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Letter to the Editors

Cation incorporation into zirconium oxide in LiOH, NaOH, and KOH solutions

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Abstract

To investigate the cation incorporation into zirconium oxide, SIMS analysis was performed on the specimens prepared to have an equal oxide thickness in LiOH, NaOH, and KOH solutions. Even though they have an equal oxide thickness in LiOH, NaOH, and KOH solutions, the penetration depth of cation into the oxide decreased with an increase in the ionic radius of cation. The cation is considered to control the corrosion in alkali hydroxide solutions and its effect is dependent on the concentration of alkali and the oxide thickness. The slight enhancement of the corrosion rate at a low concentration is thought to be caused by cation incorporation into oxide, while the significant acceleration at a high concentration is due to the transformation of oxide microstructures that would be also induced by cation incorporation into oxide. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The effect of LiOH on the Zircaloy corrosion has been studied by many researchers [1–8]. The Li incorporation into oxide [2,4], the modification of oxide nucleation or growth [6], and the dissolution and reprecipitation of oxide [7] were suggested to be the reasons for the accelerated corrosion in LiOH solution.

In the previous study [5], the corrosion characteristics of Zircaloy-4 in various alkali hydroxide solutions and the oxide microstructure by TEM were investigated, and the cation incorporation into oxide was suggested to play an important role on the corrosion acceleration. It was also reported in the previous paper [5] that, in the LiOH solution, the equiaxed grain was formed in pre- and post-transition regime, in the NaOH solution the columnar grain was formed in pre-transition regime and the equiaxed grain in post-transition regime, and in the KOH solution the columnar grain was formed in both transition regimes. However, the cation contents in the oxide were not investigated by SIMS or chemical analysis. Thus, the corrosion mechanism of Zircaloy in alkali hydroxide was not clearly evaluated in the previous study. Therefore, for the better understanding of cation incorporation into oxide, SIMS and chemical analysis were performed to observe how Li^+, Na^+, K^+ cation penetrated into the oxide. The corrosion mechanism of Zircaloy in alkali hydroxide solutions was discussed on the basis of the SIMS results in this study and the oxide microstructures by TEM in the previous study [5].

2. Experimental procedure

In this study, a recrystallized Zircaloy-4 containing 1.51 wt% Sn, 0.22 wt% Fe, and 0.11 wt% Cr was used for corrosion tests. The specimens were chemically polished using a pickling solution before the corrosion test. The corrosion tests were performed in LiOH, NaOH, KOH, RbOH, and CsOH solutions of 4.3 mmol and 32.5 mmol with equimolar M^+ and OH^- by using the static autoclave at 350°C under the pressure of 17 MPa.

The penetrations of Li^+, Na^+, and K^+ into the oxides formed in LiOH, NaOH, and KOH solutions were

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investigated by SIMS and chemical analysis to clarify the relationship between cation radius and cation incorporation. The SIMS analysis was performed on two kinds of corroded samples of the thick oxide with different oxide thicknesses and the thin oxide having an equal oxide thickness formed in LiOH, NaOH, and KOH solutions. Cameca-ims 4f SIMS was used for the analysis of the cation in the oxide. The primary ion beam of O^{2+} was used because its sensitivity is improved for the secondary ion detection of Li^+, Na^+, and K^+. The acceleration voltage of 10 kV, primary ion beam current of 200 mA, and sputtered area of 150 by 150 μm were selected. Gold coating was applied to the specimen surface with 300 Å thickness to reduce the charge effect of oxide and an electron gun was used to eliminate the stored charge during the analysis. In SIMS depth analysis, secondary ion counts were indicated as a function of sputtering time. The crater depth was measured by a surface roughness tester (α-step 300) to convert sputtering time into oxide depth. Oxide thickness was also measured by metallography, and the depth measured by the roughness tester was calibrated. Secondary ion counts were converted into the function of oxide depth based on those measurements.

