

Self-propagating high-temperature synthesis of Al₂O₃-TiC-Al composites by aluminothermic reactions

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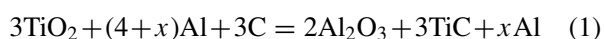
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Al₂O₃-TiC-Al composites were fabricated by self-propagating high-temperature synthesis process using aluminothermic reactions with titania, aluminum, and graphite powders. As the molar ratio x of the excessive aluminum in the reactants increases, the adiabatic temperature of the reaction and the melting rate of alumina in the products obviously decrease according to thermodynamics. This reaction is theoretically presumed to be ignited at preheat temperature of 900 K even though x is up to 13 mole. The experimental results revealed that the critical molar ratio of excessive Al, which the combustion reaction can self-sustain, is 7.66 mole with a preheat temperature of 400–500 K. The excessive aluminum favors to fill in the pores of the products, and a cylindrical Al₂O₃-TiC-Al composite with a relative density of 70% can be obtained, and its tensile strength is higher ten times than that of the Al₂O₃-TiC composite. Moreover, TiC and Al₂O₃ grains in the composites are fined as the excessive aluminum increases. Although the excessive aluminum does not take part in the combustion reaction, it strongly affects combustion process and microstructures of the products. © 2001 Kluwer Academic Publishers

1. Introduction

Self-propagating high-temperature synthesis, or combustion synthesis has been used to fabricate ceramic, ceramic/intermetallic, and ceramic/metal composites [1, 2]. Because of the advantage of using low-cost raw materials in the aluminothermic reaction, the synthesis via aluminothermic reaction was paid a great attention. Al₂O₃-TiC, Al₂O₃-TiB₂, WC-Al₂O₃, Cr₃C₂-3Al₂O₃ ceramic composites have been prepared using this technique [3–5]. However, the relatively high level of porosity in the products has led to some limitations in the application of this method for producing advanced materials. Varied densifying techniques have been explored, including hot compacting and hipping, explosive forming, and shock compaction [1]. In recent year, a novel densifying method for the combustion-synthesized products is currently being investigated which involves the use of excess metal reactant, e.g., Al, Ni, and Fe [6–10]. In this paper, excessive aluminum, indicated by the molar ratio x , was added into the reactants of the following exothermic reaction to densify the Al₂O₃-TiC ceramic composites:



2. Thermodynamic calculations

Combustion synthesis reactions are strong exothermic ones. Once ignited, extremely high temperature can be achieved in very short time. It is therefore reasonable to assume that a thermally isolated exothermic system exists because there is very little time for the heat to disperse to its surroundings. Therefore, the maximum temperature to which the product is raised can be assumed to be the adiabatic temperature, T_{ad} [11].

According to the enthalpy change between the reactants and the products, T_{ad} of Equation 1 with different excessive aluminum x and preheat temperature T_0 was calculated as shown in Fig. 1a. Melting rate of alumina in the products, R_m , was calculated as shown in Fig. 1b. A flat roof can be observed at 2303 K, which is the melting point of alumina, in the T_{ad} versus excessive Al curve. However, the melting rate R_m changes from 0 to 100% at this flat roof depending upon preheat temperature T_0 and the molar ratio x of excessive Al.

The theoretical T_{ad} can be used as a semi-quantitative evaluation to estimate whether the exothermic reaction can self-sustain or not. Merzhanov [1] suggested that a system will not become self-sustaining unless its $T_{\text{ad}} > 1800$ K. For Equation 1, when $x = 0$, T_{ad} is 2347 K at $T_0 = 298$ K. It implies that the combustion

