DIFFERENTIAL THERMAL ANALYSIS OF THE MIXTURES OF SILICON AND RED LEAD

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Abstract

There are two different opinions in the literature on the combustion mechanism of the $Si-Pb_3O_4$ system. Differential thermal analysis, X-ray diffraction and infra-red spectroscopy have been used to examine the thermal behaviour of the mixture to characterize its combustion products and judge the validity of both proposed reaction paths.

It was concluded from the results that the $Si-Pb_3O_4$ system exhibits rather complicated reaction mechanism including both gas–solid and solid–solid (proceeding below oxidant decomposition temperature) reactions whose importance depends on the fuel content of the mixture.

Keywords: combustion, reaction mechanism, silicon–red lead mixture

Introduction

Compressed mixtures of red lead (Pb_3O_4) and silicon (Si) are widely used as delay composition in detonators. Several papers have been published on the mechanism of their combustion [1–3] but some uncertainty still exists about the nature of reactions occurring in the system.

A fundamental question which arises in pyrotechnics reactions is whether the process is a real solid–solid reaction, a solid–liquid one involving either a molten fuel, or a molten oxidant, or whether the fuel reacts only with gaseous oxygen formed by the prior thermal decomposition of the oxidant, or whether some combination of these processes contributes to the overall reaction [4].

The above mentioned publications differ from each other in the explanation of the mechanism of reactions occurring in the $Si-Pb_3O_4$ system. While in [2, 3] it is supposed that the main reaction is of solid–gas nature between Si and O_2 liberated by the decomposition of Pb_3O_4 in [1], although it is accepted that the men-

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tioned reaction is taking place in the system, it is also assumed that the reaction of PbO (from decomposed Pb_3O_4) with Si is the process to release most of the heat and to occur in the solid state.

There is also a difference between reaction starting temperatures indicated in various studies [1, 3].

It therefore seemed appropriate to carry out some further thermoanalytical studies on the mixtures.

Experimental

Materials and mixing procedure

Silicon powder was 96% pure with the following particle size distribution: 38 wt% between 10 and 4 μm and 62 wt% less than 4 μm. Red lead was 99% pure (as PbO and PbO_2, with 32.3% as PbO_2) and had particle size less than 9 μm.

The compositions were mixed by hand sieving of weighed components through a mesh eight times successively. Mixtures were prepared with compositions ranging from 5 wt% Si to 55 wt% Si with 10% step.

Apparatus

A Perkin-Elmer DTA 1700 apparatus was used for this study. The DTA instrument was calibrated against the melting points of indium, tin and lead. Accurately weighed (approximately 20 mg) samples were placed into quartz containers which were then evacuated and sealed. Pure alumina powder in an identical quartz container was utilized as the inert reference material. The rate of temperature rise used was 20°C min^{-1} and the measured temperature ranged up to 800°C. All the obtained data were processed using a TA-system software package. The results are shown in Fig. 1.

Thermoanalytical measurements were supplemented with IR and X-ray analysis of solid combustion products.

Results and discussion

It can be seen from Fig. 1 that the reaction pattern consists of three exothermic peaks for all the examined compositions heated at a rate of 20°C min^{-1}, although the first exothermic peak is not very distinct for the 5% Si mixture.

The DTA curves start to leave the base lines at 370–390°C, then rise gradually and reach their first maxima at 440–455°C. The peak temperatures lie well below the decomposition temperature of red lead ($\approx$550°C), which means that a so called 'pre-reaction' [5] occurs in the system before the decomposition of the oxidant. This finding coincides with Zhong Jun's results [3] which proved the reaction to be of solid–solid nature. Silicon is oxidized by diffusion of oxygen
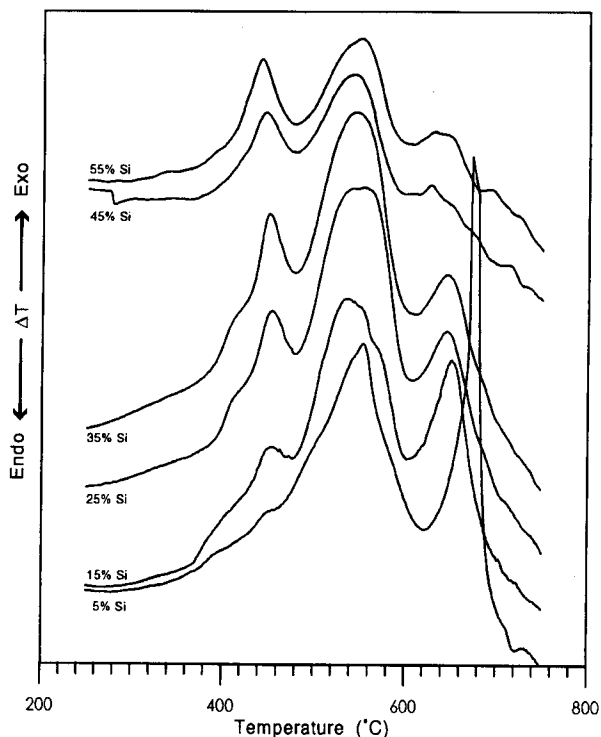
Fig. 1 DTA records for silicon-red lead mixtures heated in evacuated containers

