



# In situ analysis of creep behavior of pure Pb using electrochemical creep system

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## ABSTRACT

The control of the growth of a Pb-based alloy grid is very important for extending the life of a lead-acid battery. In this study, the creep behavior of pure Pb was investigated in air, in a highly concentrated H<sub>2</sub>SO<sub>4</sub> solution, and in a highly concentrated H<sub>2</sub>SO<sub>4</sub> solution with the intermittent electrifying to the specimen electrode, which simulated the discharge–charge process of the lead-acid battery, in order to obtain the fundamental knowledge about the growth of the Pb-based alloy grid. The growth or the creep of pure Pb in the stress range of 4.0–6.0 MPa was advanced by a dislocation creep mechanism. The creep rate in a 4.5 kmol m<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution was also accelerated by the electrifying to the electrode. This suggests that the acceleration of the creep rate is closely related to the release of dislocations near the specimen surface by the electrifying.

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## 1. Introduction

A lead-acid battery has a high electromotive force and is much cheaper when compared to other rechargeable batteries. Therefore, lead-acid batteries are used in almost all the automobiles around the world. However, the role of the battery is becoming more important since the latest cars come equipped with more electronic devices than ever. Moreover, the user's demand for extending the life of the lead-acid battery has become very strong, plus extension of both its discharge current and capacity.

By the way, it is well known that the life of the lead-acid battery is significantly influenced by the performance of the Pb-based alloy grid which holds the active materials in the electrolyte, especially the resistance of the grid against the growth. The temperature of the engine room of an automobile has increased every year and is around 80 °C during the summer, because of the boost in engine power and high-density arrangement of the parts. Therefore, for extending the life of a lead-acid battery, the development of a new Pb-based alloy grid with growth-resistance is a very important subject [1].

A Pb–Sb alloy [2,3] has usually been used as the grid material of the lead-acid battery, since its mechanical strength was high. However, the Pb–Sb alloy had a shortcoming such that it consumed the electrolytic solution and a periodic supply of water had to be carried out. Then, the VRLA battery (Valve Regulated Lead-Acid Battery) whose grid material is a Pb–Ca alloy with little consumption of the

electrolytic solution was developed. Now, a Pb–Ca–Sn alloy [4–7] is used as the grid material of the VRLA battery. Sn is added to the Pb–Ca alloy for the purpose of corrosion-resistant improvement. However, the risk that the growth rate suddenly increases in the final stage of its life has often been pointed out for the Pb–Ca alloy grids.

It seems that the growth of the Pb-based alloy grid in a lead-acid battery is a kind of corrosion creep, whose corrosion behavior is significantly influenced by electrifying to the electrodes during the charge–discharge process. Therefore, the growth rate of the Pb-based alloy grid may be greatly affected by the operating conditions of a battery, the state of the corrosion scale, in addition to the quality of the material or the shape of the grid. Although a lot of papers have been published on the corrosion creep of the Pb-based alloy, the number of the researches on the lead-acid battery in operation is limited. That is to say, the growth mechanism of the Pb-based alloy grids under the operating condition and the control methods have not yet been satisfactorily elucidated.

In this study, “electrochemical corrosion creep system” which can run a creep test under several corrosive environments was produced. The creep curves of the pure Pb were in situ measured under the following conditions: (1) in air, (2) in highly concentrated H<sub>2</sub>SO<sub>4</sub> solution, and (3) in highly concentrated H<sub>2</sub>SO<sub>4</sub> solution with an intermittent electrifying to the specimen electrode in order to obtain the fundamental knowledge about the growth of the Pb-based alloy which is the grid material of a lead-acid battery. The intermittent electrifying is modeled from the charge–discharge process of the lead-acid battery. Moreover, the influences of (a) the stress on the specimen, (b) the operating conditions, and (c) the intermittent electrifying to the specimen electrode on the steady-state creep rate of pure Pb were investigated.

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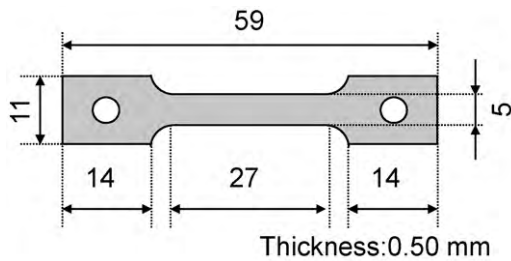


Fig. 1. Specimen coupon for creep test.

