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Short communication

Effects of PTFE activation and excess Al on combustion synthesis of SiC– and ZrC–Al_2O_3 composites

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ABSTRACT

Fabrication of SiC– and ZrC–Al_2O_3 composites was studied in PTFE-added SiO_2/Al/C and ZrO_2/Al/C combustion systems. PTFE acted as not only a reaction promoter to initiate and sustain self-propagating combustion, but a carburizing agent to facilitate evolution of carbides. Excess Al was required to improve thermite reduction of oxide precursors. Based upon the dependence of flame-front velocity on combustion temperature, the activation energies of 149.8 and 104.0 kJ/mol were respectively deduced for synthesis of SiC– and ZrC–Al_2O_3 composites from PTFE-assisted combustion. The SiC–Al_2O_3 composite with the least amount of minor phases was produced from the SiO_2/Al/C system with PTFE of 6.2 wt% and extra Al of 25%. The best yield of the ZrC–Al_2O_3 composite was obtained from the ZrO_2/Al/C system with PTFE of 3 wt% and 25% excess Al.

Alumina containing composites have been extensively studied because of their high hardness, good chemical stability, high thermal resistance, and good mechanical strength [1–4]. Compared to monolithic SiC, mechanical properties of the SiC–Al_2O_3 composite were significantly improved, including hardness, fracture toughness, flexural strength, and creep resistance [5–7]. These favorable properties of the SiC–Al_2O_3 composite led to its use in cutting tools, abrasive materials, and high-temperature structural applications. As an ultra-high temperature ceramic (UHTC), ZrC attracts considerable attention due to its excellent physical and chemical properties in ultra-high temperature ablation environments, such as high melting point, high thermal and electrical conductivity and good thermal shock resistance [8–10]. When combined with ZrC, the ZrC–Al_2O_3 composite is a candidate material for development of the thermal protection system in hypersonic aerospace vehicles, scramjet propulsion engines, and rocket motors [8–10].

With the merits of low energy consumption, short reaction time, inexpensive equipment, simplicity of operation, and in situ formation of composite components, self-propagating high-temperature synthesis (SHS) has been recognized as a promising fabrication route of advanced materials [11,12]. Moreover, combustion synthesis involving aluminothermic reduction of metal oxides represents an in situ processing method capable of producing Al_2O_3-reinforced ceramics and intermetallics [13,14]. For the SHS system characterized by an adiabatic temperature less than 1800 K or having a high activation energy barrier, chemical activation employing PTFE (Teflon) as the promoter has been effective in initiating the reaction and sustaining the combustion wave [15–18].

According to Zurnachyan et al. [15], the Si–PTFE and Al–PTFE reactions with SiF_4 and AlF_3 as the intermediates promoted low-exothermic reaction systems to produce SiC–Cu and SiC–Al cermets under the SHS mode. As reported by Musa et al. [16], the threshold amount of PTFE was 3 wt% for the SHS reaction between tantalum and graphite to produce TaC. An investigation of PTFE-activated combustion in the SiO_2/Al/C system indicated that PTFE led to formation of gas-transport species and evolution of SiC whiskers [17]. Recently, Cr_2AlC–Al_2O_3 composites were fabricated by PTFE-assisted combustion synthesis using Al, Cr_2O_3, Al_4C_3, carbon black, and graphite as the raw materials [18]. Moreover, a set of reaction mechanisms taking into account the interactions of PTFE with Al, Cr, and Al_2O_3 was proposed [18].

This study aims to prepare SiC– and ZrC–Al_2O_3 composites by the SHS process involving PTFE activation and aluminothermic reduction of SiO_2 and ZrO_2. In contrast to most of the thermite reactions, reduction of SiO_2 and ZrO_2 by Al is weakly exothermic [19]. Therefore, main goals of this study are to substantiate the role of PTFE in promoting the reduction reaction and subsequent formation of SiC and ZrC, and to examine the effect of excess Al on phase transformation. In addition, the activation energy associated with PTFE-activated combustion was deduced from measured combustion wave velocity and reaction temperature.

