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High Temperature Oxidation of Zr-2.5%wt Nb Alloys Doped with Yttrium

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Abstract: Zirconium base alloys have been utilized in LWRs (light water reactors) as fuel element cladding tubes, fuel assembly spacer grids, guide tubes in PWRs (pressurized water reactors) due to their low neutron absorption and good corrosion resistance. The oxidation resistance of Zr alloys are strongly controlled by the phase presence and composition of the alloys. The beneficial effect of yttrium content on isothermal oxidation behavior of Zr-2.5%Nb-Y(Y = 0, 0.5, 1, 1.5)in wt % alloy at high temperature has been studied. High temperature oxidation carried out in air furnace at 600,700 and 800 ^{o}C for 1, 4, and 9 h. Characterization by optical microscope showed that microstructure of Zr-2.5%Nb-Y alloys relatively unchanged. X-ray diffraction of the alloys depicted that the oxide scale formed during oxidation of zirconium alloys is monoclinic ZrO_2 and minor of tetragonal ZrO_2, while unoxidized 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. The parabolic rate constant value decreasing with increasing yttrium in Zr-2.5%Nb alloys.

Key words: Oxidation, alloy, zirconium, yttrium.

1. Introduction

The Zirconium base alloy have been widely used in the nuclear power plant reactors as cladding material for nuclear fuels due to low neutron absorption and good corrosion resistance. The extension of fuel burn-up has been one of the primary reasons in the NPP (nuclear power plant) to obtain a more economical operation of the reactors. The main restriction on a high burn-up is the WSCI (waterside cladding interaction) where the corrosion of the fuel claddings occurs by primary cooling water reactor at high temperature. Corrosion of zirconium alloys is one of the main factors in the degradation of the nuclear fuel element cladding during service [1, 2]. Zirconium and its alloys oxidized spontaneously and develop of adhesive and protective oxide scale of zirconium at high temperature. At high temperatures the oxidation continues and a uniform oxide layer forms. The kinetics of the scale growth on zirconium is controlled by the intrusion of reactive specious at the scale-base metal interface. Since the oxidation of Zr alloys is controlled by the diffusion of oxygen to the oxide/metal interface through the scale, the phase present microstructure of the oxide scale is expected to provide the most important data on the oxide growth [3].

Application of alloys at high temperatures should have resistance to chemical degradation caused by reactions oxidation between the alloy and the oxygen. The most structural alloys are not sufficiently protective above 550 °C. Therefore the addition of REE (rare earth elements) to these alloys will improve high temperature oxidation behavior of alloys. The

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effect of REE such as neodymium, yttrium, lanthanum and ytterbium has been studied by Pillis et al. [4]. From that study it was found that the additions of REE improved oxidation behavior of AISI 304L stainless steel. The oxidation behavior at high temperature on low manganese carbon steel after implanted by yttrium has been studied by Caudron et al. [5]. From the study, it can be concluded that implantation of yttrium on low manganese carbon steel improve high temperature oxidation of the alloy. The influence of REE on zirconium alloys was investigated by a number a researcher [6-8]. Bai et al. conducted implantation of yttrium on Zircaloy 4 and oxidized in air furnace at 500°C. The results showed that implantation yttrium on zircaloy 4 improve oxidation resistant of zircaloy 4. Peng et al. investigated aqueous corrosion zircalaoy 4 after implanted with yttrium in a 1 N H_2SO_4 [8]. It was found that corrosion resistance of zircaloy 4 in a 1N H_2SO_4 increase with raising implantation dose.

Zr-Nb alloys , Zirlo, M5 are develop for application in the water cooled reactor. It has been understood that Zirconium added with Nb show the better corrosion resistance when Nb content is less than 5wt.% by optimizing the heat-treatment [9, 10]. Depending on the composition and the oxidation conditions, three crystallographic structures have been reported for the ZrO_2 layer: monoclinic, tetragonal and in rare cases cubic zirconia. 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. The oxidation rate is known to depend on the composition of the material [11] .

