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Combustion characteristics of TiO_2/Al/C system

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Abstract

The formation of TiC-Al_2O_3 composite powder was studied by a combustion reaction on the system TiO_2/Al/C. The effects of the molar ratios of raw materials, compaction pressure and initial temperature of reactants on the products and combustion process were studied. The most important variable affecting the synthesis of TiC-Al_2O_3 was the molar ratio of C and Al. The highest yield of TiC-Al_2O_3 was obtained at the molar ratio of TiO_2:Al:C$=$3.0:4.0:2.7$\sim$3.0. The combustion temperature and the combustion velocity were increased with increasing preheating temperature. On the other hand, the cooling rate was decreased with increasing of preheating temperature. The cooling rate after completing the combustion was related to grain size of products. The grain size was increased with decreasing cooling rate. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: A. Ceramics; B. Chemical synthesis; C. X-ray diffraction; D. Thermodynamic properties

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1. Introduction

Self-propagating High Temperature Synthesis is potentially an energy-efficient process to synthesize many inorganic materials, including intermetallics, ceramics, and ceramic composites [1–3]. Characteristics of the process in the combustion-wave mode are self-generated high temperature (800 to 3500^{o}C), relatively rapid propagating combustion fronts (0.1 to 10cm/sec), high rates of heating (up to 10^6 deg/sec), and thermal gradients (up to 107 deg/cm) at the combustion front. The exact values of temperature,

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Table 1
Thermochemial data for TiC, Al_2O_3, TiO_2, Al and C [9,10]

Element	Temp. Range(K)	ΔH° (KJ/mole)	ΔH_m (KJ/mole)	Cp(J/Kmole)
TiC	298~1800	−183.69		$49.5 + (3.35 \times 10^{-3}T) - (14.98 \times 10^5T^{-2})$
	800~3290			$34.2 + (11.58 \times 10^{-3}T) + (74.161 \times 10^5T^{-2})$
Al_2O_3	298~1800	−1677.44	111.085	$106.61 + (17.78 \times 10^{-3}T) - (28.54 \times 10^5T^{-2})$
	1800~2327			$128.0 + (5.28 \times 10^{-3}T) - (80.235 \times 10^5T^{-2})$
	2327~3000			192.464
TiO_2		−944.79		–
Al		0		–
C		0		–

wave velocity, thermal gradients, and rate of heating are functions of the particular chemical system and experimental parameters. Both solid-solid and gas-solid combustion reactions are used to produce a variety of advanced technological materials.

Al_2O_3-TiC, Al_2O_3-ZrO_2, Si_3N_4 and TiC which have high temperature strength, high thermal shock resistance have used as advanced structural materials. Especially, the TiC-Al_2O_3 composite used for making abrasive tool and wear resistant coating to protect components of oil refining equipment has been produced by hot pressing TiC and Al_2O_3 powder. The preparation of TiC-Al_2O_3 composite powder by the SHS process was widely studied in several former researches [4–7], however the effect of carbon sources on the combustion characteristics are rare. Hence, in this study, the SHS process was applied to a system of TiO_2/Al/C for the production of TiC-Al_2O_3 composite. The reaction in this system was discussed in terms of the mixture ratio and the preheating of the pellet for the formation of fine TiC-Al_2O_3 powder when activated charcoal, carbon black and graphite used as carbon sources.

2. Experimental

The raw materials used were TiO_2 (98.56% rutile, <0.5μm; Korea Titanium Co., Korea) and Al (99.5%, <44μm; Chang Seong Co., Korea). Activated charcoal(Duksan Pharm. Co., Japan), Carbon black(LG Chemical Ltd., Korea) and Graphite (Kanto Chemical Co., Inc., Japan were used as carbon sources. The reactants(TiO_2:Al:C=3.0:3.4~4.6:1.8~3.6), were mixed by milling for 5 hours using an alumina ball mill. The mixed powders were pressed to form a pellet 40mm diameter and 50~60mm in height under a pressure of 80MPa and then dried in a drying oven of 70°C for 1 hour. The green pellet was ignited in a reactor using a tungsten coil connected to a power supply under atmosphere of argon. The green pellet was preheated by small furnace installed in combustion chamber from room temperature to 600°C. The combustion temperature, the combustion velocity and the cooling rates of the pellet were measured by a c-type (W-5%Re vs. W-26%Re) thermocouples embedded into the pellet using a data acquisition system and a personal computer. The crystal structures of reaction products were