The chemical analysis of cations was performed on the oxide formed in 4.3 and 32.5 mmol LiOH, NaOH, KOH, RbOH, and CsOH solutions for 300 days. For the analysis of cation content, the corroded samples were exposed to a solution containing HF to dissolve the metal part, and then the insoluble oxide part was dissolved in a HCl solution. The solution was diluted with water to a total volume of 25 ml, and the cation contents were analyzed by using atomic absorption (Perkin Elmer 3100). In this method, the total content of cations was analyzed from the corroded sample including oxide and metal.

3. Results

The cation contents in the oxide were measured by chemical and SIMS analysis. Fig. 1 shows the cation contents in the oxide by chemical analysis with a variation of weight gain as a function of ionic radius of cation. In 4.3 mmol solutions (Fig. 1(a)), the cation contents decreased gradually with an increase in the ionic radius from Li^+ to Cs^+. This variation of cation content is consistent with that of weight gain showing the gradual decrease with ionic radius. Therefore, it can be thought that the corrosion in a low concentration of alkali hydroxides would be controlled by the cation incorporation into the oxide. However, in the high concentration of alkali hydroxides (Fig. 1(b)), the variation of cation content in the oxide showing a slight decrease between LiOH and NaOH is inconsistent with that of the weight gain showing a rapid decrease. Therefore, it is thought that the strong acceleration of corrosion rate in a high concentration of LiOH would be controlled not only by the cation incorporation but also by other factors like oxide microstructure.

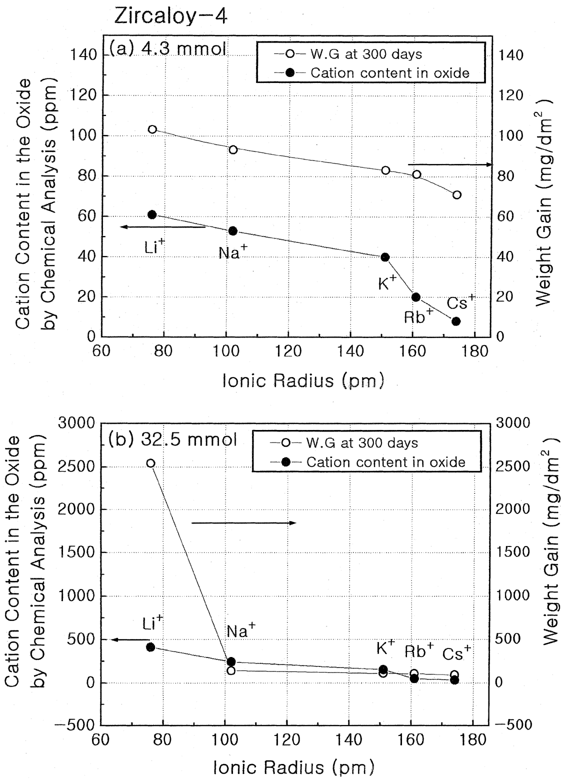

Fig. 1. Variations of cation content in the oxide by chemical analysis with an increase in the ionic radius of alkali hydroxide cation.

Fig. 2 shows the depth profile of Li^+, Na^+, and K^+ by SIMS analysis on the oxide formed for the long-term corrosion test in high concentration of alkali hydroxide as a function of distance from the oxide surface. The Li^+ content rapidly decreased from the oxide surface to 1 μm, and then the constant content was maintained up to long distance. The oxide thickness in LiOH solution was too thick to measure the Li^+ profile at metal–oxide interface. The Na^+ content by SIMS shows a rapid decrease from the surface to 0.5 μm, flat concentration to 3 μm, and a rapid decrease again. On the oxide formed in KOH solution, the K^+ content continuously decreased up to 2 μm without a flat region. The penetration depth of cation decreased in order of Li^+, Na^+, and K^+ ion. However, the fraction of penetration depth from a total layer was not clearly evaluated because each oxide thickness was quite different in the corroded samples used for SIMS analysis.

