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The energy required to ignite micropyretic synthesis. Part II: unstable Ti + 2B reaction

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Abstract In the previous study, the influences of micropyretic parameters on the ignition energy for lower exothermic heat and lower activation energy of stable Ni–Al reaction have been studied. In this study, we studied the effect of ignition energy on the unstable Ti + 2B micropyretic reaction, which has higher exothermic heat and higher activation energy. Three-dimensional maps are generated to illustrate the influences of micropyretic synthesis parameters on the required ignition energy. In addition, the comparisons in the ignition energy for the micropyretic reactions with Ni + Al and Ti + 2B are studied. The numerical calculation indicates that the changes in the ignition energy caused by the thermal conductivity for the micropyretic reaction with Ti + 2B is smaller as compared with for the micropyretic reaction with Ni + Al. However, the required ignition power is found to significantly change with the thermal conductivity for the NiAl micropyretic reaction when a higher pre-exponential factor is taken in the calculation. In addition, the difference in the required ignition energy caused by the thermal conductivity is noted to be larger for the Ni–Al micropyretic reaction with a lower pre-exponential factor.

Introduction

The previous study [1] indicated that the parameters of micropyretic synthesis reaction with Ni + Al influence the thermal profiles at ignition spot and the ignition energy. These micropyretic synthesis parameters include activation energy (E), exothermic heat (Q), pre-exponential factor (K_o), thermal conductivity (K), heat capacity (C_p), and thermal activity of the reactants and product. The calculated results in the previous study [1] have shown that the activation energy has a pronounced effect on the ignition energy for the Ni + Al micropyretic reaction. It was found that the reaction with lower activation energy is quickly ignited at the beginning of Al melting, further decreasing the ignition time and energy. The changes in the exothermic heat were noted to slightly affect the heat loss and zone length after the micropyretic reaction starts. In addition, a decrease in the pre-exponential factor (K_o) has been reported to increase the thermal conductivity. It was thus found that the rate of heat loss at the ignition spot is increased with the decrease in the pre-exponential factor. The thermal conductivity and heat capacity were also found to affect the heat loss at the ignition spot and length of pre-heating zone. A change in the thermal conductivity alters the absolute values of heat loss and zone length (vertical direction in the parameter profile), but the ignition time is only slightly dependent on changing the thermal conductivity. On the other hand, a variation in the heat capacity changes the reaction time (horizontal direction in the parameter profile), but the absolute values of heat loss and zone length are almost identical. When the changes in the thermal conductivity and the heat capacity were concurrently considered in the calculation, it was found that decreasing both parameters reduces the heat loss only after the micropyretic reaction starts. The required ignition time and energy were found to slightly decrease with the decrease in the thermal activity.

The previous study [1] also indicated that an increase in the ignition power increases the required ignition energy for the Ni + Al micropyretic reaction [1]. The changes in

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Table 1 The values of various parameters used in the numerical calculation for Ni + Al and Ti + 2B micropyretic reactions [2–6]

Parameters	NiAl	TiB_2
Activation energy (kJ/mole)	139 [5]	318 [6]
Exothermic heat (kJ/mole)	118.5 [2]	4,214 [3]
Heat capacity (300 K) (J/kg K)	537 [2]	950 [4]
Thermal conductivity (300 K) (J/ms K)	75 [4]	25 [4]
Pre-exponential factor (1/s)	4×10^8	1×10^{10}

the ignition energy caused by each micropyretic parameter were also respectively investigated [1]. It was found that an additional 40% increase in the activation energy increases the ignition energy by 44–50%. In addition to the activation energy, heat capacity also has a pronounced effect on the ignition energy for the micropyretic reaction with Ni + Al when a lower ignition power is used. The calculated results also illustrated that the percentage of change in ignition energy for the reaction with thermal activity is approximately equal to the summation of those for the reaction with thermal conductivity and heat capacity [1].

As compared with Ni + Al micropyretic reaction, Ti + 2B micropyretic reaction possesses higher activation energy, higher ratio of exothermic heat to heat capacity, and lower thermal conductivity, as shown in Table 1 [2–6]. In addition, the Ti + 2B micropyretic reaction was reported to propagate in an unstable manner due to higher activation energy. In an unstable combustion, the combustion temperature and propagation velocity are not uniform with time [7] and the combustion front propagates in an oscillatory or spin manners [8–14]. In addition, the manner of combustion front propagation is strongly dependent on the process of heat dispersion (by heat transfer and heat loss) and heat generation (by chemical reaction) [8]. Any change in the processing conditions may give rise to a variation in the velocity and temperature of the combustion propagation front and further influence the instability of the combustion front. In this study, the influences of the micropyretic parameters on the required energy and the propagation manner for the micropyretic reaction with Ti + 2B are investigated. Three-dimensional maps are also generated to illustrate the combined influences of micropyretic synthesis parameters on the required ignition energy. In addition, the comparisons in the ignition energy for the micropyretic reactions with Ni + Al and Ti + 2B are also carried out.

