The Thermal Stability of Calcium Uranates in a Hydrogen Atmosphere

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The stability and decomposition of $CaUO_4$, Ca_2UO_5, and Ca_3UO_6 on heating in hydrogen were investigated by X-ray powder diffraction and thermogravimetry. Ca_2UO_5 decomposes at 450°C into $Ca_2UO_{4.5}$ with a triclinic unit cell. At 850°C, it changes to monoclinic $Ca_2(Ca_{0.67}U_{0.33})UO_6$ which loses some oxygen up to the composition $Ca_2(Ca_{0.67}U_{0.33})UO_{5.83}$. At 1100°C, it decomposs to UO_2 solid solution and CaO. $CaUO_4$ decomposes at 900°C to $Ca_2(Ca_{0.67}U_{0.33})UO_{5.83}$ and CaU_2O_6. The decomposition products of Ca_3UO_6 at 850°C are $Ca_2(Ca_{0.67}U_{0.33})UO_{5.83}$ and CaO.

Introduction

The stability of compounds in the system UO_3–UO_2–CaO at elevated temperature in a reducing atmosphere is not known in detail. The most abundant data are found for $CaUO_4$, with a rhombohedral structure (*1*). It was reported that $CaUO_4$ could be reduced to $CaUO_{3.5}$ with only a slight increase in unit cell dimensions; this was interpreted as a loss of the O^{2-} ions at random from the lattice, with a corresponding change of U (6+) into U (5+) (*2*). However, the agreement between the literature data is poor (*3–5*). Ca_2UO_5 and Ca_3UO_6 crystallize in monoclinic forms (*6, 7*) but little is known of their stability. It has been reported that Ca_2UO_5 decomposes in air to Ca_3UO_6 and $CaUO_4$ (*4*). In vacuo, Ca_3UO_6 decomposes at 1500°C to UO_2 solid solution and CaO (*3*). It was observed that in oxygen Ca_2UO_5 and Ca_3UO_6 remained stoichiometric up to their decomposition temperatures (*8*).

The present investigations were undertaken to determine the thermal stability and decomposition products of $CaUO_4$, Ca_2UO_5, and Ca_3UO_6 in reducing atmospheres.

Experimental

Starting materials for preparation of $CaUO_4$, Ca_2UO_5, and Ca_3UO_6 were $CaCO_3$ (Merck, extra pure, 99%) and U_3O_8 (nuclear grade). Appropriate proportions of powdered materials were mixed under alcohol, dried, and pressed into pellets. Samples were calcined at 1250°C in oxygen for prolonged periods with intermittent cooling, crushing, mixing, and pressing to ensure homogeneity. X-ray analysis confirmed the presence of pure compounds only.

The compounds obtained in this way were reduced in hydrogen. Hydrogen from a cylinder was passed only through a Deoxo purifier (Heraeus type D). The oxygen

partial pressure was determined by a $ZrO_2/$CaO galvanic cell, taking air as standard. A water content of 0.1 vol% in hydrogen was calculated from the equilibrium $H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2$.

The change in stoichiometry of the compounds during reduction was investigated on a quartz helix thermobalance capable of registering mass changes of 0.3 mg. Samples, weighing 2–2.5 g, were heated in steps of 50°C.

X-ray powder patterns were obtained on quenched samples. Samples were quenched by rapidly removing them from the hot zone of the furnace to the end of a water cooled tube. A Geiger counter diffractometer using Ni-filtered $CuK\alpha$ radiation at a scanning rate of 1° 2θ min^{-1} was used to obtain structural data. The 2θ values were calibrated against the known peaks of pure Au. For qualitative X-ray analysis, a Guinier–de Wolf Nonius camera was used to scan the region 0–45°.

The density was measured by displacement of hexane in an evacuated pycnometer, with a precision of ±0.05 g/cm³.

Results and Discussion

On heating Ca_2UO_5 in wet hydrogen, no detectable weight change was observed up to 450°C. At this temperature, a partial reduction of the sample occurred and the composition changed to $Ca_2UO_{4.5}$. This composition remained stable up to 850°C. With increasing temperature a slow, continuous weight loss was observed again. At 1050°C, the sample composition calculated from the thermogravimetric data corresponded to $Ca_2UO_{4.37}$. With a further increase in temperature, considerable weight loss occurred; the sample composition at 1100°C corresponded to $Ca_2UO_{4.1}$ (Fig. 1).

X-ray analysis of samples heated at various temperatures indicated changes in crystal structure at 450°C, 850°C, and close to 1100°C. Up to 450°C, X-ray reflections of Ca_2UO_5 were in accordance with the reported monoclinic structure (6).

A triclinic unit cell was determined for the $Ca_2UO_{4.5}$ compound. The following cell parameters were calculated from the X-ray reflections by the least squares method (11): $a = 22.98$ (1) Å, $b = 9.312$ (4) Å, $c = 10.712$ (4), $\alpha = 54.89$ (5)°, $\beta = 76.54$ (5)°, $\gamma = 82.17$ (6)°. The measured d_{hkl} together with the calculated d and the corresponding indices are shown in Table I.

