

Al/TiO₂ SELF-COMBUSTION SYNTHESIS REACTION^①

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ABSTRACT Al/TiO₂ self-combustion synthesis reaction has been studied, including the effect of initial conditions of reactants on combustion temperature, combustion velocity and combustion stability etc. The reaction mechanism of Al/TiO₂ self-combustion synthesis has been studied emphatically and the dynamic reaction model has been created.

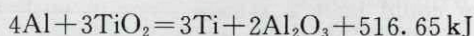
Key words aluminum titania self-combustion synthesis reaction reaction mechanism

1 INTRODUCTION

As a new way of material synthesis and compounding, self-combustion high-temperature synthesis (SHS) technology has been largely motivated by its distinctive properties. These investigations have included theoretical analyses of the mechanism of SHS and experimental demonstrations of the feasibility of the process to synthesize some metallic and ceramic materials, including composite materials^[1-3]. As a matter of fact, the reaction between Al and TiO₂ is a typical aluminothermic reaction. But being regarded as self-combustion synthesis reaction, so far the reaction between Al and TiO₂ has never been studied at home and abroad excepting for the author and their study group. Some study results has already been reported^[4,5,6]. In a subsequent paper we will present results of the effect of initial conditions of reactants on combustion process and SHS reaction mechanism between Al and TiO₂.

2 MATERIALS AND EXPERIMENTAL PROCEDURES

The SHS reaction equation in this paper is



The high purity Al powders (average 10.0 μm as shown in Fig. 1(a)) and TiO₂ powders (average 2.0 μm , Fig. 1(b)) or adding diluent alumina powders (average 0.5 μm) were mixed in a alumina ball mill with alumina balls in acetone for 24 h and dried and outgassed in vacuum.

Fig. 2 shows SHS reaction experimental scheme. Each powder mixture was pressed into a cylindrical sample 20 mm in diameter and 50 mm in height, then the green body sample was placed in the closed chamber, which was first evacuated and then filled with Ar gas at atmospheric pressure. The test sample was ignited at one end by using an electrically heated SiC rod. The sample measurement thermocouple was wolfram-rhenium with wires of 1.0 mm diameter and sample temperature measurements were monitored by a strip chart recorder. Through the watching window, the combustion propagating process could be watched and combustion velocity could be measured. The preheating furnace could be used to preheat the sample. The combusted sample laid in a special crucible was cooled to ambient temperature in experimental scheme. The process flow diagram in the studies are as follows:

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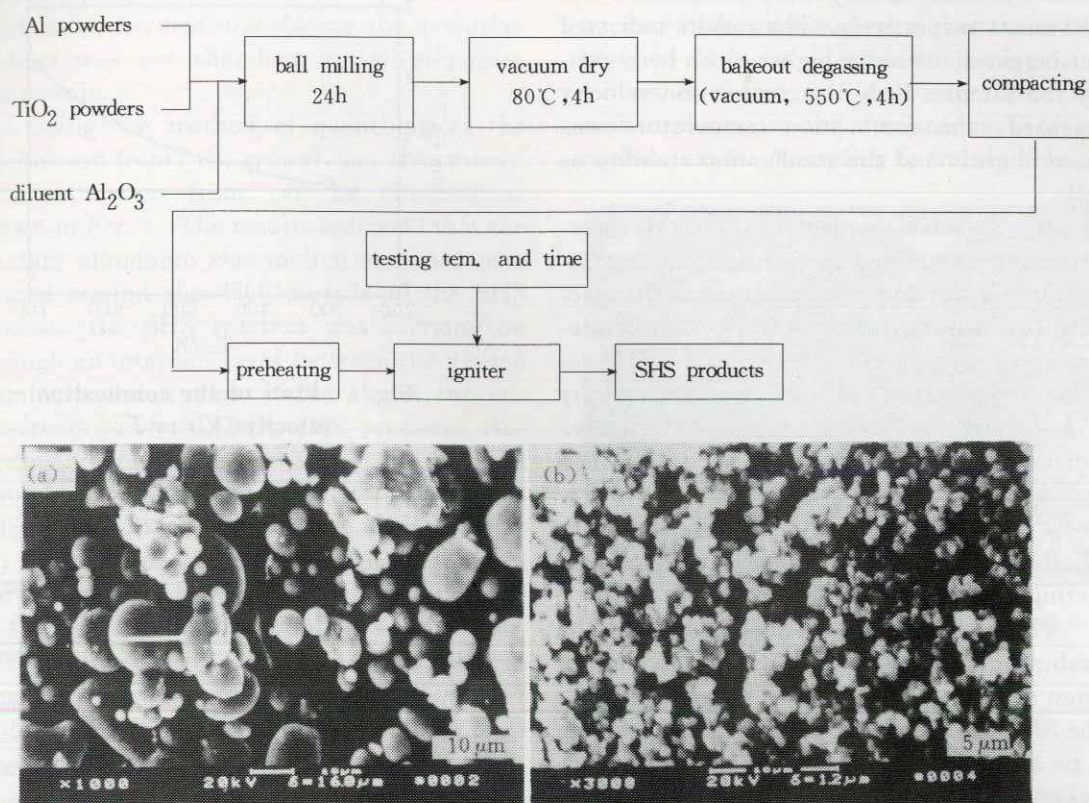