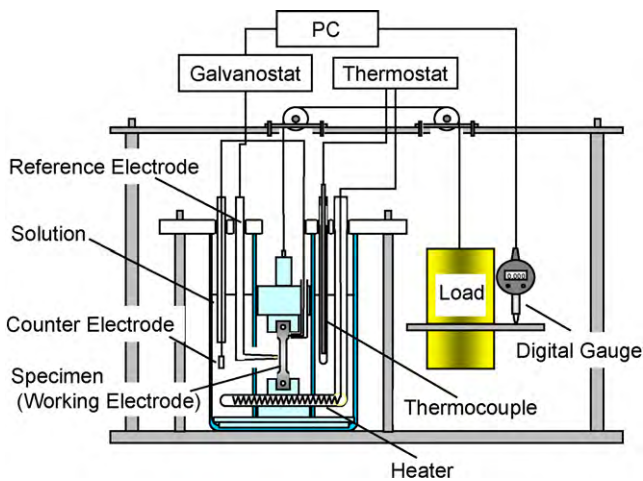


Fig. 2. Electrochemical corrosion creep system.

## 2. Experimental

### 2.1. Electrochemical creep test

A pure Pb ingot (purity; 99.99 mass%) was rolled into a 0.50 mm thick sheet. A specimen coupon of the shape shown in Fig. 1 was then punched from the rolled sheet using dies.

After ultrasonic cleaning in acetone, the specimen coupon was installed in the electrochemical corrosion creep system as shown in Fig. 2, and the creep curve was measured using a digital gauge (Mitutoyo, ID-S). Namely, the time–strain curves for the specimen coupon were measured under a constant load in the range of 4.0–6.0 MPa, (1) in air and (2) in a 4.5 kmol m<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution. The curve was also measured (3) in a 4.5 kmol m<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution with an intermittent electrifying to the specimen electrode, in which a Cu wire was soldered to it for electrical connection and was covered

with an epoxy resin. The counter electrode and the reference electrode were a Pt sheet and an Ag/AgCl electrode in 3.30 kmol m<sup>-3</sup> KCl, respectively. The intermittent electrifying was done using a potentio-galvanostat (Hokuto Denkou, HZ-5000). The electrifying with a constant current for 3.6 ks and the immersion without electrifying for 3.6 ks were constantly repeated, and the current density of the electrifying was changed from 0 to 10.0 mA cm<sup>-2</sup>. Incidentally, the authors have the empirical knowledge that the electrifying to the electrode is effective in shortening the time of the endurance test for the Pb-based alloy without loading. These electrifying conditions of the creep test were selected on the basis of the empirical and careful research. During the creep test, the load current, the potential and the strain of the specimen electrode were recorded by a computer.

After the creep test, the corrosion products on the specimen coupon were analyzed by X-ray diffraction (JEOL, JDX-3530) using Cu K $\alpha$ . The accelerating voltage and the emission current were 40 kV and 40 mA, respectively. The EPMA (JEOL, JSM-5900LV) analysis of the corrosion products was also performed using a 20 kV electron beam.

### 2.2. In situ measurement of mass change

Electrode reactions during the charge–discharge process usually undergo a mass change in addition to the charge transfer. In this study, a special system was built using a digital microbalance and the mass change of the Pb electrode was in situ measured [8,9]. That is, a plate-like electrode of pure Pb was hung in the lower part of the digital suspension microbalance (METTLER TOLEDO, AG245) with the sensitivity of 10<sup>-5</sup> g and dipped into a 4.50 kmol m<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution at 305 K. The potential and the mass of the Pb electrode were then measured during the simulated discharge–charge process, in which the electrifying to the electrode for 3.6 ks and the immersion without electrifying for 3.6 ks were constantly repeated. At this time, the current density of the electrifying was changed to 0, 0.5, 1.0, 5.0, and 10.0 mA cm<sup>-2</sup>.

