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To cite this article: R Rahbari G et al 2009 J. Phys.: Conf. Ser. 152 012055

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Combustion synthesis of TiO$_2$-Al-C/Al$_2$O$_3$ mixture in the presence of oxygen

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Abstract. Quasi-adiabatic combustion synthesis of optimized 3TiO$_2$+4Al+(3+x)C mixture in the presence of oxygen was carried out to produce TiC-Al$_2$O$_3$ composite. The influence of Al$_2$O$_3$ diluent in combusted (3TiO$_2$+4Al+3.5C+yAl$_2$O$_3$) reactant mixture was investigated. Thermodynamics studies of the system shown that self-sustaining (SS) mode of combustion wave propagation can occur for large amounts of diluents ($y = 2.5$). Diluent reduced combustion temperature and rate of reaction kinetics. Oxide (Ti$_2$O, Ti$_3$O$_5$) and intermetallic (AlTi$_2$) phases were detected when extra Al$_2$O$_3$ was added to the mixture. Semi-quantitative XRD analysis was employed to study the phase formation of products for various amounts of diluent content in the mixture. The boundary between SS and non-SS modes of wave propagation was determined. Adding Al$_2$O$_3$ diluent slightly increased density that resulted in better thermal conductivity.

1. Introduction
Combustion synthesis (CS) uses chemical reaction energy to produce various high temperature materials. The mechanism of structure and phase formation of this rapid, high temperature synthesis method requires appropriate control to produce the desired product.

Adding inert diluents to initial mixture absorb the heat and decrease the violence of combustion reaction. A diluent can be an inert component to the reactant mixture and/or one of the specific products of the combusted mixture. Adding one of the products, such as Al$_2$O$_3$, to the reactant (3TiO$_2$+4Al+3C) mixture is commonly used to control combustion process and grains grow of the product [1-3]. The diluent reduces the adiabatic temperature and decreases kinetic rate of reaction to achieve desired microstructure and properties.

TiC-Al$_2$O$_3$ composite is a promising material in industry as an abrasive tools, wear resistant coating, magnetic head recording substance as well as heatable valves and nozzles due to its attractive high temperature mechanical, chemical and electromagnetic properties. Conventionally, TiC-Al$_2$O$_3$ is produced by hot pressing of (TiC+Al$_2$O$_3$) powders consuming extensive amount of heat energy. On the contrary, combustion synthesis provides an alternative route to synthesize TiC-Al$_2$O$_3$ composite in a simple, energy saving and economic way.

Wide range of investigation has been performed on combinations of two or more components in TiO$_2$-Al-C system to produce different types of materials such as metal-ceramic and ceramic-ceramic composites [4-12]. In addition, considerable efforts have been made to investigate the reactions of
heterogeneous TiO$_2$-Al-C and TiO$_2$-Al-C-Al$_2$O$_3$ mixtures in self-sustaining reaction mode \[4, 7, 9, 10, 11\]. However, setup of an adiabatic system for combustion synthesis might raise technical difficulties and result in higher cost, so studying the synthesis under quasi-adiabatic conditions is a practical need.

Furthermore, lack of detail studies on quasi-adiabatic combustion of reactant mixtures in the presence of oxygen necessitates more efforts in this direction. In previous work \[13\], it was discussed in details that additional powders of Al and/or C is needed for production of desired TiC-Al$_2$O$_3$ composite from TiO$_2$-Al-C mixture.

This research is continued the work and focused on the combustion of TiO$_2$-Al-C mixture under quasi-adiabatic conditions with the addition of inert diluent-Al$_2$O$_3$ in the presence of oxygen. Different impacts of various diluent-Al$_2$O$_3$ fractions in the mixture on macrokinetics, and thermo-mechanical behavior of the product were studied in the project. Semi-quantitative XRD analysis revealed the phase formation and mechanism of the process. Al$_2$O$_3$-diluent absorbed heat of the exothermic reaction, so that decreased the combustion temperature. Moreover, extra Al$_2$O$_3$ reduced the contact points between reactants, decreased the reaction rate and lead the formation of intermetallic phase.

However, thermodynamic studies revealed that self-sustaining propagation of combustion wave was occurred even by adding large amounts of Al$_2$O$_3$-diluent into the reactant mixture. Experimental results showed that extra diluent decreased the porosity and consequently increased thermal conductivity of the product, slightly.

