Surface Analysis Study on ZIRLO Cladding Hulls Oxidized at Low Temperatures

저온 산화된 ZIRLO 피복관의 표면분석 연구

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Surface oxidation behavior of ZIRLO (ZIRconium Low Oxidation) hulls was investigated using an X-ray photoelectron spectroscopy (XPS) technique. The effects of oxidation time (10-336 h at 500°C) and temperature (400-700°C for 10 h) were studied. Deconvolution results of the hulls oxidized at 500°C revealed that a ZrO_2 phase appeared after 24 h (11.86%), and an increase in the ZrO_2 ratio was observed when the hulls were oxidized for 336 h (17.93%). On the other hand, the ZrO phase which employed 5.68% in the 10 h oxidized sample disappeared when the oxidation time increased to 24 h. The XPS results also showed that an increase in the oxidation temperature resulted in an increase in the ratio of ZrO , which increased from 0 to 5.68, 8.31, and 9.16% when the oxidation temperature increased from 400 to 500, 600, and 700°C, respectively. ZrO_2 phase was observed only in the sample that was oxidized at 700°C. The mechanism of ZrO formation was not conclusive, but it was suggested that a formation of hydroxide might have been accelerated at elevated temperatures leading to a formation of a $\text{Zr}(\text{OH})_4$ phase. The relationship between the surface oxidation status of the hulls oxidized at 500°C and their chlorination reaction feasibility was discussed, and it was suggested that the thickness of the oxide layer is an important parameter that determines the chlorination reaction feasibility.

Keywords: X-ray photoelectron spectroscopy, Cladding hull, ZIRLO, Oxidation, Chlorination

본 논문에서는 X선 광전자 분광법(X-ray photoelectron spectroscopy, XPS)을 이용하여 ZIRLO (ZIRconium Low Oxidation) 피복관의 표면 산화 거동을 연구하였다. 산화 시간 (10-336 시간, 500°C) 및 산화 온도 (400-700°C, 10 시간)에 따른 산화 특성 변화를 관찰하였다. XPS peak 분석 결과, 500°C에서 산화된 피복관의 산화 시간이 24 시간이 될 때 ZrO_2 peak가 11.86% 관찰되었으며, 이후 산화 시간이 길어질수록 ZrO_2 의 비율이 17.93%까지 (336 시간) 증가하는 것이 확인되었다. 반면, 10 시간 산화된 피복관에서 5.68% 존재하던 ZrO 상은 산화 시간이 24 시간으로 늘어남에 따라 사라지는 것이 관찰되었다. 산화 온도 증가에 의한 영향 분석 결과에서는 산화 온도가 400°C에서 500, 600, 700°C로 증가할 때 ZrO 상의 비율이 0% 부터 5.68, 8.31, 9.16%로 증가하는 것이 확인되었다. 이 때, ZrO_2 상은 700°C에서 산화된 시료에서만 관찰되었다. ZrO 상의 형성 메커니즘은 불명확하지만, 고온에서 공기 중의 수분과 Zr의 반응으로 인해 $\text{Zr}(\text{OH})_4$ 상의 형성이 가속되는 것으로 예상된다. 본 논문에는 500°C에서 산화된 ZIRLO 피복관과 이들의 염소화 반응 특성에 대한 논의도 포함되었으며, 염소화 반응 진행 가능성에 있어서 산화막의 두께가 중요한 역할을 하는 것으로 보여진다.

중심단어: 폐 피복관, 표면분석, ZIRLO, 산화, 염소화

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1. Introduction

Cladding hull waste is an interesting subject in the nuclear waste treatment field, owing to its large portion (about 25wt%) in used nuclear fuel (UNF) and high content of Zr (about 97wt%) [1, 2]. Currently, acid washing and compaction techniques are widely employed to manage the cladding hull waste. The acid washing is a convenient method to remove residual UNF from the cladding hulls that are stuck on the inner surface, but it is also well known that the acid washing procedure is insufficient to classify the cladding hull waste as a low-level waste [3, 4]. In addition, it was revealed that the radioactivity of ^{94}Nb , which is one of the major radioactivation products of Nb contained in ZIRLO (ZIRconium Low Oxidation) cladding hull material, exceeds acceptance limit of the Wolsong LILW (Low and Intermediate Level Waste) disposal center (WLDC) of Korea [5]. Thus, a selective recovery of Zr from the cladding hull waste is an attractive approach to minimize the generation of mid-/high-level waste regardless of UNF treatment methods. The selective recovery of Zr is also considered as a pre-treatment of dry storage systems, because a separation of cladding hulls from nuclear materials can eliminate the risk of fractured cladding and handling issues during storage and transportation [1].

