ELSEVIER

Journal of Nuclear Materials 273 (1999) 177–181

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Long-term oxidation characteristics of oxygen-added modified Zircaloy-4 in 360°C water

Hyun Seon Hong *, Seon Jin Kim, Kyung Sub Lee

Division of Materials Science and Metallurgical Engineering, Hanyang University, Seoul 133-791, South Korea

Received 26 November 1998; accepted 20 January 1999

Abstract

The effect of oxygen on the long-term oxidation behavior of modified Zircaloy-4 (Zry-4) was investigated. The modified alloys were prepared by changing the chemical compositions of Zry-4; the tin content decreased from 0.5 wt% to zero while oxygen increased from 0.1 to 0.2 wt%, 0.1 wt% Nb was added and the amounts of Fe and Cr were kept to 0.1 and 0.2 wt%, respectively. The weight gain in water at 360°C for the 270 days exposure increased with increasing oxygen content from 0.1 to 0.2 wt%. In the case of the specimens containing 0.2 wt% oxygen, the tin free specimen showed a rate transition and a much higher weight gain compared to Zry-4. Raman spectroscopy showed that the tetragonal phase in the pre-transition region transformed to the monoclinic phase after the rate transition. Furthermore, this protective structure was changed to the non-protective cauliflower-like structure in the post-transition region. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Recently, a modified Zircaloy-4 (Zry-4) alloy was developed by reducing the tin content from 1.0 wt% to zero and adding 0.1 wt% Nb and oxygen up to 0.8 wt% [1]. Oxygen was originally added to compensate for the decrease in strength resulting from the reduction of the tin content. The oxygen addition showed a marked improvement in the mechanical strength. There still exists a controversy with regard to the effect of oxygen on the oxidation resistance [1–3]. While oxygen as an impurity has been known to be harmful on the oxidation resistance of Zircaloy, Charquet et al. reported that a small amount of oxygen in the 0.25 wt% Fe–0.25 wt% V–Zr alloy did not modify the oxidation resistance [2]. In a previous study [1], it was found that higher amounts of oxygen resulted in a higher weight gain for the 120 days short-term oxidation test of the modified Zry-4, but little was known about the effect of oxygen on the long-term oxidation. In order to clarify the oxygen addition effect, therefore, it is necessary to investigate the long-term oxidation characteristics of the modified Zry-4.

In the present study, a long-term oxidation test was conducted up to 270 days in order to investigate the effect of oxygen on oxidation. The effect of oxygen on the weight gain and the rate transition was studied. The variation of the oxide structure in the modified alloys with time of exposure was also investigated.

2. Experimental procedures

2.1. Specimens

The modified Zry-4 specimens for the oxidation test were prepared by changing the chemical composition of Zry-4. Specifically the tin content was varied from 0.5 wt% down to zero and oxygen was added from 0.1 wt% up to 0.2 wt%. In addition, 0.1 wt% Nb was added and the Fe/Cr ratio of Zry-4 was reduced to 1/2 with the amounts of Fe and Cr fixed at 0.1 and 0.2 wt%, respectively. The chemical composition of the modified Zry-4 alloys is presented in Table 1.

---

* Corresponding author.

0022-3115/99/$ – see front matter © 1999 Elsevier Science B.V. All rights reserved.
PII: S 0 0 2 2 - 3 1 1 5 (9 9) 0 0 0 3 0 - 6

Table 1
Chemical composition of the modified Zry-4 alloys (in wt%)

Specimen number	Alloying elements					
	Sn	Fe	Cr	Nb	O	Zr
1	0.5	0.1	0.2	0.1	0.1	Bal.
2	0.5	0.1	0.2	0.1	0.2	Bal.
3	0.0	0.1	0.2	0.1	0.1	Bal.
4	0.0	0.1	0.2	0.1	0.2	Bal.
5(Zry-4)	1.2–1.7	0.18–0.24	0.07–0.13	0.01	0.09–0.16	Bal.

2.2. Oxidation test

The specimens for the oxidation tests were prepared by the procedures described in a previous study [1]. The oxidation tests were conducted in autoclaves filled with pure water at 360°C under a pressure of 180 bar. Oxidation test specimens with the dimensions of 10 × 25 × 1 mm^3 were prepared from the recrystallized sheet specimens which were mechanically and chemically polished before testing. The test followed the ASTM G-2 method [4]. The oxidation behavior was evaluated by the weight gain (ΔW) as a function of exposure time.

