

# Combustion synthesis of titanium carbide: theory and experiment

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The combustion synthesis of titanium carbide from elemental powders has been theoretically and experimentally studied as a model system for self-propagating high temperature synthesis (SHS) of refractory compounds. Calculations of the adiabatic temperature of combustion of graphite and titanium powders to form  $TiC_x$  have been made to show the effects of stoichiometry, dilution and the initial temperature of the reactants. Experimental observations on the stability of the combustion front, combined with theoretical predictions, lead to an estimated activation energy of  $\leq 117 \text{ kJ mol}^{-1}$  for the process. This value is at least a factor of about four too low to correspond to a diffusion-controlled process. The combustion of graphite and titanium powders was accompanied by the evolution of gases whose primary constituent was found to be hydrogen. This observation was attributed to the reaction of adsorbed moisture with titanium powder. The titanium carbide phase resulting from the combustion of compacted mixed powders of the elements was highly porous ( $\sim 50\%$  porosity). It can be obtained in high density ( $\sim 5\%$  porosity) when pressure is applied during the combustion process.

## 1. Introduction

In reactions that are sufficiently exothermic, the heat liberated is adequate to sustain the reaction by the rapid propagation of a combustion front without further addition of energy. Early interest in such reactions focused on their applications in the areas of pyrotechnics and rocket fuel. More recently, however, these reactions have been studied as possible methods for the preparation of high-temperature ceramic and intermetallic compounds. The initial studies concentrated on thermite reactions [1-3], but later investigators dealt with a wide variety of reactions and materials. Current interest in such reactions stems in part from claims that materials prepared through this method (combustion synthesis) are superior to those prepared by conventional means [4, 5]. Combustion-synthesized materials are reported to have higher purity, to be more reactive, and to possess improved mechanical properties. Higher purity is attributed to the expulsion of impurities as volatile species at the high temperatures that are typically attained during these reactions, while the improvements in reactivity and mechanical properties are attributed to the high defect concentrations resulting from the attainment of high temperature and the relatively rapid cooling rates following the formation of the product.

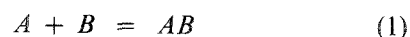
Initially, combustion synthesis was used to produce compounds from elemental reactants. Products prepared in this manner include carbides, borides, nitrides [6], and numerous intermetallics [7, 8]. More

complex reactions have been investigated to produce, for example, "metallate" compounds [9, 10]. Although typically the reactants and products in these syntheses are in the solid state, some investigations have utilized reactants in the gaseous and liquid phases to produce, for example, nitrides [11, 12].

Considerable effort has also been made to investigate the dynamics of the reaction-front propagation in combustion synthesis. Numerous analytical and experimental investigations have been made [7, 8, 13]. In general, consistent agreement between experimental observations and theoretical predictions is lacking. This is primarily the consequence of numerous simplifying assumptions incorporated into the theoretical models. The combustion of titanium and carbon powders to produce  $TiC$  was selected as a model system to demonstrate the principles underlying the combustion of solids. Previous studies [14-16] have provided experimental data for this particular combustion reaction. However, lack of sufficient detail in some of the studies indicates that further investigation is needed.

## 2. Theory

If we consider a simple reaction between elements  $A$  and  $B$  to produce the compound  $AB$ , then the enthalpy of the reaction



is the heat of formation of  $AB$  if the reaction is carried

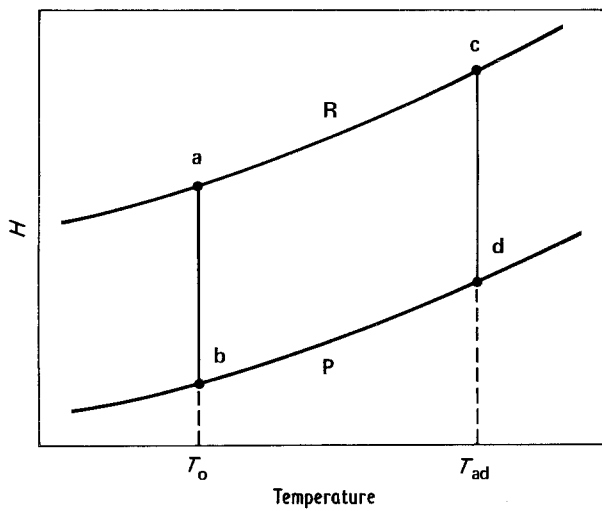


Figure 1 Schematic representation of the calculation of the adiabatic temperature.

out at standard conditions of temperature and pressure. For a thermally isolated exothermic system, the temperature to which the product is raised is the adiabatic temperature,  $T_{ad}$ . A schematic representation of this process is shown in Fig. 1 where Curves R and P represent the enthalpy–temperature dependences of the reactants and products, respectively. Accordingly, we can write

$$\Delta H_{a-b} = \Delta H_{b-d} \quad (2)$$

and, if the melting point of the product  $AB$  is higher than  $T_{ad}$ , Equation 2 becomes

$$\Delta H_{T_0}^{\circ} = \int_{T_0}^{T_{ad}} C_p(P) dT \quad (3)$$

where  $\Delta H_{T_0}^{\circ}$  is the enthalpy of the reaction at  $T_0$  and  $C_p(P)$  is the heat capacity of the solid product  $AB$ . A more general form for Equation 3 includes additional enthalpy terms accounting for phase transitions. Thus a more generalized form for the case in which the adiabatic temperature is higher than the melting point of the product is

$$\Delta H_{T_0}^{\circ} = \int_{T_0}^{T_1} C_p(P_1) dT + \int_{T_1}^{T_m} C_p(P_2) dT + \int_{T_m}^{T_{ad}} C_p(P_1) dT \quad (4)$$

where  $C_p(P_1)$ ,  $C_p(P_2)$ , and  $C_p(P_1)$  are, respectively, the heat capacities of Solid Phase 1, Solid Phase 2 and the Liquid Phase of the product;  $\Delta H_m$  is the enthalpy of fusion of the product at its melting point,  $T_m$ ; and  $T_1$  is the transition temperature between Solid Phases 1 and 2. Where sublimation of the product is significant, a term accounting for the heat contribution of this process must be included. However, since sublimation takes place over a range of temperatures, the incorporation of its effect in the energy and material balance is not straightforward. Fortunately, for most materials prepared by combustion synthesis the contribution of evaporation is negligible, with notable exceptions in the nitrides, e.g.  $AlN$  and  $Si_3N_4$ .