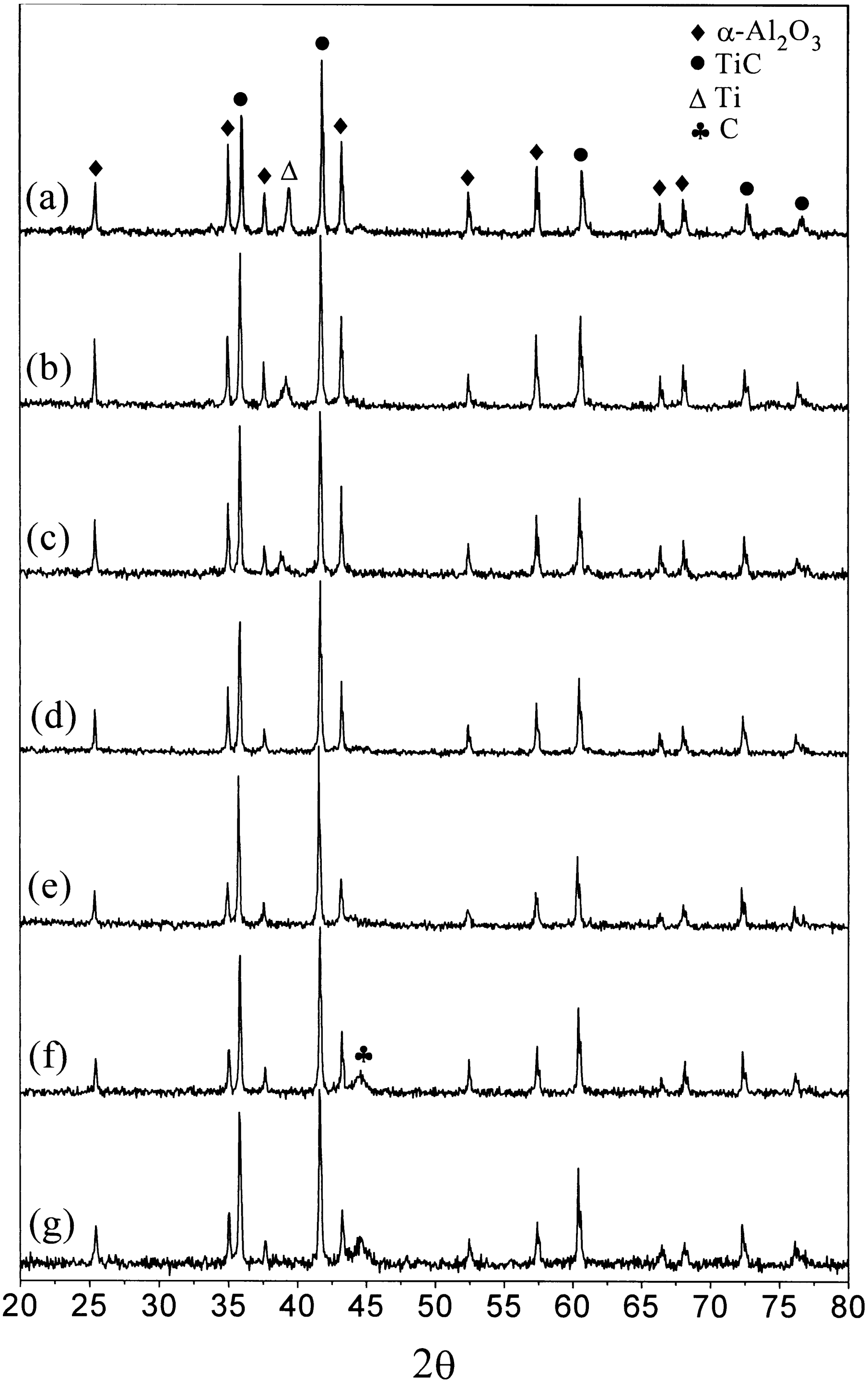

Fig. 1. X-ray diffraction patterns of reaction products varying with carbon molar ratio at TiO_2: Al=3.0:4.0(carbon source:charcoal activated):(a)1.8 (b) 2.1 (c) 2.4 (d) 2.7 (e) 3.0 (f) 3.3 (g) 3.6.

