Crystallization and degradation of zirconium oxide in various pH solutions

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Abstract

A series of modeling experiments was conducted to understand crystallization and degradation behavior of zirconium oxide occurring during corrosion of zirconium alloys. The crystallization of zirconia from amorphous $Zr(OH)_4$ was investigated through its hydrothermal treatment in various metal hydroxide solutions with different pH at 250°C for 6 h in mini-autoclaves. The degradation behavior of the tetragonal zirconia stabilized by 3 mol% Y_2O_3 was investigated at low temperatures of 90–200°C in water and LiOH solution with 3.5 and 350 ppm Li, respectively. It is demonstrated that pH is a main factor governing the crystallization of zirconia, leading to 35% tetragonal and 65% monoclinic zirconia at pH 7–10 and 100% monoclinic zirconia at pH > 12. Therefore, the change of the corrosion resistance of zirconium alloys with pH at the beginning of corrosion is suggested to be attributed to the crystallization behavior of the zirconia varying with pH. On the other hand, the tetragonal zirconia degraded due to the tetragonal–monoclinic transformation, which was accelerated only in LiOH solution, not in $LiNO_3$ or KOH. On the basis of this finding, the accelerated corrosion of zirconium alloys in LiOH solutions is discussed. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Zirconium alloys showed accelerated corrosion in LiOH solutions when pH_{25} (room temperature pH) was higher than 12 [1] or high temperature pH was higher than 10 [2], and did not show any pre-transition stage of the corrosion rate at pH_{25} > 13.5, directly jumping into the accelerated post-corrosion stage even at the beginning of the corrosion [1]. However, this accelerated corrosion did not occur in the 1 M lithium salt solutions such as $LiNO_3$, Li_2SO_4 and Li_2CO_3 [1]. One puzzling thing is that the higher accelerated corrosion of zirconium alloys always occurs in a LiOH solution only, not in other metal hydroxide solutions such as KOH, NaOH and NH_4OH under the same molar content [1–4]. In the KOH solution of pH 14 only, however, some acceleration of corrosion occurs [1]. This suggests that not only the cations but the concentration of OH ion, that is, pH,

may govern the corrosion of zirconium alloys at the same time. To date, it is not clearly understood why corrosion of zirconium alloys depends on pH and higher accelerated corrosion occurs in LiOH solution.

Garzarolli [5] proposed that the amorphous oxide formed at the oxide/metal interface initially crystallizes to fine equiaxed tetragonal zirconia, which grows and transforms at a certain critical size to monoclinic grains. Further, the oxide film of columnar monoclinic zirconia and fine tetragonal zirconia was also observed in post-transition oxides in water [6]. To the contrary, a recent TEM study showed the presence of equiaxed monoclinic grains only without any tetragonal zirconia even near the oxide/metal interface in the post-transition with accelerated corrosion by LiOH [7]. These facts suggest that the crystallization behavior of zirconia grains may depend on the pH of the solution, leading the oxide film to have different structures with pH.

Once the tetragonal oxide crystallizes on zirconium alloys, it transforms into monoclinic zirconia, thus degrading the intact oxide. It is based on the fact that after the transition, the tetragonal zirconia is transformed into

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monoclinic zirconia [8]. Since this tetragonal to mono-clinic (t–m) transformation rate is a major controlling factor to the corrosion resistance of zirconium alloys, it is necessary to elucidate the cause for the t–m transforma-tion of zirconia. Even though the cause for the t–m transformation is suggested to be related to stress relax-ation [5,8] it is still not understood what triggers the stress relaxation. Garzarolli [5] suggested that the t–m trans-formation of zirconia may be enhanced by the presence of hydrogen. However, it is to be noted that the tetragonal zirconia stabilized by 3 mol% Y_2O_3 is degraded at low temperature, which is enhanced in humid conditions such as water or steam rather than in air [9–11]. These facts seem to indicate that OH ions in aqueous solution rather than hydrogen ions trigger t–m transformation even though their role in the t–m transformation needs a better understanding. Here we assume that a similar degrada-tion phenomenon occurs in the zirconia film on zirconium alloys. Then, the corrosion of zirconium alloys can be understood by correlating the degradation behavior of tetragonal zirconia in various solutions containing alkali metal hydroxides or salts. Furthermore, enhanced cor-rosion of zirconium alloys in LiOH solutions may be at-tributed to the enhanced t–m transformation rate. To prove this hypothesis, it is necessary to investigate whether the t–m transformation is enhanced especially in LiOH solutions compared to in water of pH 7 in tetrag-onal zirconia stabilized by 3 mol% Y_2O_3.

The aim of this study is to understand crystallization and degradation behavior of zirconium oxide formed during corrosion of zirconium alloys with different pH. A series of modeling experiments was carried out to correlate corrosion of zirconium in metal hydroxide solutions such as LiOH, KOH and NaOH with the crystallization and degradation of 3 mol% Y_2O_3 stabi-lized zirconia in various solutions. The first experiment was to investigate the crystallization of zirconia at dif-ferent pH while the second one was to focus on the degradation behavior of the tetragonal zirconia in metal hydroxide solutions containing Li, Na and K ions as well as in pure water of pH 7.

