DOI: 10.24425/122441

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SURFACE CHARACTERIZATION OF METALLIC FUEL SLUGS PREPARED BY MODIFIED INJECTION CASTING

Metallic fuel slugs containing rare-earth (RE) elements have high reactivity with quartz (SiO_2) molds, and a reaction layer with a considerable thickness is formed at the surface of metallic fuel slugs. The surface characterization of metallic fuel slugs is essential for safety while operating a fast reactor at elevated temperature. Hence, it is necessary to evaluate the surface characteristics of the fuel slugs so that chemical interaction between fuel slug and cladding can be minimized in the reactor. When the Si element causes a eutectic reaction with the cladding, it deteriorates the metallic fuel slugs. Thus, it is necessary to examine the characteristics of the surface reaction layer to prevent the reaction of the metallic fuel slugs.

In this study, we investigated the metallurgical characteristics of the surface reaction layer of fabricated U-10wt.%Zr-*X*wt.%RE ($X = 0, 5, 10$) fuel slugs using injection casting. The results showed that the thickness of the surface reaction layer increased as the RE content of the metallic fuel slugs increased. The surface reaction layer of the metallic fuel slug was mainly formed by RE, Zr and the Si, which diffused in the quartz mold.

Keywords: Sodium-cooled fast reactor, Metallic fuel slug, U-Zr alloy, Surface characterization, Injection casting

1. Introduction

A prototype generation-IV sodium-cooled fast reactor (PGSFR) is being developed in combination with the pyroprocessing of spent PWR fuel. A metallic fuel is used for the sodium-cooled fast reactor (SFR), which is a representative model of a Gen-IV reactor. To maintain the sustainability of nuclear power generation, it is very important to develop the technology of the SFR, which is the most promising candidate reactor among the Gen-IV reactor candidates under development. Nuclear fuel charged in an SFR can be recycled by the pyroprocessing of spent fuel used in a light-water reactor (LWR), thereby increasing the utilization of uranium and reducing the amount of high-level waste. Currently, the most promising fuel candidate material for an SFR is metallic fuel, which is fabricated through a modified injection casting method to prevent the volatilization of the minor actinide elements, such as Am. The metallic fuel slugs were cast in quartz (SiO_2) molds of Φ5-L400 mm after induction melting in a graphite crucible with the injection casting method. Metallic fuel has many advantages: reactor safety, good neutron economy, high thermal conductivity, and excellent compatibility with a Na coolant [1-6].

A modified injection casting has been used for production of metallic fuel slugs as an alternative fabrication method. The modified injection casting prevents the evaporation of volatile elements under pressurized Ar atmosphere during the melting process [7]. The uranium-zirconium-rare earth (U-Zr-RE) alloys have a strong reactivity with quartz molds. The Si element in a quartz mold reacts and penetrates the U-Zr-RE metal fuel slug during injection casting. In particular, a large part of the reaction layer exists outside the fuel slug, which causes a reaction with the stainless steel cladding during irradiation. In this study, we fabricated the U-10wt.%Zr-*X*wt.%RE ($X = 0, 5, 10$) fuel slugs using modified injection casting, and then we investigated the metallurgical characteristics of the surface reaction layer.

2. Experimental

U-10wt.%Zr fuel slugs with RE element content of 0, 5, and 10wt.% were fabricated by the modified injecting casting method. The RE alloy lumps were fabricated using four different lanthanide elements, with an overall composition of 53, 25,16 and 6 wt.% of Nd, Ce, Pr, and La, respectively [8]. The graphite crucible was coated with Y_2O_3 using a plasma spray method and the quartz mold was coated with Y_2O_3 using a slurry coating method. The quartz mold was preheated to 600°C while the charged metal-fuel material was heated to 1470°C. The quartz mold was immersed in the melted metal fuel material at 1470°C, and Ar gas was infused to inject the molten metal into the quartz

