Zircaloy-4와 $Zr_{1.5}Nb$ 합금의 금속-산화막 계면에 대한 미세구조 분석
A microstructural analysis of the metal-oxide interface formed on Zircaloy-4 and $Zr_{1.5}Nb$

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1. Introduction

It is known that the effect of thermal redistribution of hydrides across the zirconium metal-oxide interface, coupled with thermal feedback on the metal-oxide interface, is a dominating factor in the accelerated oxidation in zirconium alloys cladding PWR fuel. Also it has been reported that the hydride redistribution induces microstuctural changes. In fact, it is well-known that tetragonal ZrO_2 forms in the metal-oxide interface in the early stage of zirconium oxidation that is protective against further oxidation. However, as the oxide grows the stress built up during the oxidation process relieves then the tetragonal phase turns into the monoclinic phase which is non-protective and stable at low stress. Therefore, it is believed that the zirconium oxidation kinetics depends on the phase transformation. In other words, if the transformation is accelerated by any stress-lowering factor, the kinetics would be fast. It has been proposed that hydride precipitates and their redistribution lower the stress built up in the metal-oxide interface and thus promote the phase transformation, ending up with the oxidation-enhancement. Therefore, in this study the effects of hydride precipitates on the phase transformation and the microstructural changes have been investigated using TEM and EDX.

2. Experimental

TEM specimen was made by FIB (Focused Ion Beam) system. The specimen has about 2 ㎛ thickness oxide film which was grown in the muffle furnace. Hydrogen content in the hydrided specimen was analyzed with the hydrogen determinator (model:RH-404) from LECO Corp. The oxide layer and metal matrix were examined using JEM-ARM1300S HVEM(High Voltage Electron Microscope) instruments and JEOL JEM2100F TEM with EDX system in KBSI(Korea Basic Science Institute).

2.1 TEM Investigations

The results of TEM analysis on the microstructural changes in the Zircaloy-4 and Zr1.5Nb specimens are shown in Fig.1 and Fig.2. It shows BFI(Bright Field Image) of oxide-metal interface of the Zircaloy-4 and Zr1.5Nb specimens. Both figures demonstrate the microstrucural and morphological changes between hydrided and unhydrided Zircaloy-4 specimens, though amorphous layer is not clearly seen in the hydrided zircaloy-4 and Zr1.5Nb specimens. The matrix texture of the pre-hydrided specimens are rougher and more coarser than that of the unhydrided ones.

2.2 Energy Dispersive X-ray microanalysis

JEOL JEM2100F TEM with EDX system was used to investigate the microstructural changes and chemical composition changes in the unhydrided and the hydrided specimens. Fig.3 shows grain boundaries and precipitates distributions and the results of EDX chemical composition analysis of precipitates in the Zircaloy-4 matrix. Fig.4 shows the results of Zr1.5Nb matrix. These figures clearly demonstrate the microstructural changes of the matrix and hydrided precipitates redistribution and their composition changes.

3. Conclusions

Microstructural analysis of metal-oxide interface in the hydrided and unhydrided Zircaloy-4 and Zr1.5Nb specimens was carried out using HVEM. Also the morphological and the chemical composition changes due to the hydride precipitates were analyzed by TEM and EDX system. TEM results from the hydrided specimens clearly demonstrate the micro-structural changes. EDX results on the Zircaloy-4 and Zr1.5Nb specimens also show the microstructural, morphological, and compositional changes due to the hydrides precipitation in the zirconium matrix.

