Synthesis and Characterization of Microwave and Conventional Combustion Synthesized Alumina-Titanium Carbide Powders*

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Al_2O_3-TiC powders were produced from microwave and conventional-combustion synthesized mixtures of TiO_2, C and Al. Different types of precursors such as rutile and anatase TiO_2, as well as carbon black, graphite and activated carbon powders were used. The different types of precursors and heating methods affected the combustion behavior. Combustion using microwaves could be achieved in less than 3 min, which was 10 times faster than conventional combustion. The composition of rutile-carbon black-aluminum gave the shortest ignition time using microwave energy, whereas the mixture containing activated carbon ignited fastest using conventional heating. Nevertheless, in both cases samples with anatase required longer time to ignite and thus gave higher combustion temperatures than ones with rutile. An incomplete combustion product observed when activated carbon was the carbon source. The synthesized powder was fragmented and angular in shape with the largest agglomerate size limited to smaller than 25 microns.

1. Introduction

Microwave processing of ceramic has been the focus of attention of numerous researchers in recent years. The effectiveness of using microwaves to promote heating for drying, calcination, binder removal, glass melting, and heating have been demonstrated in laboratories throughout the world, and some processes have found the way to become an industrial reality. Microwave processing can offer advantages over conventional firing methods, including more uniform heating, less processing time, and energy saving[1].

Microwave heating is fundamentally different from conventional processing in its heating mechanism. In microwave heating, heat is generated within the sample itself by interaction of microwaves with material. When microwaves penetrate and propagate through a dielectric material, the internal electric fields generated within the affected volume induce translational motion of free or bonded charges and also and rotate complexes such as dipoles. The resistance of these induced motions due to internal elastic and frictional forces, which are frequency dependent, cause losses and attenuate the electric field. As a result, volumetric heating occurs[2]. In conventional heating, the heat generated by heating elements is transferred to the sample surface, and then transferred to the interior by conduction.

In this work, microwave energy was applied to assist the combustion synthesis of Al_2O_3-TiC. This ceramic composite is widely used in industry for cutting tools for machining high hardness material and more recently application as a magnetic recording head substrate. This is because of its properties such as high hardness, good strength, moderate fracture toughness and chemical inertness. Generally, this commercial ceramic composite is fabricated by directly mixing Al_2O_3 and TiC powders and followed by pressureless sintering, hot pressing or hot-isostatic pressing[3]-[6]. An alternative process that has drawn much attention for the preparation of Al_2O_3-TiC composite powders is self-propagating high temperature synthesis (SHS) or combustion synthesis[7]-[10]. This method offers several advantages including its simplicity, energy efficiency and the use of low cost precursors[11],[12]. The combustion synthesis of Al_2O_3-TiC composite can be described as follows,

$$3TiO_2 + 4Al + 3C = 2Al_2O_3 + 3TiC \qquad (1)$$
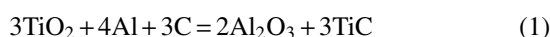
The process begins with initial reagents; once ignited, there is sufficient heat release leading to the formation of a

combustion wave that travels along the reactants, converting them to the required product. Even though SHS has been studied by many researchers, the use of microwave energy as a heating source has been limited[13]–[15]. The study of the effects of various types of precursors on microwave combustion behaviors is rare.

Hence, the purpose of this study was to investigate the effect of various types of precursors on microwave combustion behaviors of Al_2O_3-TiC composite powders. The differences of combustion behavior and powder characteristics between the microwave and conventional combustion were reported.

2. Experimental Procedure

The raw materials used in this study were TiO_2 (99.5% rutile, $1-2\,\mu m$; Alfa-aesar), TiO_2 (99.8% anatase, $0.1\,\mu m$; Sigma-aldrich), Aluminum (99.5%, $7-15\,\mu m$; Alfa-aesar), carbon black ($1.13\,\mu m$; Cabot), graphite ($6.61\,\mu m$; Hoganas) and activated carbon ($<45\,\mu m$; Carbokarn) (Fig. 1). The six compositions of reactants were mixed by ball milling with alumina ball in ethanol for 24 h (Table 1). The reactant mixtures were then dried at 105°C for 24 h and sieved through a 100 mesh to reduce the number of agglomerates.

