

# Characteristics of Reaction Propagation in Combustion Synthesis of (Ti–B–C) Systems

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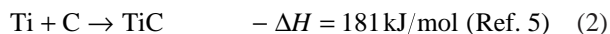
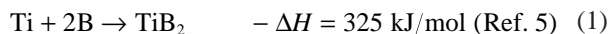
Combustion syntheses of the (Ti–B–C) system have been investigated through measurements of its reaction heats and propagation rates. In order to clarify the reaction propagation characteristics, powder mixture compositions and the constituent carbon sizes were varied. As a result of the present work, it has been confirmed that the variation of the propagation rate related to the mixture ratios of the starting powders and greatly depended on carbon size. Three regimes categorize the present propagation characteristic: when the (Ti + 2B) component is predominant, the propagation rate decreases drastically with increasing the mole fraction of (Ti + C) component because the superiority of the reaction between Ti and B decreases. In the regime of the intermediate mole fraction, the propagation rate does not change as much. As the (Ti + C) component becomes predominant, the reaction between Ti and C overcomes the reaction with B and the propagation rate becomes large. In this regime, the large specific heat of boron might affect such a tendency.

**KEY WORDS:** Combustion synthesis of (Ti–B–C) system; propagation rate; reaction heat; superiority of reaction; specific heat.

## 1. INTRODUCTION

Combustion synthesis consists of reaction propagation and structurization processes [1–4]. The former is the process by which the chemical reaction occurs in a successive zone resulting in combustion wave propagation. The latter is the process in which structurization and crystallization proceed at the zone behind the passing wave. The propagation characteristic is a principal factor that affects not only the propagation but also the structurization process [4].

Titanium diboride (TiB<sub>2</sub>) and titanium carbide (TiC) are the typical products synthesized by combustion synthesis. In both systems, with a stoichiometric mixture the following reactions occur;



The adiabatic temperatures of (1) and (2) are 3203 and 3423K [5], respectively, which are the melting points of each product. Although these values are similar, the propagation rate of (1) is very large compared to that of (2) [6]. The difference in propagation rate in both systems might be caused by the difference of phase transition at high temperature between boron and carbon [7–9]. Therefore, upon combustion synthesis in the (Ti–B–C) system, the propagation rate would be greatly altered with powder mixture ratio. Following this, the composition of final products would be varied.

The purposes of this study are to clarify dependency of the propagation rate on mixture ratio and the size effects of the reactant powder (carbon) on the reaction propagation and to discuss the predominant factors affecting propagation rate in the combustion synthesis of (Ti–B–C) systems. The reaction heat measurements were made with stoichiometric and nonstoichiometric sample mixtures. The products are revealed from the X-ray diffraction (XRD) profile. The superiority of the existing reactions is discussed, based on the mole ratio of the products, and estimated by the value of the heat of the reaction. The propagation rate measurements were made with

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stoichiometric sample mixtures. From the viewpoint of the above estimated superiority and the difference in specific heats between boron and carbon, the dependencies of the propagation rate with the sample composition in combustion synthesis of (Ti–B–C) systems and the size effects of carbon diameter on the dependencies were discussed.

Makino [10] investigated the propagation rate on samples, which are mixtures of two different carbon sizes. It had been reported that the propagation rate decreases monotonously with the mole fraction of the large carbon particle. The differences of the dependency of the propagation rate between the binary (titanium, small and large carbon in Makino's study) and ternary system (titanium, small boron and large carbon in this study) will be discussed.

## 2. EXPERIMENTAL

### 2.1. Sample Preparation

The powders of titanium (ca. 30  $\mu\text{m}$ ), amorphous boron (ca. 0.8  $\mu\text{m}$ ), and carbon were used as starting materials. These were mixed in a given composition and pressed into powder compacts of 60% packing density (15 mm  $\phi \times 10$  mm for reaction heat measurements and 25 mm  $\phi \times 30$  mm for propagation rate). The sizes of carbon powder were 3 and 25  $\mu\text{m}$ .

Based on the heat reaction measurements, sample compositions were selected, as shown in Table Ia. The samples prepared in the present work included (1) stoichiometric compositions between Ti and B/C, based on the reactions of (Ti + 2B) and (Ti + C) systems, and (2) nonstoichiometric ones. The samples from No. 1–4 are stoichiometric mixtures, where the estimated products are  $\text{TiB}_2$ ,  $\text{TiB}_2 + \text{TiC}$ ,  $\text{TiB}_2 + 2\text{TiC}$ , and  $2\text{TiB}_2 + \text{TiC}$ . The samples from No. 5–7 are nonstoichiometric mixtures, where the amounts of B/C are in excess of that of Ti, compared with the stoichiometric composition.

In the propagation rate measurements, all of samples are stoichiometric mixtures. The mole fraction of (Ti + C) component ( $X_c$ ) is changed from 0 to 1, as shown in Table Ib.