2. Experimental

Titanium (IV) Oxide (rutile; $<5$ μm; 99.9% purity; Sigma Aldrich), Al ($<10$ μm; 99.9% purity; Lab Chemical), Carbon black ($<0.02$ μm; 99.9% purity, Juhalim Co., Malaysia) and Aluminum Oxide ($<10$ μm; 99.9% purity; Sigma Aldrich) were mixed and combusted to produce TiC-Al$_2$O$_3$ composite. At first, the mixture of TiO$_2$-Al-C powders was prepared according to equation (1) to achieve the desired product under quasi-adiabatic conditions in the presence of oxygen \[13\]. For this purpose, various contents of carbon, C ($x=0, 0.5$), were examined to optimize the reaction and achieve the final TiC-Al$_2$O$_3$ product. Then, the influence of inert diluent, Al$_2$O$_3$, on the combustion of the optimized mixture was studied. In this stage, mixtures were prepared according to equation (2). All the reactants were mixed in a planetary ball mill for 6 hours. Cylindrical pellets with 20 mm in diameter and about 5 mm thickness were produced under a constant compact load of 100 MPa using uniaxial hydraulic press.

\[3TiO_2 + 4Al + (3 + x)C \quad x = 0, 0.5 \quad (1)\]

\[3TiO_2 + 4Al + 3.5C + yAl_2O_3 \quad y = 0, 0.5, 1.0, 1.5, 2.0, 2.5 \quad (2)\]

The combustion of TiO$_2$-Al-C green mixture was carried out in a tube furnace in argon and oxygen gas environment. The pellet heated up to 1100 °C and the holding time was 90 minutes. Then, the furnace was turned off and the sample was kept inside the furnace until the temperature dropped to the room temperature. On this way, possible thermo-mechanical stresses were minimized.

The combusted TiO$_2$-Al-C-Al$_2$O$_3$ compact powders were characterized by using scanning electron microscope (SEM), and x-ray diffraction (XRD) with CuK\(\alpha\) radiation. Semi-quantitative composition XRD analysis was performed to study the phase formation of the products in details. Density of the products was measured by using Archimedes method. Finally, the thermal conductivity of the products was investigated using Koh and Fortini model \[14\].

3. Results and Discussion

It is known that the combustion synthesis of (3TiO$_2$+4Al+3C) mixture includes two stages. In the first stage aluminothermic reduction of TiO$_2$ occurs according the following equation:

\[3TiO_2 + 4Al \rightarrow 3Ti + 2Al_2O_3 + Q \uparrow \quad (3)\]

Exothermic reaction between Ti and C occurs in the next stage of the synthesis as follows:

\[3Ti + 3C \rightarrow 3TiC + Q \uparrow \quad (4)\]

The proposed mechanism in (3) and (4) occurs in adiabatic closed system. But in this investigation the synthesis carried out under quasi-adiabatic conditions in the presence of oxygen. Here, mechanism
of the process is more complicated. Therefore, the optimum amount of C was found experimentally to produce the desired product [13].

The XRD result of combusted (3TiO₂+4Al+3C) and optimum reactant (3TiO₂+4Al+3.5C) mixtures are shown in figure 1. The figure shows that the combustion of (3TiO₂+4Al+3C) mixture in quasi-adiabatic conditions of the open system did not produce the desired product. However, it was observed that the optimum value of \( x = 0.5 \) would produce the desired TiC-Al₂O₃ composite. This result is in agreement with the previous work [13]. Therefore, in equation (2) the coefficient of C is considered to be equal to the optimum value, \( x = 3.5 \).

![Figure 1. XRD pattern of product for (a) (3TiO₂+4Al+3C), (b) (3TiO₂+4Al+3.5C) mixtures.](image)

3.1. The influence of diluent content on the adiabatic temperature
The calculated theoretical adiabatic temperature \( (T_{ad}) \) from the thermo-chemical parameters of the reaction can be used to predict the combustion reaction mode for a given system [15-18]. The thermo-chemical parameters of the reactants and products are given in table A1 in appendix A. The calculated adiabatic temperature \( (T_{ad}) \) for various amounts of Al₂O₃ diluent content in the mixture is shown in figure 2. It can be seen that for all the samples \( (y = 0-2.5) \), \( T_{ad} \geq 1800K \). The horizontal line corresponds to the melting point of Al₂O₃ \( (T = 2303 \text{ K}) \). Experimental investigations of combustion temperature for various Al₂O₃ diluent added into TiO₂-Al-C system were performed elsewhere [10]. The dependence of combustion temperature on diluent content showed the similar characteristics as shown in figure 2.

3.2. The influence of diluent content on the combustion wave propagation
Propagation mode of combustion wave is an important parameter of the synthesis. Heat generation due to chemical reaction as well as heat loss due to system condition and environment are defining parameters. If heat loss is not considerable comparing with heat generation (adiabatic conditions), self-sustaining mode (SS) can occur. If heat loss is considerable comparing with heat generation unsteady propagation can occur.