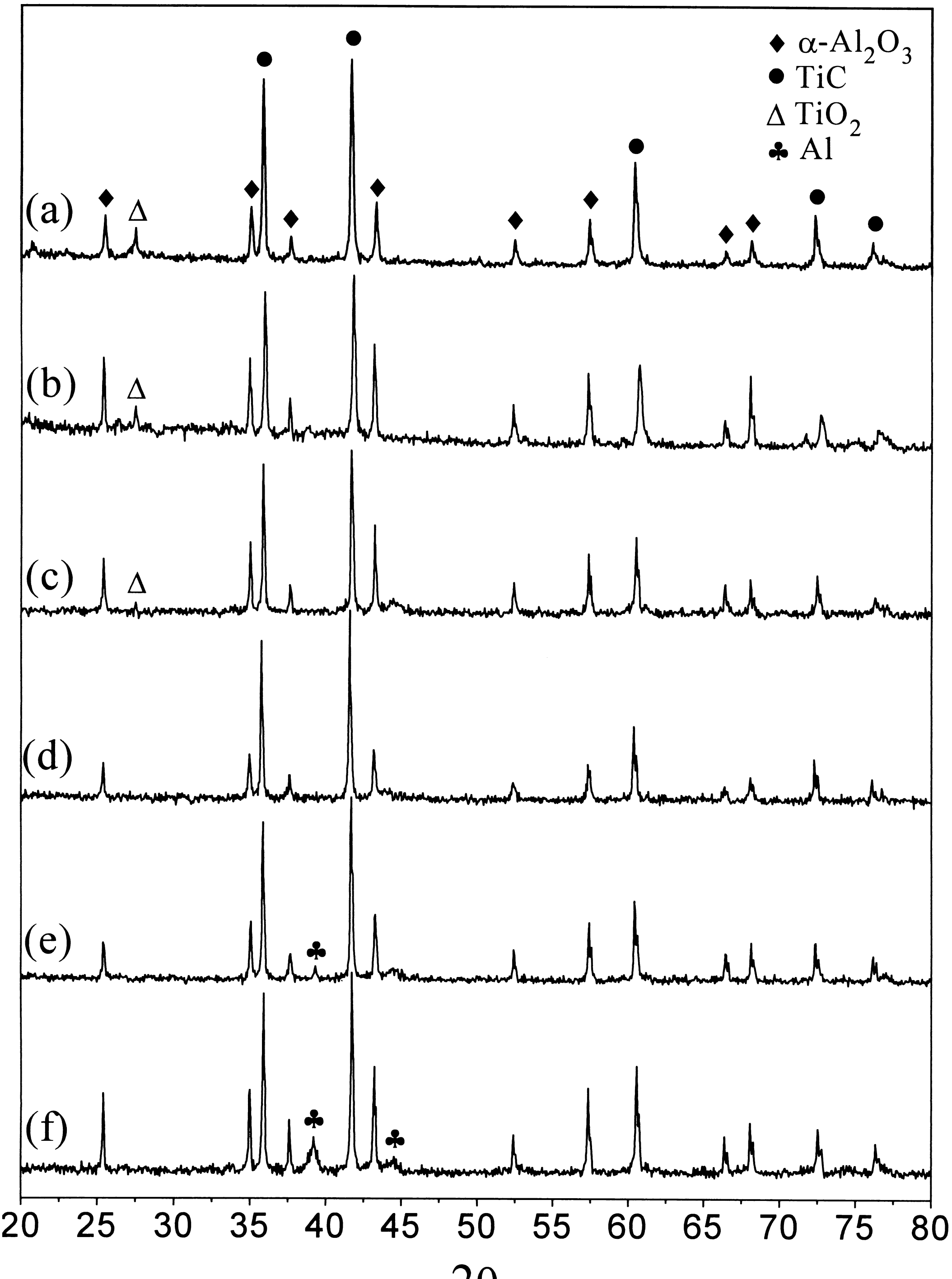

Fig. 2. X-ray diffraction patterns of reaction products varying with aluminum molar ratio at TiO_2: C=3.0:3.0 (carbon source: charcoal activated): (a) 3.4 (b) 3.6 (c) 3.8 (d) 4.0 (e) 4.2 (f) 4.6.

