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Structure of the combustion wave in the combustion synthesis of titanium carbides

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From the recorded images of combustion wave propagation during the combustion synthesis of titanium carbide, real time combustion velocities have been determined with increase of density of the compact. Results demonstrate that the combustion velocity exhibits a maximum with increase of density of the compact, and the wave propagates in a steady-state manner. Real time temperature profiles suggest that adiabatic conditions exist during the steady-state propagation of the combustion wave. Analysis of the images for the propagation of the combustion wave suggest that density plays a major role in the nature of propagation and whether the combustion wave propagates or not. Pore structural analysis of the carbides indicate collapse of the original porosity of the carbons, and the collapse of porosity is attributable to an exothermic diffusional reaction occurring between liquid titanium and carbon forming a titanium carbide product layer.

1. Introduction

In self-propagating exothermic reactions between solids, ignition of finely divided solid powders can lead to propagation of a combustion wave due to the exothermicity of the reaction between the powders. At any time during the propagation of the combustion wave, no reaction would have occurred ahead of the combustion wave while the reaction would have been complete behind the combustion wave raising the temperature of the product due to the evolved heat. Reactions of this nature were first observed by Spice and Staveley [1], and the propagation of combustion wave in such systems is treated similar to the propagation of flames in gases [2, 3]. Combustion reactions of this nature have been studied widely to understand the self-propagating solid state reactions in pyrotechnic powders due to their practical applications as pyrotechnic fuses and delay elements for explosives and detonators [4, 5]. The exothermicity and self-propagating nature of solid–solid reactions have been utilized [6] to synthesize various high temperature ceramic materials like silicides, carbides, borides and sulphides of transition metals; structural materials like nickel and copper aluminides; shape memory alloys like nickelides of titanium; and hydrides of transition metals. The technique has been called either as a "combustion synthesis" technique or as a "self-propagating high temperature synthesis" technique since a combustion wave propagates on its own through the reactants once the reaction is initiated on the surface. In the past few years, the technique has emerged as an alternative synthesis technique for the synthesis of high temperature ceramic materials [7].

Three different modes of combustion behaviour such as steady-state burning, oscillatory burning, and spin burning were noted in the synthesis of various ceramic materials, and the differences in the burning behaviour were attributed to the heat losses and to the exothermicity of the reaction [6]. It was empirically noted that a strong exothermic reaction leads to the propagation of the combustion wave [8], although it is not clear whether the system is under adiabatic conditions or not. If one were to extend the theory of flame propagation in gases to solids, one would expect a steady state burning under adiabatic conditions and the combustion wave should propagate steadily at a particular rate immaterial of the length of the compact. It is not clear whether such an extension is possible to porous compacts of solids since burning occurs in condensed state without any involvement of gaseous phase, and the physical parameters such as the density of the compact, particle sizes of the reactants, and the internal surface areas of the reactants may play a vital role during the propagation of the combustion wave.

We will examine the above issues in the combustion synthesis of titanium carbide (TiC), which can be prepared by burning titanium and carbon powders in an inert atmosphere. The heat of reaction of TiC is 44 kcal mol^{-1}, and the calculated adiabatic combustion temperature corresponds to 3210 K. This system is chosen due to its practical importance (carbides of transition metals are widely used for cutting tool applications, and recently they have drawn considerable attention due to their catalytic activity similar to those of noble metal catalysts [9], and also the earlier reports seem to suggest that this system would probably exhibit a steady-state combustion behaviour [8]. Very little information exists as related to the adiabaticity, steady-state burning, and the reaction zone thickness during the propagation of the combustion wave through the compacts of titanium and carbon. The relevant work related to the understanding of combustion process involves determining the

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effect of particle size on the extent of conversion [10], determining melting of an inner core of titanium in a titanium–carbon compact [11], and attempts to model the synthesis procedure [12, 13]. A great deal of effort has been directed towards finding commercial applications as can be judged by the number of patents on the combustion synthesis technique [6]. There has been no systematic investigation of combustion velocities and corresponding combustion wave structure. It is not known whether combustion synthesized carbides possess the required pore structure for catalytic applications or not.

The objective of the present investigation is to extend our understanding of combustion wave propagation in solids, and the influence of physical parameters on the propagation of the combustion wave in practical systems of high technological importance. The results presented here are for the combustion synthesis of TiC and the specific issues addressed include (a) the parameters influencing the combustion wave propagation, (b) the structure of the combustion wave from real time temperature profiles, and (c) the mechanism involved in the synthesis of carbides. The study is extended to determine whether a carbide with a porous structure and high surface area can be synthesized by starting with a carbon powder having a high surface area and micropores of 1 nm.

The materials and experimental methodology is briefly discussed in the next section, which is followed by presentation and discussion of experimental results.

2. Materials and experimental methodology

As-received titanium and carbon powders were thoroughly mixed in the desired C to Ti atomic ratios, and cylindrical compacts with a diameter of 19.6 mm and approximately 30 mm in length were obtained by pressing the powders using a hydraulic press in a die steel die with two plungers. Pressures in the range 70 to 400 MPa were applied uniaxially on both sides of the powdered mixture and the pressure was kept constant on each side for 3 min. Combustion synthesis experiments were carried out in a stainless steel chamber (Fig. 1 shows the schematic of the set-up), and two 12.5 cm quartz windows were used for recording the combustion wave propagation. The cylindrical compact was placed on a boron nitride disc and a tungsten ignition coil was located a few millimetres above the upper surface of the compact. The chamber was evacuated to 10 μm by flushing with argon between the evacuations. After the evacuation, the chamber was pressurized to 1.2 atm of argon and the surface of the sample was ignited by applying current to the ignition coil in the range of 40 to 50 A. Unless indicated otherwise specifically, most of the experiments were carried out by mixing titanium and carbon in the stoichiometric range, nominally referred to as $TiC_{1.0}$.

A very fine tungsten–5% rhenium and tungsten–26% rhenium thermocouple was placed in a small groove cut on the surface of the compact to obtain an ignition temperature profile. A thin layer of the powder with the same composition as that of the compact mixture was spread on the surface covering the thermocouple bead as shown in configuration A of Fig. 2a. Thermocouples were forced to the centreline of the compact to obtain real time–temperature profiles by drilling holes in the compact as shown in configuration B of Fig. 2a. The thermocouple hole was filled with the same powder as that of the compact to minimize heat losses and any errors that may be introduced to the reaction temperature due to the heat losses. A new set of thermocouples was used for each experiment since thermocouples were fused to the product after the propagation of the combustion wave.