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mold. At the beginning of induction melting, the temperature inside the chamber was room temperature and the pressure was less than 1.5 × 10^{-2} torr. In order to prevent the evaporation of the molten elements, the atmosphere was maintained in an Ar atmosphere of 400 torr during the heating. The injection casting was carried out with a higher injection pressure of 0.2 MPa. The diameter of the U-10Zr-RE fuel slugs was 5 mm and the length was 250 mm. Fig. 1 shows the metallic fuel slugs cast with the quartz mold. The metallic fuel slug was divided uniformly into three equal parts over the entire length. The microstructure, phase composition, and phase identification of the fuel slugs were analyzed using scanning electron microscope (SEM) (JSM-6610, JEOL, Tokyo, Japan), energy-dispersive X-ray spectroscopy (EDS) (Oxford Instruments, Abingdon, UK) and X-ray diffractometry (XRD) on an AXS D8 Advance instrument (Bruker, Billerica, MA, USA) equipped with a Cu K_α source (wavelength λ = 1.54060 Å).

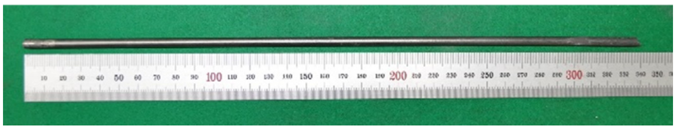

Fig. 1. Metallic fuel slugs fabricated by modified injection casting

3. Results and discussion

Fig. 2 shows the scanning electron micrographs and energy-dispersive X-ray spectroscopy of the U-10wt.%Zr fuel slug. A dark gray phase and a light gray phase were distinguished from the matrix in the top, middle, and bottom parts of metallic fuel slugs. The thickness of the surface reaction layer increased from the top to the bottom. Dark gray was formed on half of the surface reaction layer at the top part; however, the dark gray was uniformly formed to the boundary between the matrix and the surface reaction layer in the middle and the bottom. Zr mainly existed in the surface reaction layer.

Recent studies reported that Si-Zr forms a compound [9] and it is thought that a uniform Si reaction layer is formed due to the high-temperature reaction in the boundary layer between the quartz (SiO_2) template and the U-10Zr alloy. Fig. 3 and Fig. 4 show the scanning electron micrographs of U-10wt.%Zr-5wt.%RE and U-10wt.%Zr-10wt.%RE metallic fuel slugs, respectively. The figures show different shapes at the top, middle, and bottom surface reaction layers of the fuel slugs. The studies confirmed that the thickness of the surface layer increased from the top to the bottom. Fig. 5 shows the results of U-10wt.% Zr-5wt.%RE EDS mapping. The figure confirms that there were

