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Characteristics of the combustion synthesis of TiC and Fe–TiC composites

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The combustion synthesis of TiC, using the thermal explosion mode, was investigated by varying some of the process parameters including the reactant particle size, the pre-compaction pressure, and the heating rate. Based on these observations, a combustion model for the reaction was developed. When iron was added to titanium and carbon black powders, the ignition temperature was dictated by the eutectic temperature of the Fe–Ti system. Iron acted as a moderator for the reaction and led to a decrease in the combustion temperature.

1. Introduction

Self-sustaining reactions between solid elements have been of great interest to materials scientists and engineers for the last two decades. The conventional process, often referred to as self-propagating high-temperature synthesis (SHS), has received comprehensive attention. In this process a small part of the reactant sample is ignited at a high temperature, creating a combustion wave which propagates through the entire sample. A similar practice, known as thermal explosion, involves the uniform heating of the whole sample until the ignition point is reached. At this temperature, T_{ig}, a spontaneous exothermic reaction occurs allowing the temperature of the sample to rise to a maximum value known as the combustion temperature, T_{comb}.

It has been demonstrated that regardless of which mode of reaction is utilized, the products are identical and the maximum temperatures are nearly the same [1]. In theory, the highest temperature to which the product phase may be raised is the adiabatic temperature, T_{ad}, which can be calculated from thermodynamic functions [2]. In practice, because the rate of the exothermic reaction is extremely high in both the combustion and thermal explosion modes, the highest temperature to which the product is raised is often assumed to be the adiabatic temperature [2].

Sato and Munir [3] have discussed the construction of a SHS diagram (Fig. 1) which indicates the difference between the combustion and thermal explosion mode of ignition. Thermal explosion, which was the subject of this investigation, has several advantages over the conventional SHS process. These include: (a) a product of higher purity due to the elimination of the filtering effect, (b) a higher possibility of obtaining complex and/or metastable phases, and (c) the possibility of formation and densification of materials at the same time. These are the subject of other work, currently under investigation by the authors.

The combustion synthesis of TiC has been extensively studied by a number of researchers [4–10] and the Ti–C system is commonly considered to be a model system for SHS processes. There is, however, a general lack of consistency in the combustion data and no firm understanding of combustion mechanisms. The thermal-explosion mode of SHS has received less attention and the mechanism of formation of composites has been studied very little.

The objective of the work presented here was to investigate the effect of the starting materials and the operating variables on the combustion characteristics of TiC when the thermal explosion mode is used. The extremely fast reaction between two solid elements has been explained by Vadchenko *et al.* [4], who investigated the ignition and combustion process between titanium and carbon, using carbon-coated titanium wires. It was concluded that the combustion process starts at the melting point of titanium and the formation of the carbide proceeds by subsequent crystallization from a molten phase. According to this model, no reaction occurs at a temperature lower than the melting point of titanium. Mullins and Riley [5] reported an ignition temperature of 1500–1600 °C for the Ti–C system, whereas an ignition temperature of 1667 °C was reported by Advani et al. [6]. However, it was observed in the present investigation that under certain conditions a powder mixture may be ignited at temperatures much lower than the melting point of titanium. During the present study, a combustion model was developed to characterize the combustion synthesis of TiC and Fe–TiC composites.

2. Experimental procedure

Carbon black and titanium powders were mixed at an equi-atomic stoichiometric ratio. In the second part of the study, different quantities of iron powder were added to obtain composite products with iron compositions ranging from 2.7%–85%. Pellets, 11.3 mm

TABLE I Summary of the experimental conditions and results

Sample	Titanium particle size, d (μm)	Precompaction pressure (MPa)	Heating rate, (°C min^{-1})	Ignition temp. (°C)	Combustion temp. (°C)	Remarks
A1	< 45	4	350	1166	2610	
A2	< 100	4	350	1206	2500	
A3	< 100	4	250	None[b]	–	Max. temp. 1500 °C
A4	< 100	10	350	None[b]	–	Max. temp. 1350 °C
A5	< 100	2	350	1140	2620	
A6	< 100	None	350	None[b]	–	Max. temp. 1350 °C
A7	< 500[a]	4	350	None[b]	–	Max. temp. 1450 °C
A8	< 500	2	350	None[b]	–	Max. temp. 1350 °C

[a] 70% < 250 μm 10% < 100 μm.

