

**LITERATURE
REVIEW**

Chapter 1

LITERATURE REVIEW

1.1 Physical fundamentals of self-propagating high temperature synthesis (SHS)

Thermodynamic calculations of SHS reactions can be performed to determine the adiabatic combustion temperature, while kinetic studies provide information about the rate of heat release. The latter can be assessed from the wave velocity measurements or the temperature profile analysis.

1.1.1 Thermodynamic calculations of SHS reactions

Determination of adiabatic temperature T_{ad}

In order for a reaction to be self-sustaining, it must be highly exothermic and therefore be associated with a high temperature. A useful parameter which provides an indication of the possible maximum temperature attained by the product is the adiabatic combustion temperature T_{ad} . When considering a synthesis of ceramic compound by SHS process, the first step should be the calculation of adiabatic temperature. It can be calculated by assuming that the enthalpy of the reaction heats up the products and that no heat energy is lost to the surroundings. The enthalpy of the synthesis reaction for the propagating case is expressed as follows^[12]:

$$\Delta H_{r, T_0} = \Delta H_{f, T_0}$$

Where $\Delta H_{r, T_0}$ is the reaction enthalpy at the ambient temperature, T_0 usually 298 K and $\Delta H_{f, T_0}$ is the enthalpy of formation at that temperature. If $\Delta H_{r, T_0}$ is assumed to heat the reaction product, the adiabatic temperature T_{ad} can be calculated from the definition of heat capacity of the product C_p as given by the following equation^[12]:

$$-\Delta H_{r, T_0} = \int_{T_0}^{T_{ad}} C_p(\text{product}) dT$$

The high combustion temperature may produce phase's transitions e.g. melting of the products, so that the enthalpies of these transitions must also be taken into consideration.

$$\text{If } T_{ad} < T_m \text{ then } -\Delta H_{r, T_0} = \int_{T_0}^{T_{ad}} C_p(\text{product}) dT$$

$$\text{If } T_{ad} = T_m \text{ then } -\Delta H_{r, T_0} = \int_{T_0}^{T_m} C_p(\text{product}) dT + v\Delta H_m$$

If $T_{ad} > T_m$ then

$$-\Delta H_{r, T_0} = \int_{T_0}^{T_m} C_p(\text{product}) dT + v\Delta H_m + \int_{T_m}^{T_{ad}} C_p(\text{product}_{liq}) dT$$

Where T_m is the melting temperature, $C_p(\text{product}_{liq})$ is the specific heat capacity of the liquid product, ΔH_m is the enthalpy of fusion of the product and v is the fraction of the reaction product which underwent melting.

During SHS reactions the anticipated heat loss to the surroundings is significant and the measured reaction temperatures could be lower than the measured one. The calculated adiabatic temperatures serve as an important guide for the probability of a particular chemical reaction occurring in the combustion regime.

The adiabatic temperature is also substantially affected by the starting temperature T_0 , as shown in Fig. 1. If the reactants are heated to T_2 before ignition, the T_{ad} is calculated as follows^[13]:

$$-\Delta H_{r, T_2} = \int_{T_2}^{T_{ad}} C_p(\text{product}) dT$$

From Fig. 1 and Hess's law of constant heat summation, the sum of the energy during the ABD path equals that of the ACD path, such that;

$$\Delta H_{r, 298} + \int_{298}^{T_2} C_p(\text{product}) dT = \Delta H_{r, T_2} + \int_{298}^{T_2} C_p(\text{reactants}) dT$$

By substituting for $\Delta H_{r, T_2}$,

$$\Delta H_{r, 298} + \int_{298}^{T_2} C_p (\text{product}) dT = - \int_{T_2}^{T_{ad}} C_p (\text{product}) dT + \int_{298}^{T_2} C_p (\text{reactants}) dT$$

and by rearrangement, an equation of the effect of preheating of the reactants on T_{ad} is obtained,

$$-\Delta H_{r, 298} + \int_{298}^{T_2} C_p (\text{reactants}) dT = \int_{298}^{T_{ad}} C_p (\text{product}) dT$$

This equation simply states that:

Energy of the reaction + Energy supplied by pre-heating the reactants to T_2 = Energy required to heat the products to T_{ad} .

Integrating the above equation and solving the obtained equation, T_{ad} can be performed.

An empirical formula by Novikov et al. [14] has shown that a reaction will not be self-sustaining unless $T_{ad} > 1800$ K. Munir and co-workers [15,16] showed that there is an approximate linear relationship between T_{ad} and the ratio $\Delta H_{r,298}/C_{p,298}$ because of the low sensitivity of C_p to temperature changes.

Alternatively, another equation that depends on T_{ad} which has a theoretical foundation than empirical observations has been derived [17]. It has proposed that SHS reactions will occur when:

$$T_{ad} - T_{ig} / T_{ig} - T_{start} \geq C_p (\text{reactants}) / C_p (\text{products})$$

where, T_{ig} is the ignition temperature, T_{start} is the initial temperature of the reaction, $C_p(\text{products})$ is the mean specific heat between T_{ad} and T_{ig} , $C_p(\text{reactants})$ is the mean specific heat between T_{start} and T_{ig} .

