Behaviors of $\text{UO}_2\text{-WB}_2$ and $\text{UO}_2\text{-TaB}_2$ Fuels in Steam

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WB_2 and TaB_2 dispersives in UO_2 were heated in flowing steam and in static high-pressurized steam, and the reaction between steam and borides was studied by means of the X-ray diffraction method and optical microscopy.

The main results obtained are as follows:

(1) Powder compacted specimens of $\text{UO}_2\text{-WB}_2$ and $\text{UO}_2\text{-TaB}_2$ reacted with the flowing steam at 600°C . WO_2 and H_3BO_3 were formed for $\text{UO}_2\text{-WB}_2$, and Ta_2O_5 and H_3BO_3 for $\text{UO}_2\text{-TaB}_2$. It was considered that the boron element migrated out of specimens in the form of a gaseous compound. There were no reactions between UO_2 and borides in steam.

(2) In the sintered pellet specimen of $\text{UO}_2\text{-WB}_2$, there were no appreciable changes in the shape and location of the WB_2 particles even after heating at 600°C , while in the $\text{UO}_2\text{-TaB}_2$ specimen a new phase, which was considered as Ta_2O_5 , appeared in the annulus region surrounding each TaB_2 particle after heating at 600°C , although no appreciable migration of TaB_2 particles was observed.

(3) The effect of pressurizing of steam on the behaviors of $\text{UO}_2\text{-WB}_2$ and $\text{UO}_2\text{-TaB}_2$ was not recognized in the temperature range below 400°C .

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I. Introduction

In the power reactor, an extra amount of the fissionable element which exceeds the critical mass requirement is loaded as a fuel for power production. The excess reactivity produced by additional fissionable elements is usually compensated for by the negative reactivity produced by the poisoning such as the movable control rod. If poison particles are dispersed in the fuel and the simultaneous depletion of both the fissionable element and the poison element is realized during a long-period reactor operation, the number of control rods and the subsidiary mechanical system can be minimized, leading to economization of the power production. To this end, it is indispensable to select an adequate poison material.

Although several borides with a high melting point and a large neutron cross section are now regarded as being promising from the viewpoint of reactor physics, a more careful selection of them should be also made from the viewpoint of material stability under irradiation.

The requirement for the shaped dispersed poison in UO_2 is that the poison material should maintain its original shape and location of the as-manufactured state for a long-period reactor operation. During the reactor operation, cladding tubes of fuel rods are sometimes failed due to the build-up of an excessive internal gas pressure, the thermal expansion of UO_2 , and radiation damage of welded parts. In these cases, cooling water will infiltrate into the fuel rod through the defect in the cladding tube and produce steam by reacting with heated UO_2 . Robertson et al.⁽¹⁾ reported that the irradiation damage on defective UO_2 fuel rods was not so large as to disqualify the use of the fuel rods.

When cooling water infiltrates into the fuel rods of combustible dispersed poison in UO_2 , the reaction between steam and poison materials in the presence of

UO_2 must be taken into consideration in addition to the reaction between steam and UO_2 . If the original shape and location of the poison material are changed by some reaction, such a material does not satisfy the requirement as a shaped combustible dispersed poison in UO_2 .

At present, little has been known about the behaviors of combustible dispersed poisons in UO_2 which are exposed to steam. In the present study, two kinds of fuels, $\text{UO}_2\text{-WB}_2$ and $\text{UO}_2\text{-TaB}_2$, were heated at various temperatures in flowing steam and in static high pressurized steam, and the reactions between steam and poison materials in UO_2 matrix were studied by means of the X-ray diffraction method and optical microscopy.

II. Experimental

1. Specimens

Combustible poison powders used were WB_2 and TaB_2 , and their melting points are 2900°C ⁽²⁾ and 3000°C ⁽³⁾, respectively, which are higher than 2750°C ⁽⁴⁾ for UO_2 . These borides powders were supplied by Herman Starke Co., Germany, and their particle sizes ranged between 5 and 50 microns. The UO_2 powder used as the matrix was supplied by Mitsubishi Metal Mining Co.. Boride particles were blended with ceramic grade UO_2 power particles, die-pressed and then fired in hydrogen at a high temperature. The firing

Fig. 1 Outline of apparatus for heating in steam.

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temperatures were 1400°C for $\text{UO}_2\text{-WB}_2$ and 1500°C for $\text{UO}_2\text{-TaB}_2$. Blending ratios of borides to UO_2 were 3 volume percents. The densities of $\text{UO}_2\text{-WB}_2$ and $\text{UO}_2\text{-TaB}_2$ were 88 and 91 % of the theoretical densities, respectively.

