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ABSTRACT

The changes in specific surface area observed during the calcination of ammonium uranate in various atmospheres have been studied using constant rate of heating, isothermal and isochronal experiments. X-ray diffraction, thermogravimetric analysis (TGA) and differential thermal analysis (DTA) results have been used to correlate these changes with the stages of reaction which occur during the calcination. During dehydration (20 to 200°C) AU 'Type II' remains the major phase. Thermal decomposition (200 to 350°C) produces amorphous UO_3 and β-UO_3 which retain ammonia in their structure. These are subsequently converted to U_3O_8 by a self-reduction process (350 to 450°C). Reduction in a hydrogen atmosphere takes place between 450 and 510°C to produce UO_2. In an inert gas or air atmosphere β-UO_3 and $UO_{2.9}$ persist to

(continued)

much higher temperatures, and the presence of an oxidising atmosphere may completely eliminate the self-reduction reaction.

The observed specific surface area increases during dehydration and decomposition and reaches a maximum between 400 and 450°C. The major increase in the surface area is attributed to the opening up of internal porosity, formed during decomposition, by stress-induced cracking of the particles. The internal stresses are generated by the nucleation and growth of phases which have different specific volumes from that of the parent solid. The maximum surface area was observed if self-reduction occurred. The observed decrease in specific surface area at higher temperatures is due to sintering.

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AIR; AMMONIUM COMPOUNDS; CALCINATION; DECOMPOSITION; DEHYDRATION; DIFFERENTIAL THERMAL ANALYSIS; HELIUM; HIGH TEMPERATURE; HYDROGEN; REDUCTION; SURFACE PROPERTIES; THERMAL GRAVIMETRIC ANALYSIS; URANATES; URANIUM TRIOXIDE; U308; X-RAY DIFFRACTION

CONTENTS

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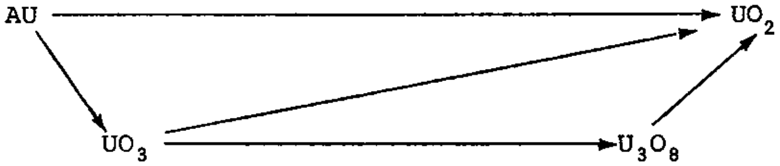
CONTENTS (continued)

1. INTRODUCTION

Uranium dioxide powders used in the fabrication of reactor fuel pellets are normally produced by the calcination of ammonium uranate (AU). This calcination may be effected *via* three different routes (Woolfrey 1968):



The AU can be directly reduced with a hydrogen atmosphere, or initially calcined in air or an inert gas to produce UO_3 or U_3O_8 and then reduced.

Recent work on the calcination of nitrate-free AU (Price 1971, Price & Stuart 1973), indicates that there are several stages of thermal decomposition:

(a) Stages I (20 - 120°C) and II (20 - 200°C) are overlapping dehydration processes involving loss of coordinated water molecules and some dehydroxylation.

(b) Stage III (200 - 350°C) involves thermal decomposition of the AU with a loss of H_2O and NH_3. However, some of the original NH_3 is retained within the solid in the form of ammoniate ($UO_3.xNH_3$).

(c) Stage IV (350 - 450°C) is a process of self-reduction by the ammonia retained in the lattice of the solid. Self-reduction may be partly or fully suppressed in an oxidising atmosphere because of prior oxidation of the ammonia.

If the calcination is performed in a reducing atmosphere a subsequent final reduction to UO_2 is observed.

The calcination of AU is generally accompanied by changes in the specific surface area of the powder (Woolfrey 1968). Surface area has a major influence on the sinterability of the UO_2 product and is often controlled as part of the powder specification. The present work, in which changes in surface area are related to the stages of decomposition, was undertaken because a survey (Woolfrey 1968) suggested that no such systematic study had been performed. The powders used in this work were typical of commercial materials in that they were precipitated from uranyl nitrate solution and thus contained residual nitrate as a major impurity; therefore it was necessary to confirm that these powders showed the same stages of decomposition as the nitrate-free material.

2. EXPERIMENTAL

The AU powders were prepared by continuous precipitation from a 0.63 molar uranyl nitrate solution with gaseous NH_3 at 42°C (Ramm & Quaass (1968). 'Batches' of AU were precipitated at pH 7.1 and 8.6. The precipitates were initially washed with demineralised water on a drum filter, and subsequently each batch was reslurried once in demineralised water and twice in ethyl alcohol. After each reslurrying the precipitate was filtered on a drum filter, then dried at ambient temperature in flowing laboratory air. The washing reduced the amount of nitrate in the solids and produced a powder with soft, friable agglomerates. The bulk powder was stored in sealed polythene jars and material for X-ray analysis was sealed in small glass bottles.

In the calcination studies, powder samples of approximately 0.5 g (1 to 2 mm bed depth) were contained in a U-shaped glass or silica tube continuously purged with hydrogen at a flow rate of 100 $cm^3\ min^{-1}$. This configuration was used to facilitate rapid removal of gaseous decomposition products. Two types of calcination studies were undertaken:

(a) Samples were heated at a constant rate (CRH) of 5°C min^{-1} to temperatures between 100 and 650°C and the surface area was measured as a function of the final temperature. These conditions approximate to those in the batch reduction processes used for UO_2 powder production.

(b) Isothermal calcinations were performed over the temperature range 300 to 900°C for up to 70 minutes. Surface area was measured as a function of time and temperature. Specimens were plunged into a preheated furnace and the desired temperature was attained within 2 to 5 minutes. These conditions approximate those which would occur during hot feeding of a continuous, pulsed or fluidised bed reactor for UO_2 powder production.

The calcination atmospheres used were hydrogen, helium and dry bottled air at a flow rate of 100 $cm^3\ min^{-1}$. The hydrogen was purified to less than 3×10^{-5} vol.% of oxygen using a catalytic deoxidiser, and dried to less than 3×10^{-4} vol.% of water vapour by passage through a liquid nitrogen cold trap. The bottled helium contained less than 1×10^{-4} vol.% of oxygen and a liquid nitrogen cold trap was used to remove water vapour.

The specific surface area of the powders was measured by the continuous flow BET method using a Perkin-Elmer Sorptometer*. Powder surfaces were

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* *Perkin-Elmer Corporation, USA.*

cleaned under a flowing stream of helium for combinations of time and temperature which preliminary investigations had shown to produce the maximum value of surface area on known AU and UO_2 powders. AU was conditioned for 18 hours at 50°C. Calcined powders were conditioned for the minimum practicable time at a temperature at least 100°C lower than the calcination temperature. The surface area was measured immediately after calcination and conditioning without the powder being exposed to atmosphere. Duplicate calcinations showed a reproducibility in the measured specific surface area of about 6 per cent.

The bulk phases present in the powder specimens were identified by X-ray diffraction in a Philips diffractometer (17 cm radius) using Cu Kα radiation with a Ni filter. X-ray crystallite size for the major peak of the predominant phase was determined from the half-maximum peak breadth with corrections for Kα-doublet broadening (Klug & Alexander 1962). No attempt was made to estimate the strain component of the broadening.

TGA, DTA and ammonia release data were provided by Mr. G. Price (AAEC private communication) for the calcination of a similar AU powder. The apparatus and techniques have been described elsewhere (Price 1971). These data were used to complement the X-ray diffraction results and to help identify the reactions which occurred during specific stages of the calcination.

3. RESULTS AND DISCUSSION

3.1 Characterisation of AU Powders

Characteristics of the AU powders are shown in Table 1. The X-ray powder pattern of the AU has been classified in terms of Cordfunke's compound nomenclature (Cordfunke 1962) for convenience, even though later results (Price & Stuart 1973) suggest that the AU system at equilibrium is continuous with no intermediate stoichiometric compounds. The two powders were very similar; both contained some nitrate and were typical of the powders normally used for fabrication of fuel pellets.