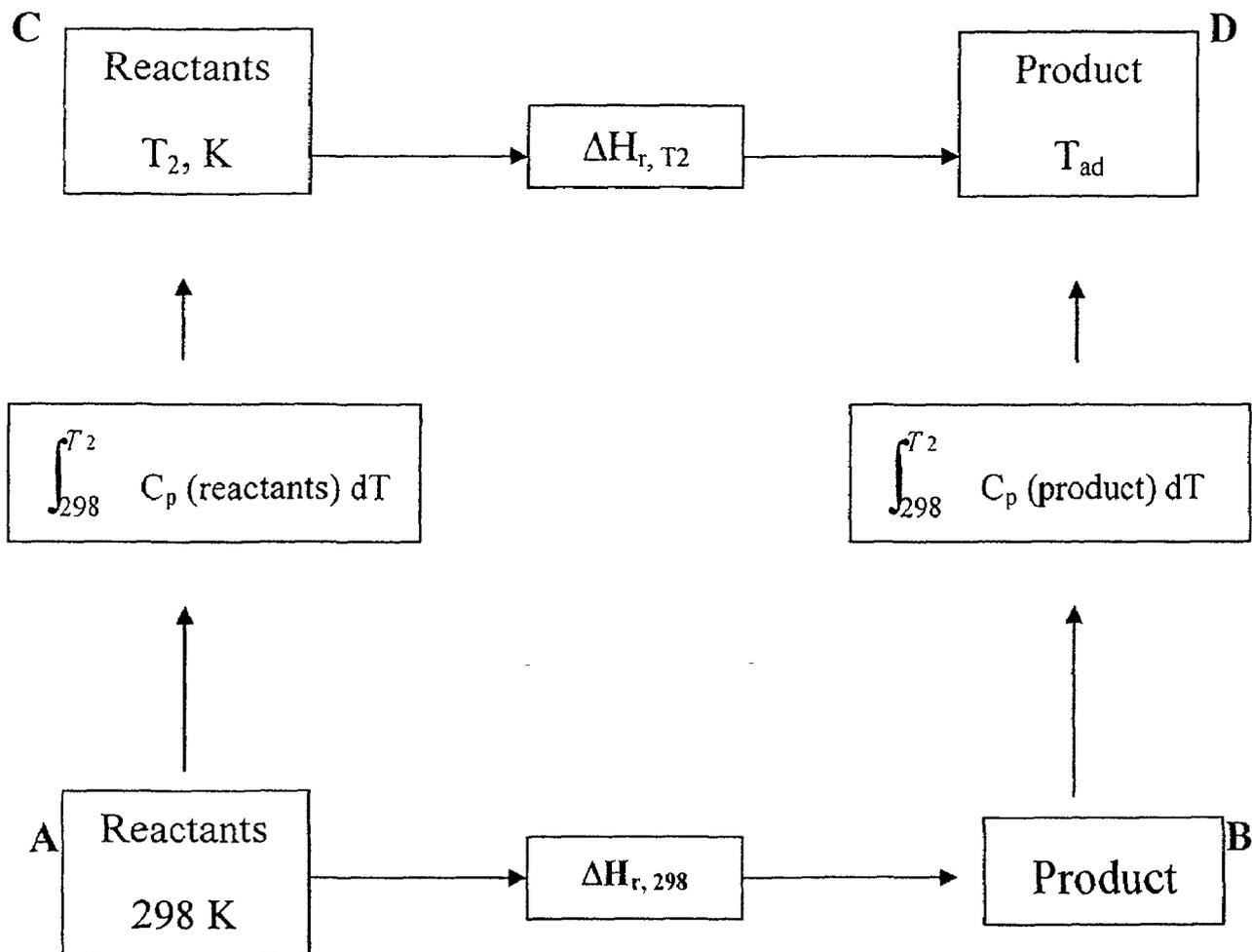


Fig. 1 Schematic heat balance for SHS reaction where AB path represents the reaction at 298 K; CD path refers to the reaction at T_2 K; AC path represents heating of the reactants from 298 to T_2 K; and BD is the path of heating up the products from 298 to T_2 K^[13].

Data of Table: 1 are shown graphically in Fig. 2, where it may be seen that SHS behavior was predicted correctly for all mentioned reactions except for $\text{Mo} + 2\text{Si} \rightarrow \text{MoSi}_2$ and $\text{Ti} + 2\text{B} \rightarrow \text{TiB}_2$ which are weakly exothermic^[17].

Table: 1 SHS Parameters for various reactions, $T_{\text{start}} = 298 \text{ K}$

| Reaction | T_{ad}, K | T_{ig}, K | $\frac{T_{\text{ad}} - T_{\text{ig}}}{T_{\text{ig}} - T_{\text{start}}}$ | $\frac{C_p(\text{reactants})}{C_p(\text{products})}$ | SHS |
|--|---------------------------|---------------------------|--|--|-----|
| $\text{Si} + \text{C} = \text{SiC}$ | 1800 | 1573 | 0.2 | 0.89 | No |
| $\text{Ti} + \text{Ni} = \text{TiNi}$ | 1552 | 1183 | 0.42 | 1.14 | No |
| $9\text{Cu} + 4\text{Al} = \text{Cu}_9\text{Al}_4$ | 1103 | 821 | 0.54 | 0.93 | No |
| $\text{Ti} + \text{Al} = \text{TiAl}$ | 1518 | 913 | 0.98 | 1.05 | No |
| $\text{Mo} + 2\text{Si} = \text{MoSi}_2$ | 1913 | 1217 | 0.76 | 0.82 | Yes |
| $2\text{Ni} + \text{Si} = \text{Ni}_2\text{Si}$ | 1600 | 965 | 0.95 | 0.91 | Yes |
| $\text{Ni} + \text{Al} = \text{NiAl}$ | 1911 | 900 | 1.68 | 0.85 | Yes |
| $\text{Ti} + \text{C} = \text{TiC}$ | 3210 | 1300 | 1.91 | 0.89 | Yes |
| $\text{Ti} + 2\text{B} = \text{TiB}_2$ | 3200 | 1173 | 1.28 | 0.81 | Yes |