## 3. Results and discussion

### 3.1. Influence of operation condition and stress on creep rate

Fig. 3 shows the creep curves of pure Pb, (1) in air, (2) in a 4.5 kmol m<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution, and (3) in a 4.5 kmol m<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution with the intermittent electrifying of 10.0 mA cm<sup>-2</sup> to the specimen electrode at 298 K. The tensile stresses applied to each end of the specimen coupon were in the range of 4.0–6.0 MPa. Although the strain rate of pure Pb was very low for in the stress of 4.0 MPa, the specimen was considerably deformed with the

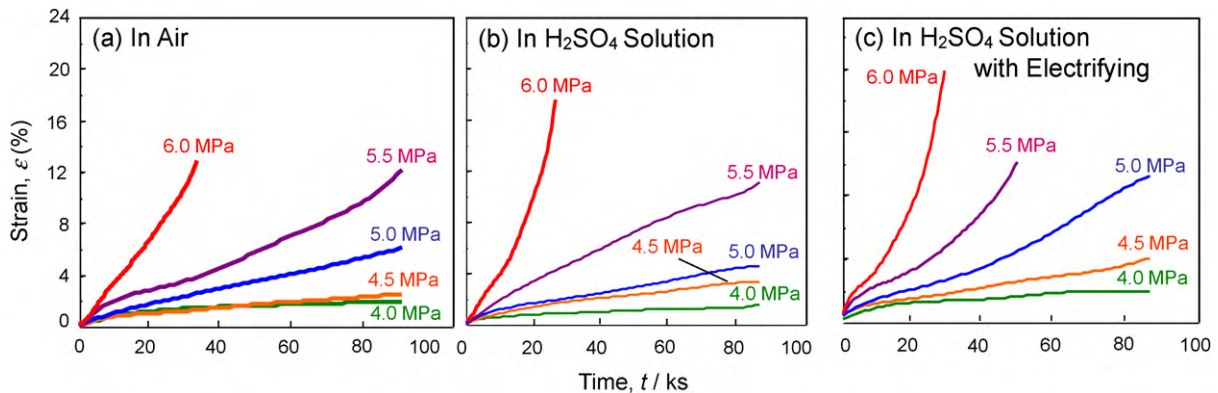
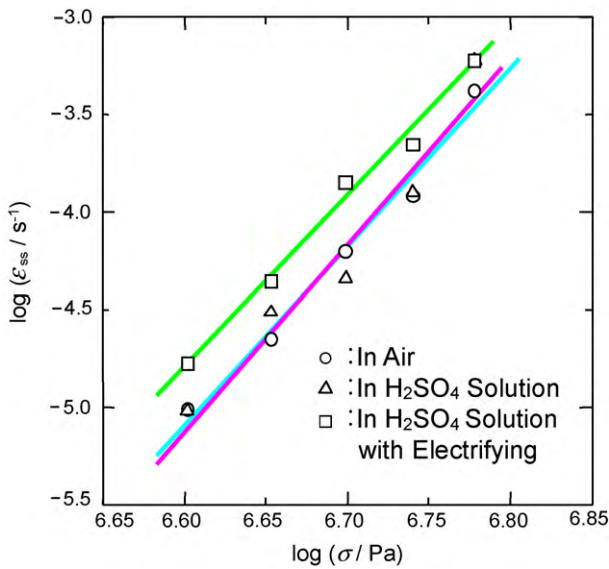


Fig. 3. Creep curves of pure Pb, (1) in air, (2) in 4.5 kmol m<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution, and (3) in 4.5 kmol m<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution with the intermittent electrifying of 10.0 mA cm<sup>-2</sup> at 298 K.