Electron microscopy of alcohol-dispersed material showed that the powders consisted of thin plates of hexagonal or related shape. The powders contained no particles larger than 0.1 μm and the average particle size appeared to be smaller at the increased pH. Selected area electron diffraction patterns indicated that the plates with well developed crystallographic shapes were single crystals, but the smaller irregularly shaped plates were often polycrystalline.

3.2 Calcination of AU

The observed changes in surface area which accompany the thermal decomposition of a solid substance are generally a function of two competing processes:

(a) Nucleation and growth of crystallites in the decomposition product can lead to an increase in surface area, if the strains resulting from the difference in specific volume between the parent and product solids are accommodated by intercrystallite cleavage. Increased surface area may also result from the formation of porous particles, if large pores or channels are left within the structure by escaping gases.

(b) A reduction in surface area may be caused by sintering and particle growth. The major driving force for the sintering process is the excess surface energy of the powder which is directly related to particle size and shape. Diffusion processes are normally involved, and hence sintering becomes relatively more important at higher temperatures.

Thus, the surface area observed during the calcination of AU will be a function of temperature, time and the decomposition sequence.

3.2.1 Calcination in hydrogen

CRH experiments. Figure 1 shows the changes in specific surface area together with TGA and DTA traces for the AU precipitated at pH 8.6, and heated at 5°C min^{-1}. Table 2 list the compounds identified by X-ray diffraction at various temperatures during the calcination.

The TGA and DTA traces are very similar to those obtained by Price & Stuart (1973) for nitrate-free AU. The additional exotherm in the DTA trace at 350°C has been identified by several investigators (Woolfrey 1968) with the decomposition of nitrate present in the AU. The close similarity between the TGA and DTA results for nitrate-free and nitrate-containing AU would indicate that similar stages of decomposition occurred in both materials.

(a) Stages I and II (20 - 200°C)

The surface area of the AU decreased significantly on heating to 100°C. No such effect had been observed during experiments to determine the optimum temperature for cleaning the surface of AU for BET measurements. However, in those experiments the sample was rapidly heated to temperature in a preheated water bath. Leitnaker, Smith & Fitzpatrick (1972) observed a decrease in the specific surface area of AU during drying operations. In the present work, examination of the AU powder by electron microscopy showed that the AU plates were attracted to each other, plane to plane, and overlapped and adhered extensively. It may be that the observed loss in specific surface area is a result of particle growth at the points of contact, and that this is more likely with a slower rate of heating where adsorbed water and water of decomposition remain available longer. Above 100°C, an increase in specific surface area occurred as dehydration proceeded.

The powders gave X-ray diffraction patterns normally associated with lower ammonia content 'compounds' (type II) and $UO_3.2H_2O$ (type I) as shown in Table 2. The diffraction patterns could be identified with those described by Debets & Loopstra (1963) but they showed line shifts of up to 0.25 degrees and changes in the relative intensities of the peaks. Cordfunke (1962) observed that type II is the most stable AU composition in the presence of a moist gas. However, his observed changes occurred by an exchange mechanism between NH_3 and water vapour from a saturated gas while, in this case, the water was liberated by decomposition and only very minor traces of ammonia were detected in the exit gas. No significant amounts of ammonia were released until 190°C. These results suggest that X-ray diffraction patterns similar to those observed for types I and II materials can be produced in higher ammonia content AU by removing only water and hydroxyl from the structure.

(b) Stage III (200 - 350°C)

During this stage there was a rapid increase in surface area starting at about 325°C. The exotherm in the DTA trace indicates that nitrate decomposition occurred at the same time (Woolfrey 1968). The maximum rate of NH_3 evolution occurred during this stage at about 330°C. At 300°C, the predominant phases were AU (type II) and $UO_3.2H_2O$(type I). Very minor amounts of β-UO_3 and $UO_3.0.8H_2O$ were identified. At 350°C, complete disruption of the AU lattice occurred. The X-ray pattern showed a high background with very broad, low, irregular peaks and few reflections could be unambiguously identified. This could be due either to the small dimension of the primary crystals, disorder within the crystal lattice, or both. The d-spacings covered by these broad peaks included the major lines for UO_3 and U_3O_8 and this is probably the material referred to in the literature (Woolfrey 1968) as amorphous UO_3 (UO_3 'A'). The TGA results show that the material present at the end of this stage is more complex than the basic UO_3 structure revealed by X-ray diffraction. The weight of the material exceeds the estimated weight of UO_3 by about 2 per cent. This is in agreement with the observations of Price & Stuart (1973) that the calcined material still contains ammonia in the form of ammoniate ($UO_3.xNH_3$). Other experimental results showed that a similar disruption of the lattice occurred in nitrate-free AU precipitated at pH 4.2, and thus was not associated with nitrate decomposition. Both β-UO_3 and UO_3 'A' are reported to hydrate in the presence of water vapour to form the compound $UO_3.0.8H_2O$ (Landspersky *et al.* 1964), which could explain the appearance of the latter phase at these higher temperatures.

(c) Stage IV (250 - 450°C)

During this stage, self-reduction occurred (DTA) with a major increase in surface area. Competition between surface generation by decomposition and surface loss by sintering resulted in a maximum in surface area at approximately 450°C. At 400°C, the material had d-spacings for the major lines which were intermediate between those for $UO_{2.9}$ and U_3O_8 ('$UO_{2.9}$ - U_3O_8'). At 450°C, the major phase was U_4O_9 with minor amounts of U_3O_8. The X-ray diffraction peaks became sharper indicating that crystallite growth had occurred. The TGA curve indicates that the bulk material had been converted to at least U_3O_8 during this stage. NH_3 evolution ceased at approximately 410°C. These results suggest that the rapid increase in surface area of the calcined powder, which occurs during this stage, is associated with the internal self-reduction step and/or the structural changes involved in recrystallisation from the highly disordered UO_3 'A' to U_3O_8.

(d) Atmospheric reduction

The DTA exotherm between 450 and 510°C indicates that reduction by the hydrogen atmosphere took place over this temperature range (Price 1971, Price & Stuart 1973), forming UO_2 (TGA). This phase subsequently gave the UO_{2+x} X-ray diffraction pattern because of air-oxidation during preparation of the sample for the diffraction measurements. A rapid loss in surface area due to sintering was observed during the reduction to UO_2. As the temperature was increased, the specific surface area stabilised at 2 to 3 m^2g^{-1}, probably for two reasons. Firstly, the excess surface energy of such low surface area powders is small and it becomes progressively more difficult to lose surface area by sintering. Secondly, the formation of $UO_{2.0}$ would assist stabilisation since it was observed in a separate experiment (Figure 2) that fully reduced UO_2 did not lose surface area until much higher temperatures. These specimens were reduced isothermally at 500°C for one hour in hydrogen and then calcined at the desired temperature. This latter effect on surface area would be due to slower diffusion rates of ions in the fully reduced material and the associated decrease in the rate of sintering.