Calculations of  $T_{ad}$  are typically made with  $T_0 = 298$  K, and thus the heat generated by the reaction of the elements is the standard heat of formation of the

product. In practice, however, reactions are not initiated at room temperature but at some elevated (ignition) temperature,  $T_{ig}$ . This will influence the results in accordance with the following relationship

$$\int_{T_{ad_1}}^{T_{ad_2}} C_p dT = \int_{298}^{T_{ig}} C_p dT + \int_{298}^{T_{ig}} \Delta C_p dT \quad (5)$$

where  $C_p$  is the heat capacity of the product,  $\Delta C_p$  is the difference between the heat capacities of the product and reactants,  $T_{ad_1}$  is the adiabatic temperature calculated for  $T_0 = 298$  K, and  $T_{ad_2}$  is the adiabatic temperature for  $T_0 = T_{ig}$ . For reactions in which the Neumann–Kopp rule is applicable, i.e.  $\Delta C_p \sim 0$ , Equation 5 simplifies to

$$\int_{T_{ad_1}}^{T_{ad_2}} C_p dT \approx \int_{298}^{T_{ig}} C_p dT \quad (6)$$

Fig. 2 demonstrates the dependence of  $T_{ad}$  on  $T_0$  for titanium carbides (TiC) for the two cases described by Equations 5 and 6.

Depending on the heat capacities and the enthalpies of formation and fusion, the product can be solid, liquid or a mixture of the two. The conditions under which these cases exist are dictated by the following relationships

$$\text{Case 1: } T_{ad} < T_m$$

$$\Delta H_{T_0}^{\circ} < \int_{T_0}^{T_m} C_p dT \quad (7)$$

$$\text{Case 2: } T_{ad} = T_m$$

$$\Delta H_{T_0}^{\circ} = \int_{T_0}^{T_m} C_p dT + v\Delta H_m \quad (8)$$

where  $v$  is the fraction of the product that has undergone melting. For this case,  $0 < v < 1.0$ .

$$\text{Case 3: } T_{ad} > T_m$$

$$\Delta H_{T_0}^{\circ} > \int_{T_0}^{T_m} C_p dT + \Delta H_m \quad (9)$$

The calculated adiabatic temperature is an upper limit and, because of heat losses, is usually not achieved in practice. Despite this, there are cases where a lowering of the adiabatic temperature is desirable and this is usually achieved by the addition of the product phase as a diluent. The effect of the addition of TiC as a diluent on the theoretical adiabatic temperature and on  $v$  for the reaction between titanium and carbon is shown in Fig. 3.

### 3. Titanium carbide

#### 3.1. Structural, physical and thermodynamic properties

Titanium carbide,  $TiC_x$ , exists as a homogeneous phase within the limits  $0.47 < x < 1.0$ . There is some uncertainty concerning the exact values of these limits, however. Experimental evidence [17] shows that for  $x = 0.45$  the material exists as a two-phase mixture of titanium and “TiC”. The phase diagram of Ti–C is shown in Fig. 4 [18]. Depending on composition (the value of  $x$ ), titanium carbide melts over the range 1918

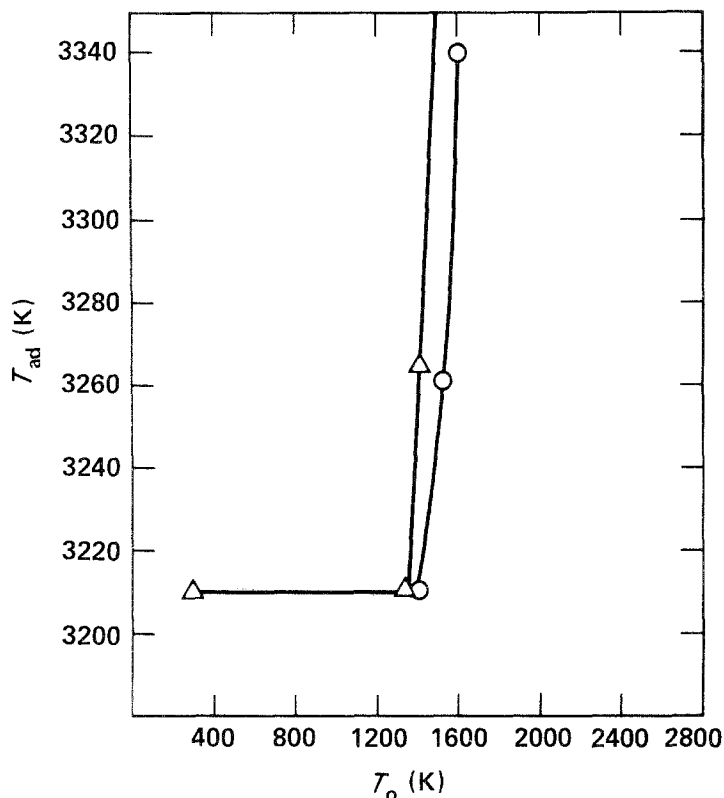


Figure 2 The dependence of the adiabatic temperature on the initial reaction temperature. (O)  $\Delta H_f$  at 298 K (Equation 6); ( $\Delta$ )  $\Delta H_f$  at temperature  $T$  (Equation 5).

to 3210 K, the highest temperature corresponding to the composition with  $x \approx 1.0$ .

