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Measurement of the Heat of Reaction of Polytetrafluoroethylene/Aluminum Composites Based on Laser Initiation

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Abstract: Polytetrafluoroethylene/aluminum (PTFE/Al) composites are reactive materials which can release energy due to exothermic chemical reactions initiated under shock loading conditions. In order to accurately measure the potential maximum heat of reaction of PTFE/Al composites in an inert atmosphere, we propose in this paper a heat of reaction measurement system based on laser initiation. Our results show that the measurement system successfully initiates the chemical reaction between PTFE and Al in an argon atmosphere. The comparison between theoretical calculations and experimental data demonstrates that our measurement method is highly accurate and exhibits excellent consistency. Thus, the heat of reaction measurement system based on laser initiation is applicable for measuring the heat of reaction of PTFE/Al composites and also other complicated reactive materials.

Keywords: reactive materials, PTFE/Al composites, heat of reaction, laser initiation

1 Introduction

The term reactive materials refers to metastable composites comprised of two or more non-explosive solid materials. These components typically do not react with each other under normal conditions. However, under a sufficiently strong impact, these components undergo rapid reactions releasing a large amount of chemical energy [1]. Some of the most typical reactive materials are PTFE/Al composites, which exhibit high energy and insensitivity, as well as unique energy release characteristics [2-4]. Thus, PTFE/Al composites have great potential in defence technologies and other industrial applications.

The heat of reaction and the heat of combustion are two important characteristics of energetic materials. A bomb calorimeter is commonly used to measure these properties. However, due to the low energy of electric ignition and the short duration of the ignition method, traditional calorimeters, ignited by resistance wire heating, are not suitable for initiating the chemical reaction in PTFE/Al composites [5, 6]. The potential maximum heat of reaction of PTFE/Al composites is normally obtained by theoretical calculations [5]. However, for PTFE/Al composites with a complex composition and due to the complex reaction products, it is difficult to determine the heat of reaction by calculation.

The combination of a light initiation system and a calorimeter, *i.e.*, the principle of a photo-calorimeter, was introduced by Magee *et al.* in 1939 [7]. However, because of the large power, the low stability of the light and also the large photo-induced thermal effect, the heat released from the chemical reaction can be easily masked by the heat produced by the strong light. As a result, the heat of the chemical reaction cannot be accurately determined. Due to their excellent monochromaticity, adjustable power density, and low attenuation during propagation, lasers have found widespread applications in the ignition and initiation of energetic materials [8-11]. By combining a laser with a calorimeter, and replacing the resistance wire with a laser to initiate the chemical reaction between PTFE and Al in an inert atmosphere, it was anticipated that the heat of reaction of PTFE/Al composites could be accurately measured.

Under the above motivation, we proposed a heat of reaction measurement system based on laser initiation. The system successfully initiates the chemical reaction between PTFE and Al in an inert atmosphere. The heats of reaction of PTFE/Al composites have been measured by using the proposed system, and the accuracy and consistency of the method have also been analyzed.

2 Principle of the Measurement

The measurement system was modified based on the traditional isothermal calorimeter. A laser was introduced into the sealed bomb to realize the initiation of samples by the laser. A semiconductor solid-state laser was used at a wavelength of 918 nm and maximum power density of 20 W. In the modified measurement system, the radiant flux and period can be adjusted by the software to meet the initiation requirements of different materials.

The heat of reaction measurement system, based on laser initiation, shares a similar measurement principle with the present constant temperature calorimeters. According to energy conversion, after successful initiation by the laser, the sum of the heat that causes the water temperature to change and the heat absorbed by the measurement system equals the sum of the laser energy and the energy released from the reaction, according to the follow relation.

$$E + m\cdot Q_m = (W_{\text{water}}\cdot C_{\text{water}} + C_J)\cdot \Delta T \tag{1}$$

where E is the laser energy during the initiation, m is the weight of sample, Q_{m} is the heat of reaction of the sample per unit weight, W_{water} is the weight of water, C_{water} is the specific heat of water, C_{J} is the heat capacity of the instrument, and ΔT is the change in water temperature during the measuring procedure.