Assuming 16 formula units in the unit cell, the calculated X-ray density of $D_c = 5.68$ g/cm³ agrees very well with the measured density of $D_m = 5.60$ g/cm³. The choice of this unit cell was also confirmed by a preliminary electron diffraction study,

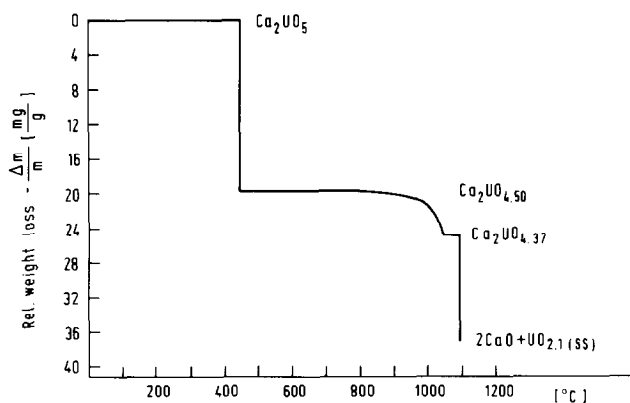FIG. 1. TG curves of Ca_2UO_5 reduction.

TABLE I

X-Ray Powder Diffraction Data for $Ca_2UO_{4.5}$

$h\,k\,l$	d_{cal}	d_{obs}	I/I_0
4 0 0	5.587	5.58	45
3 1 2	4.829	4.82	86
$\underline{1}$ 0 2	4.381	4.38	9
$\bar{4}$ 1 1	4.318	4.32	5
2 2 0	3.608	3.605	49
1 $\bar{1}$ 2	3.104	3.100	100
$\bar{2}$ 1 4	3.055	3.056	85
8 0 0	2.794	2.795	8
$\bar{3}$ 3 2	2.711	2.712	34
3 2 $\bar{1}$	2.667	2.667	45
$\bar{3}$ 3 3	2.516	2.517	5
3 3 0	2.406	2.410	12
0 1 $\bar{3}$	2.291	2.291	4
10 1 0	2.146	2.147	17
1 3 5	2.100	2.100	6
7 1 $\bar{2}$	2.079	2.079	16
10 0 $\bar{1}$	2.069	2.068	12
$\bar{6}$ 2 4	1.933	1.933	11
0 4 0	1.904	1.906	12
$\bar{4}$ 4 4	1.887	1.888	41
6 2 $\bar{2}$	1.866	1.868	9
1 3 $\bar{2}$	1.772	1.773	9
$\bar{3}$ 5 1	1.617	1.617	18
1 1 6	1.600	1.600	13
6 3 $\bar{2}$	1.566	1.566	6
2 $\bar{2}$ 4	1.552	1.552	9
15 1 2	1.530	1.532	5
2 2 $\bar{4}$	1.496	1.497	3
$\bar{5}$ 1 6	1.400	1.400	6
2 5 $\bar{1}$	1.358	1.358	2

although it seems that structural relationships between the product structure and the original structure are more complex. A more detailed account of this study will be published in a forthcoming paper.

As determined from X-ray analysis of quenched samples, at 850°C $Ca_2UO_{4.5}$ undergoes an irreversible transformation to $Ca_2(Ca_{0.67}U_{6.33})UO_6$ (9). The stoichiometry with regard to oxygen remains the same. This perovskite phase reduces further to $Ca_2(Ca_{0.67}U_{0.33})UO_{5.83}$. The reduction is very slow, the kinetics of this process depending on the surface area of the specimen. It was found that samples which are

not densely sintered reduce more rapidly.

When the perovskite phase has heated over 1100°C it decomposes to UO_2 solid solution and CaO regardless of the stoichiometry. Kemmler-Sack et al. (9) obtained the perovskite phase $Ca_2(Ca_{0.67}U_{0.33})UO_6$ from a mixture of $CaCO_3$ and $UO_2(NO_3)_2$ which was heated first in air at 600–700°C and then in wet hydrogen at a temperature up to 1100°C.

In the $Ca_2(Ca_{0.67}U_{0.33}^{4+})U^{5+}O_{5.83}$ phase one quarter of the uranium atoms are in the 4+ valent state. A perovskite phase with this ratio of uranium valences is known: $\frac{2}{3}Ca^{2+}$ is replaced by RE^{3+}, as for example in $Ba_2(RE_{0.67}U_{0.33}^{4+})U^{5+}O_{6.17}$ (10). The X-ray pattern of the perovskite phase $Ca_2(Ca_{0.67}U_{0.33}$ was evaluated similarly. Experimental data together with the calculated values and indices are shown in Table II. A monoclinic unit cell with parameters $a = 5.765$ (2) Å, $b = 5.965$ (3) Å, $c = 8.348$ (3) Å, $\beta = 90.21$ (3)° was determined. Assuming 2 formula units in the unit cell, the calculated X-ray density $D_c = 5.89$ g/cm³ compares fairly well with the measured value of $D_m = 5.70$ g/cm³. Practically the same data ($a = 5.767$ Å, $b = 5.974$ Å, $c = 8.349$ Å and $\beta = 89.8°$) were reported by Kemmler-Sack (9) for the perovskite compound $Ca_2(Ca_{0.67}U_{0.33}^{5+})UO_6^{5+}$.