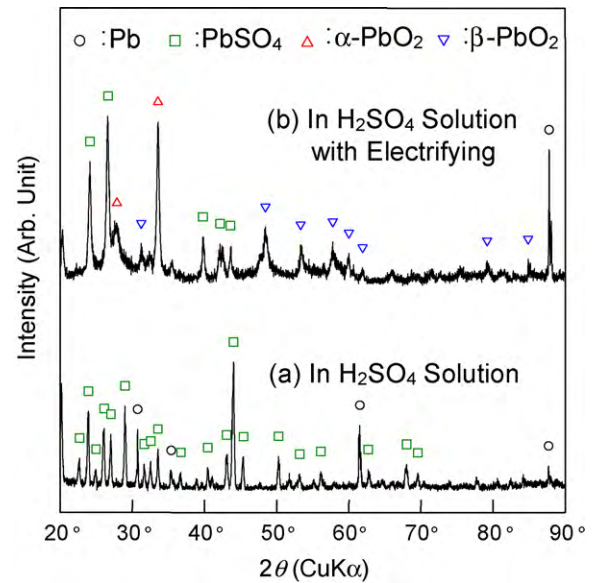
**Fig. 4.** Relationship between stress and steady-state creep rate of pure Pb, (1) in air, (2) in  $4.5 \text{ kmol m}^{-3} \text{ H}_2\text{SO}_4$  solution, and (3) in  $4.5 \text{ kmol m}^{-3} \text{ H}_2\text{SO}_4$  solution with an intermittent electrifying of  $10.0 \text{ mA cm}^{-2}$  at 298 K.

increasing stress under all the conditions. On the other hand, the creep curves in air and those in the  $4.5 \text{ kmol m}^{-3} \text{ H}_2\text{SO}_4$  solution were similar, while the creep rates in the  $4.5 \text{ kmol m}^{-3} \text{ H}_2\text{SO}_4$  solution tended to be accelerated with the intermittent electrifying to the specimen electrode.

Fig. 4 shows the relationship between stress and steady-state creep rate, which was determined from the creep curve for each stress in Fig. 3. As a result, a plot of the steady-state creep rates,  $\log \epsilon_{ss}$  for the stresses,  $\log \sigma$  revealed a linear relationship, which corresponds to the Norton rule given by the following equation:

$$\epsilon_{ss} = B\sigma^n \quad (1)$$

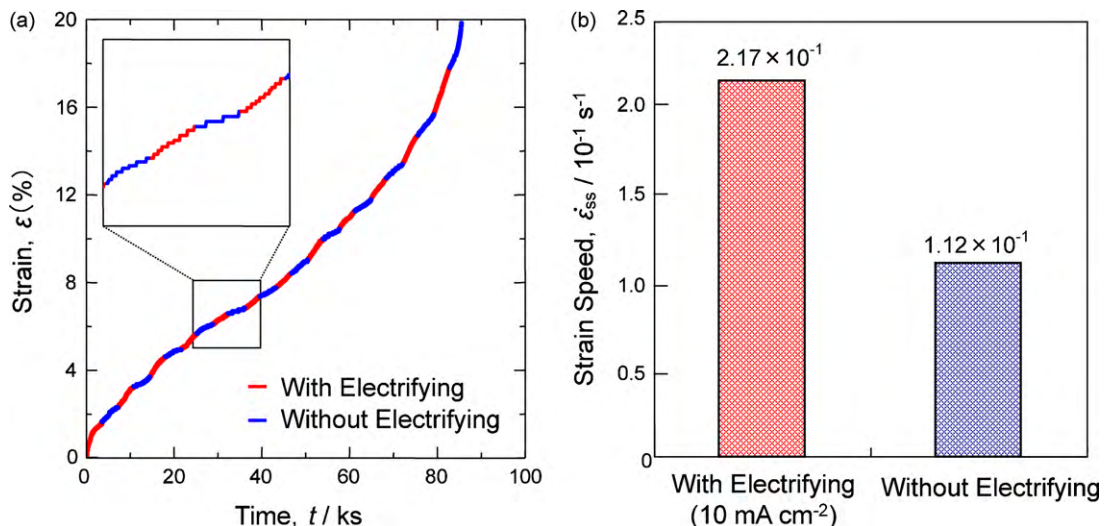
where  $n$  is the steady-state stress exponent, and  $B$  is a material constant. For the exponents,  $n$  defined as  $n = [\partial \log \epsilon_{ss} / \partial \log \sigma]$ , (1) in air, (2) in  $4.5 \text{ kmol m}^{-3} \text{ H}_2\text{SO}_4$  solution, and (3) in  $4.5 \text{ kmol m}^{-3} \text{ H}_2\text{SO}_4$  solution with the intermittent electrifying of  $10.0 \text{ mA cm}^{-2}$  were 9.1, 9.5 and 8.7, respectively. When  $n$  is around 1, the creep can be associated with a diffusion mechanism [10]. Also, the mechanism associated with dislocation movement such as dislocation