The heat capacity of the instrument (C_{J}) was obtained by calibration with benzoic acid. The system parameters were set up before each measurement. The heat of reaction of the material was automatically calculated once the measurement was complete.

3 Experimental

The starting materials were Al and PTFE powders with an average size of 7 μm (JT-4) and 25 μm (3M), respectively. Powders of Al and PTFE in different proportions were mixed uniformly. The mixed powders of about 1.0 g were then cold pressed into ϕ 12 mm disks at a pressure of ~20 MPa. The PTFE/Al disks were reweighed using a high precision electronic balance (±0.0001 g) for the calculation of the heat of reaction. Crystalline phases existing in the reaction products of the PTFE/Al composites were identified with powder X-ray diffraction (XRD) using a Cu Kα radiation.

4 Influence of Laser Characteristics on the Heat of Reaction

The reason for measuring the heat of reaction for PTFE/Al composites by the proposed measurement system was to ascertain whether the laser could successfully initiate the chemical reaction between PTFE and Al. Under the same laser absorptivity for the PTFE/Al composites, the laser energy absorbed by the material is closely related to the laser power and the radiation time in the measurement. Only under appropriate laser radiation conditions can the chemical reaction between PTFE and Al be initiated. Therefore, the effects of laser power and radiation time on the measurement of the heat of reaction for PTFE/Al composites were investigated.

4.1 Influence of laser power on the heat of reaction

Figure 1 shows the heat of reaction measurement results for a PTFE/26.5 wt.% Al composite at different laser powers with a radiation time of 10 s. It can be seen from the figure that the heat of reaction was almost zero when the laser power was 3 W, indicating that the laser failed to initiate the chemical reaction between PTFE and Al. When the laser power was greater than 6 W, the laser succeeded in initiating the chemical reaction. The heat of reaction was 7.95 kJ/g for a laser power of 6 W, and a further increase in the laser power resulted in an increase in the heat of reaction. However, the magnitude of the increase was small, with the heat of reaction being 8.40 kJ/g for a laser power of 18 W.

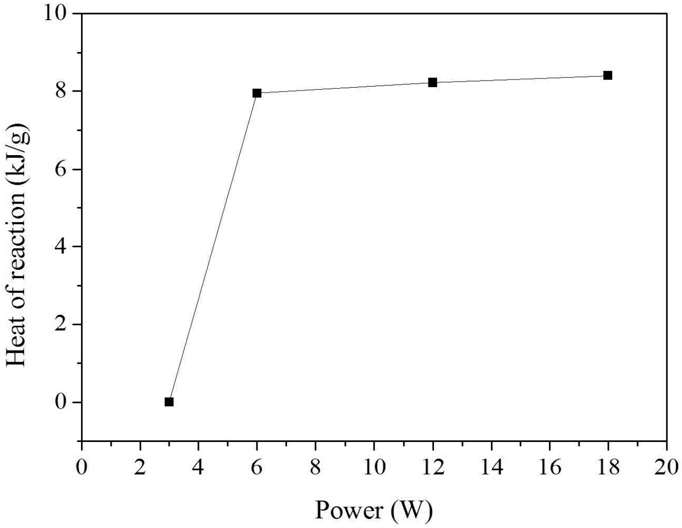

Figure 1. The heat of reaction for a PTFE/26.5 wt.% Al composite at different laser power levels but the same radiation time of 10 s