In the present study, the high temperature oxidation behavior of Zr-2.5%Nb dopped with yttrium content 0.5, 1, and 1.5 wt% were investigated under the condition of temperature 700, 800 and 900 °C in air furnace.

2. Experiments

2.1. Specimens Preparation

The chemical compositions of the Zr alloys used in this study are the Zr-2.5%Nb-X system (x = 0, 0.5, 1, 1.5) were prepared from zirconium sponge (99) Nb wire (99.9) and Y chip (99,8) in wt%. The alloys were prepared by an arc melting under a high purity argon atmosphere and remelted at least four times prior to homogenity of the as-cast structure. The arc-melted ingots were β-treated at 900 °C for 4 h in tube furnace under argon atmosphere, and finally hot-rolled after a pre-heating at 900 °C for 60 min. The chemical composition of the Zr-2.5% Nb-Y alloys used in this study is given in Table 1.

2.2 Oxidation Testing

The oxidation tests in air furnace were conducted by using tube furnace in the range temperature from 600 to 800 °C with the duration in furnace 1, 4 and 9 h. The oxidation behavior of the alloys was examined by measuring the weight gain of the sample as a function of the exposure time. After the oxidation test, the cross-section of the oxide was observed by a transmitted light optical microscopy. X-ray diffraction is used for characterization oxidized and un oxidized specimens. 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 2,400. Micro structural analysis of specimen was carried out by using an optical microscope after specimen chemically etched in a solution of 5% H_2SO_4, 10% HF, 30% HNO_3 and 55% H_2O by volume. Cross sections composition of the specimen were analyzed by SEM-EDS

3. Results and Discussion

3.1 Microstructures as Hot Roll Alloys

Fig. 1 showed microstructures of as hot roll three

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

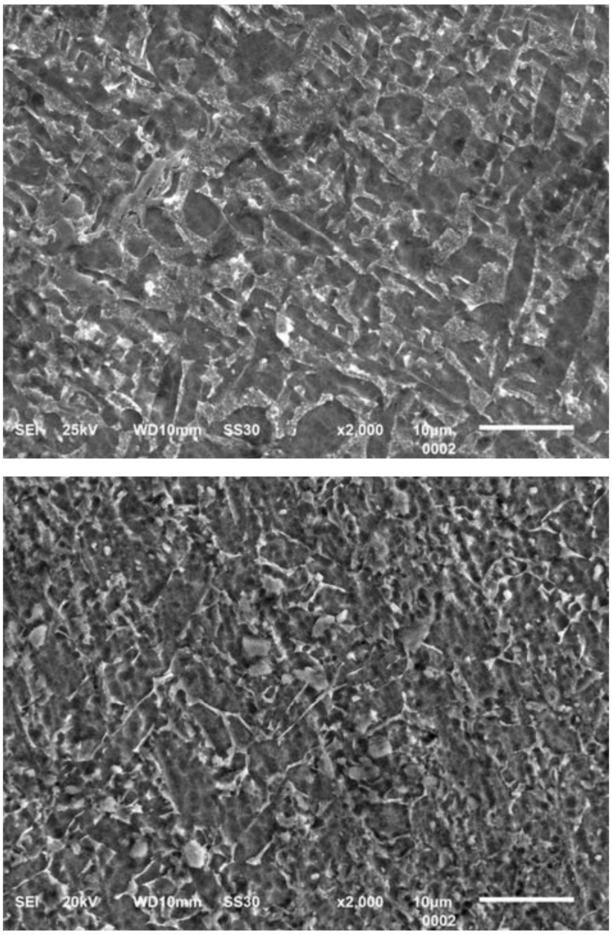


Fig. 1 Microstructures 2 different alloys Zr-2.5%Nb andZr-2.5%Nb-1%Y after hot roll.