Thus, the corroded samples having an equal weight gain of 20 mg/dm^2, which corresponds to 1.4 μm oxide

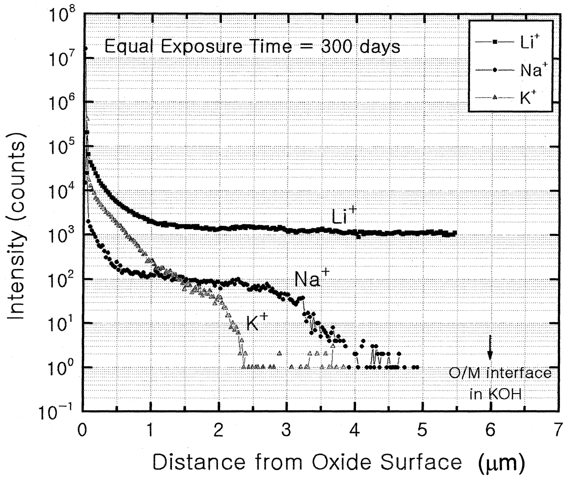

Fig. 2. SIMS depth profile of Li^+, Na^+, and K^+ in the oxide formed for long-term corrosion tests in 32.5 mmol alkali hydroxide solution.

thickness, were prepared by controlling the exposure time. The cation profiles in the oxides formed in the pre-transition regime were investigated as shown in Fig. 3. Although they have an equal oxide thickness, the penetration depth of cation was dependent on the ionic radius of cation. Li^+ penetrated up to the oxide–metal interface. The penetration depths of cation decreased in order of Li^+, Na^+, and K^+ ion. If the barrier layer is assumed as the impervious depth of cation, as shown in Fig. 4, the fraction of penetration layers from the total oxide layer decreases with an increase in the ionic radius of cation – up to 18% in the case of KOH solution.

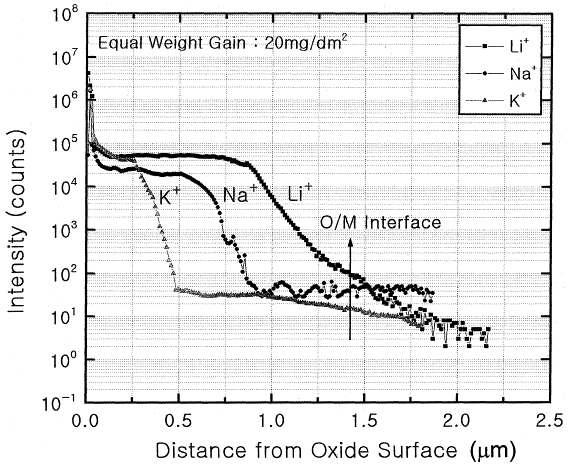

Fig. 3. SIMS depth profile of Li^+, Na^+, and K^+ in the oxide with equal oxide thickness formed in 32.5 mmol alkali hydroxide solution.

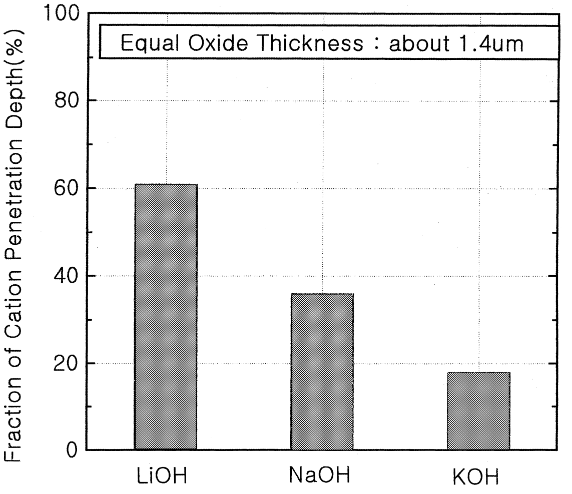

Fig. 4. Fraction of cation penetration depth in the total oxide layer formed at pre-transition regime in 32.5 mmol hydroxides.

4. Discussion

Based on the corrosion characteristics, the SIMS analysis, and the oxide microstructure [5], the discussion is classified into the two mechanistic aspects: one is related to the slight enhancement in a low concentration and in the pre-transition regime of high concentration, and the other significant acceleration in high concentration.

