and the heterogeneities in reactants and product that influence the density (ρ) and thermal conductivity (κ) profiles are also considered in the numerical calculation. Once the molar fraction at each node is set to a given heterogeneity, the volume fraction ($V_{s,j}$) of reactant s can be correspondingly determined and the thermophysical/chemical parameters at node j can be thus calculated as

$$\text{Heat capacity at node } j: C_{p_j} = \sum_s (C_{p_s} \cdot X_{s,j}) \tag{3}$$

$$\text{Density at node } j: \quad \rho_j = \sum_s [\rho_s \cdot V_{s,j} \cdot (1 - P)] \tag{4}$$

$$\text{Thermal conductivity at node } j: \quad \kappa_j = \sum_s [\kappa_s \cdot V_{s,j} \cdot (1 - P)/(1 + P/2)] \tag{5}$$

where s denotes the component involved in the reaction, including Ni, Al, and diluent NiAl in this study; and P is the porosity of a specific material. The effect of melting of reactants and product is also included in the calculation procedure.

During the numerical calculation, the porosities of the reactants and product are both assumed to be 30%. The various thermophysical/chemical parameters, such as thermal conductivity, density and heat capacity of the reactants and product, 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. In addition, the higher pre-exponential factor (K_0) value, 8×10^8 1/s, is used to be capably of illustrating the variation of the propagation velocity for the NiAl micropyretic reaction. The parameter values used in the computational calculation are shown in Table 1 [20–22] and Table 2 [5, 20]. In this study, the combustion temperature is defined as the highest reaction temperature during combustion synthesis, and the propagation velocity is the velocity of the combustion front propagation.

Table 1 The thermophysical/chemical parameters for the reactants (Ni and Al) and product (NiAl) at 300 K and liquid state [20–22]

Thermophysical/chemical parameters	Al	Ni	NiAl
Heat capacity (at 300 K) (J/(kg K))	902 [20]	445 [20]	537 [20]
Heat capacity (liquid state) (J/(kg K))	1178 [20]	735 [20]	831 [20]
Thermal conductivity (at 300 K) (J/(ms K))	238 [22]	88.5 [22]	75 [21]
Thermal conductivity (liquid state) (J/(ms K))	100 [22]	53 [21]	55 [21]
Density (at 300 K) (kg/m^3)	2700 [22]	8900 [22]	6050 [21]
Density (liquid state) (kg/m^3)	2385 [22]	7905 [22]	5950 [22]

Table 2 The values of various parameters used in the numerical calculation [5, 20]

Parameters	NiAl
Combustion temperature (K)	1912
Activation energy (kJ/mole)	139 [20]
Exothermic heat (kJ/mole)	118.5 [5]
Pre-exponential factor (1/s)	8×10^8
Time step (s)	0.00025

Results and discussion

Effect of heterogeneity in reactants

Figure 1 shows the variations of the Ni composition and the correspondingly reaction yield along the Ni + 50 at.% Al composition with 20% maximum heterogeneity in reactants. For this composition, Ni and Al compositions are respectively set to vary within 10 at.% (= 50 at.% × 20%). On account of the variations of compositions with the distance, the reaction yields are correspondingly altered at all nodes. It is noted that as the Ni composition is deviated far from the stoichiometric value (50 at.%), the difference between Ni and Al compositions increases and the reaction yield for NiAl micropyretic reaction decreases, as shown in Fig. 1. A decrease in the reaction yield is expected to decrease the exothermic heat of the reaction, further reducing the reactivity of the micropyretic reaction [23].

In addition, the occurrence of heterogeneities in reactants also influences the thermophysical/chemical parameters of the reactants at each node, as expected. Since the thermophysical/chemical parameters (including thermal conductivity, heat capacity, and density) are respectively calculated from the ratio of the reactants at each node (Eqs. 3–5), the variations of these parameters are strongly correlated with the change of the compositions. Figure 2 shows the variations of density and thermal conductivity along the specimen. In the ideal homogeneous specimen (0% heterogeneity in reactants), thermal conductivity and density remain as constants at all nodes. As heterogeneities in reactants increase, density and thermal conductivity are noted to vary with the distance. Figure 2 also shows that the magnitudes of variations of density and thermal conductivity are increased as the heterogeneities in reactants are increased.

