



## Study on the Formation of Cs-U-O from the Reaction between Cs<sub>2</sub>O and UO<sub>2</sub>†

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Reactions between UO<sub>2</sub> and Cs<sub>2</sub>O in various Cs/U compounds (atom ratios: 0.5~3.0) were investigated in a temperature range of 30 to 1100 °C using a thermogravimetric analyzer and differential scanning calorimeter. The formation of Cs-U-O was determined by the appearance of exothermic peaks at 186 °C and 240 °C in differential scanning calorimeter and weight loss depending on the Cs/U ratio from 200 °C to 250 °C and from 610 °C to 710 °C when using a TGA. By chemical analysis, it was determined that the formation of Cs-U-O increased linearly with the Cs/U ratio. From X-ray diffractometer measurements, diffraction patterns of Cs<sub>2</sub>UO<sub>4</sub> and Cs<sub>2</sub>U<sub>2</sub>O<sub>7</sub> were observed when heated to 500 °C and 1100 °C, respectively.

**Key Words:** UO<sub>2</sub>, Cs<sub>2</sub>O, Formation of Cs-U-O, TGA-DSC, XRD.

### INTRODUCTION

Cs-U-O compounds (cesium uranates) have been observed at the periphery of irradiated nuclear fuels by scanning electron microscopy and electron probe micro analysis mapping of Cs and U<sup>1</sup>. Cs-U-O compounds were generally found at the region where local burnup increased strongly. Furthermore, the fuel chemistry of Cs-U-O has become a matter of concern because of the current trend of high burnup operations of power plants. According to a report concerning the chemistry of the fuel periphery of UO<sub>2</sub>, Cs<sub>2</sub>UO<sub>4</sub> was synthesized to investigate the properties of Cs-U-O through reactions between cesium oxides or carbonate and U<sub>3</sub>O<sub>8</sub> or UO<sub>3</sub>, where the oxidation state of U was high<sup>2</sup>. In this work, as a different trial, reactions using UO<sub>2</sub> as a reactant against Cs<sub>2</sub>O were traced for samples of various Cs/U compounds (atom ratio) by measuring the weight variance and heat flow using TGA and DSC. Through chemical analysis and XRD measurements, the extent of the formation of Cs-U-O and the patterns of phases for the samples from the reactions were obtained.

### EXPERIMENTAL

**Preparation of the samples for the reaction between Cs<sub>2</sub>O and UO<sub>2</sub>:** UO<sub>2</sub> powder, which was ground well with an agate mortar, was used and particle sizes of the UO<sub>2</sub> powder were observed to be within the range of 2 to 5 μm by SEM.

Cs<sub>2</sub>O was a product of the supplier (Aldrich, metallic impurities < 1 %). The calculated amounts of Cs<sub>2</sub>O and UO<sub>2</sub> were ground and blended thoroughly in an agate mortar to give a certain Cs/U (atom ratio) value in which the Cs/U compounds ranged from 0.5 to 3. Because of the high hygroscopic property of Cs<sub>2</sub>O, the above works were all conducted in a grove box and the humidity was controlled at 0 %.

#### Measurement of the reaction between Cs<sub>2</sub>O and UO<sub>2</sub>:

The thermal properties, *i.e.*, the weight variance and heat flow during heating from 30 to 1100 °C, for the blended samples of various Cs/U compounds (0.5, 1.0, 1.5, 2.0, 2.5 and 3.0), which were prepared as described above, were measured using TGA-DSC (Scinco 1500) in a continuous argon flow and at a heating rate of 5 °C/min.

**Determination of the formation extent of Cs-U-O by chemical analysis:** Cs-U-O compounds dissolve well in an aqueous solution of approximately pH 2. However, UO<sub>2</sub> does not dissolve as well in this type of solution. The samples that were heated during the TGA-DSC measurement were treated using a pH-2 solution to dissolve and separate the U ions from unreacted UO<sub>2</sub>. Additionally, the concentrations of uranium ion that were dissolved in the pH-2 solution were determined using an inductively coupled plasma-atomic emission spectrometer (ICP-AES) and corresponded to the extent of the formation of Cs-U-O that was produced through the reaction between Cs<sub>2</sub>O and UO<sub>2</sub>.

