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A THERMOANALYTICAL STUDY OF THE IGNITION BEHAVIOUR OF URANIUM DICARBIDE

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ABSTRACT

A knowledge of the ignition behaviour of uranium and plutonium carbides is necessary to understand their high reactivity, arrive at procedures for their proper handling in various reactor and laboratory applications, and also to examine the conditions for a controlled oxidation of these carbides. This paper presents a study of the ignition behaviour of uranium dicarbide employing a thermoanalytical method. The onset of ignition of the carbide under various heating rates was investigated and the influence of the experimental variables was also examined.

INTRODUCTION

The study of the reactivity of technologically important materials forms an essential aspect of current materials research. Ignition is a high reactivity process wherein a material capable of reacting exothermically is brought to a process of rapid combustion [1]. Investigations on the ignition behaviour of materials of air-sensitive and pyrophoric nature are not only useful in understanding and controlling their high reactivity but also of relevance in their industrial applications. Carbides of uranium and plutonium belong to the category of advanced nuclear fuels [2] for use in fast-breeder nuclear reactors. A knowledge of the ignition behaviour of these carbides is necessary in order to establish procedures for their safe handling in various reactor as well as laboratory research operations and also to optimize the conditions for a controlled oxidation of the carbides to oxides, a process which is under consideration as a possible head-end step in carbide fuel reprocessing. No earlier information is available on the ignition behaviour of uranium dicarbide and in the present paper studies carried out on the ignition behaviour of uranium dicarbide employing a thermoanalytical method are presented.

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EXPERIMENTAL

Thermal analysis in the nonisothermal mode was used in the present study to determine the ignition temperature of uranium dicarbide and its dependence on various experimental variables. Uranium dicarbide required for this work was prepared by the carbothermic reduction route starting with thoroughly blended mixtures of uranium dioxide and graphite in the desired proportion, pelletizing at a pressure of 300 MPa and carrying out the carbothermic reduction process at a temperature of 1873 K in flowing high-purity argon for 10 h. The formation of uranium dicarbide was confirmed by X-ray diffraction using a Siemens model D-500 diffractometer. Thermoanalytical measurements were carried out using a Netzsch model STA 429 thermal analyser. A convenient method of measuring the ignition temperature is to monitor directly the sample temperature and its time derivative in the nonisothermal mode of thermal analysis. The carbide sample was taken in a cylindrical crucible which was in direct contact with a thin Pt versus Pt-10% Rh thermocouple. The sample was held in a silicon carbide furnace which was coupled to a PID temperature controller, programmer and a separate Pt versus Pt-10%Rh control thermocouple. The sample weight, temperature and derivative of temperature were continuously recorded while the furnace was subjected to a dynamic heating programme at a predetermined heating rate. A constant air flow at a rate of 75 ml min^{-1} was maintained in the sample chamber.

RESULTS AND DISCUSSION

As the oxidation of the sample proceeded, an increase in sample weight was noticed. At the point of ignition which usually occurred at temperatures exceeding 160 ° C, the sample temperature rose sharply due to the large amount of heat generated and deviated from the set programme as seen in a typical illustration shown in Fig. 1. The temperature which corresponds to the onset of ignition is known as the ignition temperature (T_{ig}) and the maximum deviation of the sample temperature with reference to the programmed temperature is known as the over temperature. The values of the ignition temperature and over temperature obtained under different heating rates are shown in Table 1. It is observed that the ignition behaviour is generally complex and depends on factors like heating rate, physical form of the sample, etc. The variation in the ignition temperature (T_{ig}) as a function of heating rate (β) is shown in Fig. 2. With a decrease in heating rate the ignition temperature was found to increase. When the heating rate was decreased covering the range from 20 ° C min^{-1} to 1 ° C min^{-1}, the ignition temperature was found to gradually increase from 167 to 229 ° C. As the heating rate was further lowered to 0.2 ° C min^{-1} no ignition could be