When the laser is directed onto the surface of a PTFE/Al composite, the laser energy is absorbed by the material, resulting in an increase in temperature. The temperature in the area directly irradiated by the laser increases rapidly, while the temperature in other areas is increased *via* heat conduction at a slow speed. If the energy accumulated in the laser radiation period does not raise the temperature of the PTFE/Al composite to its reaction temperature, then laser initiation fails, and thus, the system cannot measure the heat of reaction. By contrast, when the accumulated energy raises the temperature of the PTFE/Al composite to its reaction temperature, the chemical reaction between PTFE and Al may occur, with the area directly irradiated by the laser reacting first. However, if the laser irradiation is terminated at this time, when the energy released from the reaction cannot induce the chemical reaction in other areas of the composite, that is the PTFE/Al composite cannot produce a self-sustaining reaction, laser initiation also fails. As a result, the heat of reaction will not be measured, and the PTFE/Al composite will essentially retain its original shape with only a small hole left behind on the surface which was directly irradiated by the laser (Figure 2). However, if the laser irradiation is not terminated, the energy released from the reaction could be conducted to other areas to initiate reaction, and at that stage, even if laser irradiation is terminated, self-sustaining reactions will continue. Under these conditions, the laser initiation is successful, and the heat of reaction can be measured by the measurement system. For a successful initiation, as is seen in Figure 3, the resultant reaction product of a PTFE/Al composite is a fluffy black powder.

Figure 2. Small hole left on the surface of a PTFE/26.5 wt.% Al composite when laser initiation fails

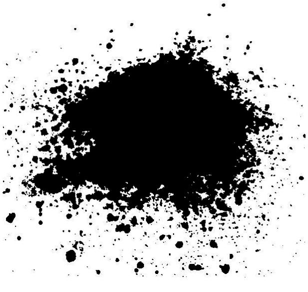

Figure 3. Reaction product of a PTFE/26.5 wt.% Al composite after a successful laser initiation

4.2 Influence of laser irradiation time on the heat of reaction

The heat of reaction of a PTFE/26.5 wt.% Al composite under different laser irradiation times was also investigated. Figure 4 shows the heat of reaction measurement results for a PTFE/26.5 wt.% Al composite at different laser irradiation time with the same laser power of 18 W. It may be seen from the figure that at a laser power of 18 W, the initiation of the chemical reaction is successful, and the heat of reaction can be measured even when the irradiation time is only 2 s. With increased laser irradiation time, the heat of reaction increased from 7.97 kJ/g to 8.40 kJ/g, with irradiation times of 2 s and 10 s, respectively. These results suggest that with a laser power of 18 W, an increase in the laser irradiation time can improve to a certain level the degree of chemical reaction of PTFE and Al. However, the heat of reaction remained almost constant even when the irradiation time was increased to 20 s. The above analyses indicate that a laser power of 18 W and an irradiation time of 10 s are the optimal laser initiation conditions for a PTFE/26.5 wt.% Al composite, under which the heat of reaction is 8.40 kJ/g.

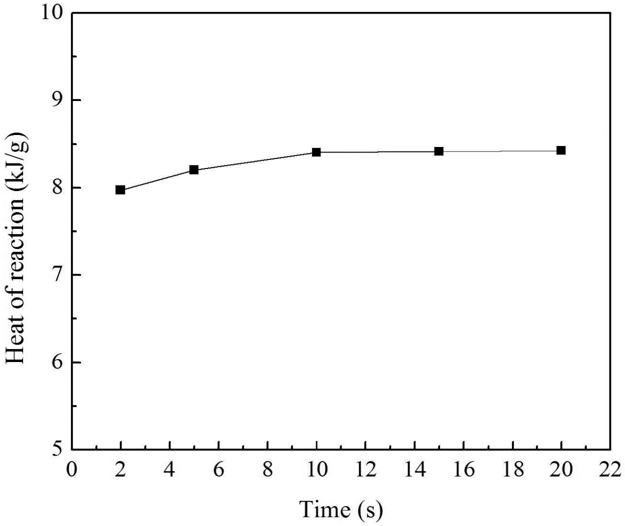

Figure 4. The heat of reaction for a PTFE/26.5 wt.% Al composite at different laser irradiation times but the same laser power level of 18 W