### 2.2. Reaction Heat Measurement

Reaction heats in (Ti–B–C) systems were measured using a vacuum flask-type adiabatic calorimeter (Ogawa sampling Co., Ltd.). Figure 1 shows a schematic diagram of the experimental apparatus. Distilled water (1800 g) was added to the vacuum flask. The sample and an iron wire are set into a bomb. After air in the bomb was re-

**Table I.** Compositions of Reactants

a. Reaction heat experiments			
Ti : B : C			
Stoichiometric composition			
No. 1	1 : 2 : 0		
No. 2	2 : 2 : 1		
No. 3	3 : 2 : 2		
No. 4	3 : 4 : 1		
Nonstoichiometric composition			
No. 5	1 : 2 : 1		
No. 6	1 : 2 : 2		
No. 7	1 : 4 : 1		
b. Propagation rate experiments			
$X_c$			
3 $\mu\text{m}$	25 $\mu\text{m}$	Ti : B : C	
0.00	0.00	1 : 2 : 0	No. 1
0.10		1 : 1.8 : 0.1	
0.20	0.20	1 : 1.6 : 0.2	
0.33	0.33	1 : 1.33 : 0.33	No. 4
0.50	0.50	1 : 1 : 0.5	No. 2
0.67	0.67	1 : 0.67 : 0.67	No. 3
0.80	0.80	1 : 0.4 : 0.8	
	0.88	1 : 0.24 : 0.88	
0.90		1 : 0.2 : 0.9	
	0.96	1 : 0.08 : 0.96	
1.00	1.00	1 : 0 : 1	

placed with argon at atmospheric pressure, the bomb was inserted the flask. For ignition, the iron wire was heated to 10A. Elapsed time until the wire was broken ( $t$ ) and average applied voltage ( $V$ ) were noted. The increase of the water temperature due to reaction heat ( $\Delta T$ ) was measured using a Beckmann's thermometer.

The reaction heat in the sample ( $q$ ) was calculated using the following equation:

$$q = C_w \Delta T - \frac{VI t}{1000} - \frac{Q_{\text{TiB}_2} W_{\text{TiB}_2}}{M_{\text{TiB}_2}} \quad (3)$$

where  $C_w$  and  $I$  are specific heat of water, including the specific heat of the vacuum flask and the bomb, and applied current for the iron wire (10A), respectively.  $C_w$  is peculiar to the configuration of each apparatus. Therefore, in this experiment, the value of  $C_w$  is calculated in advance from the increase of water temperature on the condition of heating the wire without the samples ( $10.41 \pm 0.82$  kJ/K). The third term in the above equation is applied only when  $\text{TiB}_2$  is used as the igniter.  $Q_{\text{TiB}_2}$ ,  $W_{\text{TiB}_2}$ , and  $M_{\text{TiB}_2}$  are standard reaction heat of  $\text{TiB}_2$ , mass of  $\text{TiB}_2$ , and molecular weight of  $\text{TiB}_2$  (69.52), respectively.

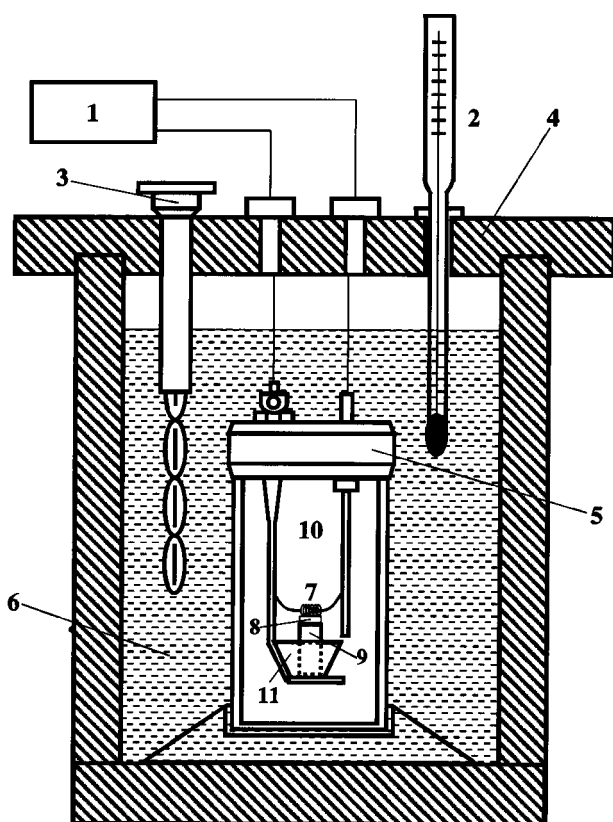


Fig. 1. Experimental apparatus for the reaction heat measurement. (1) Power supply; (2) Beckmann's thermometer; (3) stirrer; (4) vacuum flask; (5) bomb; (6) distilled water; (7) iron wire; (8) igniter; (9) sample; (10) Ar; (11) melting pot.

### 2.3. Propagation Rate Measurement

The schematic of apparatus for measurement of propagation rate is shown in Fig. 2. The sample and a tungsten wire for ignition are set in a chamber. After air in the chamber is replaced with argon at atmospheric pressure, the top of the sample is ignited by heating the tungsten wire. A combustion wave propagates from the top downward.

For detection of the passing combustion wave, K-type thermocouples are installed from the sidewall at two points: 14 and 22 mm from the ignition point and 2 mm inside the sample. The output voltages from the thermocouples are amplified 25 times and recorded as digital data through a data logger with a sampling frequency of 1 kHz. The voltage rises quickly as the combustion wave passes the thermocouple. The time at which the temperature reaches 773K is defined as a wave-passing time. The propagation rate is calculated as the value of difference of the propagation time divided by distance between the two thermocouples (8 mm).