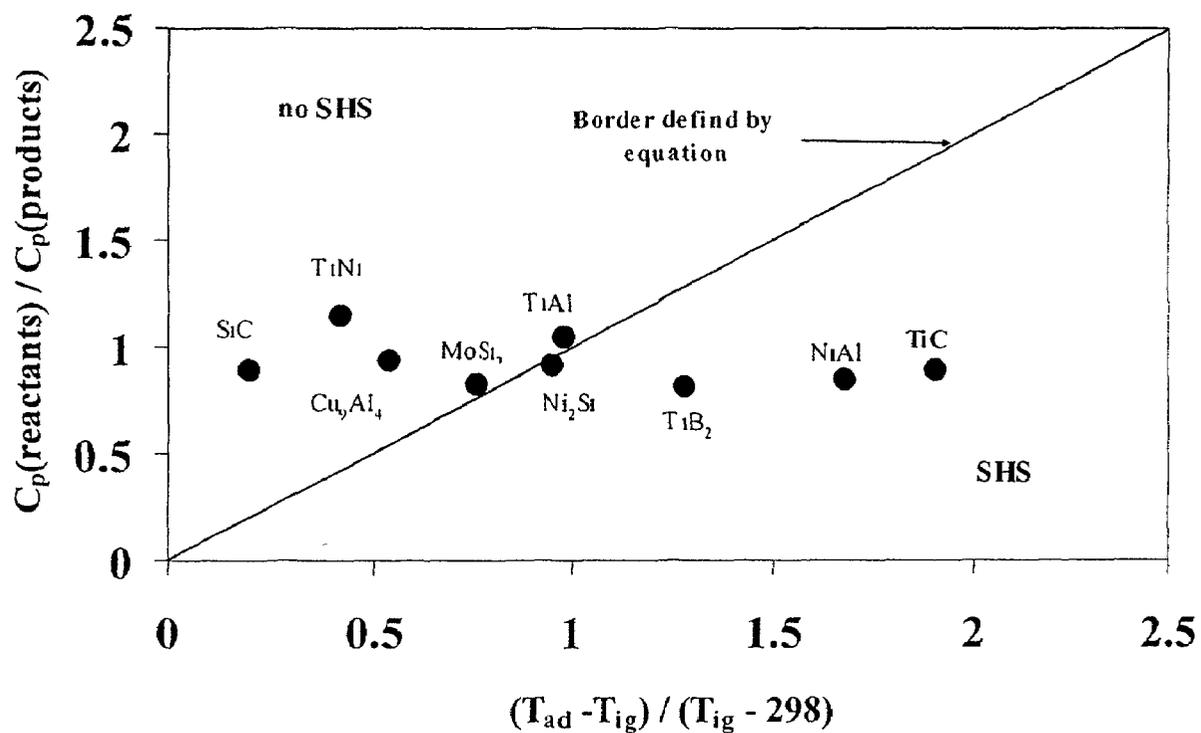


Fig. 2 Variation of C_p (reactants) / C_p (products) with $(T_{ad} - T_{ig}) / (T_{ig} - 298)$ for various reaction systems

1.1.2 Kinetic study of self-propagating combustion reactions

Kinetic investigations in self-propagating combustion synthesis reactions have primarily utilized two experimental approaches: Combustion wave velocity measurements and temperature profile determinations. In the former, the temperature dependence of the wave velocity is used to calculate the activation energy of the process and in the latter the reaction rate is used to determine the same kinetic term.

1.1.2.1 Wave velocity measurements

The general heat balance expression is used to derive a formula describing a self-propagating reaction^[18],

$$C_p \rho \cdot \partial T / \partial t = k \cdot \partial^2 T / \partial x^2 + Q \rho \cdot \phi(T, \eta)$$

where, ϕ and η are defined as, $\phi(T, \eta) = \partial \eta / \partial t$; ϕ is the kinetic function; C_p is the specific heat of the product; ρ is the product density; η is the fraction reacted at time t and T is the temperature at that time; k is the thermal conductivity of the product; x is the axial distance; Q is the heat generated from the reaction. This equation assumes no heat loss that is the sample which possesses an essentially infinite diameter and where the radial diameter is uniform so that the combustion front is planar. Assuming a homogeneous reaction, then the kinetic function $\partial \eta / \partial t$ may be expressed as,

$$\partial \eta / \partial t = k_0 (1 - \eta)^n \exp(-E/RT)$$

Where k_0 is a pre-exponential constant; R is the universal gas constant; and n is the order of the reaction. Assuming a narrow zone of the reaction, Khaikin and Merzanov^[18] derived the solution:

$$u^2 = [f(n)^a k_0 C_p R T^2] / [Q E \cdot \exp(-E/RT)]$$

Where $f(n)$ is a function that depends on the order of the reaction, n , u is the velocity of the combustion front, and a is the thermal diffusivity of

the product. By plotting $\log (u/T)$ versus $1/T$, the apparent activation energy, E , is calculated from the slope of the Arrhenius plot.

1.1.2.2 Temperature profile analysis

Generally, a temperature profile describes how the temperature develops with time. Fig. 3 is schematic representations of three important parameters associated with the propagation of a combustion wave. These parameters (Temperature T , rate of heat released ϕ and degree of conversion η) are shown for a wave traveling from right to left.

In the case depicted in Fig. 3A, the reaction is assumed to reach completion in the combustion front as evidenced by the associated values of T , η and ϕ . In contrast, Fig. 3B depicts another case in which the reaction is only partially completed within the boundary of the wave. In this case both, T and η continue to increase even after traveling of the wave to the adjacent layer^[19]. Kinetic analyses of combustion reactions depend essentially on the variations of these parameters with time.

Depending upon the heat balance equation in which an axial heat loss term is added, Boddington and co-workers^[20, 21] derived another equation which expresses the reaction rate, $\partial\eta/\partial t$, in terms of the temperature profile parameters:

$$\partial\eta/\partial t = [(\tau) t_x^{-1} + \partial\tau/\partial t - (\partial^2\tau/\partial t^2) t^*] / \tau_{ad}$$

Where, $\tau = T - T_0$ is the temperature rise, τ_{ad} is the maximum temperature rise under adiabatic condition

$$\tau_{ad} = t_r \times \tau(t_1) / (t_d - t_r) + t_d \times \tau(t_2) / (t_d - t_r) - 1 / (t_d - t_r) \times \int_{t_1}^{t_2} \tau dt$$

$$, t_x = t_d - t_r \quad \text{and} \quad 1/t^* = 1/t_r - 1/t_d$$

Where, t_r and t_d are the rise and decay times of the temperature in the remote ahead and behind the wave where no reaction can take place; $\tau(t_1)$ is the temperature difference at time t_1 in the rise region, $\tau(t_2)$ is the temperature difference at time t_2 in the decay zone.

Both t_d and t_r are obtained from the plots of $\ln \tau$ vs. t in the rise and decay zones where the slopes of the straight lines are equal to $1/t_r$ and $1/t_d$, respectively.

1.2 Historical development of self-propagating high temperature synthesis (SHS)

In the middle of twentieth century, Krapf ^[22], Wolton ^[23] and Abramovici ^[24] published several papers describing the use of the heat released from exothermic reactions to form metal-ceramic composites. In 1967, Borovinskaya, Skhiro and Merzhanov ^[25] began a systematic investigation of combustion synthesis reactions at the Institute for Chemical Physics, former U.S.S.R. Academy of Sciences.

One of their initial observations was of the violent reaction of titanium with boron to yield titanium boride (TiB_2), in which the product was found to retain its original shape with a hard and relatively dense body. The authors realized the potential of such a simple process and began to investigate the synthesis of other high value ceramic materials. This work lead eventually to the establishment of the Institute for Structural Macrokinetics in Chemogolovka near Moscow, a former U.S.S.R. Academy of Sciences institute dedicated to research in SHS.