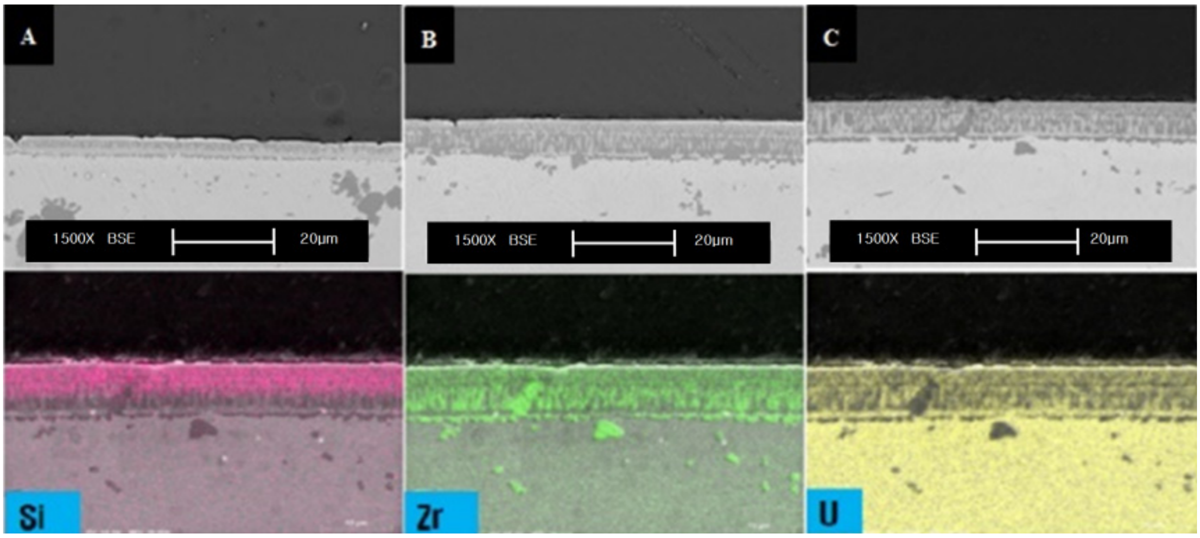

Fig. 2. Cross-sectional scanning electron micrographs and energy-dispersive X-ray spectroscopies mapping results showing the surface reaction layer of U-10wt%Zr fuel slug: (A) top, (B) middle, (C) bottom

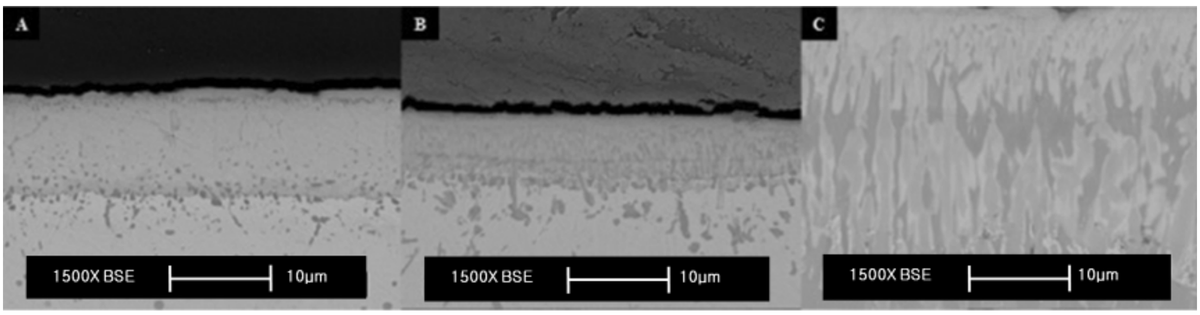

Fig. 3. Cross-sectional scanning electron micrographs showing the surface reaction layer of U-10wt% Zr 5wt.%RE fuel slug: (A) top, (B) middle, (C) bottom

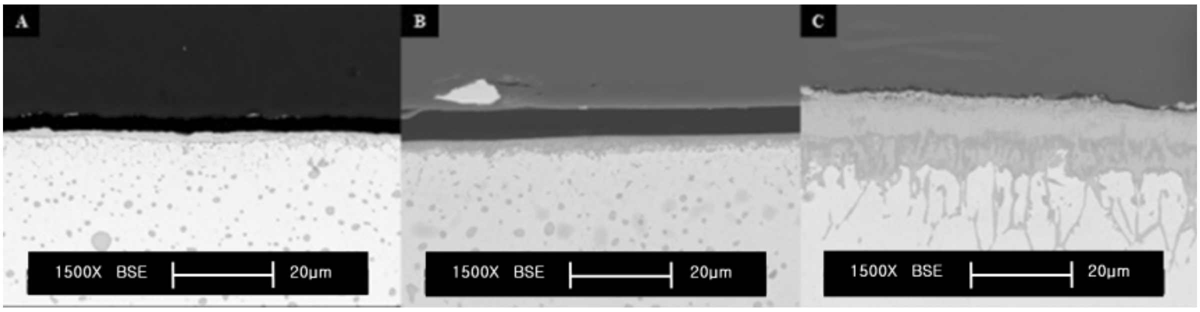

Fig. 4. Cross-sectional scanning electron micrographs showing the surface reaction layer of U-10wt% Zr-10wt.%RE fuel slug: (A) top, (B) middle, (C) bottom

