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Analysis of CRUD Flake Applied to Abnormal High Beam Current by Shielded-EPMA

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CRUD specimens, scraped from twice-burned fuel cladding in the Korean Nuclear Power Plant, were analyzed using Shielded-EPMA. The principal elements of the CRUD were identified as Ni and Fe, at an approximate ratio of 1.3 Ni/Fe. To investigate the morphology and composition of the pure metallic materials in the CRUD, coolant impurities must be removed. This can be accomplished by increasing the EPMA current to an abnormally high intensity until the impurities are melted. Normally, EPMA applications are performed at conditions of 20 kV voltage and 20 nA current. But in our study, the applied current was increased up to 1200 nA, over time increments ranging from 5 to 30 seconds. This technique was performed by opening an adjustable aperture for the gun alignment. Results showed impurities contained in the CRUD material disappeared and pure metal materials, e.g., Ni and Fe, remained. This method presents an innovative way to analyze CRUD.

Keywords: *CRUD, Shielded-EPMA, Abnormal beam current, Boling chimney hole, $NiFe_2O_4$*

1. Introduction

Unidentified materials, known as CRUD (chalk river unidentified deposit), which are activated corrosion products from BWR and PWR reactors, get deposit on the outer surfaces of fuel rods [1]. Corrosion products from reactor components may transport into the reactor core by cooling water, where they can deposit over fuel fins [2]. These deposits can be distinguished from the corrosion layer which is intrinsic to the given structural material. These corrosion layer results from a mass transfer process of corrosion/erosion products, derived from the various structural materials which is in contact with the primary coolant water circuits [3]. In consequence of longer operation cycles in PWRs results higher generation and deposition of CRUD Masses on nuclear fuel. For higher 235U enrichments need extended cycle operation that have higher peak factors and in result more boiling of sub-cooled nucleate take place on clad surface. There is a direct correlation between these fuel attributes and the amount of CRUD depositing on the fuel rods. The higher CRUD loading has resulted a number of cases of axial offset anomaly (AOA) across the globe, as well as anomalous shutdown chemistry behavior observed at some units. In particular, there is a case that report in Korea Nuclear Power Plant (KNPP) where the steam generator materials were changed from Inconel 600 to Inconel 690.

These deposits are absolutely different from the corrosion products dissolved from structural materials and piping which are into the core by the primary coolant. Steady distribution of fuel power in PWR core may disturb due to CRUD deposition [4,5]. Pressurized water reactors circulate high-temperature water that slowly corrodes Inconel and stainless steel surfaces, and the nickel/iron based corrosion products may deposit in regions of the fuel where sub-cooled nucleate boiling occurs. It is difficult to characterize directly because of the impacts of plant shutdown chemistry on the CRUD form. CRUD scrape samples from fuel and high-temperature water samples have shown that PWRs CRUD is mostly composed mostly of nickel ferrite, nickel oxide, and nickel metal with other nickel-iron-chrome spinel's. The mass density loaded CRUD on the fuel surface varies significantly [6-9].

The creation of CRUD is considered to be a form of trail that can be encountered in pine forests. As shown in Fig. 2, CRUD is like pine leaves on the trail over sand, gravel, and materials of different sizes. Therefore, when the pine forest is burned, it is assumed that the intrinsic material will remain intact. In order to investigate the mor-

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phology and composition of the pure metallic material composing the CRUD, it is mandatory to remove impurities and shapes of CRUD form. Experiments were repeatedly carried out until coolant impurities burn out and the shape disappeard. In general, EPMA application conditions are performed under 20 kV, 20 nA. But In this study, the applied current and time were increased up to 1200 nA, and 30 seconds respectively. This method cannot be performed because the analysis equipment may damage. It was a piecemeal attempt, got a good result. The ratio of pure metal, compare to volume of impurities and other water-soluble amorphous materials is absolutely low in the entire volume of the CRUD. Moreover the ratio of other minor substances, Concentrations of Li, Mn, Mo, Nb, Sb and Sn as coolant impurities are low. Which is the analyzed using ICP-MES (inductively coupled plasma mass spectrometry) analyzer.

Current in EPMA increased up to such limit that the impurities contained in the CRUD were melted. As a result, it was confirmed that the impurities contained in the CRUD material disappeared and only the pure metal material remained. Thus, in this paper, we summarized the results of the remaining metal elements shapes and composition.