In the early of 1980s low research efforts were started in the United States, and Japan. In the U.S.A., the combustion synthesis (CS) research began primarily with the DARPA (Defence Advanced Research Projects Agency) two year programs (1984-1986) ^[26]. The Ti-C and Ti-B systems were extensively studied at the U. S. Army Material Laboratories, ^[27, 28] while Rice and coworkers ^[29, 30] studied the simultaneous reaction and densification of ceramic materials and composites. Logan et al. ^[31, 32] studied the synthesis and processing of powders such as TiC, TiB_2 and $\text{TiB}_2\text{-Al}_2\text{O}_3$ composite powders through

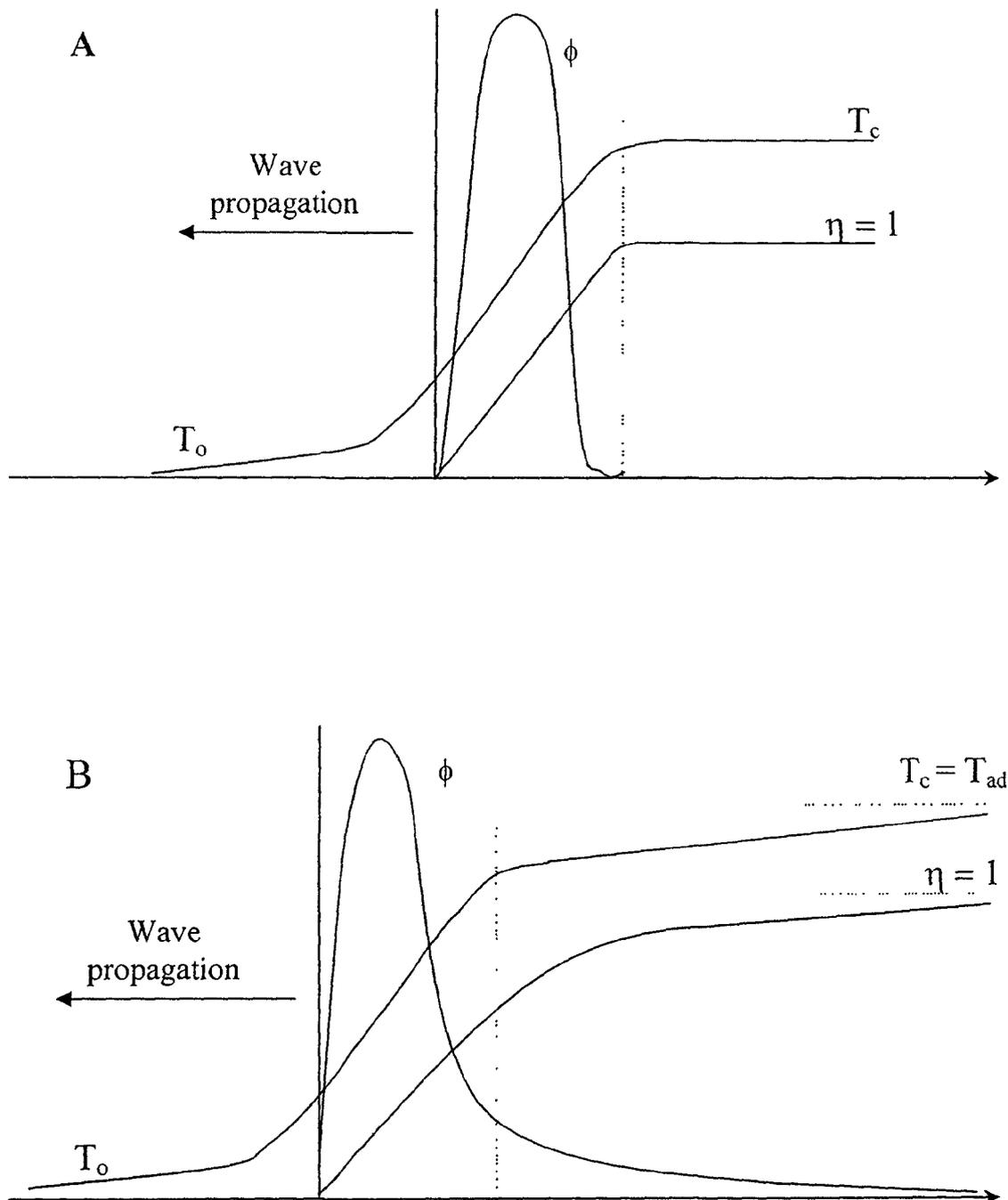


Fig. 3 Schematic representation of a combustion wave

- A. complete reaction in combustion zone
- B. Partially complete reaction in combustion zone

thermite-type reactions. The research headed by Munir and Holt^[33, 34] was aimed to provide a fundamental understanding of combustion synthesis reactions.

In Japan, the study of combustion synthesis was initiated by Koizumi and Miyamoto at the Institute of Scientific and Industrial Research of Osaka University in 1984^[35, 36]. They demonstrated that refractory ceramics such as TiB₂, TiC and SiC could be synthesized and simultaneously densified by the high pressure combustion sintering (HPCS) method; in which high pressure consolidation techniques were used in conjunction with the SHS reactions. Odawara and J. Ikeuchi, at the Tokyo Institute of Technology^[37, 38] have successfully used SHS reactions coupled with centrifugal motion as a method to deposit corrosion-resistant coatings on the inner wall of pipes. Since 1984 a large number of ceramic powders have been synthesized in Japan using SHS. Examples of the commercial use of these powders include raw materials for SiC ceramics, refractory bricks and abrasives^[36]. In 1990s the SHS process was released and propagated through the world^[39].

1.3 General characteristics of self-propagating high temperature synthesis (SHS)

Self-propagating high temperature synthesis is defined as a process that utilizes the heat evolved from an exothermic reaction to complete the reaction between the raw materials in a self-sustaining manner. It consists of three fast steps initiation, wave propagation and termination as shown in Fig. 4^[40].

The initiation step needs very high temperature with very fast heating rate. Normally, the reaction is initiated from the surface with a high heat flux supplied from heated wire, carbon electrode, electric spark, laser beam, etc. After less than one minute the reaction starts and propagates through the reactive sample in a wave style and this wave

continues its propagation until all the raw materials are reacted. In some cases, the reaction is initiated by bulk heating the compact in a furnace and carried out in the thermal explosion mode.

During the wave propagation, the sample is divided into three different regions consisting of a product, combustion wave and the reactants. Although both reactants and products can be easily identified, reactions occurring within the combustion wave are complicated. For simplicity, the combustion wave region consists of a zone for heating the reactants to a threshold temperature (ignition temperature) at which a spontaneous reaction is initiated between reactants and another one for synthesis of products. Combustion synthesis is a very interesting process since both the zone of heating and the zone of synthesis move with the propagation of the combustion wave, converting the reactants into products. It can be considered that the SHS process typically involves reaction between a metal and a non-metal (or another metal of higher melting point).

Generally speaking, before the arrival of the combustion wave, the effects of the reaction cannot be remarkable due to the low temperature and the small area of contact between the solid reactants.

