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THERMOGRAVIMETRIC STUDY OF THE OXIDATION BEHAVIOUR OF URANIUM DICARBIDE

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Systematic studies were carried out on the oxidation behaviour of uranium dicarbide in air in the temperature range 25 °C to 700 °C employing thermogravimetry, evolved gas detection X-ray diffraction and chemical analysis. The mechanistic aspects were investigated and the oxidation was found to proceed through reaction processes involving oxidation of uranium to α-UO_3 with release of chemically bound carbon, reaction of released carbon leading to the formation of CO_2 which gets liberated stepwise, decomposition of α-UO_3 to U_3O_8 and oxidation of free carbon to CO_2. Examination of the thermoanalytical behaviour of sintered graphite, UO_3, mixtures of graphite with UO_3 and with U_3O_8 supported the above findings.

Uranium and plutonium carbides are candidate materials for use as advanced fast reactor fuels. Oxidation of carbides is one of the proposed alternatives in the head end stage of the fuel reprocessing and hence studies on the oxidation behaviour of these carbides are of importance from nuclear technology point of view [1, 2]. Such oxidation studies can also be of use from a solid state chemistry point of view in order to elucidate the nature of the oxidation process, to establish its mechanism and to understand the high reactivity of these materials. Investigations on the reaction behaviour of advanced carbide fuels with air, oxygen and CO_2 have been reviewed by Matzke [1], Naito et al. [3], Ervin and Miller [4] and Sudo and Osawa [5] studied the kinetics of the oxidation of uranium monocarbide at low oxygen pressures. As far as uranium dicarbide is concerned, while considerable information exists on its formation, crystal structure and thermodynamic properties, information regarding its oxidation behaviour is not available. In the present work detailed studies were carried out on the oxidation behaviour of uranium dicarbide primarily employing thermogravimetry but also making use of chemical analysis, X-ray diffraction and evolved gas detection.

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Experimental

Preparation of materials

Uranium dicarbide was prepared by starting with thoroughly blended mixtures of uranium dioxide and graphite in the desired proportion, pelletising at a pressure of 300 MPa and carrying out the carbothermic reduction process at 1873 K in flowing argon gas for 10 hours. Carbide thus obtained from the carbothermic reduction route was used in most of the present oxidation studies. Only in a few experimental runs which were carried out to compare the rates of oxidation of UC_2 and uranium metal, arc melted UC_2 was employed. To obtain this, UC_2 pellets prepared by carbothermic reduction were placed in a shallow depression in the water-cooled copper hearth of an arc melting set-up. The arc chamber was evacuated and back filled with argon. A zirconium button was also melted to further purify the gas. The uranium dicarbide pellet was then melted three or four times for better homogeneity and the arc melted UC_2 was thus obtained. Graphite which was separately subjected to the same heat treatment as the carbothermic reduction samples is denoted as sintered graphite. α-UO_3 necessary in the present work was prepared by slow heating of uranyl peroxide hydrate to 500° and holding the temperature at that value for about 10 hours. Uranium metal foils necessary were obtained from "nuclear fuel complex", taken in 4 × 4 × 1.2 mm size and stored in silicone oil. Before thermal analysis runs the foils were washed with dilute nitric acid and dried with acetone.

Characterisation and thermoanalytical investigations

Phase characterisation of the material was done by X-ray diffraction technique for which a Siemens D-500 powder diffractometer was used, employing copper K_α radiation. Determination of the oxygen to uranium ratio of the products of oxidation was carried out by a spectrophotometric method developed in our laboratory. The details of the method are described elsewhere [6]. Samples for this purpose were dissolved in phosphoric acid saturated with sodium sulphate, centrifuged and spectra of the clear solutions were taken.