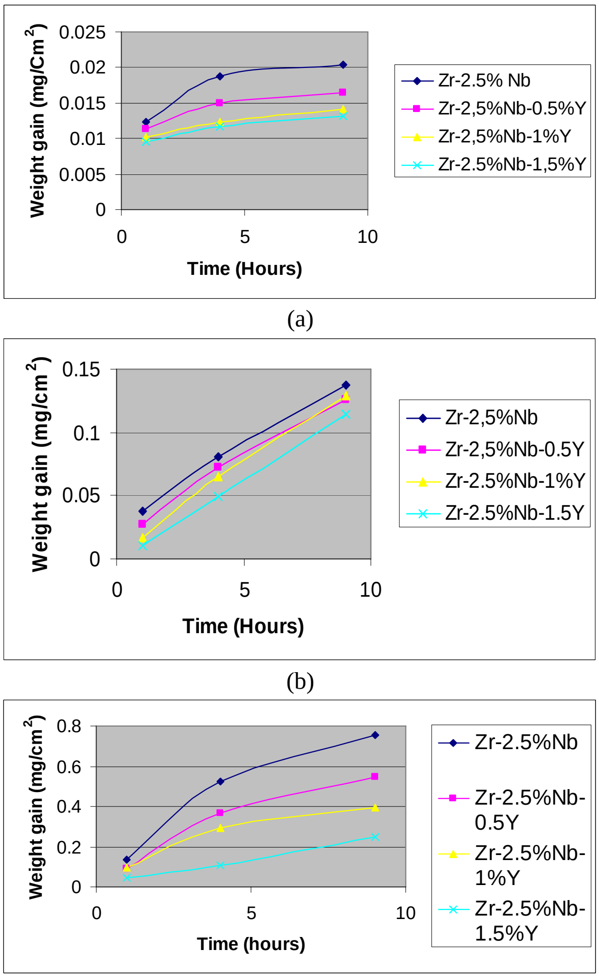
different alloys Zr-2.5%Nb, and Zr-2.5%Nb-1%Y. From the figure depicted that the microstructures of three alloys are relatively the same in apparent. The alloys consist of dendritic microstructure with interdendritic toward rolling direction.

3.2 Oxidation Kinetics

Due to the growth of zirconium oxide scale is controlled by diffusion oxygen inward through oxide scale so the phase present and microstructure of oxide scale plays an important role in the oxidation kinetic. Moreover, the pore, crack and defect of surface oxide scale may also responsible to the oxidation kinetics. The oxidation kinetic of Zr-2.5%Nb and Zr-2.5%Nb-Y with yttrium addition 0.5, 1, 1.5 wt % shows significant different. Fig. 2 shows the weight gains of Zr-2.5%Nb-Y oxidized at different temperature and time. In the 600 ^{o}C, the growth of zirconium oxide scale is controlled by 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 Fig. 4a. Compared with the oxidation weight gain of un doped Zr-2.5%Nb, it can be shown that the oxidation kinetic rate decreases with increases

Table 2 The metallic phase present of Zr-2.5%-Y alloys as Hot-roll.

Sample	Y (Wt%)	The metallic phase
Zr-2.5%Nb	0	α + β
Zr-2.5%Nb-0.5%Y	0.5	α + β
Zr-2.5%Nb-1%Y	1	α + β
Zr-2.5%Nb-1.5%Y	1.5	α + β



(a)

(b)

(C)

Fig. 2 Oxidation rate as hot roll alloy at 600 (a), 700 (b) and 800 ^{o}C (c).

Y addition. The curve with addition 1.5% Y of Zr-2.5%Nb below curve un doped Zr-2.5% Nb indicated that oxidation resistance of doped Zr-2.5%Nb is lower compared with un doped Zr-2.5%Nb.

Kinetic oxidation rate was higher at higher temperature than 600 ^{o}C. As expected that temperature will accelerated reaction oxidation rate. The alloys exhibiting unstable oxide growth also increased with temperature. 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. Similar to my results, it has been reported that the oxidation resistance of zircalloy could be improved by addition rare earth element such as yttrium and cerium [11]. The results show that development tetragonal phase of zirconia took place if the alloy contain yttrium.