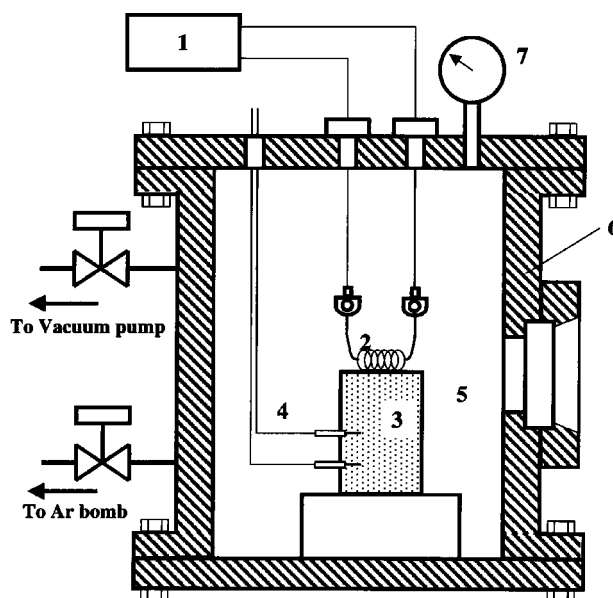


Fig. 2. Experimental apparatus for the propagation rate measurement. (1) Power supply; (2) iron wire; (3) sample; (4) thermocouples; (5) Ar; (6) chamber; (7) pressure gauge.

Because the K-type thermocouples would be broken due to high temperature following the combustion wave (over 2000 K), the temperature variation on the structurization process could be measured. W-5%Re-W-26%Re thermocouples would be used to obtain the temperature variation through the propagation and the structurization processes.

## 3. RESULTS

### 3.1. Reaction Heat

The experimental results on reaction heat for each sample are shown in Table II. In the case of stoichiometric sample mixtures (from No. 1 to 4), the reaction heat is independent of carbon powder size, under the conditions of the same initial mixture composition. However, in the case of nonstoichiometric sample mixtures (from No. 5 to 7), it depends on the size.

The products were identified by XRD. Representative XRD profiles of stoichiometric and nonstoichiometric mixture samples are shown in Fig. (3). The XRD profiles of the stoichiometric sample mixtures indicate only productions of  $\text{TiB}_2$  and  $\text{TiC}$ . Others, such as titanium,  $\text{TiB}$ , and  $\text{B}_4\text{C}$ , were not detected. The XRDs in stoichiometric samples show almost similar profiles (as shown in Figs. 3a and b). This evidence supports the above-

**Table II.** The Reaction Heats and the Mole Ratios of  $\text{TiB}_2$  to  $\text{TiC}$  in the Sample

	Heat of reaction $q$ (kJ)		Reactant [2B]/[C]	Product [ $\text{TiB}_2$ ]/[ $\text{TiC}$ ]	
	3 $\mu\text{m}$	25 $\mu\text{m}$	3 $\mu\text{m}/25 \mu\text{m}$	3 $\mu\text{m}$	25 $\mu\text{m}$
Stoichiometric composition					
No. 1	$18.43 \pm 0.79$		$\infty$	$\infty$	
No. 2	$18.22 \pm 0.79$	$18.30 \pm 0.70$	1	1	1
No. 3	$17.41 \pm 1.22$	$17.24 \pm 0.35$	0.5	0.506	0.429
No. 4	$18.71 \pm 0.53$	$18.87 \pm 0.21$	2	1.681	1.778
Non stoichiometric composition					
No. 5	$15.31 \pm 0.40$	$15.67 \pm 0.56$	1	7.333	15.393
No. 6	$12.01 \pm 0.43$	$12.12 \pm 0.41$	0.5	3.202	3.566
No. 7	$11.65 \pm 0.16$	$11.72 \pm 0.16$	2	17.868	26.027

mentioned reaction-heat independence of carbon powder size. These results suggest that the reactions (1) and (2) have occurred and all of reactants (Ti, B, and C) are consumed under stoichiometric conditions. On the other

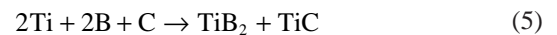
hand, in the nonstoichiometric sample mixtures (Figs. 3c and d), titanium,  $\text{TiB}$ ,  $\text{B}_4\text{C}$ , etc., were not detected except for  $\text{TiB}_2$  and  $\text{TiC}$ . Lack of nondetection of residual titanium in any of the XRD profiles is worth noting. Judging from the fact that a broad pattern could be confirmed in the XRD profiles, it is implied that the boron and carbon would remain after titanium transferred to  $\text{TiB}_2$  and  $\text{TiC}$ . As the carbon powder size becomes smaller and starting mole ratio of boron to carbon ([2B]/[C]) becomes larger, the diffraction peak of  $\text{TiB}_2$  become relatively large compared with  $\text{TiC}$ . This tendency corresponds an increase in generated reaction heat.

Since all the products are also identified to  $\text{TiB}_2$  and  $\text{TiC}$ , the reaction can be categorized with the Eqs. (1) and (2). The mole ratio of  $\text{TiB}_2$  to  $\text{TiC}$  in a final product ([ $\text{TiB}_2$ ]/[ $\text{TiC}$ ]) can be obtained, assuming that all of the titanium was reacted.

