

Isothermal Oxidation Behavior of Ternary Zr-Nb-Y Alloys at High Temperature

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Abstract. The effect of yttrium content on isothermal oxidation behavior of Zr-2,5%Nb-0,5%Y, Zr-2,5%Nb-1%Y Zr-2,5%Nb-1,5%Y alloy at high temperature has been studied. High temperature oxidation carried out at tube furnace in air at 600,700 and 800°C for 1 hour. Optical microscope is used for microstructure characterization of the alloy. Oxidized and unoxidized specimen was characterized by x-ray diffraction. In this study, kinetic oxidation of Zr-2,5%Nb with different Y content at high temperature has also been studied. Characterization by optical microscope showed that microstructure of Zr-Nb-Y alloys relatively unchanged and showed equiaxed microstructure. X-ray diffraction of the alloys depicted that the oxide scale formed during oxidation of zirconium alloys is monoclinic ZrO₂ while unoxidised alloy showed two phase α and β phase. SEM-EDS examination shows that depletion of Zr composition took place under the oxide layer. Kinetic rate of oxidation of zirconium alloy showed that increasing oxidation temperature will increase oxidation rate but increasing yttrium content in the alloys will decrease oxidation rate.

Keywords: Oxidation, Zircalloy, Zr-Nb alloy, ZrO₂, Kinetic rate

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INTRODUCTION

The Zircalloy base alloy have been widely used in the nuclear power plant reactors as cladding material for nuclear fuels element due to low neutron absorption and good corrosion resistance. In order to improve the corrosion resistance of zircalloy, the minor modifications of alloys have been conducted to heat-treatments or modification alloy with additive elements for these Zr-based alloys [1,2]. Currently, extension of fuel burn-up for the light water reactors have been conducted with the purpose from the economical aspect of Nuclear Power Plant (NPP). Therefore, further improvements should be desired for various properties of new Zr-based alloys, e.g. corrosion resistance and mechanical strength [3]. Former study shows that Nb addition to zirconium-based metals improves the corrosion resistance in high pressured water vapor. Developing Zr-based alloys with Nb addition with the chemical composition of 0.1–1.0wt.% Nb has already accomplished in the recent development [4]. Meanwhile, the Zr–2.5Nb alloy has been developed as a pressure tube material of CANDU reactors and the resistance corrosion behaviors have been investigated [5]. Furthermore, the change of micro-structures by the heat-treatment in a manufacturing process improves the corrosion behaviors of Zr–Nb alloys. So far, it has been understood that Zr-based alloys with Nb addition

shows the better corrosion resistance when Nb content is less than 1–5wt.% by optimizing the heat-treatment [6].

Corrosion of zirconium alloys is one of the main factors in the degradation of the tubes during service. Zirconium and its alloys will oxidized spontaneously and develop a self-healing layer of adhesive and protective oxide layer at high temperature. At high temperatures and in the presence of water vapor, the oxidation zirconium alloy will continue to form a uniform oxide layer. The kinetics of the oxide layer thickness growth on zirconium is controlled by the migration of oxygen ions through the existing oxide scale layer and the interaction with the metal at the metal–oxide interface [7]. Depending on the composition and the oxidation conditions, three crystallographic structures have been reported for the ZrO₂ layer: monoclinic, tetragonal and in rare cases cubic zirconias. The ratio of different oxide phases has been shown to be dependent on the material composition and on corrosion conditions testing such as temperature, pressure and chemistry composition of gas and solution. In the previous studies on oxidation of Zr metal by dry oxygen gas, its kinetics, and the nature of oxide films have been discussed [8]. The results show that the oxidation rate is known to depend on the composition of the material and follows a cubic rate law at the early stages.

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An early study [9] showed that the corrosion weight gain in air at 500°C for Zr-4 implant with yttrium improves corrosion resistance of the alloy compared with Zr-4 without implantation. Further improvement of corrosion study on hydrogen pick up has been carried out by a number of researchers. Study Zr-Y showed that addition yttrium on zirconium improve hydrogen pick up due to broadening limiting solid solubility hydrogen in Zr-Y alloy [10]

However, the present work investigated the phase structures, morphologies and chemical composition of the oxide films grown on Zr-2.5%Nb-Y at high temperature, using X-ray diffraction (XRD), scanning electron microscopy (SEM-EDS) and optical microscope. The corrosion rate and oxidation mechanism of Zr-Nb-Y is also discussed.