[b] These samples did not ignite at the maximum temperature shown.

diameter with a weight of 3.0 g, were compacted in a ceramic die rather than in a steel die which was observed to cause segregation of iron due to its magnetic effect. Other specifications and some of the experimental results are summarized in Table I. Precompacted samples were heated to ignition (or otherwise) in a graphite crucible, using an induction furnace. The furnace was first evacuated and then filled with argon to a total pressure of about 0.7 atm. This procedure was repeated two or three times to maintain a very low partial pressure of oxygen in the furnace. For each run a temperature–time response curve was obtained, using a two-colour pyrometer together with a computerized data acquisition system which could register as many as 500 readings per second. With these facilities it became possible to register the temperature change of the sample during the explosion time which was normally of less than 2 s duration.

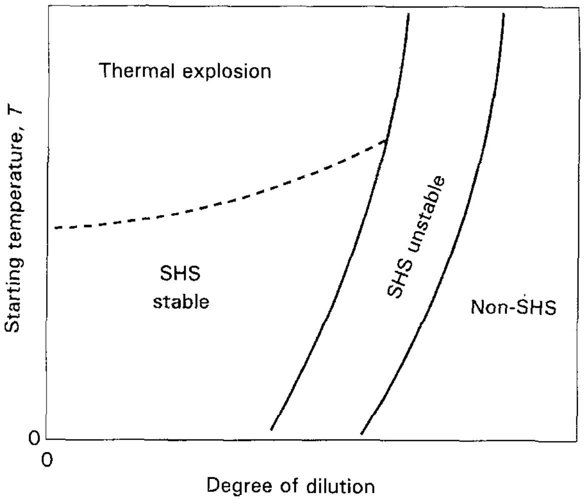

Figure 1 Schematic representation of an SHS diagram.

3. Results

3.1. Thermal explosion of compacted C–Ti powder

3.1.1. Effect of titanium particle size

When titanium powder of diameter in excess of 100 μm and carbon black were heated up to a temperature as high as 1450 °C, at a rate up to 350 °C min^{-1}, the reaction did not self-propagate. X-ray diffraction analysis showed evidence of the formation of TiC by solid-state diffusion of carbon at the TiC/Ti interface. This was confirmed by the optical micrograph in Fig. 2 which shows the development of a thin TiC layer around a titanium particle.

When titanium powder of a particle size less than 45 μm was used, a reaction was observed to occur by thermal explosion which ignited at 1166 °C and reached a combustion temperature of 2610 °C. TiC was formed as a continuous phase as shown in Fig. 3. With a particle size between 45 and 100 μm, ignition took place at 1206 °C and the maximum temperature reached was 2500 °C. Fig. 4 represents plots of temperature against time for these two reactions. The first 3–4 s of the plots show the rate at which the samples had been heating up just prior to ignition. It is evident that once ignition occurs the sample temperature rises steeply and the reaction proceeds extremely fast and is complete within 1 s.

Figure 2 Optical micrograph of a titanium particle, showing a TiC layer, produced by solid-state diffusion.

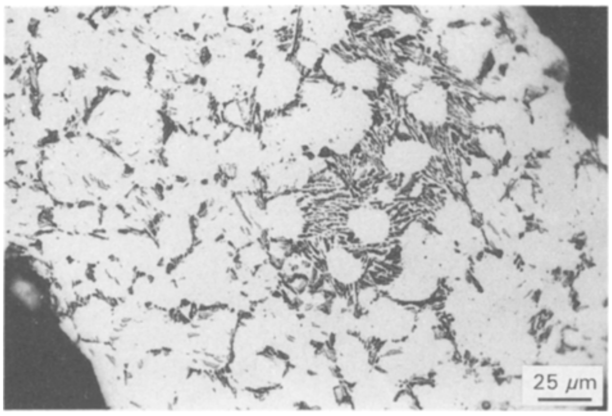

Figure 3 Optical micrograph of TiC produced by SHS reaction.