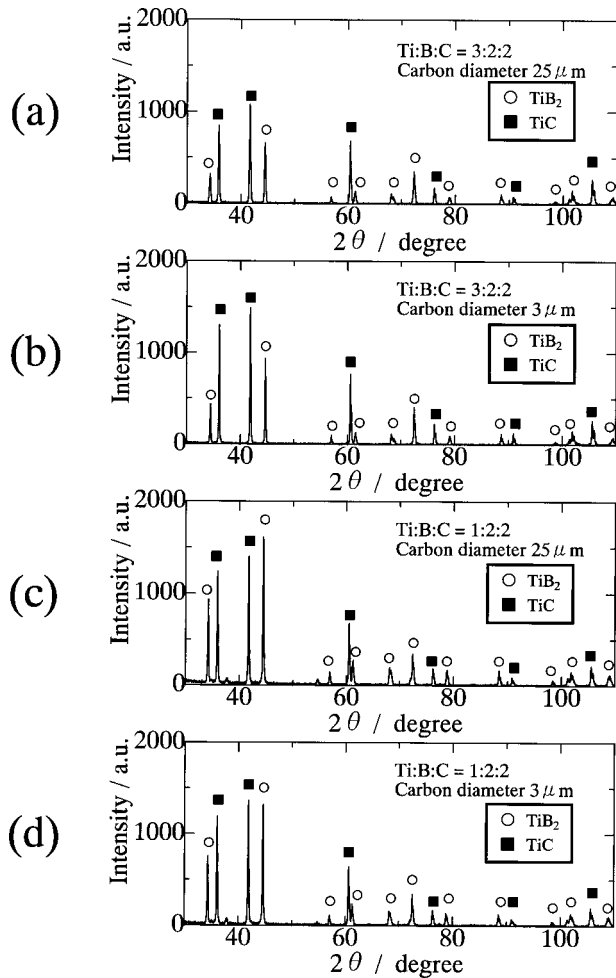
$$Q_{\text{TiB}_2} \frac{[\text{TiB}_2]/[\text{TiC}]}{[\text{TiB}_2]/[\text{TiC}] + 1} + Q_{\text{TiC}} \frac{1}{[\text{TiB}_2]/[\text{TiC}] + 1} = q \frac{M_{\text{Ti}}}{W_{\text{Ti}}} \quad (4)$$

where  $Q_{\text{TiC}}$ ,  $W_{\text{Ti}}$ , and  $M_{\text{Ti}}$  are standard heat of reaction of  $\text{TiC}$ , mass of titanium contained in the starting sample, and molecular weight of titanium (47.90).

$Q_{\text{TiB}_2}$  and  $Q_{\text{TiC}}$  were calculated from the experimental results of Nos. 1 and 2. In the case of No. 1, we assumed that only reaction (1) occurred. Consequently, we could obtain  $370.39 \pm 14.43$  kJ/mol as  $Q_{\text{TiB}_2}$ . Equation (5) represents the No. 2 experiment;

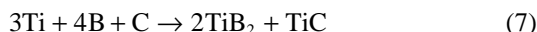
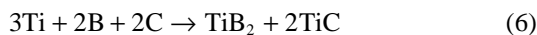


$Q_{\text{TiC}}$  was then determined as  $237.10 \pm 8.91$  kJ/mol. The mole ratio in the case of Nos. 3 to 7 was calculated from Eq. (4), using the above  $Q_{\text{TiB}_2}$  and  $Q_{\text{TiC}}$ . These results are shown in Table II.

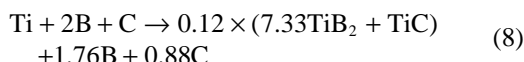


**Fig. 3.** Representative XRD profiles. (a) 3:2:2(Ti:B:C), 25  $\mu\text{m}$  (carbon powder size); (b) 3:2:2, 3  $\mu\text{m}$ ; (c) 1:2:2, 25  $\mu\text{m}$ ; (d) 1:2:2, 3  $\mu\text{m}$ .

For stoichiometric samples, the mole ratios of  $\text{TiB}_2$  to  $\text{TiC}$  are equivalent to the initial mixture ratio. Therefore, in experiment Nos. 3 and 4, the following reactions, represented by Eqs. (6) and (7), would occur, respectively (regardless of the carbon powder size).



In the No. 5 experiments, about  $3\text{ }\mu\text{m}$ , a reaction represented by Eq. (8), would be estimated as:



From the above equation, it can be seen that a much larger amount of  $\text{TiB}_2$  would be produced compared to that of  $\text{TiC}$ . This tendency is similar to that found in experiment Nos. 6 and 7. Therefore, it is determined that the reaction in  $(\text{Ti} + 2\text{B})$  system (Eq. 1) proceeds in a superior manner compared to that in  $(\text{Ti} + \text{C})$  system (Eq. 2). In case of smaller carbon size, the mole ratios of  $\text{TiB}_2$  to  $\text{TiC}$  increase. This indicates that the smaller the carbon, the easier the carbon reacts with titanium.

### 3.2. Propagation Rates

The dependencies of the propagation rate with the mole fraction of  $(\text{Ti} + \text{C})$  component are shown in Fig. 4a and b. It is confirmed that both results of 3 and  $25\text{ }\mu\text{m}$  give similar dependencies, as can be seen in the schematic diagram of Fig. 7a (see later). Three regimes categorize the tendency of the propagation rate following the increase of  $X_{\text{C}_2}$  (1) decreasing drastically in regime I,

(2) almost constant in regime II, and (3) increasing gradually in regime III. The value of  $\chi_{\text{I II}}$ , which is a transition point from the regime I to II, depends on the carbon size. Similarly, the value of  $\chi_{\text{II III}}$  depends on the size. Therefore, the smaller the carbon diameter, the narrower the range of the regime I and the broader the range of the regime III.