Isothermal and isochronal experiments. Isothermal calcination studies were carried out on the AU precipitated at pH 7.1. The results of the TGA, specific surface area and X-ray crystallite size measurements are shown in Figure 3, and the phases identified are listed in Table 3. The change in specific surface area with time can again be correlated with the stages of decomposition of AU. A typical curve is illustrated by the calcinations at 325°C (Figure 3). The specific surface area initially increased slightly but then remained steady for 45 minutes. After 5 minutes, the formation of β-UO_3 and 'AU' with line shifts indicated that stage III decomposition had commenced. 'Recrystallisation' and the formation of 'amorphous' material was not observed until 51 minutes. Surface area began to increase rapidly at 45 to 50 minutes. The formation of U_3O_8 by self-reduction (stage IV) and the associated maximum in the surface area was observed at 52.5 minutes. Self-reduction has been observed to commence in CRH experiments within 30°C of this temperature (Price 1971). The surface area then decreased in a two or three stage process, the initial collapse being extremely rapid. Irreversible changes had occurred during the formation of the maximum surface area, since only a minor amount of NH_3 (~ 0.2 wt.%) could be readsorbed into the structure at this point and the surface area change could not be reversed by such a process. The surface area subsequently stabilised briefly and then decreased relatively rapidly by sintering in the major phase, which was U_3O_8. Very minor amounts of β-UO_3 and 'AU' persisted in the product. The TGA curve did not correlate very well with the X-ray results as it indicated that the major phase was not even stoichiometric UO_3. This anomaly is probably related to the complex nature of the decomposition products which may contain ammoniate or nitrogen (Price 1971, Price & Stuart 1973). The X-ray crystallite size results showed the expected initial decrease in crystallite size followed by stabilisation. However, over the peak surface area period they showed an opposite trend to what would be predicted from the surface area results.

At 400°C (Figure 3), the surface area curve showed a similar shape with the peak moved to shorter times. The major phase present up to and including the peak in the surface area was U_3O_8. The peak showed the initial rapid collapse followed by a two stage loss in surface area. In the first stage it was lost at a fairly rapid rate but this rate was reduced dramatically when the U_4O_9 phase predominated. The X-ray crystallite size results followed a trend which might be expected from the specific surface area results. However, the crystallite size did not appear to decrease until after the maximum in surface area had been reached.

At 500°C, the surface area reached a maximum and collapsed within 5 minutes, then increased slightly and stabilised. The major phase present for all times was UO_{2+x}. The X-ray crystallite size followed the peak surface area trend but the minimum crystallite size was again after the maximum in surface area.

These isothermal results confirm that the major increase in specific surface area occurred after the bulk of the AU weight loss. They also indicate that recrystallisation of UO_3 'A' to U_3O_8 is not the sole cause of the surface area peak, since U_3O_8 was the major phase present well before the surface area peak at 400°C. The results suggest that the surface area peak is not related to any specific change in the phases present in the calcined powder. It occurred at 325°C when β-UO_3 gave U_3O_8, and at 400°C when U_3O_8 gave U_4O_9. At 500°C the product was at least UO_{2+x}. The peak in surface area did not appear to be related to crystallite size changes.

Isochronal experiments have often been used to determine the surface area changes which occur during calcinations (Woolfrey 1968). A series of calcinations was carried out in which specimens were heated at temperatures between 50 and 900°C for 60 minutes. The results are shown in Figure 4 and Table 4. It is obvious that such an approach does not show the complex situation revealed by the CRH and isothermal experiments.

The isothermal and isochronal specific surface area data, including results not recorded above, have been collated in Figure 5 as a three-dimensional representation of the contour surface. The complexity of the contour surface is evident and illustrates why a variety of correlations have been observed between the surface area of the AU precursor and product materials (Woolfrey 1968). Above 500°C, simpler correlations have been observed, as sintering has effectively reduced the surface area to a plateau region and has reduced the importance of any initial differences.

3.2.2 Calcination in helium

The CRH results for AU precipitated at pH 8.6 are shown in Figure 6 and Table 2. The DTA and TGA results were obtained in an argon atmosphere and are very similar to those obtained by Price & Stuart (1973) for nitrate-free AU. The shape of the surface area curve is similar to that observed in H_2 except that in He the peak was sharper and occurred at a lower temperature (400°C). Both these effects are associated with the absence of a reducing atmosphere; the former is due to enhanced rates of sintering, and the latter is due to the absence of any increase in surface area associated with atmospheric reduction. The results confirm that the major increase in surface area is associated with the self-reduction reaction. The rapid loss of surface area was briefly interrupted at 550°C. The DTA and X-ray results suggest that this may have been caused by the generation of fresh surface during the formation of U_3O_8. The X-ray results also show that 'AU' and $UO_{2.9}$ existed in very minor amounts up to 500 and 550°C respectively.

3.2.3 Calcination in air

The CRH results for AU precipitated at pH 8.6 and heated in air are shown in Figure 7 and Table 2. The DTA and TGA results again show a marked similarity to those reported by Price & Stuart (1973) for nitrate-free AU. The general shape of the surface area curve is again similar to those observed in H_2 and He except that the peak is not as high or as sharp. The DTA trace shows the exotherm at 350°C associated with nitrate decomposition and another at about 390°C. The latter resulted from the reaction of retained ammonia with oxygen from the calcination atmosphere (Price 1971). At this heating rate, all ammonia was effectively oxidised before self-reduction could occur; hence the absence of the normal DTA exotherm at 410°C associated with self-reduction. Ammonia evolution ceased at approximately 350°C as it was subsequently oxidised by the above process. The results show that the only major increase in surface area was associated with stage III of the decomposition. Owing to the absence of the self-reduction reaction, no further increase in surface was observed, as had occurred in H_2 and He atmospheres. The X-ray results show that β-UO_3 was retained to at least 500°C. The DTA and TGA results indicate that U_3O_8 became the predominant phase at about 600°C but the X-ray results show that it was also formed as low as 500°C. The small peak, rapid loss of surface area, and absence of any indication of surface area increase associated with the conversion of $UO_{2.9}$ to U_3O_8 at 600°C, are indicative of the rapid sintering under these calcination conditions.

The X-ray results show that in air 'AU', β-UO_3 and $UO_{2.9}$ persisted to much higher temperatures than in hydrogen. The results also confirm previous observations that β-UO_3 decomposes between 525 and 550°C (Wheeler *et al.* 1964, Hoekstra & Siegel 1958), UO_3 'A' between 430 and 450°C (Wheeler *et al.* 1964), and $UO_{2.9}$ at 550°C (Wheeler *et al.* 1964). Amorphous UO_3 existed over a much wider temperature range in air.

3.3 Particle Morphology

Examination of calcined powders by electron microscopy confirmed the observations of Doi & Ito (1964) that the shape of the precipitate persists throughout calcination at temperatures below 600°C. In general, single particles showed only a very faint, or no selected area, electron diffraction pattern. Similarly, if an AU particle showing a strong electron diffraction pattern was heated by the electron beam, the pattern faded and disappeared after about 50 minutes. This would probably be associated with the disruption of the lattice during decomposition and the formation of amorphous material.

AU-platelets calcined below 600°C developed a mottled structure which Doi & Ito (1964) attributed to the formation of "minute holes in the elementary ADU-platelets". In the present work, detailed examination of individual platelets under the electron microscope revealed only a few isolated holes through the crystals, and showed that the mottled appearance was caused by internal porosity. The porosity developed during dehydration (stages I and II) and consisted initally of generally isolated pores of approximately circular cross section with a diameter of less than 100 Å. With increasing time and temperature, a network of porosity developed. The isothermal results (Figure 3) show that the surface area rapidly increased to a maximum without any significant decrease in X-ray crystallite size. The maximum surface area is also much greater than would be predicted from the particle or crystallite size. Therefore, it must be the opening up of this internal surface, possibly by cracking of the platelets due to internal stresses, which produced the rapid increase in the observed surface area. Conversely, the initial rapid collapse of the surface area peak without any significant changes in crystallite size must have been due to the sealing up of cracks and/or collapse of some of the porosity.