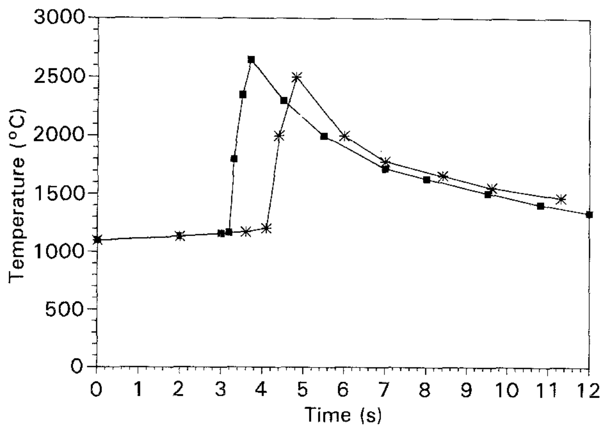

Figure 4 Variation of temperature with time for a thermal explosion of Ti–C mixture; titanium particle size, (■) < 45 μm, (*) between 45 and 100 μm.

3.1.2. Effect of heating rate

When titanium powder of particle size below 45 μm and carbon black were heated at a rate of 250 °C min^{-1} the reaction did not take place in the self-supporting manner, even after reaching temperatures as high as 1550 °C. X-ray diffraction data demonstrated that the reaction after 3 min at this temperature was incomplete. Microscopic examination showed evidence of a layer of TiC growing around titanium particles by solid-state diffusion of carbon. On the other hand, when a heating rate of 350 °C min^{-1} was used the reaction was observed to self-propagate at 1166 °C.

3.1.3. Effect of pre-compaction pressure

The effect of pre-compaction on the characteristics of the combustion reaction is shown in Table I. While a non-compacted powder mixture (i.e. loose powders) did not ignite at 1350 °C, a pre-compaction pressure as low as 2 MPa reduced the ignition temperature to as low as 1140 °C. Higher pre-compaction pressures, however, led to higher ignition temperatures. A critical pre-compaction pressure of 10 MPa was observed to exist. Above this the reactants did not react in a self-supporting manner when heated up to 1350 °C. Hence, there exists a lower and a higher pre-compaction limit which depends on the process variables such as the particle size and the heating rate.

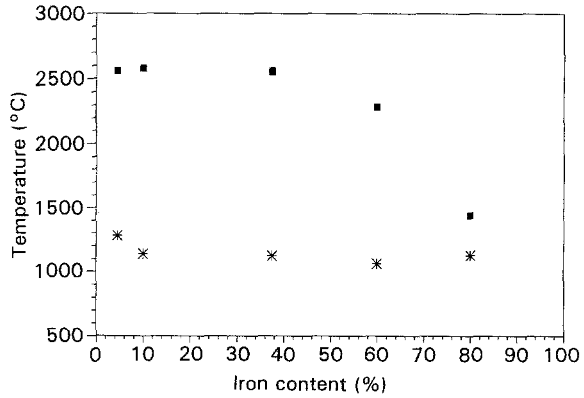

Figure 5 Plots of (*) ignition and (■) combustion temperature as a function of iron content.

3.2. Thermal explosion of compacted Fe–Ti–C powder

As dicussed above, the ignition temperature of carbon and titanium powder with a particle size in excess of 100 μm was higher than 1550 °C. Even titanium powder smaller than 45 μm did not ignite at 1550 °C when a heating rate of 250 °C min^{-1} was used. However, addition of as little as 2.7 wt % iron powder to the mixture of titanium and carbon black decreased the ignition temperature to 1250 °C, even though titanium powder in excess of 250 μm diameter was used. Fig. 5 is a plot of the ignition and adiabatic temperatures against the content of iron in the sample. It is evident that as the iron content increases, the ignition temperature decreases and reaches a minimum of 1060 °C at 60 wt % iron. For higher dilutions, the ignition temperature increases to about 1130 °C for the sample containing 80 wt % iron. The combustion temperature remains almost unchanged up to a certain dilution and then it drops to 1442 °C for the sample containing 80 wt % iron. Samples containing more than 80 wt % iron did not react in a self-supporting manner.