The starting materials adopted by this study included SiO_2 (Alfa Aesar, < 45 μm, 99.8%), ZrO_2 (Alfa Aesar, < 45 μm, 99.5%), Al (Showa Chemical, < 45 μm, 99.9%), carbon black (Showa Chemical, 20–40 nm, 99%), and PTFE ($-(C_2F_4)_n-$, Alfa Aesar, 6–10 μm). Reactant mixtures were formulated based on the stoichiometries of Reactions (1) and (2)

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for in situ formation of SiC– and ZrC–Al_2O_3 composites, respectively.

$$3SiO_2 + (4 + z)Al + (3 - x)C + xC_{PTFE} \xrightarrow{-(C_2F_4)_n-} 3SiC + 2Al_2O_3 \quad (1)$$

$$3ZrO_2 + (4 + z)Al + (3 - y)C + yC_{PTFE} \xrightarrow{-(C_2F_4)_n-} 3ZrC + 2Al_2O_3 \quad (2)$$

where C_{PTFE} represents carbon supplied from complete decomposition of PTFE and is taken into account as a part in the total carbon balance. The coefficients, x and y, ranging from 0.1 to 0.6 are considered to signify the molar content of C_{PTFE}. The coefficient, z, indicates the excess amount of Al. Besides those without extra Al ($z = 0$), test specimens are prepared with excess Al at $z = 0.5$, 1.0, and 1.5. Reactant powders were well mixed and compressed into cylindrical samples with 7 mm in diameter, 12 mm in length, and a relative density of 55%. The SHS experiment was conducted in a windowed combustion chamber under vacuum. The combustion temperature was measured by a fine-wire (125 μm) Pt/Pt-13%Rh thermocouple attached on the sample surface. Details of the experimental methods were previously reported [20].

Experimental observations showed that combustion failed to be initiated when no PTFE was added. The threshold amounts of PTFE required for inducing self-sustaining combustion in Reactions (1) and (2) were 3.0 and 2.0 wt%, which are correspondingly equivalent to $x = 0.13$ and $y = 0.2$. As a reaction promoter, PTFE is able to peel off the Al_2O_3 shell on the surface of the Al particle to enhance the reactivity of Al powders [18]. Moreover, direct reaction between Al and PTFE is highly exothermic and generates AlF_3 and carbon. Carbon produced from C_2F_4 participates in the formation of carbides. Excess Al is to compensate for the loss of Al due to evaporation and formation of AlF_3 [18]. According to the reaction mechanisms to be presented later, F_2 gas was produced during the SHS process. Due to its toxicity, the combustion chamber was purged by argon gas after each experiment.

Fig. 1 presents a combustion sequence recorded from a PTFE-added powder compact of Reaction (1) with $x = 0.2$ and $z = 0$. As illustrated in Fig. 1, a combustion wave is established upon ignition and travels downward in a self-sustaining manner. Because of formation and expelling of gas-transport species associated with PTFE, irregular cracks were created in the sample during the SHS process. As a result, the as-synthesized product was taller than the green compact and was ease to grind into powders. Similar combustion behavior was observed for Reaction (2). As reported by Musa et al. [16], the irregular combustion wave propagation and a noticeable elongation of the sample, as compared to its original height, could be ascribed to the gaseous species developed as a consequence of PTFE decomposition.