The air oxidation of UC_2 was followed by thermogravimetry employing a Netzsch model STA 429 Thermal Analyser. Slow heating rates of 1 and 2 deg/min were generally used. In addition to the usual isothermal and non-isothermal methods of heating, quasi-isothermal approach was also employed. In this technique continuous programmed heating of the sample is stopped when the rate of a reaction exceeds a preset limit. As indicated by Paulik and Paulik [7], it gives a better separation of closelying reactions compared to the usual non-isothermal approach. Weight changes corresponding to the various stages of oxidation were monitored. The thermogravimetric runs were done in air at a flow rate of 75 ml/min with the samples in wide silica crucibles. The reaction products corresponding to the intermediate stages of oxidation were soaked at the respective temperatures for a sufficient period of time, cooled and analysed. Thermogravimetric runs were taken not only with UC_2 but also with selected intermediate products of oxidation.

In a different set of experiments, carbide samples were also subjected to air oxidation coupled with evolved gas detection. The effluent gas stream together with the evolved CO_2 was bubbled through sodium bicarbonate solution containing bromophenol indicator for a sampling period of 5 minutes. In this manner continuous monitoring of the gas stream in sampling intervals of 5 minutes was continued throughout the programmed heating period. The pH change in the solution which is a measure of the absorbed CO_2 was measured before and after the bubbling of each of the gas samples.

Results and discussion

Oxidation of UC_2 is highly exothermic and when UC_2 is subjected to oxidation in the non-isothermal mode of heating, at temperatures above 200° it undergoes rapid combustion, often leading to ignition. Due to the rapidity and exothermicity of this process, some of the oxidation stages observable under smooth controlled conditions cannot be distinguished. A typical result of the detection of the evolved CO_2 gas during a non-isothermal oxidation of the carbide is shown in Fig. 1 in which two stages can be seen, the first one over the range 250–450° and the second covering the range 530–680°. Employing synthetic mixtures of UC_2 and sintered graphite, it was seen that an increase in the amount of graphite in the sample leads to an increase in the second peak. It is thus concluded that while the first peak is due to the overall process of oxidation of UC_2 the second peak is due to the oxidation of the free graphite (hereafter indicated as C_f). In order to study the oxidation of UC_2 in greater detail the oxidation runs were carried out in the quasi-isothermal mode. To start with, the carbide samples were heated to 200° at the rate of 2 or 1 deg/min, held at that temperature for 4 hours, the temperature was then raised to 260° and the samples were kept at that temperature for about 100 hours thus preventing the rapid reaction and allowing the smooth oxidation to proceed to as large an extent as possible. This stage of oxidation is referred to as Stage I. Subsequently the temperature was raised continuing the quasi-isothermal approach and selectively stopping the heating programme at various stages thus allowing the formation of the oxidation products to a reasonable degree of completeness. The various intermediate stages in the oxidation process thus delineated can be described as follows.

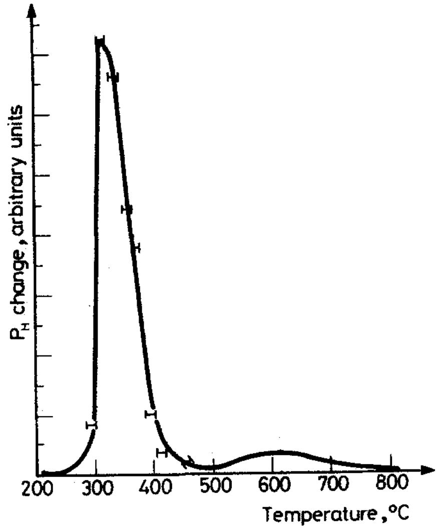

Fig. 1 Evolved gas profile in the oxidation of uranium dicarbide in continuous non-isothermal mode

Stage I (25° to 260°)

During this first stage of oxidation it is noticed that considerable weight gain occurs (Fig. 2) and the major part of the oxidation process takes place. Evolved gas sampling during this stage indicated very sluggish evolution of CO_2, in the first 20 h yielding about 1.26% of the total evolved gas and in the next 20 hours yielding only 0.71% of the evolved gas—thereby indicating that while the uptake of oxygen and