There are two technologies under research at the Korea Atomic Energy Research Institute (KAERI) for the selective recovery of Zr: chlorination and electro-refining techniques. The latter employs electrochemical reactions to dissolve and selectively recover metallic Zr by controlling an applied potential or current [6-8]. This technique has some advantages including recovery of Zr in its metallic form and relatively mild operation conditions, while the reaction rate, scale-up, and electrolyte treatment issues need verification. The chlorination process employs a simple chemical reaction between metallic Zr and chlorine gas to produce zirconium tetrachloride which sublimates at 331°C. During the chlorination process, the purity of recovered Zr is determined by the operation temperature owing to a

formation of volatile chlorides of other constituent metals such as niobium and tin [4]. Compared to the electro-refining process, it is suggested that the chlorination process is more convenient to control the reaction rate and scale-up, while a reduction of recovered ZrCl_4 should be followed if it cannot be recycled during cladding hull production [1].

The chlorination process was previously demonstrated at the Institute of Research and Innovation (IRI, Japan) [9], KAERI (Korea) [10], and Oak Ridge National Laboratory (ORNL, USA) [1]. At the IRI, a recovery of Zr from Zircaloy-2 cladding hulls was successfully demonstrated in the presence of Ni and Co, which are major sources of radioactivity of cladding hull waste [9]. At KAERI, Zircaloy-4 cladding hulls were employed for the chlorination reaction, and highly pure ZrCl_4 (99.97wt%) was recovered without further heat treatments [10]. At the ORNL, an actual cladding hull (Zircaloy-2) of UNF was employed for the chlorination reaction, and high decontamination factors (> 1200 for total radiation) were reported [1]. It should be noted that the previous reports employed Zircaloy alloys for the chlorination process because they are major cladding materials stacked in reactor site pools. However, it is well known that nowadays ZIRLO is widely employed in pressurized water reactors as well as Zircaloy alloys. Tin (~1.5wt%), iron (~0.2wt%), and chromium (~0.1wt%) are the major alloying elements in Zircaloy-4, while niobium (~1.0wt%), tin (~1.0wt%), and iron (~0.1wt%) are alloyed with Zr for ZIRLO offering enhanced corrosion resistance over the Zircaloy alloys. The enhanced chemical characteristic of ZIRLO makes it worth verifying a feasibility of Zr recovery from ZIRLO cladding hulls through the chlorination method.

We previously reported that the surface oxidation status of Zircaloy-4 cladding material played a key role in determining the feasibility of the chlorination reaction [11]. An X-ray photoelectron spectroscopic (XPS) result revealed that the Zircaloy-4 hulls oxidized at 500°C for 5 h, which was reactive to chlorine gas, contained Zr_2O_3 (83.0%) and ZrO (17.0%) phases on its surface, while the other one that

was oxidized at 700°C for 5 h had Zr_2O_3 (69.4%) and ZrO_2 (30.6%) phases on its surface and was not reactive with chlorine gas [11]. Although the relationship between the surface oxidation status and chlorination reaction feasibility is not clear yet, it is obvious that the surface oxidation status should be considered as a key parameter in designing the chlorination process. In the case of ZIRLO, only one report was presented on the chlorination reaction behavior [12]. Interestingly, it was shown that the ZIRLO hulls oxidized at 500°C for various hours (from zero to 168 h) exhibit significantly different chlorination reaction behaviors. Some reaction products were observed in the hulls oxidized for 24 h, while no signs of reaction were observed in the 72 h oxidized hulls. Thus, it might be interesting to clarify what happened to the surface of the hulls when they were oxidized at different conditions.