However by approaching of the combustion wave, the lower melting-point metal melts first, resulting in slurry consists of higher melting-point non-metal particles suspended in the molten metal. This leads to faster reaction rate as well as much higher heating rates of the reactants due to the anticipated increase in the area of contact (solid/liquid phase) thus the reaction between the metal and non-metal is greatly enhanced. The reaction takes place at the surface of the non-metal particles and continues until all non-metal particles disappeared.

Different modes of propagation of the combustion wave such as steady planar, pulsation, spinning and repeated combustion wave are

reported ^[25] depending on the experimental conditions. In the pulsating combustion, the combustion wave travels in a planar but pulsating manner, which results in materials with a laminated structure. In spinning combustion, the combustion wave is non-planar and the wave moves along in a spiral path over the surface of the sample, inside which reactants experience only heating without reaction. In repeated combustion, after the passage of the combustion wave, another wave is initiated and propagates through the burned medium, yielding the final combustion products from the intermediates.

Makino and others ^[41, 42] mentioned the typical parameters characterizing the combustion synthesis process as follows:

| | |
|--|---|
| Combustion temperature | From 1800 to 4000 K |
| Heating rates | From 10^4 to 10^6 °C/min |
| Velocity of the combustion wave | From 0.1 to 25 cm/s |
| Induction time for ignition | From 0.2 to 1.2 s |
| Ignition temperature | From 1000 to 2000 K |
| Thickness of synthesis zone | From 0.1 to 5 mm |

The reaction time involved in combustion synthesis is very short (few seconds to minutes) compared with the long heating time (several hours) involved in heating up the whole solid reactants to the desired temperature in the conventional technique. Also, the heating rate is very high compared with several degrees per minute during the conventional processes.

The combustion synthesis products may be in the form of powders, ingots, whiskers, cakes, foams, fiber or crystals. It can also be used for net-shape production of machine parts. The cost effectiveness of the SHS is normally associated with, energy savings, high combustion

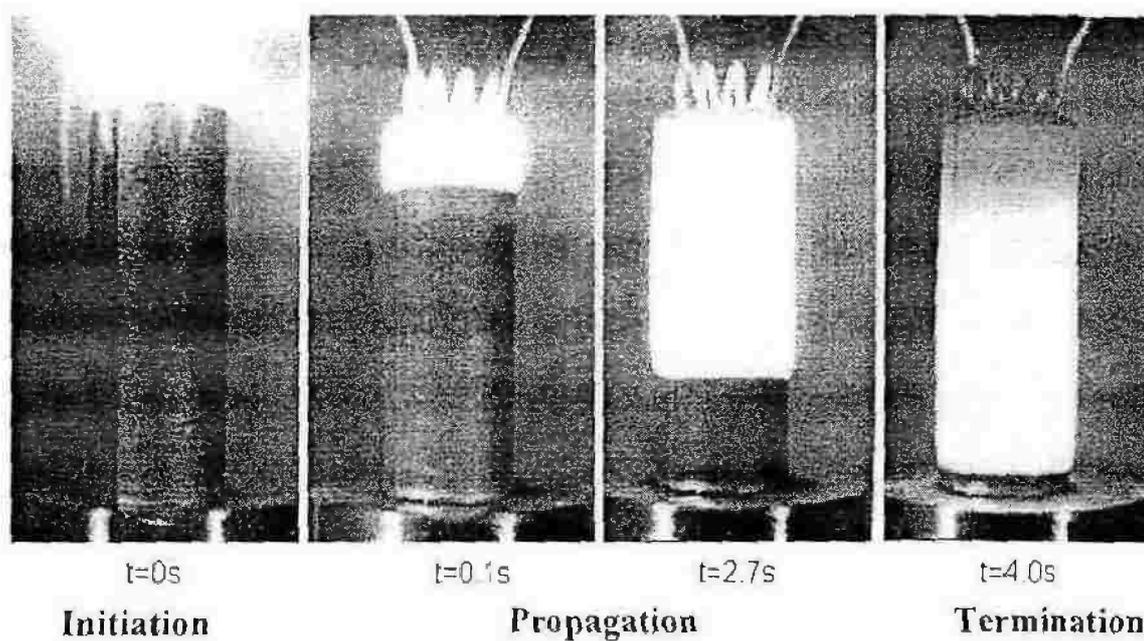


Fig. 4 Three steps of self-propagating high-temperature synthesis

temperature and burning velocity, simplicity of facilities and high quality products.

1.4 Controlling factors in SHS reactions

The SHS reactions are influenced by the density and diameter of the green compacts, amount of diluents, the starting temperature, reactants grain sizes, processing atmosphere and the stoichiometric ratio of the reactants ^[43-70].

1.4.1. Density of the green mixture

Because of kinetic limitations, self-sustaining combustion synthesis reactions cannot be initiated in very dense powder compacts. In compacts of (TiO₂ + 4 Al + 3 C), self-propagating waves can be initiated in samples with less than 78% relative density. At this and higher densities, propagation rates not only decreased but terminated due to self extinction in some cases or failed to ignite and propagate. The dependences of wave velocity and combustion temperature on the relative density of the reactants were qualitatively similar, showing maxima at a relative density of about 60 ± 10% ^[47].

1.4.2. Particle size of reactants

Some authors ^[48-51] studied the effect of particle size on a number of SHS reactions. It was reported that an increase in particle size leads to a decrease in the combustion wave velocity, reaction rate and a broadening of the combustion wave. This is attributed to the increase in the maximum size of the diffusion barrier of the reactants, which decreases the reaction rate. Bowen and Derby ^[13] stated that, the SHS reactions are enhanced by decreasing the particles sizes of the reactants, increasing the diameter of the compact, decreasing the amount of diluents and increasing the starting temperature.

1.4.3. Addition of diluents

SHS reactions can also be controlled by adding diluents to the reactants; this lowers the adiabatic combustion temperature [46, 52-57]. These additions do not take part in the reaction but they increase the specific heat of the system and thus lowering the adiabatic combustion temperature. Lowering the adiabatic temperature would result in a decrease in both the reaction rate and the combustion temperature [58, 59]. Botta and co-workers [60] used Al_2O_3 as diluents during SHS reactions to form a low melting point eutectic phase to aid densification.

