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Comparison of the air oxidation behaviors of Zircaloy-4 implanted with yttrium and cerium ions at 500 °C

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Abstract

As a valuable process for surface modification of materials, ion implantation is eminent to improve mechanical properties, electrochemical corrosion resistance and oxidation behaviors of varieties of materials. To investigate and compare the oxidation behaviors of Zircaloy-4, implantation of yttrium ion and cerium ion were respectively employed by using an MEVVA source at the energy of 40 keV with a dose ranging from 1×10^{16} to 1×10^{17} ions/cm^2. Subsequently, weight gain curves of the different specimens including as-received Zircaloy-4 and Zircaloy-4 specimens implanted with the different ions were measured after oxidation in air at 500 °C for 100 min. It was obviously found that a significant improvement was achieved in the oxidation behaviors of implanted Zircaloy-4 compared with that of the as-received Zircaloy-4, and the oxidation behavior of cerium-implanted Zircaloy-4 was somewhat better than that of yttrium-implanted specimen. To obtain the valence and the composition of the oxides in the scale, X-ray photoemission spectroscopy was used in the present study. Glancing angle X-ray diffraction, employed to analyze the phase transformation in the oxide films, showed that the addition of yttrium transformed the phase from monoclinic zirconia to tetragonal zirconia, yet the addition of cerium transformed the phase from monoclinic zirconia to hexagonal zirconia. In the end, the mechanism of the improvement of the oxidation behavior was discussed.

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1. Introduction

Zirconium alloys are noted for their low thermal neutron capture cross-section, good corrosion resistance, and adequate mechanical properties, which lead to an extensive engineering use in the nuclear industry. However, with the concept of high burn-up developing, the request for the properties of zirconium alloys becomes higher and higher. It is well known that certain modification methods such as ion beam surface processing (IBP) [1,2] can significantly improve corrosion behavior. Ion implantation, a kind of IBP, offers the possibility to introduce a controlled concentration of an element to a thin surface layer. For the purpose of studying and improving the corrosion resistance of zirconium alloys, there has been a growing interest in the application of ion implantation in recent years. He et al. [3] investigated the effect of Ar ion implantation on the aqueous corrosion resistance of Zircaloy-4, and Tang et al. [4] proved that nitrogen-implanted Zircaloy-4 could significantly decrease the passive current density.

Some researches have reported that the corrosion of zirconium alloys in pressurized water reactors (PWR) proceeds mainly through the oxidation process [5,6], and that the oxidation resistance of metals can be improved by implanting some reactive elements, such as yttrium,

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cerium and other rare earths [7–10]. In order to investigate and compare the oxidation behaviors of Zircaloy-4, yttrium and cerium were, respectively, implanted at a dose range from 1 × 10^{16} to 1 × 10^{17} ions/cm^2 to change high temperature oxidation behaviors of Zircaloy-4. Part of the work has been demonstrated in some publications [11]. What we mainly reported in the paper were the effects of yttrium and cerium implantation on the air oxidation behavior of Zircaloy-4 at 500 °C, and the mechanisms of the improvement of the oxidation behavior for these two different Zircaloy-4 samples, respectively, implanted with yttrium and cerium ions.

2. Experimental procedures

Zircaloy-4 samples were machined to 10 mm × 10 mm × 1.5 mm from a sheet of fully annealed Zircaloy-4. The composition of Zircaloy-4 is Sn: 1.4 wt%, Fe: 0.23 wt%, Cr: 0.1 wt%, Ni: 60 × 10^{-6} wt%, balanced with zirconium. Then, the samples were mechanically polished with 200–800 grade emery paper, degreased in acetone and ethanol, chemically polished in the solution of 10 vol.% HF, 30 vol.% HNO_3, 60 vol.% H_2O, rinsed in natural water more than three times and finally rinsed in deionized water.

The samples were loaded onto a steel-made sample holder in the target chamber of the MEVVA implanter at a vacuum level of 1.8 × 10^{-3} Pa. The implanted area is of 12 cm diameter. Because the implantation system has no analysis magnet, the extracted yttrium ions were measured to consist of 5% Y^+, 60% Y^{2+}, and 33% Y^{3+}, yet the extracted cerium ions consist of 3% Ce^+, 83% Ce^{2+}, and 14% Ce^{3+}. For the two kinds of ions, the doses of the implantation ions were both ranged from 1 × 10^{16}, 5 × 10^{16} to 1 × 10^{17} ions/cm^2 at the extracted voltage of 40 kV and the beam current density of 10 μA/cm^2. During implantation, no special cooling was taken for the samples and the maximum temperature of the samples was 125 °C or so.