A commercial gas flow type adsorption device was used for determining the pore structural properties of titanium and carbon powders along with combustion

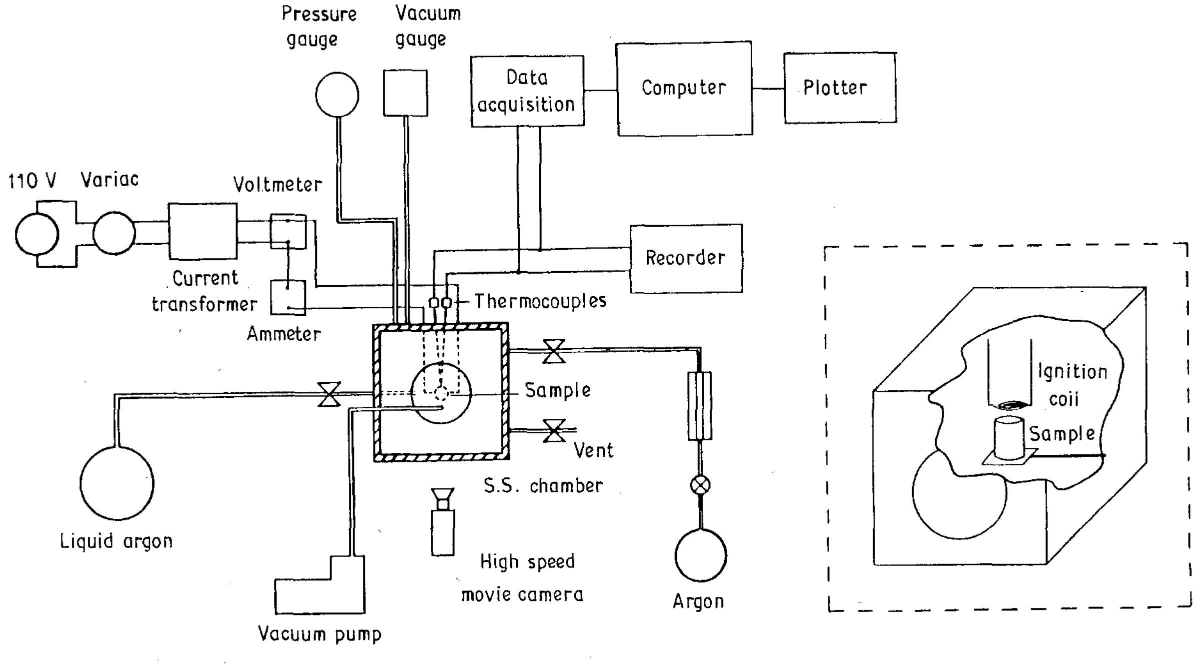

Figure 1 Schematic of the experimental apparatus for combustion synthesis of materials.

synthesized titanium carbide powders. Samples were heated at 200 °C for 12 h in vacuum to remove the trapped gases from the pore structure, and the experimental determination of surface area and pore structural parameters was carried out using nitrogen as an adsorbent as described elsewhere [14].

3. Results

A typical ignition profile obtained with a thermocouple located on the upper surface of the compact (of titanium and carbon powders) as shown in configuration A of Fig. 2a indicated a sudden rise in temperature to the maximum combustion temperature following ignition (Fig. 2b). During the passage of the combustion wave, adsorbed gases and impurities were expelled from the sides of the compact and the combustion wave separated the product, TiC, from the reactant mixture titanium and carbon, until the propagation was complete. A thermocouple located at the centreline of the compact indicated a small increase in temperature followed by an abrupt and sudden increase to 2869 K, when the combustion wave passed the location of the thermocouple. The temperature profile indicated a sudden cooling after attaining the maximum temperature and the temperature of the product dropped to 600 K in just a few minutes. The reactants titanium and carbon were converted to TiC following the propagation of the combustion wave. The heating rate calculated based on Fig. 2b is $2.9 \times 10^5\ \mathrm{K\,min^{-1}}$ while the approximate cooling rates are in the range 2 to $8 \times 10^3\ \mathrm{K\,min^{-1}}$. It should be noted that in combustion synthesis technique only the compact was at a high temperature for a few minutes while the surrounding chamber was close to the room temperature. In contrast, conventional synthesis of carbides requires heating of the reactants at a furnace temperature of 2000 to 2400 K for several hours [15].

Combustion wave propagation was recorded using a CCD solid state camera coupled with a high speed timer and a recorder. The time-resolved combustion velocities were obtained by calculating the combustion velocities from the recorded images of combustion wave propagation during the synthesis of TiC. The rate of propagation determined at several locations along the length of the pellet suggest a steady-state propagation as can be noted from the constancy of the velocity with respect to length of the compact (Fig. 3a). In the case of a 62% TMD (abbreviated for % of theoretical maximum density) compact, velocity was constant up to 2/3 the length of the compact and then dropped to a different value. This suggests that the wave propagates in a steady-state manner and then changes to an unsteady behaviour. Interestingly, the combustion velocity (averaged over the length of the compact) shown in Fig. 3b increased with increase of % TMD of the compact, followed by a decrease. Traces of the images of combustion wave propagation obtained at several % TMDs are indicated in Fig. 4. Each line denotes location of the wave at a particular time. The distance between the lines along the length

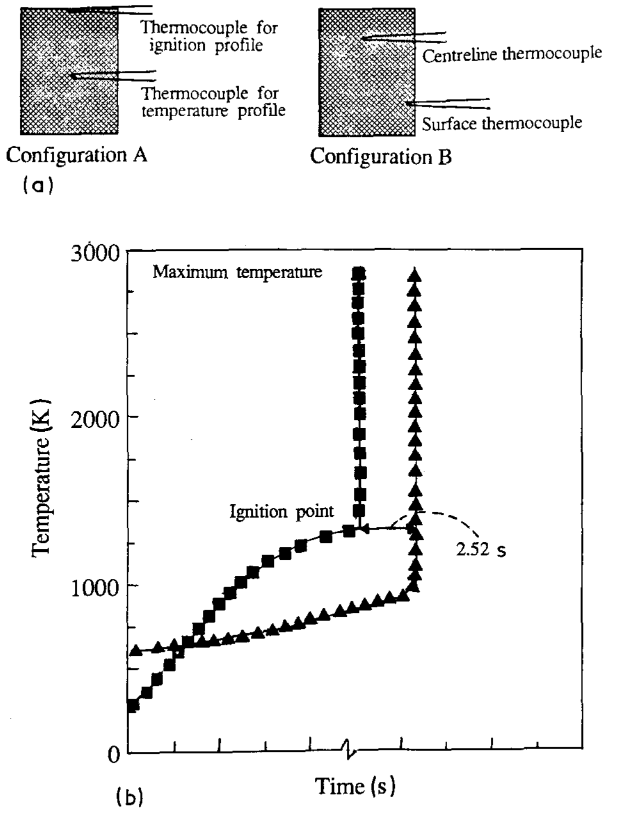

Figure 2 (a) Configurations used for obtaining ignition (■) and temperature (▲) profiles. (b) Real time ignition and heating–temperature profiles obtained during the combustion synthesis of titanium carbide with a stoichiometric mixture of titanium and carbon.

