

## DIFFERENTIAL THERMAL ANALYSIS STUDIES OF THE REACTIONS OF SILICON AND LEAD OXIDES

S. S. AL-KAZRAJI and G. J. REES

*Department of Chemical Engineering, The Polytechnic of Wales, Pontypridd, Mid-Glamorgan, Wales, U. K.*

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DTA measurements have been performed on powder mixtures of silicon/lead monoxide and silicon/lead, with the object of determining the mechanisms of reactions as the temperature is gradually raised to 900° in (a) air (b) nitrogen.

X-ray diffraction and infrared spectroscopy are used in an attempt to characterize the products of reaction. From the results obtained a tentative mechanism for reactions in air and nitrogen is suggested.

Compressed compositions, consisting of lead oxides and silicon, have utility in industry and in military applications as fuses [1]. These delay compositions were formulated to replace the older fuse materials, based on gun-powder, which were unreliable under the demanding conditions of low pressure at high altitudes, e.g. in space research. The essential difference, between the old and the new compositions, is that the latter gave rise to the formation of solids rather than gases upon combustion. The compositions are also utilised as time delays for use with detonators in the application of explosives in the mining and quarrying industries. Little published work on combustion mechanisms has appeared but Nakahara et al. [2] and Sulacsik [3] have described DTA studies on potassium permanganate/antimony and trilead tetroxide/ferro-silicon powders. In view of the widespread application of these compositions, it was decided to carry out DTA studies on mixtures of lead oxides and silicon, as an aid in understanding the mechanism of combustion.

### Experimental

Silicon powder, manufactured by a grinding process had an average particle size of 5  $\mu\text{m}$  and a surface area of 2.5  $\text{m}^2/\text{g}$ . It was 98% pure the chief impurity being metallic iron. The lead monoxide was 95% pure and had an average particle size of 4  $\mu\text{m}$ .

The particle sizes of all materials were measured using a Coulter Counter Model TA equipment and surface areas with a Ströhlein Area Meter.

### *Equipment*

A Stanton Redcroft massflow thermobalance (Model No. MFH-1), was used. This has a temperature range of 0–1400° and the rate of temperature increase used was 6°/min. Thermocouples were of Pt/Pt–13% Rh positioned under dimpled platinum crucibles 6.5 mm diameter and 10 mm deep. The crucibles rest on the thermocouples within a high purity alumina block.

### *Safety measures and experimental methods*

Appropriate precautions are necessary when dealing with mixtures of lead oxides and silicon since they are sensitive to impact, friction and static electricity. Spark-free tools and equipment are used throughout, e.g. brass sieves and camel hair brushes for mixing ingredients. The sieves are earthed and placed behind armoured glass safety screens during the mixing process. Safety clothing including gloves, face mask and goggles are also used, and the mixing operation performed in a fume-cupboard.

### *Mixing procedure*

The lead oxides and silicon powders were mixed by passing, the previously weighed and dried separate ingredients, through 75  $\mu\text{m}$  sieves five times. This ensures uniform mixing and breaks down powder agglomeration. A range of mixtures was prepared (10 g of each) and stored in a desiccator for 24 hours prior to DTA measurements. Each composition was mixed again, immediately prior to DTA measurements, to reduce segregation due to wide density difference between silicon and lead oxides.

### *DTA measurements*

Accurately weighed samples (approximately 15 mg of the mixtures) were used. The inert reference material was pure alumina powder which had been previously calcined at 1400°. The rate of temperature increase used was 6°/min. The results are indicated graphically (Figs 1–3).

### *Analysis of reaction products*

X-ray diffraction and infrared spectroscopy were used to characterize the slags obtained from the DTA measurements carried out in nitrogen and air.

## **Discussion**

DTA studies on  $\text{Pb}_3\text{O}_4$  and  $\text{Pb}_3\text{O}_4/\text{Si}$  mixtures have been published [4], and it was shown that the reactions took place at the temperature of decomposition of the oxide.