4.3 Identification of the reaction products from a PTFE/26.5 wt.% Al composite by XRD

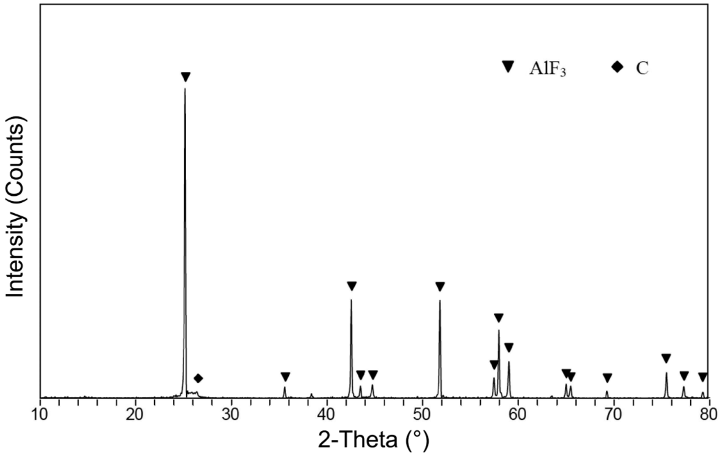

Figure 5. XRD pattern of the reaction products from a PTFE/26.5 wt.% Al composite

Figure 5 shows the X-ray diffraction (XRD) pattern of the reaction products of a PTFE/26.5 wt.% Al composite under successful initiation in an inert atmosphere. From the XRD pattern it can be seen that only AlF_3 and C diffraction peaks were present, indicating that the PTFE and Al in the composites reacted completely to form AlF_3 and C.

5 The Accuracy and Consistency of the Measurements

The accuracy of the measurements and the consistency of many measurements are important factors for determining whether the heat of reaction measurement system based on laser initiation is reliable, as well as whether the measurement results are trustworthy. To address these concerns, the accuracy and consistency of the heat of reaction measurements were analyzed as shown below.

5.1 The accuracy of the measurements

When PTFE and Al react, the reaction proceeds as follows:

$$4n\mathrm{Al} + 3(\mathrm{C_2F_4})_n \rightarrow 4n\mathrm{AlF_3} + 6n\mathrm{C} + \Delta H$$

where ΔH is the enthalpy of the reaction and is approximately −8.53 kJ/g. For the reaction of a PTFE/26.5 wt.% Al composite, PTFE and Al in the composite react completely to form AlF_3 and C. The reaction products are clearly defined. Therefore, for a PTFE/Al composite with a standard composition, the theoretical value of the heat of reaction is 8.53 kJ/g, and the measured heat of reaction was 8.40 kJ/g, which is approximately 98.48% of the theoretical value. In other words, our experimental results agree surprisingly well with the calculations.

The PTFE/Al used in these experiments was obtained by powder compaction, in which the diameter of the Al powders was ~3-4 μm. Due to the high activity of the Al powder, a thin layer of Al_2O_3 is usually formed and covers its surface [12]. As a result, the available Al content in the Al powder is reduced; in other words, the active Al content is reduced. However, in the calculation of the theoretical heat of reaction, the effect of the thin layer of Al_2O_3 formed on the surface of the Al was not taken into account, which is likely to be the main reason why the measured heat of reaction was lower than the theoretical value. The actual content of active Al in the raw Al powder was 97.11%. However, the measured heat of reaction was 98.48% of the theoretical value, which is higher than the 97.11% active Al content in the composite. This result probably occurs because at high temperature, the Al_2O_3 on the surface of Al may react with PTFE to release heat; however, the enthalpy of this process is much lower than that of the reaction between Al and PTFE [13, 14].