The lattice structure of titanium carbide is face centred cubic (NaCl type) with a reported cell parameter  $a_0 = 0.4329 \pm 0.0001$  nm [19]. As expected, however, the lattice parameter depends on stoichiometry with an experimentally-determined dependence shown in Fig. 5. The value of  $a_0$  decreases with increased deviation from stoichiometry, i.e. with a decrease in carbon content [17, 18, 20]. Pertinent thermodynamic properties of TiC are summarized in Table I. The value for the heat of formation,  $\Delta H_f^\circ$ , of this compound is subject to disagreement, as reported in the literature. The value listed in Table I is that selected by Schick [21]. In a more recent investigation [22],  $\Delta H_f^\circ$  was shown to be a function of composition, as depicted in Fig. 6. Extrapolation of the values plotted in this figure to  $x = 1.0$  gives  $\Delta H_f^\circ = -194.37$  kJ mol $^{-1}$ , which is approximately 5.4% higher than the value listed in Table I.

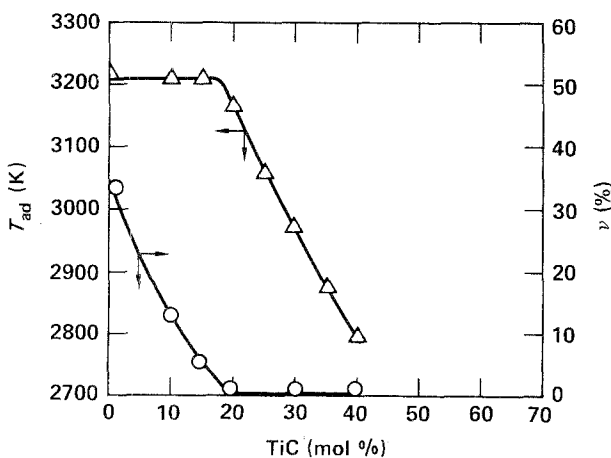


Figure 3 The influence of the addition of TiC as a diluent on the adiabatic temperature. ( $\Delta$ )  $T_{ad}$ , (O)  $v$ .

### 3.2. Adiabatic temperature calculations

The adiabatic temperature  $T_{ad}$  for TiC was calculated, as described in Section 2, using the thermodynamic properties listed in Table I. The results show that  $T_{ad} = 3210$  K, which is the melting point of TiC, and  $v = 0.33$ , as shown in Fig. 7. In these calculations  $T_0$  is assumed to be 298 K. The effect of varying  $T_0$  on the calculated  $T_{ad}$  was shown in Fig. 2 for the case where the heat of reaction is taken as the 298 K value and for the case where  $\Delta H_{298}^\circ$  is corrected for  $C_p$ .

The effect of the addition of a diluent on the adiabatic temperature was demonstrated in Fig. 3 for the case of TiC as diluent, assuming a stoichiometric product. With this assumption, similar calculations were made to show the effect of adding titanium and carbon as diluents. These results are shown in Figs. 8a and b, respectively. These results are valid for the case of TiC and carbon as diluents in the formation of stoichiometric titanium carbide, and only nominally valid for the case of titanium as diluent. The reason for this stems from the phase stability range of TiC and the fact that the heat of formation of  $TiC_x$  is a

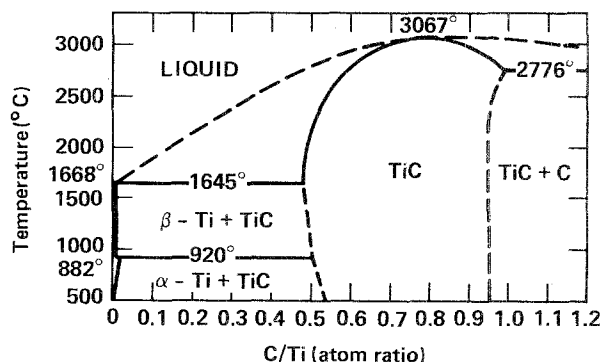


Figure 4 The titanium-carbon phase diagram (taken from Storms [18]. 882°C is the  $\alpha$ Ti to  $\beta$ Ti phase transition temperature, and 1668°C the melting temperature of titanium.

TABLE I Thermodynamic properties of  $TiC_x$

Property (units)	Value
$C_p$ ( $J K^{-1} mol^{-1}$ ) (solid)	$49.45 + 3.34 \times 10^{-3} T - 14.96 \times 10^5 T^2$
$\Delta H_{f(298)}$ ( $kJ mol^{-1}$ )	-184.46
$T_m$ (K)	3210
$\Delta H_m$ ( $kJ mol^{-1}$ )	83.6
$C_p$ ( $J K^{-1} mol^{-1}$ ) (liquid)	66.88

function of  $x$ , as shown in Fig. 6. In addition, the melting point of  $TiC_x$  is also dependent on the value of  $x$ . In order to calculate the variation of  $T_{ad}$  with composition, two assumptions have to be made: that the  $C_p$  equation and the heat of fusion for  $TiC_x$  are independent of  $x$  within the limit of stability of this phase. The results are shown in Fig. 9 along with similar results from a previous calculation [23].

### 3.3. Combustion rate calculations

The analysis of the rate of propagation of a combustion front is commonly made with the assumption that the thermophysical properties of the materials involved in the reaction are not strong functions of temperature, and that the temperature distribution parallel to the front (i.e. the radial distribution) is uniform. With these and the additional stipulation that the heat losses from the sample are convective and radiative only, the generalized form for the self-propagating combustion [24] is

$$C_p \frac{\rho \partial T}{\partial t} = \frac{k \partial^2 T}{\partial x^2} + Q \frac{\rho \partial \phi}{\partial t} - \frac{2\alpha}{r} (T - T_o) - \frac{2\epsilon \sigma_o}{r} (T^4 - T_o^4) \quad (10)$$

where  $C_p$  = heat capacity ( $J g^{-1} K^{-1}$ ),  $\rho$  = density ( $g cm^{-3}$ ),  $k$  = thermal conductivity ( $W cm^{-1} K^{-1}$ ),  $Q$  = heat of reaction ( $J g^{-1}$ ),  $\phi$  = reacted fraction,  $\alpha$  = heat transfer coefficient ( $W cm^{-2} K^{-1}$ ),  $r$  =

