Influence of the composition heterogeneity on micropyretic synthesis of TiB_2 compound

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Nomenclature

C_p	heat capacity of product (general form) (kJ/kg/K)
E	activation energy (kJ/kg)
H_R	reactant heterogeneity (%)
K_o	pre-exponential constant (s^{-1} for zero order reaction)
Q	heat of reaction (kJ/kg)
P	porosity (%)
R	gas constant (kJ/kg/K)
R_{yield_j}	reaction yield at node j (%)
T	temperature (K)
T_o	initial temperature (K)
$X_{i,j}$	molar fraction of component (species) i at node j (%)
X_i^o	original (homogeneous) molar fraction of component (species) i (%)
z	dimensional coordinate (m)
d	diameter of the specimen (m)
$f_R(j)$	generated 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
$\Phi(T, \eta)$	reaction rate (1/s)

Heterogeneous distributions of reactants are common when powders are mixed during micropyretic synthesis and the conventional modeling treatments thus far have only considered uniform systems. This composition heterogeneity directly influences the thermophysical/chemical parameters of reactants, such as thermal conductivity, heat capacity, and density. The variations of these parameters caused by composition heterogeneity are thought to significantly change both the reaction temperature and propagation velocity for micropyretic synthesis, and thus affect the product quality. Therefore, it is important to understand the influence of the composition heterogeneity on the micropyretic-synthesized products. In this study, numerical simulation is used to characterize the composition heterogeneity effect for micropyretic synthesis of TiB_2 compound.

During micropyretic synthesis, the energy equation for transient heat conduction, including the source term, containing the heat release due to the exothermic combustion reaction is used to simulate the propagation of the combustion front [1, 2]. This exothermic energy propagates the combustion front across the specimen to carry out material processing. This process can be described by the energy equation expressed as [3–5]:

$$\rho C_p\left(\frac{\partial T}{\partial t}\right) = \kappa\left(\frac{\partial T^2}{\partial^2 z}\right) - \frac{4h(T - T_o)}{d} + \rho Q\Phi(T, \eta) \quad (1)$$

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

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

For the numerical calculation, a one-dimensional sample of 1 cm long was divided into 1201 nodes (regions) to calculate the local temperature using an enthalpy-temperature method coupled with the Guass Sidel iteration procedure [3, 4].

Composition at each node was calculated from the random number ($f_R(j)$ at node j) and the assigned heterogeneity (H_R) that determines the magnitude of the variation. The sequence of the random numbers (-0.5–$+0.5$) generated from the computation was repeatedly used in the specimens with different composition heterogeneities to compare the magnitude of heterogeneity effect. For the TiB_2 stoichiometric composition, titanium (Ti) composition was first determined from a given Ti composition heterogeneity and boron (B) composition was further calculated. The compositions of reactants before the beginning of the reaction can be expressed as follows:

$$\text{Ti molar fraction at node } j\text{: } X_{Ti,j} = X_{Ti}^o(1 + H_R \cdot f_R(j)) \quad (3a)$$

$$\text{B molar fraction at node } j\text{: } X_{B,j} = 1 - X_{Ti,j} \quad (3b)$$

where $-0.5 \le f_R(j) \le +0.5$ and $j = 1, 2, \ldots, 1201$. Titanium composition heterogeneity (H_R) was taken from 0 to 18% in this study. In order to assure the sum of the compositions for all 1201 nodes equal to the stoichiometric values, the calculated Ti and B compositions of each node were adjusted so that the average values of each composition are equal to the ideal homogeneous values (Ti:B = 1:2, i.e., $\frac{1}{n}\sum_{j=1}^{n=1201} X_{Ti,j} = X_{Ti}^o = 33.33$ at.% and $\frac{1}{n}\sum_{j=1}^{n=1201} X_{B,j} = X_B^o = 66.67$ at.%). Table I shows the studied compositions with the different Ti composition heterogeneities. After the molar fractions of reactants were calculated, the reaction

TABLE I Ranges of variations for Ti + 2 B composition which corresponds to TiB_2 stoichiometric composition with the different titanium (Ti) composition heterogeneities

Titanium composition heterogeneity (%)	Range of variation of 33.3 at.% Ti composition (at.%)	Ti composition (at.%)	B composition (at.%)
0	0.00	33.33	66.67
2	0.67	33.00–33.67	67.00–66.33
4	1.33	32.67–34.00	67.33–66.00
6	2.00	32.33–34.33	67.67–65.67
8	2.67	32.00–34.67	68.00–65.33
10	3.33	31.67–35.00	68.33–65.00
12	4.00	31.33–35.33	68.67–64.67
14	4.67	31.00–35.67	69.00–64.33
16	5.33	30.67–36.00	69.33–64.00
18	6.00	30.33–36.33	69.67–63.67

TABLE II The thermophysical/chemical parameters for the reactants and product at 300 K and liquid state [6].