2. Experimental procedures

2.1. Hydrothermal treatment

As a starting material, white and amorphous $Zr(OH)_4$ powder as shown in Fig. 1 was made by pre-cipitating from NH_4OH and zirconyl chloride ($ZrOCl_2·8H_2O$) followed by filtering, drying in vacuum at 60°C and pulverizing. Then, the amorphous $Zr(OH)_4$ powder was subjected to hydrothermal treatment at 250°C under the autogenous steam pressure in mini-autoclaves containing various solutions with LiOH, KOH and NaOH, respectively. All pH data were taken
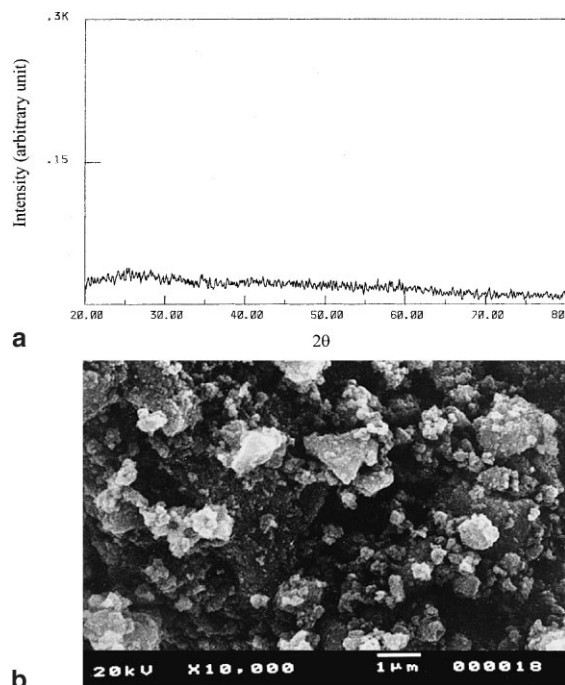

Fig. 1. Amorphous $Zr(OH)_4$ powders: (a) their X-ray diffrac-tion pattern with no diffraction peaks and (b) the particle shape.

from the test solutions at room temperature. X-ray dif-fraction analyses were conducted to identify the struc-ture of the crystallized powder after washing and drying in an oven for more than 12 h. The fraction of tetragonal zirconia was calculated following the modified equation proposed by Garvie [12] and Toraya [13] by comparing the peak intensities of tetragonal (1 1 1) and monoclinic (1 1 1) and (1 1 $\bar{1}$) obtained by scanning through 2θ an-gles of 27–33°:

$$V_m = \frac{1.311 X_m}{(1 + 0.311 X_m)},$$

$$\text{where } X_m = \frac{\left\{ I_m(1\,1\,1) + I_m(1\,1\,\bar{1}) \right\}}{\left\{ I_t(1\,1\,1) + I_m(1\,1\,1) + I_m(1\,1\,\bar{1}) \right\}},$$

V_m is the monoclinic volume fraction, I_m the peak in-tegral intensity of monoclinic zirconia and I_t the peak integral intensity of tetragonal zirconia.

2.2. Degradation of the tetragonal zirconia by t–m transformation

To simulate the enhanced degradation of the oxide film in LiOH solution grown on zirconium alloys, the tetragonal zirconia containing 3 mol% Y_2O_3 of near 100% theoretical density was subjected to annealing at temperatures of 90–200°C in pure water and lithiated solution with Li contents of 3.5 and 350 ppm, respec-

tively. The annealing was conducted in stainless steel mini-autoclaves that were quickly cooled after various annealing time intervals. From the peak intensity of tetragonal (111) and monoclinic (111) and (11$\underline{1}$), the amount of monoclinic and tetragonal crystalline phases was calculated as described above. The as-sintered tetragonal zirconia pellet was confirmed to entirely consist of tetragonal zirconia only. After exposure to either water or lithiated solutions, the FTIR (Fourier transform infrared spectroscopy) was used to identify the existence of OH$^-$ in the transformed layer.

3. Results and discussion

3.1. Crystallization of zirconia in solutions with various metallic ions and pH

Amorphous Zr(OH)$_4$ underwent crystallization through hydrothermal treatment at 250°C for 6 h. Fig. 2 shows the XRD patterns of crystallized zirconia with pH in LiOH solutions. The peak intensity of tetragonal zirconia at around 30° decreased with increasing pH and was not observed at pH > 12. Similar changes were also observed in NaOH or KOH solutions. Fig. 3 shows the quantitative fraction of crystallized monoclinic zirconia after hydrothermal treatment at 250°C for 6 h in different metal hydroxide solutions containing KOH, LiOH and NaOH, respectively. As long as pH was below 11, the crystallized zirconia consisted of 35% tetragonal zirconia and 65% monoclinic zirconia irrespective of the metal hydroxide solution. When pH increased to 12 or more, however, only 100% monoclinic zirconia was crystallized. It is surprising to note that this crystallization behavior of zirconia depends only on pH and not on the metal hydroxide solutions. Furthermore, it is to be noted that pH initiating accelerated corrosion of zirconium alloys in short-term experiments [1,14] coincidentally agrees with pH initiating the crystallization of 100% monoclinic zirconia. When pH ranged from 11 to 12, there was a sharp increase in the content of monoclinic zirconia. It is also noteworthy that the 35% of tetragonal zirconia obtained at pH 7 is in good agreement with the fraction of tetragonal zirconia (30–40%) existing in the first layer of 200 nm just next to the metal/oxide interface [8]. In essence, we can conclude that the crystallization of zirconia is governed by pH and not by the alkali metal of hydroxide solution. The accelerated corrosion in short-term experiments at high pH, therefore, is likely correlated to the formation of monoclinic zirconia only.