2.3. Microstructural analysis

In order to identify the crystal structure of the growing oxide surface, Raman spectroscopy was used. The methods of characterization of the structure of ZrO_2 by a Raman spectrometer have been reported elsewhere [5–7]. A Raman spectrometer with a 200 mW argon–ion laser source at a wavelength of 488 nm was used. The spectral range employed was from 100 to 500 cm^{-1}.

SEM investigation of the oxide structure at the metal–oxide interface was performed on specimens where the metal phase had been removed. For this experiment, one side of the specimen was ground and polished to reduce the thickness. The remaining metal was dissolved in a mixed solution of 10% HF, 45% HNO_3 and 45% H_2O.

3. Results and discussion

3.1. Oxidation behavior

The weight gain versus oxidation time curves for the five specimens including Zry-4 up to 270 days exposure are represented in Fig. 1. It is seen that the weight gain increases with exposure time during the oxidation. As shown in Fig. 1 the weight gain difference between the specimens up to 150 days exposure is not large enough to be clearly distinguished, and thus the effect of oxygen content on the weight gain is controversial in this exposure range. However, in the long-term oxidation of 270 days, it is clearly seen that the weight gain increased with increasing oxygen content as well as exposure time.

The oxidation of the specimens containing 0.5 wt% tin followed the cubic rate law up to 270 days and a

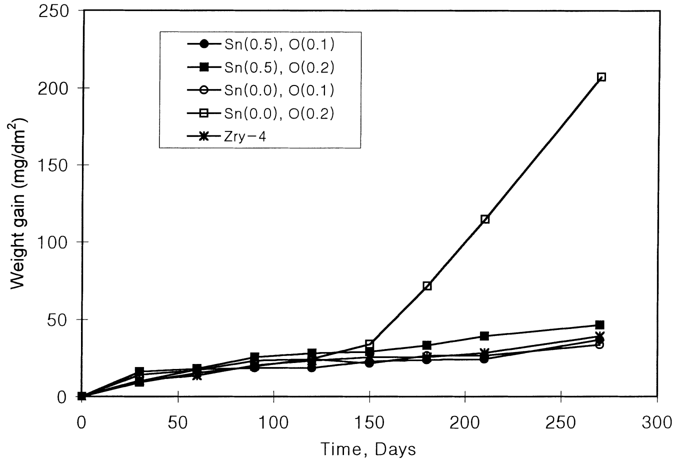

Fig. 1. Weight gain of the modified Zr alloys as a function of exposure time at 360°C.

rate transition did not occur. Weight gain of the 0.5 wt% tin specimens increased from 36.87 to 46.43 mg/dm^2 as the oxygen content increased from 0.1 to 0.2 wt%. The effect of the oxygen content on the weight gain increase can be related to the oxygen dissolution rate as discussed in the previous study [1]. During oxidation of zirconium alloys, oxygen ions diffuse from the water/ZrO_2 interface to the metal matrix following an oxygen concentration gradient built-up in the oxide layer. The diffused oxygen ions at the oxide/Zr interface move into the Zr matrix down the oxygen concentration gradient in the Zr matrix depending on the oxygen concentration of the specimen. The decrease of the oxygen concentration gradient with the addition of oxygen retards the dissolution rate of oxygen into the Zr matrix. The lower dissolution rate accelerates the formation of ZrO_2 and results in the higher weight gain. Therefore, it could be suggested that the amount of 0.2 wt% oxygen in the present specimens increased the weight gain due to the lower oxygen concentration gradient between the oxide/Zr interface and the Zr matrix.

In the case of the tin free specimen, the weight gain increased from 33.73 to 207.27 mg/dm^2 after 270 days as the oxygen content increased from 0.1 to 0.2 wt%. The 0.0 wt% Sn-0.2 wt% O specimen showed a rate transition from the cubic oxidation rate to the linear oxidation rate after the 150 days exposure as shown in Fig. 1. The other specimens did not show a rate transition up to 270 days. It was reported in a previous study [1] that the oxide layer in the pre-transition region was black and uniform. In the present long-term study, it was observed that the initial black oxide was changed to a porous white or gray oxide at the rate transition point of 150 days.

