Effect of aluminium addition on the combustion reaction of titanium and carbon to form TiC

YOON CHOI, SHI-WOO RHEE
Laboratory for Advanced Materials Processing, Department of Chemical Engineering, Pohang University of Science and Technology, Pohang 790-600, Korea

Aluminium was incorporated into the reactant mixture with a molar ratio of Ti/C of 1.0 to study the effect of its addition on the combustion reaction between titanium and carbon to form TiC. Thermal analysis of the reactant mixture and component analysis of the reaction product suggest that the combustion reaction of the Ti–C–Al system proceeds in such a way that aluminium initially reacts with titanium to form titanium aluminide compounds of $TiAl_3$, Ti_2Al, and TiAl with heat evolution, and then the reaction between titanium and carbon and the decomposition of titanium aluminide to titanium and aluminium is subsequently followed. As the amount of aluminium incorporated was increased over the range of 0 to 40 wt%, the grain size of TiC decreased from approximately 15 µm to 0.4 µm. It was also observed that most of the aluminium in the TiC–Al composite was distributed on the surface of the spherical TiC grain.

1. Introduction

Combustion synthesis, also termed self-propagating high-temperature synthesis (SHS), has been extensively applied to the preparation of refractory ceramic and intermetallic compounds because it is more energy-efficient than other conventional processes. TiC is extremely hard and has a very high melting point, which makes it attractive for wear-resistant and high-temperature applications.

TiC powder has been produced by combustion synthesis from reactant mixtures of titanium and carbon mixed with some TiC powder [1]. A dense titanium carbide has been formed by simultaneous synthesis and sintering under high pressure [2, 3] or by combustion synthesis followed by dynamic compaction [4]. Combustion parameters in the TiC combustion reaction have been theoretically discussed by Holt and Munir [5].

Kirdyashkin et al. [6] and Dunmead et al. [7] have studied the kinetics of Ti–C combustion reaction from the measurements of combustion temperature and wave velocity. Titanium and carbon interaction in the combustion reaction was investigated by Korchagin and Aleksandrov using electron microscopy [8]. The effect of carbon sources, such as amorphous carbon and graphite, on the combustion synthesis of TiC has been studied by Choi and Rhee [9].

However, little effort has been made to study the effects of aluminium incorporation on the Ti–C combustion reaction. Dunmead et al. [7] investigated the combustion reaction mechanism in the Ti–C–Ni system by measuring the combustion temperature and wave velocity with the addition of various amounts of TiC powder to the reactant mixture of titanium, car-

bon and nickel powders. In the present work, aluminium was selected as a metal additive for titanium carbide cermet because it is reactive and is used as the source of TiC–intermetallic alloy composite such as the Ti–C–Ni–Al system. Aluminium composites have a great potential because of their high strength-to-weight ratio.

The objective of this investigation was to study the effect of aluminium addition on the Ti–C combustion reaction, to provide an insight into the combustion reaction mechanism in the Ti–C–Al system. The interaction between each component in the reactant mixture was studied by differential thermal analysis (DTA) and differential scanning calorimetry (DSC) of the Ti–C, Ti–Al, Al–C, and Ti–C–Al systems. The phase transformation during the reaction of the Ti–C–Al system was also studied and their components were analysed by X-ray diffraction (XRD). The microstructure and composition of the reaction product were also investigated.

2. Experimental procedure

Table I shows the characteristics of titanium, graphite, and aluminium powders used as starting materials. Powders were mixed in a dry mixer for 5 h and cylindrical compacts, 20 mm diameter and approximately 30 mm long, were formed at pressures from 70–76 MPa in a stainless steel die with double-acting rams. The green densities of the compacts were maintained at 68% ± 2% theoretical.

Fig. 1 shows a schematic diagram of the apparatus. The sample, which was dried in a vacuum dry oven for 24 h at 573 K and 1×10^{-4} torr, was placed in a