The temperature hystereses obtained by W-5%Re–W-26%Re thermocouple are shown in Fig. 5a and b. In the  $(\text{Ti–B})$  system, the temperature rapidly decreases, just after the temperature reaches a maximum (structurization process). On the other hand, high-temperature conditions are continued in the  $(\text{Ti–C})$  system, even after maximum temperature is attained. The temperature hystereses shows a transition from the hysteresis in  $(\text{Ti–B})$  system to the counterpart in  $(\text{Ti–C})$  system with  $X_{\text{C}}$ . The temperature hystereses in the vicinity of  $\chi_{\text{I II}}$  shows bimodal profiles; the first peak, which is steep one, is caused primarily by the reaction in the  $(\text{Ti–B})$  system; the second peak, which has a shoulderlike shape, is caused primarily by the reaction in  $(\text{Ti–C})$  system.

## 4. DISCUSSION

Figure 6 shows that the relation between the mole ratio of  $\text{TiB}_2$  to  $\text{TiC}$ ,  $[\text{TiB}_2]/[\text{TiC}]$  and the mole ratio of  $2\text{B}$  to  $\text{C}$ , following the starting composition,  $[2\text{B}]/[\text{C}]$ , is based on the results of Table II. In this figure, it seems that the proportional relation exists between both mole ratios. For the stoichiometric sample, both data of 3 and  $25\text{ }\mu\text{m}$ , regardless of the carbon size, are plotted on a straight line with a unit gradient. This leads to the fact that all reactants would be consumed and the products obtained according to starting composition. For the non-

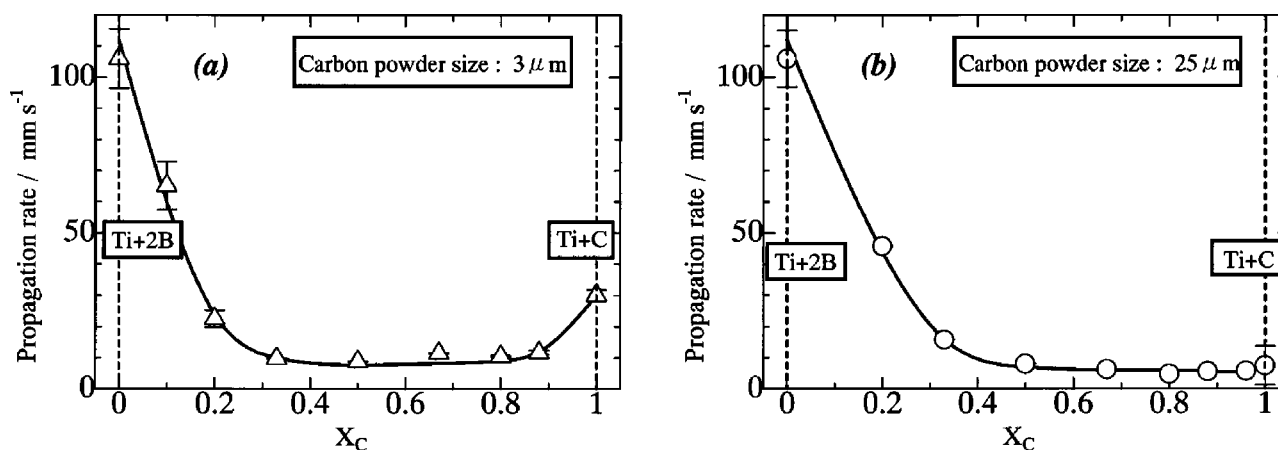


Fig. 4. Dependencies of the propagation rate with mole fraction of  $(\text{Ti} + \text{C})$  component ( $X_{\text{C}_{50}}$ ) (a)  $3\text{ }\mu\text{m}$  in carbon powder size; (b)  $25\text{ }\mu\text{m}$  in carbon powder size.