Investigation showed that thermal properties of reactants in heterogeneous powder mixtures are the limiting factor [20]. Bowen C R et al. [9] studied the finite-difference model of combustion in TiO₂-Al-C system based on heat generation and heat loss competition. The temperature profile throughout the sample shows that the significant temperature gradient \( (300 \text{ K to } 2500 \text{ K}) \) is in a small zone...
between reactants and products. However, the temperature in the reactant zone is almost constant due to low thermal conductivity of reactants. High temperature product which is very near to the maximum combustion temperature, results in negligible temperature gradient in product zone. It is shown that self-sustaining (SS-mode) and non-SS mode occurs depending on the ratios in (5). In other words, the point at which the combustion reaction becomes extinguished i.e. SS-mode converts to non-SS regime, can be determined by examining the equation (5). Density and thermal conductivity are not in the equation as an approximation. SHS mode will occur when the following condition is satisfied [9]:

\[
\frac{\left( T_{ad} - T_{ig} \right)}{\left( T_{ig} - T_0 \right)} \geq \frac{C_p(\text{reactants})}{C_p(\text{products})}
\]  

(5)

Where, \( C_p \) is average specific heat capacity in that temperature range.

Munir Z A [21] proposed another model based on activation energy of the combustion reaction to study influence of the diluent content and initial temperature on wave propagation. To estimate the SS/ non-SS behavior of the TiO\textsubscript{2}-Al-C system with Al\textsubscript{2}O\textsubscript{3} diluent, at first, the heat capacity of the reactant and products were calculated for various amounts of diluent. Then, the ratio of \( C_p(\text{reactant})/C_p(\text{diluent}) \) was calculated to find the right hand side of the equation (5). Ignition temperature was assumed to be constant \( T_{ig} \approx 1144K \) based on thermal analysis results. Furthermore, the adiabatic temperature \( T_{ad} \) was calculated for initial temperature of \( T_0 = 298 \) K. Finally, the corresponding diluents content was determined from figure 2. The results are shown in figure 3. The figure shows that for initial temperature of \( T_0 = 298 \) K, the minimum amount of Al\textsubscript{2}O\textsubscript{3} diluent that converts SS to non-SS mode is about 39.6 wt% ( \( y \approx 2.46 \)). It needs more diluents content to convert the SS to non-SS mode for initial temperatures greater than 298 K. Therefore, the SS-mode was occurred in all samples, even though the experiment was carried out under quasi-adiabatic condition in the presence of oxygen. The optical image of combustion product is shown in figure 4. All the samples retained its initial shape without any cracks or fractures after the combustion.

Figure 2. Calculated adiabatic temperature for various diluent - Al\textsubscript{2}O\textsubscript{3} content in (3TiO\textsubscript{2}+4Al+3.5C+yAl\textsubscript{2}O\textsubscript{3}) mixture.
3.3. Reactant mixtures
XRD pattern of the green compact mixture without diluent is presented in figure 5. The XRD composition analysis shows the presence of three components TiO$_2$, Al, and C in the green mixture. SEM micrographs of green compact mixture without diluent ($x = 3.5, y = 0$) and with diluent ($y = 2$) are shown in figures 6a and 6b, respectively. In figure 6a the biggest particles probably belong to Al powder, while the smaller bright particles represent TiO$_2$ powder. The particles of carbon black are very small and cannot be seen easily. In figure 6b two types of big particles represent Al and Al$_2$O$_3$ powders. Smaller particles belong to TiO$_2$.

3.4. Product composition of combusted reactant mixture without diluent
The combustion of the reactant powder for $x = 0$ as in (1) did not produce the desired TiC-Al$_2$O$_3$ composition. It is due to the quasi-adiabatic condition and the presence of oxygen in the system. Therefore, the additional Ti$_2$O phase was detected in the product along with TiC-Al$_2$O$_3$ (figure 1a). Adding extra carbon to the mixture ($x = 0.5$) directed the mechanism of the combustion to produce
expected TiC-Al$_2$O$_3$ composite (figure 1b). The reaction mechanism can be explained by considering the presence of oxygen. Al particles can be easily oxidized due to the presence of adsorbed oxygen or available oxygen in the environment. This resulted in deficiency of Al in aluminothermic reduction of TiO$_2$. Thus, carbothermal reduction of TiO$_2$ completed the reduction stage at higher temperature proposed by Woo Y C et al. studies [22]. The carbothermal reduction process is as in equation (6) [22]:

$$TiO_2(s) + 3C(s) \rightarrow TiC(s) + 2CO(g)$$

(6)

Hence, the addition of extra carbon ($x=0.5$) yielded the desired composition of the TiC-Al$_2$O$_3$ product. Microstructure of the desired TiC-Al$_2$O$_3$ composite is shown in figure 7. It features various grain size distributions of dark and bright grains with pores.

