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DIFFERENTIAL THERMAL ANALYSIS OF SOLID STATE REACTIONS UNDER COMPLETE VOLUME CONFINEMENT*

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ABSTRACT

A differential thermal analysis apparatus has been developed in which the sample is heated under conditions of complete volume confinement. The sample and reference material are tightly confined to their original volume during the heating cycle. This apparatus has been applied to the study of metal-powder–inorganic oxidant mixtures which react from the solid state to produce products which have a variety of characteristics such as a metal oxide which undergoes dissociation or has a lower density than the reactants.

INTRODUCTION

High-energy producing mixtures such as those used in propellants, explosives, and pyrotechnics often are ignited and undergo propagative combustion reactions under conditions of zero ullage, that is, confined to their original volume with no free space surrounding the reacting system. In addition, these mixtures are often stored and transported under confinement in extreme ambient temperature environment. It is therefore of great interest to study the effect of physical confinement on the thermal stability and on the kinetics and mechanisms of these reactions.

Differential thermal analysis has been extensively used to study the high temperature behavior of materials of this type but the previous work has been performed either in open DTA systems, or, if in a closed system, under conditions where a relatively large free space surrounded the sample[1–4]. Consequently, a differential thermal analysis apparatus has been developed in which the sample can be heated in a state of complete physical confinement to its original volume. The sample can, alternatively, be heated in an unconfined situation in the same apparatus and the effect of confinement on the high temperature behavior of the sample determined. This paper describes the design and construction of this apparatus and illustrates its application to a study of the effect of confinement on the solid-state reactions of some mixtures of metal powders and inorganic oxidants.

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EXPERIMENTAL

A diagram of the apparatus for performing differential thermal analysis under complete volume confinement is shown in Fig. 1. The heating block is a stainless steel cylinder $2\frac{3}{4}$ inches long and 2 inches in diameter. Two holes to accommodate the sample and reference material were drilled into the top of the block. These holes are $\frac{1}{2}$ inch in diameter for the first $1\frac{1}{4}$ inches and $\frac{1}{4}$ inch in diameter for the next $\frac{1}{2}$ inch. Two holes $\frac{1}{16}$ inch in diameter were drilled through the bottom of the heating block penetrating the center of the cavities which hold the sample and reference. Two $\frac{1}{16}$ inch diameter stainless steel-sheathed 28 gauge chromel–alumel thermocouples are fitted snugly into these holes with their tips penetrating about $\frac{1}{16}$ inch into the sample and reference cavities. These thermocouples are connected as a pair of differential thermocouples. A snugfitting brass gasket $\frac{1}{2}$ inch in diameter by $\frac{1}{4}$ inch in thickness is inserted into each of the two holes so that they rest on the ledge at the bottom of the two large diameter holes. The sample and reference materials are loaded into their respective cavities to a depth of slightly more than $\frac{1}{4}$ inch. Confinement is obtained with cylindrical stainless steel plugs $\frac{1}{4}$ inch in diameter for the bottom $\frac{1}{2}$ inch and $\frac{1}{2}$ inch in diameter for the next $1\frac{3}{4}$ inches with a flat hexagonal head on the top. These plugs fit snugly into the sample and reference cavities with the shoulder of the plugs resting on top of the brass gaskets and with the tip of the plugs tightly confining the sample and reference to their original volume of $\frac{1}{4}$ inch in diameter by $\frac{1}{4}$ inch in height.