3.2. Degradation of 3 mol% Y$_2$O$_3$ stabilized tetragonal zirconia in LiOH solutions

Since enhanced corrosion of zirconium alloys is well known to occur in LiOH solutions with high Li content,
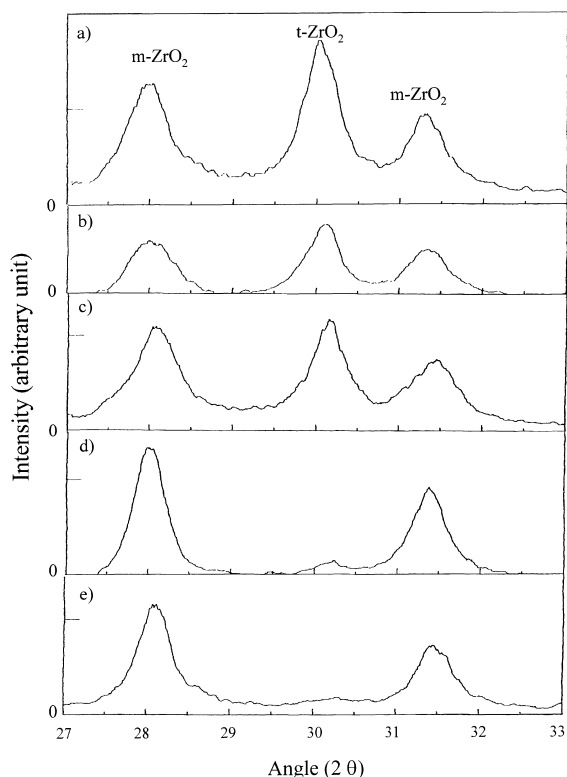

Fig. 2. X-ray diffraction pattern of the crystallized zirconia after hydrothermal treatment at 250°C in LiOH solutions with various pH: (a) pH 7, (b) pH 10.01, (c) pH 11.31, (d) pH 12.2 and (e) pH 12.3.
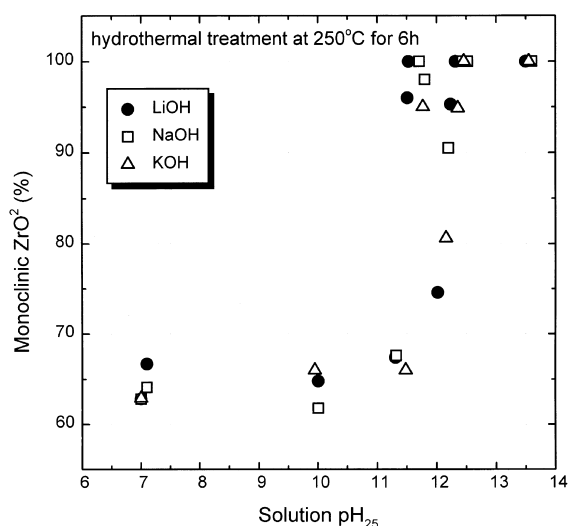

Fig. 3. Fractional monoclinic zirconia with pH after hydrothermal treatment in various metal hydroxide solutions at 250°C for 6 h.

the t–m transformation rate of zirconia is, likewise, expected to be enhanced in LiOH solutions. In order to confirm this, the tetragonal zirconia stabilized by 3 mol% Y_2O_3 was exposed to pure water, LiOH solutions with 3.5 and 350 ppm Li, respectively, at 90–250°C. Fig. 4 shows the extent of the t–m transformation of the tetragonal zirconia at the surface only. The t–m transformation proceeded so slowly at 90°C that only 15% monoclinic zirconia was formed even after 10 h. However, the t–m transformation became greater with increasing temperature so that all the tetragonal zirconia on the surface turned fully to monoclinic zirconia at a temperature as high as 200°C. Especially, the measured fraction of monoclinic zirconia at 150°C showed that the rate of t–m transformation was enhanced in 350 ppm LiOH solution as compared to that in water. At 200°C, due to the full t–m transformation at the surface, the thickness of the transformed layer was determined with X-rays by continuously removing the surface by grinding as shown in Fig. 5. Fig. 6 shows the transformed layer thickness with exposure time when the tetragonal zirconia was annealed in solutions with 350 ppm Li, 3.5 ppm Li and no Li, respectively. The t–m transformation was enhanced in the LiOH solution with 350 ppm Li compared to that in the solutions with either 3.5 ppm Li or no Li. It is worth noting that the t–m transformation advances from the surface into the interior with the flat boundary being kept between the transformed and unaffected layers as shown in Fig. 7. In addition, the transformed layer was found to be very porous with micro- and macro-pores as shown in Fig. 8, which is caused by volume expansion during the t–m transformation.