The oxidation was carried out in air at 500 °C for 100 min to study the high temperature oxidation behaviors of the Zircaloy-4 samples, and the weight gain curve was measured on the basis of the former work. To analyze the composition and the valence of the surface layer of the samples, X-ray photoemission spectroscopy (XPS) was employed in the study. In addition, glancing angle X-ray diffraction (GAXRD) was used to exam the phase transformations due to yttrium and cerium ions implantation in the oxide films.

3. Results

The effects of yttrium and cerium ions implantation on the oxidation behavior of Zircaloy-4 were studied and compared in air at 500 °C for 100 min. To investigate the repeatability of the oxidation tests, the as-received Zircaloy-4 specimens were oxidized in the same condition for two times to show their difference. On the basis of the data obtained from the oxidation tests, weight gain curves of the specimens implanted with different doses were measured. Figs. 1 and 2 represented the oxidation weight gain curves for different Zircaloy-4 specimens. As shown in Fig. 1, curve 1 represented the oxidation weight gain of the as-received sample. Meanwhile, curves 2, 3 and 4 represented the oxidation weight gain of yttrium-implanted Zircaloy-4 at a dose of 1 × 10^{16}, 5 × 10^{16} and 1 × 10^{17} ions/cm^2, respectively. Fig. 2 demonstrated the oxidation curve of

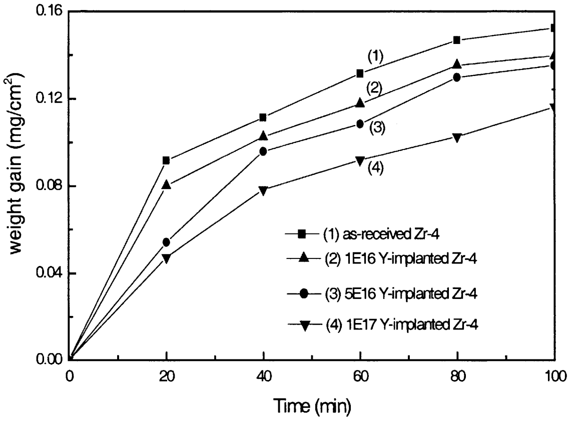

Fig. 1. The oxidation weight gain curves for (1) as-received Zircaloy-4, and for Zircaloy-4 specimens implanted with yttrium ions at a dose of (2) 1 × 10^{16} ions/cm^2, (3) 5 × 10^{16} ions/cm^2, and (4) 1 × 10^{17} ions/cm^2 at 500 °C in air.

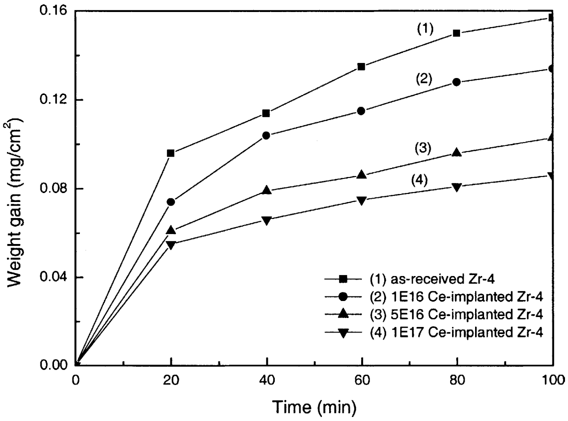

Fig. 2. The oxidation weight gain curves for (1) as-received Zircaloy-4, and for Zircaloy-4 specimens implanted with cerium ions at a dose of (2) 1 × 10^{16} ions/cm^2, (3) 5 × 10^{16} ions/cm^2, and (4) 1 × 10^{17} ions/cm^2 at 500 °C in air.

