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Oxidation properties of Zr–Nb alloys at 500–600 °C under low oxygen potentials

Tatsumi Arima *, Kensaku Miyata, Yaohiro Inagaki, Kazuya Idemitsu

Institute of Environmental Systems, Faculty of Engineering, Kyushu University, 6-10-1 Hakozaki, Fukuoka 812-8581, Japan

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Abstract

Zr–Nb alloys with 1–10 wt.% Nb content were oxidized at 500–600 °C in the CO–CO_2 gas mixtures. The oxidation weight gain increased with Nb content and the kinetics except for Zr–1Nb alloy changed from cubic rate to linear one at 600 °C for a long period of time, 7 d. The cubic rate constant was almost insensitive to oxygen potential of oxidizing atmosphere. As the oxidation resistance deteriorated, the volume ratio of tetragonal to monoclinic zirconia phase and the relevant compressive stress in oxide film decreased with increase of Nb content. Before and after oxidation, Nb re-distribution could not be observed under the present experimental condition.

Keywords: Zr–Nb alloy; Oxidation; XRD; EPMA

1. Introduction

The Zircaloy-2 and 4 have been widely used in the light water reactors, and successfully carried out a role as cladding material for nuclear fuels. Furthermore, in

* Corresponding author. Tel.: +81 92 642 3779; fax: +81 92 642 3800.
E-mail address: arimatne@mbox.nc.kyushu-u.ac.jp (T. Arima).

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order to improve the corrosion resistance, the minor modifications have been added to heat-treatments or controlling of additive elements for these Zr-based alloys [1–4]. For instance, Sn content has been lowered to 1.3 wt.% from 1.5 wt.% in Zircaloy-4 cladding now in use [4]. Recently, extension of fuel burn-up and loading mixed oxide fuel, UO_2–PuO_2, into the light water reactors have been progressed from the economical and ecological points of view. Therefore, further improvements should be needed for various properties of new Zr-based alloys, e.g. corrosion resistance and mechanical strength [4,5].

It is possible that Nb addition to Zr-based alloy improves the corrosion resistance in high pressured water vapor. Developing Zr-based alloys with Nb have the chemical composition of 0.1–1.0 wt.% Nb as shown in the recent trend [6,7]. Meanwhile, the Zr–2.5Nb alloy has been developed as a pressure tube material of CANDU reactors and the relevant corrosion behaviors have been investigated [8–10]. However, the correlation between Nb addition and corrosion behavior is not well understood. Furthermore, the change of micro-structures by the heat-treatment in a manufacturing process complicates the corrosion behaviors of Zr–Nb alloys. So far, it has been understood that Zr-based alloys added Nb show the better corrosion resistance when Nb content is less than 1–5 wt.% by optimizing the heat-treatment [7,11–13]. And it has been suggested that the corrosion resistance of Zr-based alloy added Nb is deteriorated only by β-quenching which means fast-cooling from ~1050 °C. The following heat-treatment relevant to occurrence of β-Nb phase is rather favorable [13].

In the previous studies on oxidation of Zr metal by dried oxygen gas, its kinetics, the nature of oxide films and so on have been discussed [14–20]. At the initial stage of oxidation, it was observed that the kinetics obeyed to the parabolic or cubic law, and that for the long period of time the oxidation was accelerated according to the linear rate law [16,18–20], which is called the kinetic transition. However, the reason why such a kinetic transition occurs in oxidation of Zr metal or Zr-based alloys has not been cleared so far [16]. In our previous studies on oxidation mechanism of Zircaloy-2 and -4, we concluded that oxidation kinetics of these alloys obeyed the cubic rate law at 450–600 °C for 24 h in CO–CO_2 gas mixtures and that the rate constant was insensitive to the oxygen partial pressure of oxidizing atmosphere [21,22]. Furthermore, the kinetic transition was also observed for a long period of time at 600 °C. The crystallographic analyses clarified that oxide films on these alloys showed the correlation that the volume ratio of tetragonal to monoclinic zirconia phase and compressive stress in oxide film decreased with the growth of oxide film.

For the comprehensive understanding of oxidation mechanism of Zr–Nb alloys, it is important to investigate the oxidation behavior in the dried atmosphere with the low oxygen partial pressure as well as in the water vapor. This investigation is helpful to understand the fuel-side oxidation and can give the basic information on understanding the water-side corrosion. The objective of this study is to understand the oxidation behavior of Zr–Nb alloys as a function of Nb content in CO–CO_2 gas mixtures and to discuss the experimental results especially from the crystallographic point of view.