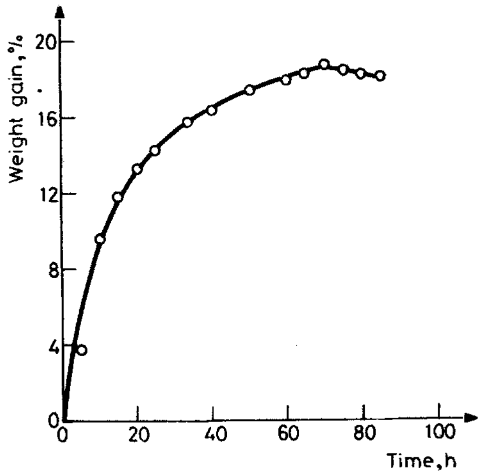

Fig. 2 Mass gain as a function of time during stage I

formation of oxide of uranium progresses, the oxidation of the carbon released (hereafter indicated as C*) consequently is very sluggish. Segregation of this released carbon and its subsequent oxidation constitute the rest of the oxidation process. It has to be also noted that the weight changes indicated in Fig. 2 constitute the effect of two processes, namely oxygen uptake for the formation of the uranium oxide intermediate and a parallel liberation of CO_2 formed from released carbon. The slow mass loss seen in Fig. 2 after a heating time of about 70 hours indicates that the second process, namely the oxidation of the released carbon is quite sluggish, presumably due to the relatively low temperature. In the examination of the mass gain at 260° in the oxidation of UC_2 samples while a single pellet of UC_2 showed a maximum mass gain of 19.2% at this stage, the mass gain when the carbide was taken in the form of small broken chips was 18.3%. However, when the carbide pellet was powdered and subjected to oxidation up to this stage, the mass gain noticed was about 16.46%. It can be seen that the uptake of oxygen corresponding to the formation of UO_3 with retention of all the released carbon in elemental form in the sample corresponds to a mass gain of about 18.3%. Similarly, the uptake of oxygen corresponding to the formation of UO_3 with liberation of all the released carbon in the form of CO_2 would result in a mass gain of 9.16%. In the case of pellet samples, the observed mass gain above 18.3% implies additional uptake of oxygen by the released carbon leading to the formation of CO_2 and its retention in the inner layers. While the CO_2 formed from the oxidation of the carbon released and segregated near the outer surface of the sample pellet can get liberated, the CO_2 formed within the inner layers of the pellet may get trapped inside as the pressure build-up would be insufficient for its liberation thus explaining the sluggish mass loss after long heating times in Fig. 2. It is also noted that when the sample is in the form of small broken chips the released carbon practically remains as such without additional oxygen uptake. Furthermore when the samples are taken in powder form it is seen that the CO_2 formed from the oxidation of part of the released carbon is getting liberated.

Measurement of the oxygen-to-uranium ratio at this stage was not possible as the solution obtained by the dissolution of the oxidation product in phosphoric acid medium was opaque with dispersed carbon particles thus precluding the necessary spectrophotometric measurements. The solution contained two types of carbon particles one being coarse and the other very fine. The solution was centrifuged, the residue washed first with 1 : 1 H_2SO_4 to remove the phosphoric acid and then with water and methanol successively. The oxidation of this filtered carbon residue in air indicated two steps, the first step being around 345° and the second one at 685° as shown in Fig. 3. Sintered graphite subjected to similar treatment as described above for the carbon residue was found to get oxidised at 680°. Similarly, when the free carbon obtained as residue from dissolution of the unoxidised UC_2 sample in phosphoric acid was washed with 1 : 1 H_2SO_4 followed by water and methanol and subjected to air oxidation, an oxidation temperature of 680° was noted. These observations indicate that the second step seen in Fig. 3 is due to the unreacted free graphite present in the sample right from the preparation step. Furthermore, an inception temperature of 340° was also noticed in the oxidation of charcoal which is primarily amorphous in nature. It can be thus noted that the carbon (C*) which is released from UC_2 consequent to the preferential oxidation of uranium, segregates and exists in amorphous form and has a reactivity quite different from that of the free carbon (C_f).