Numerical calculation procedure

The detailed numerical calculation procedure has been introduced in the previous study [1]. In the numerical calculation of the micropyretic reaction with Ti + 2B, the pre-exponential factor (K_o), 1×10^{10}, is obtained by matching the experimental and numerical values. The energy is gradually added at the ignition spot in very small timesteps (0.02 ms) until the micropyretic reaction starts. The porosity is kept at 30% in the numerical calculation. The values of the parameters used in the computational calculation are shown in Tables 1 and 2 [2–6]. In this study, the propagation velocity is the velocity of a propagating combustion front and the pre-heating zone is calculated from the end of reaction nodes (zones) until the position where the temperature is decreased to the original substrate temperature.

Table 2 The thermophysical/chemical parameters for the reactants and product at solid state (300 K) and liquid state [4]

Thermophysical/chemical parameters	Ti	B	TiB_2
Heat capacity (300 K) (J/kg K)	528	118	950
Heat capacity (liquid) (J/kg K)	700	2,800	2,055
Thermal conductivity (300 K) (J/ms K)	21.6	27	25
Thermal conductivity (liquid) (J/ms K)	11	15	13
Density (300 K) (kg/m^3)	4,500	2,450	4,400
Density (liquid) (kg/m^3)	4,110	2,080	4,100

Results and discussion

Figure 1 shows the temperature profiles of combustion fronts at various times along the Ti + 2B specimen. The

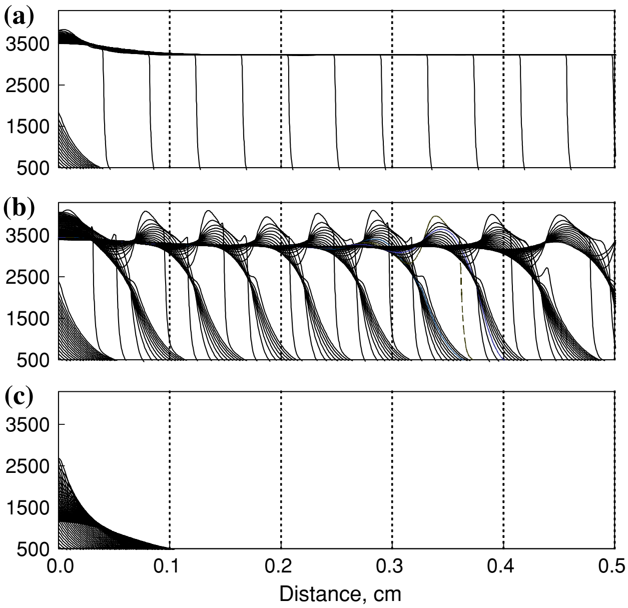

Fig. 1 Time variations of the combustion front temperature along the TiB_2 specimen with the pre-exponential factor of 1×10^{10} s^{-1}. The interval time between two consecutive time steps (profiles) is 1.0 ms. The ignition power is taken as 175 J/(ms g) in the numerical calculation. The activation energy in (**a**), (**b**), and (**c**) are 254.4 KJ/mole (80% *E*), 318.0 KJ/mole (reported experimental value *E*) [6], and 381.6 KJ/mole (120% *E*), respectively

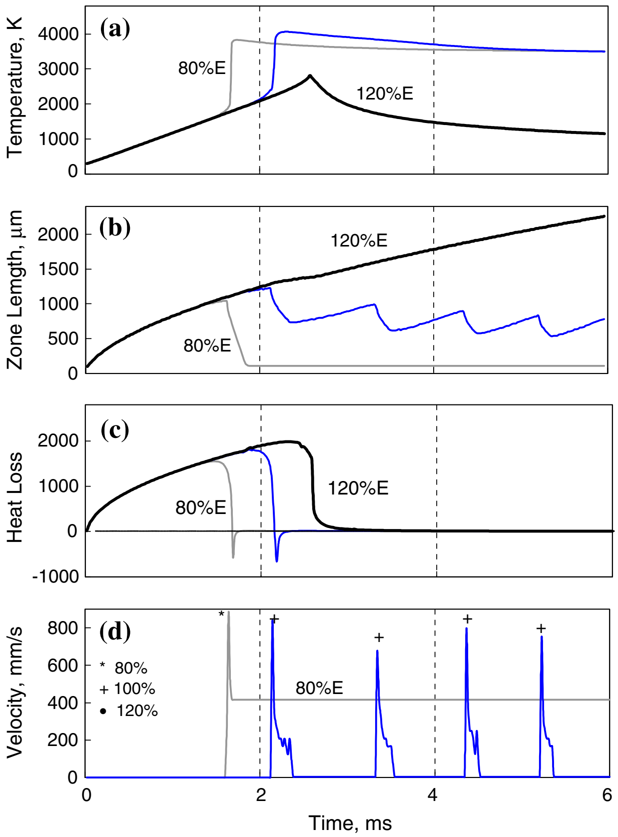

Fig. 2 The plots of (**a**) temperature, (**b**) length of pre-heating zone, (**c**) heat loss with the reaction time, and (**d**) propagation velocity. The central line in each figure denotes the Ti + 2B micropyretic reaction with the experimental value of activation energy 318.0 KJ/mole [6]. The other lines denote the reactions with the 120% (bold line) and 80% reported values of activation energy, respectively

