Analysis of CRUD Flake by Shielded EPMA

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1. Introduction

Interest in the analysis of crud materials has increased due to the evolution of the analysis process in nuclear reactor water chemistry. Chemical analysis of crud with ICP-MS as well as ICP-AES is well known as an analysis tool which can, as can other techniques like SEM and TEM give complementary information on the morphology and local composition of crud materials. However, analysis by shielded EPMA can produce specific results. Crud specimens were intensively analyzed using shielded EPMA. Also, we changed the power condition for this study. As a result, we found that part of the crud is evaporated and the main metal composition material such as iron remains.

2. Samples and methods

Crud flakes were intensively analyzed using shielded EPMA. Resolution of WDS analysis, one of the various analyzing functions of EPMA, is useful in partial analysis of very small specimens like crud flake. Such analysis is different from a chemical analysis method, in which the entire filter is analyzed. The resolution is excellent, and the data precision of that of method is comparable to the chemical analysis.

Crud specimens, which were scraped from twice-burned fuel claddings, were moved to the Irradiated Materials Examination Facility to perform the analysis.

3. Results and discussion

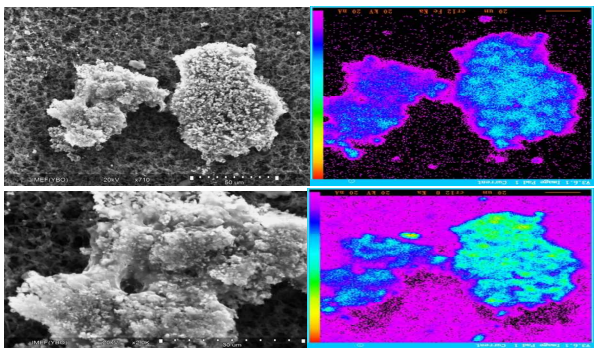
3.1. Cruds flake Analysis by EPMA WDS and SEM

The sample of crud flake was a specimen scraped from twice-burned fuel cladding in a Korean PWR. The specimen was prepared by cutting the filter after identifying each area of the filter by HIROX to locate the presence of the specimen.

The chemical composition of the crud flake measured by EPMA normal analysis is shown in Table 1.

Flake No	Thick (㎛)	Hole (㎛)	Fe	Ni	Cr	Zn	O	Ni/ Fe
No 1	12	6	18	24	2.3	0.7	55	1.3
No 2	.	.	39	57	0.8	0.2	2.5	1.5

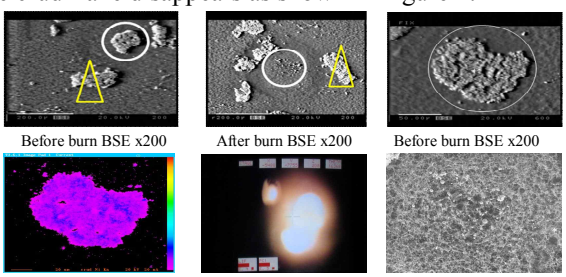
[Table 1. Chemical composition of crud flake measured by EPMA]



[Fig.1. SEM & X-ray map of flake No. 1]
(W/L/t ≒ 50/120/12 ㎛, chimney hole size ≒ 50/120/12 ㎛)

3.2. EPMA analyses of a crud flake after burn

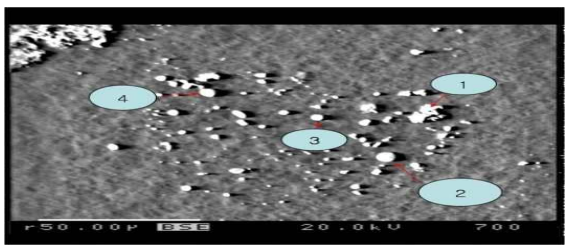
Even though the general power application condition for EPMA analysis is about 20 kV and 10 nA, the power condition applied in this analysis was 20 kV and 1200 nA applied for 5 seconds, created by opening an adjustable aperture device for gun alignment adjustment. This value of 1200 nA was the value shown on the screen, but the actual applied current was estimated to be 1,500~ 2,000 nA. It was confirmed that the crud flake disappears as shown in Figure 2.



[Fig.2. EPMA monitor, SEM BSE analysis of crud flake]
(Beam condition : 20kV, 1200nA, Beam exposure time : 5sec)

3.2.1 After burn precipitates

Fig.3. shows a typical nickel ferrate, with composition as shown in the table 2.