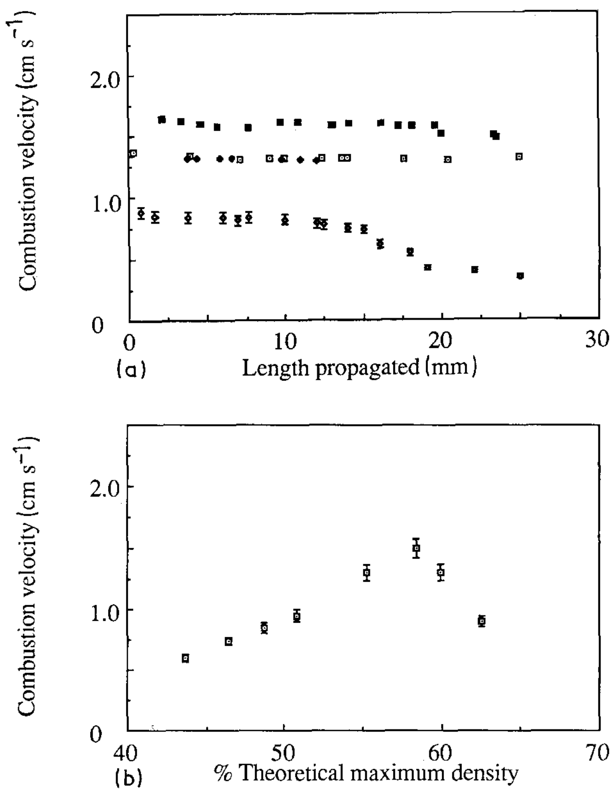

Figure 3 (a) Real time combustion velocities of compacts of Ti–C mixtures of stoichiometric composition. (□ 55.6% TMD, ◆ 55.2% TMD, ■ 58.4% TMD, ◇ 62% TMD). Compact length 22 to 30 mm, size 10 μm Ti, 11 μm C. (b) Dependence of combustion velocities of stoichiometric Ti–C mixtures on the % TMD of the compacts. (Compact length 22 to 30 mm size, 10 μm Ti, 11 μm C)

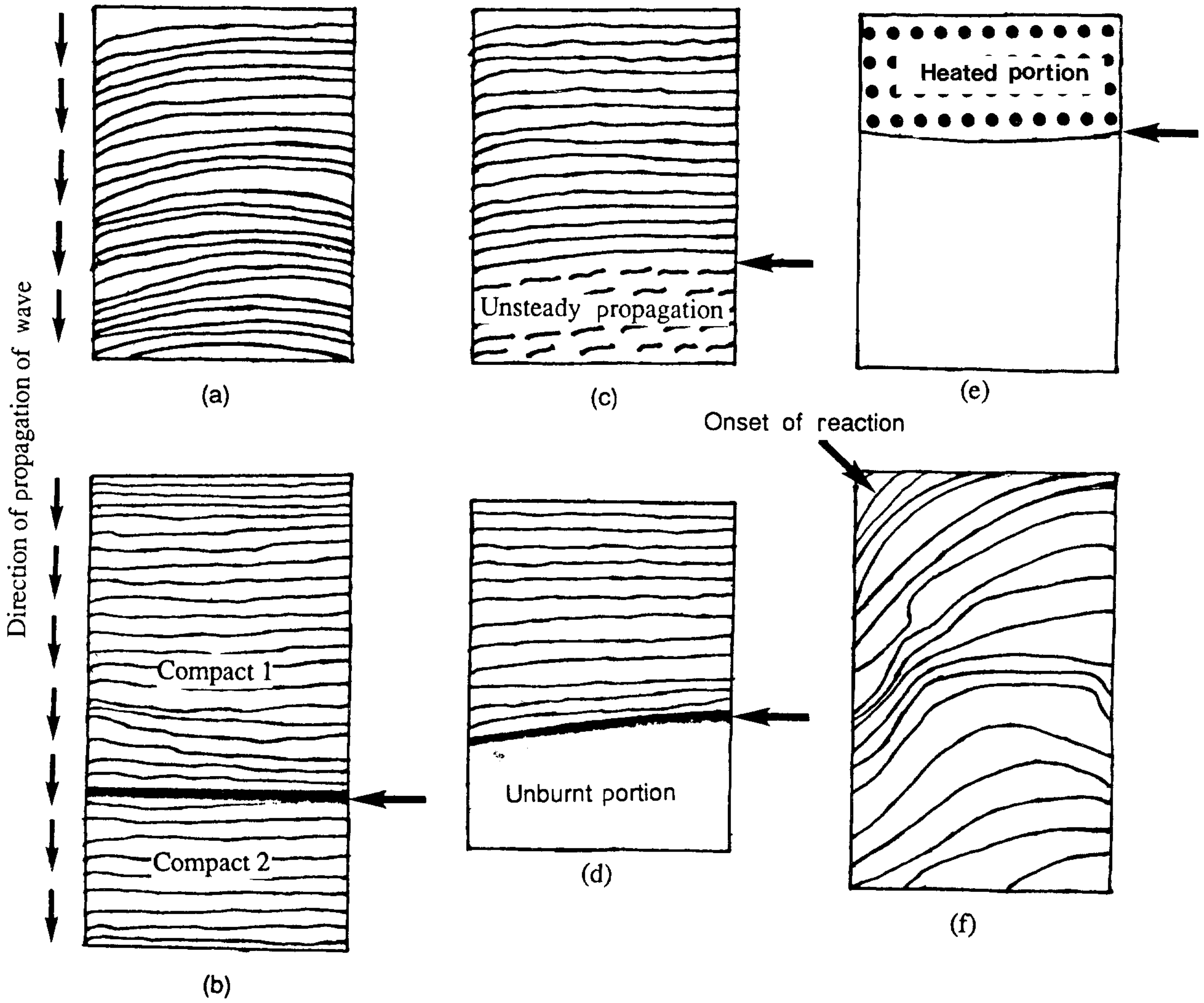

Figure 4 Structure of the combustion wave (traced from the recorded images as the wave propagated through the compacts). (a) 47.2% TMD (b) 55.6% TMD (compact 1) and 55.2% TMD (compact 2), (c) 62% TMD (d) 64.1% TMD (e) 66.6% TMD and (f) 51% TMD.