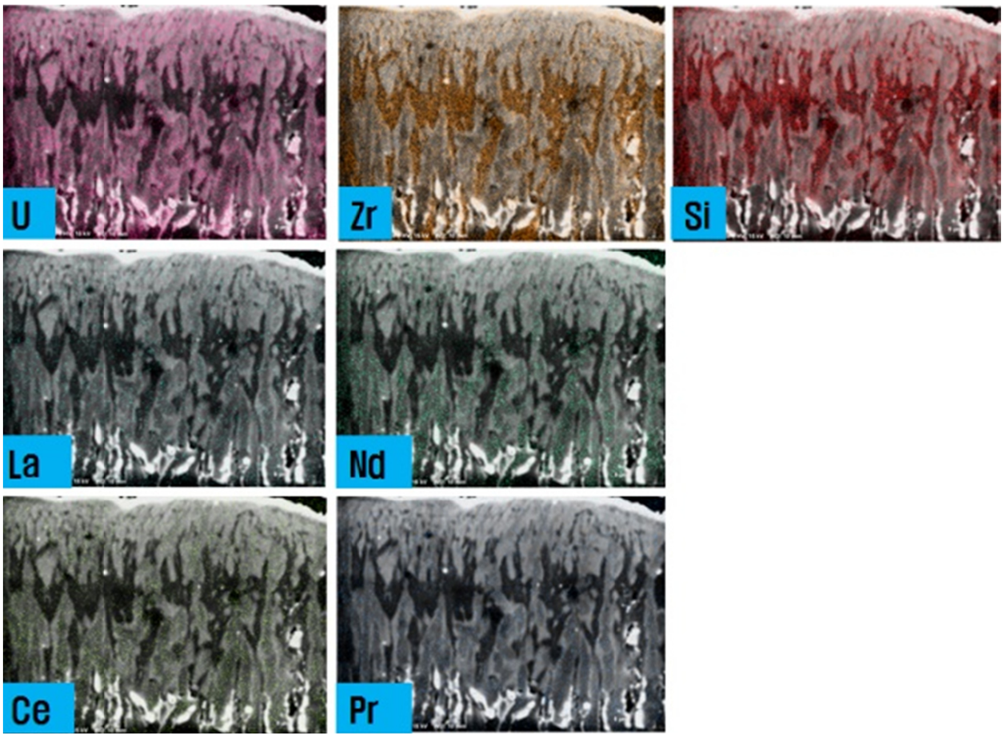

Fig. 5. Cross-sectional energy-dispersive X-ray spectroscopies mapping showing the surface reaction layer of U-10wt%Zr-5wt.%RE fuel slug: (A) top, (B) middle, (C) bottom

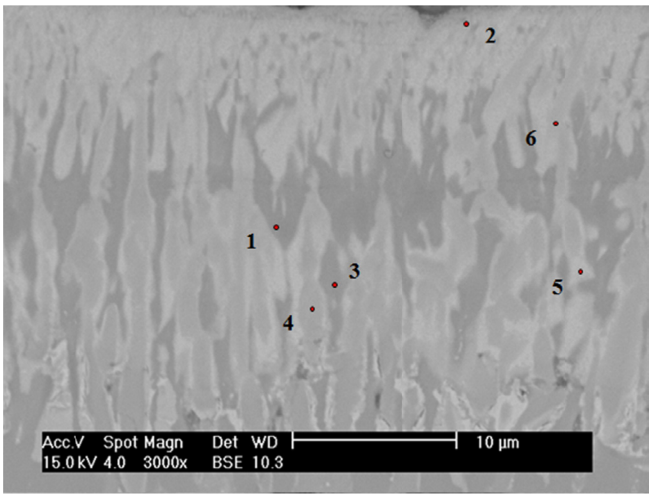

Fig. 6. Cross-sectional energy-dispersive X-ray spectroscopy points showing the surface reaction layer of the bottom of U-10wt%Zr-5wt.%RE fuel slug

several layers in surface reaction layer of U-10wt.%Zr-5wt.%RE. U and RE elements were alternately formed in a parallel shape in the surface reaction layer. Si was detected only at a certain depth in the surface layer. Fig. 6 and Table 1 show the results of the EDS point analyses on the bottom of the metallic fuel slug.

