

Nb 첨가 지르코늄 합금의 고온산화 거동 연구

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Kinetics of High Temperature Oxidation of a Nb-Added Zr Alloy in Steam

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Abstract

니오비움 첨가 지르코늄 합금 (Zr-1%Nb) 의 고온 수증기에서 산화속도에 관한 연구를 수행하였다. 산화온도는 700-1200 °C이다. 대기압수증기에서 산화될 때, Zr-1%Nb은 2차법칙을 따르는 것으로 나타났으며, 이는 900 °C이하에서 3차법칙을 따르는 지르칼로이-4와 상이한 형태를 보이고 있다. 900 °C이상에선 산화속도가 지르칼로이-4보다 약간 낮으며, 산화후 금속층의 경도가 증가하였다. 경도증가로 보아 인성의 감소가 예상되며, 따라서 니오비움 첨가 지르코늄 합금의 사고시 안전성에 대한 주의가 요구된다.

1. INTRODUCTION

Zr-base alloys are used as cladding materials for nuclear fuel in light and heavy water reactors. Zircaloy-4 (Zry-4) has been used satisfactorily as a cladding material in pressurized water reactors for several decades. Nowadays, light water reactors tend to extend their fuel cycle length to improve fuel economics, which needs a nuclear fuel of higher burn-up. Zry-4 may not satisfy the current required safety-margin for the high burn-up fuel. Hence, more corrosion-resistant Zr-base

cladding materials are being developed. One direction for the development of new Zr-base alloys is addition of Nb in alloying elements.

At high temperatures, the exothermic reaction of Zr-base alloys with steam is always a concern for the safety of nuclear power plants during accidents like LOCA (loss-of-coolant accident). The Nuclear Regulatory Commission set safety criteria for the Zr-base claddings, which are only applicable to conventional Sn-added Zr claddings. Nowadays, it becomes an important issue whether newly developed Nb-added Zr base alloys can

satisfy the current safety criteria. Hence, the difference in the kinetics of high-temperature oxidation between Nb-added and Sn-added Zr alloys should be checked. In the present paper, we compare the oxidation characteristics of Sn-added Zr-alloy (Zry-4) and those of Nb-added alloy (Zr-1%Nb alloy) at high temperatures, and discuss the possible problems when Nb-added alloy is used as claddings.

2. EXPERIMENTALS

We selected two types of specimens, i.e., Zry-4 as a Sn-added alloy and Zr-1%Nb alloy as a Nb-added alloy in the experiments. Both Zry-4 and Zr-1%Nb tubes are the commercial ones of Westinghouse, and used in the as-supply state. The tubes were cut to specimens of the length of about 15mm. Each specimen was degreased and pickled in aqueous HF/HNO₃ solution, then cleaned in hot and cold water. The chemical composition of each type of specimens is shown in Table 1. The main alloying elements of Zry-4 are Sn, Fe and Cr, while those of Zr-1%Nb alloy are Nb, Sn, and Fe.

High temperature oxidation tests were done under 1 atm steam in a vertical heater, where a specimen is hung by a Pt-wire (Fig. 1). When the goal temperature is obtained and the steam flow through the alumina tube inside heater becomes stabilized, the specimen is inserted into the center

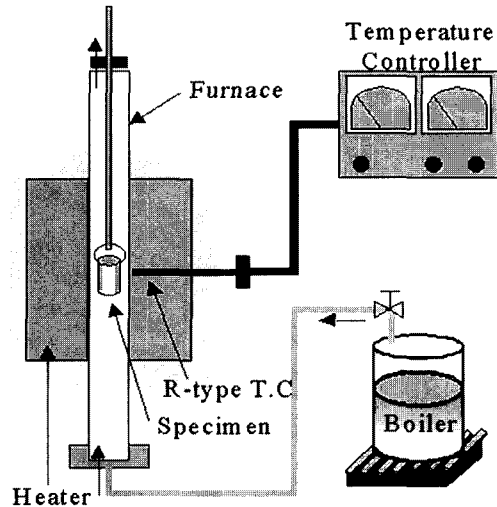


Fig. 1. Experimental setup for atmospheric steam oxidation

of the tube and pulled out of the tube after the desired oxidation is reached. The temperature range is between 700 and 1200°C. The steam flow rate is about 10g/min. After oxidation test, the specimen is molded, grounded and polished for the optical microscopic observation. For the micro-structural evaluation, the polished section was wipe-polished by etchant. The thickness of oxide and that of alpha-layer are determined by optical microscope.