TABLE I Description of precursor powders

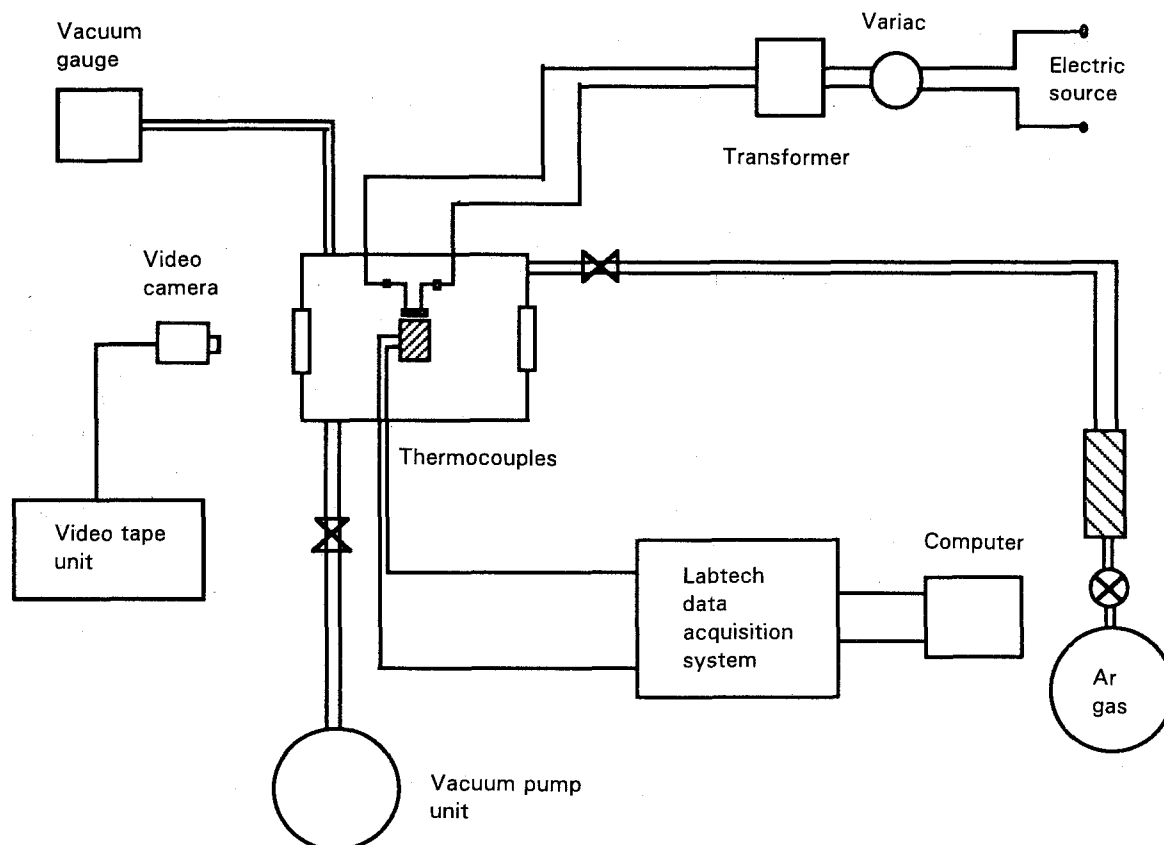|	Manufacturer	Purity (wt %)	Average particle size (μm)	Specific surface area ($m^2 g^{-1}$)
Titanium	Kojundo Kagaku Co.	99.9	30	0.56
Graphite	Kojundo Kagaku Co.	99.9	5	19.8
Aluminium	Kojundo Kagaku Co.	99.9	20	0.13

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

stainless steel chamber (270 mm high × 160 mm diameter) with two quartz windows (100 mm diameter). Tungsten filament was positioned approximately 2 mm above the top surface of the pellet for ignition. The chamber was purged and filled with argon gas before ignition. The top surface of the sample was ignited by applying a current of about 80 A to the filament.

Combustion wave velocity was measured using a video camera which was capable of scanning the reaction at 1/30 s intervals. Combustion wave velocity was also calculated from the time interval between heating profile peaks obtained from W–Re thermocouple tips (0.08 mm) at two different locations in the pellet. A data acquisition system was used to process the electrical signal from the thermocouple.

In addition to the combustion synthesis experiment, the differential thermal analysis (DTA) for compacts of reactant mixtures with a molar ratio of Al/C = 1.0, Ti/C = 1.0, and Ti/Al = 1.0 was performed by heating at the rate of 40 °C min^{-1} under an argon atmosphere. To study the reaction of the Ti–C–Al system, DSC of reactant compacts of Ti/C = 1.0 with aluminium

(10–40 wt %) was performed at a heating rate of 40 °C min^{-1} under an argon atmosphere. Samples of Al/C = 1.0, Ti/C = 1.0, Ti/Al = 1.0, and Ti/C = 1.0 mixed with 10–40 wt % Al were placed in a tubular furnace and heated to 25–1200 °C at a heating rate of 6 °C min^{-1} under an argon atmosphere.

Microstructure, phase, and chemical composition of the reaction products were investigated using scanning electron micrographs, XRD, and wavelength dispersive spectroscopy (WDS).