TABLE 1

Composition analysis of U-10wt%Zr-5wt.%RE metallic fuel slugs measured using EDS in Fig. 6. Values in atomic %

Location	Composition (at.%)							
	U	Zr	Si	La	Nd	Ce	Pr	O
1	4.5	52.2	25.9	0.07	1.84	0.21	0.1	15.0
2	17.2	36.2	32.2	0.1	3.5	2.0	0.02	8.5
3	8.2	46.6	30.8	0.01	1.5	0.4	0.08	12.1
4	15.9	42.6	2.4	1.0	6.8	1.7	5.6	23.5
5	17.9	41.1	30.9	0	2.5	0.2	0.2	8.0
6	17.2	36.2	32.2	0.1	3.5	2.03	0.2	8.5

The dark gray part of the surface layer confirmed that there was more Zr than in the light gray layer. In U, it is presumed that a U-Si compound was formed in the Si penetration region due to a small amount in the outer layer. A zone where Si was detected simultaneously with U and Zr was observed and other studies have reported that Zr-Si and U-Si form compounds with each other [9,10].

TABLE 2

Composition analysis of U-10wt%Zr-10wt.%RE metallic fuel slugs measured using EDS in Fig. 8. Values in atomic %

Loca-tion	Composition (at.%)							
	U	Zr	Si	La	Nd	Ce	Pr	O
1	0.05	10.28	7.92	3.82	28.60	13.32	1.05	34.95
2	1.10	12.04	4.05	3.29	26.03	13.28	0.80	39.41
3	0.16	44.51	20.39	0	1.65	0.96	0.	10.42
4	3.71	18.10	1.36	1.83	20.59	12.53	6.22	35.65
5	0.27	15.12	56.19	1.58	15.98	9.13	0.71	1.03
6	12.04	16.12	0.90	1.33	20.52	8.93	0.04	40.12
7	46.27	21.91	1.18	0.08	2.45	0.05	0.18	25.89

Fig. 7, Fig. 8 and Table 2 show the results of mapping and point analysis of U-10wt.%Zr-10wt.%RE fuel slug. As result of mapping analysis, Si and Zr were found mainly in the upper and lower parts of the surface reaction layer, and the RE elements were found in the middle part. The RE elements were distributed except for the Zr-Si rich zone, and there was no individual behavior among the RE elements. The distribution of RE elements in the surface reaction layer is affected by the immiscibility between U and Zr of the RE elements. Mapping and point analysis confirms that there is little distribution of U throughout the surface reaction layers. Compared with the area excluding the surface reaction layer, the distribution of RE elements was concentrated in the surface reaction layer. An area where Si and RE were simultaneously detected was also observed. Several studies have reported the reaction of Si with RE elements (La, Ce, Pr) [11,12,13]. Haefling et al. demonstrated that Nd, Ce, Pr and La are immiscible and do not react with molten U. Furthermore, the melting temperatures of Nd, Ce, Pr and La are 1,024°C, 795°C, 935°C, and 920°C, respectively [14,15]. The U-10wt.%Zr-5,10wt.%RE alloy was approximately 1,300°C, which indicated that the immiscible RE elements would still be liquid when the U-10wt.% Zr-5wt.%RE alloy solidified during cooling after casting. In this situation, it seems that Si diffuses from the quartz mold and reacts with the RE elements. Cross-sectional SEM micrographs and EDS mapping results of the surface reaction layer of the U-10wt.%Zr-*X*wt.%RE ($X = 0$, 5, 10 wt.%) fuel slugs showed slightly different morphology and microstructure according to RE content. The surface reaction layer, composed of Si, Zr, RE-rich and U-depleted zones, is formed uniformly in vertical direction of the fuel slugs. RE elements have no independent distribution by component, and the tests confirmed the RE-rich zone. This appears to be due to the immiscibility of between U and RE elements. Si from the quartz was detected in the surface reaction layer of the metallic fuel slug, but there was no Y_2O_3 slurry coating layer in the surface reaction layer of the metallic fuel slug. The surface reaction layer of U-10wt.%Zr and U-10wt.%Zr-5wt.%RE fuel slugs were formed by alternating dark gray and light gray. The surface reaction layer was observed as light gray and dark gray layers, and the dark gray