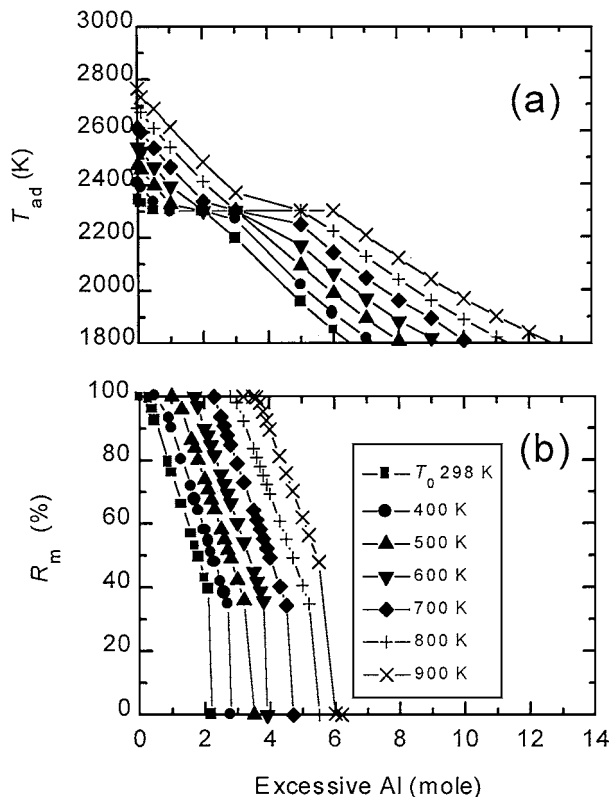


Figure 1 (a) Adiabatic temperature T_{ad} of the reaction $3\text{TiO}_2 + 3\text{C} + (4+x)\text{Al}$ and (b) melting rate R_m of alumina in the products.

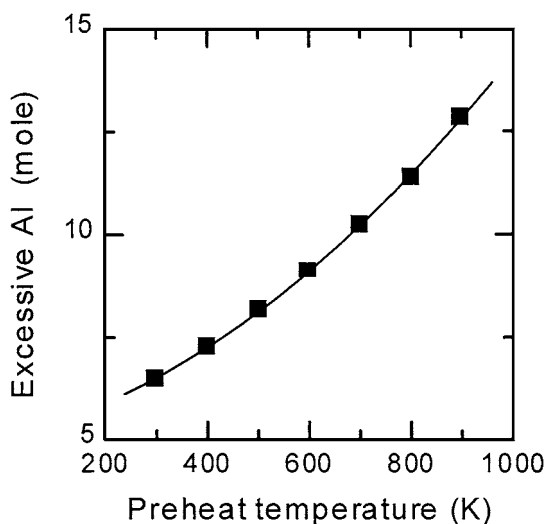


Figure 2 Critical molar ratio x_{cr} of excessive Al at varied preheat temperature T_0 .

synthesis reaction without excessive Al can self-sustain and self-propagate at any initial temperature. However, when x is greater than zero, excessive Al decreases T_{ad} of the reaction until T_{ad} is lower than 1800 K, and the combustion reaction cannot self-sustain and is extinguished. In this article, this critical molar ratio, x_{cr} of excessive Al was calculated as shown in Fig. 2 with varied T_0 . As T_0 increases, x_{cr} obviously increases.

3. Experimental procedure

Reactants were powders of titania (99% pure, anatase, average particle size of $2\ \mu\text{m}$), aluminum (99% pure, $30\ \mu\text{m}$), and graphite (99% pure, $60\ \mu\text{m}$). Appropriate amounts of these powders were mixed in accordance

with Equation 1. Mixing was done in an alumina ball-mill using alumina balls for 6 hours. Cylindrical reactant pellets with an approximate diameter and height of 20 mm were made by pressing the powder mixtures under a pressure of 180 MPa. The cylindrical pellets were subsequently ignited by an electric arc in a reaction chamber filled with flowing argon at 133 Pa. A W-3%Re/W-25%Re thermocouple inserted along the cylinder axis in the bottom of the sample was used to measure the temperature profile during the synthesis process.

The as-synthesized samples were fractured by a tensile tester to measure the tensile strength of the Al_2O_3 -TiC-Al composites. The fractured samples were examined using a scanning electron microscopy, SEM (S-520, Hitachi, Japan) and an electron probe micro-analyzer, EPMA (EPM-810, Shimadzu Electron Probe Microanalyzer, Japan). The chemical compositions were analyzed by an inductively coupled plasma atomic emission spectrometer (ARL 3520 ICP-AES, USA) and an element analyzer using powder samples. The constitutions of the products were analyzed by an x-ray diffractometer, XRD (Rigaku D/Max 2400, Japan).