The observed changes in specific surface area were very similar irrespective of the calcination atmosphere (Figures 1, 6 and 7). Electron microscopy of the calcined powders also showed that the development of the internal porosity was not affected by the atmosphere. This common pattern of behaviour suggests a common mechanism. The surface area increased during stages I, II, IIIand IV. Thus, the cracking would not appear to be associated with one particular stage of decomposition, but rather to internal stresses resulting from the nucleation and growth of phases which have different specific volumes from that of the parent solid. However, the maximum stresses appeared to be generated during the self-reduction reaction (stage IV) since the increase in surface area was several times larger than that observed in the other stages or in the absence of the self-reduction reaction. No single phase appeared to be solely responsible for the cracking (Section 3.2).

The structure of AU consists of hexagonal or pseudohexagonal layers of composition $UO_2(O_2)_\infty$, with additional O and N atoms of water and ammonia between these layers (Debets & Loopstra 1963). The loss of H_2O and NH_3 during decomposition would promote the formation of a network of porosity between these layers. Both internal porosity and cracking have been observed during the decomposition of α-$UO_2(OH)_2$ (Rundle 1971) which has a closely related structure to that of AU. Similarly, Dollimore *et al.* (1973) reported a maximum in the surface area observed, during the calcination of uranyl oxalate, which they attributed to the development and eventual collapse of internal porosity.

After the initial collapse of the internal porosity, sintering and crystallite growth complicated the mechanism of surface area decrease. Above 600°C, sintering also caused neck formation between platelets as evidenced by the formation of stronger aggregates which became more difficult to disperse with ultrasonic treatment.

4. SUMMARY

The calcination of nitrate-containing AU initially proceeds by several overlapping stages similar to those observed in nitrate-free material. They occur irrespective of the atmosphere.

(a) Stages I and II (20 to 200°C) involve dehydration processes with AU 'type II' being the most stable in the presence of moisture. The observed specific surface area initially decreases but begins to increase again above 100°C.

(b) Stage III (200 to 350°C) involves decomposition of the AU to form UO_3 'A' and β-UO_3 which retain some ammonia in their structure. Complete disruption of the lattice occurs. Any nitrate present also decomposes. A significant increase in surface area is observed during this stage.

(c) Stage IV (350 to 450°C) is a process of self-reduction by ammonia retained in the lattice of the solid to produce U_3O_8 and U_4O_9. The specific surface area reaches a maximum during this stage.

Reduction in a hydrogen atmosphere takes place over the temperature range 450 to 510°C, forming UO_2. Any associated increase in specific surface area is completely masked by the rapid loss in surface area due to sintering.

In an atmosphere of helium, β-UO_3 and $UO_{2.9}$ persist to much higher temperatures due to the absence of any reduction associated with the calcination atmosphere. The observed specific surface area peaks earlier, and the rate of loss due to sintering is faster.

In air 'AU', β-UO_3 and $UO_{2.9}$ persist to much higher temperatures, as air tends to reduce the amount of ammonia retained in the lattice and may prevent subsequent self-reduction. There is also no reduction associated with the calcination atmosphere. Amorphous UO_3 exists over a much wider temperature range. The observed specific surface area peak is smaller with a subsequent rapid loss due to sintering.

The observed increase in specific surface area is due to the opening up of internal porosity, formed during decomposition, by stress-induced cracking of the platelets. These internal stresses are generated by the nucleation and growth of phases which have different specific volumes from that of the parent solid. The maximum surface area was observed if self-reduction occurred.

5. ACKNOWLEDGEMENTS

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TABLE 1

PROPERTIES OF AU POWDERS

Property	Precipitation pH	
	7.1	8.6
NH_3/UO_3	0.728	0.705
NO_3/UO_3	0.192	0.140
Surface area (m^2g^{-1})	9.3	18.3
X-ray crystallite size (Å)	202	195
Particle size (μm)	0.1-0.01	0.1-0.01
X-ray composition type*	III *(M)*, IV *(M)*	III *(M)*, IV *(M)*

M *major*

* *Cordfunke's (1962) AU compound nomenclature is used.*

TABLE 2

EFFECT OF TEMPERATURE AND ATMOSPHERE ON THE PRODUCTS FORMED DURING THE HEATING AT 5°C min^{-1} OF AN AU PRECIPITATED AT pH 8.6

Temperature (°C)	Atmosphere		
	Hydrogen	Helium	Air
20	AU 'III, IV' (M)	AU 'III, IV' (M)	AU 'III, IV' (M)
100	AU 'II, III, IV' (M), $UO_3.2H_2O$ (M)	n.a.	AU 'II' (M), AU 'III, IV' (Mi), $UO_3.2H_2O$ (Mi)
200	AU 'II' (M), $UO_3.2H_2O$ (M), AU 'III, IV' (Mi)	n.a.	AU 'II' (M), $UO_3.2H_2O$ (M), AU 'III, IV' (Mi), $UO_3.0.8H_2O$ (Mi)
300	AU 'II' (M), $UO_3.2H_2O$ (M), AU 'III, IV' (Mi), β-UO_3 (Mi), $UO_3.0.8H_2O$ (VMi)	n.a.	AU 'II' (M), $UO_3.2H_2O$ (M), AU 'III, IV' (Mi), β-UO_3 (Mi)
350	UO_3 'A' (M), β-UO_3 (Mi), 'AU' (VMi)	UO_3 'A' (M), β-UO_3 (M), 'AU' (Mi)	β-UO_3 (M), $UO_3.2H_2O$ (M), AU 'II' (M), AU 'III, IV' (Mi)
400	'$UO_{2.9}$-U_3O_8' (M)*	n.a.	UO_3 'A' (M), β-UO_3 (Mi), '$UO_{2.9}$-U_3O_8' (VMi)*, 'AU' (VMi)
450	U_4O_9 (M), U_3O_8 (VMi)	n.a.	UO_3 'A' (M), β-UO_3 (Mi), '$UO_{2.9}$-U_3O_8' (Mi)*, 'AU' (VMi)
500	U_4O_9 (M), U_3O_8 (VMi)	β-UO_3 (M), U_3O_8 (Mi), 'AU' (VMi)	U_3O_8 (M), $UO_{2.9}$ (Mi), β-UO_3 (VMi), 'AU' (VMi)
550	U_4O_9 (M), U_3O_8 (VMi)	U_3O_8 (M), $UO_{2.9}$ (Mi)	U_3O_8 (M), $UO_{2.9}$ (Mi)
600	UO_{2+x} (M)**	U_3O_8 (M)	U_3O_8 (M)
650	UO_{2+x} (M)**	U_3O_8 (M)	U_3O_8 (M)

n.a. *not available.*

M *major.*

Mi *minor.*

VMi *very minor.*

* '$UO_{2.9}$-U_3O_8' *has d-spacings intermediate between* $UO_{2.9}$ *and* U_3O_8.

** UO_{2+x} *with* $x < 0.25$.

'AU' shows only a few major AU peaks with considerable displacement.

UO_3 *'A' is the so-called amorphous* UO_3.