2. Experimental

The surface oxidation status of the hulls was investigated using the XPS (Kratos AXIS Nova) technique. Monochromated Al $K\alpha$ (1486.76 eV) was employed to collect the spectra at 0° between the sample surface normal and the analyzer lens. A pass energy of 40 eV and step size of 50 meV were employed for the high-resolution regions scans. The charge compensation of the samples was performed during the measurement using a charge neutralizer. The measured binding energies were referenced with respect to C 1s peak at 284.8 eV. Deconvolution of the XPS peaks was performed using the XPS 4.1 software [13]. The effect of oxidation time on the surface oxidation status was studied by preparing 5 cm-long ZIRLO hulls oxidized at 500°C for 10, 24, 72, 168, and 336 h under an air atmosphere. In addition, the effect of oxidation temperature was also investigated by oxidizing the ZIRLO hulls at 400, 600, and 700°C for 10 h. Through this paper, the hull samples were denoted as 'ZIRLO-(oxidation temperature)-(oxidation time)' for convenience, and thus ZIRLO-500-72 means

Fig. 1. Experimental set-up and pictures of reaction reactants and products for ZIRLO-500-10.

ZIRLO hulls oxidized at 500°C for 72 h. In accordance with the surface oxidation status, the detailed results of our previous work [12] on the chlorination reaction behavior of ZIRLO hulls oxidized at 500°C for various periods (0-168 h) were introduced in the present study. A previously reported experimental set-up was employed for the chlorination experiments [10]. Briefly, the reactor is a vertical quartz tube which has a quartz frit in the middle so that it can hold cladding hulls at the reaction zone while gases and volatile reaction products can pass through it. The chlorination reaction was performed at 380°C for 2 h while feeding argon and chlorine gases at a flow rate of 20 mL/min for each gas. Experimental set-up of the chlorination reaction experiments is shown in Fig. 1.

3. Results and Discussion

Before getting started with the oxidation status analysis of the ZIRLO hulls, the relationship between an oxidation condition and a chlorination reaction behavior needs to be discussed, because it can help to clarify the relationship

Table 1. A summary of the chlorination reaction experimental results including the results of previous work [12]. The experiments were performed at 380 °C for 2 h under a flow of 20 mL min⁻¹ Ar and 20 mL min⁻¹ Cl₂

Samples	Reactant	Residue	Product	Weight loss
ZIRLO-bare	10.05 g	4.34 g	13.33 g	56.8 wt%
ZIRLO-500-10	10.07 g	6.56 g	7.66 g	34.9 wt%
ZIRLO-500-24	10.16 g	6.57 g	7.90 g	35.3 wt%
ZIRLO-500-72	10.09 g	10.09 g	0.00 g	0.0 wt%
ZIRLO-500-168	10.13 g	10.13 g	0.00 g	0.0 wt%

between the oxidation status and chlorination reaction behavior. A summary of the chlorination reaction behavior is listed in Table 1, including the results of our previous work [12]. The pictures of reaction reactants and products for ZIRLO-500-10 are shown in Fig. 1. It is clear, at once, that an increase in the oxidation time reduces the reaction rate of the ZIRLO chlorination reaction. It is interesting to observe that a significant change in the weight loss was observed between ZIRLO-bare and ZIRLO-500-10, while the difference between ZIRLO-500-10 and ZIRLO-500-24 is negligible. In addition, it was found that ZIRLO-500-72 is not reactive with chlorine gas meaning that these hulls were completely protected by oxide layers from chlorine gas. The weight loss behavior of ZIRLO hulls oxidized for 24 h is somewhat different from the case of Zircaloy-4 [11]: weight loss values for the Zircaloy-bare and Zircaloy-500-24 cases were 54.1 and 50.7%, respectively, meaning that the protective role of the surface oxide layer is more significant in the ZIRLO hulls. As the previous study [11] lacks the chlorination reaction behavior of the hulls oxidized for 72 and 168 h, an additional experiment was performed for Zircaloy-500-168 for comparison, and no signs of reaction were observed at the identical reaction condition of this study. These results reveal that the oxide layers formed on the surface of ZIRLO hulls impact more influence on the chlorination reaction than the oxide layers of Zircaloy-4 hulls, while both the ZIRLO and Zircaloy-4 hulls are completely protected from chlorine gas when they

Table 2. Oxide thickness values of ZIRLO and Zircaloy-4 alloys calculated using oxide thickness rate constant values offered by Natesan and Soppet [14]

