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Determination of Chemical Compositions and Oxidation States for Corrosion Products in LiCl Molten Salts

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Abstract

The mechanism of corrosion behavior has to be understood clearly to select an optimum material for handling molten salts to be used in the oxide reduction process of PWR spent fuel. In this study, the oxidation states of corrosion products on the surface of Inconel 600 and 800H as well as their chemical compositions and structural informations were determined by using XPS, ICP-AES, AAS, EPMA and XRD after the corrosion experiment with lithium molten salts at 750 ℃ for 25 hours. Nickel and oxygen were detected from the corrosion products on the surface of Inconel plates and chromium was found to be dissolved out into lithium molten salts leaving cracks on the surface. The corrosion products were identified as metal oxides such as Fe_2O_3, Cr_2O_3, NiO, $NiFe_2O_4$ and MnO by using XPS and XRD.

Key Words : chemical composition, oxidation states, corrosion products, lithium molten salts, Incone

1. Introduction

The effective management of spent nuclear fuels is very important to use them as future energy resources for a long time. In Korea, the system investigation of an advanced spent fuel management process to establish a non-proliferation model for the long-term spent fuel management has been performed by comparing the several dry processes, such as intergrate fast reactor(IFR) process developed in U.S.A. and Dimitrov dry process (DDP) developed in Russia. As a result, the lithium molten salt process is found to be the most optimum process for the advanced spent fuel management process, especially for the countries that have not yet decided a back-end nuclear fuel cycle policy.[1]

Molten salts have been widely applied to electrochemistry field especially for the production of various metals, since molten salts can dissolve various metal compounds and their vapor pressure and viscosity are relatively low at high temperature. Recently, corrosion studies for various molten salt systems were continuously increased in the fields of jet-engine, fuel-cell, solar energy, and metal refining process. Especially, regarding the corrosion behavior in molten salts, corrosion studies have been focused on the researches on the accelerated oxidation of nickel alloys by molten sulfate salts such as Na_2SO_4 which can be produced from jet-engine or gas turbine of industrial engines.[2,3]

Fe-Ni-Cr alloy has been known as a corrosion resistance material against molten salts containing chloride compounds. The composition of the alloy is 0.05 ~ 1.5 % for Mn, 18 ~ 30% for Cr, and 10 ~ 35 % for Ni (Cr/Fe = 0.33 ~ 0.7, Ni/Fe = 0.33 ~ 1.0).[4] In addition to this alloy, Fe-Ni-Cr alloy containing Si and Mo has been also used as a substitute for its high on-site workability and corrosion resistance as well. However, molten chloride system has a tendency of accelerating corrosion process, since it is strongly hygroscopic and easily hydrolyzed when exposed to air.

For the development of the advanced spent fuel management process based on the molten salt technology, it is essential to choose optimum material for the process equipment handling molten salts. In this regard, the corrosion mechanism has to be understood clearly for the selection of optimum materials for handling molten salts in the metalization process of PWR spent fuel. In this study, the oxidation state of corrosion products on the surface of Inconel 600 and 800H as well as their chemical compositions and structural informations were determined by using XPS, ICP-AES, AAS, EPMA and XRD after the corrosion experiment with lithium molten salts at 750 ℃ for 25 hours.

2. Experimental

The corrosion experiment was performed with Inconel 600 and 800H plates placed in alumina crucibles. The size of the Inconel plate was 15(W) × 20(H) × 2.5(T) mm. The plates were polished with Emery paper 1200 and cleaned with distilled water and acetone before the corrosion experiment. The lithium molten salts, LiCl-Li_2O(75:25 wt%), were then added into the crucibles for the corrosion test at 750 ℃ for 25 hours. After the corrosion experiment, the crucible was broken into several pieces and Inconel plates were collected and rinsed with distilled water and then the morphological and chemical changes on the surface of Inconel plates were investigated using SEM, EPMA, XPS and XRD.

The Powder X-ray diffraction patterns were recorded in the 2θ range of 10 ~ 70° using a diffractometer (Siemens model D5000).