Table 1
The $3d_{5/2}$ binding energies of Y and Zr in the scale

Elements	$Y3d_{5/2}$			$Zr3d_{5/2}$			
	1×10^{16}	5×10^{16}	1×10^{17}	As-received	1×10^{16}	5×10^{16}	1×10^{17}
Experimental data (eV)	161.1	161.3	161.4	186.8	187.0	187.1	187.2
Adjusted data (eV)	156.2	156.4	156.5	181.9	182.1	182.2	182.3

cerium-implanted Zircaloy-4 with a dose range from 0 to 1×10^{17} ions/cm^2 at 500 °C in air. Similarly, curve 1 represented the oxidation weight gain of the as-received sample, yet curves 2, 3 and 4, respectively, represented the oxidation weight gain of cerium-implanted Zircaloy-4 at a dose of 1×10^{16}, 5×10^{16} and 1×10^{17} ions/cm^2. Figs. 1 and 2 showed that the oxidation weight curves of as-received Zircaloy-4 specimens for two repetitive oxidation tests were very alike. Tiny difference between the two curves arose from experiment errors and could be ignored. As result, it could be deduced that comparison of the results between the oxidation tests would be helpful to show the difference of oxidation behaviors between Zircaloy-4 samples subjected to Y implantation and Ce implantation. It could be seen in Figs. 1 and 2 that the oxidation weight gain rates of the implanted specimens were smaller than that of as-received one. Furthermore, the oxidation weight gain rate decreases with the increase of the dose of the implanted ions. The tendency was same to Figs. 1 and 2. In addition, these two figures also indicated that the oxidation weight gain of yttrium-implanted Zircaloy-4 was somewhat less than that of cerium-implanted one at the same implantation dose.

XPS was employed to analyze the composition and the valence of the surface layer of the Zircaloy-4 samples. In our experiments, because of limitation of test conditions and other factors, system errors are unavoidable. XPS tests showed that the surface energy of the absorbed C on the surface of the specimen is different from the standard binding energy, 284.8 eV. This energy margin is due to the system error, and needs to be adjusted so that the system errors could be reduced or even eliminated. By comparing the surface energy of the absorbed C on the surface of the specimen with that of the standard binding energy, adjusted binding energies of the XPS spectra for different samples implanted with yttrium and cerium ions were, respectively, calculated and listed in Tables 1 and 2. The adjusted XPS spectra of $Y3d_{5/2}$ and $Zr3d_{5/2}$ were shown in Figs. 3(a) and (b), and the adjusted XPS spectra of $Ce3d_{5/2}$ and $Zr3d_{5/2}$ were shown in Figs. 4(a) and (b). For as-received sample, because ion implantation was not carried out and not any new ions were subjected to the sample, no background data for $Y3d_{5/2}$ and $Ce3d_{5/2}$ could be attained. In each figure of Figs. 3(a) and (b) and 4(a) and (b), comparing the XPS spectra obtained for the different implantation doses, it was clear that there was no significant change in shape and peak position, but a slight shift due to the experiment error. From the XPS spectra in Figs. 3(a) and (b), it showed that the binding energies coincided well with the standard values of Y_2O_3 and ZrO_2, that is, 156.4 and 182.1 eV, respectively. So, it could be said that the oxides of Y and Zr in the scale probably existed in the form of Y_2O_3 and ZrO_2. As shown in Fig. 4(a) and (b), however, the binding energies coincided well with the standard values of CeO_2 and ZrO_2, 881.9 and 182.1 eV. As a result, it could lead to a conclusion that the oxides of Ce and Zr in the scale probably existed in the form of CeO_2 and ZrO_2.

GAXRD was employed to investigate the mechanism of the improvement of yttrium and cerium addition on the oxidation behavior of Zircaloy-4. As we know, when the ion implantation tests were performed at the maximum dose of 1×10^{17} ions/cm^2, the depth distribution of implanted ions for the sample was much less than 1 μm, concretely, less than 100 nm [5]. Although the oxide thickness obviously reached a maximum of 1 μm in the oxidation tests, the information of structure transformation due to ions implantation should come from the scale below the depth of 100 nm. In our experiment, the diffraction angle at 0.3° corresponds to a theoretical

Table 2
The $3d_{5/2}$ binding energies of Ce and Zr in the scale

Elements	Ce $3d_{5/2}$			$Zr3d_{5/2}$		
	1×10^{16}	5×10^{16}	1×10^{17}	1×10^{16}	5×10^{16}	1×10^{17}
Experimental data (eV)	887.1	887.2	886.6	187.6	187.3	186.9
Adjusted data (eV)	881.7	882.0	881.8	182.2	182.1	182.1