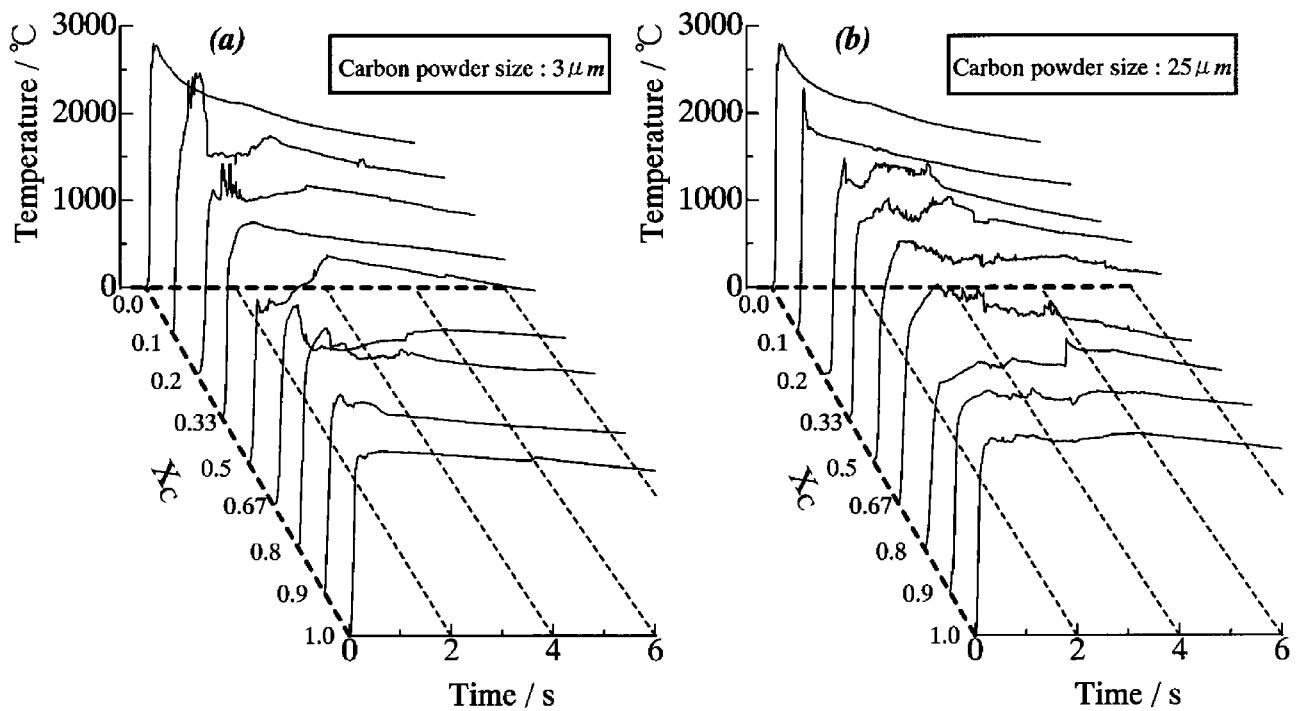


Fig. 5. Temperature hystereses in the present work. (a) 3  $\mu\text{m}$  in carbon powder size; (b) 25  $\mu\text{m}$  in carbon powder size.

stoichiometric sample, the gradients are larger than 1, and these gradients vary with carbon size. This implies that the best reaction is between titanium and boron and that the superiority of the reaction increases with smaller carbon due to an increase in the surface area per unit. Here, we define an index representing the superiority of the reaction between Ti and B to that with C, as the gra-

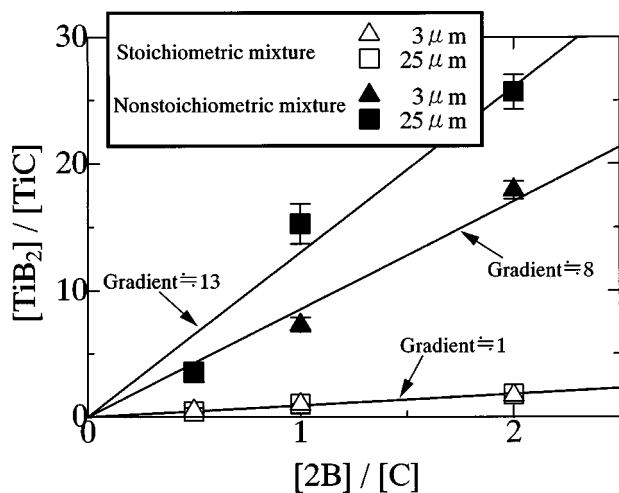


Fig. 6. Relation between the mole ratio of 2B to C ( $[2B]/[C]$ ) and the mole ratio of  $\text{TiB}_2$  to  $\text{TiC}$  ( $[\text{TiB}_2]/[\text{TiC}]$ ).

dient of the straight line for a nonstoichiometric mixture (Fig. 6). It is considered that the index would correspond to the ratio of the reaction rate in the  $(\text{Ti} + 2\text{B})$  system to that in the  $(\text{Ti} + \text{C})$  system. For carbon of 3  $\mu\text{m}$ , the reaction rate of the  $(\text{Ti} + 2\text{B})$  system is about 14 times faster than that in the  $(\text{Ti} + \text{C})$  system. For carbon of 25  $\mu\text{m}$ , the reaction rate in the  $(\text{Ti} + 2\text{B})$  system is about eight times faster than that in the  $(\text{Ti} + \text{C})$  system. These values are considered to have the following meaning: under the condition of  $X_C = 0.2$  (starting composition  $[2B]/[C] = 8/2$ ), the mole ratio of reacting boron to reacting carbon becomes  $([2B]/[C] \approx (8 \times 14)/2)$  for a carbon of 3  $\mu\text{m}$  and  $([2B]/[C] \approx (8 \times 8)/2)$  for carbon of 25  $\mu\text{m}$ . In this way, the reaction of the  $(\text{Ti} + 2\text{B})$  system proceeds better rather than the reaction of the  $(\text{Ti} + \text{C})$  system. Finally, following the starting composition,  $\text{TiB}_2$  and  $\text{TiC}$  would be generated as  $([\text{TiB}_2]/[\text{TiC}] = 8/2)$ .