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**Phase characterization:** To obtain phase information on the Cs-U-O that was formed through the reaction, the sample of Cs/U=2 that was heated during the TG-DSC was measured using a Siemens D5000 X-ray diffractometer with a scanning step of 0.02° for 10 s at each count in the range of 15° to 90°.

## RESULTS AND DISCUSSION

### Measurement of the reaction between Cs<sub>2</sub>O and UO<sub>2</sub>:

The heat flow curves from DSC for the blended samples of various Cs/U compounds are shown in Fig. 1 and they include those for each of the individual reactants, Cs<sub>2</sub>O and UO<sub>2</sub>, for a comparison with the blended samples. In Fig. 1, a common exothermic peak near 186 °C for all blended samples and an exothermic peak near 240 °C for the samples with higher Cs/U ratios than 2 are shown. However, only the endothermic peaks at 186 °C and 244 °C for the Cs<sub>2</sub>O sample disappear. The disappearance of the peaks at 186 °C and 244 °C (for only the Cs<sub>2</sub>O sample) and the appearance of the peaks near 186 °C and 240 °C (for all blended samples) in Fig. 1 could be evidence for the formation of Cs-U-O through the reaction between Cs<sub>2</sub>O and UO<sub>2</sub>. However, the exact interpretation for each individual peak in connection with the reaction process of Cs<sub>2</sub>O and UO<sub>2</sub> is not simple because the reaction between Cs<sub>2</sub>O and UO<sub>2</sub> is not currently well understood.

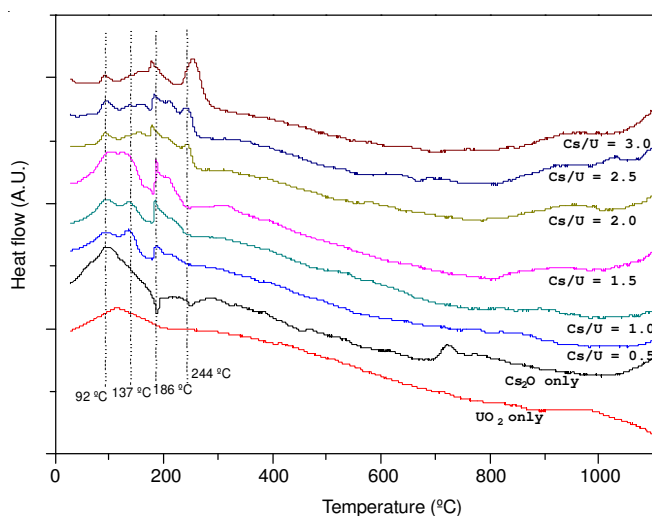


Fig. 1. Heat flow curves of DSC measurements for the reaction between Cs<sub>2</sub>O and UO<sub>2</sub>

Fig. 2 shows thermogravimetric curves for the blended samples of various Cs/U compounds and for each of the individual reactants, Cs<sub>2</sub>O and UO<sub>2</sub>. The first interesting aspect in Fig. 2 is the curve for only Cs<sub>2</sub>O. This curve shows a slight weight loss in the region from 200 to 300 °C and remarkable weight loss from 610 to 710 °C. According to previous literature<sup>3</sup>, the first, slight weight loss should be caused by evaporation of Cs<sub>2</sub>O and the cause of the large weight loss should be evaporation of Cs<sub>2</sub>O<sub>2</sub> (b.p., 650 °C) and Cs (b.p., 669.3 °C), which are the decomposed products of Cs<sub>2</sub>O through the equation,  $2 \text{Cs}_2\text{O} \rightarrow 2\text{Cs} + \text{Cs}_2\text{O}_2$  at temperatures above 400 °C. The thermogravimetric curves for the blended samples show comparable shapes in some aspects to that for only Cs<sub>2</sub>O. First, the slight weight loss for the blended samples occurs

