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Study on Formation of Chalk River Unidentified Deposits by Elemental Analysis of Metal Oxide Particles Deposited on Fuel Surface†

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Chalk river unidentified deposits (CRUD) samples were obtained from nuclear fuels during the fuel cleaning process. The samples were analyzed by EPMA-EDS for evaluating the formation of CRUD. We observed that the CRUD composed of many particles with different shapes. In the samples, we selected three different particles and measured their elemental compositions. The compositions of the particles were Cr-Ni-Zn-Fe based oxide, Co-W-Cr mixed oxide and Zr oxide, respectively. From the analysis based on elemental composition, Cr-Ni-Zn-Fe mixed oxide was considered as the mixture of Ni-Zn ferrites and Ni-Zn chromites. And, from high content of Co and W, it was thought that metal dissolution and enrichment steps were included in the CRUD formation process. Finally, we confirmed ZrO_2 layer could be removed from the fuel cladding during the fuel cleaning process.

Key Words: CRUD, Fuels, EPMA-EDS, Particle, Elemental composition.

INTRODUCTION

The behaviour of corrosion products in coolant system has been considered as an important issue for the safe operation of nuclear power plants[1-4]. The corrosion products are expected to be released from the structural materials in high temperature water. They may cause the metal oxide deposits on all surfaces in coolant system including fuels and steam generator. The metal oxide deposits are called as Chalk river unidentified deposits (CRUD), first observed in Canada deuterium uranium (CANDU) coolant system. Especially, the deposit of corrosion products on fuel clad is called as fuel CRUD. As the fuel CRUD is placed in the reactor core, it used to produce negative effects on the plant operation by reducing the heat transfer rate and generating the radioactive materials[1,5].

As CRUD originates from the corrosion product of the structural materials, the formation of CRUD depends on lots of environmental facts such as pH, temperature, redox condition, stress, impurities and so on. In addition, it also depends on the total surface area of the exposed materials. Nowadays, in nuclear power plants, the steam generator has been replacing a new one having more tubes with smaller diameter in order to mitigate the primary water stress corrosion cracking (PWSCC) of the tubes and to reduce long-term risk of crud-induced power shift. The increase of number of tubes caused the increase of the total contact surface of steam generator tubes. Therefore, more Ni species, the source of radioactive cobalt, could be released from the steam generator tubes into the reactor coolant. The new design of the steam generator makes the CRUD issue more important.

In order to investigate the influence of CRUD on the operation of coolant chemistry, many researchers have been developing the new technologies and studying the behaviour of CRUD. Especially, CRUD composition data gives the information on the source of CRUD and the CRUD formation process. In addition, the chemical information of CRUD can be used to enhance the performance of the techniques to mitigate of the radioactivity of CRUD such as the zinc addition. In general, zinc ion is added into the reactor coolant to stabilize the oxide layer formed on the surface of structural materials.

In this study, we analyzed the particles in CRUD samples by electron probe micro-analyzer (EPMA) equipped with

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energy dispersive X-ray spectrometer (EDS). It was observed that particles which were composed of Ni-Fe based oxides, Co-W containing oxide and zirconium oxide, respectively. We found some metal ingredients were enriched in CRUD particles. This means that a metal dissolution step could be included during the CRUD formation. We also estimated that zirconium oxide layer was removed from the fuel cladding surface by the ultrasonic fuel cleaning.

EXPERIMENTAL

All CRUD samples were obtained from a nuclear power plant in which the zinc addition technique was applied. The CRUD was sampled by using the paper filters during the ultrasonic fuel cleaning process. The amount of the filtered CRUD was less than 1 mg for each sample. The radioactive CRUD samples were packed in a shielded canister and moved to the radiochemical laboratory for the surface analysis. As shown in Fig. 1, the filter papers containing the CRUD samples were divided into several pieces. And then, one piece was selected for the surface analysis. The morphology and elemental composition of the CRUD sample was analyzed by EPMA (Model: JEOL JXA-8600) equipped with EDS (Model: Oxford Inka Energy).