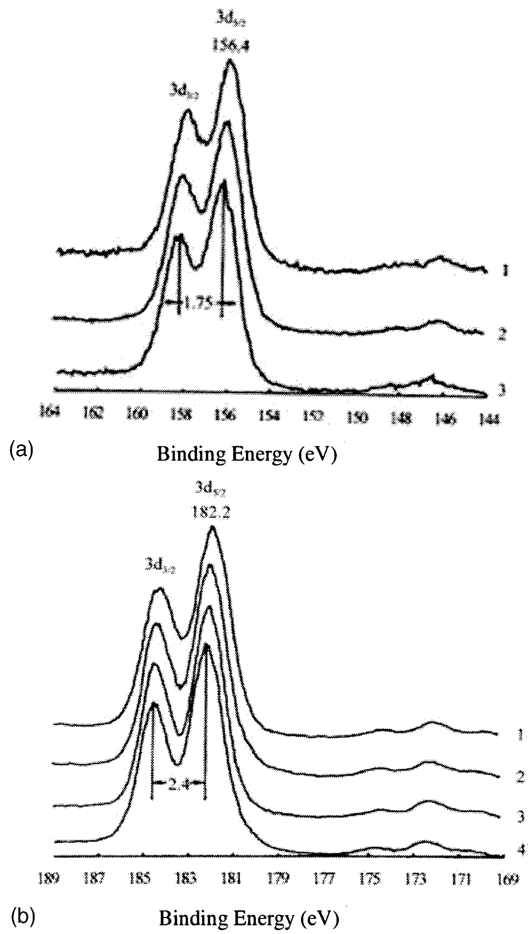

Fig. 3. The XPS spectra of $Y3d_{5/2}$ peak and $Zr3d_{5/2}$ peak in the scale. (a) The XPS spectra of $Yd_{5/2}$ peak: (1) air oxidization after 1×10^{16} ions/cm^2 implantation; (2) air oxidization after 5×10^{16} ions/cm^2 implantation; (3) air oxidization after 1×10^{17} ions/cm^2 implantation. (b) The XPS spectra of $Zr3d_{5/2}$ peak: (1) air oxidization for as-received sample; (2) air oxidization after 1×10^{16} ions/cm^2 implantation; (3) air oxidization after 5×10^{16} ions/cm^2 implantation; (4) air oxidization after 1×10^{17} ions/cm^2 implantation.

penetration depth of about 60 nm in the scale. Therefore, the angle of 0.3° was selected for the incident angle in the GAXRD experiment.

Figs. 5 and 6, respectively, showed the GAXRD spectra of yttrium-implanted Zircaloy-4 and that of cerium-implanted Zircaloy-4 at a 0.3° incident angle. As shown in Fig. 5, the oxide in the scale was almost monoclinic zirconia (m-ZrO_2) for as-received Zircaloy-4. When the samples were implanted by yttrium ions, tetragonal zirconia (t-ZrO_2) appeared in the scale. With the increase of implantation dose, the intensities of the diffraction peaks of t-ZrO_2 increased, yet the intensities

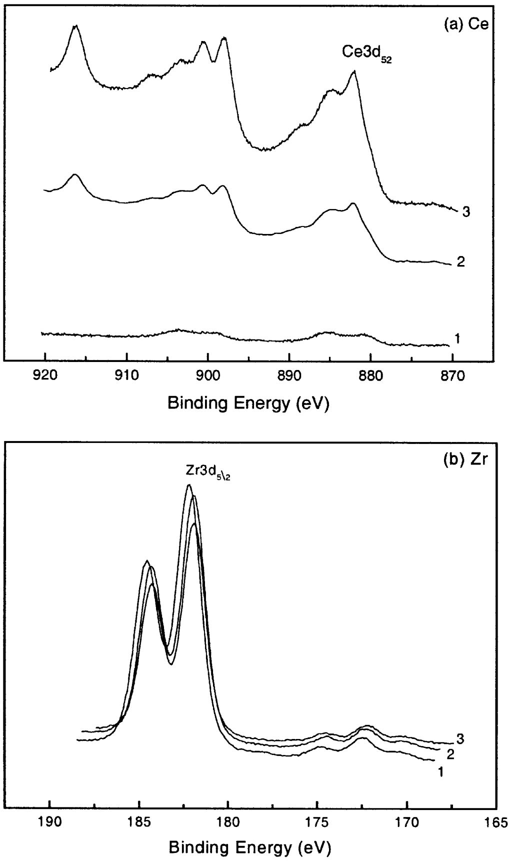

Fig. 4. The XPS spectra of (a) $Ce3d_{5/2}$ peak, and (b) $Zr3d_{5/2}$ peak in the scale: (1) air oxidization after 1×10^{16} ions/cm^2 implantation; (2) air oxidization after 5×10^{16} ions/cm^2 implantation; (3) air oxidization after 1×10^{17} ions/cm^2 implantation.