2. Samples and Methods

2.1 CRUD scraper hardware

CRUD scraper is the equipment that collect CRUD samples with suction pump and filter by scrapping the CRUD adhered on the fuel rod with scraper made of Al_2O_3. The scraper blade is used to scrape CRUD from the fuel rod, and separated CRUD is transported through the hole by Peristaltic suction pump with capacity of 0.3 hp, and collected at the bottom filter with pore size of 8 μm. The scraper structure is as shown in Fig. 1. CRUD scraping efficiency was evaluated at the laboratory. By measuring the adhesion force of the simulated CRUD on fuel cladding, it was found to be 18.6 kg/cm^2, and the result of scraping test on this simulated CRUD on fuel rod showed that over 70% of CRUD was scraped. Moreover the scrapers of Φ 9.5 ~ Φ 10.0 mm were made of Al_2O_3 and aluminum material. its scarping efficiency was measured, and the result shows, that Al_2O_3 scraper of Φ 9.6 size have best scraping efficiency. Therefore, this scraper was applied for CRUD sampling.

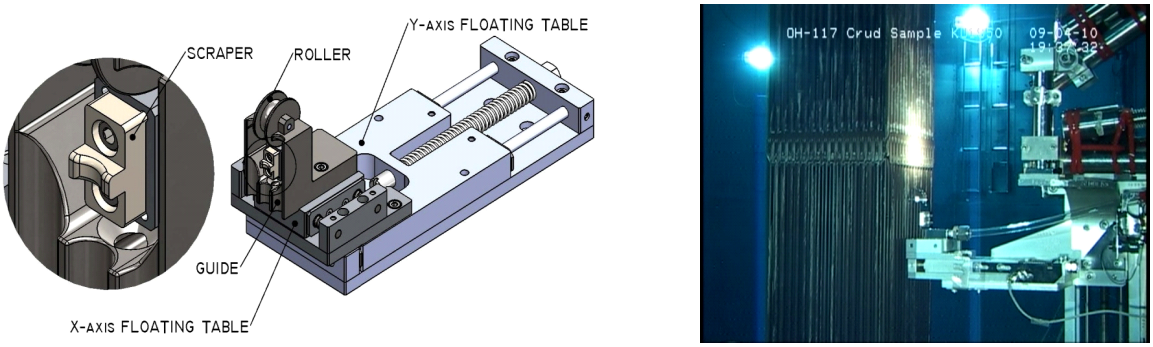

Fig. 1 The scraper structure and working in the KNPP poolside.

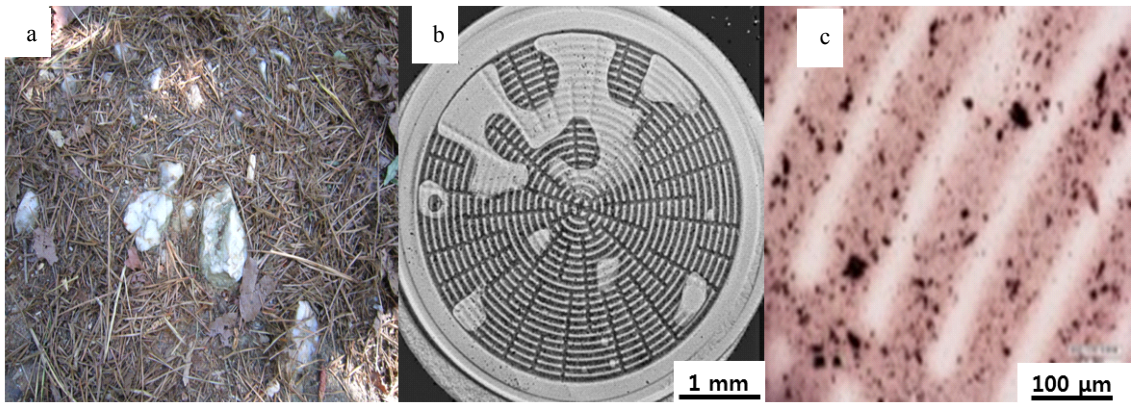

Fig. 2 Trail covered with pine leaves(a), CRUD collection filter(b) and optical photograph(c) (x350).