3. Results and Discussion

The oxidation test at 1 atm steam is shown in Fig. 2. The symbols (solid lines) indicate the weight gains of Zr-1%Nb alloy specimens with

Table 1. Chemical composition of Zry-4 and Zr-1%Nb alloy.

Alloy	Nb	Sn	Fe	Cr	O	C
Zry-4	n.a.	1.1-1.5	0.2-0.24	0.06-0.14	1090ppm	120ppm
Zr-1%Nb alloy	1.01	1.06	0.1	60ppm	1200ppm	60ppm

(Units : w/o if not specified)

time and the dashed lines are those of Zry-4. Below 900°C, transition points are observed in both alloys. Parabolic rate law is always applicable before transition in Zr-1%Nb alloy. The weight gain of Zr-1%Nb alloy at atmospheric steam can be formulated by the following equations.

Before transition,

$$\Delta W = K_p \sqrt{t}$$

$$\text{where } K_p = 7.139 \times 10^4 \exp\left(\frac{-10,665.7}{T(K)}$$

ΔW : mg/dm², and t : sec.

After the transition point (below 900°C),

$$\Delta W = Wt + K_1 + (t - t_\tau)$$

$$\text{where } Wt = 1.286 \times 10^7 \exp\left(\frac{-11,964}{T(K)}\right)$$

$$K_1 = 1.51 \times 10^2 \exp\left(\frac{-8,303}{T(K)}\right)$$

$$t_\tau = 3.23 \times 10^4 \exp\left(\frac{-2,579}{T(K)}\right)$$

The solid lines in Fig. 2 are drawn from the above kinetic equations. The oxidation kinetics of Zr-1%Nb alloy is somewhat different from that of Zry-4. The kinetics in Zry-4 at high temperatures can be divided into two regions, based on the stable oxide phase at the oxidation temperature¹⁾. Below 1000°C, monoclinic phase is stable, while tetragonal phase is stable above 1100 °C (in be-

tween 1000 and 1100 °C, a hysteresis exists). When monoclinic oxide is stable, a cubic-rate law is generally observed in Zry-4¹⁾. And, parabolic-rate law appears in the tetragonal-oxide stable region²⁾. However, when Nb is added into Zirconium as an alloying element, the whole oxidation kinetics becomes the parabolic-rate law. This cubic to parabolic rate change in the monoclinic oxide region seems one of the characteristic changes by the addition of Nb. Sn is also a mostly contained alloying element in Zr-1%Nb alloy; however, its contribution to kinetics is less dramatic than Nb. The oxidation amount of Zr-1%Nb alloy below 1000 °C is comparable to or larger than that of Zry-4. At the temperatures above 1000 °C, the oxidation rate of Zr-1%Nb alloy is lower than Zry-4.

The kinetic constant, K_p , is also compared with the values of other works (Table 2)¹⁻⁵⁾. The activation energy, Q of the Zr-1%Nb alloy is very close to that of Zry-4, however, the values of the kinetic constant, K_p , are slightly less (about 70-80 % of those of Zry-4 in 1000-1400 °C range). Oxide thickness of Zr-1%Nb alloy (symbols) is compared to that of Zry-4 (lines) in Fig. 3. The oxide layer growth of both alloys looks very close to their weight gain.