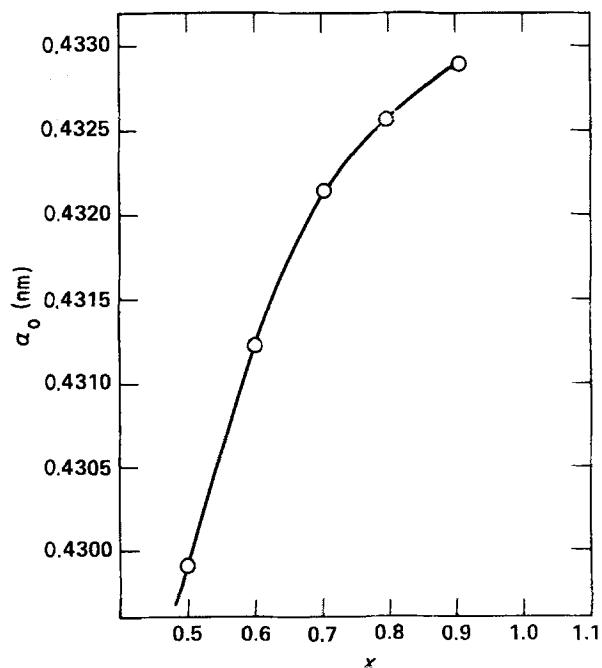


Figure 5 The variation of the lattice parameter of  $TiC_x$  with stoichiometry.

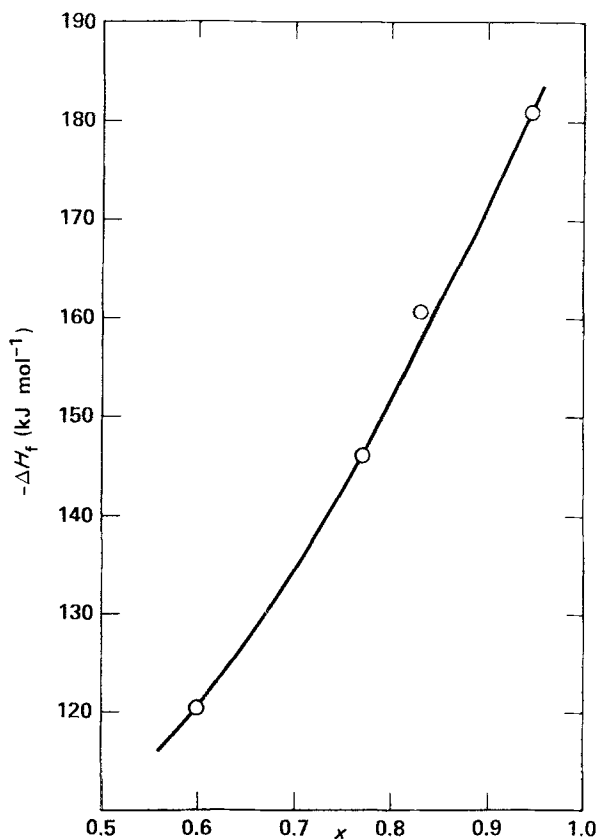


Figure 6 The enthalpy of formation of  $TiC_x$  with stoichiometry.

sample radius (cm),  $\epsilon$  = emissivity coefficient,  $\sigma_o$  = Stefan-Boltzmann constant ( $W cm^{-2} K^{-4}$ ),  $T$  = temperature (K),  $t$  = time (sec) and  $T_o$  = ambient temperature (K). The second, third and fourth terms on the right-hand side of the above equation represent, respectively, the heat generated by the reaction, the convective heat loss and the radiative heat loss. If we neglect the last two terms and express the heat-generation term as a kinetic equation for a homogeneous reaction, then Equation 10 becomes

$$C_p \rho \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} + Q \rho K_o (1 - \phi)^n \exp(-E/RT) \quad (11)$$

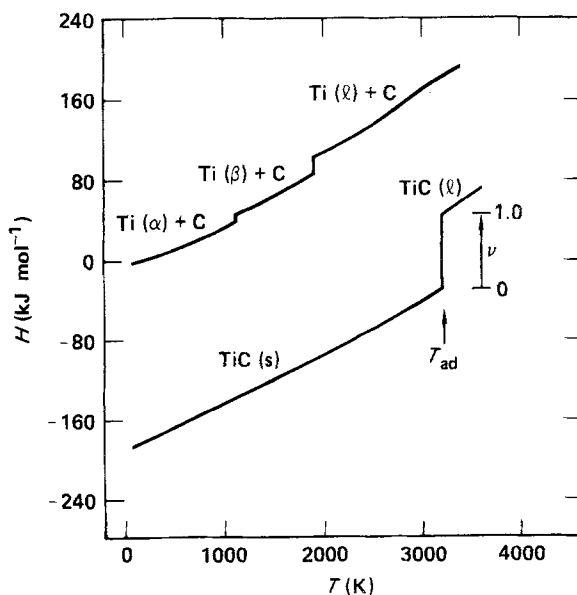


Figure 7 Thermodynamic functions and the adiabatic temperature for titanium carbide. For  $T_o = 298 K$ ,  $T_{ad} = 3210 K$  and  $\nu = 0.33$ .