ions from red lead to the surface of the fuel. Formation of the product layer (SiO_2) on the Si surface resists further reaction development, so higher fuel content provides larger surface available for the process, which is reflected by an increase in the height of the first exothermic peak with the silicon content up to the point where the amount of oxidant becomes the limiting factor ($\approx 35\%$ Si).

The second peak occurs in all DTA records at about 480°C with the maximum between 535 and 555°C. This exothermic peak is the largest and is attributed to the main reaction. The authors agree with Kazraji et al. [1] that the process involves simultaneous decomposition of Pb_3O_4 and oxidation of Si, PbO being the main reaction partner for silicon.

$$Pb_3O_4 \rightarrow 3PbO + 0.5O_2$$

$$2PbO + Si \rightarrow 2Pb + SiO_2$$

$$Si + O_2 \rightarrow SiO_2$$
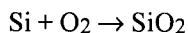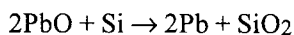
In support of this statement several arguments may be mentioned. The mixture giving the highest heat output (supposed usually to be slightly fuel rich compared to the stoichiometric one) contains 10–20% Si and the stoichiometric

composition for the simultaneous reactions PbO+Si and O_2+Si is 7.6% Si, while for the single reaction Si+O_2 it is only 2% Si. Besides, if the gas-solid reaction were the main process, all reaction products would probably contain unreacted PbO but the only compounds identified by mean of X-ray diffraction and IR spectra analysis were Pb, SiO_2, unreacted silicon for Si rich compositions and for Pb_3O_4 rich ones lead silicates.

It follows from the above mentioned decomposition reaction of Pb_3O_4 that oxygen gas constitutes only 25% of the total amount of the oxygen available for the reactions. The rest is contained in PbO which reacts with silicon in the solid state at the recorded temperatures as the melting points of PbO and Si are 888 and 1420°C, respectively. So the solid–state reaction of PbO with Si liberates the main portion of the heat evolved. This is in accordance with the fact that the burning rate of Si–Pb_3O_4 mixtures is increased with increasing density which enhances the contact of particles necessary for a solid–solid reaction.

On the other hand, we must admit that also the solid–gas reaction of Si with O_2 contributes to the heat evolution because the exothermic peaks produced by samples heated in air are higher than those heated in a N_2 environment [1, 3], and besides, there is a gas wave present in compacted mixture columns [6]. The pressure of the wave increases with decreasing silicon content. The same relationship was found for combustion temperatures [7]. These facts imply an idea that while fuel rich compositions burn mainly in the solid state, for those containing less silicon the gas–solid reaction becomes more important as higher temperatures facilitate oxidation of silicon by oxygen gas, so the air oxygen and vaporized oxides can take part in the reactions, too.

The second peak height changes in the same way with fuel content variation as the first one does because of the same reasons as mentioned above.

The third peak in the DTA traces commences at the final temperature, 605–615°C, of the second exothermic peak and reaches its maximum between 640–655°C except for the 5% Si composition which exhibits a very strong reaction at 672°C. Because of the presence of lead silicates in the combustion products as indicated by IR measurements, it is expected that the reaction occurs between unreacted PbO and SiO_2 formed during previous stages of the reaction. This reaction has been reported elsewhere [8] as producing the mentioned silicates.

The increase in peak height with increasing oxidant contents supports the idea because larger amounts of Pb_3O_4 provide more PbO available for the reaction, for fuel rich compositions the peak almost disappears and there are no silicates found in the reaction residues.

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