from 200 to 250 °C, which is a shorter temperature interval compared to that for only Cs<sub>2</sub>O, which ranges from 200 to 300 °C. Additionally, if the temperature interval from 200 to 250 °C for slight weight loss, as seen in Fig. 2, is considered with the exothermic peaks at 186 °C and 240 °C for the blended samples in Fig. 1, the slight weight loss for the blended samples in that temperature interval could be connected to the formation of Cs-U-O through the reaction between Cs<sub>2</sub>O and UO<sub>2</sub>. Secondly, in Fig. 2, unlike Cs<sub>2</sub>O, the curves for the blended samples do not show any weight loss at 610 °C. Meanwhile, a small amount of weight loss appears in the cases with Cs/U ratios that are higher than 2. It can be inferred from the lack of weight loss for the blended samples, which are mixtures of Cs<sub>2</sub>O and UO<sub>2</sub>, that Cs<sub>2</sub>O in the blended samples is consumed by the reaction with UO<sub>2</sub> and no additional Cs<sub>2</sub>O is decomposed. The weight loss for the blended samples with Cs/U ratios that are higher than 2 is thought to be caused by an excess amount of Cs<sub>2</sub>O to that of UO<sub>2</sub> in the reaction between those two reactants. The curve for only UO<sub>2</sub> does not show any weight gain by oxygen, despite UO<sub>2</sub> being easily oxidized by oxygen at temperatures near 150 °C<sup>4</sup> and from this result, it is confirmed that the oxygen content in the heating environment of the instrument (TGA-DSC) is sufficiently low even at high temperatures of up to 1100 °C and do not interfere with the oxygen oxidation reaction of Cs<sub>2</sub>O and UO<sub>2</sub>.

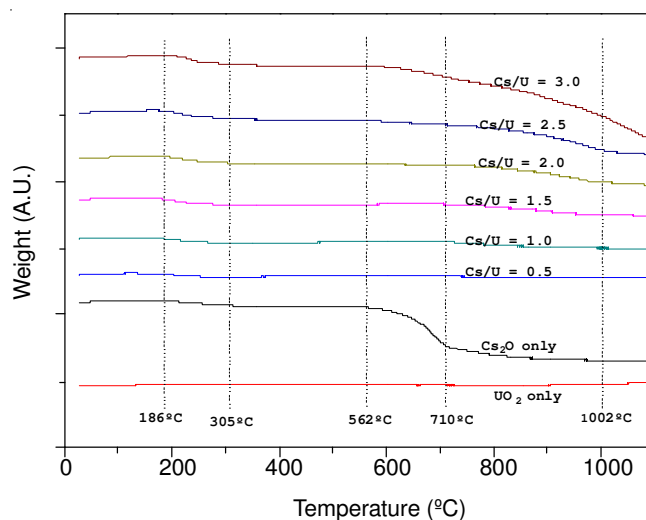


Fig. 2. Thermogravimetric measurements for the reaction between Cs<sub>2</sub>O and UO<sub>2</sub>

**Formation extent of Cs-U-O depending on the Cs/U that is added:** The formation extent of Cs-U-O, which was obtained by the chemical analysis of the U concentration as described before was plotted against the Cs/U ratio (Fig. 3), where the formation extent was  $U_{\text{dissolved}}/U_{\text{Initial}}$  ( $U_{\text{dissolved}}$ : the total amount of U that was dissolved by the pH-2 solution;  $U_{\text{Initial}}$ : the total amount of U that was initially added to the blended samples). Fig. 3 shows a linear relationship between the Cs/U ratio and the extent of formation of Cs-U-O, which means that the formation of Cs-U-O increased linearly with the Cs/U ratio. In Fig. 3, the extent of formation reached near 100 % when Cs/U was 3. This result suggests the possibility that Cs<sub>3</sub>UO<sub>x</sub> is the formula of cesium uranate that is formed through

the reaction. However, any cesium uranate of Cs/U = 3 in the formula has not been reported in the literature and it is difficult to determine the possibility of the formula of Cs<sub>3</sub>UO<sub>x</sub> with only the present result. Regarding the above results, it can be assumed that some portion of the total added amount of Cs<sub>2</sub>O into the blended samples would be consumed through other paths other than it reacting with UO<sub>2</sub>. Therefore, more Cs<sub>2</sub>O would be needed to complete (meaning 100 % of the extent of formation) of the reaction with UO<sub>2</sub> and, consequently, could give a higher Cs/U value than the real state when calculating the formula of Cs-U-O that is formed.