4. Results and discussion

Ignition of these cylindrical samples was accomplished by heating the top surface of the pellet with an electric arc for several seconds. This resulted in the formation of planar combustion waves that propagated with a stable velocity depending on excessive aluminum as shown in Fig. 3. When x was 1.58 mole, combustion velocity reached the maximum of $3.3\ \text{mm}\cdot\text{s}^{-1}$, then it decreased to the minimum of $2.0\ \text{mm}\cdot\text{s}^{-1}$ at $x = 4.74$ mole. As excessive Al increased, combustion velocity increased again to $2.8\ \text{mm}\cdot\text{s}^{-1}$ at $x = 6.96$ mole. However, more excessive aluminum resulted in a steep decrease of the combustion velocity. When x was greater than 7.66 mole, the combustion reaction could not self-sustain and was extinguished.

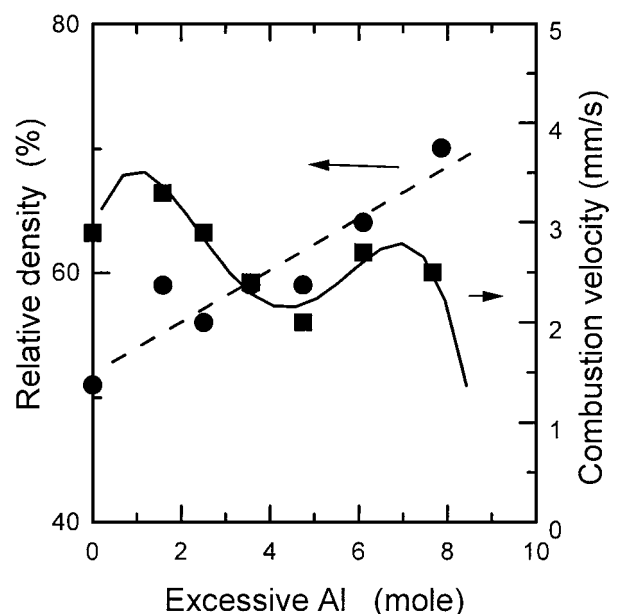


Figure 3 Combustion velocity during synthesis and relative density of the products versus the molar ratio of excessive aluminum in the reactants.

TABLE I Igniting time t_i and preheat temperature T_0 of reactions $3\text{TiO}_2 + 3\text{C} + (4+x)\text{Al}$

x (mole)	t_i (s)	T_0 (K)
0	40	433
0.75	50	491
1.58	52	522
3.56	71	500
7.66	75	550

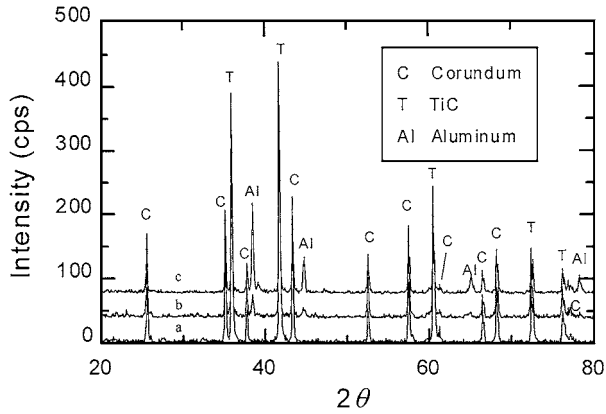


Figure 4 XRD patterns of the products using reactions $3\text{TiO}_2 + 3\text{C} + (4+x)\text{Al}$ when (a) $x = 0$, (b) $x = 0.75$ mole, and (c) $x = 2.51$ mole.

As seen from Figs 2 and 3, the experimental x_{cr} is far higher than that calculated at 298 K by thermodynamics. Preheat temperature T_0 and igniting time t_i obtained from temperature versus time profile during combustion synthesis is shown in Table I. It can be seen that the reactions in practice were ignited at 400–500 K. As the excessive Al increased, T_0 increased and t_i was postponed. It implies that igniting this exothermic reaction

is more and more difficult. Obviously, the experimental x_{cr} is very close to the theoretical one when preheat temperature is 500 K.

The chemical compositions and constitutes of the products are shown in Table II and Fig. 4. As excessive Al in the reactants increased, the Al amount in the products accordingly increased. The excessive Al has no effect on constitute of the combusted products as seen from Fig. 4. During combustion process, excessive Al does not directly take part in the reaction, and just plays a part as diluent.