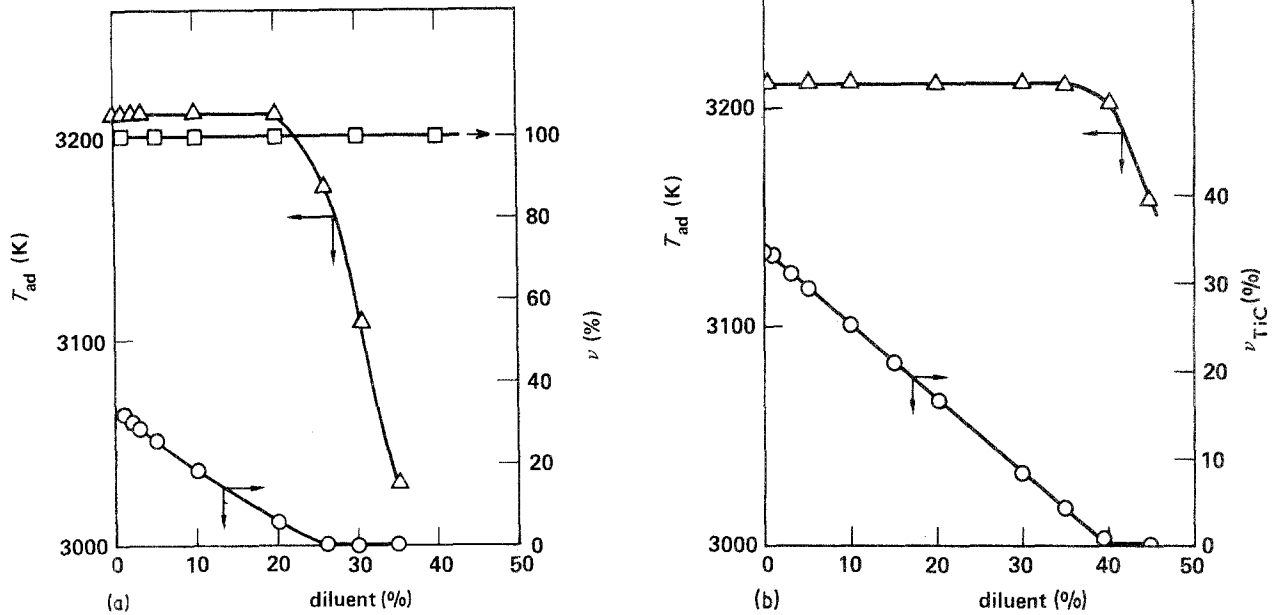


Figure 8 (a) The effect of the addition of (a) titanium and (b) carbon as a diluent on the adiabatic temperature  $T_{ad}$ , ( $\square$ )  $\nu_{Ti}$ , ( $\circ$ )  $\nu_{TiC}$ , ( $\Delta$ )  $T_{ad}$ .

where  $E$  is the activation energy for the reaction,  $n$  is the order of the reaction and  $K_0$  is a constant. A numerical solution for the above equation has been provided for  $n = 1$ , and the computer-generated results show two combustion regimes: steady-state and oscillatory. In the steady-state regime the temperature and fraction reacted profiles advance through the sample at the same rate, and the highest combustion temperature is the adiabatic temperature. On the other hand, in the oscillating regime the combustion velocity oscillates about an average value. In such a regime, a region of the sample is heated during a "slow mode" of combustion; combustion then takes place, giving rise to a "rapid mode" of advancement

of the combustion front. A criterion parameter has been numerically derived in which the limits can be used to delineate the boundary between the steady-state and the oscillating regimes. This parameter,  $\alpha_c$ , is defined [25] by

$$\alpha_c = \frac{RT_c}{E} \left( 9.1 \frac{C_p T}{Q} - 2.5 \right) \quad (12)$$

such that

$$\begin{aligned} \alpha_c \geq 1 & \quad \text{steady-state combustion} \\ \alpha_c < 1 & \quad \text{oscillating combustion} \end{aligned}$$

Moreover, the departure from a steady-state regime is qualitatively related to the departure of  $\alpha_c$  from a value of unity, i.e. the smaller the value of  $\alpha_c$ , the stronger the oscillatory nature of the combustion front. In Equation 12  $T_c$  refers to the combustion temperature.

Assuming that the reaction zone is narrow compared to the heating zone, Novozhilov [26] and Khaikin and Merzhanov [27] have calculated the velocity of a steady-state combustion as

$$U^2 = \sigma_n a \frac{C_p}{Q} \frac{RT_c^2}{E} K_0 \exp(-E/RT_c) \quad (13)$$

where  $a$  is the thermal diffusivity and  $\sigma_n$  is a constant the value of which is dictated by the kinetic order of the reaction (e.g. for  $n = 0$ ,  $\sigma = 2$ ; for  $n = 1$ ,  $\sigma \approx 1.1$ ; for  $n = 2$ ,  $\sigma \approx 0.73$ ). The other symbols of Equation 13 have been defined earlier. Thus, from simultaneous measurements of the velocity of the combustion front and the combustion temperature the value of the activation energy for the combustion process can be determined.

As stated earlier, the above theoretical analysis includes a number of simplifying assumptions and is based on the stipulation that the combustion process is a homogeneous reaction. However, considerations of real systems with finite dispersions of reactant

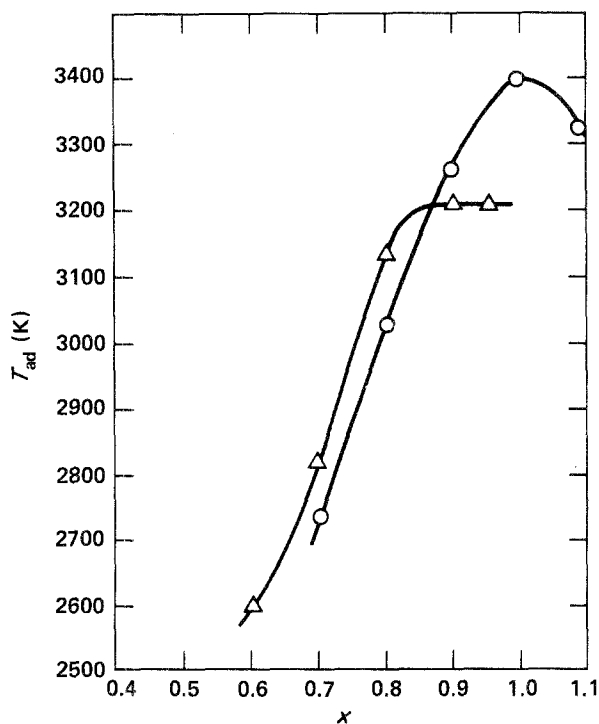


Figure 9 The variation of the adiabatic temperature of  $TiC_x$  with stoichiometry. ( $\Delta$ ) This work, ( $\circ$ ) Hardt and Valenta [23].

particles clearly show that the problem is considerably more complex and that the process is not homogeneous. Attempts to deal with some aspects of heterogeneous combustions have been made by Aldushin *et al.* [28] and Hardt and Phung [7]. The latter authors compared predicted with measured rates of combustion for the synthesis of carbides and borides of titanium and zirconium. More recent analytical [29] and experimental [30] investigations have considered the effects of stoichiometry, dilution, and the initial temperature on the rate of combustion of TiC.