of the compact coupled with the horizontal nature of the wave across the width of the compact indicates the steady state nature of the combustion wave with increase of density. The compact length was increased to determine if length of the compact exhibits any effect on the nature of the combustion wave as it passes through the reactants since the heat losses to the bottom surface of the compact would be minimized. Two compacts of same % TMD i.e. 55.6% TMD and 55.2% TMD, but of two different lengths were stacked together as shown in Fig. 4b, and the upper surface of the compact was ignited. The combustion velocities of the two compacts were the same irrespective of the length of the compact as can be seen from Fig. 3a, and increasing the length of the compact did not alter the steady-state propagation of the wave, implying that density of a compact has a determining effect on the nature of the combustion wave.

A change in the steady state nature of the combustion wave was observed with increase of % TMD at the % TMD where a decrease of combustion velocity was observed in Fig. 3b. In the case of 62% TMD compact, the combustion wave propagated steadily to 2/3 of the length of the compact (Fig. 4c) and the mode of propagation was altered (as indicated by dotted lines) due to the instabilities created by the heat losses. Extinction was observed for 64% TMD compact after propagating to about 2/3 of the length of the compact (Fig. 4d). At 66% TMD and above, the samples could not be ignited at all and a significant portion of the compact glowed due to the continuous heating of the compact (Fig. 4e). It should be noted that the composition of the compacts was essentially the same for all the images shown in Fig. 4, and only the densities of the compacts were different. In all the experiments, the diameter of the ignition coil was kept equal to the diameter of the compact and the ignition energy was supplied to the entire surface of the compact. In most cases, ignition occurred on the upper surface of the compact as a spot and quickly spread to the entire top surface of the compact and then propagated as a combustion wave. Very rarely, a compact ignited on its side (as shown in Fig. 4f), and the combustion wave propagated in an irregular manner, and finally approaching close to steady-state behaviour at the middle of the compact as seen by the parallel lines.

To determine the adiabaticity of the compact during combustion wave propagation, real time–temperature profiles were recorded by inserting two thermocouples, one at the centreline of the compact, i.e. at 9.7 mm (compact diameter = 19.6 mm), and the second one at 3.5 mm from the surface and about 12 mm from the top thermocouple, as in configuration B of Fig. 2a. The maximum temperatures and the temperature profiles are identical as shown in Fig. 5, indicating negligible heat loss along the radial direction. Furthermore, the slopes of the temperature profiles are similar, implying the existence of a true adiabatic condition resulting in a steady state propagation of the combustion wave as shown in Fig. 3a.

The heating profiles shown in Fig. 6a imply that the time involved to reach the maximum temperature decreases with increase of density corresponding to the observed increase of combustion velocity with density in Fig. 3b. The heating profiles should comprise of a preheating period in which the reactants are heated to a certain preheat temperature prior to the onset of an exothermic diffusional reaction between titanium and carbon. Although the attained maximum temperatures (Fig. 6a) were above the melting temperature of titanium, a temperature drop associated with the heat of melting was not observable in the temperature profiles. It should be pointed out that the thermocouple bead diameter influences the response time, and the observed maximum temperature. Thermocouple beads are of the order of 180 μm, and the observed values represent an average temperature over an area in the porous compacts of Ti and C. Also, the lack of availability of microthermocouples of tungsten–rhenium (which are brittle in nature) made it difficult to measure the discrete temperatures over an area corresponding to the particle sizes of Ti and C, and the lack of marked indications regarding the end of pre-heating and the onset of diffusional reaction made it difficult to unequivocally identify the end of pre-heating and the onset of reaction from the heating profiles. Pre-heating time was considered as the time required to heat the reactants to the melting temperature of titanium, and the reaction time was considered as the time involved for the reaction to occur between liquid titanium and carbon powder.

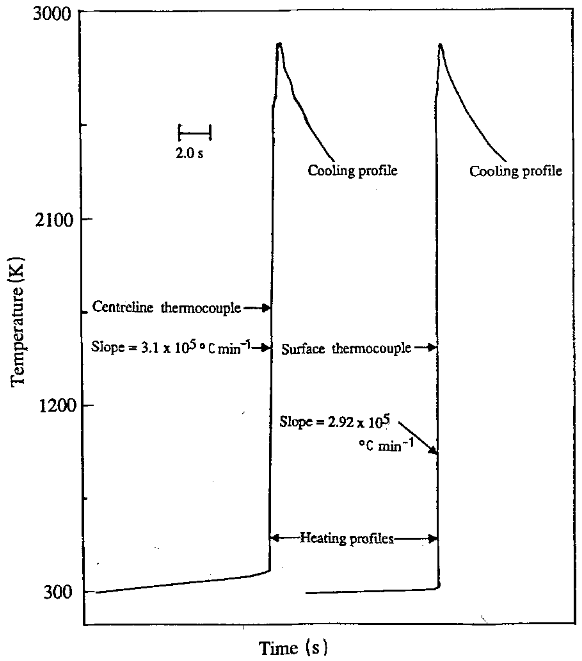

Figure 5 Temperature profiles depicting adiabaticity of the combustion wave.