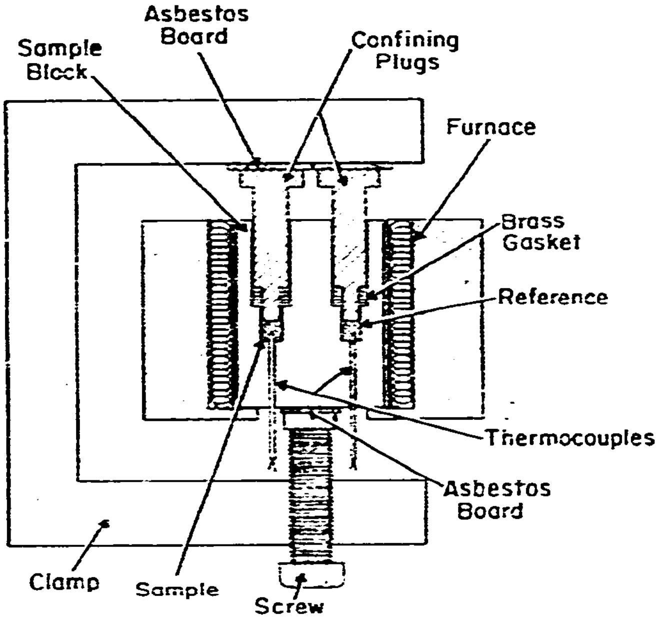


Fig. 1. Apparatus for DTA under complete volume confinement.

The heating block is placed inside an electric furnace. There is an opening in the bottom of the furnace large enough in diameter for both thermocouples to extend through but small enough to leave a rim to support the sample block. The plugs are firmly held in place with a C-clamp made of 1 inch by $1\frac{1}{2}$ inch aluminium bar stock. A piece of asbestos board is inserted between the C-clamp and the top of the plugs and between the screw and the bottom of the sample block to minimize heat loss from the block to the clamp. A controlling thermocouple is inserted in a $\frac{1}{16}$ inch diameter hole drilled into the center of the heating block near its edge and the heating rate is controlled with an F and M Scientific Company Model 240 temperature programmer. The differential temperature is plotted as a function of the sample temperature on a Honeywell Model 320 X–Y recorder. With this apparatus linear heating rates of up to 15°C min^{-1} can be obtained up to 800°C. The DTA experiments can be performed in an unconfined state with the same apparatus by simply omitting the confining plugs and thus the effects of confinement can be determined with all other conditions remaining the same.

In the first design for this apparatus confinement was obtained using threaded sample and reference cavities and threaded plugs but when this sample block was heated beyond about 400°C, the plugs became frozen in the holes making removal very difficult. However, this design could be used quite satisfactorily to study the effect of confinement on such lower temperature reactions as those of organic explosives and propellants. The design using smooth plugs, brass gaskets, and C-clamp seems to provide good confinement and the plugs can be easily removed even after heating to 800°C.

RESULTS

This DTA apparatus has been used to study the effects of total volume confinement on some reactions occurring in the solid state between powdered metals and inorganic oxidants. The mixtures selected are commonly used as delay powders, which, when ignited, burn at a controlled rate to provide a time-delay in the functioning of a munitions item. The effects of total volume confinement were found to fall into any of three categories: (1) little or no differences in the reaction between the confined and unconfined state, (2) an inhibition of the reaction due to confinement, and (3) an enhancement of the reaction when the system is confined.

An example of a reaction that is apparently little affected by the degree of confinement is that of a mixture of 65% tungsten powder, 15% potassium perchlorate, and 20% barium chromate. Figure 2 shows the DTA curves obtained for this mixture when heated at 15°C min^{-1} in both the confined and unconfined states. The two thermograms are essentially identical. The endothermal crystalline transition of potassium perchlorate from the rhombic to the cubic modification at 300°C appears on both curves followed by an exothermal reaction between the solid ingredients beginning at about 375°C. This exothermal reaction culminates in propagative combustion at 436°C in the unconfined condition and at 455°C in the confined state. The products of this reaction are barium tungstate (Ba_2WO_4), potassium chloride, and mixed oxides of chromium.

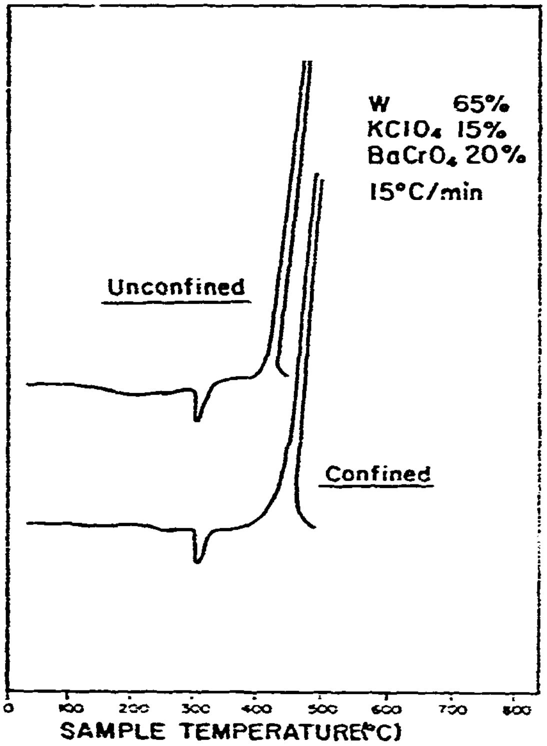


Fig. 2. DTA curve of a mixture of powdered tungsten, potassium perchlorate and barium chromate.

