Journal of Thermal Analysis, Vol. 42 (1994) 713-719

DIFFERENTIAL THERMAL ANALYSIS OF IGNITION TEMPERATURES IN A SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS REACTION

C. R. Bowen and B. Derby

Department of Materials, University of Oxford, Parks Road, Oxford, OX1 3PH, UK

Abstract

Differential thermal analysis was carried out on the self-propagating high-temperature synthesis reaction $3TiO_2+4Al+3C \rightarrow 3TiC+2Al_2O_3$. The results allow the ignition temperature of the reaction to be estimated and the reaction mechanism to be identified. The ignition temperature was 900°C and the results suggest that the reaction proceeds by an initial reaction between titania and aluminium ($3TiO_2+4Al \rightarrow 3Ti+2Al_2O_3$) and the titanium formed reacts with the carbon ($Ti+C \rightarrow TiC$).

Keywords: DTA, self-propagating high-temperature synthesis reaction

Introduction

Conventional sintering techniques to produce ceramic materials can be both time consuming and energy consuming due to the need for high temperature furnaces and long processing times. However, the technique of self-propagating high-temperature synthesis (SHS) overcomes these disadvantages by using highly exothermic reactions to produce ceramic products [1, 2]. When an SHS reaction is initiated in one area of the reactant mixture (e.g. with a resistively heated tungsten wire) there is sufficient heat release that the reaction becomes self-propagating. A combustion wave travels along the reactants converting them to the required products. The advantages of the process are that it is simple and energy efficient as once initiated no further externally applied energy is required. The processing time is reduced to seconds and the products are claimed to be of high purity as impurities are expelled during the high temperature reaction.

The aluminothermic SHS reaction,

$$3TiO_2+4Al+3C \rightarrow 3TiC+2Al_2O_3,$$

0368–4466/94/ $ 4.00

John Wiley & Sons, Limited
Chichester

has been used to produce a ceramic multiphase composite [3] which has the potential of a high hardness, high wear resistant material. The adiabatic combustion temperature, i.e. the highest temperature attained by the product during passage of the combustion wave, is calculated to be 2390 K [3].

Ignition temperature and reaction mechanism

The aim of this paper is to discuss the use of differential thermal analysis (DTA) to identify the reaction mechanism and estimate the temperature at which the reaction begins to propagate i.e. the ignition temperature (T_{ig}). The measured value of T_{ig} can be used to model the combustion wave using a finite-difference model which has been discussed elsewhere [4]. The ignition temperature is measured from the exothermic peaks which are observed on the DTA trace of the ($3TiO_2+4Al+3C$) mixture.

It can be seen that the reactant mixture consists of three phases (TiO_2, Al and C). It is unlikely that all three will react simultaneously to form the final products, therefore the reaction will begin by an initial reaction between two of the three components. Although assumptions have been made about the reaction mechanism, no experimental work has been carried out [5]. The reaction mechanism can be explored by carrying out DTA experiments on the possible interactions which can occur between each pair of the three reactants. These interactions are,

(i) $3TiO_2+4Al$

(ii) $3TiO_2+3C$

(iii) $4Al+3C$.

The DTA traces from the above mixtures are compared with the DTA trace of the complete mixture to estimate which two reactants initiate the SHS reaction. Thermodynamic calculations provide evidence about which reaction is likely to occur and X-ray diffraction (XRD) was used to identify any reaction products.

Experimental

The reactant powders consisted of TiO_2 (mean particle size 0.7 μm), Al (10 μm) and carbon black (~0.02 μm). The mixture was ball milled for eight hours and 5 mg was analysed in a DuPont 1090 DTA at a heating rate of 10 deg·min^{-1} in the temperature range 500 to 1400°C with an argon atmosphere

(flow rate 200 cm^3/min). The inert reference in the DTA was an alumina powder.

Larger samples were necessary for XRD which were prepared by cold pressing powders into a 25 mm diameter disk with a thickness of 5 mm. The reactants were placed in a glass reaction vessel with an argon atmosphere (1 atm) to prevent oxidation of the products. The reaction was initiated by means of a resistively heated tungsten wire.