micropyretic reactions are ignited by ignition power (per gram) of 175 J/(ms g) at the position 0 cm and the heating sources are removed immediately after the combustion front has been ignited. The interval time between two consecutive time steps (profiles) in Fig. 1 is 1 ms. It is found from Fig. 1b that the combustion front takes 21.04 ms to start propagating for the TiB_2 micropyretic reaction with the reported experimental activation energy (318 KJ/mole) [6]. This ignition time interval corresponds to the ignition energy of 3682.0 J/g. Figure 1b also displays an alternating increase and decrease in the temperature and propagation velocity during the combustion front propagation, indicating that the combustion front for Ti + 2B micropyretic reaction propagates in an unstable oscillatory manner. When 80% of reported experimental activation energy value is taken in the numerical calculation, the propagation manner is noted to change from unstable manner to stable manner; in addition, the ignition time is reduced from 21.04 to 16.38 ms, which corresponds to the ignition energy of 2866.5 J/g (Fig. 1a). When 120% of reported experimental activation energy is taken in the calculation, the ignition time is increased to 25.66 ms (corresponding to the ignition energy of 4490.5 J/g) and the combustion front extinguishes immediately after the start of propagation. (Fig. 1c).

Figure 1 indicates that the variations in activation energy of TiB_2 micropyretic reaction change the ignition time and correspondingly affect the energy required to ignite the micropyretic reaction. In addition, the propagation manner has been altered. The previous study [1] has shown that the micropyretic synthesis parameters influence the ignition time and energy for the stable micropyretic reaction with Ni + Al. To compare the influences of micropyretic parameters on the ignition energy between the stable and unstable micropyretic reactions, the effects of the micropyretic parameters on the ignition time and energy for the unstable micropyretic reaction with Ti + 2B are, respectively, investigated in this study.

Activation energy

The temperature profiles at the ignition point during the heating stage for the different values of activation energy are shown in Fig. 2a. All the heating rates at the ignition spot are calculated to be 1,100 K/ms when the ignition power of 175 J/(ms g) is used in the calculation. The calculated results indicate that the micropyretic reaction with smaller activation energy (80% *E*, i.e., 80% of the reported experimental value) is firstly ignited and the temperature is then sharply increased at 24,000 K/ms. After the micropyretic reaction has been ignited, the addition of external energy is stopped at the ignition spot. The length of pre-heating zone and the heat loss at the ignition spot both start to decrease. Figure 2b illustrates that the length of pre-heating zone for the TiB_2 micropyretic reaction with 80% *E* is gradually decreased to a constant value, whereas that for the TiB_2 micropyretic reaction with reported experimental activation energy (100% *E*) oscillates with the propagation. With a further increase in the activation energy to 120% *E*, Fig. 2b shows that the zone length is continuously increased. This is because the stop of the combustion front and the heat in the reaction zone is continuously transferred to the pre-heating zone. Thus, the length of pre-heating zone is increasing until the heat in the reaction zone stops transferring.

Since the heat loss is proportional to the ignition time and the ignition time is found to increase with the increase in the activation energy, the heat loss is noted to increase with the activation energy, as shown in Fig. 2c. As similar with the profiles of zone length, Fig. 2d shows that the propagation velocity for TiB_2 micropyretic reaction with 80% *E* is kept at a constant value whereas that for reaction with 100% *E* oscillates with the reaction time, indicating combustion fronts propagating in the stable and unstable oscillatory manner respectively. With a further increase in the activation energy to 120% *E*, the propagation front is extinguished and no propagation velocity is recorded in Fig. 2d.

Exothermic heat

The exothermic heat of the micropyretic reaction is released after the reaction has been ignited, thus, the exothermic heat is not expected to influence the thermal profiles at the ignition spot before the micropyretic reaction is ignited. Figure 3 shows that the temperature, zone length, and heat loss distributions are identical before the reactions are ignited. After the micropyretic reaction is ignited, the combustion front for the reaction with experimental exothermic heat is found to propagate in an unstable manner. An increase in the experimental exothermic heat (120% *Q*) offers sufficient thermal energy to propagate the combustion front in a stable manner (Fig. 3d). On the other hand, a decrease in the experimental exothermic heat (80% *Q*) causes the combustion front to stop (Fig. 3d). Due to the variations in the propagation manner, the distributions of the length of pre-heating zone, heat loss, and the variations in the propagation velocity are correspondingly changed.

Pre-exponential factor

It has been reported that the reaction with a smaller pre-exponential factor is equivalent to increasing the particle size [4], further increasing the thermal conductivity and the heat loss. Since Table 1 shows the thermal conductivity for the micropyretic reaction with Ti + 2B is less than that for Ni + Al micropyretic synthesis, the increase in the thermal conductivity caused by the pre-exponential factor is expected to only slightly influence the thermal profiles, as compared with NiAl micropyretic synthesis. Thus, it is noted from Fig. 4b and c that the length of pre-heating zone and the heat loss at the ignition spot are slightly increased with the decrease in the pre-exponential factor. In addition,