The X-ray photoelectron spectra of the corrosion products were obtained using ESCALab 220i (VG Scientific) equipped with a full 180° hemispherical electrostatic analyzer to examine the chemical state of the constituent elements. As a photon source, Mg Kα and Al Kα radiation were used. The half-width at half-maximum of the $4f_{7/2}$ line in the XPS spectrum of gold obtained by our XPS spectrometer was smaller than 1.0 eV. The energy scale of the spectrometer was calibrated using Au $4f_{7/2}$ (84.0 eV) or Ag $3d_{5/2}$ (368.3 eV), which was pressed flat on the alloy.

3. Results and Discussion

The analytical results for lithium molten salts of two different parts (obtained near metal plate and near crucible) in an aluminum crucible were tabulated in Table 1. The molten salts of both metal plate side and crucible side were firstly dissolved into distilled water and then into acid for the chemical analysis. As it can be seen in Table 1, higher concentration of chromium in lithium molten salts for the Inconel 600 was determined

Table 1. Comparison of Analytical Results of Li molten salts on Inconel 600 and 800H using ICP-AES

unit (%)	Inconel 600			Inconel 800H			Remark
	Spec. (%)	water soluble	acid soluble	Spec. (%)	water soluble	acid soluble	
Cr	16.3	0.46	0.10	21.82	<0.01	0.01	near plate
		0.52	0.09		<0.01	<0.01	near crucible
Mn	0.2	<0.01	<0.01	1.07	<0.01	0.07	ear plate
		<0.01	<0.01		<0.01	0.02	near crucible
Ni	73.66	<0.01	0.97	31.34	<0.01	0.12	near plate
		<0.01	0.88		<0.01	<0.01	near crucible
Fe	9.4	<0.01	0.41	44	<0.01	1.15	near plate
		<0.01	0.33		<0.01	0.72	near crucible
Al		1.26	0.49		1.40	2.59	near plate
		0.76	0.98		1.26	1.54	near crucible
Li		0.65	21.7		0.61	15.7	near plate
		23.1	1.16		22.5	0.85	near crucible

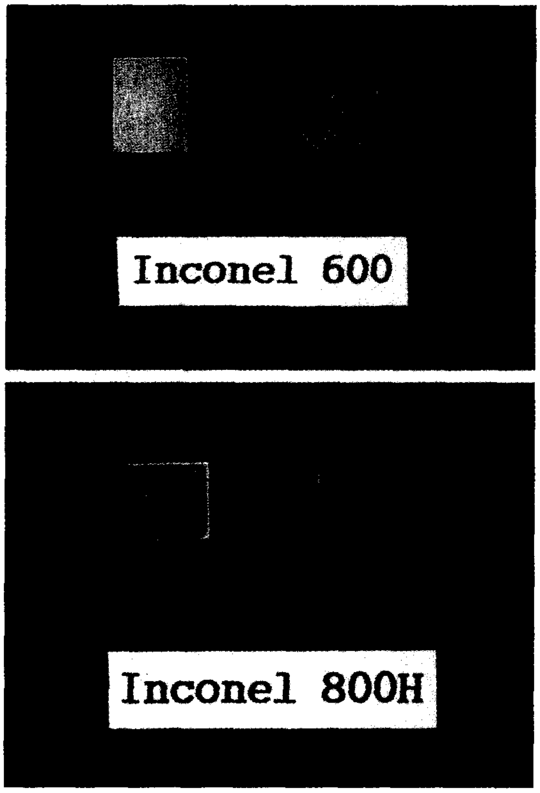

Fig. 1. Comparison of Alloys Before and After Corrosion

when compared to Inconel 800H. These results can be easily understood by comparing photographs of Inconel 600 and 800H plates shown in Fig. 1. Lithium compounds present in molten salts near crucible were found as water-soluble, while lithium compounds near metal were not water-soluble. The dissolution of lithium compounds near metal was achieved only by using acid. It can be concluded from these results that lithium in molten salts forms chemical bonds with the metals coming out of Inconel plate. Since chromium is the major metal found in molten salts after the corrosion experiment with Inconel plates, it can be thought that lithium forms chemical bond with chromium. Experimentally, lithium chromium oxide($LiCrO_2$) was identified from the XRD patterns of molten salts on the surface of the Inconel plates, in addition to lithium chloride or lithium oxide.