The heating rate and the titanium particle size did not have a significant effect on the ignition temperature when the reacting samples contained up to 80 wt % iron. For instance, an Fe–Ti–C mixture could be ignited at 1150 °C with a heating rate as low as 200 °C min^{-1} and a titanium particle size as large as 250–500 μm. The combustion temperature, however, decreased with decreasing heating rate and increasing titanium particle size.

4. Discussion

4.1. Combustion model of the thermal explosion mode

A physical and theoretical model has been developed in order to explain the experimental observations made during the thermal explosion of titanium and carbon mixtures.

When a sample of titanium and carbon is heated in an inert atmosphere at temperatures higher than 950 °C the following reaction proceeds by solid-state diffusion of carbon to the Ti/TiC interface.

$$\mathrm{Ti}_{(s)} + \mathrm{C} = \mathrm{TiC}_{(s)} \quad \Delta H^{\circ}_{298} = -184\ \mathrm{kJ\,mol^{-1}} \tag{1}$$

Because enthalpy, H, is a state function, at any temperature other than 298 K, the standard state enthalpy change (heat of the reaction) can be calculated, using the following equation

$$\Delta H^{\circ}_{\mathrm{T}} = \Delta H^{\circ}_{298} + \int_{298}^{\mathrm{T}} \Delta C_{\mathrm{p}} \mathrm{d}T \qquad (2a)$$

where

$$\Delta C_{\mathrm{p}} = C_{\mathrm{p}}(\mathrm{TiC}) - [C_{\mathrm{p}}(\mathrm{Ti}) + C_{\mathrm{p}}(\mathrm{C})] \qquad (2b)$$

When the above reaction starts, at any point in the sample two opposing thermal processes operate: heat release due to the exothermic reaction, and heat loss due to the internal temperature gradient and radiation. If at any part of the sample the rate at which exothermic heat is released becomes greater than the heat loss, there is a build up of thermal energy in that part of the sample so that its temperature increases sharply and a self-sustaining reaction is initiated. Therefore, any parameter that increases the rate of the reaction at this stage, (e.g. finer titanium powder) or decreases the rate of heat loss from the sample, (e.g. low heat conductivity) causes thermal energy to be accumulated in a part of the specimen and so can initiate a self-sustaining reaction. This model, which is shown schematically in Fig. 6, can explain the combustion synthesis of TiC by the thermal explosion mode, using titanium powder and carbon black as the starting materials. When a pellet of pre-mixed titanium and carbon is heated in a furnace the temperature of the sample and its surroundings (i.e. furnace) may follow the two paths shown in Fig. 6. At lower temperatures the sample is heated by heat transfer from the furnace, so the sample temperature is always lower than the furnace temperature (region I, Fig. 6). As soon as carbon and titanium start to react by solid-state diffusion, the slope of the line showing the sample temperature, increases due to the heat released by the exothermic reaction (region II, Fig. 6). In region II the temperature difference between the furnace and the sample depends on the rate of the reaction. If the rate of the reaction is high enough so that the rate of heat gain in the sample becomes greater than the heat loss, then the temperature of the sample will increase exponentially and this situation will lead to the ignition and combustion of the sample (region III, Fig. 6).