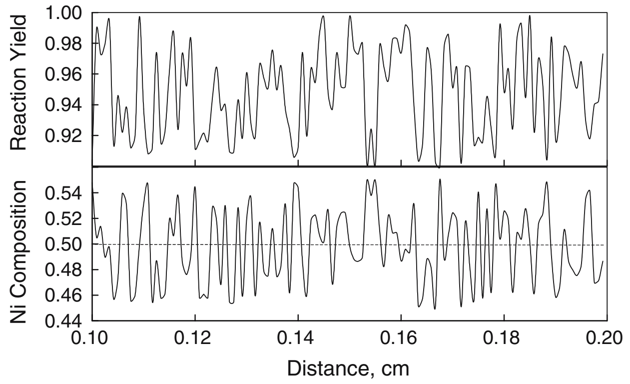

Fig. 1 The variations of the Ni composition and the correspondingly reaction yield with the distance for the NiAl compound with 20% maximum heterogeneity in reactants. No diluent is added in this composition

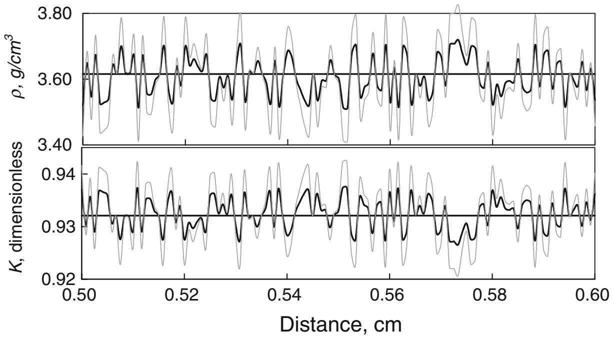

Fig. 2 The variations of density (ρ) and thermal conductivity (κ) along the NiAl reactants. The horizontal line denotes the values for the ideal homogeneous specimens. The black and gray curves denote the specimens with 10 and 20% heterogeneities in reactants, respectively

The variations of reaction yield, density, and thermal conductivity may further influence the reactivity of synthesis reaction at each node and thus change the propagation pattern and micropyretic corresponding parameters (i.e., combustion temperature and

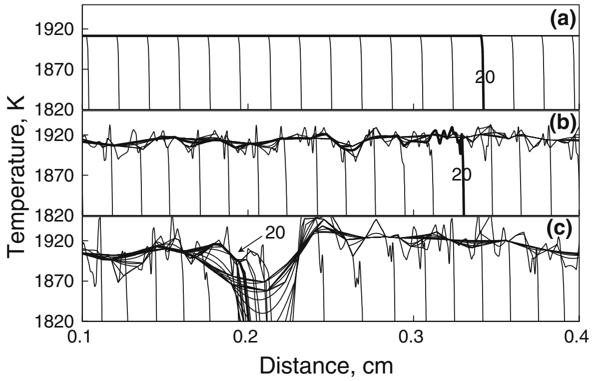

Fig. 3 Time variations of the combustion front temperature along the Ni + Al specimen. The interval time between two consecutive time steps (profiles) is 0.00025 s. The number 20 denotes the twentieth time step (0.005 s) after ignition. The heterogeneities in reactants for figures (**a**), (**b**), and (**c**) are 0, 10, and 20%, respectively

propagation velocity). Figure 3 shows the temperature profiles of combustion fronts at various times along the Ni + Al specimen for 0, 10 and 20% heterogeneities in reactants, respectively. The micropyretic reaction is ignited at the position 0 cm and the combustion front starts to propagate from left to right. It is noted from Fig. 3a that the combustion front propagates at steady state for the ideal homogeneous specimen (0% heterogeneity in reactants). The highest reaction temperature (i.e., combustion temperature) and the instantaneous propagation velocity of the homogeneous specimens are at a steady value during front propagation. When the non-homogeneous specimens are ignited, it is found that the temperature and the instantaneous propagation velocity are altered with the distance (Fig. 3b, c). The magnitude of temperature variation is also increased with the increase in the heterogeneity in reactants. The average propagation velocity is calculated to decrease from 73.4 cm/s (for the ideal homogeneous specimen) to 72.9 cm/s (for the specimen with 10% heterogeneity in reactants). When the heterogeneity in reactants is further increased to 20%, the average propagation velocity is noted to dramatically decrease in 9.13% (from 73.4 to 66.7 cm/s). The propagation front even stops half way for the composition with a further increase in the heterogeneity in reactants.

To carefully investigate the variation of the combustion temperature with the distance, the combustion temperatures of specimens with different reactant heterogeneities are calculated at each node and plotted in Fig. 4. As expected, the combustion temperature is changed periodically with the distance for the heterogeneous specimen. In addition, an increase in the heterogeneity in reactants increases the magnitude of the combustion temperature variation. Also shown in the figure is the variation of Ni content. It is noted that the combustion temperature does not strongly correlate with the variation of Ni content in time. However, as the variation of Ni content is accumulated to a certain level, the combustion temperature is found to alter periodically.