Thermophysical/chemical parameters	Ti	B	TiB_2
Heat capacity (300 K) (J/(kgK))	528	118	950
Heat capacity (liquid) (J/(kgK))	700	2800	2055
Thermal conductivity (300 K) (J/(msK))	21.6	27	25
Thermal conductivity (liquid) (J/(msK))	11	15	13
Density (300 K) (kg/m^3)	4500	2450	4400
Density (liquid) (kg/m^3)	4110	2080	4100

TABLE III The values of various parameters used in the numerical calculation [7, 8].

Parameters	TiB_2
Combustion temperature (K)	3190
Activation energy (kJ/mole)	318 [7]
Exothermic heat (kJ/mole)	4214 [8]
Pre-exponential factor (1/s)	4×10^{10}
Time step (s)	0.0005

yield at each node was further determined by:

$$R_{\text{yield,j}} = \min\left\{\frac{X_{\text{Ti,j}}}{X^{\text{o}}_{\text{Ti}}}, \frac{X_{\text{B,j}}}{X^{\text{o}}_{\text{B}}}\right\} \quad (5)$$

The porosity and composition heterogeneity effects of the reactants and product that influence the density (ρ) and thermal conductivity (κ) profiles were also considered in the numerical calculation. The thermophysical/chemical parameter values used in the computational calculation are shown in the Table II [6] and Table III [7, 8]. In this study, the combustion temperature is defined as the highest reaction temperature during micropyretic synthesis, and the propagation velocity is the velocity of the combustion front propagation.

Fig. 1 shows the distributions of the Ti and B compositions and the corresponding variations of thermal conductivity, density, and reaction yield for Ti + 66.7 at.% B compositions with different Ti maximum composition heterogeneities. The percentages of the variations are used in Fig. 1 in order to clearly compare the differences in the variations of the reactant parameters. The horizontal dash line in Fig. 1 gives the values for the ideal homogeneous specimen (0% composition heterogeneity). The black curve and the gray curve denote 8 and 18% maximum Ti composition heterogeneities, respectively. For the compositions with 8 and 18% Ti composition heterogeneities, Ti compositions are set to respectively vary within 8 and 18% whereas B compositions are correspondingly calculated to vary within 4 and 9%. However, it is found that the variation of the thermophysical/chemical parameters, including thermal conductivity and density, do not change in the same scale with the variation of Ti or B composition at each node. The variations of thermal conductivity and density are noted to only vary within 0.4 and 2.0%, for 8% maximum Ti composition heterogeneity. The magnitudes of variations of the density and the thermal conductivity are increased to 0.9 and 4.2% as the Ti composition heterogeneity is further increased to 18%. Due to the incomplete reaction caused by the composition heterogeneity, the reaction yields are decreased as compared with the ideal homogeneous specimen, as shown in Fig. 1e. A decrease in the reaction yield is expected to decrease the exothermic heat of the reaction, thus reducing the reactivity of micropyretic reaction.