TABLE 3

EFFECT OF TIME AND TEMPERATURE ON THE PRODUCTS FORMED DURING THE ISOTHERMAL CALCINATION IN HYDROGEN OF AN AU PRECIPITATED AT pH 7.1

Time (Min)	Temperature (°C)		
	325	400	500
2	*n.a.*	*n.a.*	UO_{2+x} *(M)***
5	β-UO_3 *(M)*, 'AU' *(Mi)*	U_3O_8 *(M)*, UO_{2+x} *(VMi)**	UO_{2+x} *(M)***
15	β-UO_3 *(M)*, 'AU' *(Mi)*	U_3O_8 *(M)*, UO_{2+x} *(VMi)**	UO_{2+x} *(M)***
17.5	*n.a.*	U_3O_8 *(M)*, UO_{2+x} *(Mi)**	*n.a.*
20	*n.a.*	U_3O_8 *(M)*, UO_{2+x} *(Mi)**	*n.a.*
25	*n.a.*	U_4O_9 *(M)*, U_3O_8 *(Mi)*	*n.a.*
30	β-UO_3 *(M)*, 'AU' *(Mi)*	U_4O_9 *(M)*, U_3O_8 *(Mi)*	UO_{2+x} *(M)***
45	β-UO_3 *(M)*, 'AU' *(Mi)*	U_4O_9 *(M)*, U_3O_8 *(VMi)*	UO_{2+x} *(M)***
50	β-UO_3 *(M)*, 'AU' *(Mi)*	*n.a.*	*n.a.*
51	β-UO_3 *(M)*, UO_3 'A' *(Mi)*, 'AU' *(Mi)*	*n.a.*	*n.a.*
52.5	U_3O_8 *(M)*, β-UO_3 *(Mi)*, 'AU' *(VMi)*	*n.a.*	*n.a.*
55	U_3O_8 *(M)*, β-UO_3 *(VMi)*, 'AU' *(VMi)*	*n.a.*	*n.a.*
60	U_3O_8 *(M)*, β-UO_3 *(VMi)*, 'AU' *(VMi)*	U_4O_9 *(M)*, U_3O_8 *(VMi)*	UO_{2+x} *(M)***
70	U_3O_8 *(M)*, β-UO_3 *(VMi)*, 'AU' *(VMi)*	*n.a.*	*n.a.*

n.a. *not available.*
M *major.*
Mi *minor.*
VMi *very minor.*
* UO_{2+x} *where* $x > 0.25$.
** UO_{2+x} *where* $x < 0.25$.
'AU' *shows only a few major AU peaks with considerable displacement.*

TABLE 4

EFFECT OF TEMPERATURE ON THE PRODUCTS FORMED DURING THE ISOCHRONAL CALCINATION IN HYDROGEN FOR 60 MINUTES OF AN AU PRECIPITATED AT pH 7.1

Temperature (°C)	Product
200	'AU' *(M)*, $UO_3.0.8H_2O$ *(M)*
300	'AU' *(M)*, β-UO_3 *(Mi)*
325	U_3O_8 *(M)*, β-UO_3 *(VMi)*, 'AU' *(VMi)*
350	U_3O_8 *(M)*, UO_{2+x} *(Mi)**
400	U_4O_9 *(M)*, U_3O_8 *(Mi)*
500	UO_{2+x} *(M)***
600	UO_{2+x} *(M)***

M *major.*
Mi *minor.*
VMi *very minor.*
* UO_{2+x} *where* $x > 0.25$.
** UO_{2+x} *where* $x < 0.25$.
'AU' *shows only a few major AU peaks with considerable displacement*

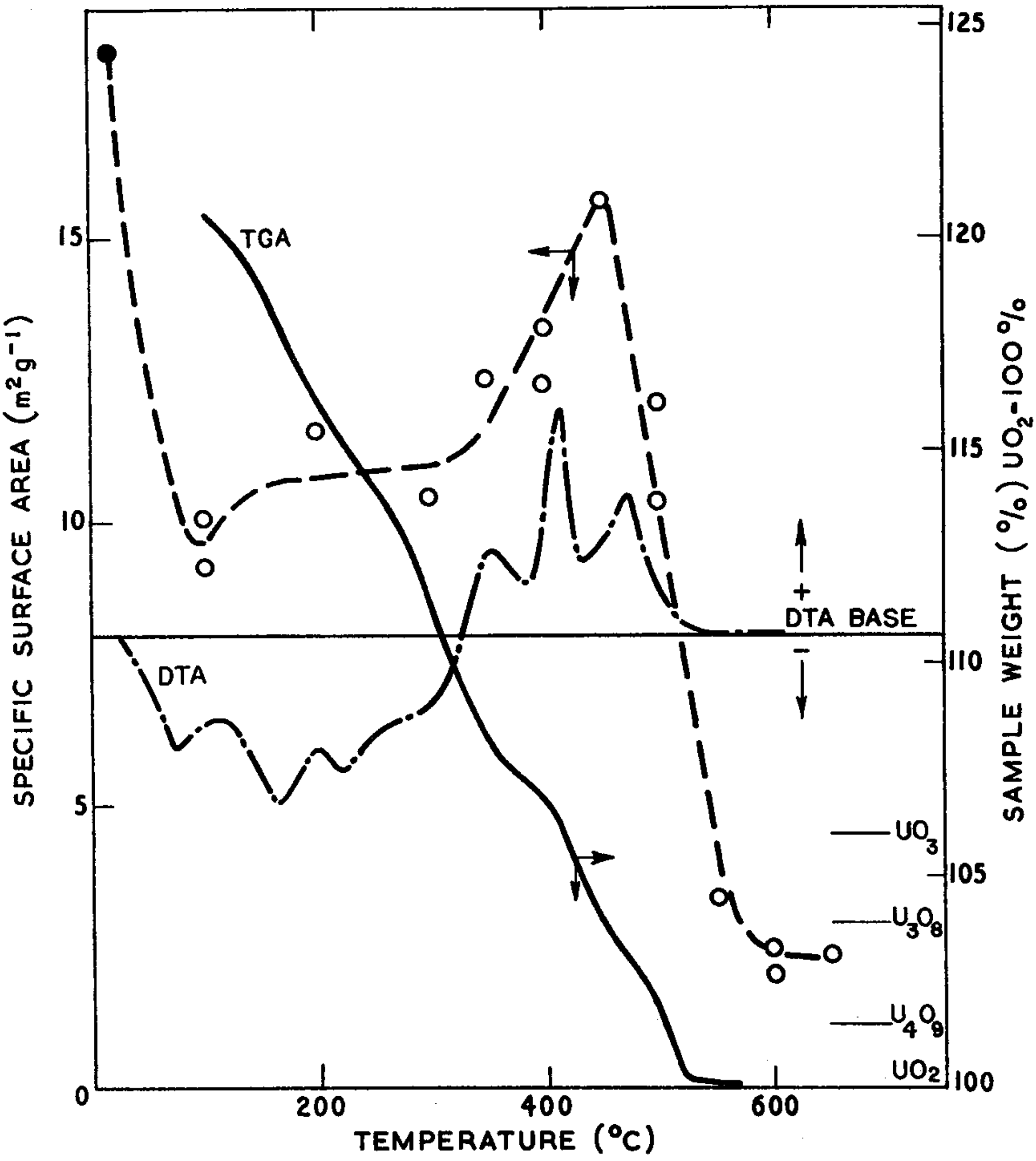

FIGURE 1. TGA AND DTA TRACES WITH OBSERVED SPECIFIC AREA FOR AN AU PRECIPITATED AT pH 8.6, HEATED AT 5°C min^{-1} IN HYDROGEN