The ignitions were performed in a 2.45 GHz microwave furnace with a chamber dimension of $13.5 \times 13.5 \times 13.5$ cm (model MHTD-1800-2.4 kW, Linn High Therm GMBH, Germany). The maximum power output is 2.4 kW. The sample powder was put in an alumina crucible, which was placed at the center of the microwave cavity. The ignition was carried out under argon atmosphere with a flow rate of 1.67 lit/min. The ignition and combustion temperatures were measured by infrared pyrometer (model Pyroskop 217-LWL, Kleiber). The schematic of the microwave combustion system is shown in Fig. 2 (a). Conventional combustion was conducted in a tube furnace under an argon atmosphere. The samples were placed in refractory boats located at the hot zone of the furnace. Samples were heated to a temperature of 1 200°C at a heating rate of 5°C/min and then cooled down to room temperature at the same rate. The near surface temperatures of the samples were measured with a K-type thermocouple. Combustion behavior was observed from a minimum of 6 repeated runs. After both combustion processes, synthesized powder was milled with alumina ball in ethanol for 96 h to reduce particle size. The powder product was then dried and sieved through 325 mesh and prepared for further characterization.

The phase analysis was performed by X-ray diffractometry (XRD; model JEOL, JDX-3530). The morphology of the combustion-synthesized powder was observed with scanning electron microscope (SEM; model JEOL, JSM5401). The chemical composition was analyzed by an energy dispersive spectroscope (EDS; model Oxford
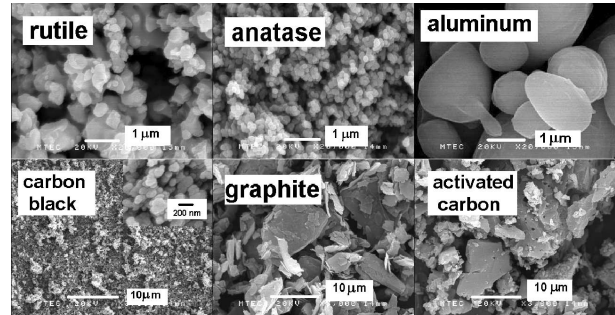

Fig. 1   SEM micrographs of reactant materials

Table 1   Six compositions with various TiO_2 and C used in TiO_2-Al-C combustion system

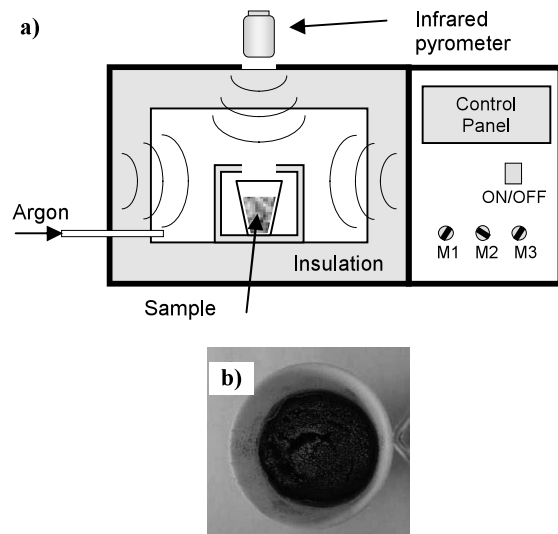| composition	reactants	
	TiO_2	C
TC1	rutile	carbon black
TC2	rutile	graphite
TC3	rutile	activated carbon
TC4	anatase	carbon black
TC5	anatase	graphite
TC6	anatase	activated carbon

Fig. 2   (a) Schematic illustration of microwave combustion system and (b) microwave combustion synthesized product

Inca 300). The particle size, surface area, and density of powders were measured by Particle Size Analyzer (Mastersizer-S), BET method (Coulter SA3100), and pycnometer (Ultrapycnometer 1000), respectively.