Fig. 1 SEM micrographs of reactants Al powders(a) and TiO₂ powders(b)

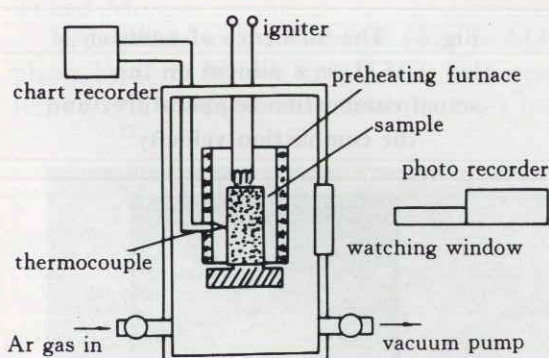


Fig. 2 Experimental scheme for SHS reaction

3 RESULTS AND DISCUSSION

The reaction initial conditions include

powder size, green body density, sample diameter, preheating temperature and diluent content etc. For the convenience of study work, the standard conditions were assumed as follows: average diameter of the aluminum powder titania powder, and alumina powder be 10.0 μm, 2.0 μm and 0.5 μm respectively; sample diameter 20.0 mm, green body density 3.124 g/cm³, no diluent and not preheating (ambient temperature).

Aluminum powder size has not affected the combustion velocity and the combustion temperature. For in the front of combustion wave, aluminum powders were molten (shown in Fig. 7), aluminum powder of effective size had less influence on combustion process. But because of the reaction mechanism between Al and TiO₂, TiO₂ powders had much influence on combustion velocity. When TiO₂ powders average size were 2.0 μm and 0.5 μm,

the combustion velocity were 2.51 mm/s and 5.81 mm/s respectively. The results indicated that bigger diameter or higher green body density the samples had, the combustion velocity increased, the combustion temperature was raised slightly and the combustion stability as well.

Fig. 3 shows the dependence of the adiabatic temperature and the actual reaction temperature on the initial temperature of the reactants (preheating temperature— T_0), preheating the reactants can increase the SHS reaction temperature, the combustion velocity (Fig. 4) and combustion stability effectively. Because the sample has been preheated in a way during the ignition, the actual temperature was higher than the adiabatic temperature (T_{ad}) calculated theoretically with low preheating temperature as shown in Fig. 3.

The actual reaction temperature and the combustion velocity decreased through the addition of Al_2O_3 as a diluent as shown in Fig. 5. The SHS process would become more unstable or be difficult to ignite and propagate with increasing the content of Al_2O_3 as a diluent. Fig. 6 is the photograph of typical pulsating combustion with the addition of Al_2O_3 as a diluent, because Al_2O_3 as a diluent needs to