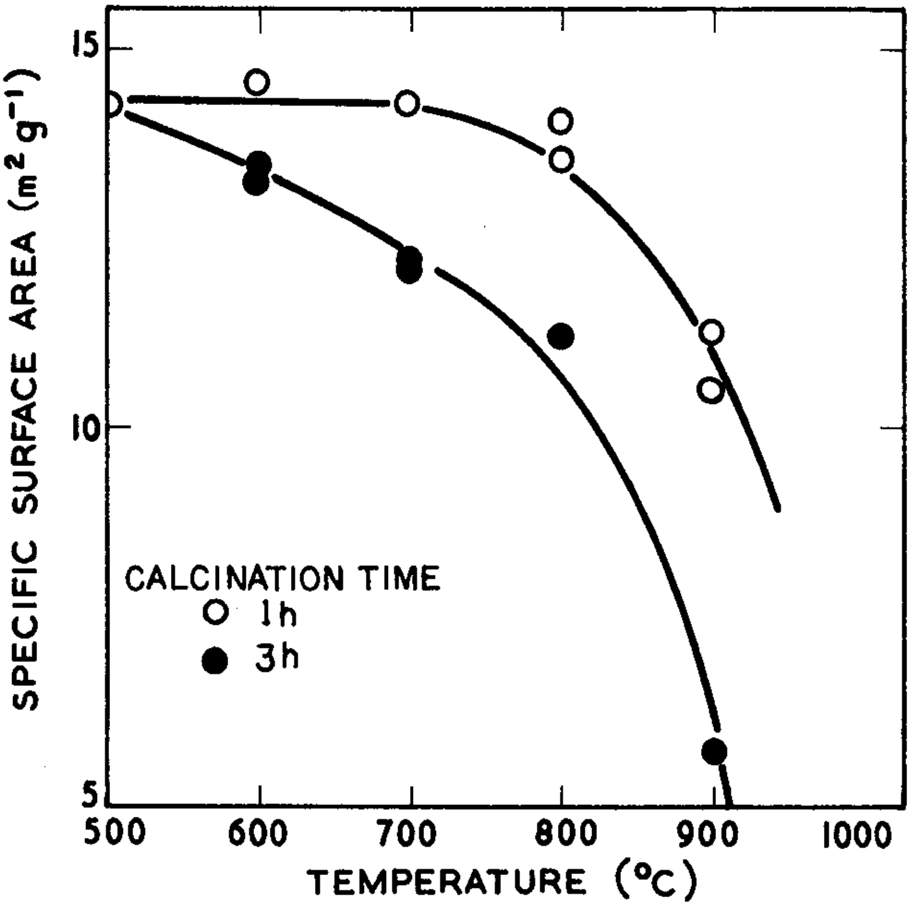

FIGURE 2. OBSERVED SPECIFIC SURFACE AREA FOR AN AU
PRECIPITATED AT pH 7.1, REDUCED AT 500°C
FOR 60 MINUTES IN HYDROGEN AND
RECALCINED AT TEMPERATURE

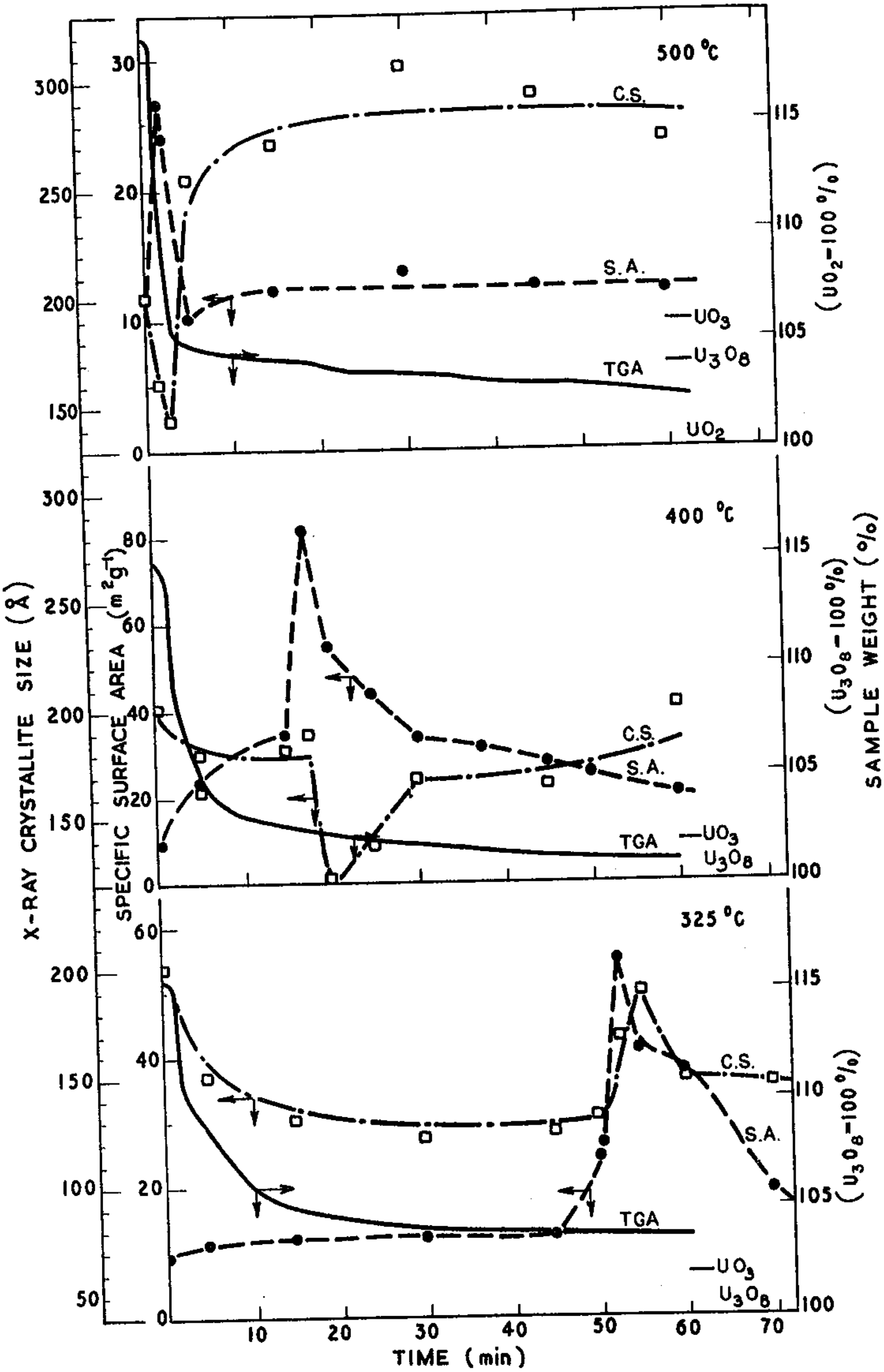

FIGURE 3. TGA TRACE, OBSERVED SPECIFIC AREA AND X-RAY CRYSTALLITE SIZE FOR AN AU PRECIPITATED AT pH 7.1, CALCINED ISOTHERMALLY IN HYDROGEN

