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Reassessment of oxidation-induced amorphization and dissolution of Nb precipitates in Zr–Nb nuclear fuel cladding tubes

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ABSTRACT

The surface oxide film of a Zr–2.5Nb alloy subjected to long term corrosion at 633 K in simulated primary coolant of pressurized water reactors has been analyzed. The primary concerns were whether Nb precipitates exhibit amorphization upon oxidation, and whether they dissolve into the matrix, as suggested by previous studies. Their behavior is of particular interest, from the viewpoint of engineering, as the mechanism of improving corrosion resistance of Zr fuel cladding by Nb addition, and from the viewpoint of basic materials science, as the critical condition of solid-state amorphization. If amorphization and dissolution proceed simultaneously, it would follow that amorphization occurs at conditions where both O and Nb atoms are mobile; under such conditions diffusion-induced amorphization has never been observed. It was found that the Nb precipitates exhibited amorphization without dissolution. Some of the inconsistencies among the previous studies were found to be artifacts of materials characterization methods. The final configuration of precipitates was amorphous Nb_2O_5, which is distinct from the other Nb oxides in terms of its dielectric nature with a wide band gap. The matrix initially contained a large amount of Nb greater than the solubility. Although the excess Nb atoms did not precipitate by thermal aging alone, oxidation was found to enhance their precipitation at this temperature. It appears that amorphization can occur even when the motion of atoms is not frozen-in.

1. Introduction

Niobium as an alloying element of zirconium alloys has attracted much attention in nuclear materials science as this element drastically improves the performance of Zr-based fuel cladding tubes of light water reactors against water corrosion and its resultant hydrogen uptake [1-2]. Based on this empirical knowledge, manufacturers have developed advanced Zr–Nb alloys optimized for extended burn-up operations such as ZIRLO™, M5® and J-Alloy™ [2], though the mechanism of improving corrosion resistance by Nb addition still remains unclear [1]. In these alloys Nb atoms are dispersed mainly in the form of β-Nb precipitates having a body-centered cubic (bcc) structure. The primary concern of the present study is the behavior of Nb precipitates upon corrosion. In the case of Zircaloys that contain $Zr(Fe,Cr)_2$ and $Zr_2(Fe,Ni)$ as second phase particles, those precipitates are known to dissolve into the matrix (ZrO_2) upon corrosion with emitting Fe, Cr and Ni. In particular, redistribution of Fe has been considered to suppress nodular corrosion [1,22]. Likewise, dissolution of Nb precipitates in the surface oxide film may be a possible mechanism underlying the excellent performance of Zr–Nb alloys. Although many research groups have analyzed the Nb precipitates in the surface oxide film of Zr–Nb alloys, the results are somewhat inconsistent from each other (Table 1). For instance, amorphization

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Table 1
Comparison between previous studies and the present study in terms of corrosion conditions and the results. As for characterization methods, TEM represents 'diffraction contrast image', and STEM represents 'Z-contrast image', respectively. SAD is the abbreviation of selected area diffraction.

	Lithium	Boron	Temperature	Characterization	Amorphization	Dissolution
Lin et al. [3]	(1) 0 (2) 3.2×10^{-4}M LiOH (pH = 10.5)	(1) 0 (2) 0	(1) 673 K/24 h (2) 583 K/176 days	TEM, SAD, EDS, EELS	(1) Yes (2) Yes	(1) ? (2) ?
Pêcheur et al. [4]	5-10 wt ppm (pH = 10.9–11.2)	650 wt ppm	636 K/unknown period	TEM, SAD, EDS	Yes	?
Kim et al. [5]	0	0	633 K/150 days	HR-TEM	Yes	Yes
Zhang et al. [6]	0	0	633 K/420 days	HR-TEM	Yes	?
de Gabory et al. [7]	0	0	633 K/280 days	TEM, EDS	Yes	?
Yao et al. [8]	0.01M LiOH (pH = 12)	0	633 K/14 days	HR-TEM, STEM	No	?
Sakamoto et al. [9-10]	(1) 1M LiOH (pH = 14) (2) 0	(1) 0 (2) 0	(1) 563 K/1 day (2) 673 K/10 days	STEM, EDS	(1) ? (2) ?	(1) Yes (2) No
Wei et al. [11]	2 wt ppm (pH = 10.5)	1000 wt ppm	633 K/unknown period	APT	?	?
Sundell et al. [12]	0	0	608 K/unknown period	APT	?	?
The present study	2.2 wt ppm (pH = 10.5)	500 wt ppm	633 K/13,000 h (542 days)	TEM, STEM, NBD, EDS, EELS, APT	Yes	No