2.2 Methods

63 specimen filters taken from KNPP were observed under an optical microscope. As shown in Fig. 2, the sample adhered to the filter was optically observed to find a CRUD lumps. The part that seemed to be CRUD was cut with scissors and attached it using carbon tape of high current conductivity. In order to increase the conductivity, carbon evaporation was carried out of about 50 Å thickness. Prepared specimens were observed under SEM (scanning electron microscope) to check CRUD flake. The filter obtained by the scratch method is different from filter obtained by using ultrasonic system in the number of CRUD lumps. After the CRUD identified by SEM, specimens were moved to EPMA for quantitative analysis. EPMA (electron probe micro analyzer, SX-50R, CAMECA, Paris, France) was used in this study, all those appropriate parts are shielded with lead and tungsten to reduce any effect of radiation. To analyze the iron and nickel characteristics, LIF (lithium fluoride) crystal was used, on the other hand oxygen and boron was analyzed using a Polar crystal. Normally surface of the CRUD is very rough, so it was analyzed in beam mode. The size of incident beam on the specimen got increased from 5,000 to 15,000 times. These analytical methods are suitable for the case where, slope and shape of the specimen surface is rough. In order to remove the impurities adhering to the CRUD, the current was abnormally raised and the analytical method of the newly produced metallic material was set to fix mode. Note that the movement of the specimen should be stopped for accurate analysis to extremely small, round specimens. And all the motors involved in the motion of specimen stage of the EPMA were stopped. In such a state, even small specimens can be analyzed.

3. Results and Discussion

3.1. CRUD analysis by using EPMA and SEM

Prior to carrying out this study, EPMA analysis was performed on several specimens. As shown in Fig. 3. CRUD was shaped as W/L/t ≒ 50/120/12 μm, and the boiling chimney hole size was observed to be: ≒ 6 μm. As for the shape of surface the area contacting the coolant,

CRUD materials dissolved in the coolant were shown to be deposited in precipitated form. Precipitation growth is form like very small particles gradually grow, rather than being deposited as a big flake. Other CRUD flakes are considered to be CRUD in areas that have contacted the cladding as the surface is flat as it contacts the cladding, and the boiling chimney hole is not clear. As for the shape of these CRUD flakes, precipitations that reached a relatively consistent size were observed. In the x-ray map analyzed by the WDS (wavelength dispersive spectrometer) of this mass, the upper part of the mass has more deposits than the lower part, and iron shows a relatively even distribution, while oxygen is higher in the upper part than in the lower. As for the shape of this CRUD flake, precipitations that reached a relatively consistent size are observed. While an x-ray map of iron and nickel analyzed by WDS of this mass shows a generally even distribution, the concentration distribution of oxygen is not shown. The results of a quantitative analysis ranging by 5,000, 8,000, and 10,000-times magnification, are shown in Table 1. The Ni/Fe ratio of 1.4 obtained by EPMA analysis is typical value of the fuel CRUD.

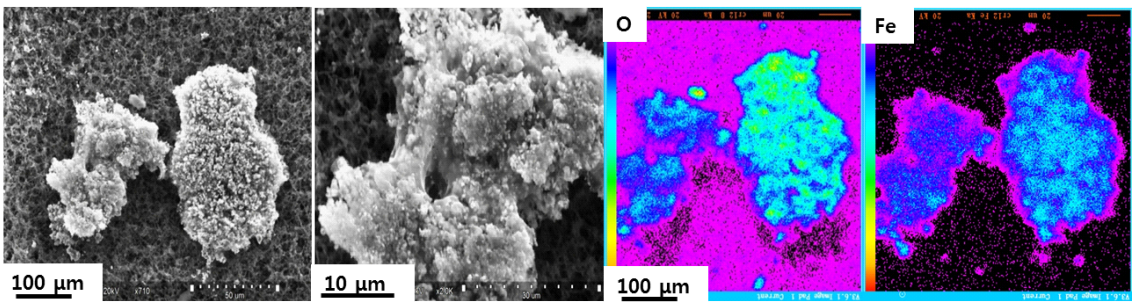

Fig. 3 SEM and x-ray map of a CRUD flake. Applied to normal beam current injection.