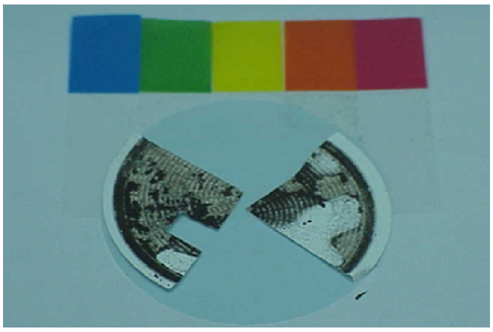

Fig. 1. A photo of filter paper containing CRUD sample (black particles) divided into several pieces.

RESULTS AND DISCUSSION

Fe-Ni-Cr-Zn oxide particles: The commonly observed CRUD is known as the nickel ferrite of which composition is Ni-Fe mixed oxide[3]. And the transition metals such as Ni, Co and Zn were known to form their ferrites, respectively. As Cr is an alloying element of steam generator tube, Cr could be found in CRUD particles with Ni and Fe.

A CRUD sample was observed which is mainly composed of Fe-Ni-Cr-Zn. Fig. 2 shows the microscopic photo of the sample and the element distribution maps obtained by EPMA. The elemental composition of the sample was shown in Table-1. In the element distribution maps, 4 metal elements were distributed in a same position in the center of the photo. From the analysis of the maps and the elemental composition data, these 4 metallic elements were chemically coexisted forming a particle. From the reported information on CRUD[1,3,6], it was easily expected that the particle is formed as Ni-Zn ferrites and chromites. Fe, Ni and Cr are definitely come from the structural materials. However, Zn ion was added into the coolant to reduce the radioactivity of reactor coolant system. As the CRUD samples were collected after Zn addition in the plant, the presence of Zn in CRUD sample is evidence that Zn ion was successfully included into the metal oxide layer.

