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Letter to the Editors

Corrosion and microstructural characteristics of Zr–Nb alloys with different Nb contents

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Abstract

To improve their corrosion resistance and mechanical properties, Nb is added to most of the advanced Zr-based alloys. So, in this study, a systematic investigation was performed on Zr–*x*Nb alloys ($x = 0.1$–2.0 wt%) to establish the optimized Nb content and annealing temperatures which were applied during manufacturing process. A corrosion resistance of Nb-containing Zr alloys was considerably affected by the Nb content as well as annealing temperature. The good corrosion resistance was obtained when the Nb content was controlled to be 0.2–0.3 wt% and the annealing temperature of the high Nb-containing alloys during the manufacturing process was performed at 570 °C. From the microstructural investigations by using TEM/EDS, the corrosion resistance was controlled by the Nb solubility in alpha Zr and the type of β-phases which were determined by the annealing temperature.

1. Introduction

Zr-based alloys are being used as fuel cladding and structural materials for nuclear reactors, since these alloys have a good irradiation stability, corrosion resistance, and mechanical properties in a reactor environment. Recently, more advanced Zr-based alloys have become necessary for enhanced operating conditions such as an increased burn-up and higher operation temperatures [1–4]. The tendency that Nb was selected as a major alloying element in the Zr-based alloy is a common characteristic for the newly developed fuel claddings. So, it is necessary to investigate the effect of the Nb-content and the effect of an annealing after a beta quenching on the corrosion of Zr–*x*Nb binary alloys, for developing advanced nuclear fuel cladding materials with an improved corrosion resistance.

The investigation on the corrosion behavior as well as the phase transformation of Zr–Nb alloys have been performed by many researchers. Some of them have reported that the Zr alloys containing a low Nb content showed a good corrosion resistance [5,6]. From a study of the effect of the β phase on a corrosion, it has also been reported that corrosion rate of Zr–Nb alloy increased with the formation of the β_{Zr} phase but it decreased with the formation of the β_{Nb} phase [7–9]. Especially, the solid solution effect of Nb-content and the type and fraction of β_{Zr} phase on corrosion were systemically studied for the water quenched and annealed Zr–Nb alloys [8]. The correlation between the microstructural properties such as Nb-content, type of precipitates and oxide characteristics was studied for the Zr–*x*Nb alloys which were isothermally annealed at 570 and 640 °C [9]. As such, the corrosion rate of Nb-containing Zr alloys is known to depend on the Nb content in the matrix and the type of β-phases.

However, the corrosion behavior of the Zr–*x*Nb alloys which were manufactured by the application of different annealing temperature during cold working process was not classified in the previous studies. So, the corrosion behavior of Zr–*x*Nb alloys having different manufacturing process was investigated in this work.

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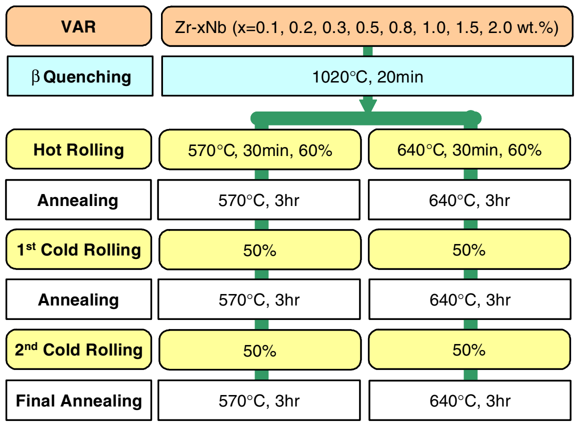

Fig. 1. Chemical composition and manufacturing process of the Zr–*x*Nb alloys.

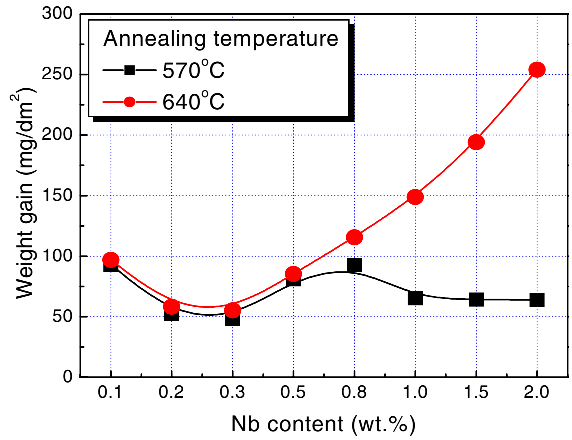

Fig. 2. Corrosion behaviors of the Zr–*x*Nb alloys with the Nb content and annealing temperature corroded at 360 °C for 150 days.