Fig. 2 Specimen assembly used for heating in pressurized steam.

Fig. 3 X-ray diffraction charts on the powder compacted specimens of $\text{UO}_2\text{-WB}_2$ heated in steam flow.

Table 1 The result of X-ray diffraction on powder compacted specimens of $\text{UO}_2\text{-WB}_2$ and WB_2 powders heated in steam flow.

Specimen identity	Heating temp. ($^\circ\text{C}$)	Product identified
$\text{UO}_2\text{-WB}_2$		
# 1	200	UO_2 , WB_2
# 2	400	UO_2 , WB_2
# 3	600	UO_2 , WO_2
WB_2		
# 4	200	WB_2
# 5	400	WB_2
# 6	600	WO_3

In addition to the sintered pellets, the powder compact specimens of UO_2 60 wt% and borides 40 wt% were prepared for X-ray diffraction studies.

2. Experimental procedure

(1) Heating in steam flow

The outline of the measuring apparatus is shown in Fig. 1. The steam of distilled water was flown over the specimen placed in a boat made of quartz. After replacing the air existing in the furnace tube with steam, the specimen was heated. The specimen temperature was measured by the thermocouple inserted in a dummy UO_2 pellet set near the specimen and was controlled by a temperature regulator. The specimen was then heated at temperatures of 200° , 400° and 600°C for two

hours. After heating, the specimen was cooled by continuously flowing steam until the specimen temperature and the furnace tube reached the steam temperature.

(2) Heating in pressurized steam

A quartz holder was inserted in a stainless steel tube of 3 mm in thickness and 20 mm in outer diameter, one end of which was welded with a stainless steel end-plug (Fig. 2). After setting the specimen on the quartz holder, a stainless steel end-plug with a hole 1.5 mm in diameter at its center was welded to another end of the tube and then distilled water was injected with an injection tube through the hole with precautions to prevent the contact between water and the specimen. The hole was sealed by welding after injecting water into the tube. The reason for using an end-plug with a center hole is to prevent the pressure build-up in a tube by minimizing the temperature increase in the welding procedure. The specimen assembly prepared by the above process was set longitudinally in a furnace with nichrome wires and heated at 300° , 350° and 400°C for 2 hours. The pressure of steam in the specimen assembly was estimated as the saturated vapor pressure at each temperature. After cooling, the tube was cut and the specimen in it was taken out for further experiments.

III. Results

1. $\text{UO}_2\text{-WB}_2$

(1) X-ray diffraction of powder compacted specimens

Fig. 4 X-ray diffraction charts on WB_2 powders heated in steam flow.

products identified were UO_2 and WO_2 , while boron and boron compounds such as B_2O_3 were not detected. The steam which was passed through the specimen was condensed at the outlet of the furnace and used for chemical analysis. A large quantity of H_3BO_3 was found in the steam condensate formed by passing through the specimen heated at $600^\circ C$.

As a possible reaction mechanism, it is considered that WO_2 and B_2O_3 are formed at first and then H_3BO_3 are formed by the reaction⁽⁵⁾⁽⁶⁾ between B_2O_3 and steam. Although the formation of boron hydride is likely to occur in the intermediate stage, the hydride will easily transform into H_3BO_3 by reacting with steam. In the present case, uranium compounds such as UB were not detected.

As reference, the WB_2 powder was heated under the same condition as for the powder compacted UO_2 - WB_2 specimens. The results of X-ray diffraction are shown in Fig. 4 and Table 1. The

Photo. 1 Microstructure of pellet specimen of UO_2 - WB_2 heated in steam flow. ($\times 106$)
(polished and etched on fractured surface)

(a) as-manufactured state (b) heated at $200^\circ C$ (c) heated at $400^\circ C$ (d) heated at $600^\circ C$
Even after heating at $600^\circ C$, no effect on WB_2 particles is observed.

Powder compacted specimens of UO_2 60 wt% and WB_2 40 wt%, which were heated in a flowing steam at 200° , 400° and $600^\circ C$, were analyzed by the X-ray diffraction method. The results are shown in Fig. 3 and Table 1. The table shows that a reaction occurs at $600^\circ C$, but not at 200° and $400^\circ C$. The reaction

table shows that some reaction occurs at $600^\circ C$, but not at 200° and $400^\circ C$. The reaction product identified was WO_3 .

(5) H. Meszel, H. Schulz and H. Deckert: *Z. Anorg. Ch.*, **220** (1934), 49.

(6) L. Hackspill, A. P. Kieffer: *Ann. Chim.*, **14** (1930), 227.