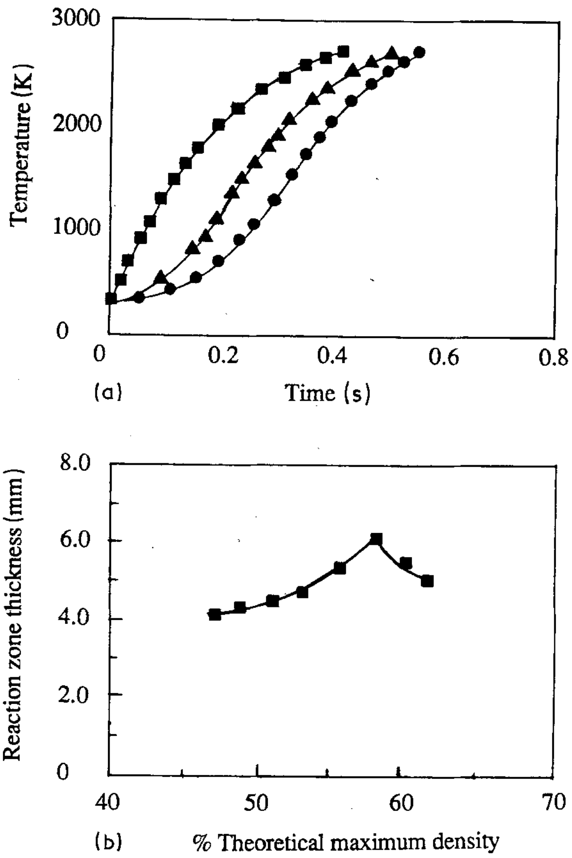

Figure 6 (a) Heating Profiles of compacts of stoichiometric composition. (● 47% TMD, ▲ 53% TMD, ■ 55.6% TMD). (b) Dependence of reaction zone thickness on the % TMD of the stoichiometric Ti–C compacts.

The temperature profiles of 52 to 55% TMD compacts were, therefore, recorded by recording the e.m.f. of thermocouples using a fast Nicolet storage oscilloscope, and were analysed in an attempt to determine the pre-heating and reaction times. The Nicolet recorded millivolt traces did not indicate any abrupt rise or discontinuities at the melting point of titanium from which the pre-heating time could have been determined, therefore, the "total time involved to reach the maximum temperature" is considered as the reaction time. The product of reaction time and combustion velocity is considered as the reaction zone thickness, therefore the heating profiles shown in Fig. 6a indicate temperature distribution within the reaction zone, while Fig. 6b denotes the relation between the reaction zone thickness and the % TMD of the compact. Note that the reaction zone thickness increases with increase of density, and then shows a decrease similar to the combustion velocity plot shown in Fig. 3b. Since the time required to reach the maximum temperature is lower for the compacts shown in Fig. 6a, it is reasonable to expect that the reaction occurs in a narrower zone. Since the reaction time considered here includes a pre-heating time and the combustion wave propagated to a finite distance within that time, the reaction zone thickness plot of Fig. 6b implies the extent of conversion of Ti and C powders to TiC as the wave propagates through the length of the compact. According to Azatyan *et al.* [10], the sum of the heating and maximal temperature zones (considered as thickness of the combustion zone) correspond to about 3.9 mm in the synthesis of TiC with 180 μm of Ti and small size of carbon at a pressure of 10 atm. Although this was the only isolated experiment found in the literature, their combustion zone thickness falls broadly within the range of values of Fig. 6b.

Increase of average particle size of Ti in the range 1.6 to 74 μm while keeping the average particle size of carbon at 11 μm indicated a significant decrease in the combustion velocity (Fig. 7a). When the average particle size of Ti was increased to 140 μm, the compact could not be ignited at all. Increase of the average particle size of carbon also showed a similar trend when the compacts of Ti and C mixture were burnt by keeping Ti size (1.6 μm) and density (56% TMD) constant. In contrast, Azatyan *et al.*'s [10] results indicate propagation of the wave at a pressure of 10 atm even when compacts with particle sizes of < 280 μm Ti and 250 to 280 μm Ti powder at a carbon size of < 1 μm were ignited. The heating profiles of larger particle sizes of Ti (Fig. 7b) indicate that the time involved to reach the maximum temperature increases with increase of particle size of Ti. This implies a slower rate of heat release. Compacts with larger particle sizes of Ti glowed intensely for notably longer periods of time, and this is reflected in the cooling profiles shown in Fig. 7c. The differences in both heating and cooling profiles with increase of particle sizes must be viewed with respect to the time scales involved in attaining the maximum temperature during the synthesis of TiC. The low heating rates, longer cooling times or glow periods imply continuation of an exothermic diffusional reaction even after the propagation of the wave.

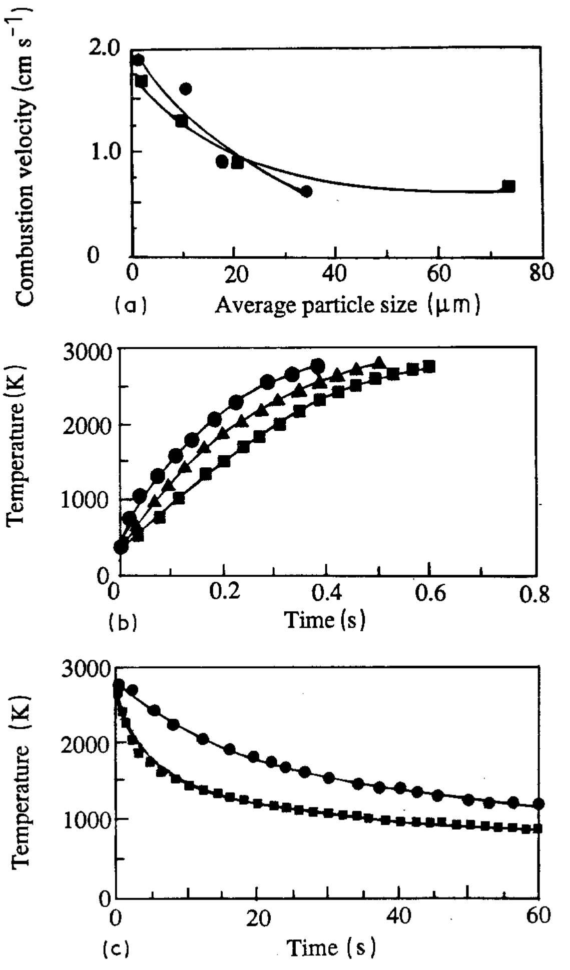

Figure 7 (a) Dependence of particle size of Ti (■) and C (●) on the combustion velocities of stoichiometric Ti–C compacts. (b) Heating and cooling profiles of stoichiometric Ti–C compacts with variation of particle size of Ti. (● 10 μm, ▲ 21 μm, ■ 74 μm) (c) As (b) (● 74 μm, ■ 10 μm)

Reduction of C to Ti ratio increases the amount of Ti present and a drop in temperature should be noticeable due to the time, and heat of melting required to melt the excess Ti. This is indeed observed as can be noted from Fig. 8, which indicates that a compact with C to Ti ratio of 0.72 indicated a drop in the temperature profile almost at the melting point of Ti. The heating profile suggests that the heat generation not only terminated at the melting point of titanium but further heat release and attainment of maximum temperature occurred rather slowly for $TiC_{0.72}$ compact as compared to the initial heating period. A comparison of Fig. 6a and Fig. 8 shows similar heating profiles for stoichiometric composition and for $TiC_{0.91}$, but addition of a diluent, TiO_2, to a stoichiometric composition decreased the combustion temperature significantly without any indication of a discontinuity at the melting point of Ti. The diluent was chosen such that it would evaporate completely at the combustion temperature.