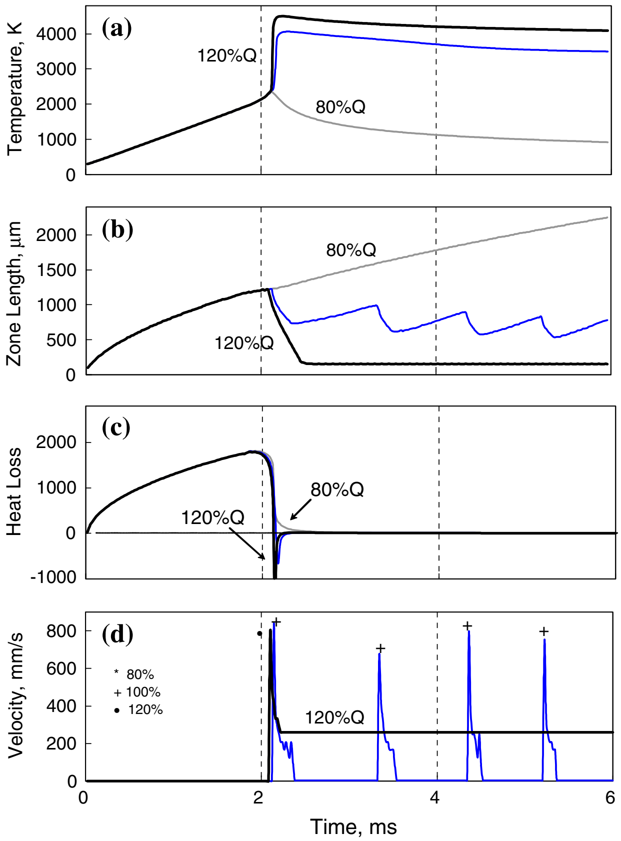

Fig. 3 The plots of (**a**) temperature, (**b**) length of pre-heating zone, (**c**) heat loss with the reaction time, and (**d**) propagation velocity. The central line in each figure denotes the Ti + 2B micropyretic reaction with the experimental value of exothermic heat 4,214 KJ/mole [3]. The other lines denote the reactions with the 120% (bold line) and 80% reported values of exothermic heat, respectively

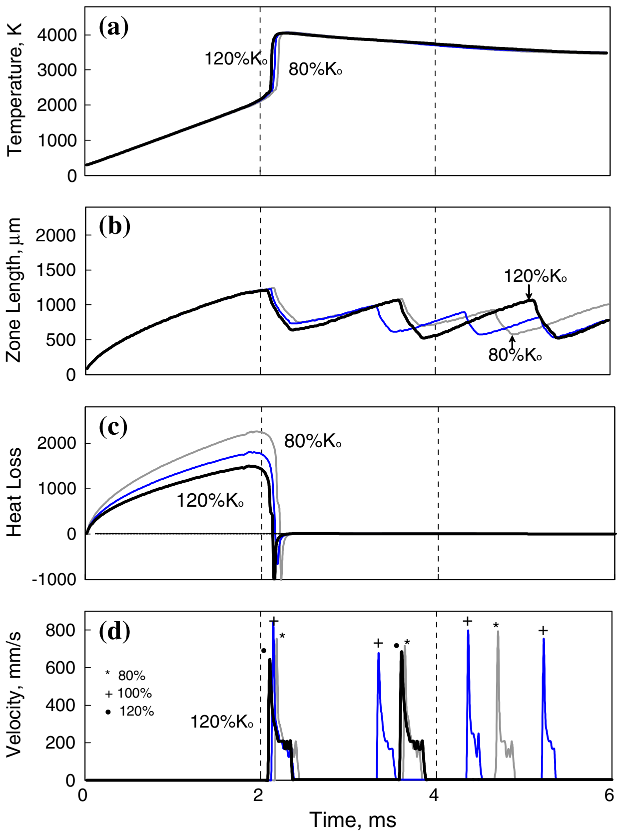

Fig. 4 The plots of (**a**) temperature, (**b**) length of pre-heating zone, (**c**) heat loss with the reaction time, and (**d**) propagation velocity. The central line in each figure denotes the Ti + 2B micropyretic reaction with the pre-exponential factor, $1 \times 10^{10}\ \mathrm{s}^{-1}$. The other lines denote the reactions with the 120% (bold line) and 80% values of pre-exponential factor, respectively

Fig. 4a and d shows that the temperature profiles at the ignition spot and propagation manner are also slightly dependent on the pre-exponential factor.

Thermal conductivity

As discussed in the previous study [1], a lower thermal conductivity reduces the heat loss and the reaction with a lower thermal conductivity can be quickly ignited. Table 2 also shows that the thermal conductivity for the reaction with Ti + 2B is lower than that for the reaction with Ni + Al. Therefore, the ignition time and temperature variations at the ignition spot are not expected to change with the thermal conductivity. In addition, the variations in the thermal conductivity are also noted to slightly change the zone length and heat loss at the ignition spot. Figure 5d shows that the propagation manner is noted to change to a stable mode when the lower thermal conductivity (80% *E*) is taken in the calculation.