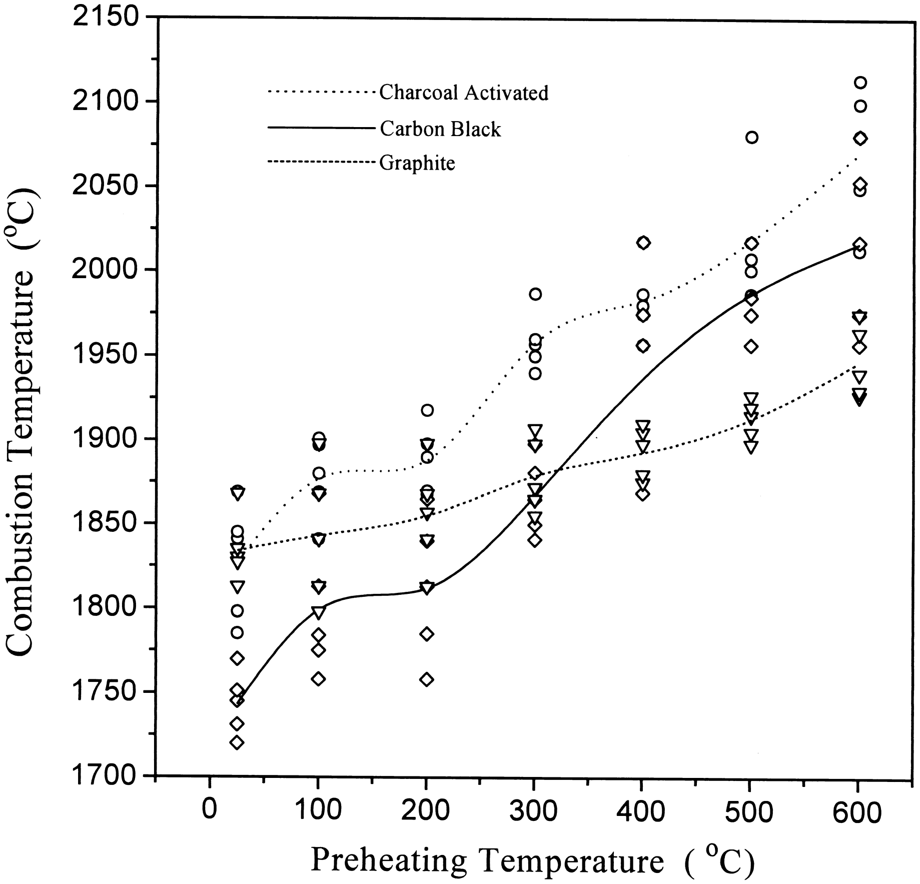

Fig. 3. The effect of the preheating temperature on the combustion temperature.

analyzed using X-ray powder diffraction (XRD) and the microstructure was investigated using scanning electron microscopy (SEM).

3. Results and discussion

The adiabatic temperature (T_{ad}) can be used as a general indication of the temperature at the combustion front. It can also be used in a semiquantitative way to ascertain whether the synthesis of a given material can be accomplished by a self-propagating method. It has been empirically suggested that combustion reactions will not become self-sustaining unless $T_{ad} \geq 1800K$ [8]. The reaction of this experiment can be represented as follows:

$$3TiO_2 + 4Al + 3C \rightarrow 3TiC + 2Al_2O_3 \quad (1)$$

The theoretical adiabatic temperature of this reaction can be calculated using thermodynamics data in Table 1 as follows;