Table 1. Chemical composition of CRUD flakes at area measured by EPMA normal analysis (at%)

No	Thick	Hole	Fe	Ni	Cr	Zn	O	Ni/Fe
No 1	12 (μm)	6 (μm)	18.2	24.1	2.3	0.7	54.7	1.3
No 2	.	.	39.0	57.0	0.8	0.2	2.5	1.5

Table 2 CRUD Mass by ICP-MES Analysis, μg/filter (Oxygen Not Included)

Filter	F/A	Rod	Span	Dose (mR)	B	Fe	Ni	Cr	Zr	Li, Mn, Mo, Nb, Sb, Sn, Zn
8	S50	9	5B2	20	20.4	34	52	10.8	20.4	< 4.0 μg/filter
10	S50	9	6A2	110	50.4	284	228	22.8	52	< 4.0 μg/filter

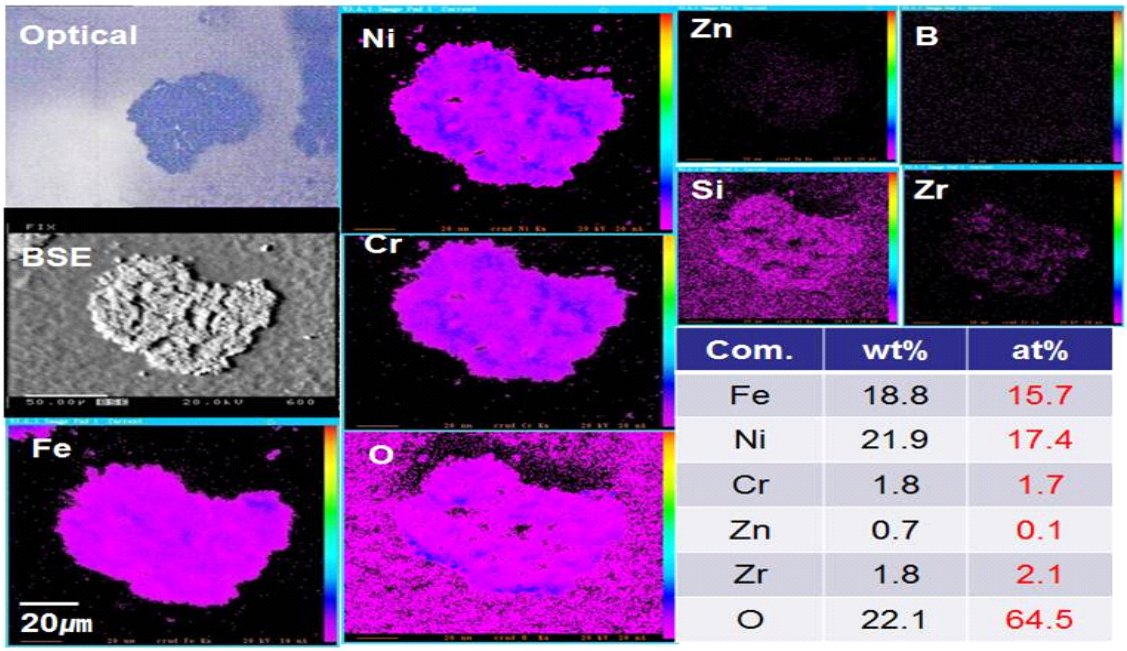

Fig. 4 Before abnormal high beam current injection (Beam condition: 20 kV, 20 nA).

3.2. CRUD analysis applied to abnormal high beam current injection (Burning)

3.2.1 Abnormal high beam current condition

It is because of the following reason why we try to burn the CRUD by applying such an abnormally high beam current. The creation of CRUD is considered to be a form of trail that can be encountered in pine forests. As shown in Fig. 2, we think that CRUD is a form in which pine leaves on the trail are sand, gravel, and materials of different sizes. Therefore, when the pine forest is burned, it is thought that the intrinsic metal material will remain. Even though general power application condition for EPMA analysis is about 20 kV and 20 nA, the power condition applied to this analysis was 20 kV and 1200 nA applied for 5 to 30 seconds, created by opening an adjustable aperture device for gun alignment adjustment. As shown in Fig. 4, We can see the value shown on the screen, and the actually applied current is estimated to be 1,500 ~ 2,000 nA.

Repeated experiments were carried out with the impurities surrounding the CRUD until just before the burning, with the remaining material being applied for 5 to 30 seconds after burning. Attention is required since this application condition can cause big damage of the device.