Heat capacity

Since the Ti + 2B micropyretic reaction has higher exothermic heat and smaller heat capacity, the variations in the heat capacity are expected to dramatically affect the temperature profiles at the ignition spot. Figure 6 shows the reaction with smaller heat capacity (80% C_p) is quickly heated for a given input energy. A sharp increase in the temperature also increases the transferred heat from the ignition spot. Thus, the zone length and heat loss are noted to be larger at the initial stage. On the other hand, the heating rate is decreased and the ignition time is correspondingly increased when a higher heat capacity is taken in the numerical calculation. Thus, the zone length (Fig. 6b) and heat loss (Fig. 6c) then decrease with the heat capacity due to a longer ignition time. Figure 6d also shows that the propagation manner of the combustion front is changed from stable, unstable, to extinguishing manner respectively when the heat capacity is gradually increased. As compared with the thermal conductivity, heat capacity has a

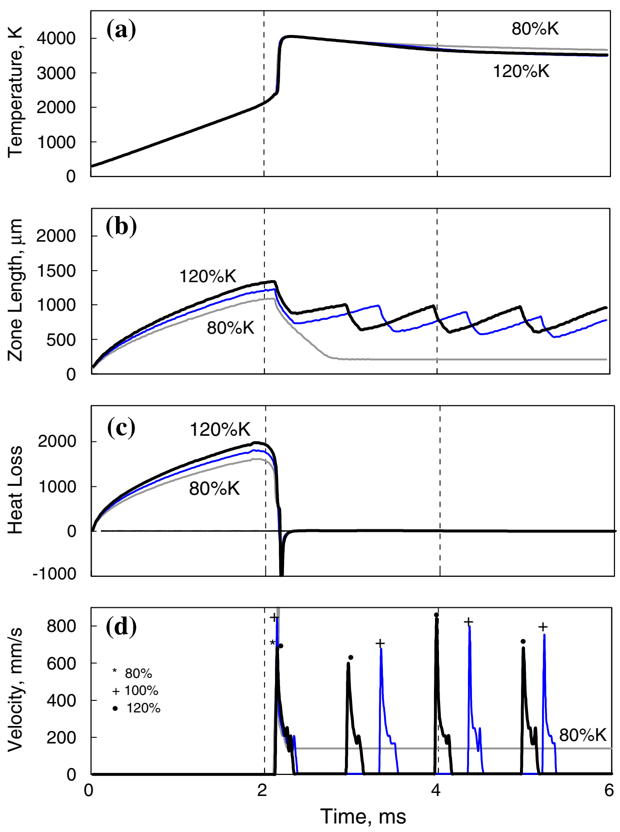

Fig. 5 The plots of (**a**) temperature, (**b**) length of pre-heating zone, (**c**) heat loss with the reaction time, and (**d**) propagation velocity. The central line in each figure denotes the Ti + 2B micropyretic reaction with the experimental value of thermal conductivity. The other lines denote the reactions with the 120% (bold line) and 80% experimental values of thermal conductivity, respectively

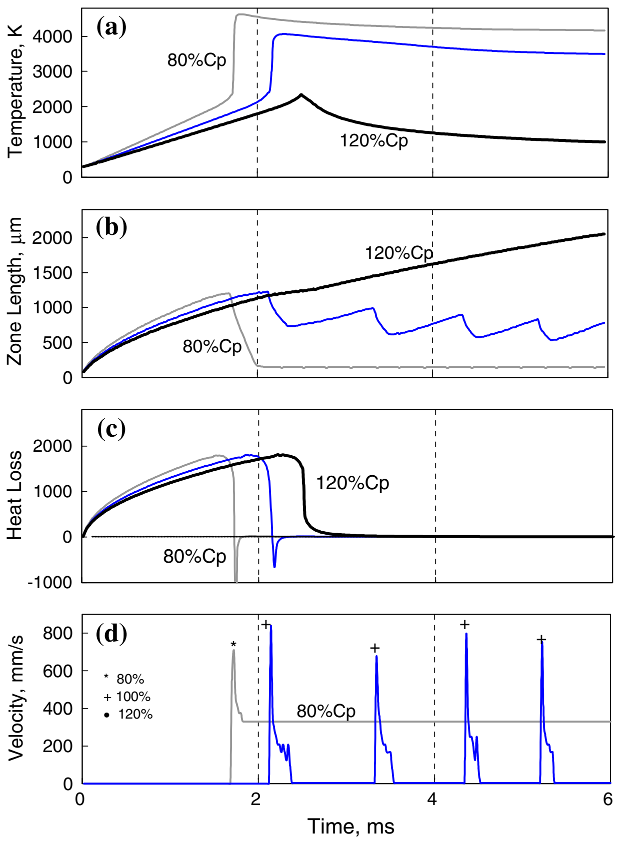

Fig. 6 The plots of (**a**) temperature, (**b**) length of pre-heating zone, (**c**) heat loss with the reaction time, and (**d**) propagation velocity. The central line in each figure denotes the Ti + 2B micropyretic reaction with the experimental value of heat capacity. The other lines denote the reactions with the 120% (bold line) and 80% experimental values of heat capacity, respectively

pronounced effect on changing the ignition time and energy for the micropyretic synthesis with Ti + 2B.

Thermal activity

The previous study has shown that an increase in the thermal activity raises the increased rate of temperature, especially after the micropyretic reaction has been ignited [1]. Thus, the heat loss at the ignition spot and the length of pre-heating zone are expected to be influenced by the thermal activity only after the micropyretic reaction has been ignited, as shown in Fig. 7. As the same as observed in the study of micropyretic synthesis with Ni + Al [1], the heat loss and zone length are decreased for the reaction with a smaller thermal activity. In addition, the stable propagation manner is also noted on account of less heat loss.