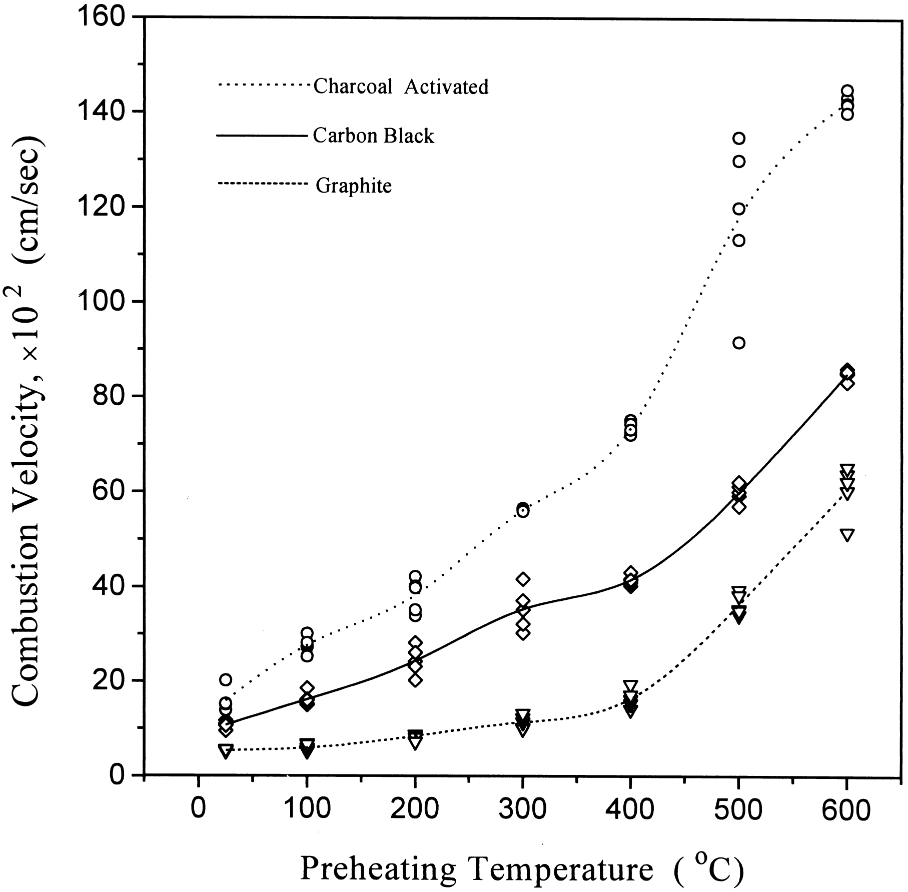

Fig. 4. The effect of the preheating temperature on the combustion velocity.

$$Q = (-\Delta H^0_{298}) = \int_{298}^{T_{ad}} \sum C_p(products)dT \tag{2}$$

$$\begin{aligned}\Delta H^0_{298} &= (3\Delta H^0_{298,TiC} + 2\Delta H^0_{298,Al_2O_3}) - (3\Delta H^0_{298,TiO_2} + 4\Delta H^0_{298,Al} + 3\Delta H^0_{298,C}) \\ &= -1071.58 kJ/mol\end{aligned}$$

$$(-\Delta H^0_{298}) = \int_{298}^{T_{ad}} \sum C_p(products)dT$$

$$Finally,\ 1071580 = \int_{298}^{1800} (3C_{p,TiC(s)} + 2C_{p,Al_2O_3(s)})dT$$

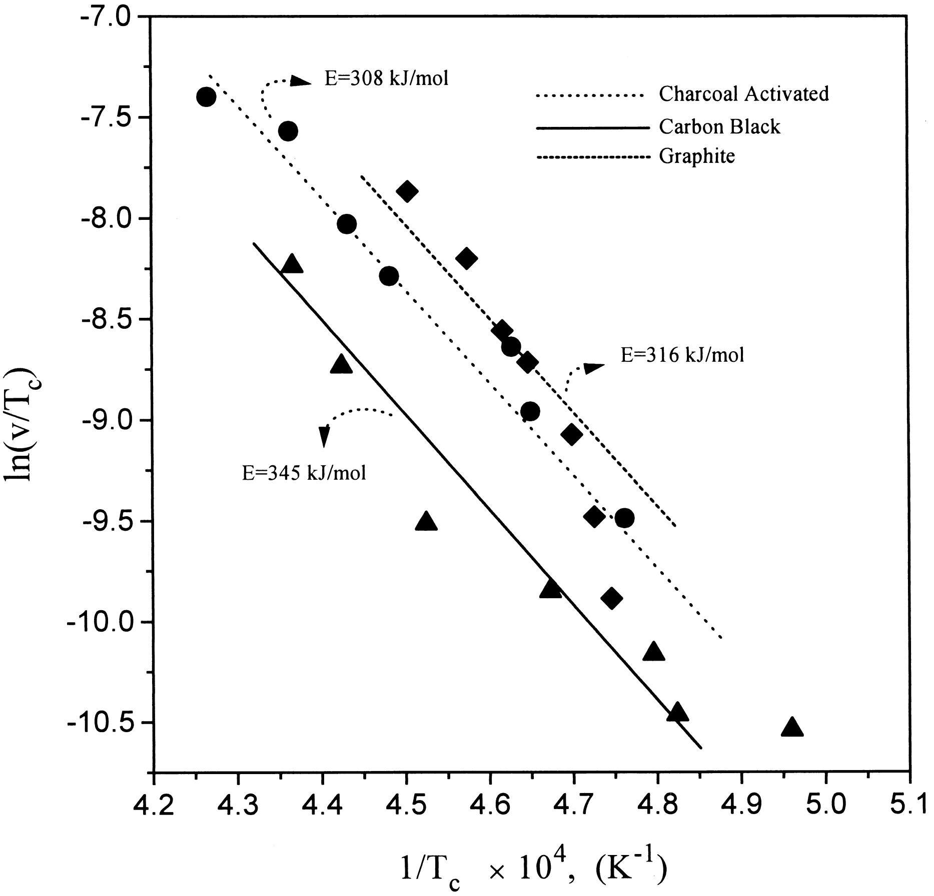

Fig. 5. Arrhenius plot of Al_2O_3-TiC combustion reaction varying with carbon source.