Mixtures of other powdered metals with potassium perchlorate do not appear to be affected by the degree of confinement. The presence of any powdered metal catalyzes the release of oxygen from the solid potassium perchlorate which leads to propagative reaction. Other reactions which were found to be little affected by the degree of confinement were the boron–barium chromate system and mixtures of zirconium powder, molybdenum trioxide and chromium sesquioxide (Cr_2O_3).

A reaction which seems to be inhibited by complete volume confinement is that between powdered antimony and potassium permanganate. DTA curves (15 °C min^{-1}) for this mixture in both the confined and unconfined states are presented in Fig. 3 along with curves for the individual ingredients. Both curves for the binary composition show a small exothermal reaction between 250 and 300 °C and then another at about 425 °C. In the unconfined condition this second exotherm represents a propagative combustion of the mixture leaving a sintered residue. In the confined state, however, this second exotherm reaction is not propagative and the reaction products are in the form of a loose powder. On examining the curve for potassium permanganate it becomes apparent that the first exotherm in the curves of the mixtures is due to a thermal decomposition of the potassium permanganate to manganese dioxide and potassium manganate

$$2KMnO_4 \rightarrow MnO_2 + K_2MnO_4 + O_2.$$

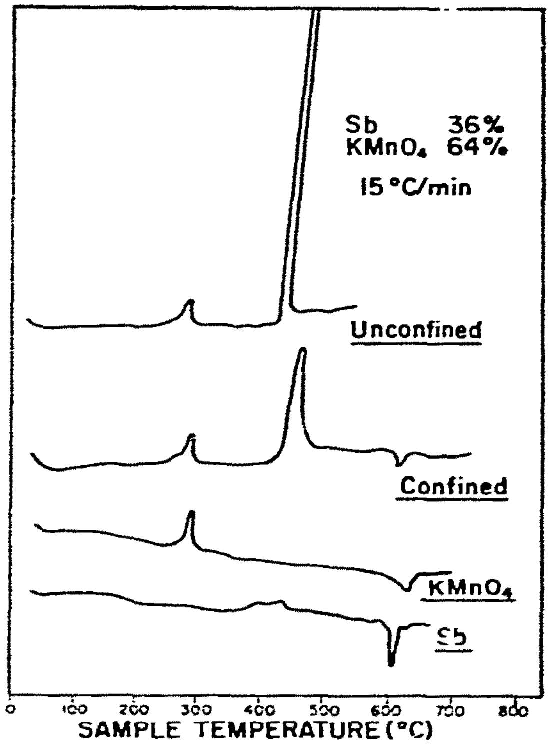
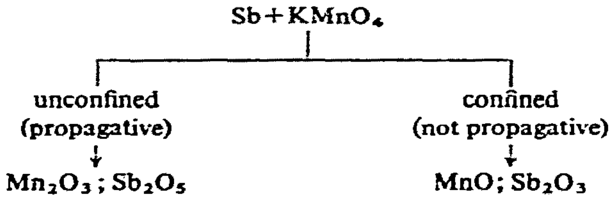


Fig. 3. DTA curve of the reaction between powdered antimony and potassium permanganate.

The second exotherm for the mixtures is then a reaction of powdered antimony with manganese dioxide and potassium manganate. The products of this reaction in both the confined and unconfined states were determined by x-ray diffraction and found to be as shown in Scheme 1.



Scheme 1.