5.2 The consistency of the measurements

Table 1 lists the heat of reaction for PTFE/26.5 wt.% Al measured repeatedly 5 times under the same conditions, of a laser power of 18 W and an irradiation time of 10 s. It can be seen from the table that the relative standard deviation (RSD) was 0.72% for the 5 measurements, indicating that the results measured for this system exhibit excellent consistency.

Table 1. Heat of reaction measurements for a PTFE/26.5 wt.% Al composite

Measurement	1	2	3	4	5
Heat of reaction [kJ/g]	8.42	8.34	8.35	8.41	8.49
RSD [%]	0.72				

6 The Heat of Reaction of PTFE/Al Composites with Different Al Contents

In practice, the composition of PTFE/Al needs to be adjusted to change the characteristics of the composite in order to meet the demands of different applications. Indeed, the contents of PTFE and Al often deviate from the standard composition. Due to these deviations and based on the above results, the constructed heat of reaction measurement system based on laser initiation has been used to measure the heat of reaction of PTFE/Al composites with different Al contents. A laser power of 18 W and an irradiation time of 10 s were used in all of the measurements.

Figure 6 shows the measured heat of reaction results for PTFE/Al composites with different Al contents. The calculated results of the heat of reaction are also given in the figure with the assumptions that the activity of Al in the composites is 100%, the compositions with less than the standard ratio in the material all react completely, and the reaction products are only AlF_3 and C.

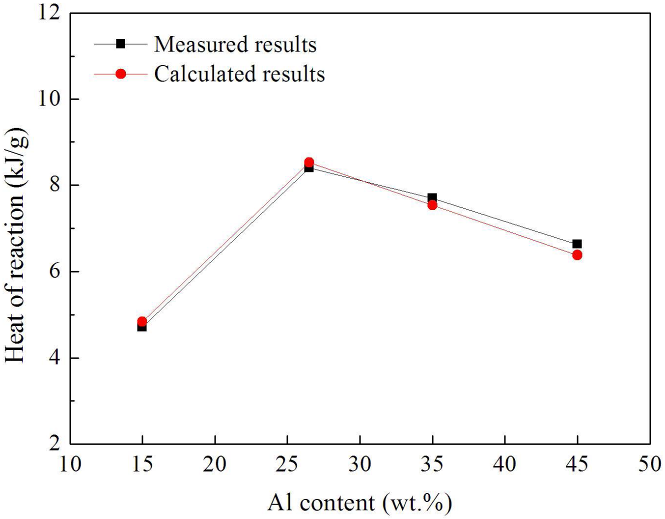

Figure 6. Heats of reaction of PTFE/Al composites with different Al contents

It may be seen from Figure 6 that when the content of Al is 26.5 wt.%, the measured and calculated results for the PTFE/Al composites both reached their maximum values. However, when the Al content was 15 wt.% and 26.5 wt.%, the measured results were lower than those of the calculated results, *i.e.*, 2.69%

and 1.52% lower, respectively. When the content of Al was 35 wt.% and 45 wt.%, the measured results were higher than the calculated results, *i.e.*, 2.12% and 3.92% higher, respectively.

Due to the formation of Al_2O_3 on the surface of Al powder in the raw material, which causes a decrease in the active Al content, the measured results for PTFE/26.5 wt.% Al is lower than that of the calculated result. To explain the differences between the measured and calculated results for the other compositions, the reaction products of PTFE/Al with different Al contents were analyzed by XRD, as can be seen in Figure 7.