3. Results and Discussions

3.1 Combustion behavior

The adiabatic temperature (T_{ad}) is used as an indication whether the synthesis of material can be accomplished by a self-propagating method. It has been empirically suggested that the combustion reaction will not

become self-sustaining unless $T_{ad} \geq 1\,800$ K. The theoretical adiabatic temperature of equation (1) calculated using thermodynamics data is $2\,546$ K ($2\,273°$C)[7]. Therefore, it could be assumed that the SHS reaction would be possible. As evidenced in Fig. 2 (b), Al_2O_3-TiC composites were successfully synthesized by microwave energy. The samples were combusted initially at the center and propagated outwardly. In this TiO_2-Al-C system, carbon will absorb microwave energy, then heat rapidly transfers to the other reactants and ignition occurs[14]. The sequential reaction proceeded in three stages: melting of aluminum, aluminothermic reduction of TiO_2, and finally TiC synthesis. As-combusted powders were rigid and irregular in shape, as seen in SEM micrograph in Fig. 3. The conventional combustion process was found to be more violent than microwave, an amount of dust was emitted. Moreover, densified powders and a greater size of agglomerate were observed. This was thought to occur because conventional combustion took a longer time than the microwave process and so a liquid phase would probably be present in the powder products for longer periods.

The microwave ignition behaviors of various compositions were shown in Fig. 4. Ignition is indicated by a sharp rise in temperature. It can be seen that the recorded combustion temperature values, T_c, in these cases (564 – $1\,255°$C) were very far from the adiabatic temperature because of a large amount of heat loss due to a large chamber size microwave furnace.

As seen in Fig. 4, samples with anatase as TiO_2
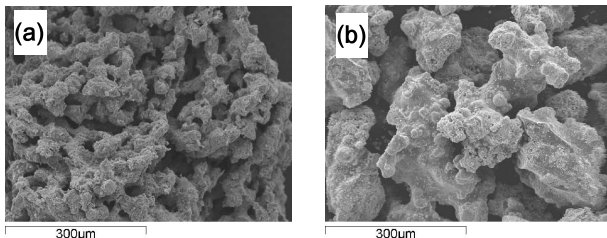

Fig. 3 SEM micrograph of as-combustion synthesized powders from (a) microwave heating, and (b) conventional heating
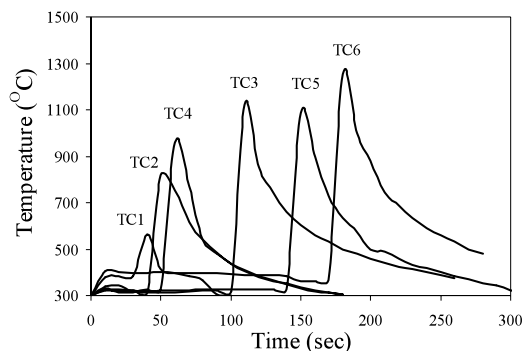

Fig. 4 Temperature profiles during the mw-combustion reaction of various $3TiO_2 + 4Al + 3C$ samples

source (TC4-TC6) required longer time to ignite and thus gave higher combustion temperatures than ones with rutile (TC1-TC3). The increasing of ignition time resulted in a large amount of heat accumulation and thus a high combustion temperature could be obtained. In addition, when anatase (0.1 μm) was used, it may have been possible for a continuous anatase phase to act as a barrier between carbon-aluminum particle contacts. The heat transfer efficiency from carbon particles, highly mw-absorbing material, to aluminum particles decreased. Thus it would take longer time for the initial reaction between TiO_2 and Al to occur. Furthermore, it was noticed that various types of carbon used also influence the ignition time (t_{ig}). Comparing among carbon sources, the mixture containing activated carbon took the longest time to ignite and also showed the highest combustion temperature. The difference in the particle size along with the ability to absorb microwave energy of these carbon sources plays a significant role in the ignition behavior.