References

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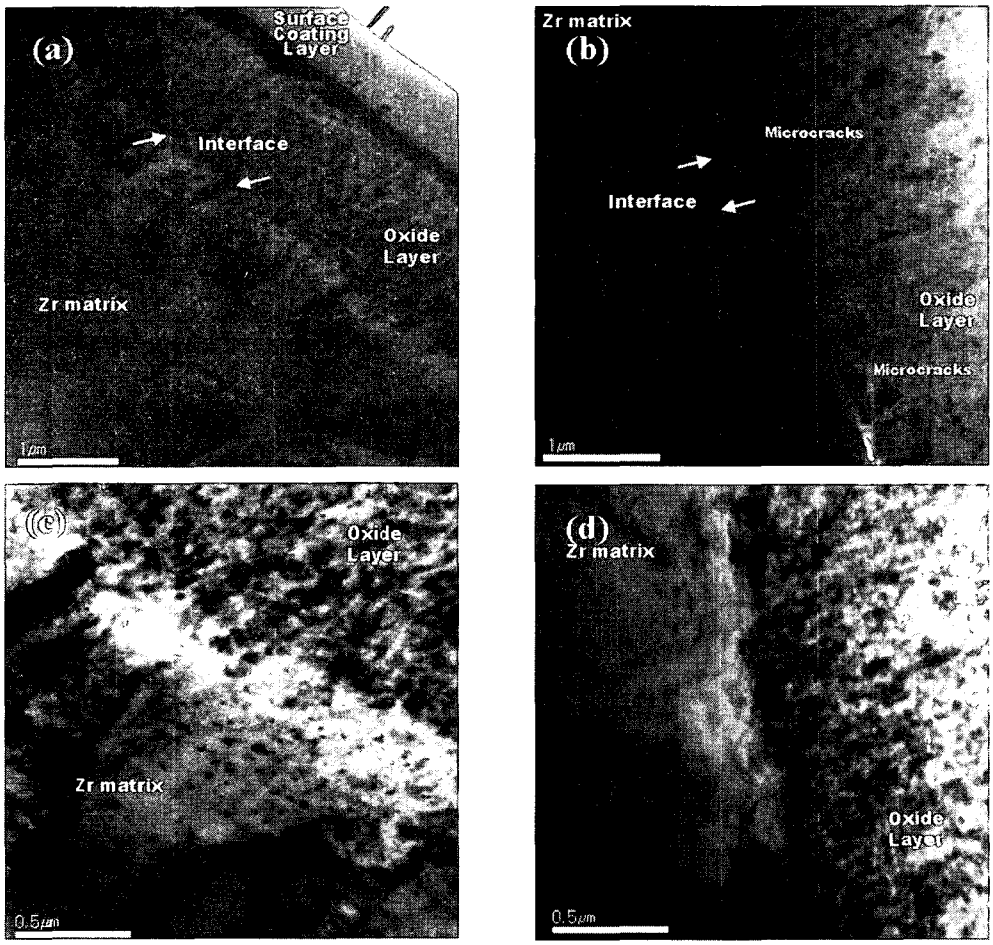


Fig. 1. (a)(c) Micrograph of unhydrided Zircaloy-4 Interface. (b)(d) Micrograph of 651ppmH hydrided Zircaloy-4 Interface.