Differential thermal analysis and thermodynamics

Figure 1 is the DTA trace of the complete reaction. It is characterised by an initial endotherm at 660°C which is due to melting of the aluminium phase. On heating to higher temperatures two exotherms are observed with onset temperatures of 900 and 1020°C. The exothermic temperature difference (ΔT) between the reactant mixture and reference alumina is very small (less than 1°C) when compared to large compacts which rapidly reach a temperature of over 2000 K. This is due to the small 5 mg sample having significant heat losses. In large samples, where heat losses are less severe, it is likely that the self-heating associated with the first exotherm heats up the reactants to ignite the components which give rise to the second exotherm. The ignition temperature is therefore defined as the onset of the first exotherm at 900°C. Figure 2 is a graph of free energy (ΔG) *vs.* temperature for some possible reactions which can occur between the reactants of titania, aluminium and carbon. At the ignition temperature of 900°C the reaction between titanium is the most exothermic and is likely

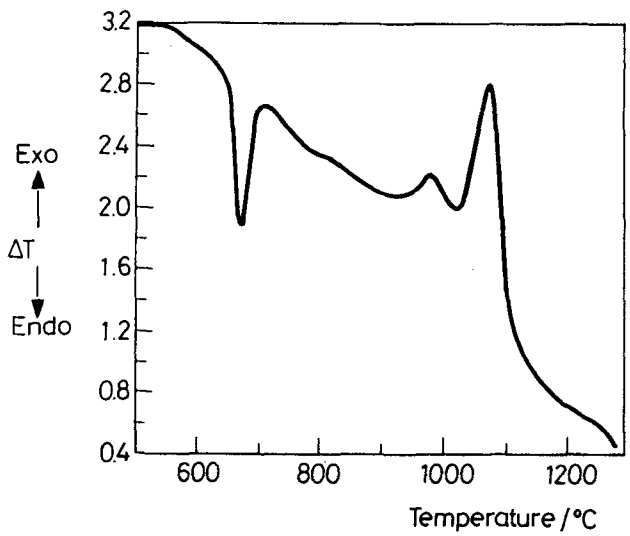

Fig. 1 DTA trace of the complete $3TiO_2+4Al+3C \rightarrow 3TiC+2Al_2O_3$ reaction

to occur. The aluminium is present in the liquid phase at this temperature and is likely to be the most reactive.

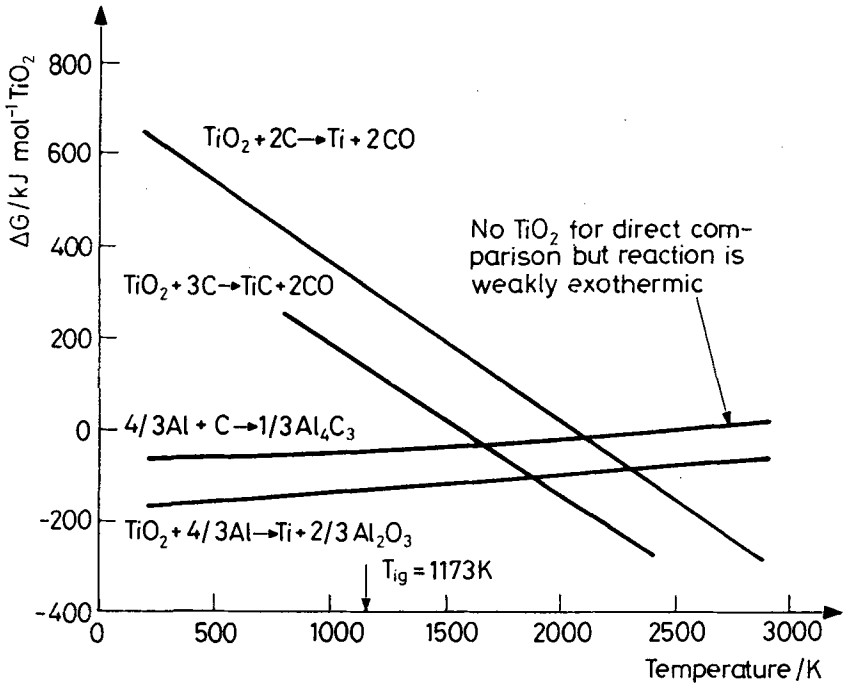

Fig. 2 ΔG *vs.* temperature for some possible reactions between the three reactants. At the ignition temperature (1173 K) the reaction between TiO_2 and Al is the most exothermic