As expected, the t–m transformation of zirconia, advancing from the surface to the interior, increased with an increase in annealing temperature and time, and furthermore, was enhanced with Li content in the LiOH

Fig. 5. Determination of the transformed layer thickness by X-ray after exposure of 3 mol% Y_2O_3 stabilized zirconia to pure water and LiOH solution with 3.5 and 350 ppm Li, respectively at 200°C for 2 h.

solution. These results indicate that the t–m transformation is associated with a kind of diffusion process. This process would be controlled by lattice diffusion: This is because the fastest diffusion process in 3 mol% Y_2O_3 stabilized tetragonal zirconia is the lattice diffusion even at a temperature as low as 250°C, the coefficient of which has been found to be 2×10^3 times the surface diffusion coefficient [15]. Since OH^- can diffuse faster that O^{-2} due to a lesser charge and similar size [9], diffusion of OH^- in the zirconia lattice seems to be reasonable. If the oxygen vacancy in the zirconia lattice increases due to the substitutional solution by the cation in the solution [1,16,17], OH^- diffusion becomes faster, resulting in the thicker transformed layer. The much thicker transformed layer in LiOH solution with 350 ppm Li, as shown in Figs. 6 and 7, provides evidence of this hypothesis.

Conversely, if the metallic cations in the solution cannot replace the zirconium ions due to the larger ionic radius, then we expect no effect of metallic cations on the
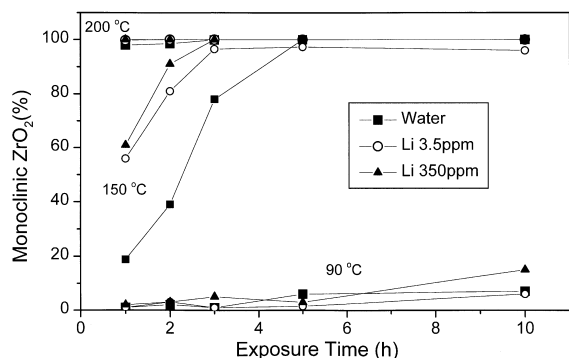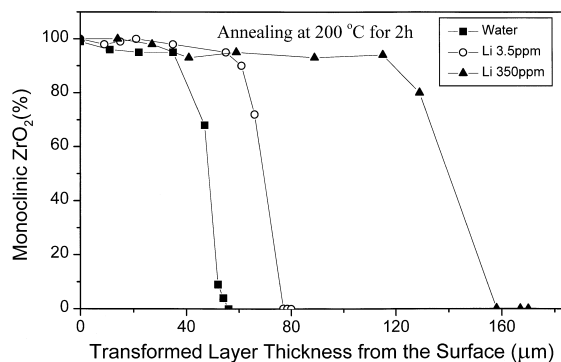

Fig. 4. The fraction of monoclinic zirconia at the surface of the tetragonal zirconia stabilized by 3 mol% Y_2O_3 after its exposure to the respective solution with Li content varying from 0 to 350 ppm at various temperatures of 90–200°C.
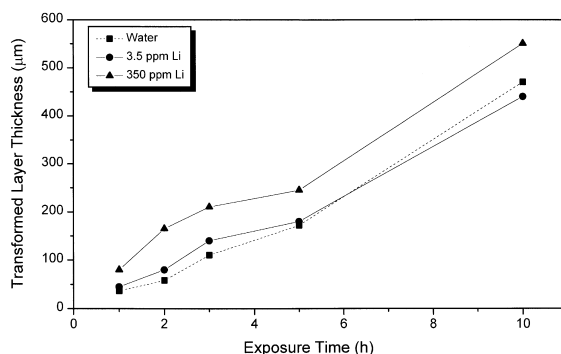

Fig. 6. Evolution of the transformed layer thickness with exposure time when 3 mol% Y_2O_3 stabilized zirconia is exposed to water and LiOH solution with 3.5 and 350 ppm Li, respectively.
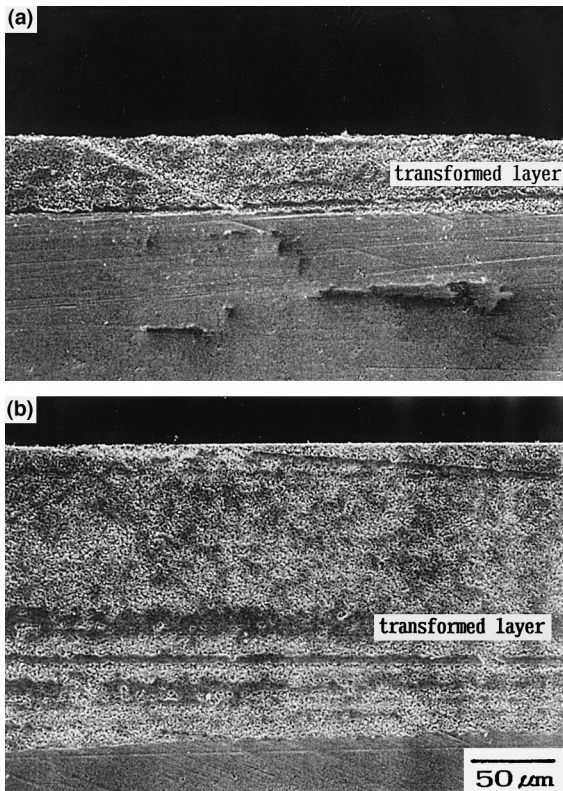
Fig. 7. Microstructures of the transformed layer in 3 mol% Y_2O_3 stabilized zirconia after annealing at 200°C for 2 h in (a) water and (b) LiOH solution with 350 ppm Li.