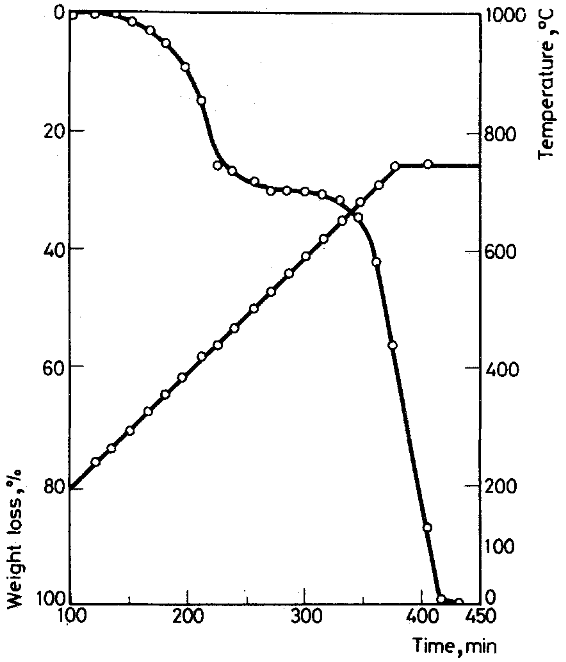

Fig. 3 Thermogravimetric representation of the oxidation behaviour of filtered carbon residue

It was also interesting to note that pellets with relatively low density (< 9.95 g/cm^3) could retain their physical integrity during the oxidation not only up to this stage I but also through the subsequent stages. However, pellets with higher density got broken down and pulverised even at the slow heating rates employed and controlled reactions conditions. This implies that in high density pellets the limited amount of CO_2 formed from the released carbon does not get retained but gets liberated leading to the breakdown of the integrity of the pellet.

Based on the above described observations the first stage in the present oxidation process can be represented as $[UO_3 + (C^*O_2)_t + C^* + (C^*O_2)_1 + C_f]$ where C^*O_2

indicates the CO_2 formed from the oxidation of a part of the released carbon (C*) and subscripts *t* and *l* indicate the trapped and liberated gas. The X-ray diffraction pattern of the oxidation product at this stage has shown it to be amorphous in nature.

Stage II (260° to 410°)

While stage I includes the controlled oxidation process for prolonged intervals up to 260°, a typical pattern of changes that occur in the subsequent stages by extension of thermogravimetric investigations to higher temperatures in the quasi-isothermal mode is shown in Fig. 4. The selection of the temperature halts for studying the progress of the reaction was done after a number of trials with careful examination of the reactivity behaviour. In the temperature range 260° to 410°, a two-step mass loss was observed indicated as II(a) and II(b). The changeover from stage II(a) to stage II(b) can be noted to be at about 375°. The oxidation product obtained at 410° after a soak time of 64 hours at the same temperature was seen to be orange red in colour with some black spots and a few cracks. Evolution of the CO_2 gas formed from the oxidation of the released carbon is considered responsible for the cracks. Complete oxidation of the released carbon by about 410–420° is also clearly indicated by the first step of the oxidation pattern for the filtered carbon residue shown in Fig. 3. The black spots are noted to be due to the free carbon in the sample. As shown in Table 1, X-ray diffraction studies of the product of oxidation at 410° indicated the same to be α-UO_3. Analysis of the oxygen-to-uranium ratio of this oxidation product also indicated the same to be UO_3 as shown in the Table. It was also seen that the two steps II(a) and II(b) observed for samples in the form of pellets or broken chips got merged into a single step when the samples were in

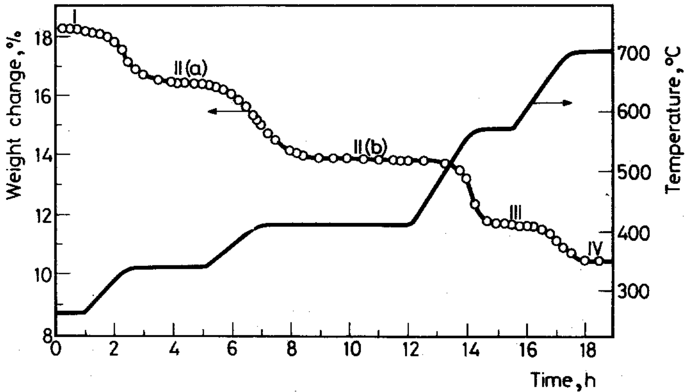

Fig. 4 Thermogravimetric representation of the weight changes at temperatures ⩾260 °C

powder form. Different rates of formation/liberation of the CO_2 from the surface and inner layers of pellets or broken chips seem to be resulting in the two steps at this stage. The reaction product at the end of this overall stage II can be represented as α-UO_3+C_f.