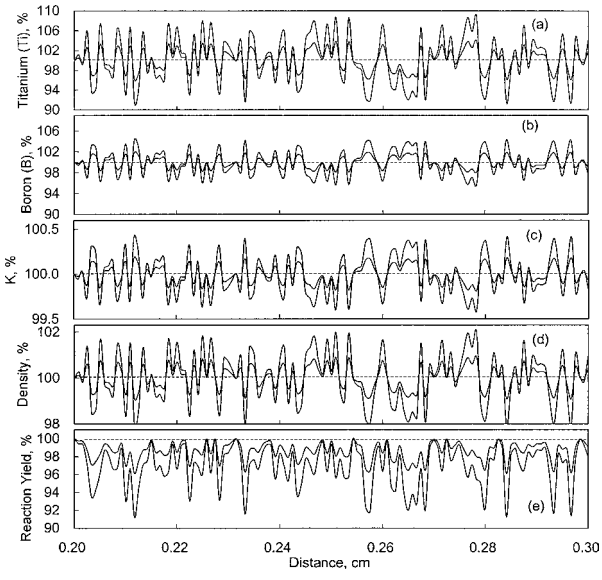

Figure 1 The variations of (a) titanium (Ti) composition, (b) boron (B) composition, (c) thermal conductivity (κ), (d) density, and (e) reaction yield with the distance for the Ti + 2 B system with different Ti composition heterogeneities. The horizontal dash line, black curve, and gray curve denote 0, 8, and 18% maximum Ti composition heterogeneities, respectively. In the ideal homogeneous specimen (0% Ti composition heterogeneity), Ti composition, B composition, density, and reaction yield are 33.33 at.%, 66.67 at.%, 2.343 gm/cm^3, and 100%, respectively.

The variations of thermophysical/chemical parameters and reaction yield along the specimen further change the propagation pattern, combustion temperature, and propagation velocity. Fig. 2 shows the temperature profiles of combustion fronts at various times along the TiB_2 specimen for the 0, 8 and 18% maximum Ti composition heterogeneities, respectively. The micropyretic reaction is ignited at the position 0 cm and the combustion front starts to propagate from left to right. Since the activation energy for Ti + 2 B micropyretic reaction is relatively higher than other micropyretic reactions, the combustion front of TiB_2 system has been found to propagate in a rather unstable manner [9]. In such an unstable propagation, the temperature and propagation velocity of the combustion front are periodically changed with the distance; as seen in

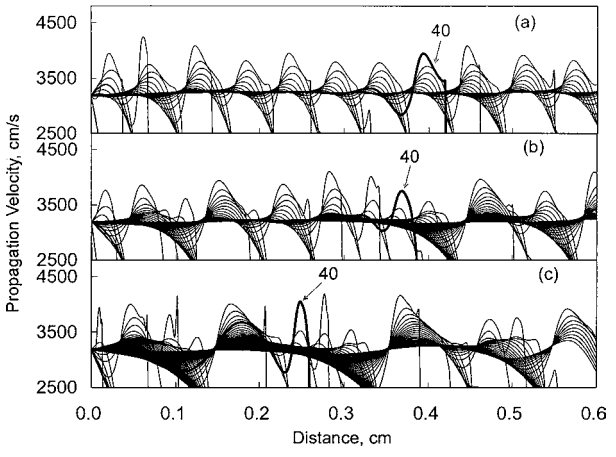

Figure 2 Time variation of the combustion front temperature for the Ti + 2 B system described above. The interval time between two consecutive time steps (profiles) is 0.0005 s. The Ti maximum composition heterogeneities in (a), (b), and (c) are 0, 8 and 18%, respectively. The number 40 shown in the figure denotes the fortieth time step that is equivalent to 0.02 s after ignition.

Fig. 2 the TiB_2 combustion front oscillates periodically in a succession of rapid and slow changes.

Fig. 2 also shows that an increase in the Ti composition heterogeneity decreases the average values of the combustion temperature and propagation velocity. It is found from Fig. 2 that the combustion front takes 0.02 s (40 time steps) to propagate ∼0.4 cm for the ideal homogeneous specimen. For the specimen with 18% Ti composition heterogeneity, the propagation velocity is dramatically decreased and the combustion front is noted to only propagate ∼0.25 cm in the same time interval. Fig. 3 shows the average propagation velocity is initially slightly increased and then is decreased with the Ti composition heterogeneity. There is almost a plateau in the curve between 8 and 15%, which is followed by a rapid fall in velocity with Ti composition heterogeneity.

The range of temperature variation is also found to increase with the Ti composition heterogeneity during TiB_2 oscillatory propagation. Fig. 2 also shows that the variation of the temperature is within ∼1340 K (from 2740 to 4080 K) for the specimen with 0% Ti composition heterogeneity. The ranges of temperature oscillatory are further increased to ∼1500 and ∼1750 K, respectively, as the Ti composition heterogeneities are

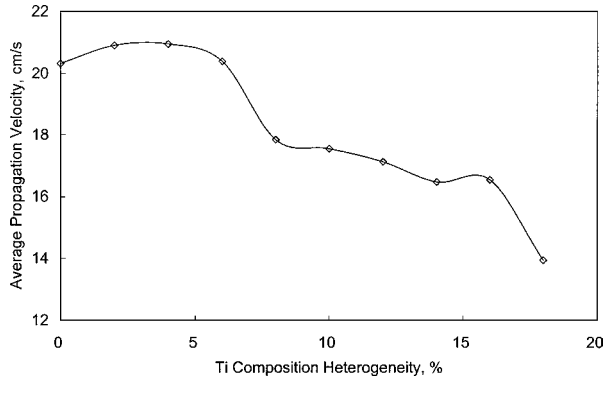

Figure 3 The average propagation velocity for the TiB_2 micropyretic reaction as a function of Ti composition heterogeneity.