Figure 3 shows the DTA traces for the three mixtures of $3TiO_2+4Al$, $3TiO_2+3C$ and $4Al+3C$. On heating a complete mixture of $3TiO_2+4Al+3C$ the reaction between TiO_2 and Al will be the first to proceed as it has the lowest ignition temperature. The ignition temperature and shape of the DTA trace of $3TiO_2+4Al$ is also very similar to that of the complete reaction Fig. 1. The DTA traces of $4Al+3C$ and TiO_2+C have much higher exotherm temperatures and different shapes when compared to Fig. 1, therefore the complete reaction must occur by an initial reaction between titania and aluminium. The presence of two exothermic peaks in the DTA trace may be due to the formation of intermediate aluminiumtitanates or intermediate titanates.

X-ray diffraction of reaction products

The DTA traces and thermodynamic data provide evidence that the SHS reaction is initiated by a reaction between TiO_2 and Al, however the reaction

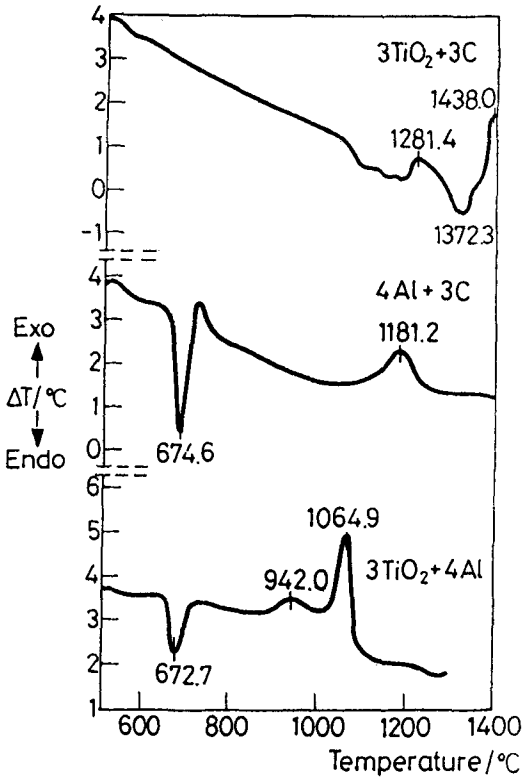

Fig. 3 DTA traces for the mixtures of $3TiO_2+3C$, $4Al+3C$ and $3TiO_2+4Al$. The shape and onset temperature of the exotherms for the $3TiO_2+4Al$ trace is very similar to that of the complete reaction shown in Fig. 1

which takes place between TiO_2 and Al is unknown. The reaction can be estimated by making a mixture of $3TiO_2+4Al$ undergo an SHS reaction and examining the reaction products. Under normal conditions $3TiO_2+4Al$ will not undergo SHS as the possible reactions are not highly exothermic. By rapidly heating titania and aluminium to high temperatures it is possible for the mixture to undergo an SHS type reaction as preheating provides more heat energy to sustain the reaction. The rapid heating is achieved using the experimental configuration in Fig. 4 where the mixture to be heated is placed on a compact of $3TiO_2+4Al+3C$. The complete SHS reaction is initiated and rapidly heats up the $3TiO_2+4Al$ mixture positioned above it. The reaction products of the $3TiO_2+4Al$ reaction were measured by XRD and consisted of titanium and alumina (Fig. 5). The reaction is therefore,

$$3TiO_2+4Al \rightarrow 3Ti+2Al_2O_3.$$

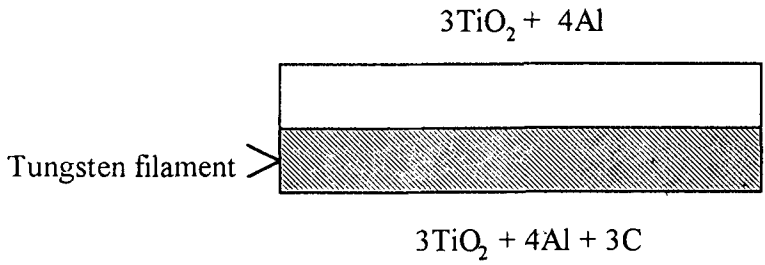

Fig. 4 Experimental configuration to rapidly heat a mixture of titania and aluminium to produce a SHS reaction