In the mixtures containing rutile phase (TC1-TC3), the one with rutile-carbon black ignited fastest. This may be because it provided the best reactant particle arrangements and particle contact between titania-aluminum, which is believed to be the initial reaction during synthesis. When graphite was mixed with the rutile, graphite particle size (6 – 7 μm) was close to Al particle size (7 – 15 μm), thus smaller mw-transparent rutile particles (1 – 2 μm) would be distributed among larger particles of both graphite and Al. This structure resulted in longer ignition time. However, the mixture of rutile-activated carbon-aluminum was observed to have the longest ignition time. A possible explanation for this was that the heat generated within activated carbon (45 μm) was shared between aluminum and rutile phase. The same trend has also been found in the mixtures containing anatase phase (TC4-TC6).

Nevertheless, all of the reactant mixtures in the microwave process were rapidly ignited about ten times faster than in the conventional process. The ignition times required for microwave processed samples containing rutile (TC1-TC3) and anatase (TC4-TC6) were approximately 40, 55, 114 sec and 60, 153, 178 sec, respectively. While the microwave-ignited powders could be achieved within about 3 minutes, it would take about 3 hours for conventionally ignited samples (Fig. 5).

It was also found that the microwave processed samples ignited at lower temperatures in the range of 305 – 365°C as compared to conventionally processed ones, 859 – 910°C. In the conventional process, ignition temperatures and times were affected by carbon sources in that they decreased as the particle size of carbon increased. However, those samples using carbon black (TC1) could be ignited faster than graphite (TC2), which was not observed in the case of the anatase system. This was thought
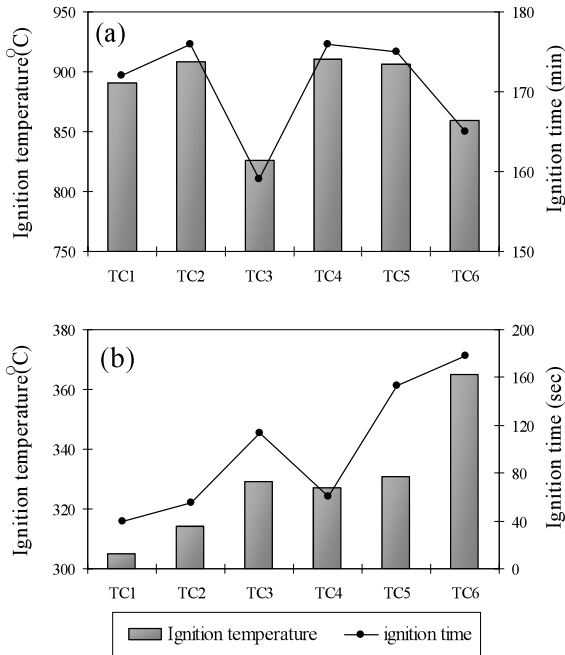
Fig. 5   Effect of composition on ignition temperature and time of (a) conventional, and (b) microwave combustion synthesized powders

(a)

(b)

Fig. 6   X-ray diffraction patterns of (a) conventional and (b) microwave synthesized powders with different TiO_2 and C source (A = Al_2O_3, T = TiC, * = Ti_3AlC)

to be because the carbon black might form a small agglomeration. The proportional decrease in ignition temperatures with ignition times was not observed in microwave cases.

In contrast to microwave processing, for conventional processing the mixtures containing activated carbon (TC3, TC6) ignited fastest (Fig. 5 (a)). It is believed that when the larger 45 μm activated carbon particles are present, the smaller 1 – 2 μm rutile (or 0.1 μm anatase) and 7 – 15 μm aluminum is the continuous phase. This particle arrangement could promote the initial reaction between titania and aluminum as previously discussed, thus resulting in the fastest ignition. In addition, the heat generated by heating elements in the tube furnace was transferred to the sample surface, and then conducted to the interior; therefore all reactant powders could experience the same temperature before ignition took place. For the microwave processed mixtures (Fig. 5 (b)), the heat source of TC3 and TC6 samples was mainly dependant on the microwave absorption efficiency of activated carbon. The competition for the amount of heat generated within activated carbon between aluminum and rutile phase would result in a longer ignition time as previously mentioned.