Above 860 °C, the cross-sectional view of each specimen shows the well-known three-layer

Table 2. Parabolic rate constants in Zr alloys. $K_p = A \exp(Q/RT)$

Temp. range (C°)	A (mg/dm ²)	Q (kcal)	Materials	Reference
1000 - 1850	20.2×10^4	22.75	Zr	3
1050 - 1580	1.91×10^4	16.7	Zry-2, Zry-4	4
1000 - 1300	7.24×10^4	20.83	Zry-4	1
1050 - 1500	6.02×10^4	19.97	Zry-4	2
700 - 1100	4.873×10^4	20.4	Zr-1w/oNb	700 - 1200
7.139×10^4	21.2	Zr-1%Nb alloy	This work	5

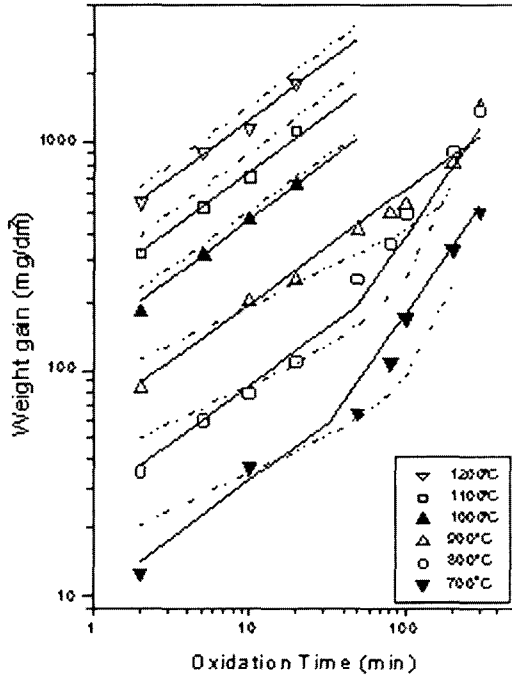


Fig. 2. Weight gain of Zr-1%Nb alloy in 1atm Steam. (dashed lines: Zry-4)

structure - oxide, oxygen-stabilized α -layer and prior β -layer (or, α' - layer). Fig. 4 displays the 3-layer structure in the specimens of Zry-4 and Zr-1%Nb alloy oxidized at 1200°C for 5 minutes. The

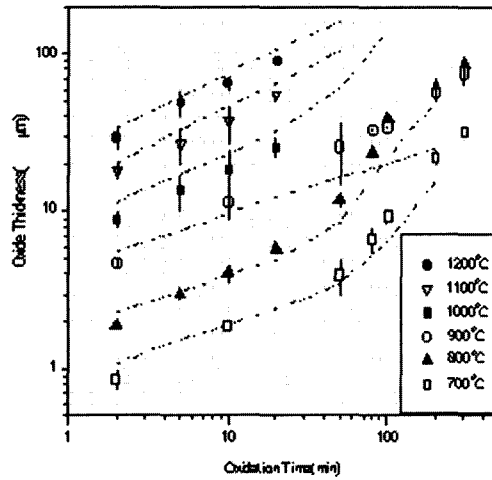


Fig. 3. Oxide thickness of Zr-1%Nb alloy (dashed lines: Zry-4)

oxide layers of both alloys have columnar structures. The oxide layer in Zr-1%Nb alloy looks thinner as was shown in Fig. 3.

The prior β -layer of Zr-1%Nb alloy has finer Widmannstatten structure than that of Zry-4. The distinction between α - and prior β - layers in Zry-4 is clearly noticeable, while the distinction is somewhat not clear in Zr-1%Nb alloy. Some microcracks are observable between α - and prior-

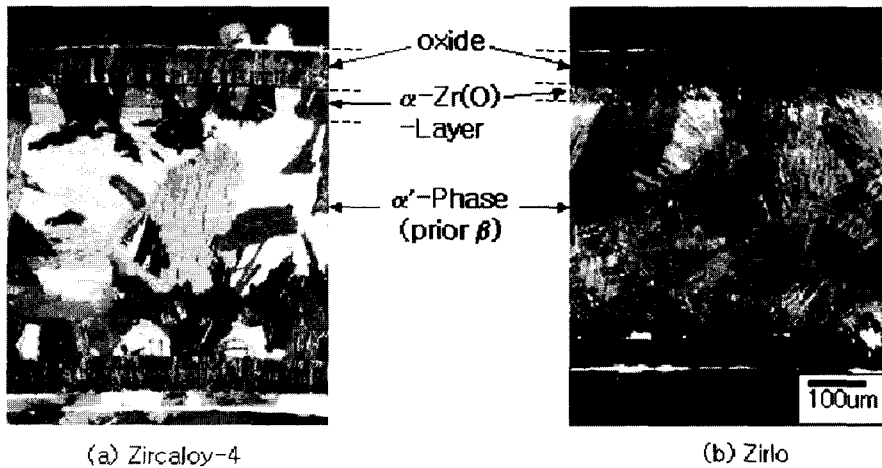


Fig. 4. Cross-sectional view of Zry-4 (a) and Zr-1%Nb alloy (b) specimens.