Reaction mechanisms which would account for the differences in reaction products are as follows:

In both cases the potassium permanganate decomposes before reaction with the antimony

$$2KMnO_4 \rightarrow MnO_2 + K_2MnO_4 + O_2.$$

In the unconfined state

$$2MnO_2 \rightarrow Mn_2O_3 + \tfrac{1}{2}O_2$$

$$2Sb + \tfrac{5}{2}O_2 \rightarrow Sb_2O_5$$

When confined the MnO_2 dissociation is suppressed and the reaction with antimony is

$$2Sb + 3MnO_2 \rightarrow 3MnO + Sb_2O_3.$$

An instance of a reaction being seemingly enhanced by confinement is that of a mixture of 65% powdered zirconium, 25% ferric oxide, and 10% silicon dioxide. Figure 4 shows the DTA thermograms for this reaction. At a heating rate of 15 °C min^{-1} in the unconfined state two regions of exothermal reaction occur, the first between 250 and 325 °C, and the second from 475 to 650 °C, but there is no propagative ignition. When heated under conditions of zero ullage, however, there is some slight exothermal reaction in the 250 to 325 °C region and then propagative ignition occurs at about 400 °C. The reaction products as determined by x-ray diffraction are listed in Scheme 2.

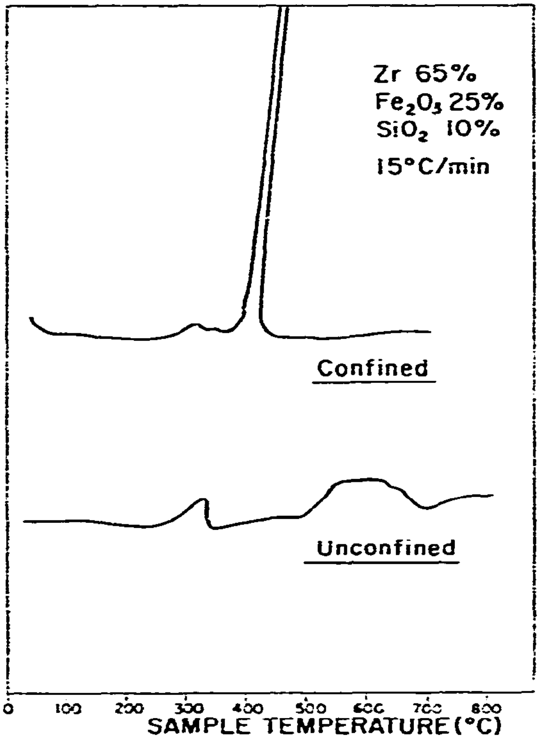
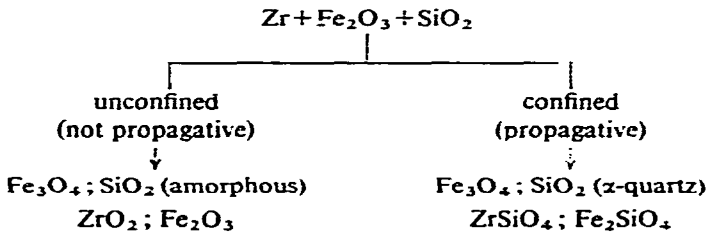


Fig. 4. DTA curve of a mixture of powdered zirconium, ferric oxide, and silicon dioxide.

Looking at the products of the unconfined reaction it can be seen that the reaction did not go to completion. Under confinement, however, the reaction products



Scheme 2.

show the result of propagative reaction with the formation of silicates and the high temperature α-quartz modification of the excess silicon dioxide. It has been noted that when a pressed column of this mixture is burned the column undergoes an apparent two-fold expansion in volume due to the porous nature of the residue. The effect of total volume confinement on the reaction may be that this expansion is prevented, keeping the reacting ingredients in close contact, thus, inhibiting heat loss from the reaction, and therefore, enhancing the possibility of propagative combustion.

CONCLUSIONS

Although this apparatus has been developed to study the effect of total volume confinement on the propagative reactions of mixtures of powdered metals and inorganic oxidants it could also be applied to other explosives and propellants. In addition, in a situation of the bulk storage of materials which can undergo self-heating, such as wool, hay, coal, fertilizers, etc. the material inside the bulk is under confinement and this method of DTA under confinement might profitably be used in studies of the thermal stabilities of materials such as these[5].

ACKNOWLEDGEMENT

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