3. Results and discussion

Fig. 2 shows the combustion wave velocity as a function of the amount of aluminium incorporated into the reactant mixture with molar ratio of Ti/C = 1.0. It was observed that aluminium addition over the range 0–40 wt % resulted in a decrease of the combustion wave velocity from 2.61 cm s^{-1} to 0.74 cm s^{-1}, except near 20 wt %.

In steady-state combustion mode it is usually assumed that the combustion reaction is homogeneous, proceeding only in a narrow zone close
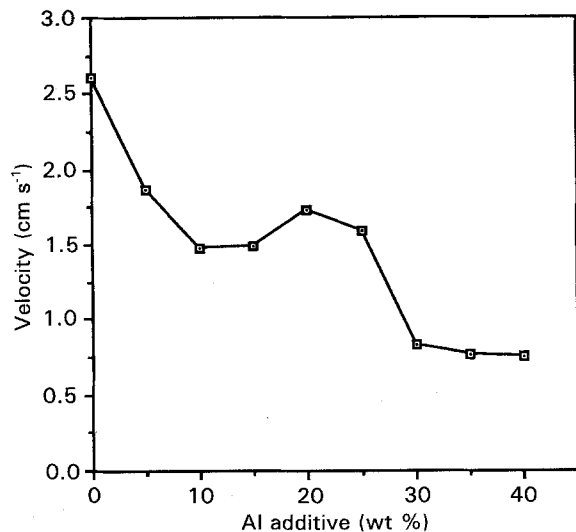
Figure 2 Combustion wave velocity as a function of the amount of aluminium addition to a sample with a Ti/C [molar ratio] = 1.0.

Figure 3 DTA curves of compacted reactant mixtures with a molar ratio of (a) Al/C = 1.0, (b) Ti/C = 1.0, and (c) Ti/Al = 1.0 at a heating rate of 40 °C min^{-1}.

to the maximum temperature. It is also assumed that the convective and radiative heat losses during the reaction can be neglected, and the activation energy is much greater than the thermal energy of the molecules. In addition, the thermal diffusivity in this case is much greater than the mass diffusivity in a condensed system. Then the combustion wave velocity is expressed as [10, 11]

$$u^2 = k'\left(\frac{kRT_c^2}{\rho Q E}\right)k_0 \exp\left(-\frac{E}{RT_c}\right)$$ (1)

where E is the activation energy (J kg^{-1}), k the thermal conductivity (W m^{-1} K^{-1}), k_0 the pre-exponential constant, k' a function of the reaction order and reaction completeness, Q the heat of reaction (J kg^{-1}), T_c the combustion temperature (K), u the combustion wave velocity (m s^{-1}), and ρ the average density of the powder compact (kg m^{-3}). The combustion wave velocity increases exponentially with increasing combustion temperature, proportional to the thermal conductivity of the sample and inversely proportional to the porosity.

If aluminium served only as a diluent which did not react with titanium and carbon, the increased amount of aluminium incorporation should result in a continuous decrease of combustion wave velocity. The result in Fig. 2 suggests that aluminium serves not only as a diluent in the Ti–C system but also as a reactant. Aluminium exists in the molten state above 935–2400 K. Therefore, it should participate as a liquid and a vapour phase in the combustion reaction of the Ti–C–Al system. It is considered that liquid aluminium in the sample should contribute to the porosity decrease and the thermal diffusivity increase of the sample, and might induce an increase of the combustion wave velocity. The slight increase of combustion wave velocity in Fig. 2 is attributed to the participation of aluminium in the combustion reaction of the Ti–C–Al system and also the increase of thermal diffusivity in the sample.