1.4.4. Preheating the compacts

Preheating of the reactants before ignition in the presence of inert atmosphere results in increased adiabatic combustion temperatures [61-66]. The raise in adiabatic temperature enhances the reaction rate and increases the combustion velocity. This phenomenon has been used for low exothermic reactions that do not undergo SHS reaction [67]. In addition, preheating the sample has been shown to have a significant effect on the microstructure of the formed ceramic because the combustion temperature can be raised above the melting point of one of the products [68]. Alternatively, if the total amount of reactants is heated simultaneously to the ignition temperature e.g. by inserting the reactant compact into a furnace, a thermal explosion combustion mode occurs. In this case the reaction takes place simultaneously throughout the whole sample without wave propagation [69, 70].

1.5 Properties of titanium carbide and aluminum oxide composites

TiC/Al₂O₃ composites are among the "advanced" ceramic that have been widely used in industries as cutting tools and wear resistance coatings because of their high hardness, chemical stability, good strength and toughness at elevated temperatures, and excellent wear resistance^[71]. Another modern application is the use as magnetic head slider substrates because they have high requirements for oxide-carbide homogeneity and microscopic wear resistance^[72].

1.5.1. Titanium carbide

Representative values of physical properties of titanium carbide^[73] are given in Table 2. Since TiC exists as a homogeneous phase over a relatively wide range of compositions and the solubility of C in Ti is approximately 3 % as shown in Fig. 5, the product of the synthesis of Ti and C has been found to be the carbide phase, a solid solution, or a combination of these two phases depending on the experimental conditions and the characteristics of the starting materials^[74].

Table: 2. Properties of titanium carbide

| Property | Value |
|--|-----------------------------------|
| Density (g/cm ³) | 4.8 |
| Melting point (°C) | ~3100 |
| Boiling Point °C | 4820 |
| Hardness (kg/mm ²) | 3000 |
| Young's Modulus (kg/mm ²) | 4.6 x 10 ⁴ |
| Specific heat capacity (cal/cm s °C) | 0.2 |
| Thermal expansion coefficient (deg C ⁻¹) | 0.08 -1.1, 7.2 x 10 ⁻⁶ |
| Crystal lattice | Cubic |

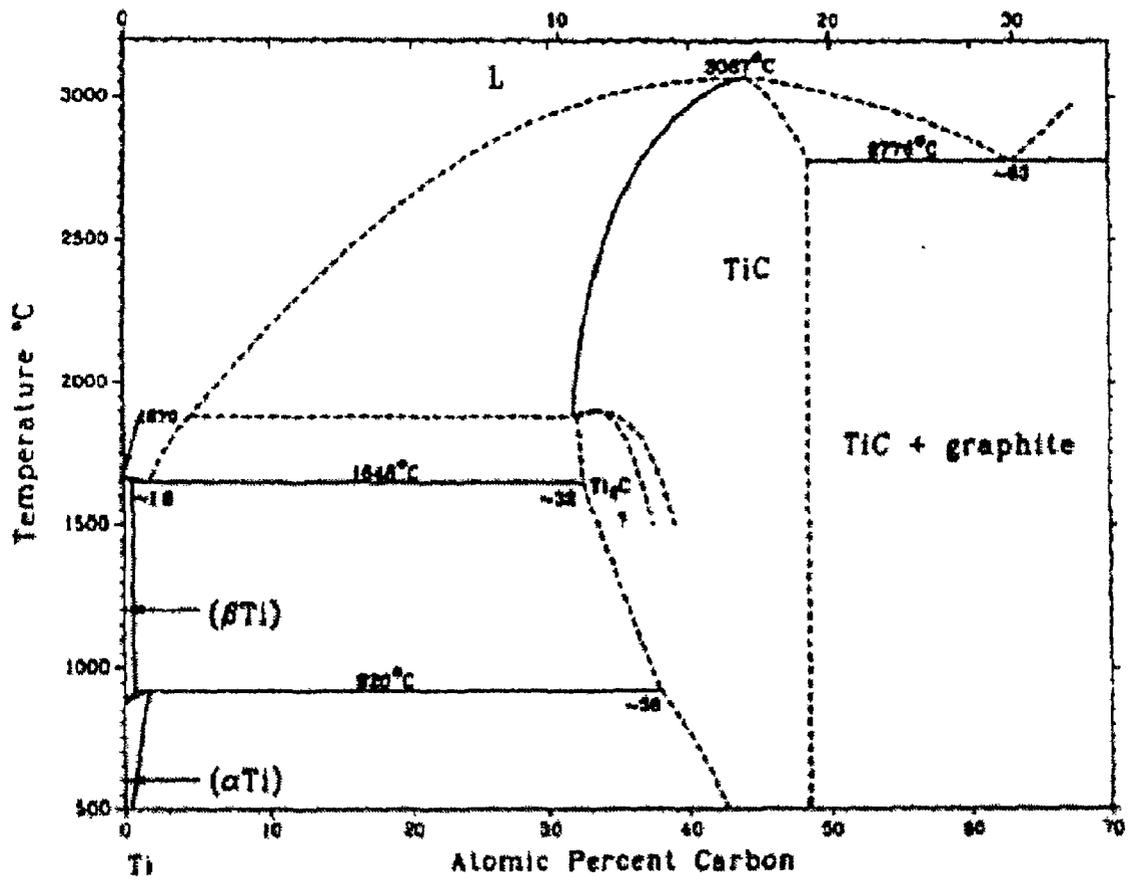


Fig. 5 Titanium-Carbon phase diagram [74]

1.5.2. Aluminum oxide

Whiskers of alumina have a tensile strength of nearly 2 magnitudes higher than ordinary bulk material. For example, normal alumina ceramics are characterized by a tensile strength of 30-60 kp/mm², while alumina whiskers ^[75] have a tensile strength between 2000 and 3000 kp/mm². Selected values of physical properties of alumina are shown in table 3 ^[73].

Table: 3. Properties of Alumina ceramics

| Property | Value |
|--|----------------------|
| Melting point | 2053 °C |
| Apparent relative density | 3.4 - 3.7 |
| thermal expansion Coefficient | 7.5 - 7.9 |
| Tensile strength(kg/cm²) | 1400 - 1750 |
| Compression strength(kg/cm²) | 10000 - 28000 |
| Bonding strength | 2800 - 4200 |
| Wear strength(kg cm/cm²) | 5.6 - 6.2 |
| thermal conductivity(cal.cm/cm² s°C) | 0.040 - 0.45 |
| Water absorption (%) | 0.0 - 0.00 |

1.6 Synthesis of titanium carbide/aluminum oxide composites

Titanium Carbide can be synthesized by variety of ways, such as vapor or plasma synthesis, sol-gel processing, metal oxide carburization and by self-propagating high-temperature synthesis [76-95].