Required ignition energy

The correlation of the required energy to ignite the reactions with the different micropyretic synthesis parameters are illustrated in the Fig. 8. To compare the differences between the micropyretic reactions with Ni + Al and Ti + 2B, the same ignition powers are used in the calculation of the Ti + 2B micropyretic reaction. The calculated results show that 3,914 J/g and 4,288 J/g are, respectively, required to ignite the Ti + 2B micropyretic reaction when the ignition powers of 397 J/(ms g) and 1,191 J/(ms g) are taken in the calculation. As compared with the micropyretic reactions with Ni + Al [1], it is found that the energy required to ignite the micropyretic reaction with Ti + 2B are 2–3 times higher. Figure 8 illustrates that the activation energy is still a major parameter to influence the ignition energy. In addition, the required energy for the Ti + 2B micropyretic reaction ignited by a lower ignition power (397 J/(ms g)) is also found to be less than that with a higher ignition power (1,191 J/ms g). Similar experimental results are also observed in the previous numerical study of Ni + Al micropyretic reaction [1] and the experimental study of the Nb + C micropyretic reaction [15]. Due to a lower heat capacity for the micropyretic reaction with Ti + 2B, the variations in the heat capacity significantly

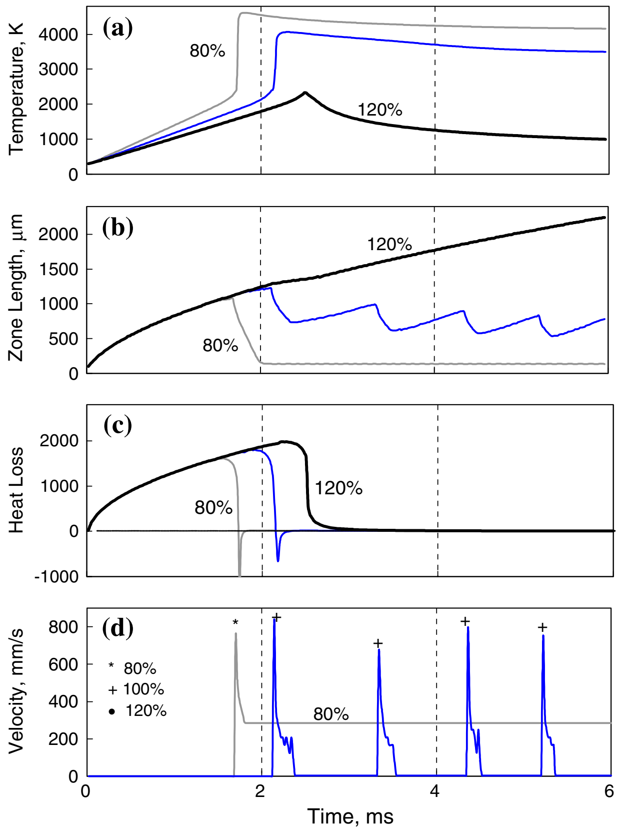

Fig. 7 The plots of (**a**) temperature, (**b**) length of pre-heating zone, (**c**) heat loss with the reaction time, and (**d**) propagation velocity. The central line in each figure denotes the Ti + 2B micropyretic reaction with the experimental value of thermal activity. The other lines denote the reactions with the 120% (bold line) and 80% experimental value of thermal activity, respectively

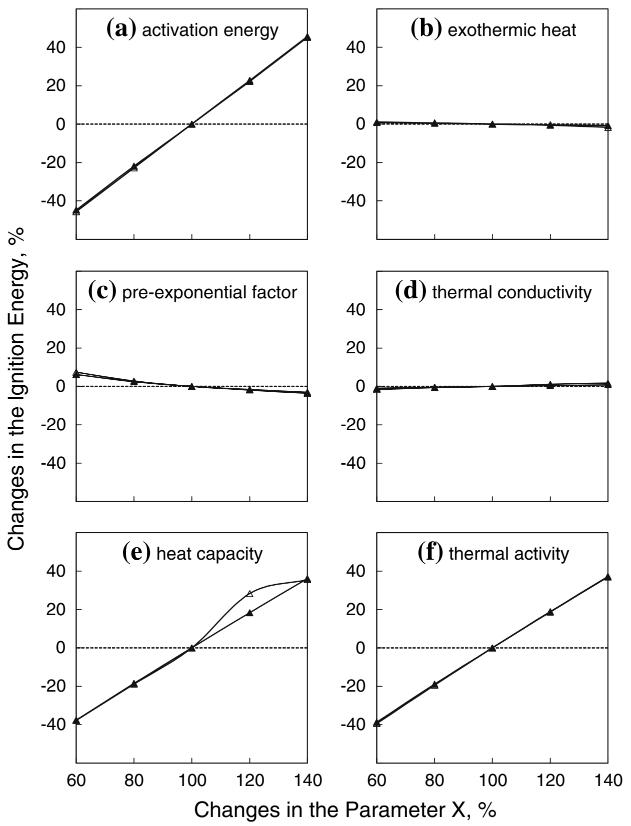

Fig. 8 The influence of the changes in the parameters (**a**) activation energy, (**b**) exothermic heat, (**c**) pre-exponential factor, (**d**) thermal conductivity, (**e**) heat capacity, and (**f**) thermal activity on the ignition energy. The TiB_2 micropyretic reactions are, respectively, ignited by a higher ignition rates of 1,911 J/(ms g) (solid symbols) and a lower ignition rates of 397 J/(ms g) (open symbols)

affect the heating rate of the specimen and hence the ignition energy. Thus, Fig. 8 shows that the energy required to ignite the reaction is increased to 36.1% when the heat capacity is increased to 140% of reported experimental value.