Cross-section of both Inconel plates after the corrosion experiment were polished and their SEM images were investigated as shown in Fig 2.

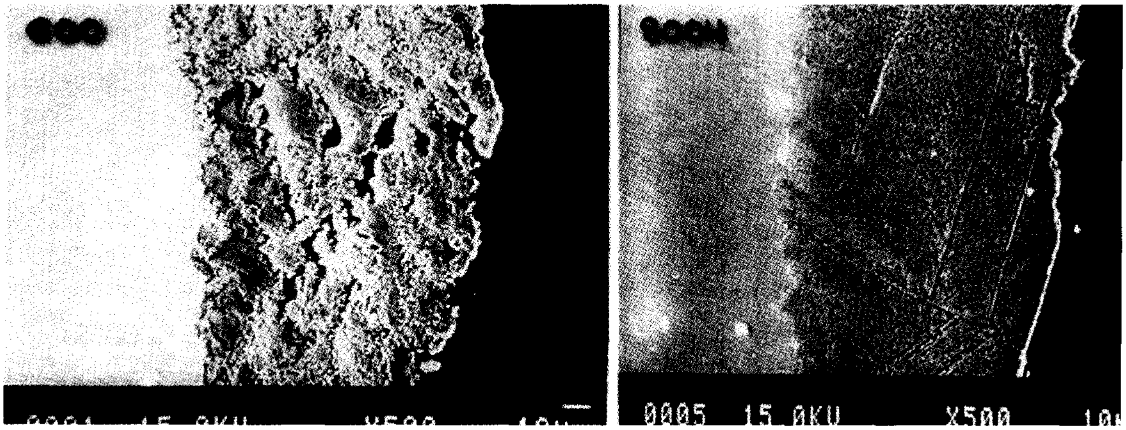

Fig. 2. Comparison of SEM Images of Inconel 600 and 800H

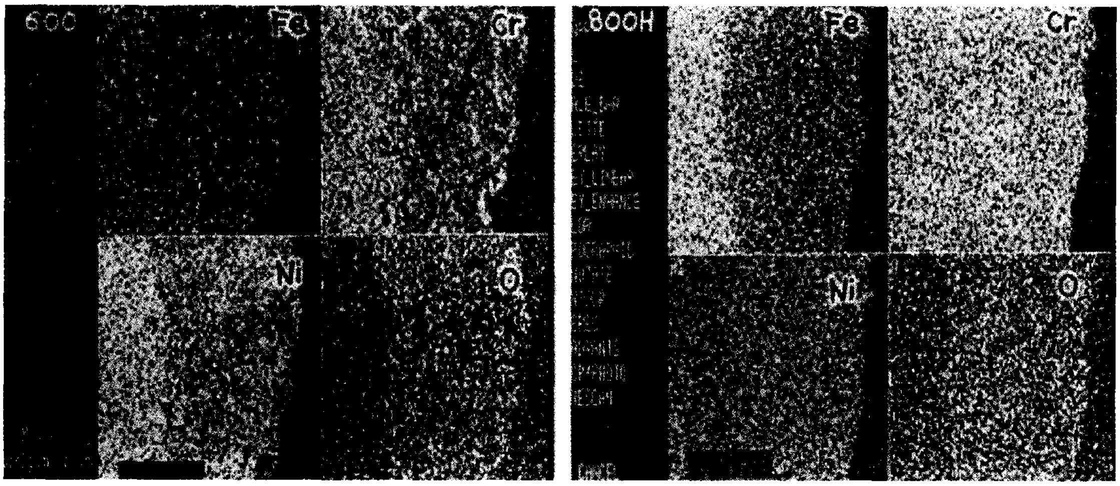

Fig. 3. Comparison of Elemental Mapping Images of Inconel600 and 800H

Elemental mapping images of both Inconel plates after the corrosion experiment were also compared in Fig. 3. Coarser view or relatively larger size of crack in corrosion product part of Inconel 600 can be clearly seen in Fig. 2, compared to that of Inconel 800H. The position corresponding to the cracks shown in SEM images of corrosion products indicated the absence of chromium and nickel, as shown in Fig. 3, agreed well with analytical results of molten salts as mentioned previously. Presence of oxygen in Fig. 3 also indicates that the metals on the surface of Inconel plate were oxidized into metal oxides such as Fe_2O_3, Cr_2O_3, NiO, and MnO. These results were confirmed by XRD measurement of corrosion products. It can be concluded from the results that chromium in Inconel 600 more easily forms lithium compound (found to be $LiCrO_2$) with lithium molten salts than that of Inconel 800H. Since the lithium compound is quite soluble in molten salt, it left the cracks in corrosion products after all as shown in Fig 2.