3.2   Phase transformation and microstructure

The confirmation of the product phases was made by X-ray diffraction analysis. XRD analysis of conventional and microwave ignited Al_2O_3-TiC powder with various compositions was provided in Fig. 6. For TC1, TC2, TC4 and TC5, the XRD patterns indicated a complete conversion of reactants to Al_2O_3 and TiC product (53:47 wt%),
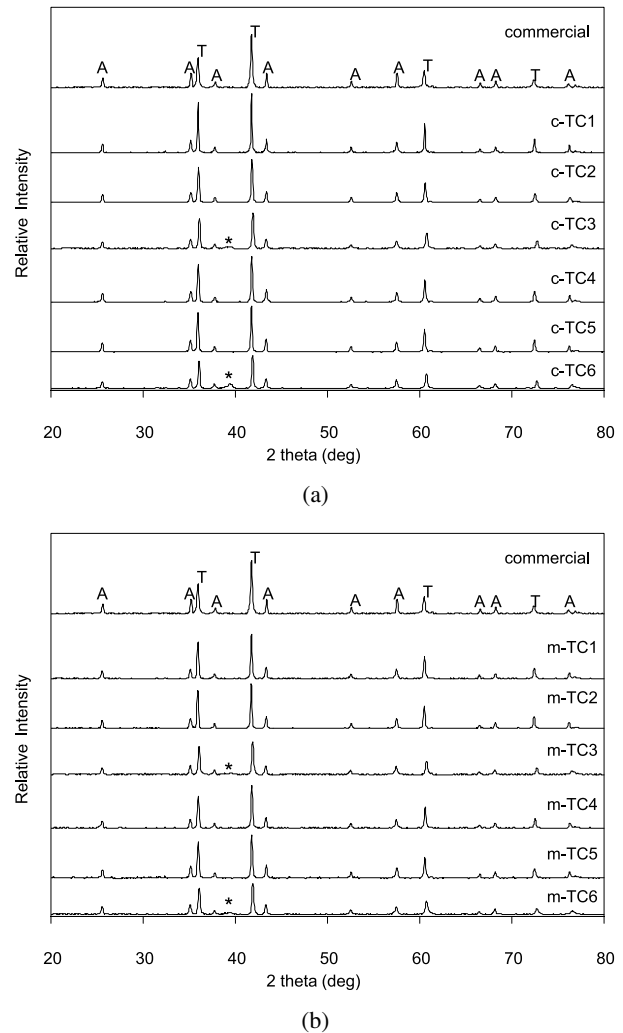
which was not different from the mixture of 53% Al_2O_3 and 47% TiC commercial powder. Two XRD patterns containing activated carbon, (TC3) and (TC6), found not only TiC and Al_2O_3 but also a Ti_3AlC signal. The weak peak of Ti_3AlC phase resulted in a decrease of Al_2O_3 and TiC peak intensity in the final product. An incomplete combustion might be related to ignition behavior aforementioned; samples conventionally