The weight gain due to oxidation as function of time related to parabolic rate law :

$$W^2 = Kpt \tag{1}$$

where W (mg·cm^{-2}) is weight gain, and Kp (mg^2 cm^{-2}s^{-1}) the parabolic rate constant, and t (s) the oxidation time. The parabolic rate constant obtained by Eq. (1) are tabulation in Table 3. Parabolic rate constant for Zr-2.5%Nb more lower compared with Zr-2.5%Nb doped with yttrium at all temperature. Its mean that inward diffusion oksigen in oxide scale in undoped Zr-2.5%Nb alloy more higher compared with doped alloy. Early studies by Arima shows that the value parabolic rate constant for Zr-2.5%Nb alloy at temperature 800 ^{o}C was 0.17 while in this experiment 0.1624.

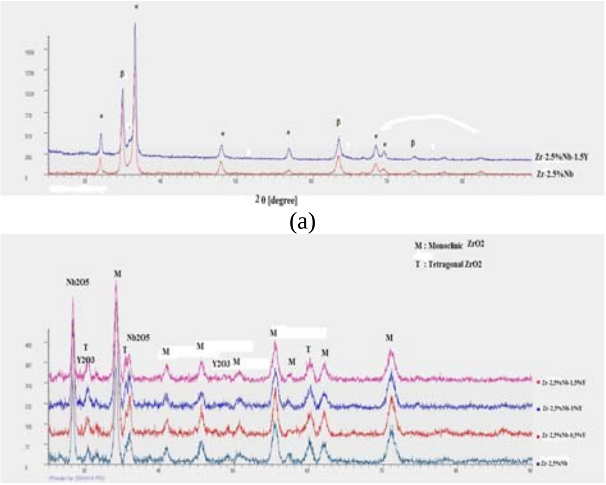
Fig. 3 shows the X-ray diffraction patterns for Zr–2.5%Nb,and Zr-2.5%Nb-1.5%Y before oxidation (a) and Zr-2.5%Nb, Zr-2.5%Nb-0,5%Y, Zr-2.5%Nb-1%Y and Zr-2.5%Nb-1.5%Y after oxidized at 800 ^{o}C for 1 h (b). In Fig. 3a, it can be seen that the diffraction patterns showed the presence of α and β zirconium phase before the alloy was oxidized. After oxidation the main oxide dominated by monoclinic zirconia's phases ZrO_2. Although the surface of this specimen was most oxidized other phases could be observed in the diffraction patterns of tetragonal zirconium, Nb_2O_5 and Y_2O_3 phase are shown in Fig. 3.

4. SEM-EDS Cross Section Oxidized Alloys

SEM-EDS examination cross section oxidized alloy

Table 3 Parabolic rate constants at 600,700 and 800 ^{o}C.

Paduan	Suhu (^{o}C)		
	600	700	800
Zr-2.5 Nb	0.0002	0.051	0.1624
Zr-2.5%Nb-0,5% Y	0.00001	0.042	0.0838
Zr-2.5%Nb-1,0% Y	0.00007	0.042	0.0462
Zr-2.5%Nb-1.5% Y	0.00006	0.032	0.0151



(a)

(b)

Fig. 3 XRD patterns (a)before oxidation alloy Zr–2.5%Nb and Zr-2.5%Nb-1.5%Y (b)after oxidized at 800 ^{o}C for 1 h–2.5%Nb, Zr-2.5%Nb-0,5%Y Zr-2.5%Nb-1%Y and Zr-2.5%Nb-1.5%Y.