In order to understand the corrosion mechanism, the determination of the oxidation

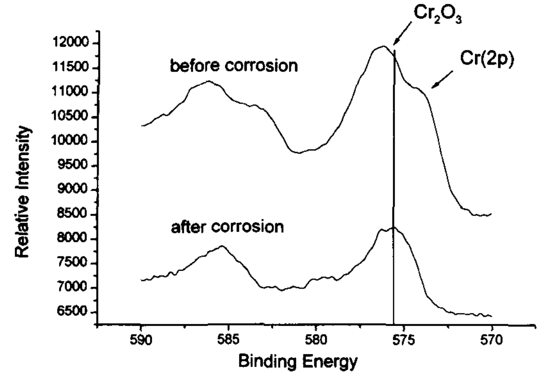

Fig. 4. Comparison of X-ray Photoelectron Spectra of Cr 2p Levels Before and After Corrosion Experiment

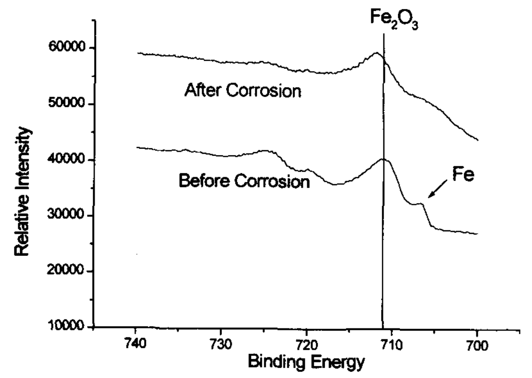

Fig. 6. Comparison of X-ray Photoelectron Spectra of Fe 2p Levels Before and After Corrosion Experiment

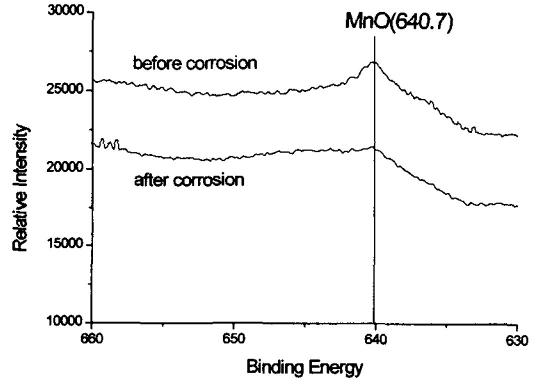

Fig. 5. Comparison of X-ray Photoelectron Spectra of Mn 2p Levels Before and After Corrosion Experiment

states of corrosion products on the surface of various alloys are very important eventually for the selection of optimum material for handling molten salts in the metalization process of PWR spent fuel. The oxidation state of metal oxides were investigated by using XPS, which core level chemical shifts can provide a general explanation for the bonding patterns that occur at the surface of the Inconel plate. X-ray photoelectron spectra of Cr, Mn, Fe and Ni 2p levels before and after the corrosion experiment were compared in Fig. 3 - 6. Fig. 3 shows absence of Cr(2p) and small shift of binding energy for Cr_2O_3 was observed after the corrosion experiment. The shift of binding energy shown in Fig 3 is probably due to the presence of $LiCrO_2$. There was no changes in X-ray photoelectron spectra for manganese before and after the corrosion experiment as shown in Fig. 5. This may be due to the very little manganese content in corrosion products of Inconel plates.

Fig. 6 shows small core level shift of Fe_2O_3. In case of Ni, however, a new peak was found at high binding energy area in addition to the peak shift for nickel oxide as shown in Fig. 7. This result indicates the presence of a new nickel compound, probably a mixed oxide such as $NiFe_2O_4$ and $NiCr_2O_4$.