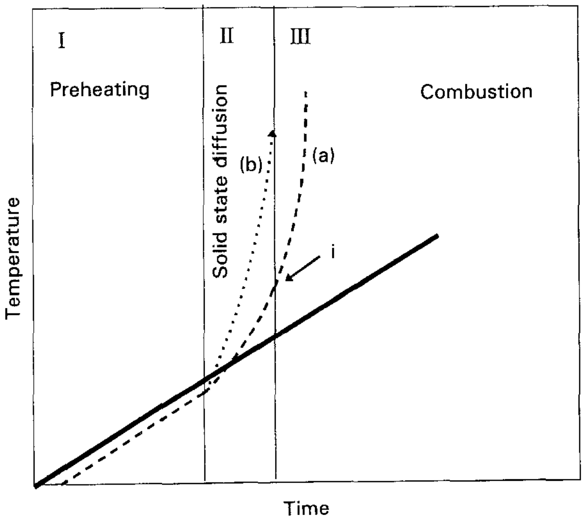

Figure 6 Schematic representation of temperature profile during thermal explosion. (———) Furnace temperature. (a) Sample temperature, (b) ignition point temperature.

As mentioned above, the initiation of the reaction might happen at one or more points, rather than uniformly in the whole sample. This is due to the heterogeneous nature of the samples which may have a broad particle-size distribution and density variation. Usually, ignition starts at fine titanium particles assuming the minimum temperature gradient is maintained for the reaction to proceed. The resulting local temperature increase could then ignite the entire sample. Curve (B) in Fig. 6 shows schematically the temperature of a particular region of the sample where ignition is initiated. When the temperature of that particular part reaches the melting point of titanium, the heat released by the exothermic reaction between titanium and carbon raises the temperature of the sample to such a level that the reaction becomes self-sustaining and is complete within a few seconds. Because combustion can start at one or more points and everything happens so fast, it is very difficult to define exactly the ignition temperature. However, it seems to be sensible and convenient to define it as the mean sample temperature just before the explosion, that is the temperature that the pyrometer shows when it is focused on the sample (point "i" in Fig. 6).

Using this model, it is possible to explain the experimental results obtained from the study of the ignition temperature as a function of the heating rate, the titanium particle size and the amount of pre-compaction. It seems all these variables affect the shape of the curves in region II. For example, at higher heating rates, when a given temperature is reached, the thickness of the TiC layer obtained by solid-state diffusion will be smaller and, therefore, the diffusion flux is greater. This leads to a higher temperature gradient and the width of region II becomes smaller. Consequently, an increase in the heating rate would lead to a decrease in the ignition temperature. It is obvious that a lower heat loss has almost the same effect as the higher heating rate.

The influence of pre-compaction on the ignition temperature arises from its influence on the thermal conductivity of the whole compact. As explained before, the higher the thermal conductivity the higher the rate of heat loss and so the more difficult ignition. The higher and lower pre-compaction limits, as mentioned above, can be explained by the fact that the compaction density plays a dual rule. A higher value of pre-compaction density increases the contact points of the reactants which results in an enhanced reaction rate and thereby makes ignition easier. On the other hand, it also tends to increase the thermal conductivity which frustrates the ignition. The volumetric heat capacity of the samples, also, increases with pre-compaction pressure, with a net effect on the ignition temperature. A sample with higher volumetric heat capacity requires a greater quantity of thermal energy to raise the temperature of the sample to the critical value for ignition, and thereby delaying or preventing ignition.

4.2. Theoretical explanation of the combustion model

In modelling the combustion process the following assumptions were made:

1. Combustion initiates in a small region inside the pellet, as shown in Fig. 7. For simplicity this region is assumed to be cubic with alternate layers of titanium and carbon.
2. The thickness of the titanium layer is equal to the titanium particle size.
3. The heat transfer within the cube is fairly fast so that there is no temperature variation between alternate layers.