Effect of heterogeneity in diluent

To illustrate the effect of the heterogeneities in NiAl diluent on micropyretic reaction, the heterogeneities in reactants are temporarily neglected in this section, i.e., the heterogeneities in reactants are taken to be zero. With the heterogeneity in reactants is set to zero and the diluent amount is set to 20% of composition, the diluent composition will therefore vary within 4% as the 20% heterogeneity in NiAl diluent is taken. Such a small composition variation correspondingly results in a tiny variation of the thermophysical/chemical parameters. It is thus found from Fig. 5 that the magnitudes of the variations for thermal conductivity and density are dramatically decreased as compared with those in Fig. 1. A decrease in the variations of the reaction yield and the thermophysical/chemical parameters is correspondingly to reduce the effects of heterogeneity in diluent on lowering propagation velocity and combustion temperature.

Figure 6 shows the temperature profiles of combustion fronts at various times along the NiAl specimen with 20 at.% diluent for three different diluent heterogeneities, 0, 10, and 20%, respectively. Consistent with the fact that the heterogeneities in diluent only slightly affect density and thermal conductivity (Fig. 5), the combustion temperature is also only

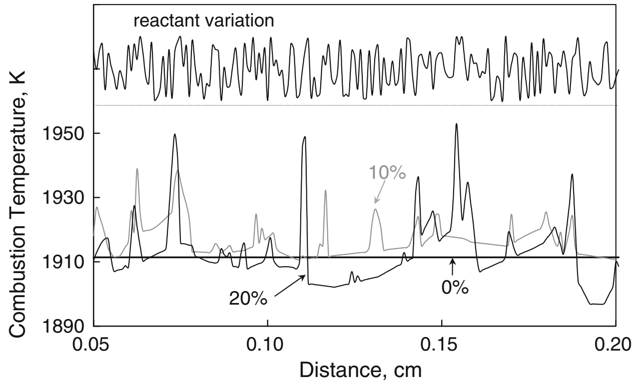

Fig. 4 The plots of the combustion temperatures at different positions for the specimens with 0, 10, and 20% heterogeneities in reactants, respectively. Also shown in the upper part of the figure is the variation of Ni composition

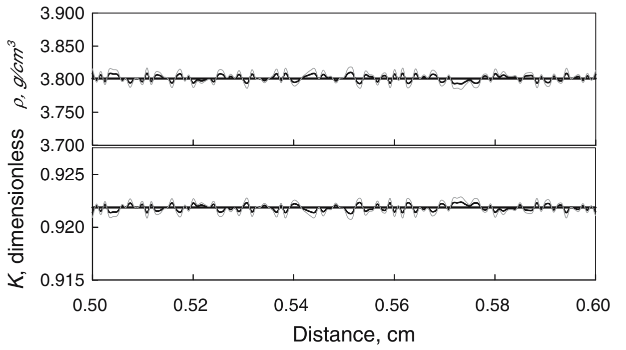

Fig. 5 The plots of density (ρ) and thermal conductivity (κ) along the NiAl reactants with 20 at.% diluent. The horizontal line denotes the values for the homogeneous specimens. The black and gray curves denote the specimens with 10 and 20% heterogeneities in diluent, respectively

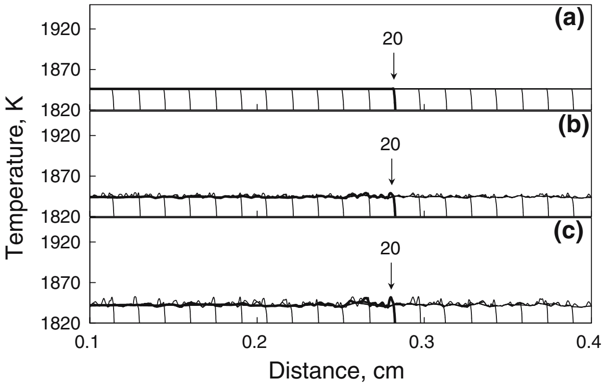

Fig. 6 Time variations of the combustion front temperature at various times along the NiAl specimen with 20 at.% diluent. The interval time between two consecutive time steps (profiles) is 0.00025 s. The number 20 denotes the twentieth time step (0.005 s) after ignition. The heterogeneities in diluent for figures (**a**), (**b**), and (**c**) are 0, 10, and 20%, respectively

slightly altered with the distance (Fig. 6). Figure 6 also shows that the propagation velocity is slightly dependent on the heterogeneity in diluent. The combustion fronts for the specimens with different diluent heterogeneities are noted to propagate at the same propagation velocity, even the heterogeneity in diluent has been enhanced to 20%.

The combustion temperatures for specimens with different diluent heterogeneities are also calculated at each node and are plotted with the distance in Fig. 7. It is noted from Fig. 7 that the combustion temperature is also changed periodically with the distance for the heterogeneous specimen, but the range of variation is significantly decreased as compared with those plots for the specimens with different reactant heterogeneities in Fig. 4. As expected, the magnitude of the combustion temperature variation is also increased with the increasing heterogeneity in diluent. It is also noted that the oscillatory (variation) frequency is decreased as the heterogeneity in diluent increases. In addition, Table 3 shows that average values of the combustion temperature are only slightly decreased as the heterogeneity in diluent is increased. These observations suggest that the heterogeneity in diluent has a smaller effect than the heterogeneity in reactants, on changing the propagation pattern.