transformed layer. This hypothesis was confirmed by annealing 3 mol% yttria-stabilized tetragonal zirconia at 200°C for 5 h in various solutions – water, LiOH with 350 ppm Li, KOH with 350 ppm K and LiNO$_3$ with 350
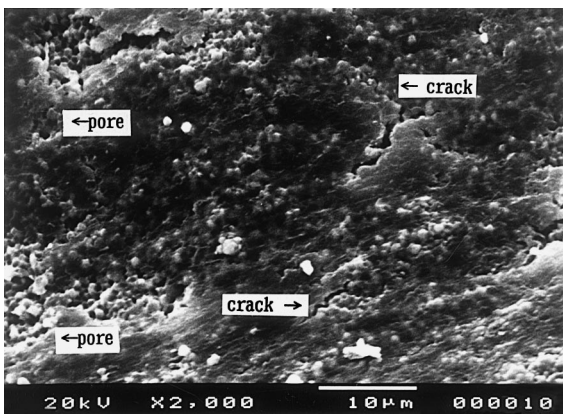
ppm Li. Since K (1.33 Å) ion is much larger than Zr ion (0.80 Å) [18], little change in the t–m transformation is expected in the KOH solution as well as in LiNO$_3$ with pH 7. As expected, the transformed layer under the KOH solution of 350 ppm K was equivalent to that in water as shown in Fig. 9. Further, the enhanced t–m transformation occurred only in LiOH solution and not in LiNO$_3$ even with the same content of Li. This fact indicates that the t–m transformation is influenced by metallic cation type and OH$^-$ concentration as well.

The strikingly enhanced t–m transformation only in the LiOH solution with 350 ppm Li as shown in Fig. 9 is likely related to the considerable extent of oxygen vacancies produced by the substitutional solution of Li ions in the zirconia lattice [1]. In case Li dissolves substitutionally in the zirconia lattice, an increase in the oxygen vacancy concentration can be expressed with Li contents in the solution:

$$\Delta C_v = k(C_{Li}) \times 7.88 \times 10^{17} \mathrm{atom/cm^3}/C_{v_{inZrO_2}},$$

where ΔC_v is the increase in the concentration of oxygen vacancy, C_{Li} the Li concentration in the solution (ppm), $C_{v\ in\ ZrO_2}$ is $\sim 5 \times 10^{20}$ atoms/cm^3 in 3 mol% Y_2O_3 stabilized ZrO_2 [19], and K is assumed to be a constant of 2.5. Thus, $\Delta C_v = 0.0039\ (C_{Li})$. Consequently, the increase in the concentration of oxygen vacancy, ΔC_v amounts to $\sim 1.4\%$ at the concentration of 3.5 ppm Li, leading to little effect of Li on the transformed layer as shown in Fig. 6. On the contrary, ΔC_v is equal to $\sim 137\%$ at 350 ppm Li, which is in relatively good agreement with the relative ratio of the transformed layer thickness at 350 ppm Li over that in water.

It is worth noting that the t–m transformation proceeds uniformly over the whole surface of the specimen, keeping the very flat transformed layer, which is parallel to the surface as shown in Fig. 7. This means that the interaction of OH$^-$ with vacancies building up tensile stress around the occupied vacancy site occurs uni-

Fig. 8. Enlarged microstructure of the transformed layer with micro- and macro-cracks in the tetragonal zirconia stabilized by 3 mol% Y_2O_3.
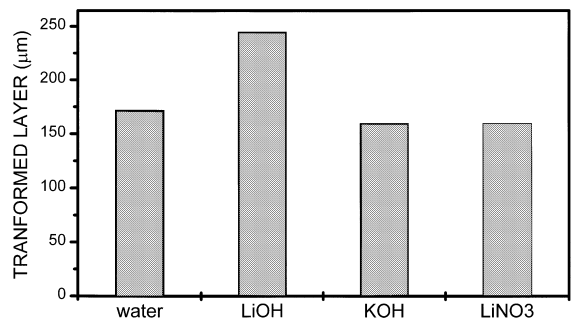

Fig. 9. The degradation of the tetragonal zirconia stabilized by 3 mol% Y_2O_3 by the t–m transformation in various solutions: (a) water, (b) LiOH solution with 350 ppm Li$^+$, (c) KOH solution with 350 K$^+$ and (d) LiNO$_3$ solution with 350 ppm Li$^+$.

formly, ending up with the onset of the t–m transformation across the interacted area. Thus, the t–m transformation would relieve the stress build-up, leading to the formation of a porous layer with micro- and macropores caused by the volume expansion as shown in Fig. 8. However, if the t–m transformation arises from the formation of Zr–OH bonds locally at the stressed site such as cracks as suggested by Yoshimura [9], the flat transformed layer would not be obtained.