Fig. 3a–c show the DTA curves of pellets with a molar ratio of Al/C = 1.0, Ti/C = 1.0, and
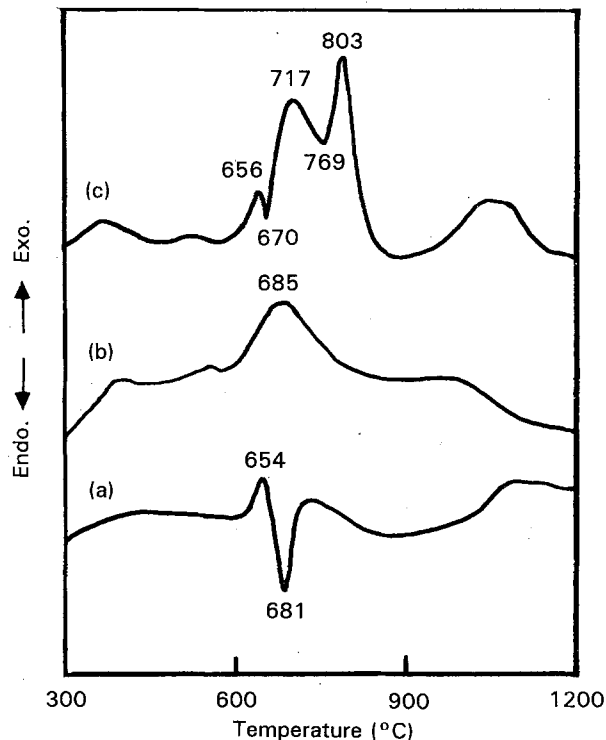
Ti/Al = 1.0, respectively, with the heating rate of 40 °C min^{-1}. Fig. 3a shows only one endothermic peak with the onset at 654 °C and the minimum at 681 °C, which corresponds to the melting of aluminium. This indicates that any exothermic reaction between aluminium and carbon to form aluminium carbide did not occur. Fig. 3b shows a slight exotherm near 685 °C. However, with a heating rate of 10 °C min^{-1}, no exotherm was observed near 685 °C. Component analysis of the sample heated to 685 °C confirmed that no self-sustained reaction between titanium and carbon to form TiC was initiated. The high heating rate in the DTA experiment, which results in the high exotherm in the DTA curve, and the interface reaction between titanium and carbon to form the thin titanium carbide layer, whch is not self-sustained and the very slight oxidation on the titanium metal surface by adsorbed moisture, may be the reasons. Fig. 3c shows two exothermic peaks with maximum at 717 and 803 °C. The peaks correspond to the exothermic reaction between titanium and aluminium to form titanium aluminide compounds. The results of Fig. 3 suggest that the Ti–Al reaction to form titanium aluminide compounds is more favourable than Ti–C and Al–C reactions in the combustion reaction kinetics of the Ti–C–Al system.

Fig. 4a and b show the X-ray diffraction patterns of samples with molar ratio of Ti/Al = 1.0 heated to 655 °C and 1200 °C, respectively, with a heating rate of 6 °C min^{-1} under an argon atmosphere. Fig. 4a indicates that the reaction between titanium and aluminium to titanium aluminides is initiated below the melting point of aluminium. It also shows that at 655 °C, TiAl$_3$ is the most abundant component in the
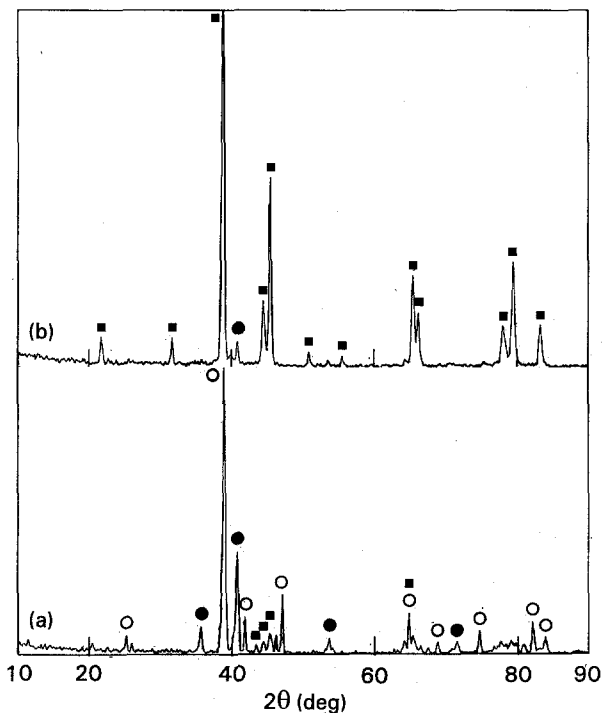
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Figure 4 X-ray diffraction patterns of samples with a molar ratio of Ti/Al = 1.0 heated to (a) 655 °C and (b) 1200 °C with a heating rate of 6 °C min^{-1} under an argon atmosphere. (■) TiAl, (●) Ti$_2$Al, (○) TiAl$_3$.

Figure 5 DSC curves of compacted reactant mixtures with a Ti/C [molar ratio] = 1.0 mixed with (a) 10, (b) 20, (c) 30, and (d) 40 wt % Al.

product followed by Ti$_2$Al and TiAl, as shown in Fig. 4a. Fig. 4b shows that TiAl is a major phase at 1200 °C. The phase diagram of the Ti–Al system shows that the reaction product from the molar ratio of Ti/Al = 1.0 is TiAl. It indicates that in the reaction of Ti/Al = 1.0, TiAl is the equilibrium composition but the reaction rate for TiAl$_3$ formation is faster than that for TiAl. It is believed that the first exotherm in Fig. 3c mainly corresponds to the reaction for TiAl$_3$ formation, while the second exotherm mainly corresponds to the reaction for TiAl formation.