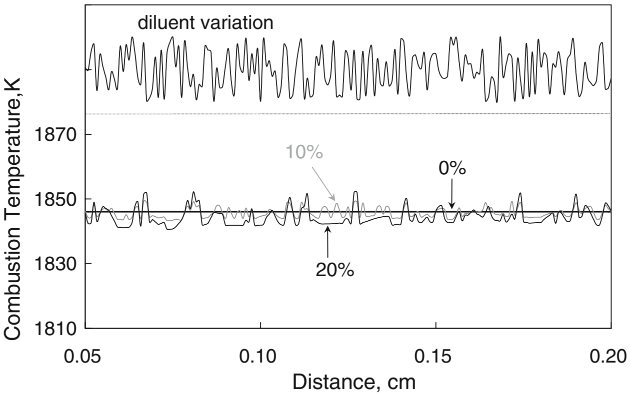

Fig. 7 The plots of the combustion temperatures at different positions for the specimens with 0, 10, and 20% heterogeneities in diluent (20 at.%), respectively. Also shown in the upper part of the figure is the variation of Ni composition

Table 3 The average combustion temperatures for the NiAl stoichiometric compositions with 20 at.% diluent for the different heterogeneities in diluent

Heterogeneity in diluent, %	Combustion temperature, K
0	1846.38 ± 0.09
5	1845.52 ± 0.10
10	1844.64 ± 0.11
15	1843.77 ± 0.12
20	1842.78 ± 0.11

The heterogeneous effect for each parameter

The discussion above shows that the heterogeneities in reactants and diluent first alter the compositions at each node, and then further change the reaction yield, density, thermal conductivity, and heat capacity. The temperature, propagation velocity, and propagation manner are thus correspondingly changed along the specimen. To illustrate the magnitude of the heterogeneous effects caused by each parameter on the propagation velocity, each parameter is also assumed as independent of composition heterogeneities to calculate propagation velocity. It is noted that as the exothermic heat of reaction is assumed as constant during the numerical calculation, the calculated propagation velocities are enhanced from 66.8 cm/s (normal 20% heterogeneity in reactants) to 70.9 cm/s (Table 4). The calculated results also show that the propagation velocities are respectively increased to 68.5 and 67.3 cm/s when the heat capacity and reactant density are taken as constant values. These calculated results show that the reduction in the exothermic heat and the variation of heat capacity caused by the heterogeneity in reactants are the major factors to reduce the propagation velocity.

Summary and conclusions

The effect of heterogeneities in composition on micropyretic synthesis is investigated by using numerical simulation. It is found that the heterogeneities in reactants and diluent directly change the reaction

Table 4 A change in the propagation velocity caused by the variation of individual parameter for the specimens with 20% heterogeneity in reactants

Conditions	Propagation velocity
Homogeneous reaction	73.4 ± 0.0 cm/s
Reaction with 20% heterogeneity in reactants	66.8 ± 3.4 cm/s
Reaction with 20% heterogeneity in reactants (except Q = constant)	70.9 ± 3.7 cm/s
Reaction with 20% heterogeneity in reactants (except ρ = constant)	67.3 ± 2.9 cm/s
Reaction with 20% heterogeneity in reactants (except K = constant)	66.7 ± 4.7 cm/s
Reaction with 20% heterogeneity in reactants (except C_p = constant)	68.5 ± 2.3 cm/s

In the numerical calculations of the heterogeneous specimens, the exothermic heat (Q), density (ρ), thermal conductivity (K), and heat capacity (C_p) are respectively taken as constant to calculate the propagation velocity

yield and the thermophysical/chemical parameters of reactants, such as thermal conductivity and density, at each node. The combustion temperature and the propagation velocity of the combustion front are thus altered, as a result. However, the combustion temperature does not directly correlate with the composition variation in time. As the composition variation is accumulated to a certain level, the combustion temperature is thus changed periodically.

The propagation velocity of the Ni–Al reaction without diluent is decreased from 73.4 to 70.9 cm/s and 66.7 cm/s as the heterogeneity in reactants is increased from 0 to 10% and 20%, respectively. As the diluent becomes heterogeneous but the heterogeneity in reactants is neglected in the numerical calculation, the variations of density and thermal conductivity are less than those caused by heterogeneity in reactants. Thus, the magnitudes of the variations of propagation velocity and combustion temperature for the compositions with heterogeneity in diluent are correspondingly decreased. The generated results also show that the reduction of the exothermic heat and the changes in the heat capacity caused by the heterogeneities in composition are the key factor to reduce the propagation velocity of the combustion front during Ni + Al heterogeneous micropyretic reaction.

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