If within dt s the thickness of each TiC layer increases by dx and the temperature of the cubic region increases by dT due to the release of exothermic heat, then dT can be expressed by

$$\mathrm{d}T = \frac{\mathrm{d}(H_1 - H_2)}{nvC_\mathrm{p}} \qquad (3)$$

where H_1 is the heat release within the cubic region due to the exothermic reaction, H_2 is the heat loss to the surroundings, C_p is the molar heat capacity at constant pressure, v is the volume of the cubic region, and n is the total number of moles of TiC and/or (Ti + C) per unit volume of the cubic region (i.e. no volume change by the reaction). Because

$$\mathrm{d}H_1 = -(\Delta H_\mathrm{f})nl^2\mathrm{d}x\left(2\frac{l}{d}\right) \qquad (4)$$

and

$$\mathrm{d}H_2 = K(T - T_\mathrm{s})nvC_\mathrm{p}\mathrm{d}t \qquad (5)$$

where ΔH_f is the molar enthalpy of formation of TiC, d is the thickness of one titanium plus one carbon layer, l is the length of each side of the cube, T is the temperature of the cubic region, T_s is the temperature of the surroundings, and K is a constant depending on the thermal conductivity and geometry and is defined per second. The number of TiC layers in the cubic region are $(2l/d) - 1$. For very small values of d, $(2l/d) - 1 \approx 2l/d$. Thus

$$\mathrm{d}T = \frac{(-\Delta H_\mathrm{f})nl^2\mathrm{d}x(2l/d) - K(T - T_\mathrm{s})nvC_\mathrm{p}\mathrm{d}t}{nvC_\mathrm{p}} \qquad (6)$$

and

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{-2\Delta H_\mathrm{f}}{dC_\mathrm{p}} \cdot \frac{\mathrm{d}x}{\mathrm{d}t} - K(T - T_\mathrm{s}) \qquad (7)$$

In the above equation dx/dt, which represents the rate of growth of TiC, is a function of temperature.

Equation 7 shows that the smaller the reactant particle size, that is the smaller the value of d, the larger the value of dT/dt and so the higher the sample temperature after a given time which in turn results in a larger dx/dt. On the other hand, the higher the rate of growth of TiC, dx/dt, the higher the rate of increase in temperature, dT/dt. This positive feed-back exponentially increases the temperature of the cubic region and causes the initiation of the self-supporting reaction.

With the aid of this thermal model which is in agreement with the combustion model, it is possible to explain the effect of most variables, such as particle size, on the combustion behaviour of Ti–C mixtures.

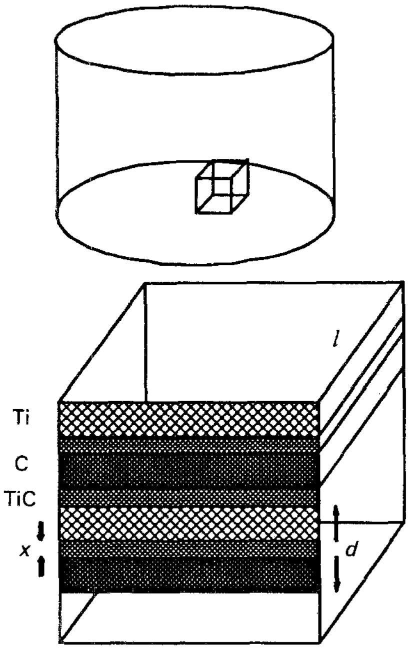

Figure 7 Schematic representation of powder layers.

4.3. Combustion characteristics of the Fe–Ti–C system

The ignition and combustion characteristics of iron, titanium and carbon powders can be explained by the fact that during the heating period, titanium and iron powders react in the solid state to produce $FeTi_2$ which is an eutectic compound having a melting point of 1085 °C. At the ignition temperature, which almost matches the melting point of the Fe–Ti alloy, carbon dissolves in the molten droplets of $FeTi_2$ and the subsequent production of TiC releases enough heat to initiate a self-sustaining reaction. This model was examined by heating a pre-compacted mixture of Fe–Ti–C to 1100 °C and quenching the sample just before ignition. SEM inspection of this sample showed some liquid droplets around the iron particles as shown in Fig. 8. Because the maximum temperature attained by the sample was well below the melting point of both iron and titanium, it is suggested that