Maps for ignition energy

To understand the combined influences of micropyretic parameters on the ignition energy, the maps for energy required to ignite the micropyretic reactions with the various parameter values are also generated in this study. In addition, the comparisons in the ignition energy maps between the micropyretic reactions with Ni + Al and Ti + 2B are also investigated. The thermophysical/chemical parameters and related results for the micropyretic reaction with Ni + Al have been shown in the previous study [1] and the ignition power is taken as 397 J/(ms g) for both the reactions in the numerical calculation. Figure 9 shows the correlation of thermal conductivity and pre-exponential factor with ignition energy for the micropyretic reactions with Ni + Al and Ti + 2B. In Fig. 9, the 100% value of micropyretic parameter denotes the reported experimental value in the calculation and the number 60%, for example, denotes the 60% value of reported experimental value in the calculation.

It has been reported that a decrease in the pre-exponential factor is equivalent to increasing the particle size of the reactant [4]. The amount of heat loss is thus increased with the particle size and pre-exponential factor. The micropyretic reaction with Ni + Al possesses a higher thermal conductivity as compared with the micropyretic reaction with Ti + 2B. Thus, the heat loss is expected to be significantly enhanced for the reaction with Ni + Al when a lower pre-exponential factor is taken in the calculation. Figure 9a illustrates that the required ignition energy is increased by 8.8 % (from 1,131 to 1,231 J/g) for the Ni + Al reactions with a higher pre-exponential factor (150% K_o) as the thermal conductivity is increased from 60% to 140 % of reported experimental value. When the pre-exponential factor is further decreased from 150% to 50% K_o, the required ignition energy is increased by 15.4% (from 1,548 to 1,787 J/g). Due to a smaller thermal conductivity for the micropyretic reaction with Ti + 2B, the ignition energy is

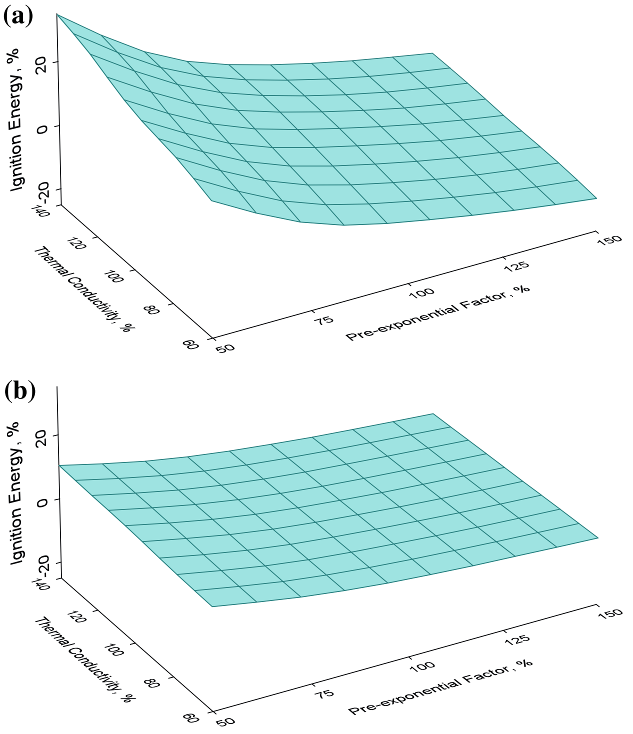

Fig. 9 The maps for the changes in the required ignition energy (in percentage) caused by thermal conductivity and pre-exponential factor (in percentage) for the micropyretic reactions with (**a**) Ni + Al and (**b**) Ti + 2B. The numbers 0.6 and 1.4 on X and Y axes, respectively, denote 60% and 140% of reported experimental values. The ignition energy in Figs. 9–11 are calculated, respectively, as 1,310 and 3,914 J/g for the micropyretic reactions with Ni + Al and Ti + 2B by taking the experimental values [1–6]

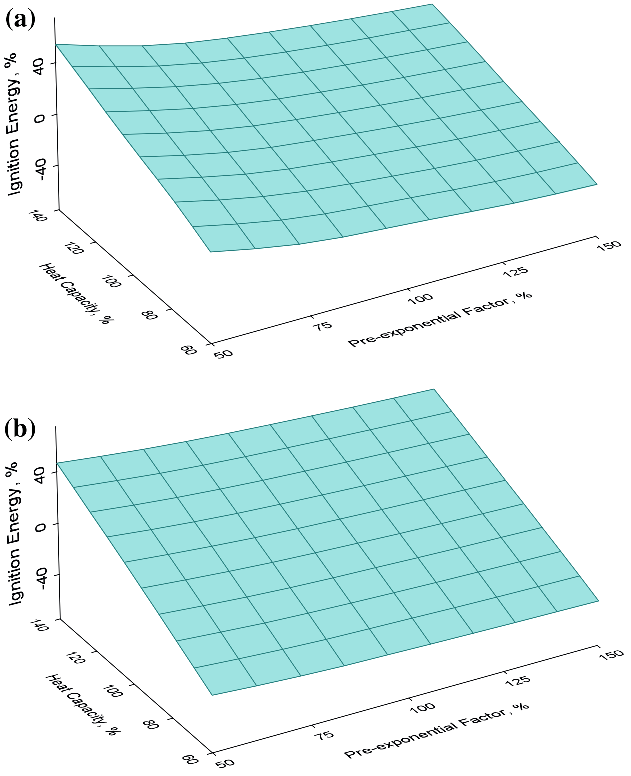

Fig. 10 The maps for the changes in the required ignition energy (in percentage) caused by heat capacity and pre-exponential factor (in percentage) for the micropyretic reactions with (**a**) Ni + Al and (**b**) Ti + 2B