This means that in the compound $Ca_2(Ca_{0.67}U_{0.33})UO_6$ a quarter of the U^{5+} ions can be reduced to U^{4+} without change in the cell dimensions.

On heating above 1100°C in wet hydrogen, the perovskite phase decomposes with further reduction of uranium. The X-ray powder pattern showed the presence of UO_2 solid solution and CaO.

$CaUO_4$ was found to be stable on heating in hydrogen up to 300°C. With increasing temperature, weight loss was detected. Compositions, calculated from weight changes, were $CaUO_{3.57}$ at 450°C and $CaUO_{3.5}$ at 650°C. The weight remained stable up to 900°C. These results are in agree-

TABLE II

X-Ray Powder Diffraction Data for
$Ca_2(Ca_{0.67}U_{0.33})UO_{6-0.17}$

h k l	d_{cal}	d_{obs}	I/I_0
0 1 $\bar{1}$	4.853	4.86	25
1 0 $\bar{1}$	4.752	4.76	15
1 0 1	4.735	4.74	15
0 0 2	4.174	4.19	80
1 1 0	4.145	4.15	80
0 2 0	2.982	2.98	36
1 1 $\bar{2}$	2.945	2.95	100
1 1 2	2.931	2.94	100
2 0 0	2.880	2.88	26
1 2 $\bar{1}$	2.526	2.52	10
1 0 3	2.502	2.50	8
2 1 $\bar{1}$	2.481	2.48	7
0 2 2	2.427	2.424	12
2 0 $\bar{2}$	2.376	2.375	9
2 0 2	2.368	2.367	7
0 0 4	2.087	2.084	15
2 2 0	2.073	2.075	35
1 3 0	1.880	1.880	13
1 1 4	1.862	1.864	13
2 2 $\bar{2}$	1.858	1.859	22
2 2 2	1.854	1.854	20
3 1 0	1.829	1.829	9
1 3 2	1.713	1.714	21
1 3 $\bar{2}$	1.715		
0 2 $\bar{4}$	1.710	1.709	27
0 2 4	1.710		
2 0 $\bar{4}$	1.693	1.693	7
2 0 4	1.687	1.688	10
3 1 $\bar{2}$	1.677	1.678	16
0 0 5	1.670	1.672	21
3 1 2	1.673		
3 2 1	1.585	1.585	2
0 4 0	1.491	1.492	7
2 2 $\bar{4}$	1.473	1.472	8
2 2 4	1.469	1.467	10
0 4 1	1.468		
2 2 4	1.469		
2 0 5	1.442	1.442	5
2 1 5	1.402	1.404	5
1 3 4	1.396	1.396	7

ment with the results reported by Tagawa (5), who observed that on heating in hydrogen with a heating rate of 2°C/min $CaUO_4$ was reduced to $CaUO_{3.55}$ and to $CaUO_{3.5}$ at 750°C.

The stoichiometry of the quenched re-

duced samples of $CaUO_4$ was redetermined after heating by oxidation of samples at 700°C in the oxygen. It has been stated that samples with stoichiometry lower than $CaUO_{3.57}$ oxidize quickly in air to form $CaUO_{3.8}$.

Gunier X-ray powder diffraction showed no line shifting for samples with stoichiometry greater than $CaUO_{3.57}$.

A phase change was detected above 900°C. At this temperature $CaUO_{3.5}$ decomposes to the perovskite compound Ca_2 $(Ca_{0.67}U_{0.33})UO_{6-x}$ and $CaU_2O_{6\pm y}$. Above 1100°C, the compounds decompose to UO_2 solid solution and CaO.

The structure of Ca_3UO_6 was also found to remain stable on heating in hydrogen up to 850°C. At this temperature, the composition of the sample was $Ca_3UO_{5.87}$. Guinier X-ray diffraction patterns of $Ca_3UO_{5.87}$ showed no line shifts compared to Ca_3UO_6.

Above 850°C, $Ca_3UO_{5.87}$ decomposes to $Ca_2(Ca_{0.67}U_{0.33})UO_{5.83}$ and CaO. The presence of the reduced perovskite compound $Ca_2(Ca_{0.67}U_{0.33})UO_{5.8}$ at 850°C confirms the thermodynamic stability of this phase.

Decomposition of $CaUO_4$, Ca_2UO_5, and Ca_3UO_6 on heating in hydrogen can be summarized schematically follows.
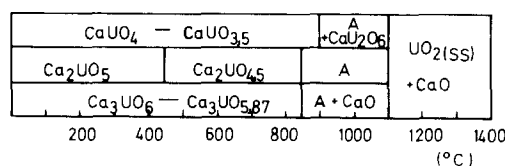
$A = Ca_2(Ca_{0.67} U_{0.33}^{IV}) U^V O_{6-0.17}$

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