#### 4. Experimental observations

##### 4.1. Combustion synthesis of TiC

Mixtures of graphite and titanium powders were combusted in two forms: loose powders and pressed pellets. Powders of titanium and graphite (–325 mesh) were mixed in the ratio of 19.0 wt % C and 81.0 wt % Ti to give a nominal C/Ti ratio of 0.936. This ratio is slightly below the maximum value (0.967) for the single-phase TiC region in the Ti–C phase diagram [18]. Experience has shown that during the combustion process some titanium is lost and thus the final C/Ti ratio will be slightly higher than the starting value. The mixed loose powders were combusted in a graphite crucible inside a chamber evacuated to a pressure of 0.2 Pa. Ignition of the powder was achieved by placing a heated tungsten coil (1.5 cm diameter wire with a current of 65 A) approximated 3 mm above the mixture. Following combustion, the total carbon content was determined and the C/Ti ratio was evaluated as 0.953. When TiC was combustion-synthesized in pellet form, the powder mixture was pressed to give a density of  $2.1 \text{ g cm}^{-3}$  and the resulting pellet was ignited in a glove-box under an argon atmosphere. Fig. 10 shows the microstructure of an etched titanium carbide produced by the combustion of titanium and carbon in pellet form. As can be seen in this figure, significant (50%) porosity exists in the final product. A spectrochemical analysis of the resulting TiC was made and is reported in Table II along with corresponding analyses for the starting powders. These results show a significant decrease in the level of impurities as a result of combustion.

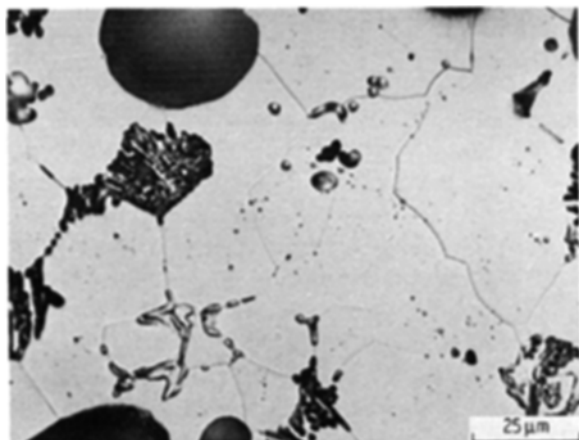


Figure 10 Micrograph of etched titanium carbide produced by combustion synthesis.

TABLE II Emission spectrochemical analysis of powders

Element	Composition (wt ppm)		
	C	Ti	TiC
Al		3000 to 4000	1000 to 2000
Ca	3	2000	30
Ar		1000	300
Mg		100	< 3
Si	10	100	100
Ba		< 30	< 30
Mn		20	20
Sr		10	< 1
Fe		5	100
B		< 3	80
Cu		< 3	< 3
Cr		< 1	6
Ni		< 1	10

The exceptions (iron, nickel, chromium and boron) are cases in which the impurities were introduced in the powder preparation process subsequent to combustion.

Preliminary experiments on the rate of combustion of TiC have been made. In one series of such investigations it was observed that the addition of 10% TiC as a diluent shifts the combustion process from a steady to a non-steady (oscillating) one. Moreover, measurements of the combustion temperature,  $T_c$ , indicated that the addition of 10% TiC as a diluent caused a decrease in  $T_c$  from 2720 to 2518 K. It is interesting to relate these observations to the analytical predictions concerning the boundary between steady-state and oscillating regimes, as defined by the parameter  $\alpha_c$  in Equation 12. Fig. 11 shows the relationship between the activation energy for combustion,  $E_c$ , and the combustion temperature,  $T_c$ , for the stable/unstable combustion boundary, i.e. for  $\alpha_c = 1.0$ . The experimental observations referred to above are qualitatively in agreement with the theoretical anticipations of Fig. 11. For any given value of  $E_c$ , a reduction of  $T_c$  can bring about a transition from a stable combustion to an unstable combustion if the decrease in  $T_c$  results in the crossing of the boundary shown in the figure.

In all cases for “stoichiometric” (undiluted) combustion of Ti + C, the combustion front proceeded in a steady-state fashion. This observation, when related to the theoretical analyses presented in Fig. 11, leads to a predicted activation energy  $E_c < 117 \text{ kJ mol}^{-1}$ .

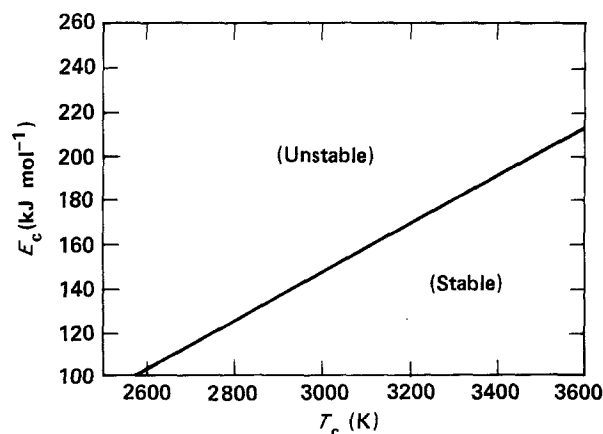


Figure 11 The variation of the activation energy for combustion with the combustion temperature (Equation 12).

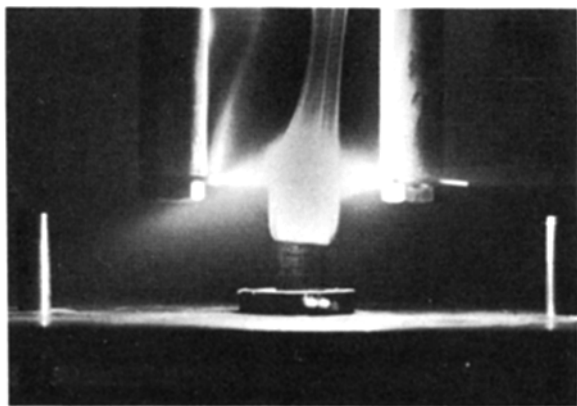


Figure 12 Gas evolution during combustion Ti + C.