Fig. 5 shows the DSC curves of pellets with molar ratio of Ti/C = 1.0 (including 10, 20, 30, and 40 wt % Al) which was heated at a rate of 40 °C min^{-1} under an argon atmosphere from room temperature to 1200 °C. It shows an endotherm over the range 651–692 °C and another exotherm in split form over the range 692–1115 °C. The first endotherm corresponds to the melting of aluminium, as already described. It is considered that the other exotherm was initiated by the Ti–Al reaction because it was easily initiated in the low-temperature region, as already described in the Ti–Al system.

The adiabatic temperatures of TiAl$_3$ and TiAl formation calculated thermodynamically from the heat of formation and heat capacity data are approximately 1546 and 1559 K, respectively. These are theoretical maximum temperatures without any heat losses. If we assume that the initial temperature is about 800 K because the Ti–Al reaction is initiated near the melting point of aluminium, the elevated adiabatic temperatures are approximately calculated to be 1955 and 1971 K, respectively. These temperatures are high enough to initiate the Ti–C reaction to form TiC. Therefore, it is believed that the Ti–C
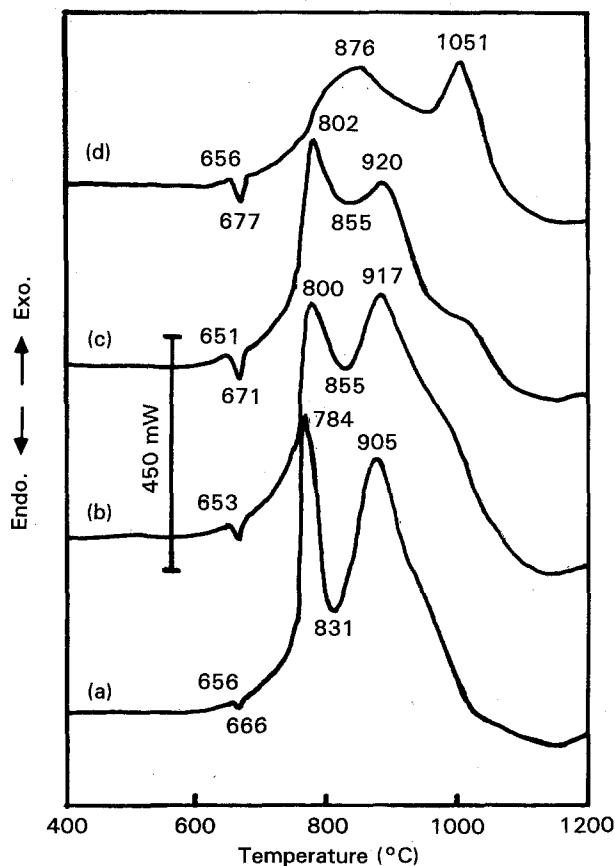
reaction in the Ti–C–Al system is initiated by the heat of reaction between titanium and aluminium.

It has been reported that TiAl$_3$ and TiAl compounds decompose at 1613 and 1733 K, respectively [12]. Therefore, it is expected that TiAl$_3$, Ti$_2$Al, and TiAl phases formed by the Ti–Al reaction decompose to titanium and aluminium from the heat of the Ti–C reaction initiated by the Ti–Al reaction. This contributes to the highly exothermic peaks over the temperature range 692–1115 °C. A pellet with a molar ratio of Ti/C = 1.0 mixed with 40 wt % Al was heated to 693 °C under an argon atmosphere. The temperature corresponds to the onset of the exotherm, as shown in Fig. 5d. Through XRD analysis, it was confirmed that the reaction product consisted of TiC and aluminium and no other titanium aluminides were detected. In fact, this is also the case for combustion synthesis, as will be confirmed in Fig. 6. It was reported that the self-sustained Ti–C reaction to form TiC is initiated at approximately 1600 °C [5]. This is too far above 693 °C even if we consider that the ignition temperature could depend on the heating rate. This proves that the Ti–C reaction in the Ti–C–Al system is initiated even at low temperatures by the heat of the Ti–Al reaction to form titanium aluminide, and the decomposition of titanium aluminide from the heat of the Ti–C reaction follows by the heat of the Ti–C reaction.