$$+ \int_{1800}^{2327} (3C_{p,TiC(s)} + 2C_{p,Al_2O_3(s)})dT$$

$$+ \Delta H_{m,Al_2O_3} \int_{2327}^{T_{ad}} (3C_{p,TiC(s)} + 2C_{p,Al_2O_3(l)})dT$$

$\therefore T_{ad} \approx 2546K$

Therefore, we can assume that the SHS reaction of Eq. [1] will be possible from the preceding theoretical result. Actually, the combustion temperature, T_c, measured in this system was about 1700~2250K because of heat losses.

The effect of the carbon molar ratio on the XRD of product without preheating sample is represented in Fig. 1. The molar ratio of carbon was changed from 1.8 to 3.6mole, because the value of x in TiC_x compound is in the range of 0.6~1.0, then the content of the total

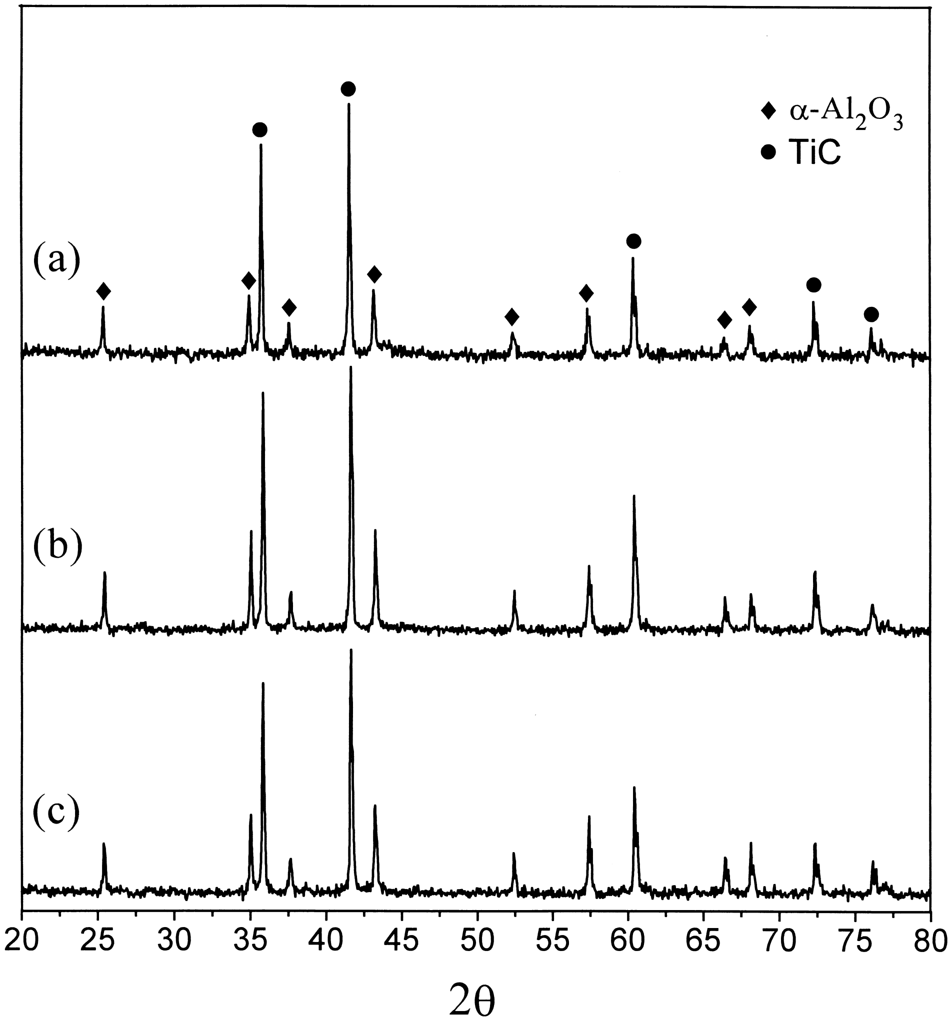

Fig. 6. X-ray diffraction patterns of reaction products varying with carbon source(TiO_2: Al: C=3.0:4.0:3.0); (a) charcoal activated (b) carbon black (c) graphite.