The ratio of pure metal, compare to volume of impurities and other water-soluble amorphous materials is absolutely low in the entire volume of the CRUD. Also the ratio of other minor substances, Concentrations of Li, Mn, Mo, Nb, Sb, Sn as coolant impurities are very low as shown Table 2, which is the result by using ICP-MES analyzer.

3.2.2. Before abnormal high beam current injection

The shape and composition of a specific CRUD were analyzed before applying an abnormally high beam current. As show in Fig. 4, the shape of the CRUD is W/L/t ≒ 100/70/10 μm, and boiling chimney hole size is hard to observe. It is because that the surface of the specimen is contacts cladding, and the crack that would have been used as a passage of heat released from the cladding. While iron shows generally even distribution and concentration of oxygen is clearly different at the upper part from the lower part. And the distribution of nickel shows a big concentration difference by specific area,

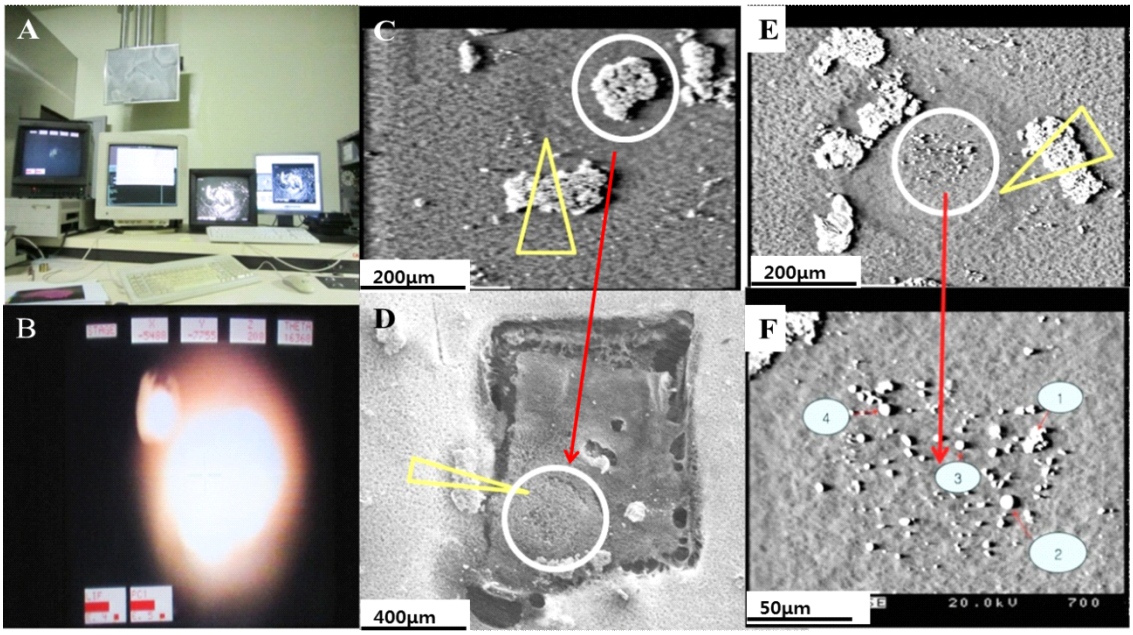

Fig. 5 EPMA monitor(a), Burning spot on monitor(b), CRUD flake before and after burning (c, d) and Close-up image of after burning CRUD (e, f). (Beam conditions: 20 kV, 1200 nA, Beam exposure time: 5 sec)

same as the concentration distribution of Cr. Zr component was observed as shown in Fig. 4. The presence of Zr component in the CRUD is likely to be the part of the test surface that was in contact with fuel cladding, that is ZrO_2. And the weight of iron and nickel, which are the representative constituents of CRUD, are over 20% respectively. The composition ratio of iron and nickel, Normalized at%, Ni/Fe = 1.11.