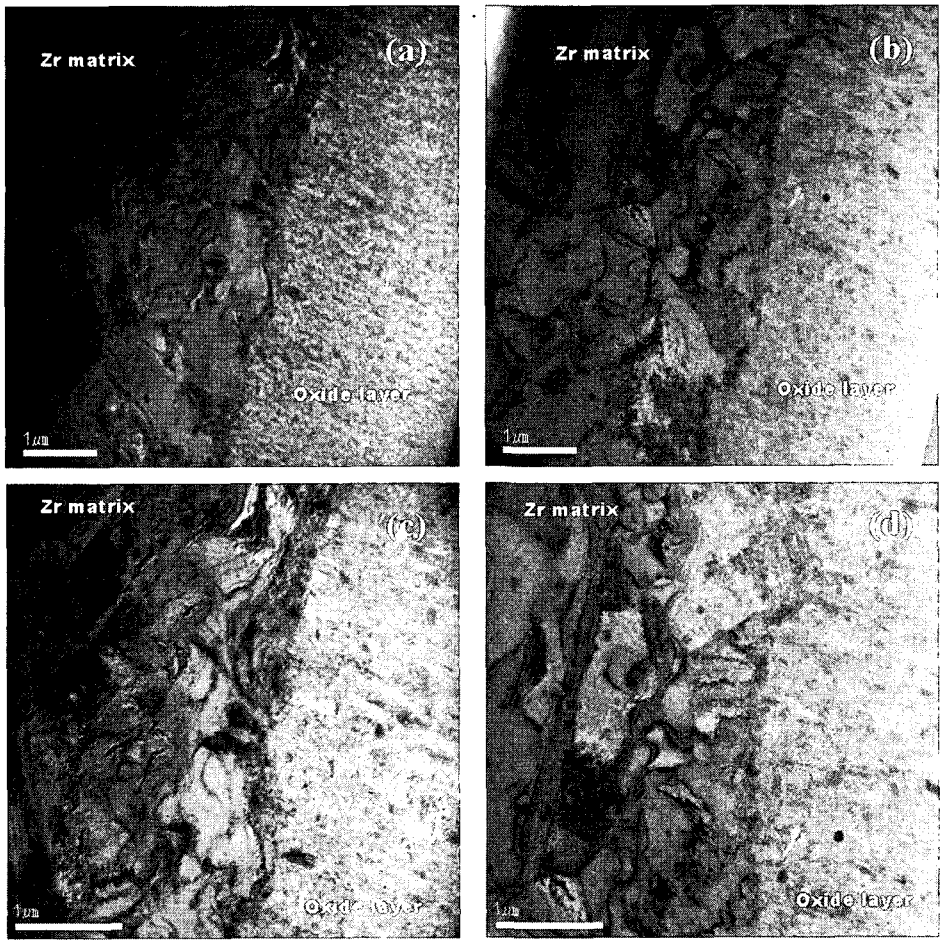
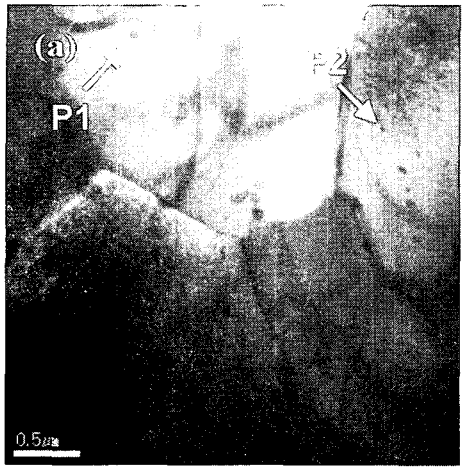


Fig. 2. (a)(c) Micrograph of unhydrided Zr1.5Nb Interface. (b)(d) Micrograph of 52.4ppmH hydrided Zr1.5Nb Interface.

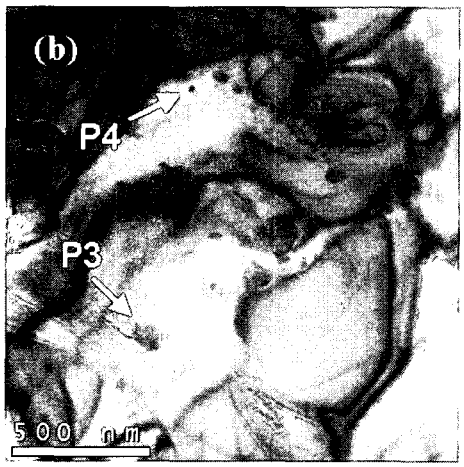


Element		(keV)	Counts	mass%	Error%	At%	K
Cr K		5.411	4422.28	4.17	0.04	6.62	0.3657
Fe K		6.398	11339.92	11.88	0.02	17.55	0.4063
Zr L		2.042	32308.43	83.28	0.01	75.36	1.0000
Sn L	*	3.443	276.60	0.68	0.63	0.47	0.9531
Total				100.00		100.00	

[EDX Results of Large Precipitate P1]

Element		(keV)	Counts	mass%	Error%	At%	K
C K		0.277	11118.29	27.92	0.00	72.39	1.0978
Cr K		5.411	4743.96	3.97	0.04	2.38	0.3657
Fe K		6.398	9937.15	9.24	0.02	5.15	0.4063
Zr L		2.042	25676.34	58.73	0.01	20.05	1.0000
Sn L	*	3.443	63.96	0.14	2.65	0.04	0.9531
Total				100.00		100.00	

[EDX Results of Small Precipitate P2]