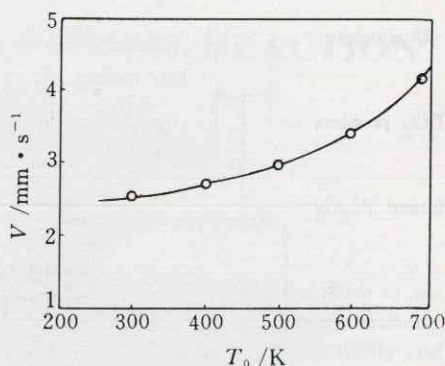


Fig. 4 Plots of the combustion velocity (V) vs T_0

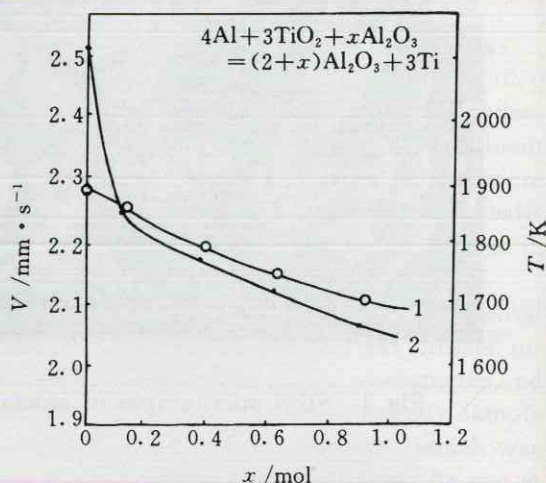


Fig. 5 The influence of addition of Al_2O_3 as a diluent on the actual combustion temperature^[1] and the combustion velocity^[2]

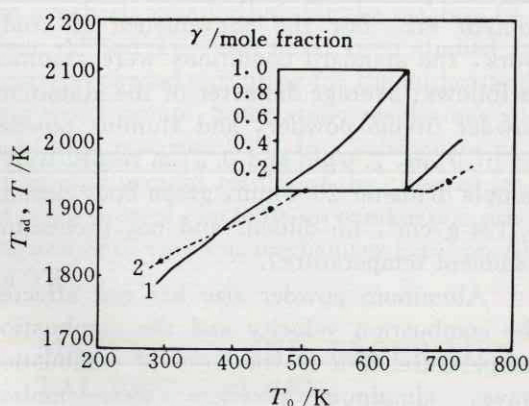


Fig. 3 The dependence of the T_{ad} (1) and the actual reaction temperature (T) (2) on the initial temperature (T_0) of the reactants (γ -mole fraction of Ti theoretically)

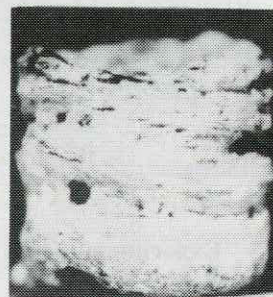


Fig. 6 The photograph of typical pulsating combustion with the addition of Al_2O_3 as a diluent [$x = 0.8$, $T_0 = 200^\circ C$]

absorb a part of heat in the SHS process, the combustion became unstable or the evolution of heat was not abundant to self-propagate frontwards.

Using the method of quenching at the combustion front, the typical, net structure of the combustion front can be obtained as shown in Fig. 7. The results indicated that the reactant aluminum was molten and then permeated around the TiO₂ particle in the SHS process, the SHS reaction was carrying on through an interface layer between the molten aluminum and titania. Fig. 8 shows the microstructure of Al/TiO₂ SHS product. According to the reference [7, 8], we make an assumption that the intermediate layer be the SHS product Ti·Al₂O₃, so there should not be any influence on the SHS reaction mechanism and the product phase when the product Ti·Al₂O₃ was added into the initial reactants directly. In fact the product phases of the SHS reaction were very complex with adding Ti·Al₂O₃ properly, there existed remarkable reaction between Al and Ti (shown in Fig. 9). The X-ray analysis has denied the previous assumption, this is to say the interface layer can not be the product Ti·Al₂O₃. For the chemical reaction between Ti and Al can carry out easily, the layer must stop the reaction between Ti and Al.

According to the reference [6] the Al₂O₃ phase being a diluent in Al/TiO₂ SHS reaction, Al₂O₃ adding in the initial reactants had

not changed the SHS product phase sorts. So we may make an assumption that the interface layer be Al₂O₃ or intermediate oxidate of aluminum as shown in Fig. 10, the outer is the molten aluminum and the inner is Ti-O intermediate oxide. According to the reaction mod-