Another convincing evidence to this proposal is to find out the existence of OH ions in the transformed layer. Fig. 10 shows the infrared absorption spectra of the tetragonal zirconia stabilized by 3 mol% Y_2O_3 before and after annealing in water or a LiOH solution with 350 ppm Li. The peak at the wave length of 3200–3300 cm^{-1} definitely demonstrates that the OH ion is strongly bonded to the zirconia lattice. Conclusively, the oxygen vacancies are the most probable site for OH ions to be adsorbed, letting the t–m transformation advance from the surface to the interior as shown in Fig. 5.

3.3. Corrosion of zirconium alloys in various pH solutions

3.3.1. Crystallization of zirconia on zirconium alloys

The above results show the crystallization of zirconia strongly depends on pH of the solution. Here, we propose a hypothesis that similar crystallization behavior of zirconia can occur in the oxide grown on the zirconium alloys. Then, many unresolved issues related to corrosion of zirconium alloys can be explained. First, no appearance of the pre-transition corrosion stage at a pH as high as 13.5 [1,14] can be related to the formation of 100% monoclinic zirconia as shown in Fig. 3. This is because the monoclinic zirconia of a larger lattice parameter cannot maintain the lattice coherency with the metal substrate at the oxide/metal interface compared to the tetragonal one of a smaller lattice parameter [20],
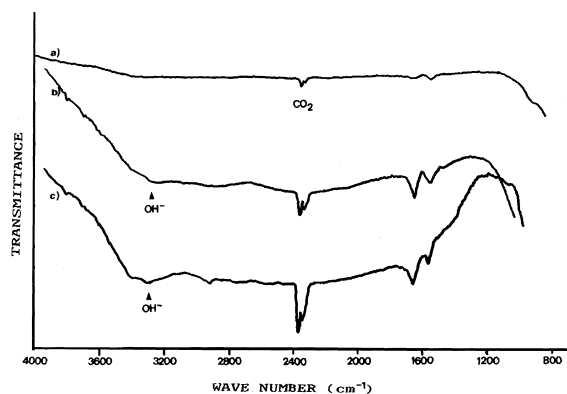

Fig. 10. The infrared absorption spectra of the tetragonal zirconia before (a) and after annealing in either water (b) or lithiated solution with 350 ppm Li (c).

leading to the formation of the pores in the oxide film. This is supported by the fact that the monoclinic equiaxed zirconia grains are observed in the oxide film near the oxide/metal interface in the accelerated corrosion stage [7]. Second, no enhanced corrosion rate in short-term tests even in the LiOH solution of pH 7–11 [1,14] is also attributed to the formation of tetragonal zirconia as shown in Fig. 3, leading to the appearance of a dense oxide film where corrosion proceeds slowly. Supportive evidence to this hypothesis is that the fraction of the tetragonal zirconia in the dense oxide layer [8] is very similar to that determined through the crystallization of zirconia as this study demonstrated. Thus, it is concluded that pH of the solution determines the crystallization of the oxide at the oxide/metal interface, attributing the enhanced corrosion at a pH as high as 14 to the crystallization of the full monoclinic zirconia. However, the cause for the crystallization of the monoclinic zirconia at a high pH is yet to be understood.

3.3.2. Degradation of the oxide film on zirconium alloys by the t–m transformation

After the dense oxide film is formed on zirconium alloys in solutions of 7–11 pH, it will degrade by the t–m transformation as demonstrated by [6,8,21]. Godlewski suggested that the cause for the t–m transformation is related to compressive stress [8,21]. However, this cannot explain the continuous occurrence of the t–m transformation in the oxide before the transition despite continuous build-up of the compressive stresses [21]. Further, the stress effect cannot explain different corrosion behaviors of zirconium alloys in various solutions. However, the modeling experiment shown in Figs. 6 and 9 demonstrated that the t–m transformation takes place independently of stress, suggesting that the t–m transformation is caused by the interaction of OH^- with the oxygen vacancies in the oxide film. Since the zirconia oxide film underwent a degradation by the t–m transformation from the surface exposed to OH ions in water, the porous oxide film of monoclinic equiaxed zirconia grains will start to form first from the surface as shown in Figs. 5 and 7 [8]. There is supportive evidence to the formation of a porous oxide film of equiaxed monoclinic zirconia only in the outermost oxide film near the oxide/water interface [7]. Furthermore, the flat transformed layer as shown in Fig. 7 may explain the uniform corrosion pattern of zirconium alloys.

The key evidence to the interaction of OH^- with oxygen vacancies is the existence of OH^- in the oxide film formed on zirconium alloys. There were two cases experimentally having confirmed the presence of OH^- in the oxide by using either a mass spectrometer or an infrared spectroscopy [8,22]. In addition, Roy's observation [23] that tritium adsorbed in the oxide lattice is immobile and further strong bonding of tritium to the oxide film occurs in T_2O but not in T_2 provides further

supportive evidence. Furthermore, Elmoselhi et al. [24] also reported that deuterium in the oxide is very immobile suggesting that deuterium in the oxide has likely bonded to pores. However, as to the possible sites for the adsorption of OH^-, we suggest that the accessible site to which hydrogen is bonded to as hydroxyl is the oxygen vacancy. Assuming that the oxygen deficit of the intact substoichiometric oxide is equivalent to 3 a/o [1], the maximum concentration of hydrogen bonded to the oxide layer can be calculated: when all the oxygen vacancies are assumed to be filled up with OD^-, the maximum deuterium concentration is calculated to be 0.09 wt%. This agrees perfectly with the maximum deuterium concentration of 0.09 wt% measured at the surface of the intact oxide [24]. Consequently, it is reasonable to think that hydrogen is bonded to the oxygen vacancies in the oxide as OH^-. Furthermore, an increase in deuterium concentration in the oxide under D_2O steam by 20 times as much as that under D_2 gas as reported in Ref. [24] also supports the adsorption of deuterium as OD^- to the oxide. Consequently, it is reasonable to draw a conclusion that the interaction of OH^- with the oxygen vacancies occurs in the oxide film, triggering the t–m transformation. Thus, a decrease in the compressive stress in the oxide after the transformation as shown in Ref. [5,8] is the effect of the t–m transformation, not its cause.