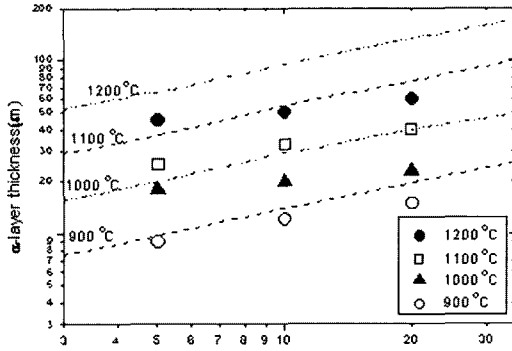


Fig. 5. α -layer growth with time. Symbols : Zr-1%Nb alloy, dash lines : Zry-4.

β -layers in Zr-1%Nb alloy. We set the thickness of α -layer in Zr-1%Nb alloy as the length between the boundaries of oxide and fine microcracks. Fig.5 is the comparison graph of the thickness of α -layers in Zry-4 and Zr-1%Nb alloy with oxidation time. As shown in Fig. 4, the α -layer growth rate of Zr-1%Nb alloy specimens (symbols) is lower than that of Zry-4 (dashed lines). And, the kinetics is also different. In Zry-4, α -layer growth follows the time dependency of the power of ~ 0.5 ($t^{0.5}$). However, the slope of the time dependence is quite different in Zr-1%Nb

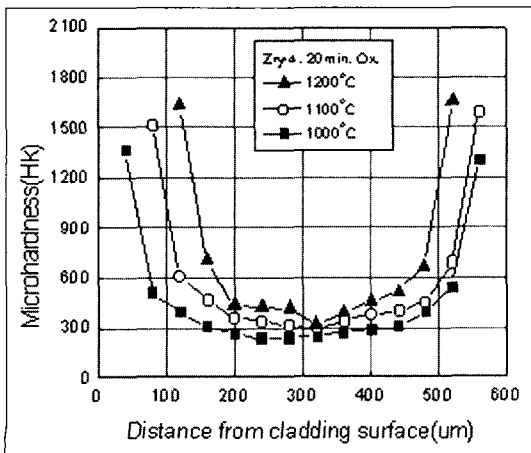


Fig. 6. Hardness of Zry-4 after 20 minute oxidation

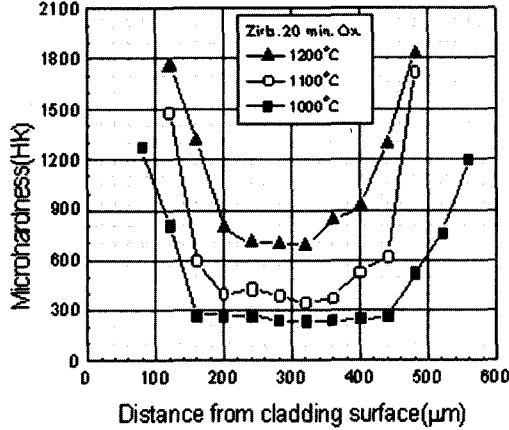


Fig. 7. Hardness of Zr-1% Nb alloy after 20 minute oxidation.

alloy, usually with the power of $0.2 \sim 0.35$ ($t^{0.2 \sim 0.35}$).