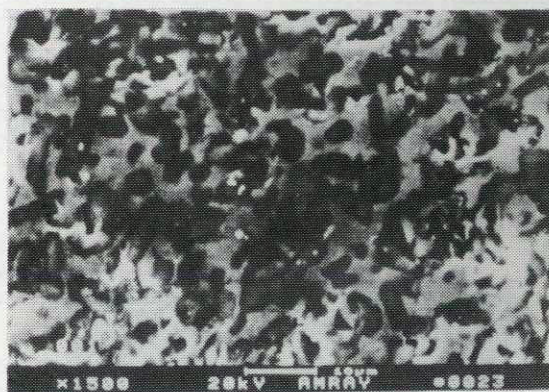


Fig. 8 Microstructure of Al/TiO₂ SHS products

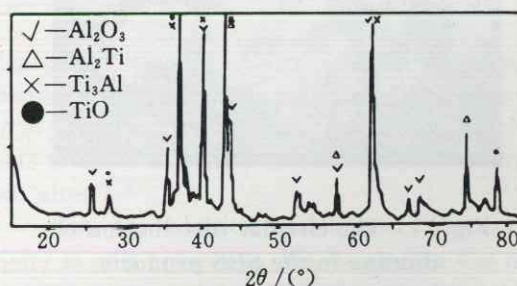


Fig. 9 XRD patterns of the combustion products with adding Ti·Al₂O₃ in the initial reactants

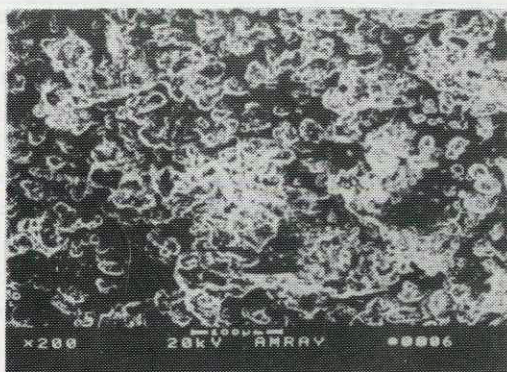


Fig. 7 The net structure of Al/TiO₂ SHS combustion front

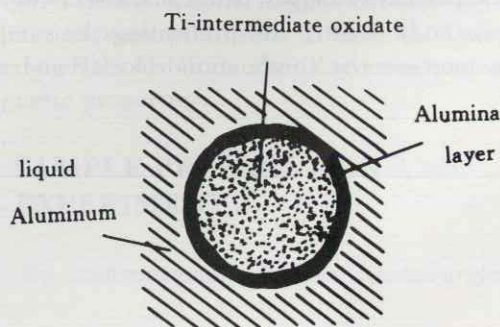


Fig. 10 Scheme drawing of Al/TiO₂ SHS reaction model

el, a layer of Al_2O_3 forms between the liquid aluminum and TiO_2 powders by diffuse of oxygen. The Al_2O_3 layer thickens by the reaction of aluminum and oxygen atoms which diffuse through the Al_2O_3 layer. A sort of "crack" effect will happen as the layer reach a certain thickness, the Al_2O_3 layer cracks and dissolves into aluminum liquid, the molten aluminum permeates and envelopes the Ti-O particles, then a new Al_2O_3 layer forms again by neucleation. The SHS reaction happens repeatedly till the end. According to the reaction model, the circular Al_2O_3 layer has been demonstrated in the SHS products as shown in Fig. 11.

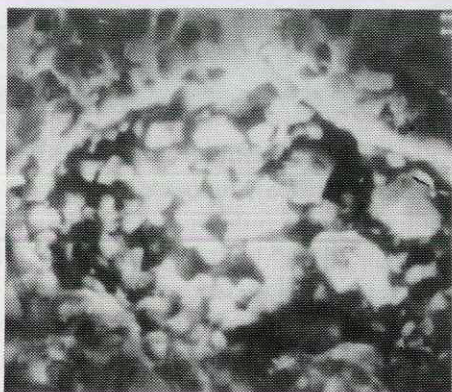


Fig. 11 The circular distribution of alumina in the SHS products

4 CONCLUSIONS

(1) The initial conditions of the reactants have influence on the SHS process. Smaller TiO_2 particles, bigger pellet diameter, higher green body density and preheating the sample can increase the combustion velocity and the

combustion stability; The addition of Al_2O_3 as a diluent decreases the combustion temperature, the combustion velocity and makes the combustion mode unstable;

(2) The liquid aluminum circles the TiO_2 particles in Al/ TiO_2 combustion front. The interface layer between the liquid aluminum and TiO_2 particles can not be the SHS products $\text{Ti}/\text{Al}_2\text{O}_3$. The interface layer may be alumina or intermediate oxidate. The Al-O layer thickens by diffusing or permeating through the crystal interface, then the Al_2O_3 layer cracks and dissolves into the aluminum liquid. The liquid aluminum permeates and envelopes the Ti-O reactant and a new Al-O layer forms again by neucleation. The reaction carries on repeatedly till the end.

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