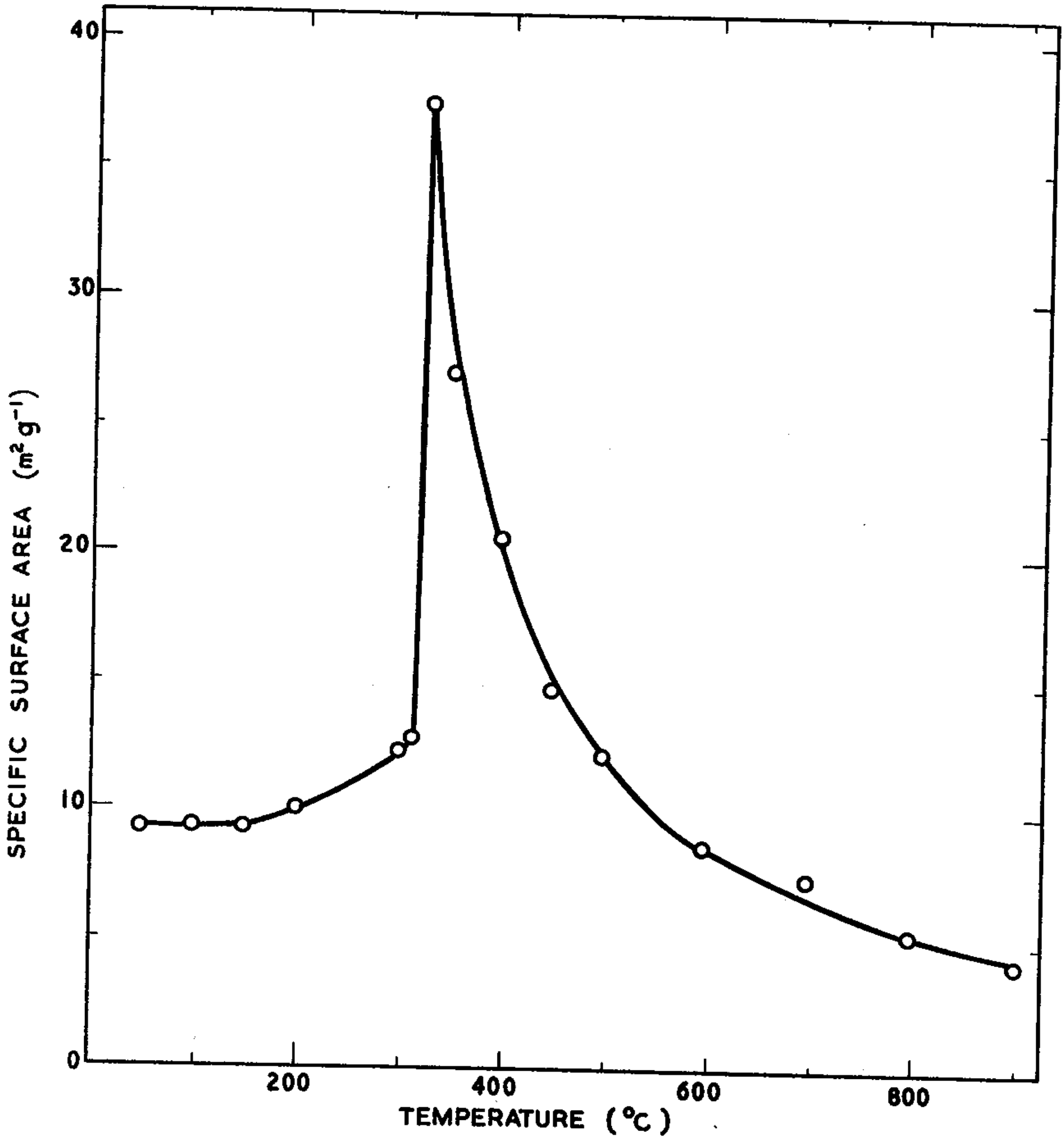

FIGURE 4. THE EFFECT OF TEMPERATURE ON THE OBSERVED SPECIFIC SURFACE AREA FOR AN AU PRECIPITATED AT pH 7.1, HEATED ISOCHRONALLY FOR 60 MINUTES IN HYDROGEN

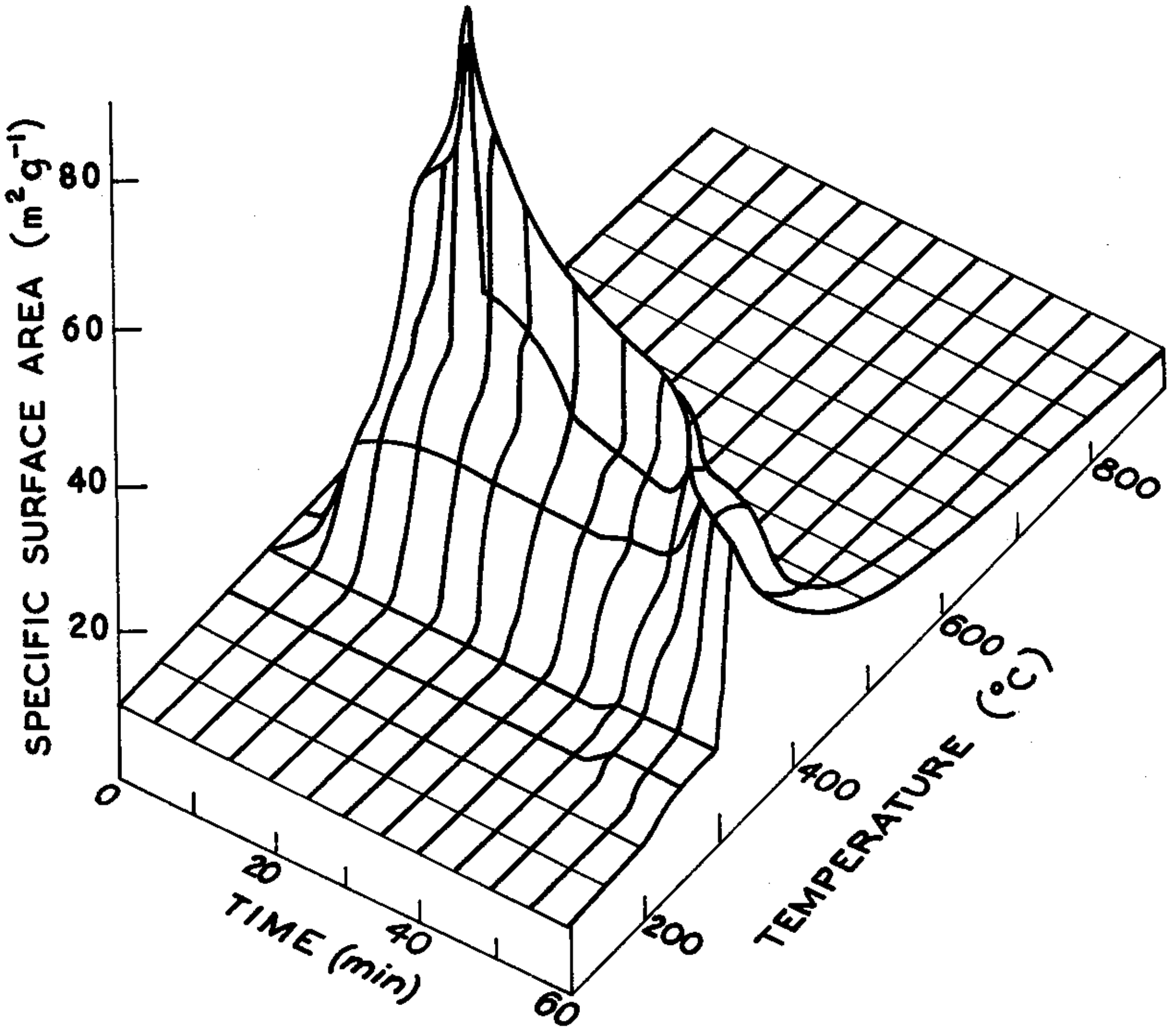

FIGURE 5. THE EFFECT OF TIME AND TEMPERATURE ON THE OBSERVED SPECIFIC SURFACE AREA FOR AN AU PRECIPITATED AT pH 7.1, CALCINED ISOTHERMALLY IN HYDROGEN