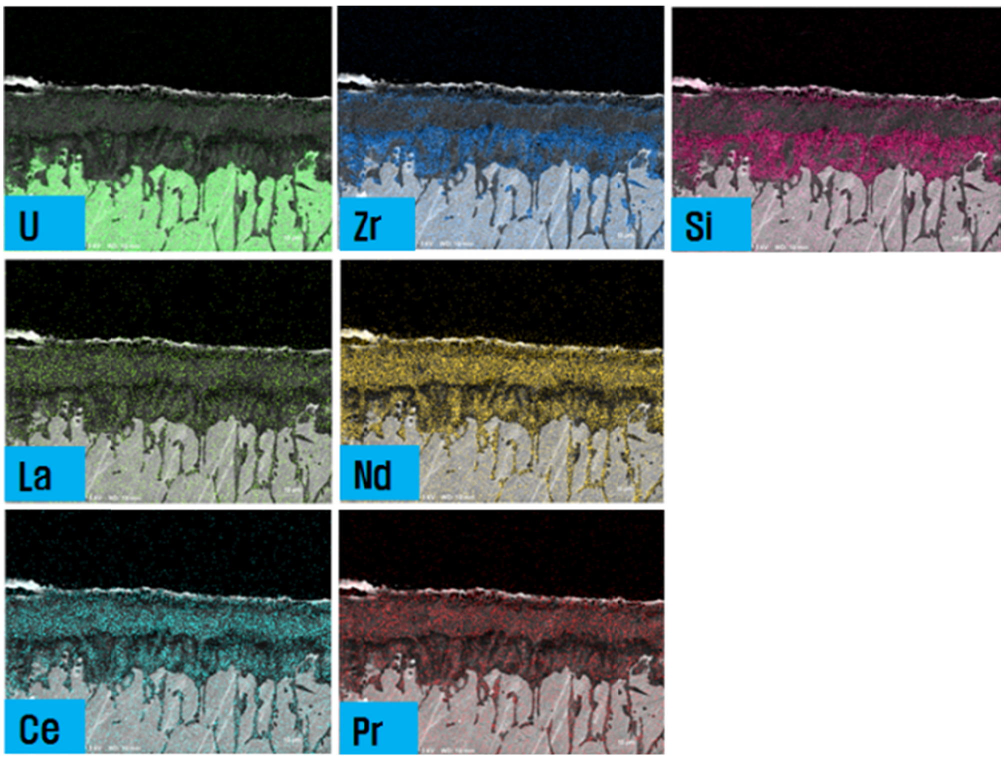

Fig. 7. Cross-sectional energy-dispersive X-ray spectroscopy mapping showing the surface reaction layer of the bottom of U-10wt%Zr-10wt.%RE fuel slug

portion contained a large amount of Zr. There was a non-uniform composition in the surface reaction layer, which was associated with diffusion of Si and migration behavior of the RE elements and Zr components during dissolution and solidification. Fig. 9 shows the XRD pattern of U-10wt.%Zr-10wt.%RE fuel slug. The major components at surface reaction layer were found to be RE-oxide, RE-hydroxide, RE-silicide, and Zr-silicide. RE-hydroxide and RE-oxide were assumed to be formed with the contamination of oxygen and moisture in the air. Zr-silicide and RE-silicide were also formed on the surface of the fuel slug. It is thought that Si element, diffused from quartz mold, reacted with RE and Zr elements on the surface of the fuel slug through diffusion during injection casting.

