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Depth profile of chemical states of alloying elements in oxide layer of Zr-based alloys

K. Sakamoto [a,*], K. Une [a], M. Aomi [b], K. Hashizume [c]

[a] Nippon Nuclear Fuel Development, Co., Ltd., 2163 Narita-cho, Oarai-machi, Ibaraki-ken 311-1313, Japan
[b] Global Nuclear Fuel Japan Co., Ltd., 3-1 Uchikawa 2-chome, Yokosuka-shi, Kanagawa-ken 239-0836, Japan
[c] Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka-shi, Fukuoka-ken 812-8581, Japan

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ABSTRACT

To understand the basic oxidation kinetics of alloying elements which is considered to be strongly related with the corrosion and hydrogen pickup, the depth profiles of chemical states of alloying elements (Cr and Fe) were measured in the oxide layer of Zr-0.5Sn-1.0Cr-0.5Fe alloys. The depth profiles were obtained by combinations of a surface-sensitive XANES and an extremely low energy Ar ion sputtering. The XANES measurements revealed that the chemical states of alloying elements (Fe and Cr) varied with the depth in the oxide layer. Especially in the oxide layer formed in steam, a decrease of the fractions of oxidation states was significant rather than that in LiOH solution. In the oxide layer formed in steam, the oxidation rate of chromium was faster than iron by a factor of approximately 2.

1. Introduction

Understanding of corrosion and hydrogen pickup properties of Zr-based alloys is of industrial and scientific interest. Several studies revealed that these properties could be controlled by optimizing the alloying elements in the Zr-based alloys such as tin, iron, chromium, nickel and niobium. However, the mechanistic understanding on the role of those alloying elements has not been comprehensively clarified. The oxide layer formed on the Zr-based alloy should serve as a main barrier against the corrosion and hydrogen pickup while those phenomena occur through the oxide layer. Therefore, the characterization of the alloying elements in the oxide layer is expected to provide important insights into the material development.

From those viewpoints, we have started the studies on the characterization of alloying elements in the oxide layer of Zr-based alloys (Une et al., 2009, Submitted for publication; Aomi et al., 2009) The oxidation states of the alloying elements (Fe, Cr and Ni) in the oxide layers of Zr–Sn–Fe–Cr–(Ni) alloys were also evaluated by the X-ray absorption near-edge structure spectroscopy (XANES) measurements using synchrotron X-ray(Sakamoto et al., 2010). However, the oxidation states of alloying elements evaluated were averaged values in whole oxide layers because the XANES measurements were performed by using the powdered oxide layers that had been removed mechanically from the surface of corroded specimens. Since the oxidation states are expected to vary with the depth in the oxide layers, the evaluation of those depth profiles is also needed to understand the oxidation kinetics of the alloying elements in the oxide layers.

In the present study, we focused on the chemical state of the alloying elements in the oxide layer to understand the basic oxidation kinetics of alloying elements which is considered to be strongly related with the corrosion and hydrogen pickup. In the measurements, the depth profiles of chemical states of alloying elements (Cr and Fe) were evaluated in the oxide layer of Zr-0.5Sn-1.0Cr-0.5Fe alloys.

The depth profiles were obtained by combinations of a surface-sensitive XANES and an extremely low energy Ar ion sputtering. The conversion electron yield - XANES (CEY-XANES) was applied as a surface-sensitive XANES technique, since the detection depth of CEY-XANES was less than 50 nm from the sample surface in the case of X-ray energy at Cr and Fe K-edges. In the sputtering process, the rf-glow discharge (rf-GD) sputtering using extremely low energy Ar was employed to suppress surface damages as low as possible.

2. Experimental

2.1. Sample preparation

Strips of Zr-0.5Sn-1.0Cr-0.5Fe alloy were corroded in steam (673 K, 10 days) or 1 M LiOH-containing water (563 K, 12 days). The

* Corresponding author.
E-mail address: kan.sakamoto@nfd.co.jp (K. Sakamoto).

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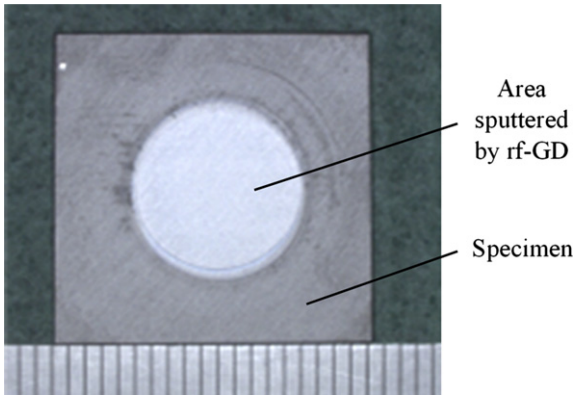

Fig. 1. Specimen surface after rf-GD sputtering (Corroded in steam, approximately 0.4 μm removal).

resulting thicknesses of oxide layer were respectively 1.3 and 20 μm. The hydrogen pickup fractions (PUFs) of Zr-0.5Sn-1.0Cr-0.5Fe alloy were approximately 15%.