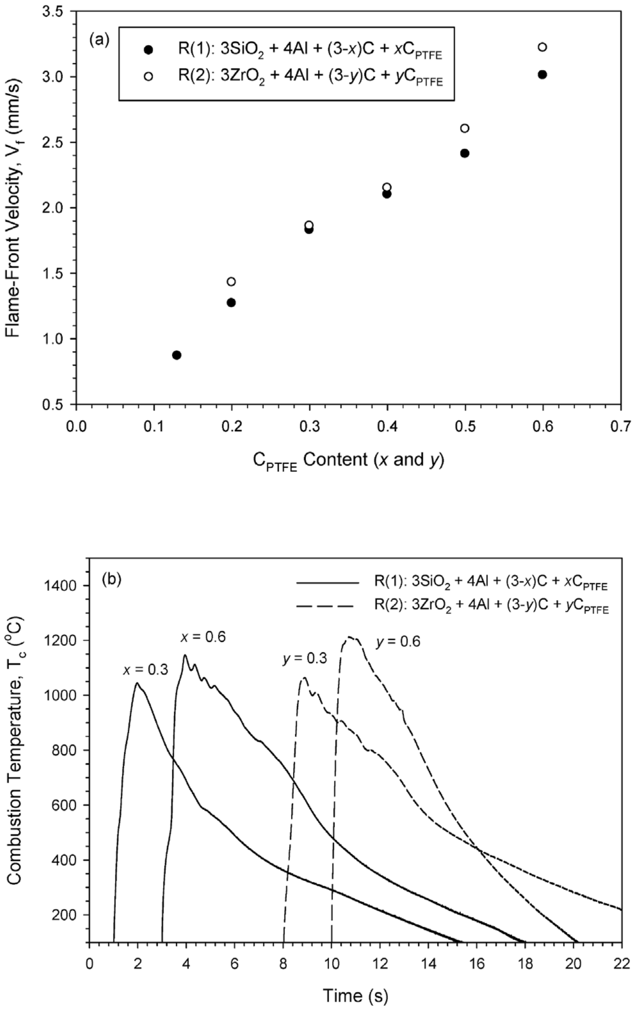

Fig. 2. Effects of PTFE content on (a) flame-front velocity and (b) combustion temperature of Reactions (1) and (2) for formation of SiC– and ZrC–Al_2O_3 composites.

The flame-front propagation velocity (V_f) was increased by increasing PTFE content. As reported in Fig. 2(a), the combustion wave velocity increases from 0.87 mm/s at $x = 0.13$–3.0 mm/s at $x = 0.6$ for Reaction (1) containing no excess Al. The flame-front velocity of Reaction (2) is slightly higher and increases from 1.43 to 3.22 mm/s for $y = 0.2$–0.6. Acceleration of the combustion wave on account of an increase of PTFE confirms the role of PTFE in chemical activation. Fig. 2(b) depicts typical combustion temperature profiles. The abrupt rise in temperature signifies rapid arrival of the combustion wave and the peak value corresponds to the combustion front temperature (T_c). The increase of combustion temperature with PTFE is presented in Fig. 2(b) and under the maximum amount of PTFE (i.e., $x = y = 0.6$), the peak combustion temperatures reach up to 1146 and 1212 °C for Reactions (1) and (2), respectively. The increase of T_c with PTFE

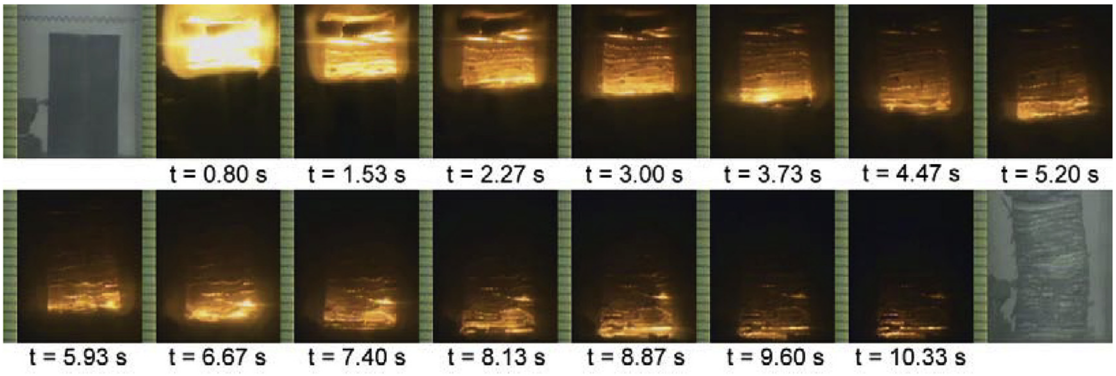

Fig. 1. A sequence of recorded images illustrating self-sustaining combustion wave propagating along a sample of Reaction (1) with $x = 0.2$ and $z = 0$.