The radial hardness profile of the specimens was also measured. Fig. 6 and 7 show the results of hardness measurements (micro Vickers) of Zry-4 and Zr-1%Nb alloy specimens, respectively. The oxide hardness was not included in the Figures. The hardness decreases sharply in α -layers, then the value decreases slowly or stays constant in prior β -region. The hardness is known to depend on the oxygen content in metal, and α -layer has higher hardness number than β -layer. The oxidation temperature dependency of hardness in prior β -layers in Zr-1%Nb alloy is quite different from that of Zry-4. Hardness values increase with the oxidation temperature, probably due to the higher oxygen content in the matrix during oxidation at higher temperatures. Hardness of metal matrix (β -layer) increases more strongly with oxidation temperature in Zr-1%Nb alloy than in Zry-4.

The increase of hardness in metal matrix is important from the viewpoint of severe accidents, since the hardness decrease means the reduction of ductility in Zr-1%Nb alloy. Bonmert, et al.,

checked the safety margin of Zr-1%Nb alloy at severe accident conditions⁹. NRC requires the calculated equivalent cladding reacted (ECR) must not exceed 17% of the cladding wall thickness during accidents. Ring compression test indicates the ductility at 5% of ECR in Zr-1w/oNb alloy is already lower than that of 18% ECR in Zry-4 cladding⁵.

The reason for the hardness increase seems from the increase of oxygen content in metal matrix. The higher hardness of Zr-1%Nb alloy (β -region) means that Zr-1%Nb alloy has higher oxygen content in metal matrix than Zry-4 does. Hence, it is highly probable that Zr-1%Nb alloy has the higher equilibrium oxygen concentration in β -phase at the phase boundary than Zry-4. Nb, a bcc structural element, tends to stabilize β -phase that is bcc. So, it is reasonable to think that β -phase contains more oxygen if Nb is added.

Pawel⁶ and Brown et al.⁷ measured the diffusion coefficient of oxygen in β -phase by fitting the calculation of diffusion equation with metalographic data. The characteristic time of diffusion in the β -layer ($t = l^2/D$, $l = 0.035$ cm) can be approximately calculated. Table 3 indicates the diffusion coefficient and the characteristic time at each temperature for the specimen used. Comparing the oxidation time (20 min.) to the characteristic time, the oxygen concentration in prior β

Table 3. Diffusion coefficient of oxygen in β -phase and characteristic time. Specimen half-length is about 0.035cm.

Temp. (°C)	Diff. coeff. (cm ² /sec) ^{6,7}	Char. time (min.)
1200	$1.5 \sim 1.7 \times 10^{-6}$	12 ~ 14
1100	$7.1 \sim 8.6 \times 10^{-7}$	24 ~ 29
1000	$3.0 \sim 3.8 \times 10^{-7}$	53 ~ 67

-region is nearly saturated at least in the specimen oxidized at 1200°C. Hence, the amount of oxygen concentration difference, that makes the hardness difference in metal layers, should be the difference in the equilibrium oxygen concentration of β -phase between Zr-1%Nb alloy and Zry-4.

The oxygen content increase in the metal layer makes the metal harder and more brittle. The embrittlement due to the higher concentration of oxygen in the metal layer of Zr-1%Nb tubes after oxidation can be an issue in the fuel safety even after the severe accident. Hence, care should be taken for the fuel safety analysis during and after the severe accident, if Nb added Zr base alloys are used in nuclear reactors.

4. CONCLUSION

High temperature steam oxidation behaviors of Zr-1%Nb alloy and Zry-4 were compared. Oxidation tests with destructive analyses were done to get the kinetics, and testing temperatures were 700 - 1200°C. The conclusions of this study are as follows ;

- The kinetics of Zr-1%Nb alloy follows the parabolic rate law, and is expressed by,

$$\Delta W(\text{mg}/\text{dm}^2) = 7,139 \times 10^4 \exp\left(\frac{-10,667.7}{T(\text{K})}\right) \sqrt{t} \text{ (sec)}$$

- Below 900°C, a transition point to linear rate appears. The oxidation rate above 900°C is slightly less than that of Zry-4.
- The hardness of metal layer increases in Zr-1%Nb alloy after high temperature oxidation. This increase seems due to the increased solubility of oxygen in the metal layer. Nb, a sta-

bilizer of bcc structure, is believed to be the reason for the increase.

- The increase in hardness and brittleness in the metal layer of Nb added Zr base alloys after oxidation should be a concern for the fuel safety in the severe accidents.

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