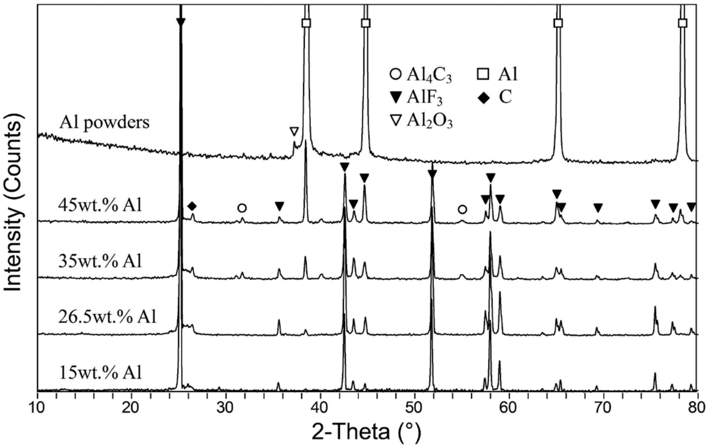

Figure 7. XRD patterns of the reaction products of PTFE/Al composites with different Al contents

It can be seen from Figure 7 that the reaction products are the same for PTFE/Al composites with Al content of 15 wt.% and 26.5 wt.%, *i.e.*, AlF_3 and C. By contrast, for PTFE/Al composites with higher Al content, the reaction products include not only AlF_3 and C phases, but also Al and Al_4C_3 phases. These results indicate that when Al is in excess in a PTFE/Al composite, in addition to the reaction of Al and PTFE, some Al also reacts with the former reaction product C to form Al_4C_3. The reaction process is as follows:

$$4Al + 3C \rightarrow Al_4C_3 + \Delta H$$

where ΔH is the enthalpy of reaction and is approximately −207.28 kJ/mol, implying that the reaction is exothermic. These analyses indicate that for PTFE/Al composites with Al contents greater than 26.5 wt.%, the heat of reaction includes not only the heat of reaction between Al and PTFE but also the heat of the carbonization reaction between excess Al and the reaction product C. However, the carbonization reaction was not taken into account in the calculations. As a result, the measured heat of reaction is higher than that calculated for the PTFE/35 wt.% Al and PTFE/45 wt.% Al composites. The greater the excess of Al, the more Al becomes involved in the carbonization reaction to form Al_4C_3. Therefore, the difference between the measured and calculated heat of reaction values increases.

For PTFE/Al composites with an Al content less than 26.5 wt.%, the PTFE will be in excess. The excess PTFE will decompose at the high temperature resulting from the reaction between Al and PTFE, and this process will absorb a portion of the energy released from the reaction between PTFE and Al. However, this process has not been considered in the calculations, which is one of the main reasons why the measured heat of reaction is lower than the calculated results for the PTFE/15 wt.% Al composite.

It can be seen from the above analysis that for PTFE/Al composites with different Al contents, the difference between the heat of reaction obtained by theoretical calculations and experimental measurements is not only significant when the Al content is 26.5 wt.%. However, for PTFE/Al composites with other compositions, due to the presence of other additional reactions, the theoretical calculation is not accurate, while the measured heat of reaction is more accurate. For multiple components, reactive materials such as PTFE/Al/W, THV/Hf, THV/Zr, the reaction products are even more complex (THV is a mixture of three different fluoropolymers: tetrafluoroethylene (TFE), hexafluoropropylene (HFP) and vinylidene fluoride (VF)). As a result, it is difficult to assess the heat of reaction for these composites through theoretical calculations. However, the heats of reaction for the composites with complex components can be accurately measured by using the method developed in this paper. The heats of combustion of this class of reactive materials can also be measured using the above system.

7 Conclusions

The heat of reaction of PTFE/Al composites has been measured by using a heat of reaction measurement system based on laser initiation. The results show that the system can successfully initiate the chemical reaction between PTFE and Al in an argon atmosphere. Comparison with theoretical calculations and reproducible experiments demonstrates that the measured results are highly accurate and exhibit excellent consistency. For PTFE/Al composites with multiple components, due to the presence of other additional reactions, it is difficult to assess the heat of reaction for these materials through theoretical calculations alone. Our experimental results based on the laser initiation method described here pave the way for accurate measurement of the heats of reaction of reactive composite materials with complex components.

Acknowledgments

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