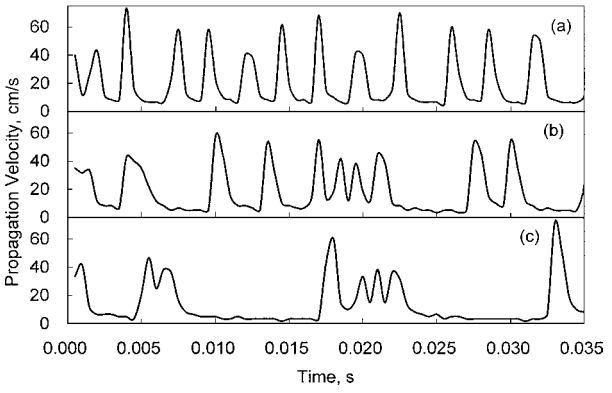

Figure 4 Time variation of the instant propagation velocity of the TiB_2 specimens. The Ti maximum composition heterogeneities in (a), (b) and (c) are 0, 8 and 18%, respectively.

enhanced to 8 and 18%. In addition, the oscillatory frequency of combustion front is also changed with the composition heterogeneity. It is noted from Fig. 2a that the combustion front oscillates at a constant of 400 s^{-1} between 0.15 and 0.45 cm for the ideal homogeneous specimen (0% composition heterogeneity). On the other hand, when the heterogeneous specimens are ignited, the combustion front oscillates irregularly and oscillatory frequency decreases with the increasing Ti composition heterogeneity.

Fig. 4 shows the variations of the instantaneous propagation velocity with reaction time; the oscillatory frequency is decreased as the Ti composition heterogeneity is increased. A similar phenomenon was also found as the TiB_2 diluent was added in the micropyretic synthesis of TiB_2 compound [9]. It has been reported that a greater diluent content reduces the average propagation velocity and oscillatory frequency, and increases the oscillatory amplitude [9]. The composition heterogeneity is noted to have a similar effect.

This study investigates the Ti composition heterogeneity effect on micropyretic synthesis using a numerical simulation. It has been shown that composition heterogeneity influences the reaction yield and the thermophysical/chemical parameters, such as thermal conductivity, heat capacity and density. Furthermore it also changes the combustion temperature and propagation velocity of the combustion front. An increase in the composition heterogeneity decreases the average values of combustion temperature and propagation velocity, but also decreases the oscillatory frequency and increases the oscillatory amplitude of the unstable TiB_2 combustion front. Such an oscillatory phenomenon has also been reported when the diluent is added in the micropyretic synthesis of TiB_2 compound. These observations suggest that the effects caused by the composition heterogeneity are similar those resulting from the addition of TiB_2 diluent during micropyretic synthesis.

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References

1. H. P. LI, *Acta Metall.* **51** (2003) 3213.
2. H. P. LI, *Mater. Chem Phys.* **80** (2003) 758.
3. M. G. LAKSHMIKANTHA, A. BHATTACHARYS and J. A. SEKHAR, *Metall. Trans.* A **23A** (1992) 23.
4. M. G. LAKSHMIKANTHA and J. A. SEKHAR, *J. Amer. Ceram. Soc.* **77**(1) (1994) 202.
5. A. G. MERZHANOV and B. I. KHAIKIN, *Prog. Energy Combust. Sci.* **14** (1988) 1.
6. E. A. BRANDES and G. B. BROOK, "Smithells Metals Reference Book" (Butterworth-Heinemann Ltd., 1992).
7. T. S. AZATYAN, V. M. MAL'TSEV, A. G. MERZHANOV and V. A. SELEZNEV, *Fiz. Goreniya Vzryva* **16**(2) (1980) 37.
8. G. V. SAMSONOV and I. M. VINITSKII, "Handbook of Refractory Compounds" (IFI/Plenum, New York, NY, 1980) p. 128.
9. H. P. LI, *J. Mater. Res.* **17**(12) (2002) 3212.
10. G. K. DEY, A. ARYA and J. A. SEKHAR, *J. Mater. Res.* **15**(1) (2000) 63.

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