3.2.3. After abnormal high beam current injection

Even though the general power application conditions for EPMA analysis are about 20 kV and 10 nA, We increased the current conditions until the CRUD start to burn. The end of the power condition was 20 kV and 1200 nA. To increase the current condition, we created current by opening an adjustable aperture device for gun alignment adjustment on the EPMA. When the current up to 1200 nA, we could see the current value displayed on the screen. The value of the current displayed on the screen was 1200 nA, but in our opinion it is assumed that the value of the current actually applied will be much higher. This is because it is difficult to generate a constant current when the adjustable aperture device for gun alignment is opened. In other words, since the current flow can be very large and variable, we estimate that the final current value applied to the CRUD sample was estimated to be 1,500 ~ 2,000 nA.

When we applied the current up to 1200 nA, we were able to identify the burning spot on the monitor. After applying the current for 5 seconds, we could observe that the shape of the CRUD was changed as shown in Fig 5. As shown in Fig. 2, we as we initially thought, CRUD is a kind of pebbles or sand grains buried in the leafy bushes piled up on the pine tree trail. During burning, all non-metallic materials, coolant impurities and sludge were disappeared. As shown in Fig. 5, it must be the material that forms most of the CRUD. Therefore, metal materials of pure CRUD are judged to be very small volume in the overall CRUD. The reason for this phenomenon is considered to be charging, which is a phenomenon that occurs due to insufficient current flow.

Charging means; when very large amount of electron shot from a gun is projected to a paper filter which is a nonconductive material, even though the specimen is carbon deposited, electron congestion momentarily occurs at the CRUD when the electron cannot get out by earth. In charging, heat is created from the interaction when a large amount of electron temporarily collides with specimen with poor conductivity. It is considered that part of CRUD is evaporated and main metal composition material such as iron remains. Attention is required since the application of this condition can big damage the device.

3.2.4. After burn, remained metallic CRUD precipitate no1 ~ no 4 analysis

3.2.4.1. Remained metallic CRUD precipitate no1

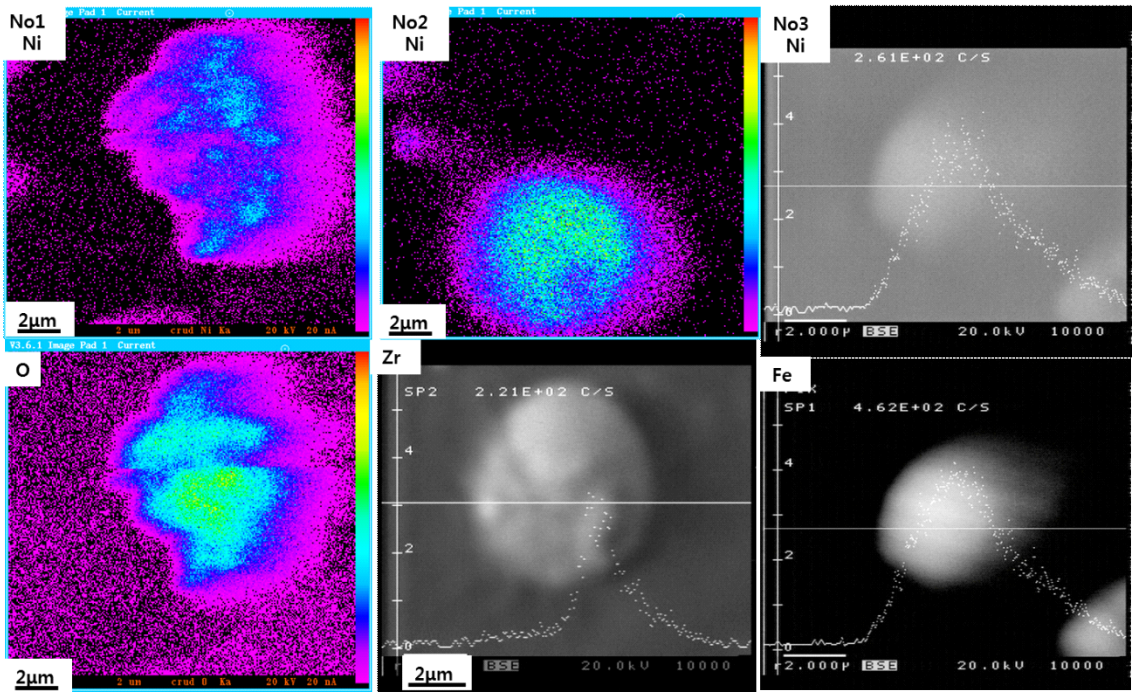

Fig. 6 After burn, remained metallic CRUD precipitate no1~no 3 analyses (SEM x10,000).