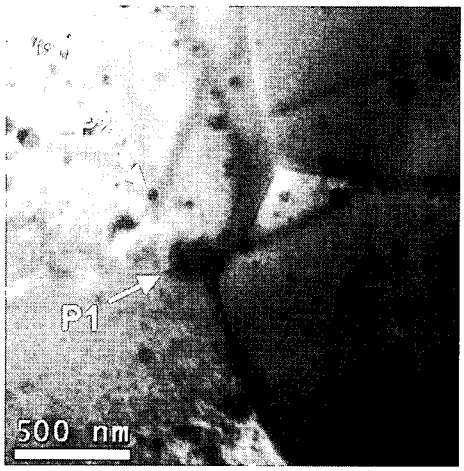
Element		(keV)	Counts	mass%	Error%	At%	K
Cr K	*	5.411	32.60	0.03	9.62	0.06	0.3657
Fe K		6.398	5451.82	6.35	0.05	9.99	0.4063
Zr L		2.042	32383.38	92.90	0.01	89.42	1.0000
Sn L	*	3.443	262.04	0.72	1.08	0.53	0.9531
Total				100.00		100.00	

[EDX Results of Large Precipitate P3]

Element		(keV)	Counts	mass%	Error%	At%	K
Cr K		5.411	1843.02	1.49	0.23	2.55	0.3657
Fe K		6.398	2600.54	2.33	0.16	3.72	0.4063
Zr L		2.042	43275.63	95.55	0.01	93.26	1.0000
Sn L	*	3.443	297.05	0.63	1.30	0.47	0.9531
Total				100.00		100.00	

[EDX Results of Small Precipitate P4]

Fig. 3. (a) Micrograph and EDX results of unhydrided Zircaloy-4 matrix. (b) Micrograph and EDX results of 651ppmH hydrided Zircaloy-4 matrix.

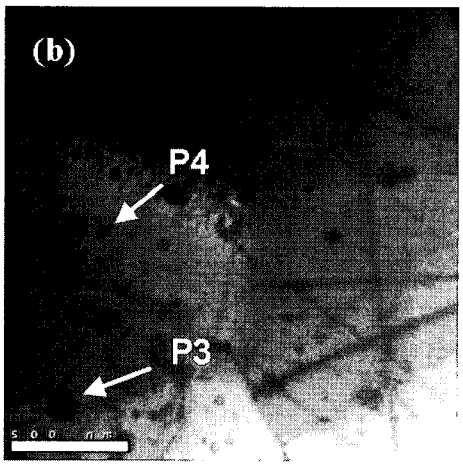


Element	(keV)	Counts	mass%	Error%	At%	Compound	mass%	K
Cr K	5.411	2251.23	20.18	0.05	30.76			0.3657
Zr L	2.042	2876.48	70.49	0.04	61.27			1.0000
Nb K	16.581	309.24	9.34	0.70	7.97			1.2325
Total			100.00		100.00			

[EDX Results of Large Precipitate P1]

Element	(keV)	Counts	mass%	Error%	At%	Compound	mass%	K
Cr K	5.411	1891.40	20.03	0.05	30.54			0.3657
Zr L	2.042	2627.07	76.06	0.04	66.12			1.0000
Nb K	16.581	109.57	3.91	1.68	3.34			1.2325
Total			100.00		100.00			

[EDX Results of Small Precipitate P2]



Element	(keV)	Counts	mass%	Error%	At%	Compound	mass%	K
C K	0.277	3232.28	12.80	0.01	52.60			1.0978
Cr K	5.411	517.63	0.66	0.21	0.65			0.3657
Zr L	2.042	22480.97	81.11	0.01	43.88		1.0000	
Nb K	16.581	1214.61	5.40	0.18	2.87			1.2325
Total			100.00		100.00			

[EDX Results of Large Precipitate P3]

Element	(keV)	Counts	mass%	Error%	At%	Compound	mass%	K
C K	0.277	3826.62	14.12	0.01	55.50			1.0978
Cr K	5.411	227.17	0.28	0.49	0.25			0.3657
Zr L	2.042	23817.73	80.06	0.01	41.43			1.0000
Nb K	16.581	1337.01	5.54	0.17	2.81			1.2325
Total			100.00		100.00			

[EDX Results of Small Precipitate P4]

Fig. 4. (a) Micrograph and EDX results of unhydrided Zr1.5Nb matrix. (b) Micrograph and EDX results of 52.4ppmH hydrided Zr1.5Nb matrix.