This value is considerably lower than the activation energies of carbon diffusion in TiC [31, 32] ( $\sim 400 \text{ kJ mol}^{-1}$ ) and titanium diffusion in TiC [33] ( $737 \text{ kJ mol}^{-1}$ ). We anticipate that the interaction between titanium and carbon particles with finite sizes would involve a diffusion process following the formation of the first layer of product. Thus the exceedingly low  $E_c$  estimated on the basis of Equation 12 raises doubt about the validity of this equation, and suggests that the simplifying assumptions of the theoretical analysis may not be valid.

#### 4.2. Gas evolution

Rapid-speed motion picture records of the combustion of Ti + C showed evidence of substantial gas evolution (Fig. 12). Various experiments were made to determine the nature and source of the evolved gases. An obvious source is the evolution of adsorbed gases. Thus, to determine the effect of adsorbed gases, mixtures of titanium and carbon, in pellet form, were combusted in a vacuum chamber of known volume. The non-condensable gases evolved during combustion were identified by mass spectrometric analysis. As shown in Table III, the major gas produced during combustion was hydrogen (86.96 vol %). Carbon monoxide, the next most abundant gas, accounts for 12.13 vol % of the total. The ratio of hydrogen to carbon monoxide as well as the total quantity of evolved gases is a function of powder characteristics such as surface area and type of carbon, i.e. crystalline or amorphous. In this particular experiment, the titanium powder was  $-325$  mesh with an average particle size of  $22 \mu\text{m}$ . The crystalline graphite is a spectroscopic grade powder with an average particle size of  $10 \mu\text{m}$ . If we assume that the hydrogen originates from water vapour adsorbed on the powders, then water vapour amounts to  $\sim 0.1\%$  of the total weight of the initial reactants.

TABLE III Evolution of gases

Gas	Evolution (mol %)	Standard deviation
N <sub>2</sub>	0.827	0.014
CO	12.13	0.04
H <sub>2</sub>	86.96	0.39
CH <sub>4</sub>	0.068	0.003
Total	99.98	—

Total amount of evolved gases =  $7.4 \times 10^{-3}$  moles.

It has been observed that metals with a strong tendency for oxide formation, e.g. chromium, evolve significant quantities of hydrogen when heated in vacuum [34]. Residual water in the vacuum system reacts with the surface oxide to produce the observed hydrogen. The precise cause of the evolution of large amounts of hydrogen in our combustion experiments remains unresolved. Heating the powder prior to combustion in a good vacuum system should reduce the amount of evolved hydrogen if adsorbed water vapour is the major contribution.

#### 4.3. Sintering

It has repeatedly been asserted that an important advantage of combustion-synthesized powders is their relatively high reactivity [5]. Specifically, it has been suggested that such powders sinter more readily than those produced by conventional methods. An investigation was conducted to determine the relative sinterability of combustion-synthesized titanium carbide powders. The results, described in more detail elsewhere [35], showed that combustion-synthesized TiC powders are less sinterable than commercial powders. A detailed analysis of the stoichiometry of the synthesized powders showed the presence of free carbon in the final product. Not only was the free carbon indicative of an incomplete combustion, but its amount was found to correlate with the oxygen content of the TiC sample. Higher free-carbon contents correlated with higher oxygen content. Similar observations have been made by Nezhevenko *et al.* [36] on combustion-synthesized ZrC powders. The role of free carbon in the sintering of TiC was explicitly demonstrated by a series of experiments using commercially available titanium carbide. A series of experiments was performed using samples with varying contents of added carbon. These were sintered under identical conditions at two temperatures. Volumetric shrinkage data for samples sintered for 60 min at 1723 and 1843 K are shown in Fig. 13 as functions of the percentage of free carbon added to the commercial TiC powder. At both temperatures the shrinkage increased with decreasing free-carbon content. It should be noted here again that the commercial powder had a near-stoichiometric composition and thus little free carbon.

A comparison of the microstructures resulting from the sintering of combustion-synthesized and commercial TiC powders can be made by examining Figs. 14 and 15. The grain structure shown in both figures is the result of sintering for 60 min at 1816 K. Both microstructures are characterized by regions of large grains within regions of smaller grains. Furthermore, the grains of the sintered commercial powder are approximately a factor of two larger than those of the sintered synthesized powder. As stated earlier, the synthesized powder contained free (unreacted) carbon and this would suggest that free carbon inhibits grain growth during the sintering of titanium carbide.

The effect of stoichiometric deviations of TiC on its sinterability was also investigated. Samples with C/Ti ratios ranging from 0.7 to 0.95 were synthesized and subsequently sintered. The activation energies for the

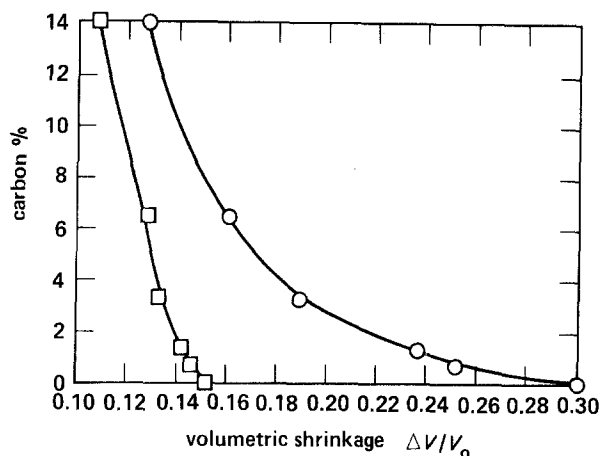


Figure 13 The effect of the free-carbon content on the shrinkage of sintered titanium carbide. Temperature (O) 1843 K, (□) 1723 K.

sintering of these samples were determined from the temperature dependence of shrinkage data for all samples. The results are plotted in Fig. 16 as  $Q$ , the activation energy, against the C/Ti ratio. The results clearly show that the activation energy decreases with increasing C/Ti ratio.