only increased by 1.1% and 3.4% for the reaction with 150% K_o and 50% K_o, respectively, when the thermal conductivity is increased from 60% to 140% of reported experimental value, as shown in Fig. 9b.

The correlations of heat capacity and pre-exponential factor with the ignition energy for the micropyretic reactions with Ni + Al and Ti + 2B are shown in Fig. 10a and b, respectively. Since the ratio of exothermic heat to heat capacity for the reaction with Ti + 2B is much higher than the reaction with Ni + Al, the temperature at the ignition spot is easily enhanced. The required ignition time and energy for the reaction with Ti + 2B are noted to decrease. Thus, the difference in the required ignition energy for the reaction with Ti + 2B (77%, Fig. 10b) caused by the heat capacity is much larger than the reaction with Ni + Al (60%, Fig. 10a). A similar comparison in the heat capacity and activation energy with ignition energy between two reactions is plotted in Fig. 11. Again, the change in the ignition energy for the reaction with Ti + 2B is larger due to a higher activation energy and a lower heat capacity.

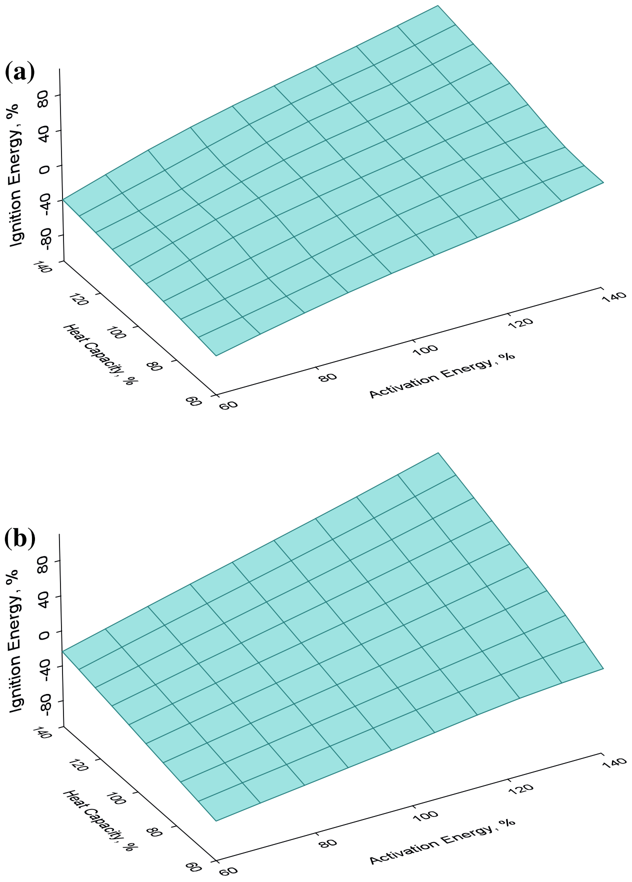

Fig. 11 The maps for the changes in the required ignition energy (in percentage) caused by heat capacity and activation energy (in percentage) for the micropyretic reactions with (**a**) Ni + Al and (**b**) Ti + 2B

Summary and conclusions

The numerical calculations indicate that the activation energy and the heat capacity are the major parameters to determine the energy required to ignite the unstable Ti + 2B micropyretic synthesis. The change in exothermic heat is noted to affect the thermal profiles at the ignition spot only after the micropyretic reaction has been ignited. Thus, the ignition energy is slightly dependent on the exothermic heat. In addition, the ignition time and energy are found to slightly depend on the thermal conductivity and pre-exponential factor. These studied micropyretic parameters not only change the ignition time and energy, but also alter the propagation manner of a combustion front after the reaction with Ti + 2B is ignited.

The maps for the required ignition energy are also generated in this study. In addition, the comparisons in the ignition energy maps between micropyretic reactions with Ti + 2B and Ni + Al are also carried out. It is found that the required energy is dramatically enhanced for the micropyretic reaction with Ti + 2B when the activation energy and heat capacity are concurrently increased. The increment is found to decrease for the micropyretic reaction with Ni + Al due to a lower activation energy. The numerical calculation also illustrates that the changes in the ignition energy caused by the thermal conductivity is small for the micropyretic reaction with Ti + 2B. However, the required ignition power is found to significantly change with the thermal conductivity for the NiAl micropyretic reaction when a higher pre-exponential factor is taken in the calculation. This is because that NiAl reaction possesses a higher thermal conductivity and a lower pre-exponential factor aids to magnify the effect of the thermal conductivity. Thus, the difference in the required ignition energy caused by the thermal conductivity is noted to be larger for the Ni–Al micropyretic reaction with a lower pre-exponential factor.

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