processed ignited too fast to complete the reaction entirely or an insufficient amount of heat was conducted from activated carbon to titania and aluminum phases under microwave energy. Another explanation might be because of impurity in activated carbon. Typically, very high temperatures are reached in exothermic reactions and all the volatile impurities evaporate producing high purity product. In this work, a large amount of heat loss in the microwave furnace chamber decreased combustion temperature down to a point that the impurity in product (TC3) and (TC6) may have remained. Further in-depth investigation is needed.
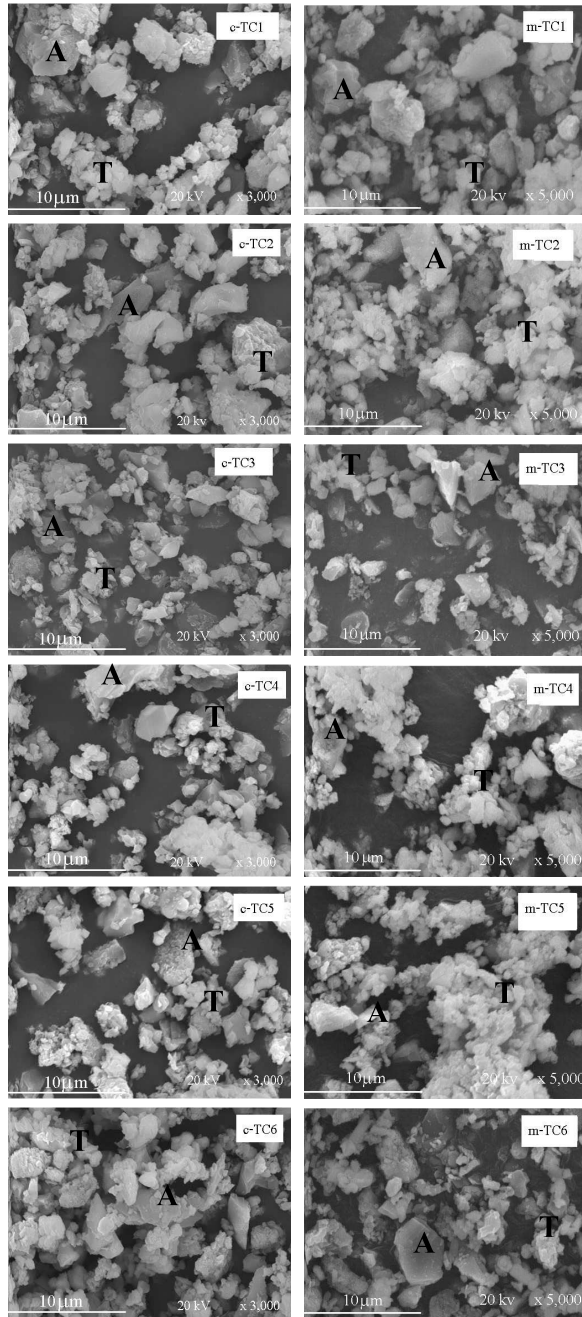
Fig. 7 SEM micrographs of the (a) conventional and (b) microwave combustion synthesized powders made with various precursors
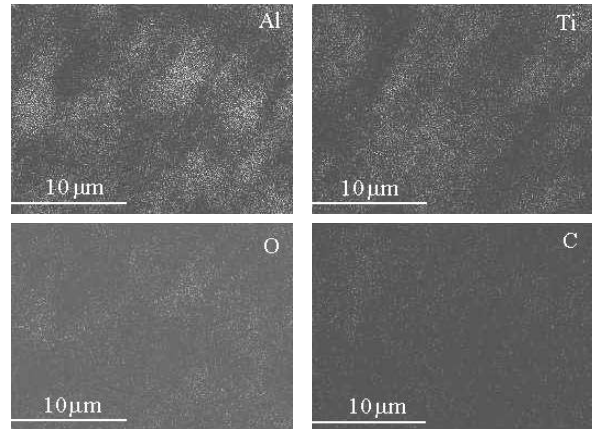