It is well known that the oxidation resistance of Zry-4 is improved as the tin content decreases. In the present study, both the 0.5 wt% and zero tin specimens containing 0.1 wt% oxygen showed a better oxidation resistance compared to Zry-4 containing 1.5 wt% tin. However, in the case of the specimens containing 0.2 wt% oxygen, the tin free specimen showed a rate transition at 150 days exposure and a much higher weight gain compared to Zry-4. This 0.0 wt% Sn–0.2 wt% O specimen showed a better oxidation resistance than Zry-4 in the previous 120 days test, but the specimen showed a reduced oxidation resistance than Zry-4 in the present 270 days test.

Consequently, it was found in the present study that the weight gain of the modified Zry-4 generally increases with increasing oxygen content from 0.1 to 0.2 wt%, and decreases with decreasing tin content from 1.5 to 0.5 wt% and zero in the modified 0.1 wt% oxygen containing Zry-4. However, the reduction of the tin content down to zero degrades the oxidation resistance of the modified 0.2 wt% oxygen containing Zry-4.

3.2. The characteristics of oxide

The oxide of the modified Zry-4 in the pre-transition region was reported to be a mixture of the tetragonal and monoclinic phases in the previous study [1]. The amount of the tetragonal phase in the oxide was quantitatively evaluated using the laser Raman spectroscopy analysis and the amount of the tetragonal phase was found to be in the range of 38.5–35% in the pre-transition region. It was speculated that the oxide layer is under high compressive stress and such stress might stabilize the oxide in its tetragonal form, which is normally stable only at temperatures above 1100°C [8]. Furthermore, the compressive stress was relaxed during the outward growth of the oxide, and the tetragonal phase became destabilized and transformed to the monoclinic phase.

The laser Raman spectroscopy results of the oxide structure in the 0.0 wt% Sn–0.2 wt% O specimen for the 120 and 180 days exposures in the present study are shown in Fig. 2. Fig. 2(a) illustrates that the oxide structure in the specimen at 120 days is a mixture of both the tetragonal and monoclinic phases. However, the oxide at 180 days is composed of only the monoclinic phase as shown in Fig. 2(b). It was thought that the tetragonal phase in the pre-transition region was transformed to the monoclinic phase at the rate transition.

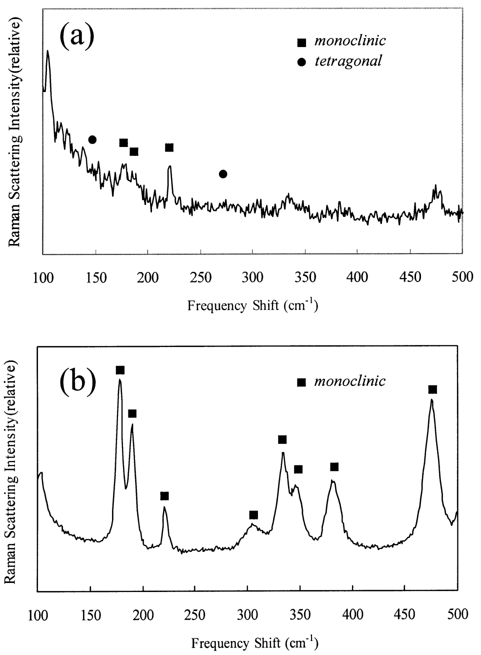

Fig. 2. Raman spectroscopy analyses of the oxide structure in the 0.0 wt% Sn–2 wt% O specimen: (a) 120 days exposure (pre-transition region), (b) 180 days exposure (post-transition region).

This tetragonal-to-monoclinic transformation is known to be governed by a martensitic transformation [9,10]. Thus, it is believed that the whole amount of the tetragonal phase was abruptly and completely transformed to the monoclinic phase at the critical point of the rate transition during oxidation at 360°C.

According to Godlewski [11,12] the oxide of zirconium alloys which was formed during oxidation at 400°C was made up of about 40% tetragonal phase and 60% monoclinic phase in the pre-transition region. After the transition, the oxide layer had a low concentration of the tetragonal phase of about 5–7%. This amount might be stabilized by oxidation of the precipitates. The oxidation of the precipitates is accompanied by a volume change that leads to the formation of a stress field around the precipitates and can stabilize the tetragonal phase. Contrary to this result, it was found in the present study that the oxide of the post-transition region was composed of only the monoclinic phase as shown in Fig. 2(b).