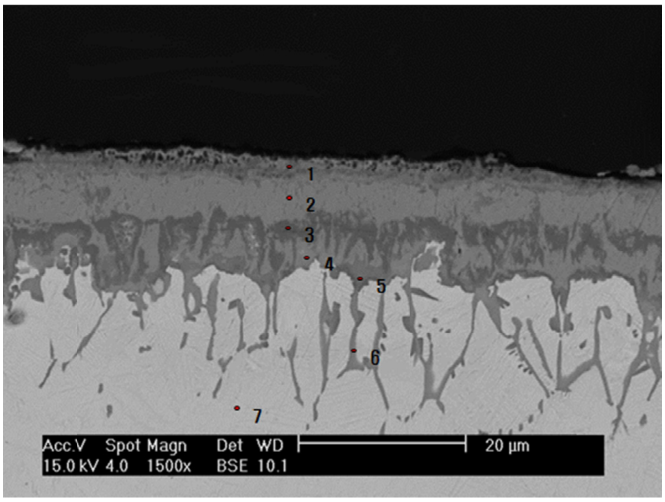

Fig. 8. Cross-sectional energy-dispersive X-ray spectroscopy points showing the surface reaction layer of the bottom of U-10wt%Zr-10wt.%RE fuel slug

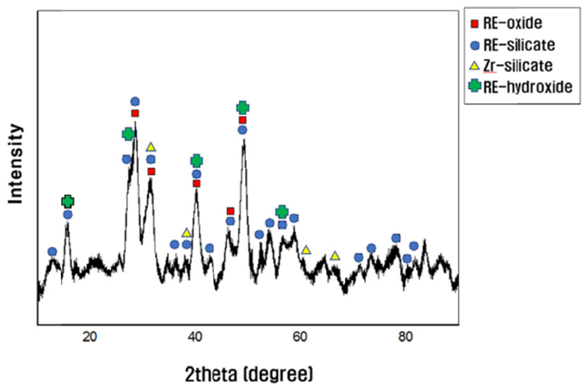

Fig. 9. X-ray diffraction pattern showing the surface reaction layer of the bottom of U-10wt%Zr-10wt.%RE fuel slug

4. Conclusions

The characteristics of the surface reaction layer of U-10Zr-*X*RE(*X* = 0, 5, 10) fuel slugs cast using a quartz mold coated with Y_2O_3 were evaluated to prevent the formation of a surface reaction layer. In the surface reaction layer of the U-10wt.%Zr, a Zr-rich zone was formed and the diffusion of the Si element was observed. In the surface reaction layer of U-10wt.%Zr-5wt.%RE, a Zr-rich zone and RE-rich zone were formed and the Si element was diffused. The diffusion shape of the Si element was similar to that of a U-10Zr fuel slug. The surface reaction layer of U-10wt.%Zr-10wt.%RE was formed with a Zr-rich zone and a RE-rich zone. The shape of the surface reaction layer and the distribution of the Si element were different in comparison with U-10wt.%Zr-5wt.%RE. The immiscibility between a RE element and a U element affects the formation of a surface reaction layer. For this reason, it causes the depletion of the U element at the surface reaction layer of the U-10wt.%Zr-5wt.%RE and U-10wt.%Zr-10wt.%RE metallic fuel slugs. The surface reaction layer was formed with Zr and RE compounds. It is thought that Si element, diffused from quartz mold, formed the compounds with RE and Zr elements during injection casting.

Acknowledgments

This work has been carried out under the Nuclear Research and Development Program supported by the Ministry of Science and Technology in the Republic of Korea.

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