#### 4.4. Simultaneous synthesis and densification

As reported in Section 4.1, the combustion of compressed pellets of titanium and carbon powder form a porous (~50%) TiC product (Fig. 10). The porosity is caused by a combination of factors such as differences in molar volume between reactants and products, outgassing of adsorbed impurity gases, and porosity in the compressed reactant pellets.

If the combustion of the reactants could be combined with a densification step, then the overall operation could become an attractive ceramic fabrication process. One of the distinct features of solid-state combustion is the high temperature (~3075 K for TiC) achieved during combustion. It is possible that the application of high pressure during or subsequent to the combustion step may densify the product.

In our experimental procedure, a mixture of titanium and carbon powder was loaded into a graphite die with a 2.5 cm diameter hole. Pressure on the double-acting graphite rams compressed the powder to about 60% of theoretical density. The die was heated at a rate of 1200 to 1400 K min<sup>-1</sup> to the ignition point

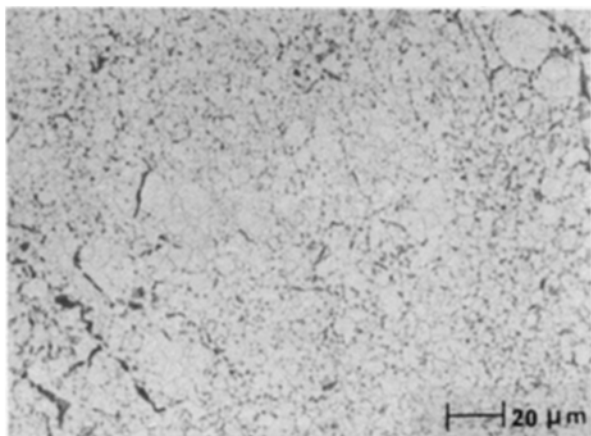


Figure 14 Microstructure of sintered combustion-synthesized titanium carbide.

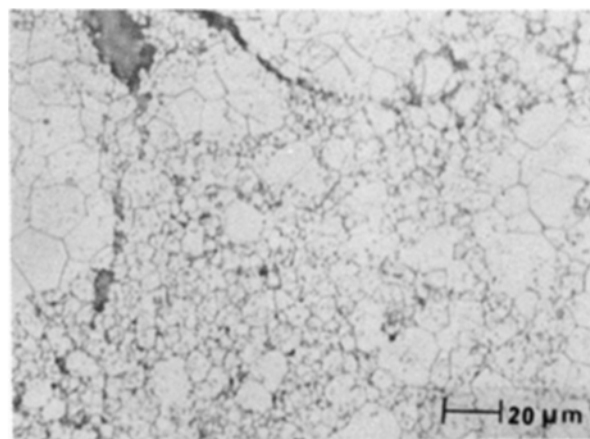


Figure 15 Microstructure of sintered commercially obtained titanium carbide.

(~1873 K) of the powder mixture. Rather than a combustion front moving through the powder at the ignition point, the reaction takes place simultaneously throughout the compressed pellet. This type of reaction has been referred to as a "thermal explosion". During the heat-up, only a slight pressure was applied to the powder, but after ignition a pressure of 27.6 MPa (4000 psi) was applied to the hot TiC. From the temperature of ignition (~1873 K) the temperature rapidly climbed to ~3075 K. The application of pressure must be within a second or two of the time that the TiC is at the maximum temperature. Compacts of TiC having a relative density of 95% of theoretical were prepared in this manner. An etched cross-section of a polished sample is shown in Fig. 17 where the average grain size is 18 μm.

Careful control of several experimental parameters is necessary to achieve the high-density TiC product. If pressure is applied during the heat-up, then adsorbed gases such as H<sub>2</sub>O may blow the die apart. The pressure must be applied after the initiation of the reaction or the initial powder must be degassed. The selection of the proper rate of heating and volume/surface ratio of the powder compacts is important to the densification process. Other methods of ignition and application of pressure are being investigated to optimize the process.

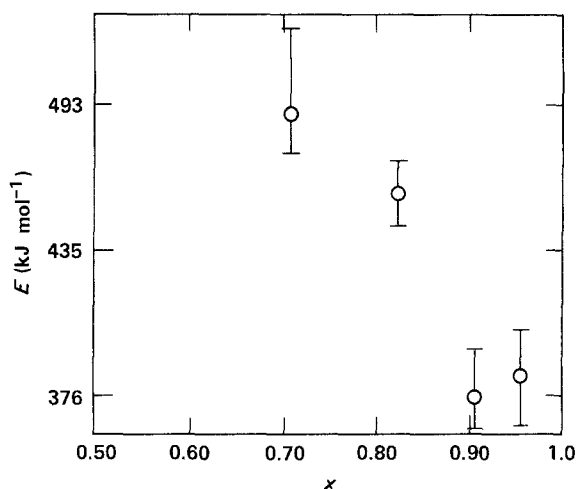


Figure 16 The variation of the activation energy for sintering with the stoichiometry of TiC<sub>x</sub>.



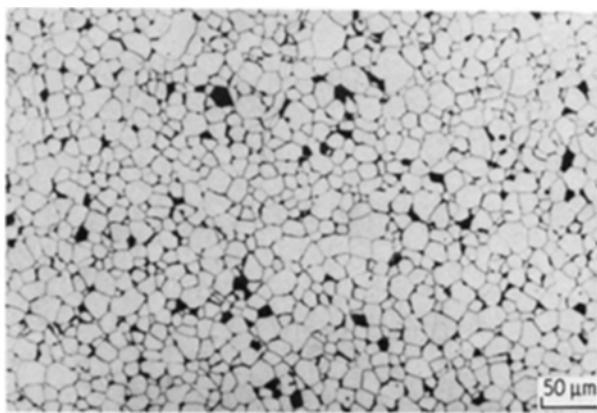


Figure 17 Etched cross-section of combustion-synthesized titanium carbide prepared under pressure.

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