In regarding core level shifts for the mixing of two metal oxides(A_mO_n and M_xO_y) to form a mixed oxide($A_zM_sO_t$) system, if metal A is more basic than M, then the relative covalency of M will make A in $A_zM_sO_t$ more ionic than that for A in A_mO_n.[5] As a result, the binding energy of A in A_zM_sOt will usually be larger than that for A in A_mO_n. In our system, since nickel is more basic than chromium

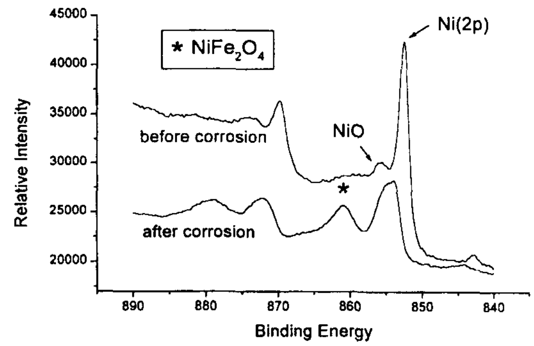

Fig. 7. Comparison of X-ray Photoelectron Spectra of Ni 2p Levels Before and After Corrosion Experiment

or iron, it can be concluded from the results of chemical shift to higher binding energy in Fig. 7 that the formation of mixed metal oxide such as $NiFe_2O_4$ or $NiCr_2O_4$ is possible .

As shown in Fig. 8, the X-ray diffraction pattern of the corrosion products of the Inconel 600 plate provided that the mixed metal oxide corresponding to the new XPS peak shown in Fig. 7 was $NiFe_2O_4$. The XRD peak for $LiCrO_2$ is found to be extremely weak since it is slightly soluble in water.

4. Conclusions

In this work, two different Inconel plates (600 and 800H) were compared with respect to their corrosion behavior in lithium molten salts. The oxidation state of corrosion products on the surface of Inconel 600 and 800H as well as their chemical compositions and structural informations were determined using XPS, ICP-AES, AAS, EPMA and XRD after the corrosion experiment at 750 ℃ for 25 hours.

The analytical results for lithium molten salts and XRD data indicated that chromium coming out of the Inconel plate by corrosion formed lithium chromium oxide($LiCrO_2$) with lithium molten salts.

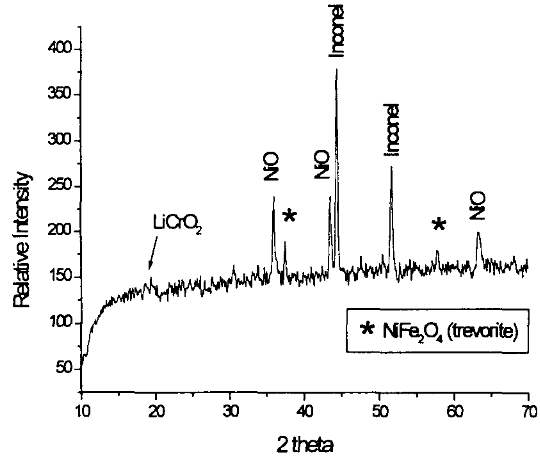

Fig. 8. X-ray Diffratogram of Inconel 600 After Corrosion

It can be also concluded from these results that chromium in Inconel 600 more easily forms lithium compound with lithium molten salts than that of Inconel 800H. Since the lithium compound is quite soluble in molten salt, it left the cracks in corrosion products after all.

The presence of oxygen shown in elemental mapping images of both Inconel plates and also small core level shift in X-ray photoelectron spectra of Cr, Fe and Ni 2p indicated that the metals on the surface of Inconel plate were oxidized into metal oxides such as Fe_2O_3, Cr_2O_3, and NiO by corrosion. In case of Ni, a new peak in X-ray photoelectron spectra was shown up at high binding energy area in addition to the peak shift for nickel oxide. The result indicates that a new mixed metal oxide such as $NiFe_2O_4$ is formed during the corrosion process, as confirmed by the X-ray diffraction study.

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