To understand the effect of the initial micro- (< 2 nm), and meso- (2 to 50 nm) porosity of carbon powder on the pore structural properties of carbides, several graphitic and activated carbon powders with varying surface areas in the range 8 to 2500 m^2 g^{-1} were utilized in the synthesis of carbides of titanium. Surface areas of the carbides were observed to be very

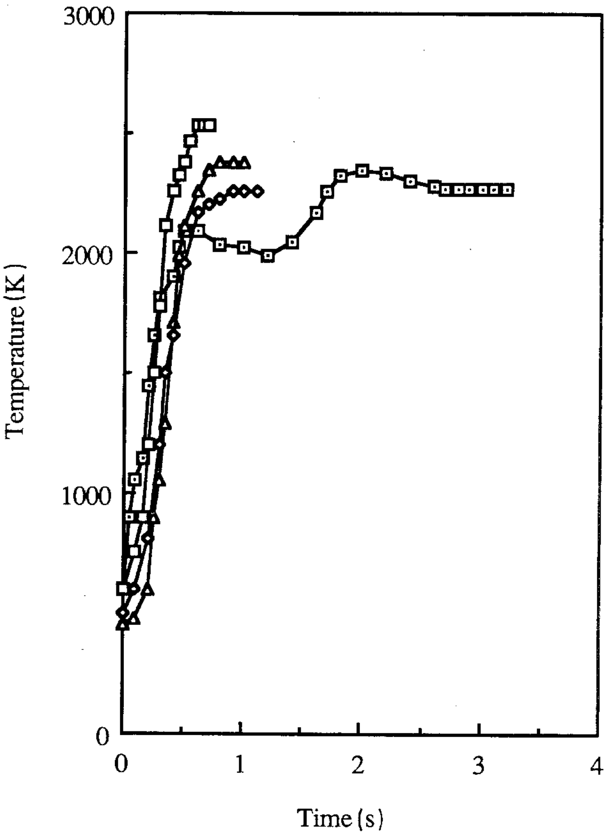

Figure 8 Effect of nonstoichiometry (□ C/Ti = 0.91, ⊡ C/Ti = 0.72) and dilution (Δ diluted with 10% TiO_2, ◇ diluted with 20% TiO_2) on the heating profiles of Ti–C compacts.

low immaterial of the type of carbon (graphitic or activated) used and its surface area. A typical case is illustrated here with an activated carbon, AX-21, which had a surface area of $2500\,m^2\,g^{-1}$. Adsorption–desorption isotherm of the carbon powder indicated a Type I isotherm (Fig. 9) indicative of the microporous nature of the carbon. When combustion synthesis was carried out using activated carbon, AX-21, and titanium powder of 11 μm, the carbide exhibited an adsorption–desorption isotherm resembling a mesoporous solid. The total volume of nitrogen adsorbed was significantly lower than the original activated carbon powder and the shape of the isotherm clearly suggests the collapse of the original microporosity and specific surface area. Indeed, the specific surface area decreased from 2500 to $4.3\,m^2\,g^{-1}$, and the total pore volume occupied by the internal pores, was about three orders of magnitude lower.

Since addition of TiO_2 decreases the combustion temperature significantly, stoichiometric compositions of Ti–C mixture containing both the graphitic and activated carbons were diluted with various amounts of TiO_2 to determine if high surface area carbide can be prepared by decreasing the combustion temperature of the compact. Due to the high combustion temperatures generated during the synthesis of TiC, TiO_2 evaporated completely leaving only TiC. This was confirmed by X-ray diffraction analysis of the carbides. Dilution of the Ti–C mixture by 10% TiO_2 exhibited a very minimal effect in increasing the surface areas of the carbides. The surface area increased from 4.3 to $8.4\,m^2\,g^{-1}$. It should be noted that the maximum specific surface area, $8.4\,m^2\,g^{-1}$, obtained with combustion synthesis technique is higher than $0.1\,m^2\,g^{-1}$ achieved with most conventional techniques. Interestingly, dilution of the original mixture even up to 20% TiO_2 did not result in the retention of even 1% of the original porosity of microporous carbon powder.

4. Discussion

The reaction mechanism involved in the synthesis of carbides should consist of melting of Ti followed by the diffusional reaction between liquid Ti and C. Compacts with C to Ti ratios of 0.66, 0.72, and 0.78 indeed indicated melting of Ti and its capillary spreading. Heat generation is terminated for these compacts at the melting point of titanium and further rise of temperature is observed to be much slower than the initial heating period involved up to the melting point of Ti. The temperature profiles of stoichiometric compacts did not, however, indicate any slowing down of the reaction at the melting point of Ti, although they exhibited combustion temperatures much higher than the melting point of Ti. It is possible that the response time of the thermocouple is not adequate to record the small changes in temperature occurring at the rates of $10^5\,K\,min^{-1}$. Melting of Ti must have occurred with the stoichiometric composition without which the high temperatures and high heating rates of the order of $10^5\,K\,min^{-1}$ cannot be explained. It may, however, be noted that most solid–solid reactions occur rather slowly in the absence of a liquid phase at the reaction temperature. The melting of Ti should be followed by the initial reaction of liquid Ti and carbon giving rise to a product layer on the surface of the carbon or possibly