Stage III (410° to 560°)

During this stage which is indicated in Fig. 4 a sharp mass loss corresponding to the decomposition of the UO_3 intermediate is noticed starting at about 520° and complete by 560°. The oxidation product was kept for 12 hours at 560° and the O/U values of the oxidation product as shown in Table 1 were in the vicinity of 2.70 indicating the formation of U_3O_8. Although the theoretical value of O/U for this oxide is 2.667, the existence hypo as well as hyper stoichiometry for this oxide and a wide range of O/U values is well understood and discussed elsewhere [8, 9]. In order to examine this stage further α-UO_3 prepared separately in the laboratory was subjected to thermal analysis and it was seen to decompose to U_3O_8 with a sharp mass loss starting at 530°. Thus the reaction process in this stage III corresponds to the decomposition of α-UO_3 to U_3O_8 and hence the oxidation product at the end of this stage can be represented as $U_3O_8+C_f$.

Table 1 Characterisation of cooled intermediates of air oxidized UC_2 at respective temperatures

T, °C	Time, h	XRD	O/U	Physical characteristics
R.T.	—	UC_2+C	—	Black pellet
260	100	Amorphous	AA	Blackish brown pellet (140% volume increase)
410	64	α-UO_3	2.97	Orange red pellet with cracks (fine black spots)
560	12	—	2.73 2.68	Black pellet with cracks
665	6	U_3O_8	2.66 2.63	Black pellet with cracks

"AA" mixture of UO_3 and fine carbon particles.

Stage IV (560° to 690°)

In this stage, as shown in Fig. 4, a one step mass loss was observed. From an examination of the second peak in the evolved gas profile shown in Fig. 1 and of the second step during the oxidation of the carbon residue shown in Fig. 3 it was seen that this stage corresponds to the oxidation of free carbon (C_f). When synthetic mixtures of UC_2 with varying amounts of sintered graphite were subjected to oxidation it was seen that the mass loss during the last stage (stage IV) increased with increase in graphite content in the sample thus further confirming that the oxidation of free carbon is the reaction process during this stage. The final product at the end of this stage is thus U_3O_8 X-ray diffraction patterns as well as the O/U ratios of the product also supported this.

General observations

With a view to examine further the behaviour of free carbon present in the graphite form in the samples, the oxidation behaviour of sintered graphite, UO_3 and sintered graphite mixture as well as U_3O_8 and sintered graphite mixture was also investigated. The oxidation of sintered graphite occurred starting from 680° both when the graphite was taken as such and also as a mixture with U_3O_8. However, when a mixture of UO_3 and sintered graphite was taken, first the decomposition of UO_3 occurred in the range 530° to 560° and subsequently the oxidation of sintered graphite took place starting from 640°, the same temperature at which the oxidation of the free carbon started in the carbide oxidation. Thus it is noted that the presence of U_3O_8 freshly formed from UO_3 in the sample had a catalytic effect and lowered the oxidation temperature of graphite by 40 deg.

Another observation made in the present studies was that aged carbide samples show higher reactivity towards oxidation. The carbide samples are known to pick up moisture and oxygen during storage and it is considered that under the present conditions of oxidation the liberation of the absorbed moisture causes cracking of the surface oxide scales, thus exposing fresh inner layers of the matrix and leading to enhanced reactivity. As part of the oxidation behaviour studies in metal-carbon systems, efforts were made to analyse the conditions for the release and oxidation of bound carbon and to investigate the thermodynamic and kinetic aspects of the equilibria involving metal, CO_2, metal oxide and carbon.