Increasing the excessive Al in the reactant remarkably densifies the synthesized products. As shown in Fig. 3, when $x = 7.66$ mole, the relative density of the product obviously increased from 51% without excessive Al to 70%. The aluminum in the product, which has a lower melting point of 933 K, is in liquid during the post-combustion stage, and infiltrates the pores in the products. The densifying effect with excessive Al is notable for the combustion-synthesized composite. The combusted samples without excessive Al were fractured with 0.6–0.9 MPa by a tensile tester. However, the samples with excessive Al of 1.58 mole were fractured with 7–9 MPa. Tensile strength of the Al_2O_3 -TiC-Al composite is higher ten times than that of the Al_2O_3 -TiC composite.

Although the excessive Al does not participate in the combustion reaction, it decreases the grain size of the products. As shown in Fig. 5, increasing excessive Al strongly decreases the final size of the products. Both of TiC and corundum are fined as excessive Al increases. The authors [5] have investigated the structure formation in the combustion synthesis of Al_2O_3 -TiC composite, and found the final grain size of the products

TABLE II Chemical compositions of the synthesized products using reactions $3\text{TiO}_2 + 3\text{C} + (4+x)\text{Al}$ (wt%)

x (mole)	Al	Ti	C	Ca	Fe	Co	Ni	Cr	O
0	27.3	36.3	9.54	0.001	0.04	0.06	0.08	0.08	Bal.
0.75	29.9	29.1	8.40	0.05	0.01	0.05	0.01	0.04	Bal.
1.58	31.3	28.8	7.93	0.04	0.02	0.04	0.07	0.05	Bal.
2.51	32.4	29.4	6.93	0.04	0.02	0.05	0.01	0.04	Bal.
3.56	38.4	30.8	5.96	0.03	0.02	0.05	0.01	0.04	Bal.

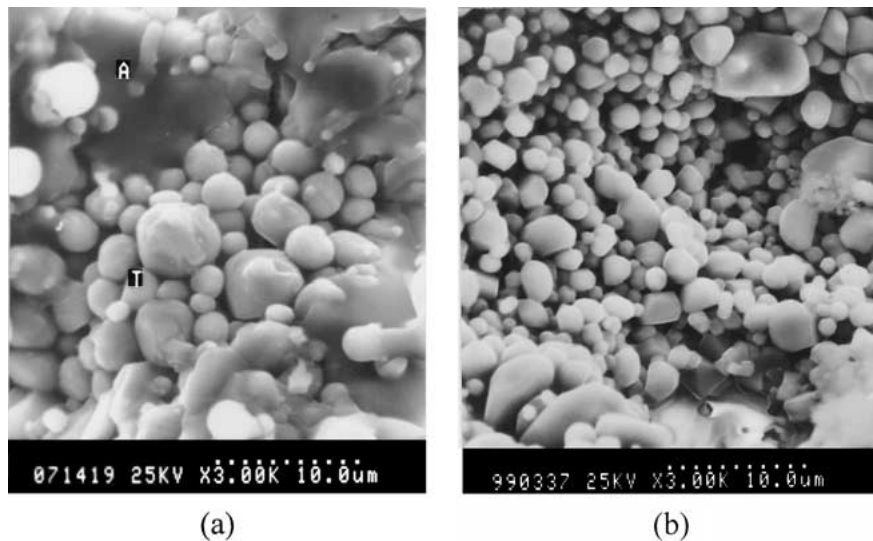


Figure 5 SEM micrographs of the products (a) without and (b) with 0.75 mole excessive aluminum.

depending on the cooling rate in the post-combustion stage. As seen from Fig. 1, excessive Al decreases the adiabatic temperature of the exothermic reaction; therefore, the resident time of the products at high temperature decreases. Lack of enough time, thus, TiC and Al₂O₃ grains cannot grow up. Excessive Al favors fining the grains of the products.

5. Conclusions

In the self-propagating high-temperature synthesis of Al₂O₃-TiC-Al composites, the critical molar ratio of the excessive Al, which the reaction cannot self-sustain and is extinguished, is 7.66 mole. Excessive Al remarkably densifies the products, both in the relative density and tensile strength of the products. Excessive Al in the reactant has no effect on constituents of the products, but fines grains of Al₂O₃ and TiC in the final products.

Acknowledgments

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