TABLE-1
ELEMENTAL COMPOSITION OF CRUD SAMPLE SHOWN IN Fig. 2

Element	Weight %
Si	1.35
Cr	30.31
Fe	43.13
Ni	16.81
Zn	8.40
Total	100

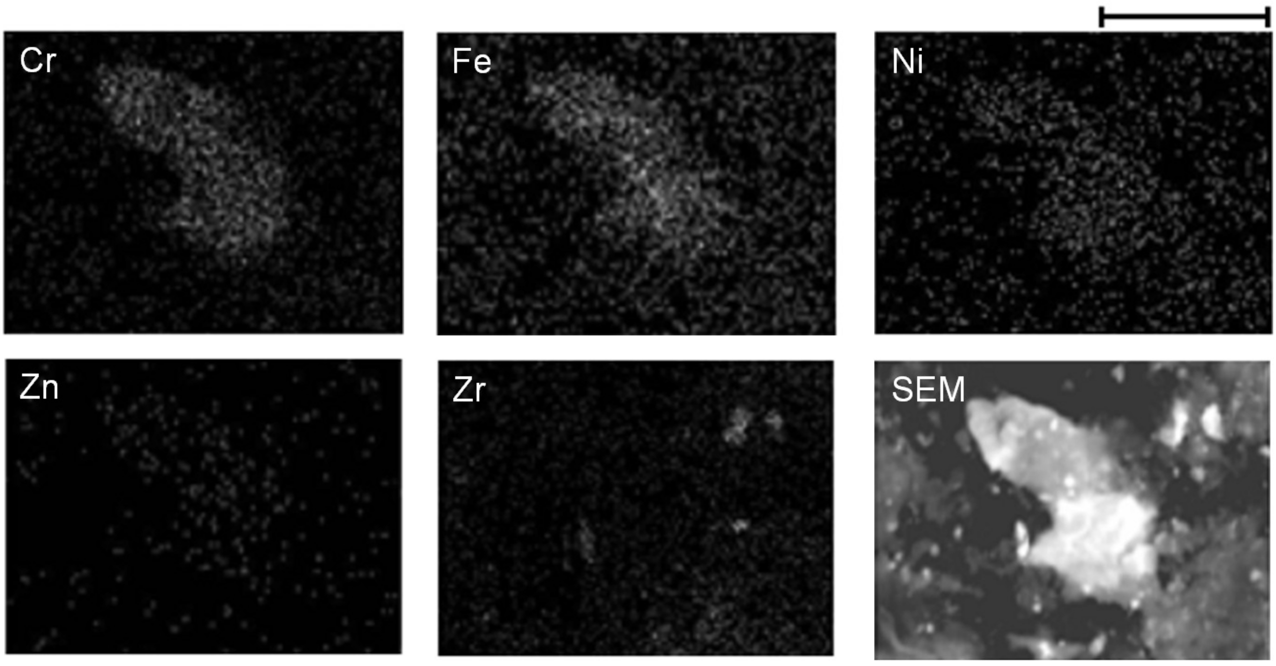

Fig. 2. Element distribution maps of a CRUD sample (scale bar: 10 μm)

Co-W-Cr oxide particles: As Co and W are minor alloying elements of structural materials, these two elements are expected to be minor component in CRUD. Especially, Co element is carefully controlled in the alloy manufacture process, because Co is a source element of radioactive Co. However, we found a particle composed of Co and W elements with high concentration.

Fig. 3 shows a CRUD sample which was composed of many particles with different shapes. In the figure, 5th positions representing each shape were designated by the position numbers. The elemental composition of each position was shown in Table-2. The major composition of the particles, besides the composition at position 1, was evaluated as nickel ferrite. At point 1, the major composition was Co-W-Cr mixed oxide which was quite different from others. And their concentration values were higher than those of structural metals. This is evidence that the CRUD formation process includes a metal dissolution reaction, an enrichment step and a precipitation (or crystallization).

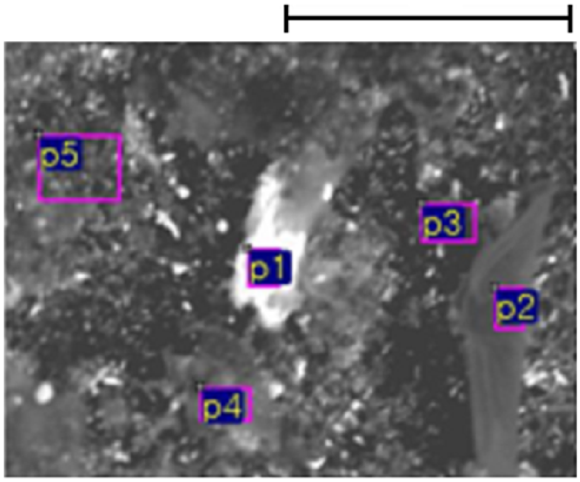

Fig. 3. SEM photo of CRUD sample with different shapes (scale bar: 30 μm)

TABLE-2
ELEMENTAL COMPOSITION OF EACH POSITION SHOWN IN Fig. 3

Element	Weight %				
	P1	P2	P3	P4	P5
Si	–	18.44	14.11	9.96	15.45
Cr	43.36	8.81	8.39	9.66	13.14
Fe	6.21	30.74	34.92	26.9	37.15
Co	33.06	–	–	–	–
Ni	2.35	17.44	11.94	16.51	20.34
W	15.01	–	–	–	–
Zn	–	–	5.46	6.21	–
Zr	–	24.58	25.19	30.76	13.91
Total	100	100	100	100	100

Zirconium oxide particles: As zirconium metal is oxidized spontaneously and formed a very protective zirconium oxide layer, Zr alloys have very good performance in corrosive media such as high temperature water. In addition, as Zr is a stable element under neutron radiation, Zr alloys have been used as fuel cladding materials for a long time.