EXSPERIMENTAL

The chemical composition of the Zr-Nb-Y alloys used in this study is given in Table 1. The alloys were prepared by arc-melting furnace under argon atmosphere. Prior homogeneity, the alloys were

re-melting at least four times. The ingots were then β quenching heat treatment at 900°C for 4 hours. Before the oxidation tests, the specimens were grinded by emery paper from grit 500 to 1000. Then all the specimens were rinsed and cleaned by ultrasonic cleaner in an acetone. The oxidation tests in air furnace were conducted by using tube furnace. The test temperature was controlled by PID and range temperature from 600 to 800°C with the duration in furnace 1 hour. During oxidation, the weight gain of specimen was measured with scale. After oxidation, oxidized and un oxidized specimens were analyzed by x ray diffraction for phase present analyzed. For the optical microscope examination, the specimen embedded in an epoxy resin and then the surfaces of the sections were mechanically grinding from grit 800 to 2400. Micro structural analysis of specimen was carried out by using an optical microscope after specimen chemically etched in a solution of 5% H₂SO₄, 10% HF, 30% HNO₃ and 55% H₂O by volume. Cross sections compositions of the specimen were analyzed by SEM-EDS.

TABLE 1. Chemical composition of Zr-2,5%Nb-Y alloys (wt%)

Specimens	Zr	Nb	Y
Alloy-1	97.5	2.5	0
Alloy-2	97	2.5	0.5
Alloy-3	96.5	2.5	1
Alloy-4	96	2.5	1.5

RESULTS AND DISCUSSION

1. Microstructures as heat treatment alloys

Figure 1 (a), (b) and (c) showed microstructures of as heat treatment three different alloys Zr-2,5%Nb, Zr-2,5%Nb-0.5%Y and Zr-2,5%Nb-1%Y. From the figure depicted that the microstructures of three alloys are relatively the same in apparent. The alloys consist of equaxed microstructure in the grain with grain boundaries relatively large.

2 X-ray diffraction alloys before and after oxidation

Figure 2 shows the X-ray diffraction patterns for Zr-2,5%Nb before oxidation (a) and Zr-2,5%Nb-1%Y after oxidized at 600°C for 1 hour (b). In Figure 2 a, it can be seen that the diffraction patterns showed the presence of α - β zirconium phase before the alloy was oxidized. After oxidation the main oxide dominated by monoclinic zirconia's phases ZrO₂. Although the surface this specimen was most oxidized other phases could be observed in the diffraction patterns of α - β zirconium phase shown in Figure 2.

3. SEM-EDS cross section oxidized alloys

SEM-EDS examination cross section oxidized alloy Zr-2,5%Nb and Zr-2,5%Nb-1,5%Y after oxidation at 600°C and 700°C, respectively for 1 hour showed in Figure 3. It is seen that increases oxidation temperature will increase the width of oxide layer. Oxidation at 700°C thicker compared with oxidation at 600°C. The oxide layer formed on the surface alloy free of pore and dense. Depleted zone in Zr-2,5%Nb after oxidation at 600°C for 1 hour contain 78.8wt%Zr. The Zr-2,5%Nb-1,5%Y alloy was oxidized at 700°C for 1 hour and depleted zone of the alloys contain 85,53 Zr.

Figure 4a shows the weight gains of Zr-2,5%Nb-Y oxidized at different temperature for 1 hour. While Figure 4b shows weight gain of the specimen plotted with alloys composition at different temperature. In the temperature testing, the growth of zirconium oxide is control by inward diffusion of oxygen through the oxide layer. There is different value of weight gain observed at different alloys. Addition Y in the alloys will decrease the weight gain. In other word, additional Y in the alloys will improve

resistance oxidation of its alloy as seen in Figure 4b. Figure 4b also depicts that increasing temperature will

increase weight gain during oxidation.