carbon in the product should be between 1.8 and 3.0 mole from eq. [1]. As the carbon content increased, the unreacted Ti diminished and was completely eliminated when the carbon content was over 2.7 mole shown in Fig. 1. Further, the XRD patterns in Fig. 1 now show the presence of carbon when the value of C in the ratio TiO_2:Al:C exceeds 2.7. Fig. 2 shows the X-ray diffraction patterns of the products with various Al molar ratios. As the Al molar ratio increases, the amount of unreduced TiO_2 is seen to decrease until the Al:TiO_2 reaches a ratio of 4.0:3.0 when all the TiO_2 is completely reduced. Peaks of Al appear above that ratio because of an excess of Al over stoichiometry.

Figures 3 and 4 show the effect of the preheating temperature on the combustion temperature and the combustion velocity of the reactions varying with carbon source. As expected, the combustion temperature and the combustion velocity of the reaction increased

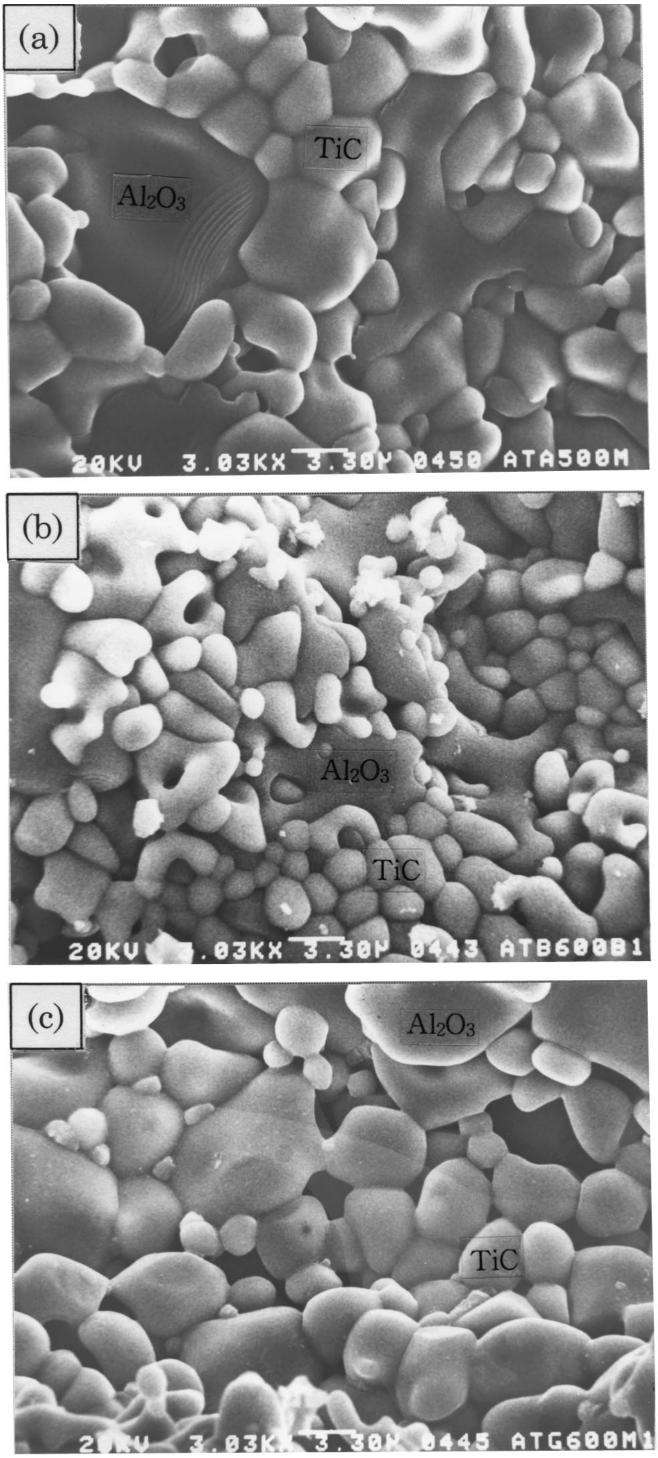

Fig. 7. SEM photomicrographs of synthesized products varying with carbon source: (a) charcoal activated (b) carbon black (c) graphite.