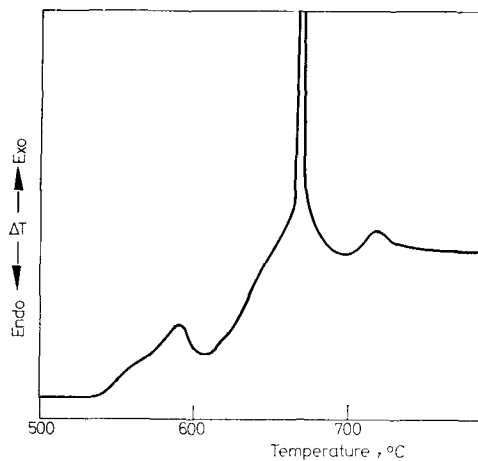


Fig. 1. DTA for PbO/Si (70/30 w/w) heated in air to 900°

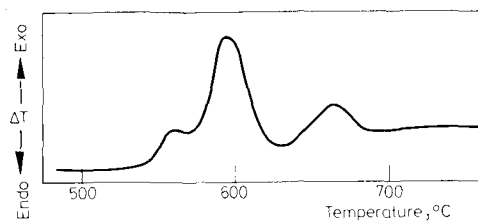


Fig. 2. DTA for PbO/Si (70/30 w/w) heated in N<sub>2</sub> to 900°

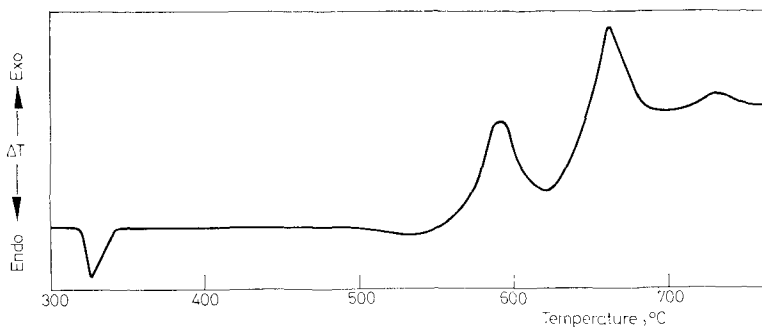
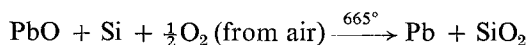
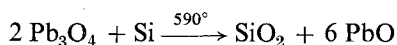
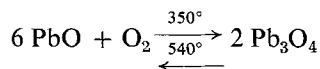


Fig. 3. DTA for Pb/Si (70/30 w/w) heated in air to 800°

In this work powder mixture of PbO/Si (70/30 w/w) were investigated by DTA in air. From Figure 1 it is seen that an exothermic shoulder is formed starting at 540° which reached a maximum at 590°. The second exothermic reaction takes place at 610°, the rise being gradual at first but very sharp when the temperature reached 665° then cooling rapidly.

These reactions follow the same pattern, in temperature of occurrence and relative size of peaks as for Pb<sub>3</sub>O<sub>4</sub>/Si reactions [4]. Initially, the monoxide is converted to red lead at temperatures above 350°:



In these compositions the Si is in excess and reactions occur on the surface and the second exothermic reaction is enhanced at the higher temperature, to favour the movement of reactants to penetrate the product layer which forms around the constituents.

When the same composition was studied under nitrogen, the second reaction is less violent due to absence of atmospheric oxygen (Figure 2).

In the case of Pb/Si (70/30 w/w) investigated by DTA in air (Figure 3) the lead melts at 327° and, as shown elsewhere [5] it is partially oxidized by oxygen from air to PbO, and at temperatures above 350° the monoxide is converted to Pb<sub>3</sub>O<sub>4</sub> and the reactions thereafter are the same as those of Pb<sub>3</sub>O<sub>4</sub>/Si mixtures. There is a third peak, much smaller than the second and this is possibly the reaction product of PbO and SiO<sub>2</sub> reported elsewhere [6].

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**RÉSUMÉ**— Des mesures d'ATD ont été effectuées sur des mélanges pulvérulents de silicone/monoxyde de plomb et silicone/plomb, afin de déterminer les mécanismes réactionnels quand la température est augmentée graduellement jusqu'à 900° dans l'air et dans l'azote.

La diffraction des rayons X ainsi que la spectroscopie infrarouge ont été utilisées pour tenter de caractériser les produits de réaction. Un mécanisme possible est proposé à partir des résultats obtenus pour les réactions dans l'air et dans l'azote.

**ZUSAMMENFASSUNG** — DTA-Messungen wurden an pulverförmigen Mischungen von Silizium/Bleimonoxid und Silizium/Blei zur Bestimmung der Reaktionsmechanismen bei stufenweiser Erhöhung der Temperatur auf 900° in a) Luft und b) Stickstoff, durchgeführt.

Röntgendiffraktion und Infrarotspektroskopie wurden zur Charakterisierung der Reaktionsprodukte eingesetzt. An Hand der erhaltenen Ergebnisse wird ein möglicher Reaktionsmechanismus in Luft und in Stickstoff vorgeschlagen.

**Резюме** — Были проведены ДТА измерения смесей порошков кремний/моноокись свинца и кремний/свинца при постоянном повышении температуры до 900° в воздушной атмосфере и в атмосфере азота с целью определения механизмов реакций. С целью идентификации продуктов реакции использовали рентгено-дифракционную технику и инфракрасную спектроскопию. На основе полученных результатов предложен предварительный механизм реакций в воздушной атмосфере и в атмосфере азота.