Fig. 6 shows XRD patterns of samples combustion synthesized from the reactant mixture with molar
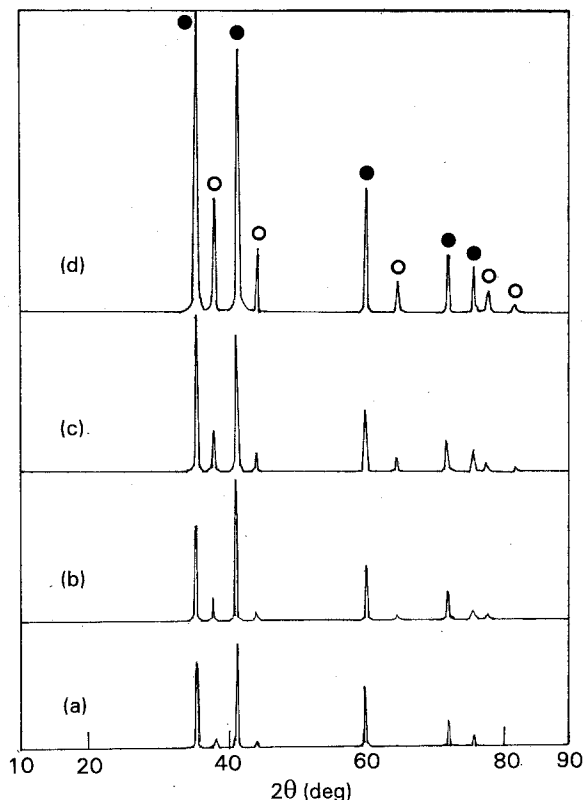
Figure 6 X-ray diffraction patterns of reaction products combustion-synthesized from the samples with a Ti/C [molar ratio] = 1.0, mixed with (a) 10, (b) 20, (c) 30, and (d) 40 wt % Al. (●) TiC, (○) Al.

ratio of Ti/C = 1.0 mixed with Al (10–40 wt %). The reaction products consist of TiC and aluminium phases. The increase of aluminium incorporation resulted in the increase of aluminium peak intensity. This confirms that the decomposition of titanium aluminide also occurs in the combustion reaction of the Ti–C–Al system, as already described in the thermal

analysis. Thermal analysis is very applicable to a study of the combustion reaction of the Ti–C–Al system although the combustion reaction, which is characterized by the very high heating rate and the propagation of the wave front, is different from the thermal explosion system such as thermal analysis.

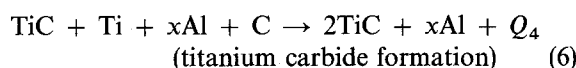Based on the results, the combustion reaction mechanism in the Ti–C–Al system may be summarized as follows:

$$2Ti + 2C + xAl \rightarrow 2TiC + xAl + Q \text{ (kJ mol}^{-1}) \quad \text{(overall reaction)} \quad (2)$$

$$2Ti + 2C + xAl \rightarrow TiAl_x + Ti + 2C + Q_1 \quad \text{(titanium aluminide formation)} \quad (3)$$

$$TiAl_x + Ti + 2C \rightarrow TiAl_x + TiC + C + Q_2 \quad \text{(titanium carbide formation)} \quad (4)$$

$$TiAl_x + TiC + C \rightarrow TiC + Ti + xAl + C - Q_3 \quad \text{(titanium aluminide decomposition)} \quad (5)$$