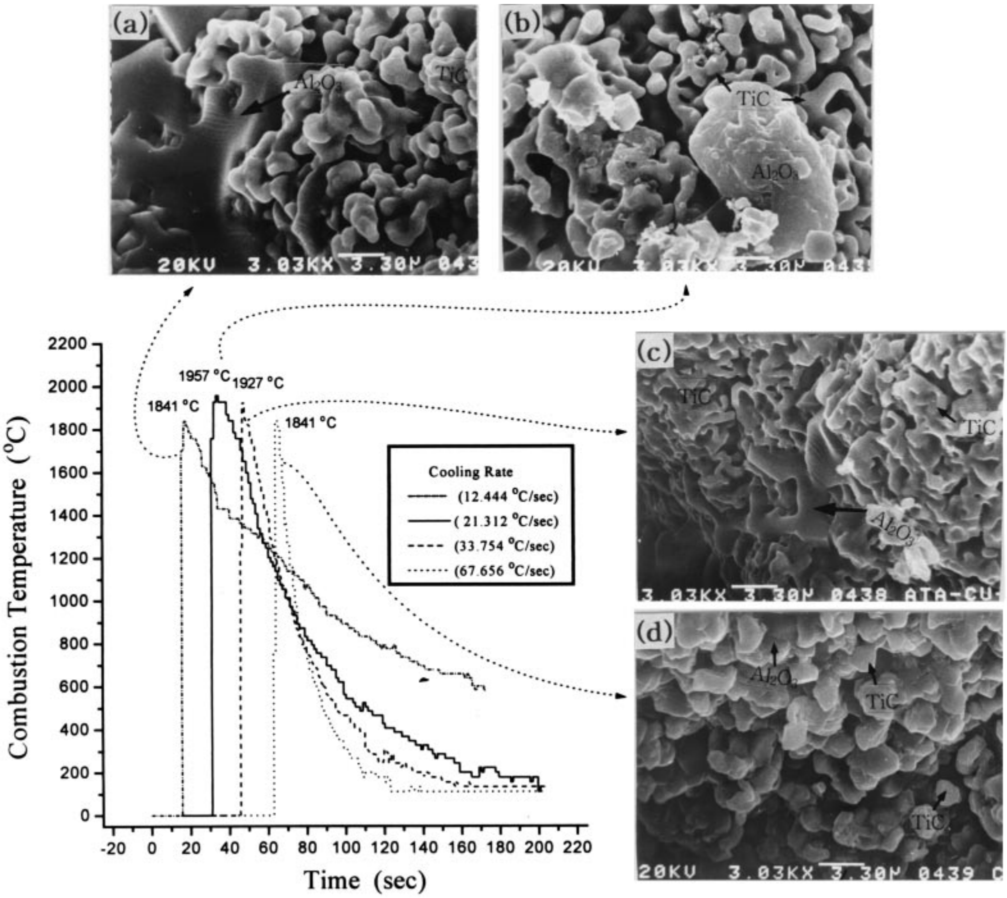

Fig. 8. SEM photographs of synthesized products with various cooling rate.

as the preheating temperature increased. According to these figures, charcoal as carbon source has the highest combustion temperature and velocity of all. In room temperature, the combustion velocity was 0.5~1.5mm/sec varying with carbon source. When the initial temperature of reactants is 600°C, the combustion velocity of charcoal activated, carbon black and graphite were 14.2mm/sec, 8.65mm/sec and 6.06mm/sec respectively. Fig. 5 shows the activation energy which is calculated using measured combustion temperature and velocity on the combustion reaction. It shows that activated charcoal, graphite and carbon black values are 308kJ/mol, 316kJ/mol and 345kJ/mol respectively.

Figures 6 and 7 show that the X-ray diffraction patterns and the microstructure of the product vary with the carbon source at TiO_2:Al:C=3.0:4.0:3.0 mole. These figures show that crystal structure and microstructure of the product was not affected by carbon sources.

In this work, we used a wedge type copper mold to investigate microstructure of reaction product as to the different cooling rates. The cooling rate is changed according to the diameter of the wedge by the large heat conductivity of copper. Fig. 8 shows the temperature profile and microstructure at different mold positions (TiO_2:Al:C=3.0:4.0:3.0, activated charcoal without preheating). As the cooling rate become faster, the grain size become smaller. We can see the result that the Al_2O_3 particles grew bigger and TiC particles seem to be sintered in Fig. 8(a), the slowest cooling rate. In the case of fastest cooling rate, Fig. 8(d), the grain size of alumina becomes smaller (up to 3∼4μm) and the grain size of TiC is about 2μm independently. So, the grain size of product depends on the cooling rate after the combustion reaction.

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