The Study on the formation of Cs-U-O compounds in UO_2 fuel

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1. Introduction

Cs-U-O compounds as the reaction products between UO_2 and Cs has been found experimentally at the periphery in UO_2 fuels that were used at high power [1]. These Cs-U-O compounds have aroused an interest because the properties of thermal expansion and thermal conductivity of these newly formed compounds could influence the integrity of nuclear fuel.

Even a proof of Cs-U-O compounds formation in UO_2 fuels by distribution mapping of Cs and U by Scanning Electron Microscopy (SEM) and Electron Probe Micro Analysis (EPMA) was reported [2], the exact chemical formula of the compounds has not been measured directly. In this work, some simulated experiments were performed in order to investigate the formation of Cs-U-O in UO_2 fuels. Supposing CsI or Cs_2O were cesium species in UO_2 fuels, the reaction behaviors and products between UO_2 and these Cs compounds were studied by using TG-DSC and XRD.

2. Experimental

2.1. Reaction of UO_2 and Cs_2O

Mixed powder samples of UO_2 and Cs_2O, where Cs/U (atomic ratio) = ~2, ~4, were prepared by weighing in the glove box. The samples were heated in argon atmosphere from 30℃ to 400 ℃ with heating rate of 10℃/min. and holding 24 hours at 400 ℃ by using TG-DSC. And the color of reaction products were observed visually and crystal structures of the sample phases were measured by XRD.

2.2. Reaction of UO_2 and CsI

Mixed powder samples of UO_2 and CsI were prepared and heated by the same manner with the upper case of UO_2 and Cs_2O. And also the reaction products were observed visually and crystal structures of the sample phases were measured by XRD.

2.3. Temperature condition for the formation of Cs-U-O from the reaction of UO_2 and Cs_2O

In order to know the temperature condition for the formation of Cs-U-O in the reaction of UO_2 and Cs_2O, mixed samples of UO_2 and Cs_2O were heated at several temperatures holding 24 hours, which are at 100℃, 150℃, 200℃, 250℃, 300℃, 350℃, 400℃, observing the color change of the sample.

3. Results and discussion

2.1. Reaction of UO_2 and Cs_2O

For both cases of Cs/U (atomic ratio) = ~2, ~4, color change from black to orange which could be thought to be a proof of the occurrence of chemical reaction between UO_2 and Cs_2O appeared after heating (Fig. 1).

When comparing the properties of reaction products of two cases, Cs/U (atomic ratio) = ~2 and ~4, in the reaction, the reaction product of Cs/U = ~4 was very hygroscopic, but on the other hand that of ~2 was not. And the reaction product of Cs/U = ~2 contained trace amount of black particle residuals in the orange sample which should be uranium oxide compounds remained in the reaction, but on the other hand that of ~4 did not contain any black particles. From the hygroscopic property and the absence of uranium oxides in the reaction product of Cs/U = ~4, it could be thought that the initial amount of Cs_2O is excess against UO_2 in the reaction and so hygroscopic Cs_2O remained as an excess in the product. From the absence of hygroscopic property and the existence of trace uranium oxides in the reaction product of Cs/U = ~2, it could be thought that Cs/U = ~2 is proper stoichiometric mole ratio for the reaction.

From XRD measurement as shown in Fig.2, it was confirmed that orange sample is Cs-U-O compounds which are mainly Cs_2UO_4 with $Cs_4U_5O_{17}$ as a minor phase (Fig. 2).

2.2. Reaction of UO_2 and CsI

In the case of CsI, the Cs-U-O compounds were not produced dissimilarly with the preceding case of the reaction between UO_2 and Cs_2O.

2.3. Temperature condition for the formation of Cs-U-O from the reaction of UO_2 and Cs_2O

By the observation of distinct color change from black to orange, it was known that temperature requirement for the formation of Cs-U-O compounds in the reaction of UO_2 and Cs_2O is the temperature higher than 350℃.

4. Conclusion

It is suggested that Cs-U-O compounds could be formed at the periphery in UO_2 fuels through the reaction between UO_2 and Cs_2O at the temperature condition higher than 350℃ and that the main product of the reaction would be Cs_2UO_4.

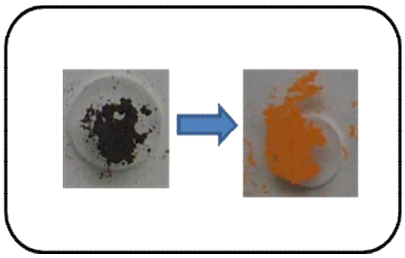

Fig. 1. Color change after heating the mixture of UO_2 and Cs_2O.

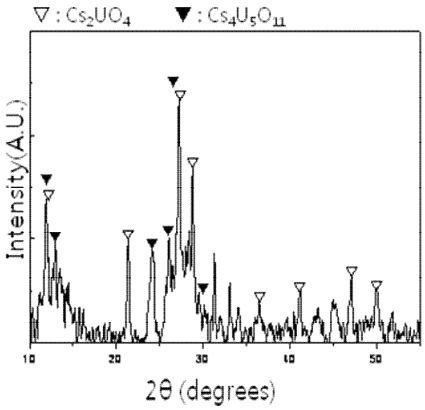

Fig. 2. XRD patterns of reaction products of UO_2 and Cs_2O.

REFERENCES

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