The influence of the tin content on the monoclinic/tetragonal ratio of ZrO_2 in the present study was studied by Raman spectroscopy. The tin content less than 0.5 wt% did not affect the monoclinic/tetragonal ratio in the present study. According to Harada [13] the oxide structure in 0.12Fe–0.1Cr–0.055Ni–Zr alloys (wt%) was changed with the tin content. In the specimen with tin less than 0.1 wt%, oxide surface consisted of monoclinic and tetragonal ZrO_2. In the specimen containing 2.20 wt% tin, only monoclinic ZrO_2 was observed at the oxide surface. So, he suggested that tin stabilizes the monoclinic phase. In the present specimens, however, the tin content had no influence on changing the oxide structure.

The difference in oxide topographies formed in the oxidation of the 0.0 wt% Sn–0.2 wt% O specimen for 120 days and 180 days is shown in Fig. 3. Fig. 3(a) illustrates that the oxide in the pre-transition region is characterized by a granular structure of small crystallites and appears to be dense. This structure changes to a cauliflower-like structure for the 180 days exposure, corresponding to the post-transition region, as shown in Fig. 3(b). The cauliflower-like granules are typical structures found in the oxide of the post-transition region [14,15]. They are porous and non-protective, and the weight gain in the post-transition region as shown in Fig. 1 increases linearly with oxidation time. The tetragonal-to-monoclinic transformation is reported to be associated with a large volume change (3–5%). This is sufficient to exceed elastic and fracture limits and can only be accommodated by cracking [16]. The volume expansion occurring in the tetragonal-to-monoclinic transformation causes microcracks to form around the crystallites clusters. Cracks are propagated around the clusters of some crystallites. The clusters are finally separated, and the oxide becomes porous as shown in Fig. 3(b). Therefore, it is considered that the cauliflower-like structure is formed by the cracks caused by volume expansion of the tetragonal-to-monoclinic transformation.

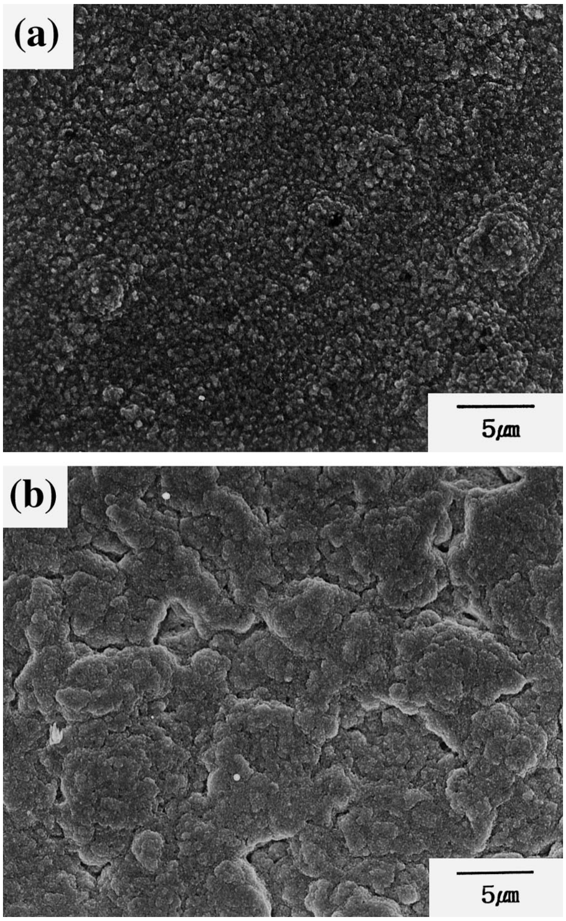

Fig. 3. SEM photographs of oxide formed during oxidation of the 0.0 wt% Sn–0.2 wt% O specimen: (a) 120 days exposure (pre-transition region), (b) 180 days exposure (post-transition region).

It is well known that zirconium and its alloys have a rather high value (1.56) of the Pilling–Bedworth ratio. Consequently, during the oxidation of zirconium alloys, the volume changes lead to the development of a compressive stress in the oxide and of a tensile stress in the metal of zirconium. The high compressive stress might stabilize the tetragonal phase in the oxide. When the compressive stress is released for some reasons, the tetragonal phase is destabilized and transforms to the monoclinic phase. Interstitial oxygen ions can increase the lattice parameter of α-zirconium [17]. It is probable that the increased lattice parameter causes a decrease of the Pilling–Bedworth ratio, and consequently a reduction of the compressive stress in the oxide and a destabilization of the tetragonal phase. Therefore, in the present study, the tetragonal-to-monoclinic phase transformation is probably caused by a stress reduction in the oxide.