Fig. 6 shows a typical nickel ferrite like the composition shown in Table 3. The distributed locations of nickel, ion and oxygen are different. In particular, iron shows a higher composition in the lower part of the specimen. Oxygen shows a similar concentration distribution as iron. According to M. Haginuma, The formation of nickel ferrite, which is known to be the main composition of fuel CRUD, is an important subject in relation to reactor coolant chemistry, which is also formed by an exchange reaction between Ni 2^{+} in the coolant and $Fe2^{+}$ in the Fe_3O_4 lattice [10]. The results of the x-ray map, as shown in in Fig. 6.

Table 3 After burning, remained metallic quantitative analyses. (Beam conditions: 20 kV, 20 nA)

	Fe	Ni	Zn	Cr	O	Ni/Fe
No1						
wt %	30.36	16.52	0.37	0.84	17.74	
At %	27.80	14.39	0.21	0.83	56.69	0.52
No2						
wt %	28.39	20.89	0.42	1.66	0.00	
At %	56.33	39.43	0.70	3.54	0.00	0.70
No3						
wt %	25.54	20.10	0.43	0.70	0.38	
At %	54.20	40.58	0.78	1.61	2.82	0.75
No4						
wt %	19.04	18.28	0.39	1.62	5.73	
At %	32.56	29.73	0.57	2.97	34.18	0.91

Agree with M. Haginuma's paper, which we confirmed.

3.2.4.2. Remained metallic CRUD precipitate no2

Table 3 shows the average value achieved by analyzing the no. 2 parts of the specimen. The ratio is Ni/Fe = 40/56 and there is zero oxygen. The Zirconium mass shown in the lower part of the picture is considered to be either scrapes off the cladding surface or precipitated from colloid that was present in the coolant. In the x-ray map of oxygen, the results of quantitative analysis shows there is no oxygen in the mass. Therefore, it is considered that this is not ZrO_2, present as oxide on the surface of cladding, but zirconium colloid dissolved in coolant or another masses. Zirconium is present both in precipitated and independently form because it does not have metal affinity with nickel or iron.

3.2.4.3. Remained metallic CRUD precipitate no3

No.3 shows the same characteristics as no. 2. In terms of iron and nickel traces, the same distribution curve is spotted at the same location under exactly same analysis conditions. This means that this is a full employment condition. The melting temperature at this point is considered to be around over 1,000 ℃ (Ni melting point 1,450 ℃), however, to make a more accurate analysis, it is necessary to collect the specimen in a new way, or to find another appropriate method using devices such as a TGA.

3.2.4.4. Remained metallic CRUD precipitate no4

No. 4 has a ratio of Fe/Ni/O = 1/1/1. It has an oxide condition different form other masses. Here, the material that has been dissolved as a particulate or ion phase in the coolant is present in the CRUD with an exchange reaction between Ni 2^+ in the coolant, $Fe2^+$ in the Fe_3O_4 lattice = NiFe, in the exchange reaction between Ni 2^+ in the coolant, $Fe_2[OH]_3$ in the $Fe_3O_4 + 3H_2O$ = NiFeO [11,12]. More research is required to determine the composition and distribution of such materials. When an appropriate method of specimen collection and research is developed, it would be useful data like above analysis data for identification the basic component of CRUD.

4. Conclusions

During this study, EPMA power conditions were changed for experimentation. Even though the general power application conditions for an EPMA analysis are about 20 kV and 20 nA, the power conditions applied to this analysis were 20 kV and 1200 nA during 5 to 30 seconds The result were found that, part of the CRUD was evaporated, and the main metal composition, such as iron, obtained. The ratio of pure metal, compared to the volume of impurities and other water-soluble amorphous materials, is absolutely low in the entire volume of the CRUD. Fuel CRUD is generally composed of $NiFe_2O_4$, NiO, Ni^0 etc. During quantitative analyses the remaining metallic CRUD precipitate No1~4. $NiFe_2O_4$ was found at at No1 specimen, boll type pure Ni/Fe material at No3, and Fe/Ni/O = 1/1/1 at No4 specimen. The results from this experiment may be different from the composition of CRUD. However, this method is a new analytical method among various methods of analyzing CRUD by EPMA.

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