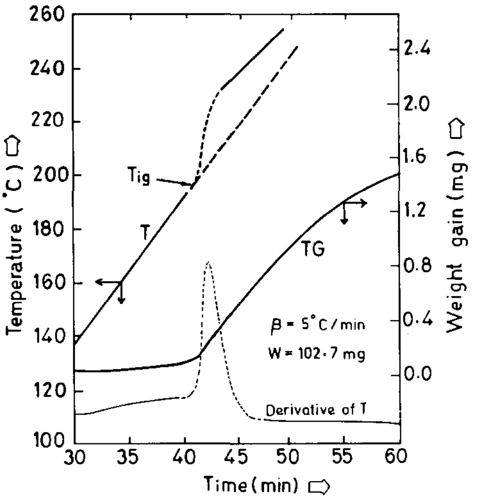

Fig. 1. Thermoanalytical representation of the ignition of uranium dicarbide.

noticed, thereby indicating that at sufficiently slow heating rates ignition can be prevented altogether.

Another method found useful in preventing the ignition of the carbide at a given heating rate is to hold the sample temperature at a value below the ignition temperature for a sufficiently long time and allow the oxidation of the sample to proceed to as large an extent as possible before raising the temperature any further. This approach, which is an adaptation of the general quasi-isothermal approach, is considered to be very useful especially

TABLE 1

Effect of heating rate on the ignition behaviour of uranium dicarbide

Sample No.	Sample weight (mg)	Heating rate (°C min^{-1})	Ignition temperature (°C)	Over temperature	Remarks
1	102.3	20	167	35	Dry air used
2	102.7	10	184	33	Dry air used
3	102.7	5	198	21	Dry air used
4	104.9	2	216	28	Dry air used
5	102.7	1	229	30	Dry air used
6	102	0.2	No ignition		Dry air used
7	102.3	5	201	21	Dry air used
8	131.5	5	197	–	Dry air used
9	102.3	5	204	25	Air containing moisture ($p_{H_2O} \sim$ 24 mmHg) used

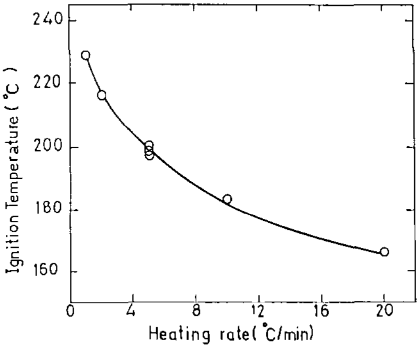

Fig. 2. The variation in the ignition temperature of uranium dicarbide as a function of heating rate.

when carrying out controlled oxidation of the carbides and studying the kinetic and mechanistic aspects of the oxidation process.

As shown in Fig. 3, a linear correlation is seen between the reciprocal of the ignition temperature and log β and it appears that the initiation of the ignition process is governed by the magnitude of the heat flux across the multilayer reaction zone. The influence of the heating rate on reaction temperatures in general has been described by Garn [3] and the effect of the surface heat flux on heterogeneous ignition processes has been discussed by Williams [1] and Linan and Crespo [4]. As seen from Table 1, the over temperature for the ignition of the carbide observed in the present study has an average value of 28 ± 7 °C. No specific correlation is seen between the over temperature and the heating rate. The ignition temperature was found to be generally lower for powders compared to pellets or pellet fragments. The relatively large surface area and the consequent higher reactivity of the powders are evidently the reason for this.

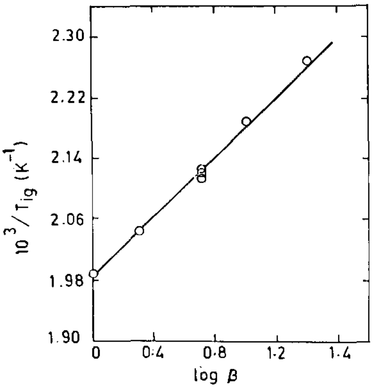

Fig. 3. The linear correlation of the reciprocal of the ignition temperature with the logarithm of the heating rate.

It appears that the oxidation of the carbide is accompanied by the growth of porous oxide with poor thermal conductivity as layers on the carbide matrix; the heat generated from the process sets into motion an autocatalytic reaction which manifests in thermal runaway conditions with rapid catastrophic oxidation. The ease of detection of the onset of ignition in various sample-container materials followed the order platinum > fused silica > recrystallized alumina. It was also found that the presence of moisture ($p_{H_2O} \simeq 24$ mmHg) in the oxidizing air atmosphere did not have any significant effect on the ignition temperature or the pattern of ignition.

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