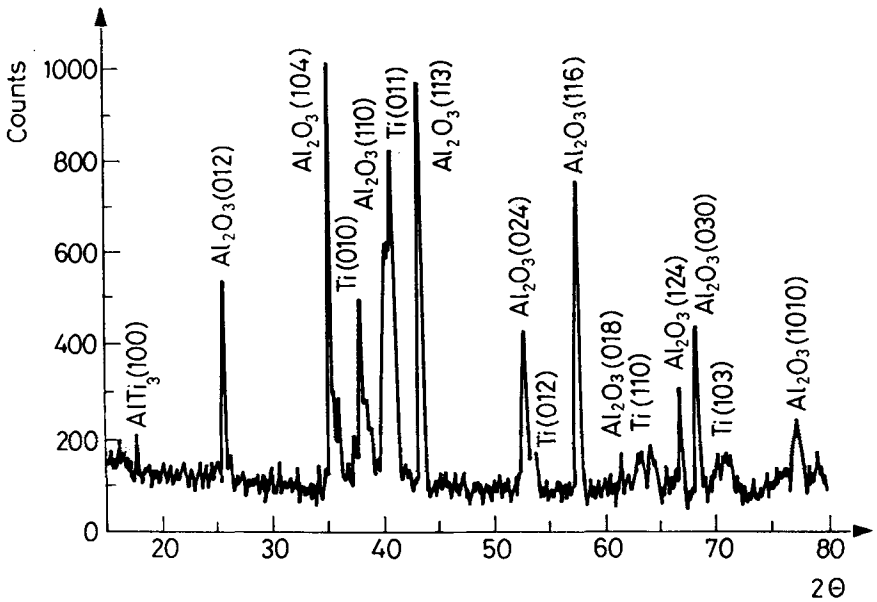

Fig. 5 X-ray diffraction of the $3TiO_2+4Al$ reaction products

If carbon is present then the titanium would react with the carbon to form TiC. Similar experiments were conducted on mixtures of 4Al+3C and $3TiO_2$+3C but no reactions were observed.

Conclusion

Differential thermal analysis, thermodynamic calculations and XRD of reaction products have estimated the ignition temperature and reaction mechanism of the SHS reaction,

$$3TiO_2+4Al+3C \rightarrow 3TiC+2Al_2O_3.$$

The results suggest that the reaction proceeds in a two stage process where,

(i) the aluminium phase melts and reacts with the titania.

$$3TiO_2+4Al \rightarrow 3Ti+2Al_2O_3 \text{ at } 900°C$$

(ii) the titanium reacts with the free carbon

$$Ti+C \rightarrow TiC$$

to produce the final $TiC-Al_2O_3$ ceramic composite.

* * *

The authors would like to thank the SERC and Cooksons Technology Centre for funding the work through a research studentship.

References

1 Z. A. Munir and U. Anselmi-Tamburini, Mat. Sci. Rep., 3 (1989) 277.
2 H. C. Yi and J. J. Moore, J. Mat. Sci., 25 (1990) 1159.
3 C. R. Bowen, S. Hüllsman and B. Derby, 2Proc. 2nd European Ceramic Society Conference, Eds. G. Ziegler and H. Hausner, 1991 p. 631, Deutsche Keramische Gesellschaft, Köln, Germany.
4 C. R. Bowen and B. Derby, Brit. Ceram. Proc., 50, Fabrication Science and Technology, Ed. D. Thompson.
5 S. Adachi, T. Wada, T. Mihara, Y. Miyamoto and M. Koizumi, J. Am. Ceram. Soc., 73 (1990) 1451.

Zusammenfassung — Mittels DTA wurde die selbstaufrechterhaltende Hochtemperatur-Synthesereaktion $3TiO_2+4Al+3C \rightarrow 3TiC+2Al_2O_3$ untersucht. Die Ergebnisse erlauben eine Schätzung der Zündungstemperatur und eine Identifizierung des Reaktionsmechanismus. Die Zündungstemperatur betrug 900°C und die Ergebnisse lassen darauf schließen, daß es sich bei der Zündungsreaktion um die Reaktion zwischen Titanoxid und Aluminium handelt ($3TiO_2+4Al \rightarrow 3Ti+2\ Al_2O_3$) und daß das entstandene Titan dann mit dem Kohlenstoff reagiert ($Ti+C \rightarrow TiC$).