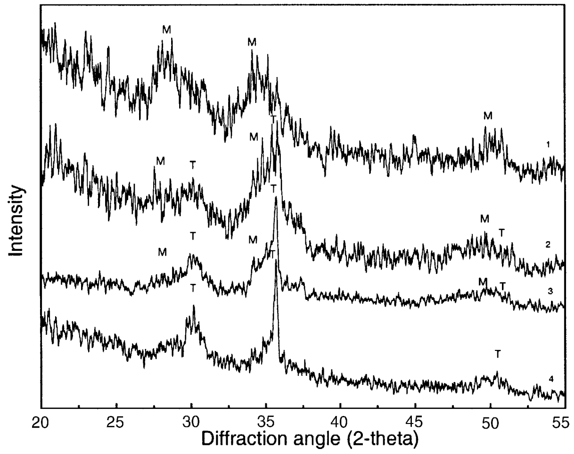

Fig. 5. GAXRD spectra at 0.3° incident angle of Zircaloy-4, which implanted with (1) as-received Zr-4; (2) 1×10^{16} Y/cm^2; (3) 5×10^{16} Y/cm^2; (4) 1×10^{17} Y/cm^2 and then oxidized in air at 500 °C for 100 min. M represents m-ZrO_2, T represents t-ZrO_2.

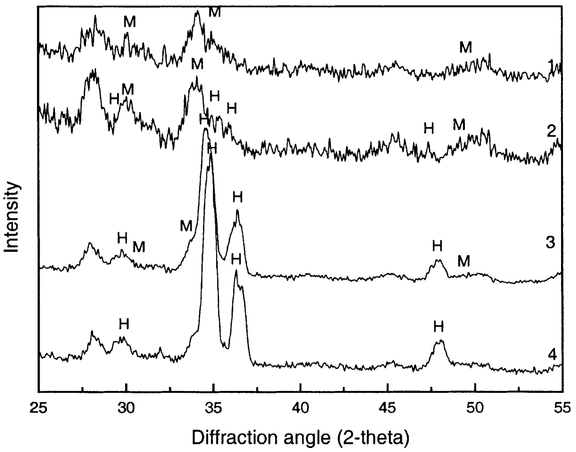

Fig. 6. The GAXRD spectra at 0.3° incident angle of Zircaloy-4 implanted with cerium at (1) 0, (2) 1×10^{16} ions/cm^2, (3) 5×10^{16} ions/cm^2, and (4) 1×10^{17} ions/cm^2, and then oxidized in air at 500 °C for 100 min. M represents monoclinic zirconia, H represents hexagonal zirconia.

of the diffraction peaks of m-ZrO_2 decreased. When the dose increased up to 1×10^{17} ions/cm^2, almost no diffraction peaks of m-ZrO_2 could be found. This result indicated that with the yttrium ion implantation, the phase of the oxide transformed from m-ZrO_2 to t-ZrO_2. Fig. 6 represented that when the samples were implanted by cerium ions, hexagonal zirconia began to exist in two chemical formulas: ZrO_{1-x} and $ZrO_{0.35}$. Similarity to Fig. 5, with the increase of implantation doses of cerium, the intensities of the diffraction peaks of m-ZrO_2 decreased, yet the intensities of the diffraction peaks of hexagonal zirconia increased. When the implantation dose increased up to 1×10^{17} ions/cm^2, almost no diffraction peaks of m-ZrO_2 could be found, that was, almost all the phase of m-ZrO_2 transformed to H-ZrO_2.

4. Discussion

It is well known that when the oxide film grows on the matrix during oxidation of Zircaloy-4, the tetragonal zirconia (t-ZrO_2) first emerges. T-ZrO_2, an unstable phase, transforms into the m-ZrO_2 promptly, and then the stress emerging from lattice misfit, becomes larger and larger in the oxide film. When the stress is accumulated enough to some critical value, the oxide film would crack and the fresh oxygen can easily arrive at the matrix and react with zirconium.