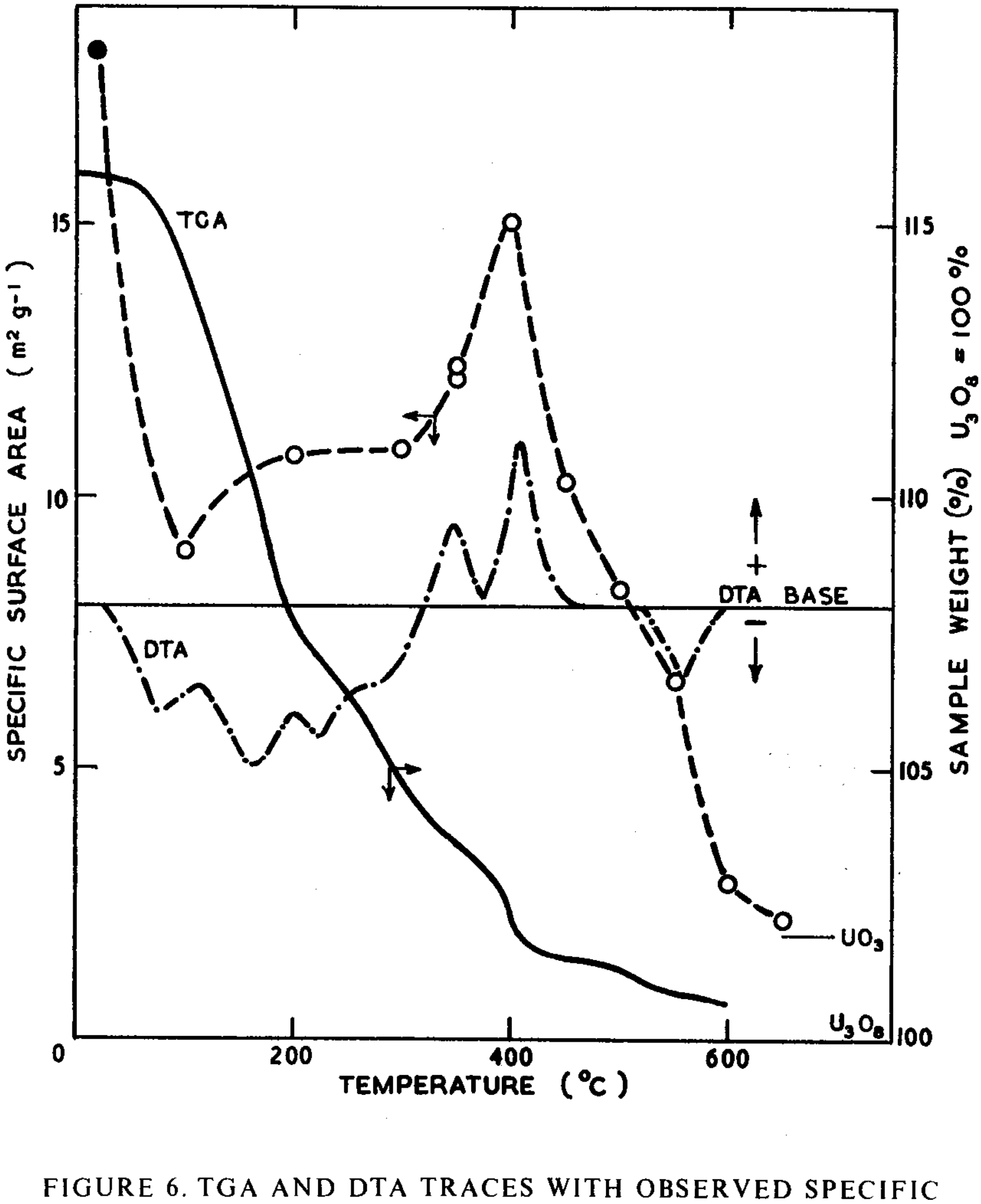

FIGURE 6. TGA AND DTA TRACES WITH OBSERVED SPECIFIC SURFACE AREA FOR AN AU PRECIPITATED AT pH 8.6, HEATED AT 5°C min^{-1} IN HELIUM

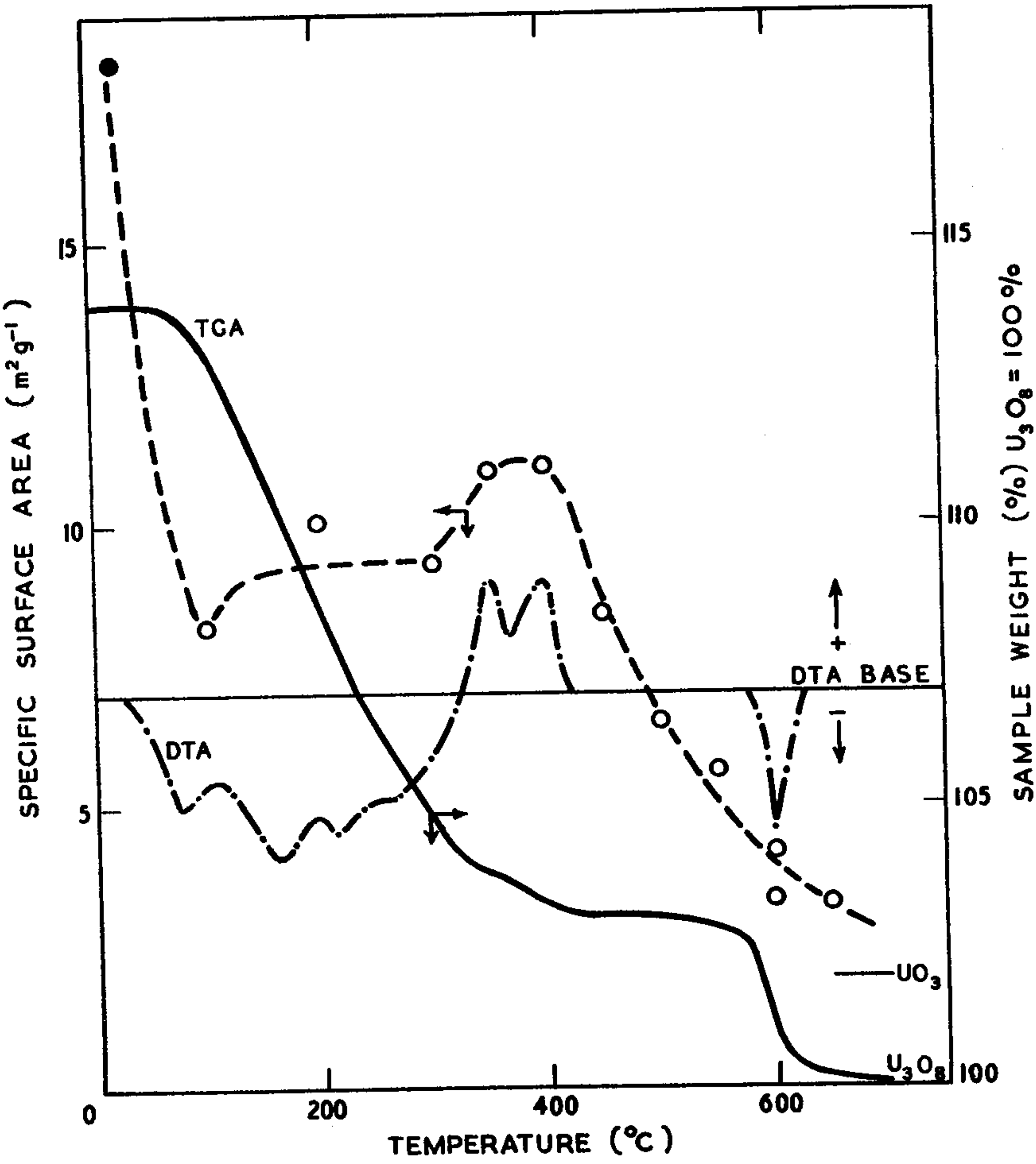

FIGURE 7. TGA AND DTA TRACES WITH OBSERVED SPECIFIC SURFACE AREA FOR AN AU PRECIPITATED AT pH 8.6, HEATED AT 5°C min^{-1} IN AIR