A TEM study on the oxide grown on Zr–0.5 wt% Sn–0.4 wt% Fe alloy shown in Fig. 11 demonstrates that the oxide film consists of the columnar zirconia near the oxide/metal interface and very fine equiaxed grains away from that. This means that the crystallized oxide grains grow in columnar shape to maintain good lattice coherency between zirconia, with a larger lattice parameter, and zirconium, subjecting the oxide film to compressive stress [5,8,21]. From this view point, the crystallization of tetragonal zirconia with a small lattice
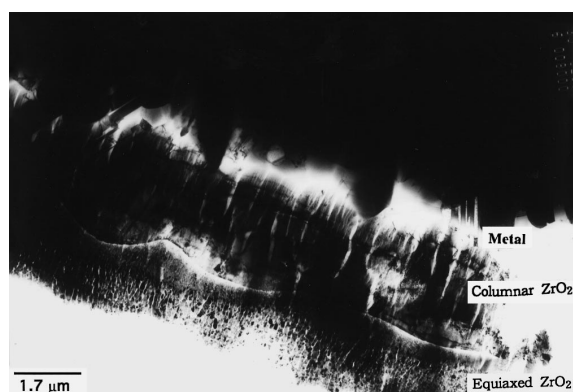
parameter is more favorable than that of monoclinic zirconia with a larger lattice parameter [20], thus leading to the formation of the dense oxide layer. This explanation can be supported by referring to the fact that the stress relaxation by the dissolution of the metal substrate causes the tetragonal zirconia to transform to a monoclinic one [8]. In other words, the oxide film subjected to compressive stress is more resistant to the t–m transformation. On the other hand, the bulky tetragonal zirconia stabilized by 3 mol% Y_2O_3 subjected to little compressive stress is far less resistant to the t–m transformation and seems to undergo considerable degradation even at a temperature as low as 200°C as shown in Fig. 4.

3.3.3. Corrosion of zirconium alloys in pure oxygen and steam

Garzarolli also reported similar observation that the monoclinic equiaxed grains were seen in oxides formed in H-containing environments such as water or steam but not in oxides formed in dry oxygen [2]. This suggests that the presence of OH ion enhances the t–m transformation, resulting in the formation of monoclinic equiaxed grains. Thus, it is expected that the corrosion of zirconium alloys would slow down in dry oxygen because of non-availability of OH^-. A complementary corrosion testing was conducted on Zircaloy-4 both in steam and in dry oxygen at 400°C. As expected, the corrosion resistance of Zircaloy-4 was higher in dry oxygen rather than in steam at least before the onset of the accelerated corrosion as shown in Fig. 12. However, it is yet to be analyzed whether the oxide film formed in dry oxygen consists of only tetragonal zirconia grains as reported [2].

Thus, it is concluded that the interaction of OH ions with oxygen vacancies is the main cause for the degradation of the oxide film. In addition, increased concentration of OH ions to over pH 13 seems to crystallize

Fig. 11. A TEM micrograph showing the columnar and equiaxed zirconia grains in the oxide film on Zr–0.5 Sn–0.4 Fe that was corroded in water to a weight gain of 80 mg dm^{-2}.
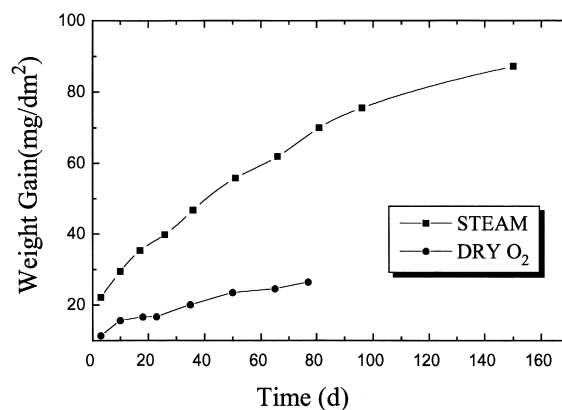

Fig. 12. Weight gain of Zircaloy-4 with time after corrosion in steam under 10.3 Mpa and in dry oxygen under 0.1 MPa.

monoclinic zirconia oxide only as shown in Figs. 3 and 4, leading corrosion to be accelerated [1,2]. In addition, no enhanced corrosion of Zircaloy-4 in 1 M LiNo₃ or 0.1 M KOH [1–3] can be explained by referring to no enhanced t–m transformation rate in LiNO₃ with 350 ppm Li or KOH with 350 ppm K compared to that in water as shown in Fig. 9.