(a)

(c)

(b)

Photo. 2 Microstructure of pellet specimen of $\text{UO}_2\text{-WB}_2$ heated in pressurized steam. (polished and etched on fractured surface) ($\times 106$)
 (a) heated at 300°C and 87.6 kg/cm²
 (b) heated at 350°C and 168.6 kg/cm²
 (c) heated at 400°C and 340.0 kg/cm²
 There were no changes in the microstructures after heating up to 400°C.

Fig. 5 X-ray diffraction charts on the powder compacted specimens of $\text{UO}_2\text{-TaB}_2$ heated in steam flow.

(2) Microstructure of the pellet specimen heated in steam flow

Photo. 1 (a) shows an optical micrograph of the fractured and polished surface of $\text{UO}_2\text{-WB}_2$ as prepared. This specimen had many cracks and voids.

As shown in Photo. 1 (b), there is no marked change in the microstructure of the specimen heated at 200°C for two hours in steam flow and poison particles maintained their original shapes and positions. Even after heating at 600°C, its effect on WB_2 particles was not observed (Photo. 1 (c)). Of course, on the surface where WB_2 was exposed directly to steam, the reaction between WB_2 and steam was the same as that of powder compact, while in the inside portion, a greater part of the pellet specimen, no reaction occurred in the temperature range studied.

The reason why no reaction occurred seems that the steam could not infiltrate into the inside of the pellet, since the interconnection of voids and cracks in the $\text{UO}_2\text{-WB}_2$ pellet specimen was incomplete in contrast with the powder compact specimen.

(3) Microstructure of the pellet specimen heated in pressurized steam

In the actual reaction operation, a pressurized steam is considered to react with UO_2 and poison materials in a nearly static state, when the defect is produced in the cladding tube. As described in the items

of experiment, the specimens were heated at 300°, 350° and 450°C in saturated vapor pressures of water, which were 87.6 kg/cm², 168.6 kg/cm² and 340 kg/cm², respectively. Dimensional measurements, which were done before and after heating, indicated no swelling in the

Table 2 The result of X-ray diffraction on powder compacted specimens of UO₂-TaB₂ and TaB₂ specimens heated in steam flow.

Specimen identity	Heating temp. (°C)	Product identified
UO ₂ -TaB ₂		
# 7	200	UO ₂ , TaB ₂
# 8	400	UO ₂ , TaB ₂
# 9	600	UO ₂ , Ta ₂ O ₅
TaB ₂		
# 10	200	TaB ₂
# 11	400	TaB ₂
# 12	600	Ta ₂ O ₅

Fig. 6 X-ray diffraction charts on TaB₂ powders heated in steam flow.

diameter of the specimen assembly.

Photo.2 shows the microstructures of fractured and polished surfaces of the specimens. There are no changes in the microstructures after heating in pressurized steam up to 400°C as in the case of heating in steam flow at 200° and 400°C.

2. UO₂-TaB₂

(1) X-ray diffraction of powder compacted specimens

The results are shown in Fig. 5 and Table 2. The table shows that the reaction does not occur at 200° and 400°C, but occurs at 600°C. The products were identified as UO₂ and Ta₂O₅, in which boron and boron compounds such as B₂O₃ were not detected. Chemical analysis of the steam, which was condensed at the outlet of the furnace after passing through the specimen heated at 600°C, showed the presence of a large quantity of H₃BO₃. The probable mechanism of the disappearance of boron in the powder compacted specimen is that Ta₂O₅ and B₂O₃ were formed at first and then H₃BO₃ were formed by the reaction between B₂O₃ and steam. It is also possible that boron hydride was formed and was flown away while reacting with H₂O, although the reaction in the intermediate stage could not be confirmed.

As reference, TaB₂ particles were heated in the same condition as UO₂-TaB₂. The results of X-ray diffraction are shown in Fig.6 and Table II.

(2) Microstructure of the pellet specimen heated in steam flow

The specimen heated at 200°C has almost the same microstructure as that before heating. As shown in Photo.3 (A) and (B), white colored TaB₂ particles are dispersed in the UO₂ matrix.

The different microstructures from (A) and (B) are observed in Photo. 3 (C). There are many zones whose color was changed by a (7 vol % HNO₃ + 2 vol % H₂O₂ + 1 vol % H₂O) etchant. In spite of the appearance of the above dark-colored zone, most TaB₂ particles retained their original shapes and location. As shown in (D), which shows the microstructure of the specimen heated at 600°C, the annulus region surrounding TaB₂ particles were not etched, while other matrix regions were etched. Although the identification of the annulus region of TaB₂ particles was not made by X-ray diffraction, which showed only UO₂ patterns because of the low TaB₂ content in the sintered pellet specimen, the region is considered to consist of Ta₂O₅ which was formed by the reaction of the surfacial part of TaB₂ particles and steam diffused in UO₂.