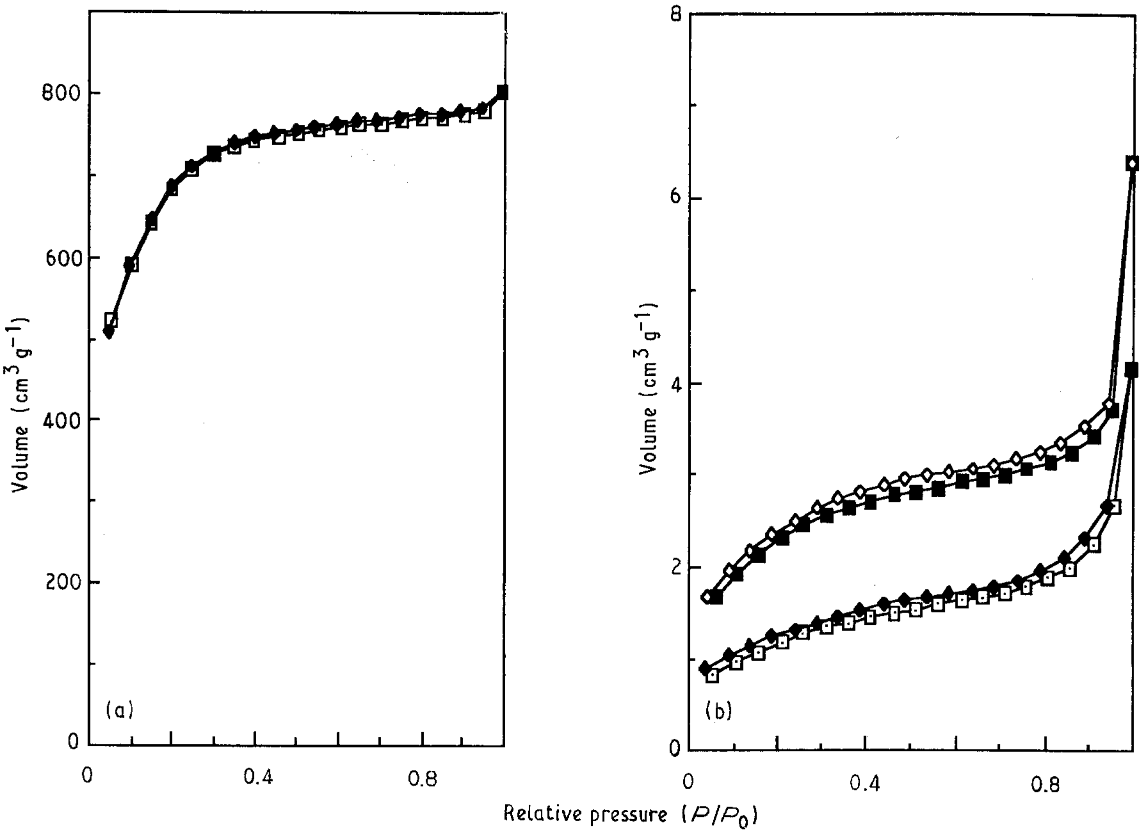

Figure 9 Adsorption–desorption isotherms of (a) activated carbon and (b) combustion synthesized stoichiometric carbide with (◇ ■) and without (◆ ⊡) the addition of 10% TiO_2 as diluent.

in the pore structure of carbon provided that carbon has meso- and micro-porosity. The energy liberated due to the reaction of liquid Ti and carbon at the reaction front supplies the energy for the propagation of the combustion front. The product layer on the carbon powder may slow down further diffusional reaction as can be inferred from the drop in the temperature profile of $TiC_{0.72}$ (Fig. 8) after reaching its maximum temperature followed by a constant temperature region. Therefore, formation of a carbide using combustion synthesis should involve melting of Ti, initial formation of a product followed by a final diffusional reaction.

In pressed powder compacts, conduction is the primary means of heat transfer and the observed phenomena with increase of % TMD may be explained based on the heat transfer in porous media. With increase of % TMD, the interfacial contacts increase and the heat transfer to the next layer of reactants is enhanced. This accelerates the heat transfer to the adjacent layer of reactants and liberates significant heat to maintain a steady-state propagation of the wave. This is reflected in the adiabaticity of the system during the propagation of the wave (Figs 4 and 5). At still higher % TMD values, the internal void volume decreases and the interfacial contacts increase significantly, resulting in an increase in the effective thermal conductivity of the compact. With increase of thermal conductivity, the increased rate of heat transfer from the combustion wave to the reactants ahead of the combustion wave decreases the temperature necessary at the reaction front to maintain a steady-state propagation of the wave. This creates instabilities in the wave, altering the mode of combustion and decreasing the combustion velocity. With further increase of the conductivity, heat transfer from the combustion wave to the reactants ahead of the wave is increased resulting in an extinction of the wave.

As the % TMD value is increased to 66% TMD, thermal conductivity approaches close to the metallic conductivity (the value will be somewhere between the conductivities of Ti and C) and the ignition energy supplied on the surface of the compact is transferred quickly to almost the entire length of the compact. This decreases the temperature necessary for the ignition of the compact and prolonged supply of ignition energy to the surface of the compact results only in heating and glowing of the compact without initiation of an exothermic reaction between Ti and C.

Our experiments with increase of particle sizes of Ti and C indicated a decrease in the combustion velocity. The decrease of combustion velocity may be attributed to the lower rates of heating and possibly due to low heat release rates with increase of particle size. The lower heat release rates with increase of particle size of Ti strongly suggests a lowering of the exothermic diffusional reaction between Ti and C. We did not observe self-sustaining combustion when the average particle sizes of Ti and C were 148 and 11 μm, respectively, but instead, combustion wave propa-