When Zircaloy-4 is implanted by a certain reactive element, some new phenomena will appear during its oxidation. For yttrium ion-implanted Zircaloy-4, the implanted yttrium will react with oxygen and form Y_2O_3. It has been reported that the oxygen vacancies, which produced by the substitution of Y^{3+} for Zr^{4+}, are the reason why yttrium can stabilize ZrO_2 [12,13]. Thus, the transition from tetragonal phase to monoclinic phase would be delayed. As a result, the stress in oxide film would be much smaller than that of as-received samples and the toughness of the oxide film by yttrium ion implantation is improved. So the oxide film would grow compact and the oxygen is difficult to diffuse through the oxide film to react with the matrix. Consequently, the oxidation rate slows down. For cerium-implanted Zircaloy-4, however, the implanted cerium, a very reactive element, should react with oxygen prior to zirconium element, and forms CeO_2. Because of the substitution of Ce^{4+} for Zr^{4+}, the oxygen vacancies subsequently produced thus led to the appearance of the chemical formulas of ZrO_{1-x} and $ZrO_{0.35}$, which existed in the hexagonal phase in the scale. In other words, the implantation of cerium brought about the transition of zirconia from monoclinic phase to hexagonal phase, and made the volume of zirconia decrease rapidly and greatly. As a result, the stress in the oxide film diminished significantly and the toughness of the oxide film by cerium ion implantation was improved. It could be concluded that with the increase of the implantation dose of cerium, the oxide film would grow compacter and compacter, and the oxygen would become more and more difficult to diffuse through the oxide film to react with the matrix. Consequently, the oxidation rate would naturally decrease.

From the above argument, it can be concluded that the enhancement of oxidation behavior with addition of yttrium ion implantation is attributed to the yttrium stabilized-zirconia and the structure transformation, from m-ZrO_2 to t-ZrO_2, is the chiefly reason for the significant reduce of oxidation. On the other hand, for cerium-implanted Zircaloy-4, when the sample was exposed to air at the temperature of 500 °C, cerium, a very active element, would have precedence over zirconium to be oxidized. Because of the substitution of Ce^{4+} for Zr^{4+} in the oxide film, opportunities for the combination of Zr^{4+} and O^{2-} decreased greatly, which brought out the increase of Zr^{4+} in intervening spaces. Relatively, it might be expressed in some sense that cerium addition led to the decrease of O^{2-} and the increase of Zr^{4+} in the zirconium oxide, thus resulted in the appearance of the chemical formulas of ZrO_{1-x} and $ZrO_{0.35}$. The zirconium oxide of these two chemical formulas existed in the hexagonal phase in the scale. That is why the structure of zirconia transformed from monoclinic phase to hexagonal phase, and for the reason of this transformation, the oxidation of Zircaloy-4 could be improved by cerium ion implantation.

Compared with the samples implanted with Y and Ce, it is obvious that the difference of their oxidation behavior consists in two aspects: one is the phase transition as above narration, the other is the chemical formula of the zirconia. For yttrium implantation samples, zirconia exists in ZrO_2. Whereas, for cerium implantation samples, zirconia exists in two chemical formulas: ZrO_{1-x} and $ZrO_{0.35}$. Because of more oxygen vacancies produced in the scale of cerium-implanted Zircaloy-4, the oxidation behavior became more difficulty for the specimens implanted with cerium than for the specimens implanted with yttrium.

5. Conclusions

Implantations with yttrium and cerium ions were employed to investigate the oxidation behavior changes of Zircaloy-4 in air at 500 °C for 100 min. It is indicated that the oxidation weight gain of implanted specimens are pervasively lower than that of as-received Zircaloy-4, and the oxidation weight gain decreases with the increase of implantation dose of yttrium or cerium. Furthermore, the oxidation weight gain of yttrium-implanted Zircaloy-4 was somewhat less than that of cerium-implanted one at the same implantation dose. The mechanism of the oxidation behavior improvement of Zircaloy-4 by yttrium addition was due to the phase transformation from m-ZrO_2 to t-ZrO_2. For cerium-implanted Zircaloy-4, however, the mechanism was due to the phase of zirconia transforming from monoclinic phase to hexagonal phase.

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