After the first CEY-XANES measurement, the surfaces of the specimens were removed by the rf-GD sputtering. The rf-GD sputtering was performed by Horiba TENSEC at a power of 25 W and at an Ar gas pressure of 550 Pa using a pulsing mode. The sputtered area was approximately 10 mm in diameter, as shown in Fig. 1. Surface profiles with a surface profiler revealed that the center of sputtered area of approximately 7 mm in diameter was removed flat, so the center area less than 7 mm in diameter was used in the following CEY-XANES measurements. Table 1 shows the sputtered-depth (i.e. oxide thickness), which were estimated on a basis of the sputtering rate obtained in the preliminary experiments (approximately 0.3 nm/s).

2.2. XANES measurements

All XANES experiments were performed at the BL11 in the SAGA Light Source (SAGA-LS). All measurements were conducted at room temperature and the absorption spectra were recorded at the iron and chromium K-edges. All XANES measurements were summarized in Table 2.

In order to evaluate the formal valence of the alloying elements in the oxide layer, the XANES spectra of metallic and oxide reference samples were also measured. The metallic and oxide reference samples were Fe (0), FeO (+2), Fe_3O_4 (+2, +3), Fe_2O_3 (+3) for iron and Cr (0), Cr_2O_3 (+3) for chromium. Those reference samples were mixed with boron nitride powder to prevent the self-absorption of fluorescence. All XANES measurements of the reference samples were performed by the transmission detection mode.

The corroded Zr-0.5Sn-1.0Cr-0.5Sn strips were set on the CEY detector with a conductive connection tape. And, the CEY detector was aligned to 5° from the direction of synchrotron radiation X-ray and filled He gas. In addition to the corroded Zr-0.5Sn-1.0Cr-0.5Sn strip, as-received (un-corroded) one was also measured.

Table 1
Summary of oxide thickness of the specimens for CEY-XANES measurements.

Corrosion condition	Oxide thickness (μm)	Sputtering time (min)
Steam 673 K for 10 days	1.3	0
	0.9	20
	0.6	35
	0.3	50
1M LiOH aq. 563 K for 12 days	20	0
	11	450

Table 2
Conditions of XANES measurements.

	Specimen	Oxide thickness (μm)	Detection mode
Fe K-edge	FeO(II)	–	TR
	Fe_3O_4(II + III)	–	TR
	Fe_2O_3(III)	–	TR
	As-received	–	CEY
	Steam 673 K for 10 days	1.3	CEY
		0.9	CEY
		0.6	CEY
		0.3	CEY
	1M LiOH aq. 563 K for 12 days	20	CEY
		11	CEY
Cr K-edge	Cr_2O_3(III)	–	TR
	As-received	–	CEY
	Steam 673 K for 10 days	1.3	CEY
		0.9	CEY
		0.6	CEY
		0.3	CEY
	1M LiOH aq. 563 K for 12 days	11	CEY

TR: Transmission mode.
CEY: Conversion electron yield mode.

3. Results

3.1. Analysis of XANES spectra

The analysis of XANES spectra was conducted by using the Athena software (version 0.8.059, Ifeffit 1.2.11c). The XANES spectra of the specimens corroded in steam and LiOH solution were respectively compared in Figs. 2 and 3. As can be seen in those absorption spectra of the reference samples, the threshold energy E_0 that is defined as the energy of the first inflection point of the absorption spectrum increased with the formal valence of Fe and Cr. The formal valences in the oxide layers were estimated by using XANES spectra of the reference specimens and the as-received sheet.

In the oxide layer formed in steam, as shown in Fig. 2, clear depth dependences were observed at both Fe and Cr K-edges. Both Fe and Cr were oxidized completely at the surface of the oxide layer, whereas some metallic Fe and Cr existed in the oxide layer. The fraction of metallic states increased with the depth in the oxide layers.

In the oxide layer formed in LiOH solution, as shown in Fig. 3, there were no significant depth dependences at both Fe and Cr K-edges. In the case of Cr K-edge, the CEY-XANES measurement was not performed but it could be easily expected that Cr was completely oxidized at the surface of the oxide layer because Cr was observed to be completely oxidized at even middle of the oxide layer.

3.2. Estimation of oxidation states

The fraction of oxidized alloying elements was evaluated by using the “linear combination fitting” function of Athena software. In this “linear combination fitting”, an unknown spectrum is fitted by a linear combination of standard spectra. In the present study, the XANES spectra of the as-received strip was used as standard spectra for the metallic state, and those of the oxide reference samples were for the oxidation state(s). In the case of the fitting of XANES spectra of Fe K-edge, all XANES spectra of the oxide reference samples (FeO, Fe_3O_4, Fe_2O_3) were used as the standard spectra and fractions attributed to the oxide reference samples were