Some authors investigated the synthesis of titanium carbide by SHS from elemental powders of titanium and carbon [96-100].

Choi et al. [96] studied the fabrication of fine fiber TiC by SHS method from titanium and carbon fiber with and without the addition of aluminum metal powder. The study showed the possibility of formation of aluminum carbide in addition to TiC composite (92 % density) containing TiC fiber and aluminum metal by SHS followed by Hot Isostatic pressing (HIP).

Pijje and Li et al. [97] prepared Al-TiC composites by SHS using titanium, carbon and aluminum with and without fluxing agents, (Na_3AlF_6) which used as activator. It reduced the delay time of SHS reaction by a factor of 3 – 5, and increased the melt over-heating temperature by 20-40 K. The titanium and carbon yield in the composites is promoted in case of fluxing sample.

R. W. Rice and Wei-Chang Lee [47, 98] investigated the effect of the addition of aluminum metal powder on the ignition temperature and reaction mechanisms of Ti-C system via SHS process. The reaction between titanium and aluminum was believed to occur before the ignition of the reaction between titanium and carbon. It was found that the addition of 30 wt % Al decreased the ignition temperature from 1700 to 1050 °C. Also, the ignition temperature decreased as the green compact density increase and reached to a minimum (1185 °C) at 60 wt % of theoretical density.

In-Hyuck Song [99] discussed the different steps for formation of Al-TiC composites by exothermic reaction from Ti-Al-C system as

follows, carbon and titanium powder were surrounded by liquid aluminum as a first step, after that, titanium powders reacted with aluminum and changed into TiAl_3 , whisker-shaped Ti_3AlC_2 as an intermediate was clearly observed, finally TiC particles were formed with a smooth surface.

N. Zarrinfar ^[100] studied the effect of initial powder mixture proportions on the stoichiometry of TiC_x produced by SHS of Ti + C and Cu + Ti + C mixtures. When no copper was present, the carbide stoichiometry closely followed that of the starting powders. In the presence of copper, the lattice parameter of the TiC_x is always higher than that observed with no copper for the same C/Ti ratio in the starting powders, due to the dissolution of some titanium into copper and formation of Ti_2Cu_3 and Ti_3Cu_4 .

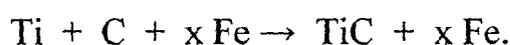
C. Curfs and co-workers ^[101] investigated the SHS reaction of the quaternary system Al–Ni–Ti–C followed by time-resolved powder diffraction, using a third generation X-ray synchrotron source, with a time-scale of 100 ms allowing a detailed study of the reaction mechanism. The reaction starts with the synthesis of TiC followed by melting of Al and Ni and a subsequent formation of NiAl during cooling. The TiC formation begins through a solid state reaction. The final product is composed of small, round TiC particles embedded in a continuous matrix of NiAl.

Z.Y. Fu and co-Workers ^[102] used the elemental powders of Ti, C, Ni, B, and Fe to fabricate TiC–Ni and TiB_2 –Fe composites by SHS plus dynamic mechanical pressing (pressing speed of 80 mm/s), which combines synthesis and densification in one step was named SHS/IP. The propagating rates increased with increasing the metal contents and reached to maximum value (1.2 cm/s) for TiC–20 mol % Ni and 4.5 cm/s for TiB_2 –30 mol % Fe. With the increase of the metal content, the

adiabatic and combustion temperatures decreased, finally, the calculated activation energies are 166 kJ/mol for TiC–20 mol % Ni and 399 kJ/mol for TiB₂–40 mol %Fe.

C. Deidda et al. ^[103] studied the effect of the mechanochemical activation (the milling time) on SHS parameters (combustion temperature and velocity of the reaction) to prepare titanium carbide from elementary powder. The combustion temperature increased from 1947 °C to 2137 °C according to a linear trend as the time of mechanochemical activation increased from 50 min to 275 min. Also, the velocity of the reaction increase from 9 mm/s to 35 mm/s.

Roberto Licheri and co-workers ^[104] investigated the synthesis of titanium carbide/iron composite by means of self-propagating reactions to be subsequently employed for plasma spray deposition. In this work, titanium, graphite and iron powders, were mixed according to the stoichiometry of the following reaction:



as the amounts of iron in the starting mixture was augmented to 50 wt% the combustion temperature decreased from 2427 °C to 1527 °C and wave propagation decreased from 1.75 cm/s to 0.7 cm/s. The reaction maintained the self-propagating mode if the Fe content is equal to or less than 60 wt %.

H.Y. Wang and co-workers ^[105, 106] studied the effect of Al content on the SHS reaction of the Ti–C system in molten magnesium. The results showed that preheating temperature has a great effect on the SHS reaction. For a preheat temperature of 450 °C, in situ TiC/Mg composite was fabricated successfully ^[105]. Also TiC particulate sizes were decreased from ~5.0 to ~1.0µm when Al content in the system ranged from 20 to 40 wt. %. In situ formed TiC/Mg composite utilizing the SHS

reaction of molten magnesium and Ti–C system with a 30 wt. % Al content was synthesized successfully. Microstructural characterization showed relatively uniform distribution of TiC particulates in the matrix material and the presence of minimal micro-porosity. Also an increase in the properties of hardness and wear resistance were noticed ^[106].

Han Jie-Cai and co-workers ^[107] showed the possibility of formation of dense TiC–xNi cermets with Ni contents of 10–50 wt % by combining combustion synthesis with isostatic pressing (IP). With increasing Ni content in TiC–xNi, to 50 wt %, the combustion wave velocity decreased from 4.8 to 1.9 cm/s and combustion temperature decreased from 2627 to 1627 °C. The microstructures consisted of spherical TiC grains embedded in a nearly continuous Ni binder. The nickel additives change the shape of TiC grains from angular to spherical. The size of the particles decreased from 16 to 2 μm with an increasing amount of metal addition. Hardness and transverse rupture strength tests indicate that the properties of the SHS/IP material are within the range of conventionally processed cermets and that material with 20 wt% Ni addition is excellent.

Z. Xinghong and co-workers ^[108] reported that TiC/TiB₂ ceramic–matrix composites were produced by SHS combined with hot isostatic pressing using Ti, B₄C and carbon powder. All the synthesized compacts contained TiB₂ and TiC two phases with no unreacted B₄C, Ti or carbon. The typical microstructure of compacts consisted of the clubbed TiB₂ grains and equiaxed or irregular TiC grains. The ceramic prepared from the composition (72.2 wt % Ti and 27.8 wt % B₄C) owned the maximum value of the bending strength (450 MPa) and compression strength (2.68 GPa) which is higher than the TiC/TiB₂ prepared by reactive synthesis. The introduction of more clubbed TiB₂ grains into TiC/TiB₂ ceramics

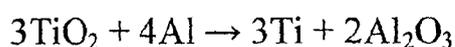
resulted in a drastic increase in the fracture toughness. The optimal ratio of the reactant powder was determined, which is Ti: B₄C equals to 3:1.