In Fig. 4, it was shown the SEM photo and the element distribution maps of a CRUD sample. From the elemental composition in Table-3 and the distribution maps, the particle is definitely composed of ZrO_2. Besides this particle, we found many ZrO_2 particles with different shape in other CRUD samples. In addition, it was reported[3] that Zr was one of the major metallic elements of CRUD obtained from the ultrasonic fuel cleaning. Therefore, it is confirmed that ZrO_2 layer could be removed from the fuel cladding surface during the ultrasonic fuel cleaning process.

TABLE-3
ELEMENTAL COMPOSITION OF CRUD SAMPLE SHOWN IN Fig. 4

Element	Weight %
Fe	1.74
Zr	98.26
Total	100

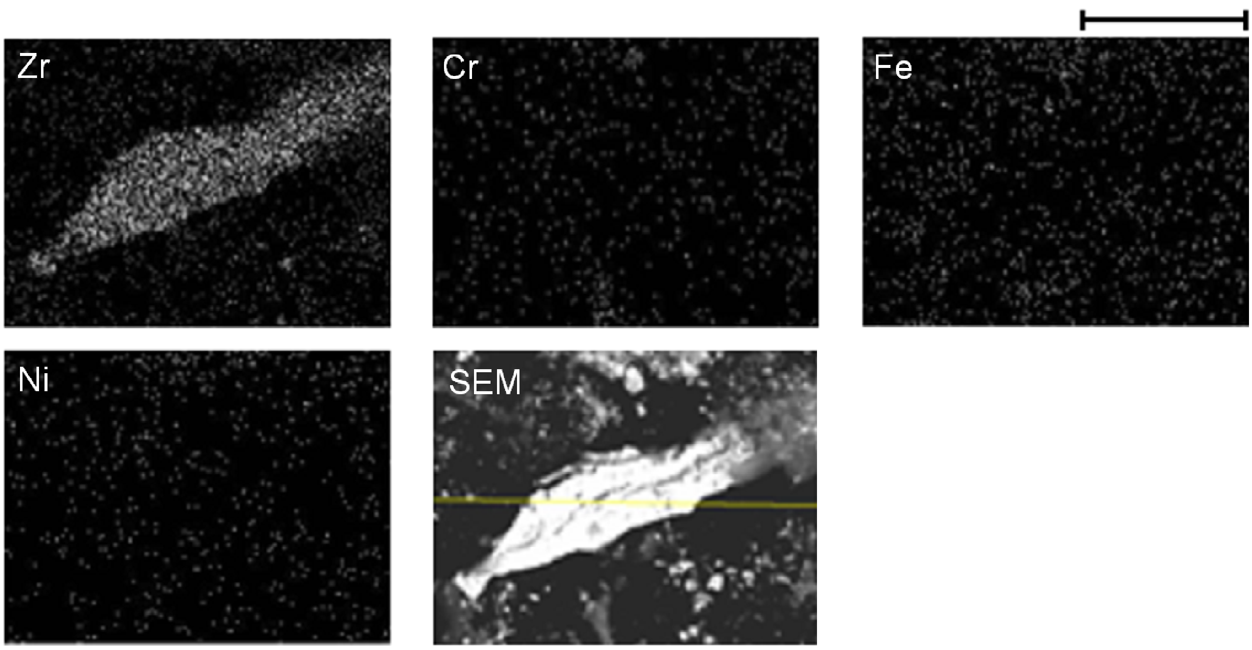

Fig. 4. Element distribution maps of CRUD sample (scale bar: 10 μm)

Conclusion

The fuel CRUD was composed of many kinds of particles with different shapes. We focused on the elemental compositions of three different particles. First, for Cr-Ni-Zn-Fe mixed oxide particle, these four elements had the same distribution on the elemental distribution maps. It was evaluated that the particle was composed of Ni-Zn ferrites and chromites. Second, we found a Co-W-Cr mixed oxide particle in the nickel ferrite based CRUD. From high concentration of Co and W, it was concluded that metal dissolution reaction and enrichment step were included in the CRUD formation process. Last, for Zr oxide particle, we confirmed that ZrO_2 layer were removed from the fuel cladding surface during the ultrasonic fuel cleaning process.

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