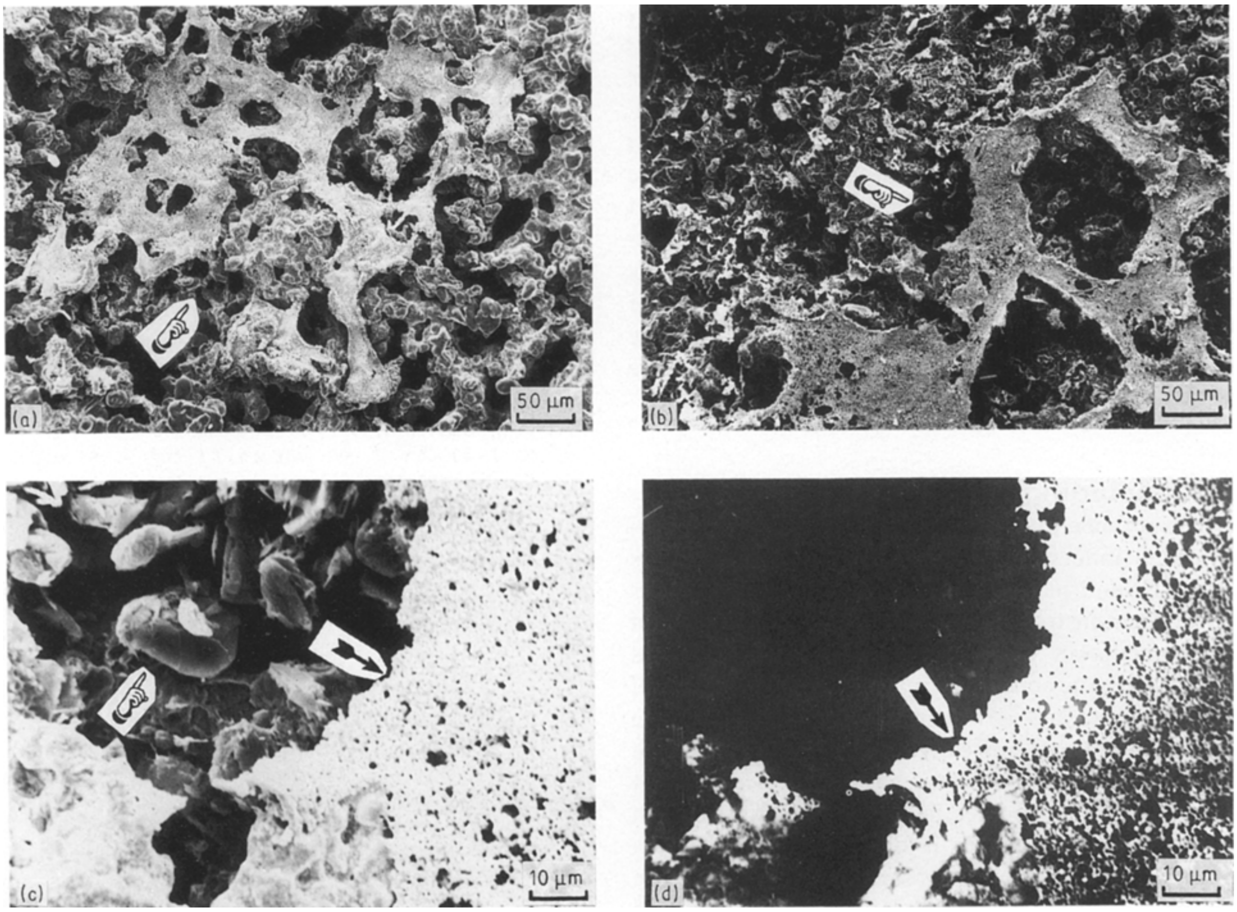

Figure 10 SEM pictures of compacts of Ti with average particle size of 148 μm and carbon with an average size of 10 μm, (a) reacted portion, (b) and (c) unreacted carbon particles, and (d) backscattered image of molten layer of Ti. Portions of interest are indicated with pointers.

gated to just a few mm. In contrast, Azatyan *et al.*'s [10] report that titanium in the range 125 to 160 µm, 250 to 280 µm and polydisperse with $\leqslant$ 280 µm (with carbon of $\leqslant$ 1 µm, argon pressure of 10 atm) underwent self-sustaining combustion. An examination of burnt portion under SEM revealed portions which were reacted fully (Fig. 10a), and the areas which retained the original particle sizes of Ti and C (Fig. 10b). Interestingly, we observed a molten layer, which was confirmed by EDAX to be Ti layer (Fig. 10c and d). This observation strongly suggests that a uniform mixing of components takes place due to the capillary spreading of liquid Ti. Shkiro and Borovinskaya's [11] experiment with a cast cylinder of Ti surrounded by a stoichiometric mixture left a hole of the size of cast Ti after the combustion synthesis, suggesting that liquid Ti does indeed flow as observed in the present work.

An analysis of the pore structure of combustion synthesized carbides indicates that the original pore structure of carbon is lost after the combustion synthesis. A simple calculation of cross-sectional area of liquid Ti (based on the molar volume of liquid Ti, avogadro number and packing factor) suggests that capillary diffusion of liquid Ti into carbon pore structure is highly probable since the cross sectional area is only a few tenths of nanometres and the carbon pore structure contains mesopores. The mesopores present on the surfaces of carbon could act as arteries to micropores. The capillary spreading of liquid Ti is aided by its low viscosity, 0.052 g cm^{-1} s^{-1}, and the high diffusivity of liquid metal (i.e. 10^2 to 10^5 times greater than corresponding solids) [16]. This capillary diffusion is responsible for the exothermic diffusional reaction giving rise to pure TiC, and for the loss of microporous structure of activated carbon, AX-21. The extent of loss due to high temperature is difficult to predict in combustion synthesis technique since high temperatures are present only for very short periods of time. The decrease of combustion temperature by adding a diluent like TiO_2 resulted in only a marginal increase of surface area. This suggests that loss of porosity of original carbon is mainly due to the capillary diffusion of liquid Ti in to the carbon pore structure resulting in a pure carbide.

5. Concluding Remarks

The experimental data suggest that combustion velocities are influenced by the physical factors such as %TMD, and particle sizes of Ti and C. The results further demonstrate that a steady-state propagation of the combustion wave occurs when the compact is under adiabatic conditions immaterial of the length of the compact, and a transition from a steady-state propagation to an unsteady propagation occurs with increase of density. It may, however, be noted that differentiation of pre-heating and reaction time from the temperature profiles is difficult due to the extremely high heating rates observed in the combustion synthesis of TiC with smaller sizes of titanium and carbon. The adiabaticity of the compact resulted in the absence of heat losses at the surface as the combustion wave progressed through the compact resulting in a pure carbide without any unreacted components on the surface of the compact.

Synthesis of TiC consists of an initial diffusional reaction of liquid Ti and C at the combustion front, mainly occurring during the passage of the combustion front and additional reaction leading to completion during the cool down period. Completion of the reaction during cool down period is much more pronounced with the larger particle sizes of reactants. X-ray diffraction analysis of carbides suggested a 100% conversion, without requiring any post-heating for homogenization as is done with the conventional processes. It should be noted that capillary spreading and diffusion of liquid Ti at the combustion front leads to a carbide consisting of macro- and meso-pores. Utilization of a very high surface area carbon for the synthesis of TiC leads to a very low surface area carbide. The importance of the technique lies in its ability to convert a mixture of Ti and C to a high strength TiC. This, of course, is illustrated by the speed at which combustion wave propagates through the compacts of a mixture of titanium and carbon.

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