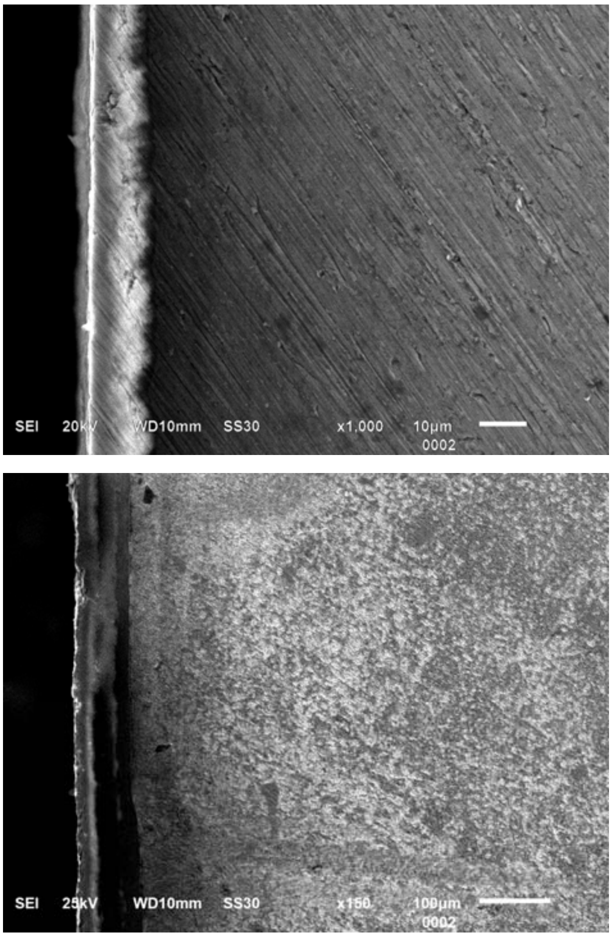


Fig. 4 Cross section alloys (a) Zr-2.5%Nb and (b)Zr-2.5%Nb-1.5%Y after oxidation at 700 for 9 h.

Zr-2.5%Nb and Zr-2.5%Nb-1.5%Y after oxidation at 700 °C, for 9 h are showed in Fig. 4. It is seen that increases oxidation temperature will increase the width of oxide layer. The oxide layer formed on the surface alloy free of pore and dense. Depleted zone in Zr-2.5%Nb after oxidation at 700 °C for 9 h contain 78.8wt%Zr. The Zr-2.5%Nb-1.5%Y alloy was oxidized at 700 °C for 9 h and depleted zone of the alloys contain 85.53 Zr. It can be concluded that addition yttrium on Zr-2.5%Nb alloy improve oxidation resistant at high temperature.

5. Conclusions

High temperature oxidation tests were conducted for Zr-2.5%Nb doped and undoped with yttrium at 600, 700 and 800 °C. The oxidation kinetic related to parabolic rate law and the weight gains of the dopped Zr-2.5% Nb samples with yttrium were smaller than that of undopped Zr-2.5% Nb and the higher yttrium dopped the better the oxidation resistance. Xrd analyses showed that the oxides of Y, Nb and Zr existed in the form of Y_2O_3, Nb_2O_3 and ZrO_2. The mechanism of the oxidation behavior improvement of Zr-2.5%Nb doped by yttrium addition was due to the role of Y_2O_3. Parabolic rate constant undoped alloy with Y higher than doped alloy with Y.

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References

[1] J. Lin, H. L. Li, and J. A. SZpunar. Mater. Scien. Eng. A 381 (2004): 104-112.
[2] N. Ni, S. L. Perez, and M. Jenkins. Scripta Materialia 62 (2010): 564-7.
[3] T. Arima, and et al. Corrosion Science 47 (2009): 435.
[4] M. F. Pillis, and et al. Mat. Res. 9 (2006): 4.
[5] E. Coudron, and H. Buscail. Applied Surface Science 158 (2000): 310-329.
[6] J. Xu, X. Bai, and Y. Fan. J. Mater. Sci. 35 (2000): 6225-9.
[7] X. Bai, J. Xu, A. Jin, F. He, and Y. Fan. Nuclear Instrumen and Methods in Physic Research B 160 (2000): 49-53.
[8] D. Q. Peng, and et al. Applied Surface Science 221 (2004): 259-271.
[9] R. J. Perez, and A. R. Masih. Journal Nuclear Materials 360 (2007): 242-254.
[10] S. A. Nikuli, and et al. Journal Nuclear Materials 418 (2011): 1-7.
[11] T. Arima, and et al. Progress in Nuclear Energy 51 (2009): 307-312.