TiC/Al₂O₃ composites can be produced by exothermic reaction using low cost TiO₂ as a reactant; therefore, the expensive of high-cost metallic Ti starting powders is eliminated. In addition to, we have in Egypt a large amount of TiO₂ ore (Rutile ~85-90 % TiO₂) present in black sand at Damietta beach. The researches in Central Metallurgical Research and Development Institute (CMRDI) used rutile to produced pure TiO₂, so we are thinking to use these efforts to produce an important TiC/Al₂O₃ composite.

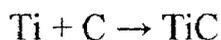
Barry H. Robin et al. ^[109] fabricated TiC/Al₂O₃ from commercially available reactants of TiO₂, Al, and C by the SHS and subsequent dynamic consolidation of the hot products using explosives as well as one GPa to achieve near full densification over 95 % of theoretical density. Products appeared to be well-bonded and exhibited a fine, interconnected composite microstructure.

The effect of Al addition in the SHS of 3TiO₂ + 3C + 4Al reaction was studied by H. J. Feng and co-workers ^[110]. The relative green compact density increased from 48 to 75 % with increase in the excess amount of Al used in the reaction system from 0 to 9 moles. When the relative green compact density increased the ignition temperature of the reaction increased from 950 to 1130 °C and decreased the volume fraction of open pores from 0.5 to 0.27 as well as closed pores from 0.22 to 0.06.

Differential thermal analysis (DTA) was carried out on the SHS reaction of 3TiO₂ + 3C + 4Al by C. R. Bowen and B. Derby ^[111]. The ignition temperature was 900 °C and the reaction proceeds by an initial reaction between titania and aluminum metal:



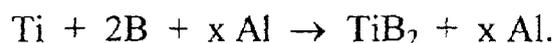
and then titanium formed reacts with the free carbon:



to produce the final TiC/Al₂O₃ ceramic composite.

The effect of Titania particle size on the combustion temperature has been studied by Feng and Moore ^[112] who examined various TiO₂ powder size in the range from 50 to 200 μm. Pyrometer measurements indicated that as the reactant particle size increased the combustion temperature decreased, then leads to a decrease in wave velocity.

The wave velocity increases with a small addition of excess aluminum (5 wt %) and then begins to decrease at higher addition of diluents with the reaction failing to propagate at 40wt% excess aluminum. An increase in wave velocity with increasing liquid diluents has been observed by Fu et al. ^[57] in the reaction:



The Laminar structure of the product is not affected with additions of 5 to 20wt % excess aluminum. At 30wt% the product microstructure becomes irregular.

Duangduen Atong and David E. Clark ^[113] produced Al₂O₃-TiC powders by SHS using microwave heating (MH) and microwave hybrid heating (MHH). The results showed no significant difference in the characteristics of powders ignited by two heating methods (MH and MHH); though a clear difference in ignition behavior was observed. Nevertheless, it was found that both MH and MHH ignited powders showed no significant difference in their properties. The average values of powder densities, particle sizes, and specific surface areas were in the range of 3.7–3.8 g/cm³, 1.4–1.5 μm, and 1–1.2 m²/g, respectively.

The effect of an addition of ZrO₂ nanoparticles on the combustion synthesis of TiO₂ –Al –C system was investigated by Q. Dong et al. ^[114]. The results of thermodynamic calculations shows that about 10 wt %

ZrO₂ nanoparticles addition reduces the adiabatic temperature from 2398 to 2327 K (the melting point of Al₂O₃). The fraction of molten Al₂O₃ varied from 100 to 78 % with the addition of ZrO₂ in the range of 0-15 wt. %. The combustion wave velocity decreased from 3.8 to 1.2 mm/s with increasing ZrO₂ content. The combustion product is a mixture of Al₂O₃, TiC and ZrO₂. XRD analysis indicated that the combustion products are mainly Al₂O₃, TiC and tetragonal ZrO₂ where Al₂O₃ grains are crystallized from the amorphous phase. TiC and ZrO₂ particles with a diameter of approximately 20 nm are distributed randomly in the Al₂O₃ particles and some amorphous regions.

1.7 Oxidation behavior

L. Zhang, X.N. Zhang and co-workers ^[115, 116] investigated the oxidation behavior of in situ synthesized TiC/Ti-6Al composite by thermal gravity analyzer (TGA). Oxidation behavior at high temperatures basically follows a parabolic law. The weight gain increases with the time and temperature of oxidation and reached to maximum (2.6 mg/cm²) at 20 h and 800°C. The activation energy of oxidation process is calculated to be 255.7 kJ/mol.

Z. Li and co-workers ^[117] studied the Oxidation behavior of Ti₃Al-TiC composites were fabricated through mechanical milling and hot isostatic pressing (HIP) using Ti, Al, and TiC as starting materials. Ti₃Al-TiC composites exhibited a lower oxidation rate than the cast Ti₃Al at 700 and 800 °C in air. The total oxidation mass gains were apparently affected by the ball milling time, of order 4 < 2 < 8 < 16 h. The composite samples exhibited superior scale spallation resistance except the sample one of four h milling at 800 °C. It is believed that the oxide scales with the properties of dense, easy to deform, strong adherence, and good interfacial connections have good protective ability.

Isothermal oxidation of sintered titanium carbide (TiC) ceramics produced by HIP processing was examined by A. Onuma et al. [118]. It was carried out at temperatures of 900 to 1200 °C for 1 to 50 h. in O₂/Ar (dry oxidation), O₂/H₂O/Ar (wet oxidation) and H₂O/Ar (H₂O oxidation) with oxygen and water partial pressures (P_{O₂} and P_{H₂O}) of 5 kPa. The oxidation rates at 900 °C in dry and wet atmospheres were not greatly changed, but slightly accelerated in H₂O. At 1000 °C, the oxidation rates became higher in the order of H₂O>wet>dry atmosphere. Above 1100 °C, the oxidation rates were almost the same as in wet and H₂O atmospheres, but higher than in the dry condition. Cracking occurred in the scale product corresponding with inflection points on the isothermal oxidation curves. X-ray diffraction analysis showed that the oxide scale obtained consisted of TiO₂ under all conditions.