of Nb precipitates has been confirmed in various Zr–Nb alloys including both model [3,5–6] and commercial alloys [4,7] subjected to various corrosion conditions (e.g. with [3–4] and without lithium [5–7]) at 583–673 K; however, an exception has recently been reported by Yao et al. [8]. In their high-resolution transmission electron microscopy (HR-TEM) observation they could visualize lattice fringes at the interior of all Nb precipitates visible on scanning transmission electron microscopy (STEM) Z-contrast images. Their observation suggested that bcc Nb precipitates turn first into the stable Nb_2O of space group (SG) #88, and gradually transform to o-Nb_2O_5 (SG #55) and m-Nb_2O_5 (SG #139). Since they examined only those located in the vicinity of the oxide/metal interface, it is not known whether the Nb_2O_5 (SG #55 and #139) is their final configuration. On the other hand, another HR-TEM observation by Kim et al. [5] concluded that bcc Nb precipitates first transform to a mixture of metastable Nb_2O (SG #80) and amorphous phase in the initial stage (near the oxide/metal interface), next turn fully amorphous in the middle stage, and finally dissolve into the matrix in the last stage, as any precipitates were not detected near the free surface. Later, based on X-ray energy dispersive spectroscopy (EDS) elemental mapping, Sakamoto and Une et al. [9–10] reported that Nb precipitates dissolve into the matrix in the case of lithiated water corrosion but not in the case of without lithium. Since they did not perform structure analysis, it is not known whether amorphization occurred in their specimens prior to dissolution. The EDS results of Sakamoto and Une et al. are apparently inconsistent with the HR-TEM results of Kim et al. who performed corrosion tests in distilled water (Table 1). As for dissolution of precipitates, atom probe tomography (APT) by Wei et al. [11] and Sundell et al. [12] showed that the concentration of Nb contained in the matrix of surface oxide film is even smaller than that of the base metal, and that segregation of Nb did not occur at the oxide/metal interface and at grain boundaries and dislocations in the oxide film. These APT results may be an indication that dissolution of Nb precipitates does not always occur.

The relationship between amorphization and dissolution of precipitates is of interest not only from the viewpoint of engineering but also from the viewpoint of basic materials science as the critical condition for solid-state amorphization. Previous electron energy loss spectroscopy (EELS) analysis by Lin and Woo [3] revealed that the amorphous Nb precipitates are non-metallic in nature; i.e., amorphization is induced by introduction of O atoms. On the other hand, dissolution of Nb precipitates is achieved via diffusion of Nb atoms. If these two reactions occur simultaneously, it would follow that amorphization occurs even when both O and Nb atoms are mobile. To date, amorphization has been confirmed to occur in various diffusional reactions such as metal-metal diffusion couples [13–16], oxide-oxide couples [17], hydrogenation of intermetallic compounds [18–19], oxidation of metals [20], etc. Their common denominator is a large difference in the diffusivity of constituent elements [21]. Previous studies suggested that, at least within experimental resolution, amorphization occurs when only one element is mobile whereas the other is practically immobile [15,21].

With these in mind, in the present study, amorphization and dissolution of Nb precipitates have been assessed by means of TEM/STEM, EDS, EELS and nano-beam diffraction (NBD). We will demonstrate that some of the inconsistencies among the previous studies are artifacts of these characterization methods. The material examined in the present study was a Zr–2.5Nb fuel cladding tube subjected to long term corrosion (up to 13,000 h) at 633 K in simulated primary coolant of pressurized water reactors (PWRs). This alloy was originally developed as a prototype of advanced fuel cladding tube material optimized for extended burn-up operations [23–24]. In these corrosion conditions the Zr–2.5Nb alloy exhibited superior corrosion performance to conventional low-Sn Zircaloy-4 (Fig. 1); the corrosion weight gain at 13,000 h was ~40% smaller. Our previous APT analysis revealed that prior to the corrosion test the Zr matrix initially contained Nb ~0.5 at.% and the Nb precipitates contained Zr ~10 at.% (Table 2) [24]. The composition of Nb precipitates was also determined by X-ray diffraction [25]. The composition estimated from their lattice spacing based on the Vegard's law was Nb–9Zr. These solute concentrations are greater than their solubility at 633 K; i.e., they are thermodynamically non-equilibrium in the state of supersaturation. Since the diffusivity of Nb is of particular concern in the present study, thermal stability of precipitates during the corrosion tests has also been investigated.

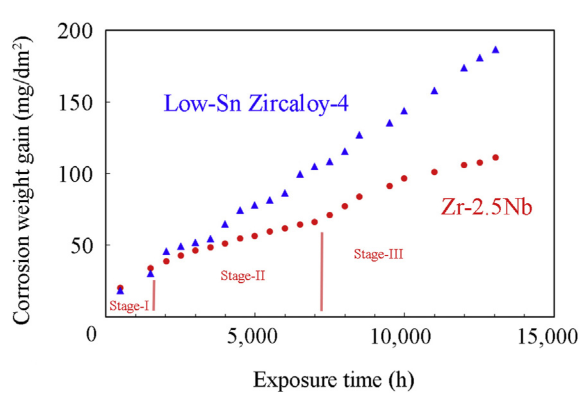

Fig. 1. Corrosion weight gain versus exposure time of the Zr–2.5Nb alloy and reference low-Sn Zircaloy-4: autoclave corrosion at 633 K in PWR-simulated water.