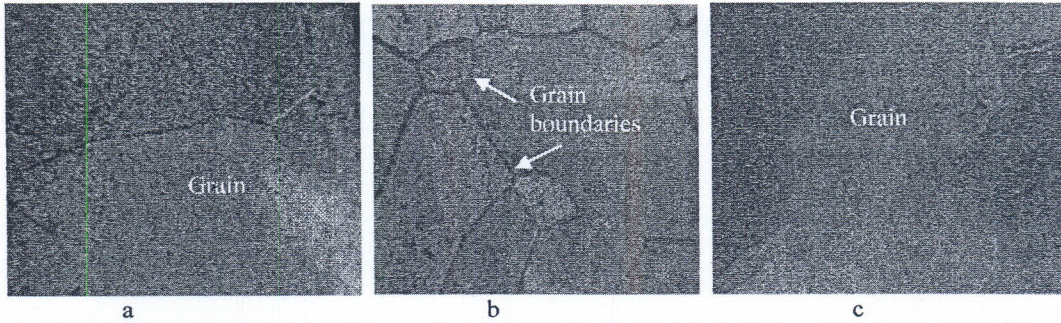


FIGURE 1. Microstructures 3 different alloys Zr-2,5%Nb, Zr-2,5%Nb-0,5%Y and Zr-2,5%Nb-1%Y 30X

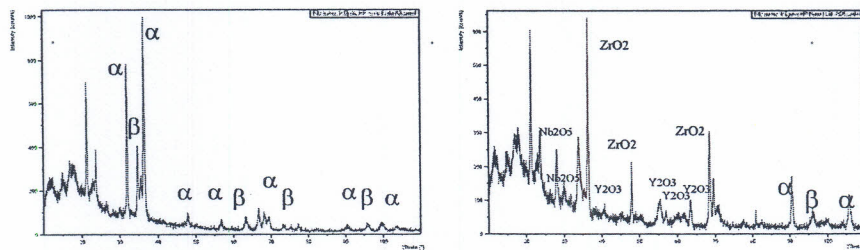


FIGURE 2.. XRD patterns before oxidation alloy Zr-2,5%Nb and Zr-2,5%Nb-1%Y after oxidized at 600°C for 1 hour

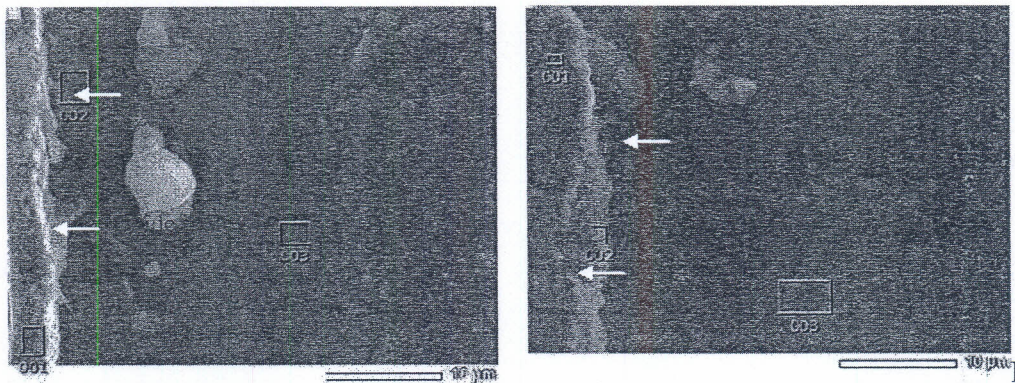
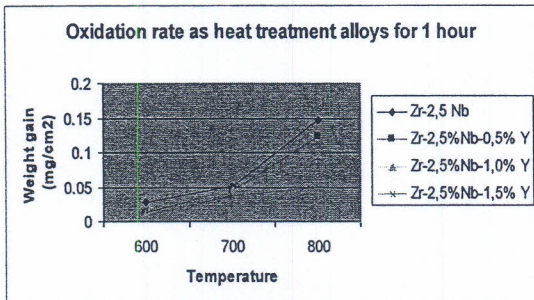
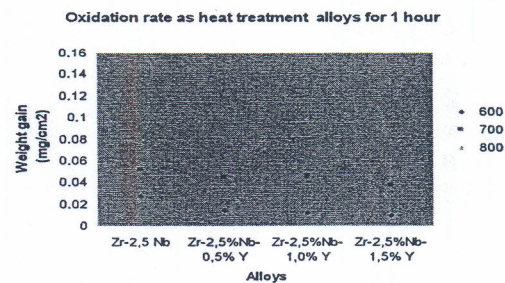