(3) Microstructure of the pellet specimen in pressurized steam

The pellet specimens were heated at 300°, 350° and 400°C under saturated vapor pressures of water. There were no remarkable changes in TaB₂ particles as in the case of UO₂-WB₂, (Photo.4).

IV. Discussion

(1) The temperature of UO₂ was limited to below 600°C for the convenience of the experimental apparatus and procedure. Considering the temperature distribution in UO₂ during the reactor operation, the results obtained in this experiment must be interpreted

Photo. 3 Microstructure of pellet specimen of $\text{UO}_2\text{-TaB}_2$ heated in steam flow. (polished etched on fractured surface) ($\times 106$)
 (a) as-manufactured state (b) heated at 200°C (c) heated at 400°C (d) heated at 600°C
 New phase, which is considered as Ta_2O_5 appeared in the annulus region surrounding TaB_2 particles.

Photo. 4 Microstructure of pellet specimen of $\text{UO}_2\text{-TaB}_2$ heated in pressurized steam. (polished and etched on fractured surface) ($\times 106$)
 (a) heated at 300°C and 87.6 kg/cm^2
 (b) heated at 350°C and 168.6 kg/cm^2
 (c) heated at 400°C and 340.0 kg/cm^2
 There were no changes in the microstructures after heating up to 400°C .

as explaining the phenomena in such a part of UO_2 fuel as its temperature is kept below 600°C . Usually, the surface part of a fuel corresponds to such a part as mentioned above.

(2) Although powder compacts are used mainly for X-ray diffraction analysis, the behavior of the powder

compacts during the reactor operation can be interpreted as follows.

It is known that a sintering phenomenon and densification occur in the central part of the powder compacted UO_2 fuel when irradiated under the condition of a high fuel surface heat flux. However, the sintering

phenomenon is not substantially observed, when irradiated under the condition of low fuel surface heat flux⁽⁷⁾. When defects are produced in cladding in the case of low heat flux irradiation, steam can easily enter into the every part of the compact and reacts with poison particles, since there are linked voids in the powder compact.

As a result of the reaction between steam and poison boride particles, borides were oxidized and WO_2 and Ta_2O_5 were formed for $\text{UO}_2\text{-WB}_2$ and $\text{UO}_2\text{-TaB}_2$, respectively. While the above reaction does not occur at the part of UO_2 near the cladding tube, where temperature is nominally below 600°C , the reaction will occur at the central part where temperature exceeds over 600°C .

When defects are produced under high heat flux irradiation, a sintering phenomenon and densification occurs appreciably in the central part of powder-compacted UO_2 and the structure of central part becomes similar to that of the sintered pellet, while the powder state is maintained at the surface part of UO_2 . In this case, poison is oxidized in a part of UO_2 when the temperature exceeds over 600°C , but is not high enough to cause the sintering phenomenon, while the central part shows a similar reaction as in the sintered pellet.

(3) In the case of the sintered pellet, it is estimated that there is no appreciable difference in the behavior

of the pellets between low and high heat flux irradiations. Combustible poison dispersions will show a stable behavior, even if defects are produced in the cladding tube.

V. Conclusion

(1) Powder compacted specimens of $\text{UO}_2\text{-WB}_2$ and $\text{UO}_2\text{-TaB}_2$ have reacted with the flowing steam at 600°C . WO_2 and H_3BO_3 were formed for $\text{UO}_2\text{-WB}_2$, while Ta_2O_5 and H_3BO_3 for $\text{UO}_2\text{-TaB}_2$. Boron has migrated from the specimens in the gaseous state. There was no reaction between UO_2 and borides in steam.

(2) In the case of the sintered pellet specimen of $\text{UO}_2\text{-WB}_2$, there was no appreciable change in the shape and location of WB_2 particles even after heating at 600°C , while in the case of $\text{UO}_2\text{-TaB}_2$ a new phase, which was considered as Ta_2O_5 , appeared in the annulus region surrounding TaB_2 particles after heating at 600°C , although any appreciable migration of TaB_2 particles was not observed.

(3) There was no appreciable effect of pressurizing of steam on the behaviors of $\text{UO}_2\text{-WB}_2$ and $\text{UO}_2\text{-TaB}_2$ in the temperature range below 400°C .

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