3.3.4. A hypothesis for enhanced corrosion in LiOH solutions

Although enhanced corrosion of zirconium alloys in a highly lithiated solution is a well-known phenomenon, it has not been resolved to date why enhanced corrosion occurs only in a LiOH solution with high Li content but not in a solution with low concentration of Li [1–3]. However, the results shown in Fig. 6 indicate that the considerable t–m transformation occurs only in the solution with 350 ppm Li, suggesting that the enhanced corrosion at high LI content is attributed to the enhanced t–m transformation rate at high Li content. Therefore, it seems quite reasonable to assume the substitutional solution of Li into the zirconia lattice as described above, resulting in increased oxygen vacancies in proportion to Li content in the solution [1,16,19]. Thus, the much increased interaction of OH^- with oxygen vacancies would occur in the solution with 350 ppm Li as opposed to that in the solution with 3.5 ppm Li, leading to the enhanced t–m transformation as shown in Figs. 6 and 7 and eventually to enhanced corrosion only at 350 ppm Li. In addition, the incorporation of Li in the oxide [2,22] is expected to produce increased pH near the oxide/metal interfaces. Once pH in the oxide increases to over 12, as opposed to the nominal pH in the solution, only then the oxide film of 100% monoclinic zirconia only will start to form instead of the dense oxide of some tetragonal and monoclinic zirconia, thus leading to acceleration of corrosion. The point that all tetragonal zirconia transforms to monoclinic zirconia seems to correspond to a transition of the corrosion rate from cubic to linear [8].

On the contrary, K ions (0.95 Å) and Na ions (1.33 Å) [18] cannot enter the zirconia oxide substitutionally due to their larger size, producing little change in oxygen vacancies. This would lead to little interaction of OH ions with oxygen vacancies in KOH or NaOH, eventually contributing to similar corrosion behavior as in water. However, when the pH of the solution reaches as high as 14, then the crystallized oxide consists of monoclinic zirconia irrespective of metal hydroxides only as shown in Fig. 3, leading to accelerated corrosion at pH 14. This hypothesis can explain why zirconium alloys show an enhanced corrosion rate only in 1 M KOH, not in 0.1 M KOH as reported in [1]. On the other hand, no enhancement of the corrosion rate in LiNO₃ [1,3] consistently demonstrated that OH ions are the main factor governing the degradation of zirconia by the

t–m transformation. Since pH of LiNO₃ is around 7, the crystallized oxide in LiNO₃ solution is likely a dense oxide film containing tetragonal and monoclinic zirconia as shown in Figs. 2 and 3. Once the dense oxide forms, the degradation behavior of the dense oxide film in LiNO₃ would follow that in water as observed in Fig. 9.

In summary, we can describe the corrosion process of zirconium alloys: first, pH determines the crystallization of the initial oxide film grown on zirconium alloys. In a high pH solution with pH > 13.5, the crystallized oxide consists of only monoclinic zirconia and the accelerated corrosion without any pre-transition stage in short term tests seems to be a result of this. At pH 7–10, the dense oxide film arises due to the crystallization of 35% tetragonal zirconia and 65% monoclinic zirconia, leading to the appearance of pre-transition stage as was observed in corrosion of zirconium alloys in water. Once the dense oxide film is formed, it degrades first from the oxide surface by the t–m transformation. This degradation of the oxide film is dominantly enhanced in LiOH solutions containing high Li content due to the enhanced t–m transformation rate.

4. Conclusion

The crystallization behavior of zirconia from amorphous $Zr(OH)_4$ demonstrates that only pH determines the crystal structure of the zirconia, crystallizing 35% tetragonal oxide and 65% monoclinic zirconia at pH of 7–10, and only monoclinic zirconia at high pH over 13.5, irrespective of the mental hydroxide solution. This crystallization behavior of zirconia can explain why pH is a main factor governing the corrosion rate of zirconium alloys, suggesting that enhanced corrosion in a high pH solution is attributed to the porous oxide film of 100% monoclinic zirconia.

The degradation of the tetragonal zirconia by the t–m transformation was enhanced only in LiOH solution with 350 ppm Li, but not in NaOH, KOH or LiNO₃ solutions with the same cation concentration. Furthermore, no enhanced t–m transformation rate occurred in solutions with no Li or 3.5 ppm Li. The t–m transformation is likely driven by tensile stress due to the interaction of OH ions and oxygen vacancies. The increased oxygen vacancy concentration by the substitutional solution of Li into the zirconia matrix may contribute to the increased interaction of OH ions with oxygen vacancies, accelerating the t–m transformation.

By correlating these results with corrosion of zirconium alloys in various pH solutions, we suggest that corrosion of zirconium alloys is governed by the t–m transformation of the zirconia, the rate of which is determined by the concentration of OH ions and oxygen vacancy as well. The enhanced corrosion of zirconium alloys in LiOH solution with high Li content is a result

of enhanced t–m transformation in LiOH solution, which is caused by the increased concentration of oxygen vacancies probably by the substitutional solution of Li into the zirconia. On the contrary, no enhanced corrosion of zirconium alloys in KOH or NaOH solution seems to confirm that a change of oxygen vacancy concentration caused by the solution of metallic cations into the oxide film is a key to controlling t–m transformation.

Acknowledgement

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