The variation of the propagation rate with the mole fraction of  $(\text{Ti} + \text{C})$  component shows the peculiar tendency seen in Fig. 7(a). In addition to the starting composition, for discussion of propagation tendency, the above-mentioned mole ratio by the superiority of the reaction should be taken into account. Since the propagation is caused by the transfer of the heat generated in the chemical reaction to the successive zone, the propagation phenomena are dominated by the counterbalance be-

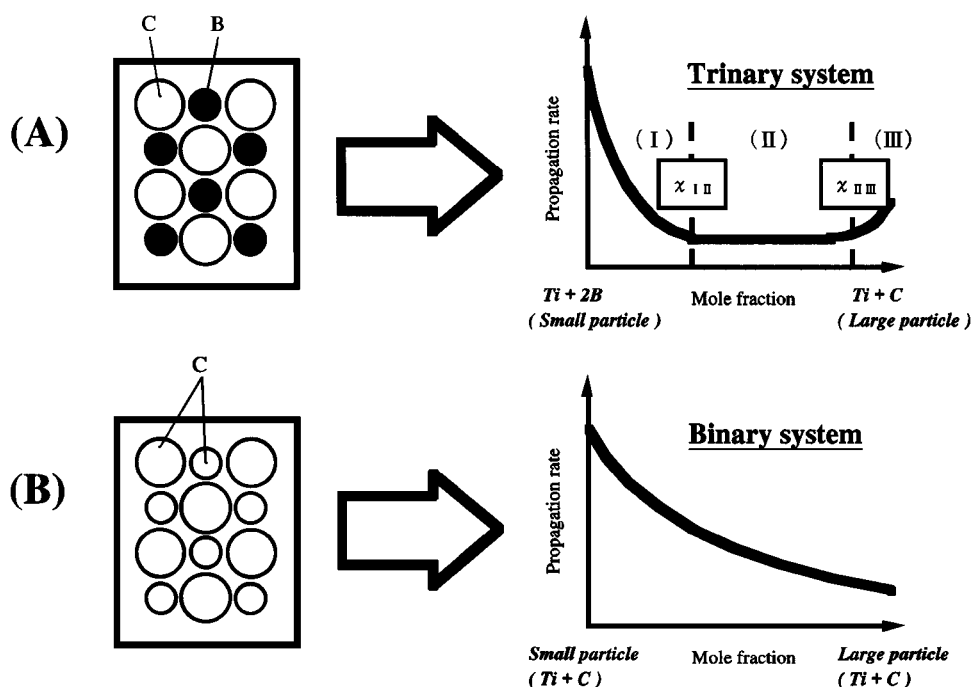


Fig. 7. Comparison of propagation rate dependency between ternary and binary system.

tween heat release and absorption [6]. The tendency in the experimental results will be discussed as follows—from the viewpoint of the mole amount of reactants, the reaction heat, or the specific heat.

The reaction heat per unit mole of  $\text{TiB}_2$  ( $Q_{\text{TiB}_2}$ ) is larger than that of  $\text{TiC}$  ( $Q_{\text{TiC}}$ ). Therefore, the smaller  $X_C$ , the greater the reaction heat generated in propagation. Since the amount of reacted boron in propagation would be more overwhelming than carbon, due to the greater superiority of the  $(\text{Ti} + 2\text{B})$  reaction (Fig. 6), the heat release by boron becomes more effective in a small  $X_C$  region.

The specific heats of boron ( $Cp_B$ ) is larger than that of carbon ( $Cp_C$ ) [5]. The role of heat sink by the specific heat of boron becomes more effective because  $2Cp_B > Cp_C$  [1 mole of titanium, 2 moles of boron, and 1 mole of carbon react in reactions (1) and (2), respectively]. Therefore, the smaller  $X_C$  is, the larger the bulk specific heat in a sample becomes for heat absorption.

In the regime I, the effect of the heat release is very large. The substance reacting with titanium is almost boron, because the superiority of the reaction in the  $(\text{Ti} + 2\text{B})$  system is remarkably large. Therefore, the propagation rate is dominated by the reaction in the  $(\text{Ti} - \text{B})$  system. The heat generated by the reaction in the  $(\text{Ti} - \text{C})$  system is small and the existence of carbon contributes to heat absorption rather than the heat release. Thus, one

can conclude that carbon may play a role as the inert substance. Therefore, the propagation rate decreases drastically with  $X_C$ .

It is considered that the transition from the regime I to II would be due to a decrease of the reaction heat. The reaction heat could not drive the combustion wave at this turning point  $\chi_{I II}$ . The propagation is then dominated by the reaction in the  $(\text{Ti} - \text{C})$  system, where the propagation rate is low. The bimodal profile shown in Fig. 5 indicates this transition. When the superiority of the reaction in the  $(\text{Ti} + 2\text{B})$  system is larger (larger carbon size), the generated heat driving the combustion wave is larger and transition point of  $\chi_{I II}$  shifts to left in the Fig. 7a.

In the regime II, although the propagation rate is dominated by the reaction in the  $(\text{Ti} - \text{C})$  system, the mole amount of boron concerned with the reaction is greater than that of carbon. In this region, a decrease of the propagation rate due to the reaction heat decrease might counterbalance the increase of the propagation rate due to the increase of specific heat. It is considered that the transition from the regime II to III would occur at the transition point  $\chi_{II III}$ , where the mole amount of carbon concerned with the reaction relatively overcomes that of boron. When the superiority of the reaction in the  $(\text{Ti} + 2\text{B})$  system is larger (carbon powder size become larger), the relative mole amount of boron compared to carbon

increases and transition point of  $\chi_{II\ III}$  shifts to the left (Fig. 7a).