FIGURE 3. Cross section alloys (a) Zr-2,5%Nb and (b) Zr-2,5%Nb-1,5%Y after oxidation at 600 and 700, respectively for 1 hour

4. Kinetic Oxidation



(a)



(b)

FIGURE 4. Oxidation rate a) As heat treatment alloy for 1 hour at 600, 700 and 800°C and b) as alloys function

Figure 4a shows the weigh gains of Zr-2,5%Nb-Y oxidized at different temperature for 1 hour. While Figure 4 b weight gain of the specimen plotted with alloys composition at different temperature. In the temperature testing, the growth of zirconium oxide is control by inward diffusion of oxygen through the oxide layer. There is different value of weight gain observed at different alloys. Addition Y in the alloys will decrease the weight gain. In other word, additional Y in the alloys will improve resistance oxidation of its alloy as seen in figure 4 b. The figure also depicted that increasing temperature will increase weight gain during oxidation.

5. Discussion

As β quenching heat treatment alloys show equaxed microstructure as seen in Figure 1 with α and β phase. Basically, all cast alloys after solidification in the furnace showed big grain microstructure with matrix α -phase due to long order cooling during solidification. After β quenching heat treatment, phase present in the as cast Zr-2,5%Nb-Y alloys can be explained as follows. During arc melting, all solid Zr, Nb and Y become liquid metal at 1800°C during arc melting in copper crucible cooled by flowing water. Liquid metal starts solidified under 1800°C and start solidified until 900°C finished. Then, under 900°C, the core of β phase transformed partly became α -phase. The sequence phase evolution of Zr-2,5%Nb-Y alloys as describes L phase \rightarrow β phase \rightarrow α + β phase. X-ray diffraction studies of as β heat treatment alloys showed that phase present in the alloys dominated by α phase and minor β phase. After β quenching heat treatment the β phase present in the alloys increase.

Kinetic oxidation rate was higher at higher temperature than 600°C. As expected that temperature will accelerated reaction oxidation rate. The alloys exhibiting unstable oxide growth also increased with temperature. The thickness of oxide film formed on Zr-2,5%Nb-1,5%Y oxidized at 700°C is thin that of Zr-2,5%Nb oxidized at 600°C as seen in Figure 3. The relationship between oxidation weight gain and Y content in the alloy showed that changes in alloying content caused significant differences in high temperature oxidation behavior. The Z-2,5%Nb-Y alloys with high Y content more resistance oxidation compare with Zr-2,5%Nb alloys. Some Zr-2,5%Nb-1%Y alloys showed stable oxide growth with protective behavior compared with Zr-2,5%Nb Alloy. From EDS analysis, composition of Zr beneath the oxide scale showed that alloy with Y contain 85,53 wt% while Zr-2,5%Nb alloy contain 78%. It means that outward diffusion of Zr relative small for Zr-2,5%-1%Y compared with Zr-2,5%Nb alloy. Oxygen

inward diffusion decreased due to development oxide scale Y_2O_3 for Y doped Zr-2, 5% Nb alloy during oxidation.

CONCLUSION

The isothermal oxidation behaviors of the Zr-2,5%Nb alloys with 0.5–1.5wt.% Y content have been performed at 600, 700, and 800°C In association with isothermal oxidation of Zr-2,5%Nb-Y at different Y content and temperature, it can be concluded that:

- (1). The main phase present in the zircalloy Zr-2.5%Nb-Y after β quenching is α and β phase with equaxed microstructure
- (2). The phase present of oxide scale Zr-2,5%Nb-Y formed during oxidation is ZrO_2 monoclinic
- (3). For All alloys showed that the accelerated rate of oxidation increase with increasing temperature
- (4). The oxidation weight gain of the specimen decrease with Y content in alloys
- (5) Addition yttrium improved oxidation Zr-Nb alloy.

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