In order to understand the oxidation behaviour better, the course of oxidation of UC_2 and uranium metal was examined on a comparative scale. For this purpose, as it is preferable to have each of these materials close to their respective theoretical densities and with similar surface area, arc melted UC_2 was selected for a comparative study with uranium metal. The pattern of oxidation for the carbide and uranium metal is shown in Fig. 5. The rates of oxygen uptake by the carbide and the uranium metal were shown to be about 1.4×10^{-3} and 6.25×10^{-3} oxygen moles per mole of U per second. It can be seen that for the uranium carbide, while uranium in the lattice gets preferentially oxidized, segregation of the consequently released carbon could be the rate determining step thus leading to a lower rate of oxidation of the carbide.

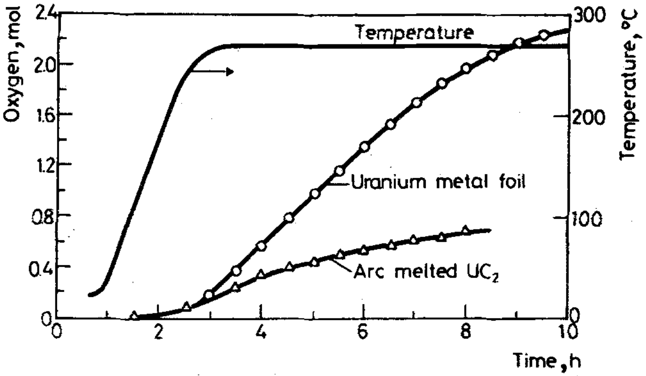

Fig. 5 Comparison of the oxidation behaviour of uranium metal and uranium dicarbide

Conclusions

The oxidation behaviour of uranium dicarbide in air was studied in the temperature range 25–700° employing thermogravimetry and supported by evolved gas detection as well as X-ray diffraction and chemical analysis of the intermediates. The oxidation of the carbide involved the intermediate α-UO_3 and oxidation of released as well as free carbon. With a controlled increase in temperature, the oxidation was shown to be proceeding through a series of reaction processes which involved preferential oxidation of uranium to form α-UO_3 with consequent release of the chemically bound carbon, reaction of the released carbon leading to formation of CO_2 which gets liberated stepwise, decomposition of UO_3 to U_3O_8 and finally oxidation of the free carbon. Examination of the thermoanalytical behaviour of graphite, UO_3 and mixtures of U_3O_8 and graphite as well as UO_3 and graphite under similar experimental conditions also supported the above findings.

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Zusammenfassung — Das Oxydationsverhalten von Urandikarbid in Luft im Temperaturbereich zwischen 25 und 700 °C wurde mittels Thermogravimetrie, Gasprodukteanalyse, Röntgendiffraktion und chemischer Analyse systematisch untersucht. Studien des Mechanismus ergaben, daß die Oxydation über Teilschritte abläuft, die folgende Schritte beinhalten: Oxydation von Uran zu α-UO_3 unter Freisetzung chemisch gebundenen Kohlenstoffes, Reaktion des freigesetzten Kohlenstoffes unter Bildung von CO_2, das schrittweise entweicht, Zerfall von α-UO_3 zu U_3O_8 und Oxydation von freiem Kohlenstoff zu CO_2. Diese Feststellungen wurden durch Untersuchung des thermoanalytischen Verhaltens gesinterter Graphit- und UO_3-Proben sowie Mischproben von Graphit mit UO_3 bzw. U_3O_8 bekräftigt.

Резюме — Методами ТГ, обнаружения выделяющегося газа, рентгеноструктурным и химическим анализом проведено систематическое исследование окисления дикарбида урана в атмосфере воздуха и интервале температур 25–700°. Изучены общие аспекты и найдено, что окисление протекает через реакционные процессы, включающие окисление урана до α-UO_3 с выделением химически связанного углерода, реакцию окисления углерода до двуокиси углерода, выделяющейся ступенчато, разложение α-UO_3 до U_3O_8 и реакцию окисления свободного углерода до двуокиси углерода. Исследование термоаналитического поведения спёкшегося графита, UO_3, смесей графита с UO_3 и U_3O_8 подтверждают вышеприведенные соображения.