Fig. 8 EDS analysis of rutile-carbon black-aluminum product

Table 2 Characteristics of microwave combustion synthesized powders

Batch	Particle size (μm)				Specific Surface area (m²/g)	Density (g/cm³)
	D (0.1)	D (0.5)	D (0.9)	D [4,3]		
TC1	0.68	3.9	15.84	6.58	7.55	4.04
TC2	0.43	2.15	8.19	3.84	16.26	4.94
TC3	0.48	2.21	7.16	3.29	6.31	5.08
TC4	1.62	5.36	15.53	7.5	4.09	5.18
TC5	0.48	2.96	13.1	5.28	9.64	5.01
TC6	0.68	4.27	24.16	9.22	3.60	5.12
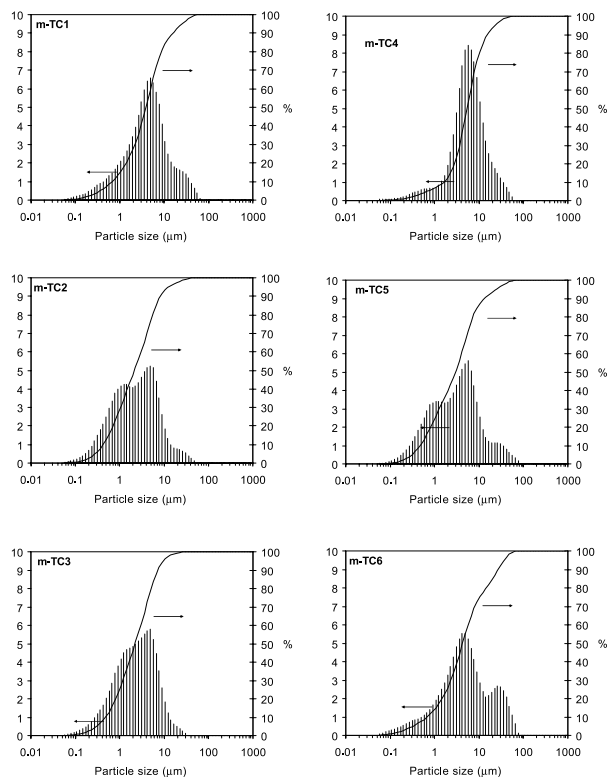
Fig. 9 Size distribution of the microwave combustion synthesized powders

The corresponding microstructures of these milled-composite powders are shown in Fig. 7. The powders were fragmented and still remained in a lot of agglomerate. A cluster of small TiC and angular shaped Al_2O_3 particles appeared. All compositions did not show any significant difference in morphology. The presence of carbon, oxygen, aluminum and titanium in EDS analysis showed the consistent dispersing of Al_2O_3 and TiC phase (Fig. 8).

3.3 Powder characterization

The characteristics of microwave ignited powders are

Table 3 Characteristics of conventional combustion synthesized powders

Batch	Particle size (μm)				Specific surface area (m²/g)	Density (g/cm³)
	D (0.1)	D (0.5)	D (0.9)	D [4,3]		
TC1	0.68	3.91	13.96	6.38	8.97	4.33
TC2	0.77	4.26	15.28	8.9	4.87	4.98
TC3	0.99	6.11	24.41	9.88	3.40	4.83
TC4	0.94	5.14	21.75	8.8	4.44	5.11
TC5	1.28	5.76	24.84	9.79	3.99	4.95
TC6	0.51	2.82	8.01	4.36	4.30	4.56

illustrated in Table 2. Pycnometry analysis showed that the densities for all powders were in the range of $4.05 - 5.18$ g/cm³. The increase of density corresponded to the combustion temperature. That is, higher combustion temperature resulted in higher density of product. Size distribution of powders is shown in Fig. 9. As observed, TC2-, TC3-, TC5-, and TC6-powders product exhibited an almost bimodal size distribution. However the mean diameters (D [4,3]) of these 6 combusted powders were in the range of $3.29 - 9.22$ μm with the largest size limited to less than 25 μm. The product with anatase as TiO_2 source had a little bit larger size than groups of rutile. One of the reasons might be because the higher combustion temperature resulted in a higher density of agglomerated powders that were too difficult to comminution by ball milling. The characteristics of conventionally ignited powders were not quite different from microwave processed ones (Table 3).

4. Conclusion

Al_2O_3-TiC powder were successfully synthesized under microwave energy in a very short time of less than ten minutes. The different type of precursors affected the combustion behavior and also the characteristics of the powder obtained. The mixture of rutile-carbon black-aluminum yielded the fastest ignition time under microwave energy, whereas the mixture containing activated carbon ignited fastest under conventional heating. For microwave processed powders, the highest combustion temperature was observed in a mixture of anatase-activated carbon-aluminum as precursors. Two XRD patterns containing activated carbon found not only TiC and Al_2O_3 but also a Ti_3AlC signal. The synthesized Al_2O_3-TiC powders were all in fragmented and angular shape. Powders are agglomerated with a size range of $0.5 - 25$ μm. From this preliminary result of microwave processing, it can be concluded that the mixture of rutile, graphite, and aluminum was a good candidate that can produce a pure product with a high density and appropriate size suitable for further application.

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