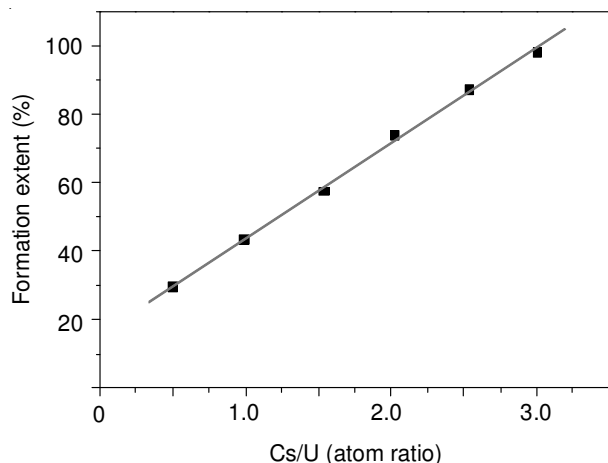


Fig. 3. Formation extent of Cs-U-O depending on the Cs/U ratio of the blended samples

**Phase characterization:** From the XRD measurements for the samples that were heated at 500 °C and 1100 °C as shown in Fig. 4, the diffraction patterns of Cs<sub>2</sub>UO<sub>4</sub> at 500 °C and Cs<sub>2</sub>U<sub>2</sub>O<sub>7</sub> at 1100 °C were observed. It was found that Cs<sub>2</sub>O could react with UO<sub>2</sub> to produce Cs<sub>2</sub>UO<sub>4</sub>, which is a well-known cesium uranate, when heated to 500 °C. The phase Cs<sub>2</sub>U<sub>2</sub>O<sub>7</sub> at 1100 °C is thought to result from the reported reaction<sup>2</sup>:

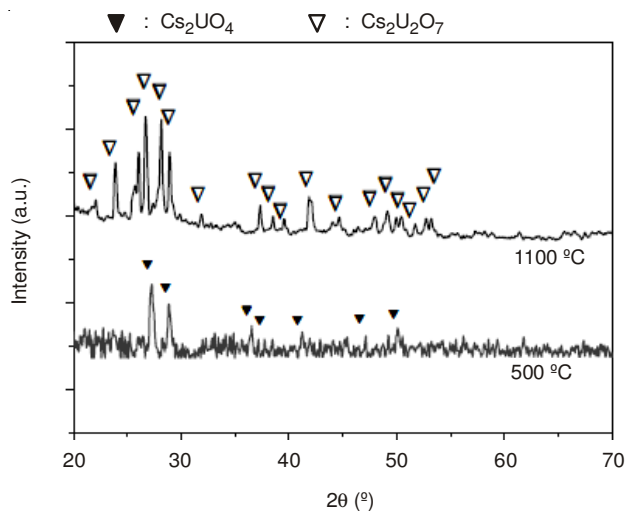


Fig. 4. XRD patterns for the reaction products of Cs<sub>2</sub>O and UO<sub>2</sub>

## Conclusion

The appearance of exothermic peaks at 186 and 240 °C from DSC and the weight loss depending on the Cs/U ratio from 200 to 250 °C and from 610 to 710 °C from TGA could be evidence for the formation of Cs-U-O resulting from the reaction between Cs<sub>2</sub>O and UO<sub>2</sub>. Through chemical analysis, it was determined that the formation of Cs-U-O increased linearly with the Cs/U ratio. From diffraction patterns, it was shown that Cs<sub>2</sub>UO<sub>4</sub> was produced when the blended sample of Cs/U=2 was heated to 500 °C and Cs<sub>2</sub>U<sub>2</sub>O<sub>7</sub> was produced from the same sample, when it was heated to 1100 °C.

## ACKNOWLEDGEMENTS

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