In region III, the effect of the specific heat would remarkably appear. The role of boron as an inert substance with large specific heat instead of a role as the heat generator is considered. The decrease of the amount of boron with increasing  $X_C$  leads to a gradual increase in propagation rate.

In the (Ti–B–C) system, it is clear that the propagation rate depends on changes with  $X_C$ . These can be categorized in three regimes and these characteristics in the regime can be explained by considering the superiority of the reaction in the (Ti + 2B) system and the difference in specific heat. Some characteristics are given in Table III.

The tendencies of the propagation rate in stoichiometric binary (titanium, small and large carbon) and trinary systems (titanium, small boron, and large carbon) will now be considered. Because all titanium will be finally be transferred to  $TiB_2$  and  $TiC$  in a stoichiometric sample, we focus on the particle size of boron and carbon, and then will discuss the difference of the tendency in both systems. It was reported by Makino [10] that the propagation rate in the binary system decreases monotonously with increasing mole fraction of the large carbon particle (Fig. 7b). The monotonous decreasing tendency in the binary system can be easily recognized, because the reaction with smaller carbon proceeds better as compared to that with the larger carbon [9]. On the other hand, considering only the powder size, the small boron and the large carbon in the present study might correspond to the small and the large carbon in the binary system. Thus, it is considered that the differences of the tendency between the binary and the trinary system could be caused by the following factors: (1) superiority of the reaction between titanium and small particle (boron or carbon), (2) the total reaction heat per unit mass, and (3) the specific heat per unit mass. The effect of superiority of the reaction in the (Ti + 2B) system becomes large due to the phase-transition difference at high temperature between boron and carbon, in addition to the powder size difference. Furthermore, judging from  $Q_{TiC} < Q_{TiB_2}$  the

reaction heat varies drastically with the mole fraction of small particle (carbon) in the (Ti–B–C) system. Consequently, the drastic decrease of the reaction heat would not be observed in binary system. Thus, region I becomes wider than that in trinary system. On the other hand, region III would not exist, because of the difference of the specific heat between the small and the large particles. This is why the propagation rate decreases monotonously with increasing mole fraction of small particles. It is clear that not only the size effect, but also the differences of the reaction rates (the superiority between the reactions), the specific heats, and the reaction heats would play a great role in the peculiar tendency of the trinary system.

## 5. CONCLUSIONS

The propagation rate in the (Ti–B) system differs greatly different from the propagation rate in the (Ti–C) system. The reaction heats and the propagation rates are measured in order to clarify the predominant factors and the size effects of the reactant powder (carbon) on the reaction propagation in combustion synthesis of the (Ti–B–C) systems. The experiments were performed on the stoichiometric sample mixtures and nonstoichiometric samples (the amounts of B/C are in excess of that of Ti compared with stoichiometric composition).

In the (Ti–B–C) system, only  $TiB_2$  and  $TiC$  in the products were detected, except for residual boron or carbon. Products such as  $TiB$ ,  $B_4C$ , and remaining titanium have not been detected. In the stoichiometric mixture,  $TiB_2$  and  $TiC$  are produced at a ratio which corresponds to the starting mixture ratio between (Ti + 2B) and (Ti + C) components. It is considered that all of boron and carbon would be reacted with titanium. On the other hand, in the nonstoichiometric mixture, it is considered that the boron and carbon would remain after all titanium transferred to  $TiB_2$  and  $TiC$ , judging by the fact that a broad pattern could be confirmed in XRD profiles. Furthermore, it is clear that  $TiB_2$  can be produced overwhelmingly more than  $TiC$ . These results imply that the reaction in (Ti + 2B) system proceeds better than that in the

**Table III.** Propagation Characteristics in Each Region

	Regime I	Regime II	Regime III
Primary reaction	(Ti–B) system	(Ti–C) system	(Ti–C) system
Mole amount	Boron $\geq$ carbon	Boron $\geq$ carbon	Carbon $\geq$ boron
Dominant factor	High superiority of (Ti + 2B) reaction		High specific heat of boron
Propagation velocity	Decrease with $X_C$	Almost constant	Increase with $X_C$



(Ti + C) system. This tendency of the superiority of the reaction in (Ti + 2B) system decreases in with larger carbon particles.

The characteristics of propagation rate are roughly categorized in three regions following the mole fractions of (Ti + C) component in the reactants,  $X_C$ . When  $X_C$  is small, the propagation rate decreases drastically with increasing  $X_C$  (regime I). When  $X_C$  is large, the propagation rate increases gradually with  $X_C$  (regime III). Between regime I and III, the propagation rate is almost constant (regime II). The ranges of these regimes vary with the carbon size. The smaller the carbon diameter, the narrower the range of the regime I and the broader the range of the regime III, because the smaller carbon would react more easily with titanium. In regime I, the reaction between titanium and boron is predominant and carbon may play a role as an inert substance because of the greater superiority of the reaction in the (Ti + 2B) system compared to the (Ti + C) system. On the other hand, in the regime III, the reaction between titanium and carbon is

predominant and boron may play a role as an inert substance because of the larger specific heat of boron. The specific heats and the reaction heats would play a great role in the peculiar tendency of the (Ti–B–C) system.

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