ZIRLO					
At 500°C	10 h	24 h	72 h	168 h	336 h
	2.08 μm	3.22 μm	5.58 μm	8.52 μm	12.05 μm
For 10 h	At 400°C	At 500°C	At 600°C	At 700°C	
	0.32 μm	2.08 μm	11.85 μm	19.90 μm	
Zircaloy-4					
At 500°C	10 h	24 h	72 h	168 h	336 h
	1.76 μm	2.73 μm	4.72 μm	7.21 μm	10.20 μm
For 10 h	At 400°C	At 500°C	At 600°C	At 700°C	
	0.33 μm	1.76 μm	18.59 μm	26.15 μm	

are oxidized at 500 °C for 72 - 168 h. It might be natural to suspect the thickness of oxide layers as a reason for the reduced chlorination reaction rate. Previously, Natesan and Soppet reported air oxidation rate constants for Zircaloy-4, ZIRLO, and M5 alloys at various temperatures [14]. Oxide thickness values calculated using the values offered by Natesan and Soppet are listed Table 2. Here, it should be noted that the rate constant values for a pre-breakaway case were employed, because a breakaway (peeling-off of oxide layers) behavior was not observed in the samples of the present study. As shown in the table, the thickness of oxide layer was almost doubled when the oxidation time increased from 24 to 72 h, and it is suggested that 5.6 μm is thick enough to protect ZIRLO hulls from chlorine gas. A comparison between the ZIRLO and Zircaloy-4 hulls might be meaningful, and it was shown that, when oxidized at 500 °C, the ZIRLO hulls exhibit thicker oxide layers and a lower chlorination reaction rate than the Zircaloy-4 hulls.

The relationship between the oxidation conditions and chlorination reaction behavior was further investigated by employing the XPS technique. Fig. 2 shows the XPS measurement and deconvolution results of the ZIRLO hulls oxidized at 500 °C for up to 336 h. Detailed information of

Fig. 2. The XPS measurement and deconvolution results for Zr 3d_{5/2} peaks of the ZIRLO hulls oxidized at 500°C for (a) 10, (b) 24, (c) 72, (d) 168, and (e) 336 h under an air atmosphere.

Table 3. The deconvolution calculation results of the XPS measurement results of the ZIRLO cladding hulls. The peak position of Zr $3d_{5/2}$ peak is denoted, and ratio of each oxidation state was determined using the peak areas of Zr $3d_{5/2}$ peaks

Ox. temp.	Ox. time	ZrO	Zr ₂ O ₃	ZrO ₂
500℃	10 h	180.64 eV 5.68%	182.04 eV 94.32%	
500℃	24 h		181.95 eV 88.14%	182.83 eV 11.86%
500℃	72 h		181.76 eV 90.14%	182.50 eV 9.86%
500℃	168 h		181.79 eV 91.84%	182.61 eV 8.16%
500℃	336 h		181.93 eV 82.07%	182.62 eV 17.93%
400℃	10 h		182.15 eV 100%	
500℃	10 h	180.64 eV 5.68%	182.04 eV 94.32%	
600℃	10 h	180.59 eV 8.31%	181.93 eV 91.69%	
700℃	10 h	180.85 eV 9.16%	182.11 eV 81.42%	183.46 eV 9.42%

the deconvolution calculation results are listed in Table 3. As shown in the Figure and Table, a small portion of ZrO phase was observed in the ZIRLO-500-10 sample, while the Zr₂O₃ phase was identified as the major component even when the oxidation time is increased up to 336 h. Interestingly, the ratio of ZrO₂ phase did not change significantly when the oxidation time increased from 24 to 168 h (11.86 - 8.16%), but a meaningful increase was observed in the ZIRLO-500-336 sample (17.93%). Recalling that ZIRLO-500-24 was reactive with chlorine gas while ZIRLO-500-72 was not, and that the ratio of ZrO₂ phase was 11.86 and 9.86% for each sample, it is suggested that, in this case, the ratio of ZrO₂ is not a key parameter that determines the chlorination reaction feasibility. This result is not in line with our previous results for the Zircaloy-4 hulls, where it was concluded that ZrO can provide a pathway for chlorine gas, while Zr₂O₃ and ZrO₂ cannot [11]. However, the chlorination reaction result of ZIRLO-500-24 (35.3% weight loss) shows that the chlorination reaction can proceed in the absence of ZrO when the thickness of the oxide layer is thin enough (about 3.22 μm). A gap in the reactivity between side walls and cutting edges should be considered,

Fig. 3. The XPS measurement and deconvolution results for Zr $3d_{5/2}$ peaks of the ZIRLO hulls oxidized at (a) 400, (b) 600, and (c) 700°C for 10 h under an air atmosphere.