It is reported that Ca and Mg exist as impurities in Zry-4 [18]. The concentrations of Ca and Mg are less than 30 and 20 ppm by weight, respectively. These elements in forms of CaO and MgO are well known to stabilize the tetragonal structure of zirconia when their contents are higher than 3 mol% [16]. Interstitial oxygen ions might interact with Ca and Mg ions to form CaO and MgO oxides, and so they might stabilize the tetragonal structure. However, in the present study, the amounts of Ca and Mg were analyzed to be 2 and 3 ppm, respectively. It is speculated that the contents of these elements are too small to affect the oxide structure. Consequently, it is considered that the addition of oxygen can affect the rate transition by stress relaxation in the oxide rather than by the formation of CaO and MgO.

4. Conclusions

1. The weight gain for the 270 days exposure increased with increasing oxygen content from 0.1 to 0.2 wt%. The weight gain decreased with decreasing tin content from 1.5 to 0.5 wt% and zero in the modified Zry-4 containing 0.1 wt% oxygen. However, the reduction of the tin content down to zero degraded the oxidation resistance of the modified Zry-4 containing 0.2 wt% oxygen.
2. The oxide structure after 120 days was a mixture of both the tetragonal and monoclinic phases, however, the oxide after 180 days was composed only of the monoclinic phase. It is thought that the tetragonal phase in the pre-transition region completely transformed to the monoclinic phase at the rate transition.
3. The oxide in the post-transition region has cauliflower-like structure. It is considered that this structure was formed by cracks caused by the volume expansion of the tetragonal to monoclinic transformation.
4. Interstitial oxygen ions in the zirconium matrix at the oxide/zirconium interface were believed to reduce the compressive stress in the oxide. The reduced compressive stress caused the tetragonal monoclinic phase transformation.

References

[1] H.S. Hong, S.J. Kim, K.S. Lee, J. Nucl. Mater. 238 (1996) 211.
[2] D. Charquet, J.P. Gros, J.F. Wadier, in: Proceedings of the International Topical Meeting on LWR Fuel Performance, Avignon, France, 21–24 April, 1991, Van Muysewinkel, Brussels, 1991.
[3] B. Lustman, F. Ferez, Metallurgy of Zirconium, McGraw-Hill, New York, 1955.
[4] ASTM G-2, Standard Test Method for Corrosion Testing of Products of Zirconium, Hafnium, and Their Alloys in Water at 680°F or in Steam at 750°F, 1993, p. 47.
[5] D.R. Clar, F. Adar, J. Am. Ceram. Soc. 65 (1982) 284.
[6] R.C. Gavie, P.S. Nicholson, J. Am. Ceram. Soc. 55 (1972) 303.
[7] V.G. Keramidas, W.B. White, J. Am. Ceram. Soc. 57 (1974) 22.
[8] P. Aldebert, J. Traverse, J. Am. Ceram. Soc. 68 (1985) 34.
[9] B. Cox, Atomic Energy of Canada, Report AECL-9382, 1987.
[10] G.K. Basal, A.H. Heuer, Acta Metall. 22 (1974) 409.
[11] J. Godlewsky, J.P. Gros, M. Lambertin, J.F. Wadier, H. Weidinger, in: Proceedings of the Ninth International Symposium on Zirconium in the Nuclear Industry, ASTM-STP, vol. 1132, 1991, p. 316.
[12] J. Godlewsky, in: Proceedings of the Tenth International Symposium on Zirconium in the Nuclear Industry, ASTM STP, vol. 1145, 1994, p. 663.
[13] M. Harada, M. Kimpara, K. Abe, in: Proceedings of the Ninth International Symposium on Zirconium in the Nuclear Industry, ASTM-STP, vol. 1132, 1991, p. 368.
[14] Y. Ding, D. Northwood, Corros. Sci. 36 (1994) 259.
[15] G. Wikmark, P. Rudling, B. Lehtinen, B. Hutchinson, A. Oscarsson, E. Ahlberg, in: Proceedings of the 11th International Symposium on Zirconium in the Nuclear Industry, ASTM-STP, vol. 1295, 1996, p. 55.
[16] R. Stevens, Zirconia and Zirconia Ceramics, Magnesium Elektron Publication, Twickenham, 1986.
[17] R.M. Treco, Trans. Am. Inst. Min. Eng. 197 (1953) 344.
[18] J.H. Schemel, Zirconium Alloy Fuel Clad Tubing, Sandvik Special Metals Corporation, Washington, DC, 1989.