2. Experimental procedure

The alloys containing 0.1–2.0 wt% Nb were prepared by the manufacturing process shown in Fig. 1. The alloy was prepared by the vacuum arc remelting method with sponge zirconium and high purity (99.99%) niobium and then this ingot was β solution treated at 1020 °C for 20 min. The quenched ingot was hot-rolled after a pre-heating at 570 °C and 640 °C for 30 min and cold-rolled two times to a final thickness of 0.8 mm. Between the rolling steps, the cold-rolled sheet was intermediate-annealed at 570 °C and 640 °C for 3 h.

Samples for the corrosion test, 25 by 20 by 0.8 mm in size, were cut from the manufactured strip, mechanically ground up to 1200 grit SiC paper, and then pickled in a solution of 5 vol.% HF, 45 vol.% HNO_3 and 50 vol.% H_2O. The final thickness of the corrosion test samples after pickling was 0.56 mm. The corrosion test was performed in a static autoclave with distilled water under the condition of 360 °C and 18.9 MPa according to the procedure of ASTM G2-88. The corrosion behavior were evaluated by measuring the weights gains of the corroded specimens. The microstructure observation and the precipitates analysis of the samples were performed by using a transmission electron microscope (TEM) equipped with EDS.

3. Results and discussion

3.1. Corrosion behaviors

Fig. 2 shows the results of the corrosion test of the Zr–*x*Nb alloys tested at 360 °C for 150 days. It was observed that the corrosion behaviors of the Zr–Nb binary alloys were quite different depending on the Nb content and the intermediate annealing temperature during the manufacturing process. The corrosion behavior of the Zr–*x*Nb alloys was changed with the Nb content and the intermediate annealing temperature. The corrosion behavior of the low Nb containing alloys in the range of 0.1–0.8 wt% were very similarly regardless of the annealing temperature of 570 °C and 640 °C. As the Nb content increased, the weight gain was decreased up to about 0.3 wt% Nb, and it was increased with an increasing Nb content up to 0.8 wt% in both samples annealed at 570 °C and 640 °C. However, in the range of a high Nb content from 1.0 to 2.0 wt%, the corrosion rate of the alloys was considerably changed with the annealing temperature. The corrosion rate of the sample annealed at 570 °C was much lower than that of the sample annealed at 640 °C, and the corrosion rate of the sample annealed at 640 °C was considerably increased with Nb content. This result of the corrosion behavior is similar to the previous result [9] which is studied for the isothermal annealing effect after β-quenching of Zr–*x*Nb alloys.

3.2. Microstructure characteristics

Fig. 3 shows the TEM micrographs of the second phase particles of Zr–*x*Nb alloys with the annealing temperature. The type and volume fraction of the second phase particle were changed by increasing the Nb content and annealing temperature. In the Zr–0.2Nb alloy annealed at 570 °C and 640 °C, the second phase particle of a small size was observed and the type of the second phase particle was revealed as a Zr_3Fe precipitate by using the TED/EDS and SAD analysis. The formation of a Zr_3Fe type precipitate resulted from the Fe as an impurity contained in the zirconium. In the range of 0.8–2.0Nb of the alloys, the type and size of the second phase particles in the sample were clearly changed by the annealing temperature. In the alloys annealed at 570 °C, $Zr(NbFe)_2$ type precipitates were mainly observed in the matrix of the Zr–0.8Nb alloy and a β_{Nb} phase was mainly observed in the matrix of the Zr–1.0Nb, Zr–1.5Nb and Zr–2.0Nb alloys. In the alloys annealed at 640 °C, $Zr(NbFe)_2$ type precipitates were mainly observed in the matrix of the Zr–0.8Nb alloy and the β_{Zr} phase was mainly observed in the matrix of the Zr–1.0Nb, Zr–1.5Nb and Zr–2.0Nb alloys.