Fig. 4. The XPS measurement results of N 1s peaks of the ZIRLO hulls oxidized at 400, 500, 600, and 700°C for 10 h under an air atmosphere.

because the XPS results represent the oxidation status of side walls while the chlorination reaction prefers cutting edges [15]. The photograph of ZIRLO-500-24 shown in ref. [12] can give a hint on this issue, because some holes are clearly shown on the side wall of the reaction residue proving that chlorine gas was reactive with ZIRLO-500-24 along the side wall. Thus, it can be concluded that, for the chlorination reaction, the thickness of the oxide layer is a key parameter as is the surface oxidation status.

The effect of oxidation temperature on the surface oxidation status was also investigated using the XPS technique, and the deconvolution results are shown in Fig. 3. Detailed information of the deconvolution results are listed Table 3.

Fig. 5. The XPS measurement and deconvolution results for O 1s peaks of the ZIRLO hulls oxidized at (a) 400, (b) 500, (c) 600, and (d) 700°C for 10 h under an air atmosphere.

First, it is interesting to observe that the ratio of ZrO increases with an increase in the oxidation temperature: at 400°C, no signs of ZrO were observed while the portion of ZrO increased up to 9.16% in ZIRLO-700-10. As shown in the Zircaloy-4 hulls [11], it was expected that the portion of ZrO decreases while that of ZrO₂ increases with an increase in the oxidation temperature. However, the XPS results revealed an opposite results, and the ratio of ZrO₂ was only 9.42% for ZIRLO-700-10, which was 28.6-32.7% in Zircaloy-700-5 [11]. This result was further studied by analyzing the XPS signals of nitrogen, because it was reported that oxidizing the ZIRLO hulls under an air atmosphere could produce a ZrN phase [16, 17]. Fig. 4 shows the XPS measurement results for nitrogen 1s peak, and clearly, no signs of nitrogen are noticeable in all samples. Thus, the possibility was eliminated that the increased ratio of ZrO with increasing oxidation temperature might have come from the formation of the ZrN phase. The formation of zirconium hydroxide such as Zr(OH)₄ instead of ZrO was also suspected, because the oxidation experiments did not employ dry air, leaving room for a reaction between zirconium and water. The XPS measurement and deconvolution results for the oxygen 1s peak are shown in Fig. 5. Generally, the XPS peaks of oxygen in a zirconium compound have two positions: one from ZrO₂ (at 530.0 eV) and the other from Zr(OH)₄ (at 531.2 eV) [18, 19]. The deconvolution results revealed that the ratio of ZrO₂ increased with an increase in the oxidation temperature, but it should be noted that a significant portion (41.1%) of oxygen is still remaining in its hydroxide form even after oxidation at 700°C. Thus, it can be suggested that the increase in ZrO ratio with increasing oxidation temperature came from the formation of the Zr(OH)₄ phase. This result also suggests that the reaction between Zr and water included in the air is significantly accelerated at higher temperatures to produce Zr hydroxides.

4. Conclusions

The XPS results revealed that increasing the oxidation time at 500°C produces a greater ZrO₂ phase, although the relationship between oxidation time and ZrO₂ ratio is not linear. It was also shown that the chlorination reaction can proceed without a ZrO phase when the oxide layer is thin enough (around 3.2 μm), meaning that the oxide layer thickness should be considered as a key parameter during the hull chlorination process. The effect of oxidation temperature was also investigated, and it was shown that the ratio of ZrO increased from 0 to 5.68, 8.31, and 9.16% when the ZIRLO hulls were oxidized at 400, 500, 600, and 700°C for 10 h, respectively. The possibility of a ZrN phase formation was eliminated owing to a lack of nitrogen peaks in the XPS measurement results. The XPS peak analysis on the O 1s peaks revealed that 41.1% of oxygen is still remaining in its hydroxide form even in the ZIRLO-700-10 sample, suggesting that the increased ZrO ratio might have come from a formation of Zr hydroxide forms such as Zr(OH)₄.

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