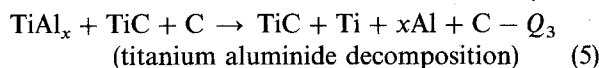$$TiC + Ti + xAl + C \rightarrow 2TiC + xAl + Q_4 \quad \text{(titanium carbide formation)} \quad (6)$$
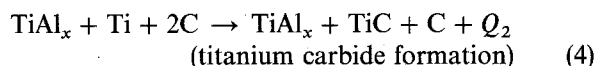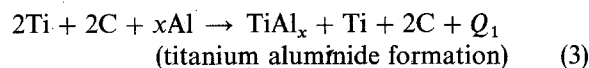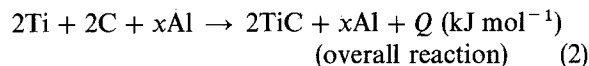
Fig. 7 shows scanning electron micrographs of fractured surfaces of combustion-synthesized samples, which were formed from the sample with Ti/C = 1.0 (including 0, 10, 20, 30, and 40 wt % Al). The grain size of the reaction products was decreased from approximately 15 µm to 0.4 µm when aluminium was incorporated into the sample with Ti/C = 1.0 over the range 0–40 wt %. This is attributed to the decrease of the combustion temperature because grain growth of reaction product is an exponential function of the combustion temperature. In addition, the aluminium phase might prevent the diffusion of carbon between TiC grains. It is reported that the grain growth of TiC in the combustion reaction between titanium and carbon is controlled by the carbon diffusion through titanium carbide [13–15] or liquid titanium [6, 7].
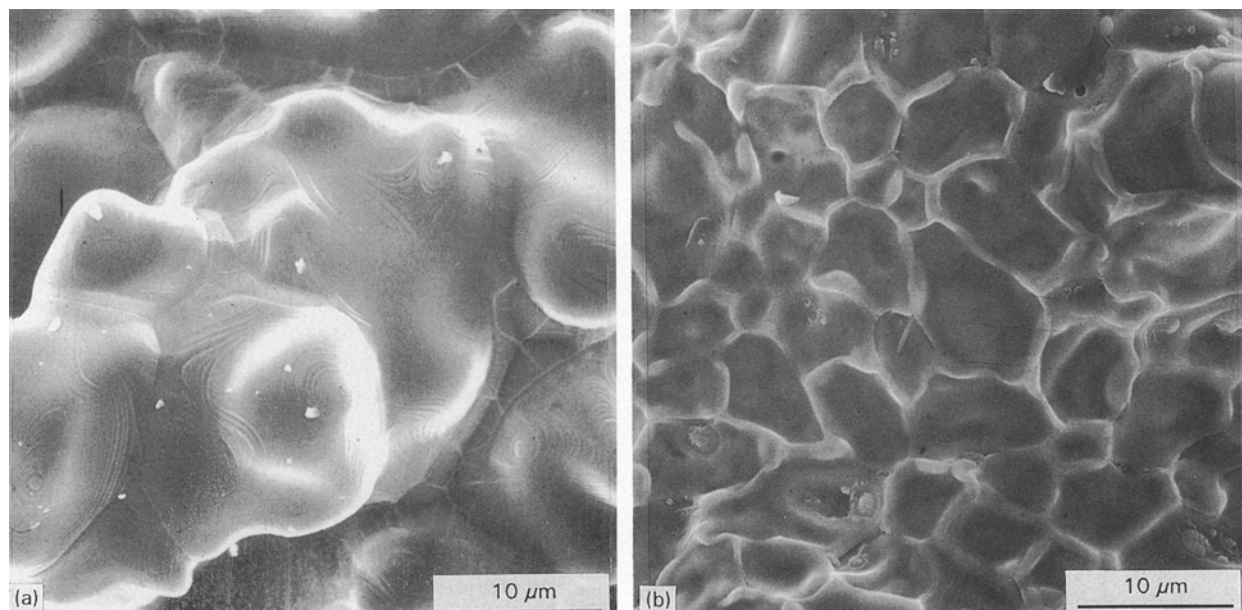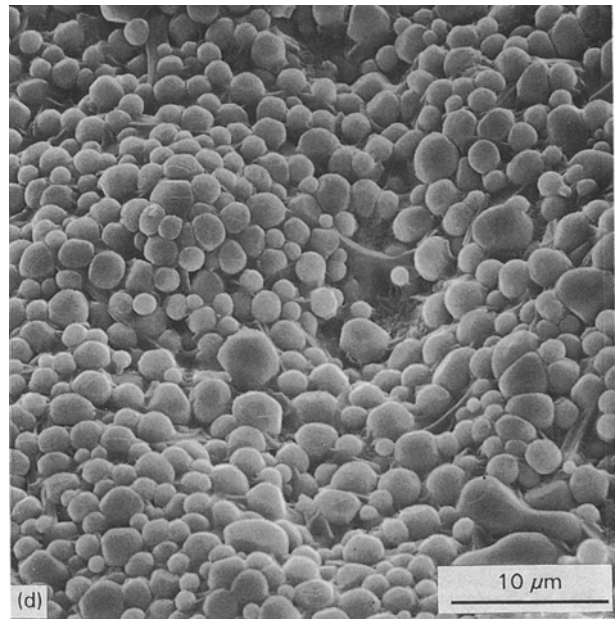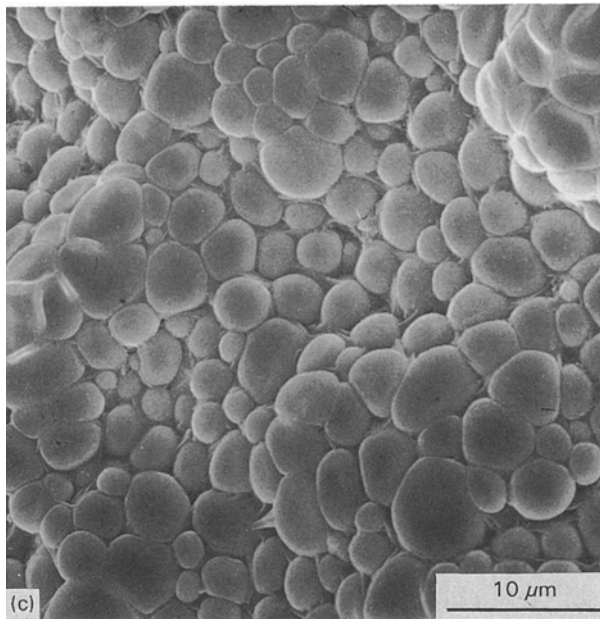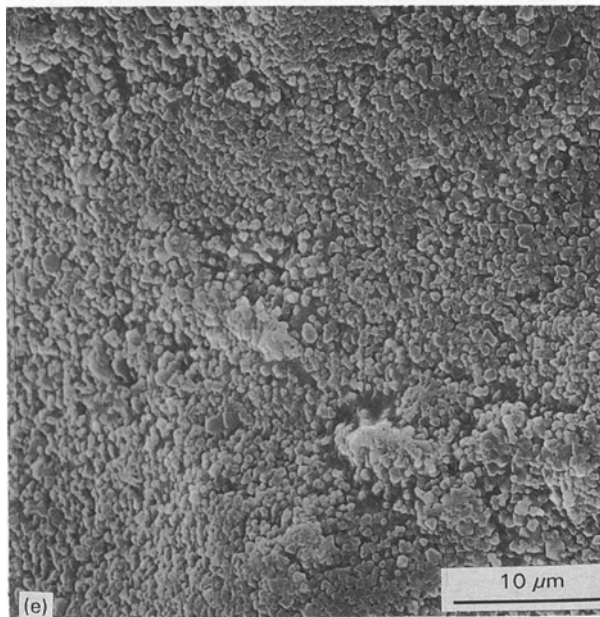