[Fig.3. BSE of flake after burning]
(Beam condition : 20kV, 1200nA, Beam exposure time : 5sec)

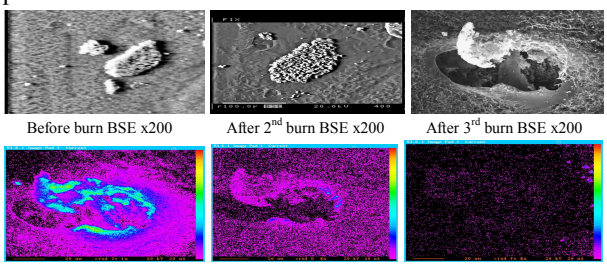
No 1						
	Fe	Ni	Zn	Cr	O	Ni/Fe
wt %	30.36	16.52	0.37	0.84	17.74	NiFe2-xO4
At %	27.80	14.39	0.21	0.83	56.69	0.52
No 2						
wt %	28.39	20.89	0.42	1.66	0.00	
At %	56.33	39.43	0.70	3.54	0.00	0.70
No 3						
wt %	25.54	20.10	0.43	0.70	0.38	
At %	54.20	40.58	0.78	1.61	2.82	0.75
No 4						
wt %	19.04	18.28	0.39	1.62	5.73	
At %	32.56	29.73	0.57	2.97	34.18	0.91

[Table 2. Quantitative analysis of crud flake after burning by EPMA]
(Beam condition : 20kV, 1200nA, Beam exposure time : 5sec)

3.3. EPMA analyses of crud flake in 2nd burn &3nd burn

The power was projected to the same location under the same application conditions for 30 seconds. As can be seen in the figure, the crud flake disappeared, also, it is possible to see damage on the filter paper, unlike the situation when the power was projected once. Damage like this seems to have been made when the crud flake material is ripped or melted down while it is changing to another shape, as in the figure. However, it is not that the paper itself was burned in the high vacuum environment.

As can be seen in the Figure 4, while the composition of zirconium is clearly shown, it was found that oxygen is not present. This conforms to the result that zirconium was not present as an oxide when the primary burn was performed.



[Fig.4. BSE & x-ray map of crud flake after 3rd burn by EPMA]
(Beam condition : 20kV 1200nA, Exposure time:2nd 5sec, 3rd 30sec)

As the melting temperature of zirconium is higher than that of iron and nickel, no change was observed when the power was applied for 5 seconds under the same conditions; then, change was observed when the sample reached a higher temperature. Even when the power was projected unilaterally for 30 seconds, if the crud material can be divided by temperature using TGI and the like, research on the essence of crud would be possible. It is a unique property zirconium that it also has the shape of general crud. Generally, it has been generally thought that zirconium cannot be dissolved by coolant because it is a stable material; however, zirconium is not only present in the crud flake form, but it is also present as a particulate, not as an oxide. Also, it was found that zirconium was not extracted from the oxide layer of the cladding during crud collection. If there is ZrO_2 on the oxide layer of the cladding, it would not have crud flake form and the presence of oxygen would have been clearly identified.

In conclusion, it was found out that the composition of the dissolved material present in the coolant is of various materials, including zirconium.

4. Conclusion

A detailed analysis was performed for the crud flake scraped from twice-burned fuel cladding by EPMA. Crud was shaped as W/L/t ≒ 50/120/12 ㎛ and crud flake thickness size was observed to be ≒ 4~25 ㎛, also we observed boiling chimney hole size at ≒ 4~6 ㎛.

We changed the power condition for this study. Even though the general power application condition for EPMA analysis is about 20 kV and 10 nA, the power condition applied to this analysis was 20 kV and 1200 nA for 5 to 30 seconds, created by opening an adjustable aperture device for gun alignment adjustment. As a result, we found that part of the crud is evaporated and the main metal composition material, such as iron remains.

The power was projected to the same location under the same application condition for 30 seconds. There was damage to the filter paper, unlike the situation in which the power was projected for 5 seconds. The damage seems to have been made when the crud flake material was ripped or melted while it was subject to the high current beam.

Also, it was found that the crud was not extracted from the oxide layer of the cladding during crud collection. If there is ZrO_2 on the oxide layer of the cladding, it would not have crud flack form and the presence of oxygen would have been clearly identified. In conclusion, it was found that the composition of the dissolved material present in the coolant is of various materials, including zirconium.

REFERENCES

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[2] "Effects of Crud Buildup and Boron Deposition on Power Distribution and Shutdown Margin", NRC Information Notice 97-85 (1997).