![Figure 6.](image)

(a) SEM micrograph of (3TiO$_2$+4Al+3.5C) mixture. (b) SEM micrograph of (3TiO$_2$+4Al+3.5C+2Al$_2$O$_3$) mixture.

3.5. Semi-quantitative phase analysis of combusted reactant mixtures with diluent

XRD patterns of combusted (3TiO$_2$+4Al+3.5C+$y$Al$_2$O$_3$) powder mixtures were collected from diffracted CuK$_\alpha$ radiation. Semi-quantitative composition analysis of the products was performed using “Reference Internal Standard Method” proposed by Chung [23]. The method includes 5-10% of error.

The semi-quantitative phase analysis of products for various values of diluent ($y=0, 0.5, 1.0, 1.5, 2.0$ and $2.5$) is shown in table 1. The results showed that after adding extra carbon ($x=0.5, y=0$), the combustion product contained only two phases: TiC (45 wt %) and Al$_2$O$_3$ (55 wt %). Adding Al$_2$O$_3$-diluent up to about ($y=1.0$) into the initial mixture increased the Al$_2$O$_3$ fraction in the same amount that consequently decreased TiC phase fraction in the product. This could be predicted theoretically as proposed by Moore J J et al. [11]. Moreover, it can be explained based on the calculated adiabatic temperature given in figure 2. According to thermodynamic estimation, when the diluent content $y \lesssim 0.058$, combustion temperature could reach above melting point of Al$_2$O$_3$ (figure 2). At that temperature, Al$_2$O$_3$ is fully melted.

In the region of about ($y<1$) the horizontal line is corresponding to the melting of Al$_2$O$_3$ in the system. It means that combustion temperature was stabilized at melting point of Al$_2$O$_3$ ($T=2303$ K). This was not limited to newly formed Al$_2$O$_3$ but included Al$_2$O$_3$ from diluent. Additional diluent ($1<y<2$) decreased the adiabatic temperature (figure 2) that resulted in detection of a new phase Ti$_2$O in the product which is illustrated in the table 1.

The lowering of adiabatic temperature results in decreasing the propagation velocity. Diluent slows the reaction kinetics and decreases interfacial contact area between Al and TiO$_2$ which results in the
formation of intermetallic compounds [24]. The reaction heat was absorbed by extra diluents and consequently another oxide phase (Ti$_3$O$_5$) was formed in the product. Finally, adding more diluent powders to the reactant mixture directed the mechanism of the combustion to produce intermetallic compound (AlTi$_2$). From the previous reports, the intermetallic compounds were formed by diffusion of Ti into molten Al and were existed as intermediate phase during the reaction [24-25]. Obviously, these variations of composition influence on the microstructure and properties of the final product.

Figure 7. Micrograph of TiC-Al$_2$O$_3$ composite product produced by adding extra carbon (x = 0.5).

Figure 8. Relative density, thermal conductivity and porosity of combusted mixture at room temperature for various diluent content (y).

Table 1. Semi-quantitative phase analysis of combusted (3TiO$_2$+4Al+3.5C+yAl$_2$O$_3$) mixture.

| Amount of Al$_2$O$_3$ diluent, (y) | Weight fraction of product |
|-----------------------------------|-----------------------------|
|                                   | Al$_2$O$_3$ | TiC   | Ti$_2$O | Ti$_3$O$_5$ | AlTi$_2$ |
| 0.0                               | 0.55        | 0.45  | 0.00    | 0.00        | 0.00      |
| 0.5                               | 0.59        | 0.41  | 0.00    | 0.00        | 0.00      |
| 1.0                               | 0.62        | 0.37  | 0.01    | 0.00        | 0.00      |
| 1.5                               | 0.67        | 0.27  | 0.06    | 0.00        | 0.00      |
| 2.0                               | 0.68        | 0.29  | 0.03    | 0.00        | 0.00      |
| 2.5                               | 0.69        | 0.20  | 0.00    | 0.09        | 0.02      |

3.6. Thermo-Mechanical properties

Adding Al$_2$O$_3$ diluent into the reactant mixture directed the mechanism of the combustion synthesis to produce small amount of oxide and intermetallic phases along with the main TiC-Al$_2$O$_3$ product. Furthermore, additional diluent powder not only changed the density of the mixture, but also influenced on the porosity of the compact pellet. Thermal conductivity of reactant and product depends on the porosity. Heat transfer in the system occurs in three mechanisms of conduction, convection and radiation. Any changes in the porosity vary the contribution part of each mechanism of heat transfer inside the sample. It is obvious that under quasi-adiabatic conditions of the experiment and the presence of oxygen porosity has more significant influence in the process.