Figure 7 (a) and (b)

As the aluminium incorporation is increased, the morphology changes to spherical and mono-dispersed small particles. This can be explained by noting that surface energies in the system, where liquid aluminium surrounds TiC particles, become the lowest by maintaining spherical form. A considerable amount of aluminium is evaporated in the sample during the combustion reaction of the Ti–C–Al system because of its high vapour-pressure, and TiC particles are coated with aluminium.

Fig. 8 shows the distribution of elements in the polished surface of the reaction product formed from the sample with Ti/C = 1.0 mixed with 10 wt % Al. The TiC particle coated with a thin aluminium layer was observed. This also confirms that aluminium participating in the reaction between titanium and carbon was segregated at the surface of TiC particles. This is due to the high vapour pressure of aluminium, the difference in specific gravity of TiC and aluminium, and the low solubility of carbon in liquid aluminium [16, 17].
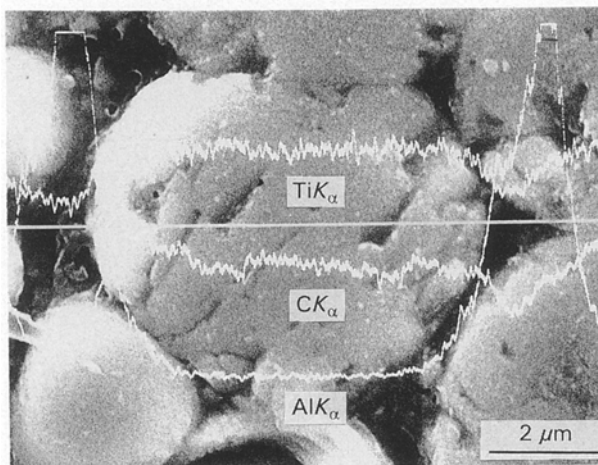
4. Conclusion

The effects of incorporating 0–40 wt % aluminium into the reactant mixture with a molar ratio of Ti/C of 1.0 were investigated. Based on the study of the reaction between each component in the Ti–C–Al system, the combustion reaction mechanism of the Ti–C–Al system was suggested. The reaction between titanium and aluminium to form titanium aluminides in the combustion reaction of the Ti–C–Al system initially occurred and this subsequently initiated the reaction between titanium and carbon which was followed by the decomposition of titanium aluminides. Aluminium incorporation (0–40 wt %) into Ti/C = 1.0 results in the size reduction of spherical TiC particles from

Figure 8 Concentration profiles of titanium, carbon and aluminium on the polished cross-section of the reaction product combustion-synthesized from the sample with a Ti/C [molar ratio] = 1.0 mixed with 10 wt % Al.

approximately 15 μm to 0.4 μm, and the TiC grain surface was coated with a thin layer of aluminium.

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