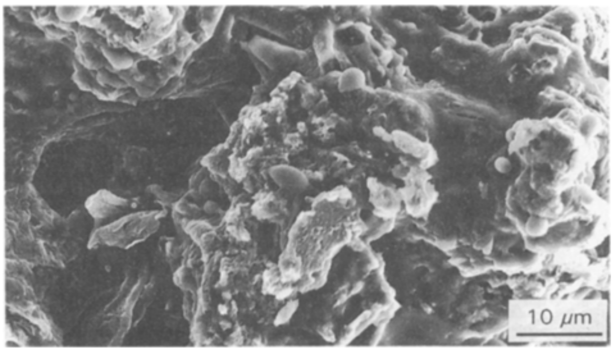

Figure 8 Scanning electron micrograph of an iron particle. Sample had been quenched just prior to thermal explosion.

diffusion of either carbon or titanium in iron has produced the low melting point phase. Point analysis of these particles, using X-ray fluorescence, confirmed the latter.

5. Conclusion

The present study has shown that the reactant particle size has an important effect on the nature of the combustion synthesis of TiC. For a titanium particle size in excess of 100 μm no ignition was possible even after heating to 1550 °C. The coarse titanium powder was believed to reduce the rate of the reaction by solid-state diffusion, and also absorb the exothermic heat of the reaction and therefore act as a moderator. When titanium of a smaller particle size was used, the reaction occurred in a self-supporting manner. The ignition temperature decreased by decreasing the reactant particle size as a result of greater contact between the reactants, and thereby a higher rate of evolution of the exothermic heat. At low heating rates the reaction did not ignite because of the gradual build-up of a TiC layer around titanium particles. By contrast, at higher heating rates, the reaction was self-sustaining as it ignited prior to the formation of a substantial TiC layer. The effect of the processing variables, such as pre-compaction, particle size, and heating rate, on the ignition temperature was in agreement with the combustion model which has been developed. The addition of iron to titanium and carbon black changed the characteristics of the self-propagating reaction. In this case the ignition temperature was dictated by the eutectic temperature of the Fe–Ti system. Increasing the amount of iron led to a decrease in the combustion temperature as more of the exothermic heat was absorbed.

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References

1. Y. S. NAIBORODENKO, V. I. ITIN and K. V. SAVITSKII, *Sov. Powder Metall. Ceram.* **7** (1970) 562.
2. J. B. HOLT and Z. A. MUNIR, *J. Mater. Sci.* **21** (1986) 251.
3. N. SATO and Z. A. MUNIR, in "Proceedings of the Symposium on High Temperature Materials V", Vol. 9–18, edited by W. B. Johnson and R. A. Rapp (Electro Chemical Society, Pennington, NJ, 1990) p. 99.
4. S. G. VANDCHENKO, YU. M. GRIGOR'EV and A. G. MERZHANOV, *Combust. Explos. Shock Waves* **12** (1976) 606.
5. M. E. MULLINS and E. RILEY, *J. Mater. Res.* **4** (1986) 408.
6. A. H. ADVANI, N. THADHANI, H. A. GREBE, R. HEAP, C.COFFIN and T. KOTTKE, *Scripta Mettall. Mater.* **25** (1991) 1447.
7. A. G. MERZHANOVA, G. G. KARYUK, I. P. BOROVINSKAYA, S. Y. SHARIVKER, E. I. MOSHKOVSKII, V. K. PROKUDINA and E. G. DYAND'KO, *Sov. Powder Metall. Met. Ceram.* **266** (1981) 709.
8. V. M. SHKIRO, V. N. DOROSHIN and I. P. BOROVINSKAYA, *Combust. Explos. Shock Waves* **16** (1980) 370.
9. A. SAIDI, A. CHRYSANTHOU and J. V. WOOD, in "Third Euro-Ceramics", Vol. 1, edited by P. DURAN and J. F. FERNANDEZ (Fuenza Editrice Iberica S.L. Spain, 1993) p. 97.
10. D. C. HALVERSON, K. H. EWALD and Z. A. MUNIR, *J. Mater. Sci.* **28** (1993) 4583.

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