The corrosion result in low concentration (4.3 mmol) of alkali hydroxide shows that the corrosion rate decreases gradually with an increasing ionic radius of alkali cation. This phenomenon would be caused by the difference of ionic radius between cation and Zr^{4+}. It would be easy to substitute Li^+ for Zr^{4+} in the oxide layer due to the similar ionic radii ($Li^+ = 76$ pm and $Zr^{4+} = 72$ pm) whereas substitution would be very difficult for Na^+, K^+, Cs^+, and Rb^+ due to the big difference in ionic radius between cation and Zr^{4+}. Also, it can be said that the slight enhancement of the corrosion rate in LiOH solution is induced owing to the easy substitution of Li^+ for Zr^{4+} in the oxide layer, indicating the formation of many anion vacancies, by the similar size of their ionic radii. This hypothesis is supported by the variation of cation contents measured in this study, namely, the gradual decrease of cation concentration with an increasing ionic radius of cation. Therefore, the slight enhancement of the corrosion rate in a low concentration of LiOH would be controlled by Li^+ incorporation into the oxide.

Regarding the corrosion behaviors in the high concentration of alkali hydroxide, the corrosion behaviors in the pre-transition regime showed the gradual decrease with an increase in the ionic radius [5]. The SIMS analysis on the samples showed that the penetration depth decreased and the ratio of barrier layer to total layer increased with an increase in the ionic radius of cation. Even in the high concentration of alkali hydroxide, the corrosion behavior in pre-transition regime is well consistent with the depth of the barrier layer in the oxides formed in LiOH, NaOH, and KOH solution. Therefore, it is thought that the corrosion in pre-transition regime of high concentration would be controlled by the cation incorporation.

However, in the post-transition regime of high concentration, it was observed that corrosion rate was significantly accelerated in only LiOH but slightly in other alkali hydroxides. The cation concentration in the oxide by chemical analysis decreased gradually with an increase in the ionic radius. Therefore, the cation concentration in the oxide is not clearly consistent with the corrosion behaviors in alkali hydroxide solutions.

In SIMS analysis on the thick oxide formed in LiOH, NaOH, and KOH solutions for 300 days, it was observed that Li^+ could be penetrated to the very long distance but Na^+ and K^+ up to only 3 and 2 μm, respectively, as shown in Fig. 2. Therefore, from the corrosion behavior in the high concentration and the cation content by SIMS and chemical analysis, it is considered that the strong acceleration of the corrosion rate in high concentration would be caused by not only cation incorporation but also other factors.

In the previous study [5], it was investigated from the TEM study on oxide that, even if they had an equal oxide thickness, the oxide morphologies were quite different depending on the alkali hydroxide. In the LiOH solution the equiaxed structure was formed in both regimes of pre- and post-transition, in the NaOH solution the columnar structure in pre-transition and the equiaxed structure in post-transition regime, and in the KOH solution the columnar structure in both transition regimes. Therefore, it is thought that the cation in alkali hydroxide can affect the oxide characteristics including oxide morphologies and oxide growth mechanism.

In a high concentration of alkali hydroxide solution, LiOH accelerates the corrosion due to the early transformation of oxide morphology from columnar to equiaxed structure. On the other hand, KOH is effective to maintain stable oxide morphology. Therefore, the strong acceleration of corrosion in high concentration of LiOH is mainly caused by the transformation of the oxide microstructure, which would be resulted from the cation incorporation into the oxide. However, it is not clear in this study how the cation incorporation induces the transformation of the oxide microstructure.

It is reported that the acceleration of corrosion in LiOH solution is caused by the preferential oxide dissolution and reprecipitation [7]. However, there is no indication for oxide dissolution in alkali hydroxide solutions from the corrosion test used in this study. It is not clear whether alkali hydroxides induce the oxide dissolution because the topography to find the oxide dissolution was not investigated in this study.

5. Conclusions

The cation controls the corrosion in alkali hydroxides with equimolar M^+ and OH^-. The effect of cation on the corrosion is dependent on the alkali concentration and the oxide thickness.

The slight enhancement of corrosion in a low concentration is controlled by the cation incorporation into oxide, which results in the increase of anion vacancy and the decrease of the barrier layer.

The strong acceleration of corrosion in a high concentration is mainly controlled by the transformation of oxide microstructures, which would be also caused by the cation incorporation into oxide.

Acknowledgements

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