A semi-empirical model for evaluation the thermal conductivity was proposed by Koh and Fortini [14]. In this model the effective thermal conductivity is given as a function of porosity and thermal conductivity of dense material as follows:

$$\lambda_{eff} = \lambda_0 \frac{1-P}{1+11P^2}$$ (7)
Where,
\( \lambda_{\text{eff}} \) - Effective thermal conductivity, Wm\(^{-1}\)K\(^{-1}\)
\( \lambda_0 \) - Thermal conductivity of dense material, 20 Wm\(^{-1}\)K\(^{-1}\)
\( P \) - Porosity,

Semi-empirical results of thermal conductivity, porosity and measured density of the products for various amounts of diluent \((y)\) at room temperature are shown in figure 8. The trend of changes in relative porosity, density, and thermal conductivity demonstrates tight correlations. Overall density value obtained is less than theoretical density \((4.436\text{gcm}^{-3})\). The figure illustrated a slight change in thermal conductivity.

4. Conclusion
Combustion synthesis of \(3\text{TiO}_2+4\text{Al}+(3+x)\text{C}\) mixture in the presence of oxygen was resulted the optimum value of \(x = 0.5\) to produce desired \(\text{TiC-\text{Al}_2\text{O}_3}\) product. Addition of \(\text{Al}_2\text{O}_3\)-diluent into the mixture directed the mechanism of the process to form oxide \((\text{Ti}_2\text{O}_3, \text{Ti}_3\text{O}_5)\) and intermetallic \((\text{AlTi}_2)\) phases. Thermodynamics studies of the system showed that self-sustaining mode of combustion wave propagation can occur for large amounts of diluents \((y = 2.5)\). Presence of diluent in the initial mixture reduced combustion temperature and reaction rate. Adding \(\text{Al}_2\text{O}_3\) diluent slightly increased density that resulted in better thermal conductivity.

5. Acknowledgements
This work was funded via Vot-F internal research fund from University of Malaya. Through research grant No. F0159/2007B.

6. Appendix A

| Table A1. Thermo-chemical data for reactants and products of (\text{TiO}_2-\text{Al-C-\text{Al}_2\text{O}_3}) system [19]. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Element        | Temp. Range (K) | \( \Delta H^0 \) kcal/mol | \( \Delta H_{\text{m}} \) kcal/mol | \( \Delta H_{\nu} \) kcal/mol | \( C_P \) (cal/Kmole) |
| TiC            | 298-3290        | -44.0            | 17.0            | 0               | 11.939+0.234x10^3T-3.531x10^2T^2+0.451x10^6T^2 |
| Liquid     | 3290-3500        | .               | .               | 15.0            |                        |
| Al\(_2\)O\(_3\) | 298-1273       | -400.0          | 26.0            | 27.43+3.06x10^3T-8.47x10^5T^2  |
| alpha         | 1280-2303       | 5.24            | 25.48+4.25x10^3T-6.82x10^5T^2  |
| gamma         | 2303-3000       | 34.623          | 2.6             | 15.023+2.715x10^3T-2.380x10^5T^2 |
| Liquid     | 298-2143         | -225.8          | 16.0            | -               | 4.94+2.96x10^5T        |
| TiO\(_2\)      | 298-932          | 0               | -               | 15.023+2.715x10^3T-2.380x10^5T^2 |
| Al            | 298-932          | 0               | -               | 4.94+2.96x10^5T        |
| Liquid     | 932-1650         | 2.6             | -               | -               | 7.6                  |
| C             | 298-1155         | 0               | -               | -               | 0.026+9.307x10^3T-0.354x10^5T^2-4.155x10^6T^2 |
| Liquid     | 1155-1933        | 0               | 4.45            | 5.841+0.104x10^3T-7.559x10^5T^2  |
| Ti            | 298-1933         | 5.296+2.458x10^3T  | 8.5             | 5.296+2.458x10^3T  |
| alpha         | 1155-3575        | 4.739+1.894x10^3T  | -               | 4.739+1.894x10^3T  |
| liquid        | 1933-3575        | 8.5             | -               | -               | 8.5                  |
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