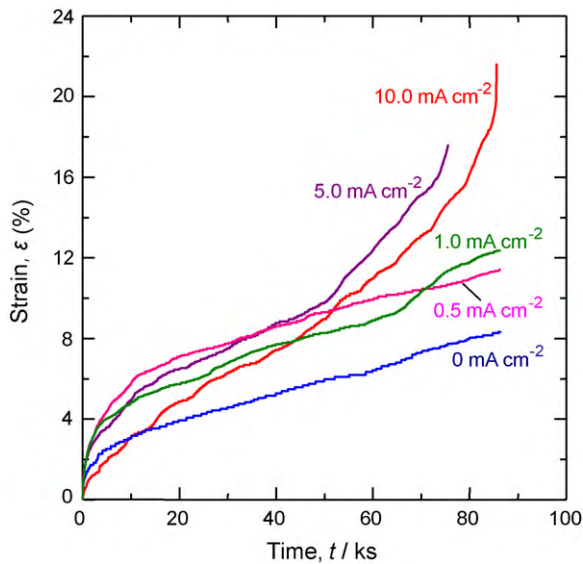
**Fig. 5.** XRD patterns of the specimen coupons after the creep test, (a) in the  $4.5 \text{ kmol m}^{-3} \text{ H}_2\text{SO}_4$  solution, and (b) in the  $4.5 \text{ kmol m}^{-3} \text{ H}_2\text{SO}_4$  solution with an intermittent electrifying of  $10.0 \text{ mA cm}^{-2}$  at 298 K.

creep is attributed to  $n > 6$  [2,11,12]. Therefore, these high  $n$  values probably support the fact that the creep deformation of pure Pb under constant stresses in the range from 4.0 to 6.0 MPa is related to the mechanism associated with a dislocation movement. Moreover, Fig. 4 clarified that the steady-state creep rate in the  $4.5 \text{ kmol m}^{-3} \text{ H}_2\text{SO}_4$  solution with the intermittent electrifying of  $10.0 \text{ mA cm}^{-2}$  was the highest when compared to those under the other two creep conditions.

Fig. 5 shows the XRD patterns of the specimen coupons after the creep test. The electrode surface after the creep test in  $4.5 \text{ kmol m}^{-3} \text{ H}_2\text{SO}_4$  solution was covered with  $\text{PbSO}_4$ . On the other hand,  $\alpha\text{-PbO}_2$  and  $\beta\text{-PbO}_2$  were identified in addition to the  $\text{PbSO}_4$  in the case of the creep test in the  $4.5 \text{ kmol m}^{-3} \text{ H}_2\text{SO}_4$  solution with the intermittent electrifying of  $10.0 \text{ mA cm}^{-2}$ . The immersion potential of the specimen coupon under the former condition was around  $-0.30 \text{ V}$  vs. NHE, at which the generation of  $\text{PbSO}_4$  as shown by Eq. (2) is the only reaction. On the other hand, the electrode potential of pure Pb during electrifying of  $10.0 \text{ mA cm}^{-2}$  rose to nearly  $2.4 \text{ V}$

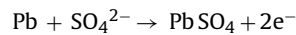


**Fig. 6.** Influence of electrifying to the specimen coupon on the creep strain of pure Pb in the  $4.5 \text{ kmol m}^{-3} \text{ H}_2\text{SO}_4$  solution at 298 K.

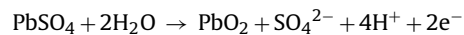


**Fig. 7.** Creep curves of pure Pb under a 5.0 MPa stress in a 4.50 kmol m<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution at 305 K with electrifying, whose current density was varied from 0 to 10.0 mA cm<sup>-2</sup>.

vs. NHE under the latter conditions. Therefore, it can be interpreted that the oxidation from PbSO<sub>4</sub> to PbO<sub>2</sub> as shown by Eq. (3) occurred in addition to the generation of PbSO<sub>4</sub> [9,13].



$$E^\circ = -0.360 + 0.0295\text{p}(\text{SO}_4^{2-}) \quad \text{V vs. NHE} \quad (2)$$



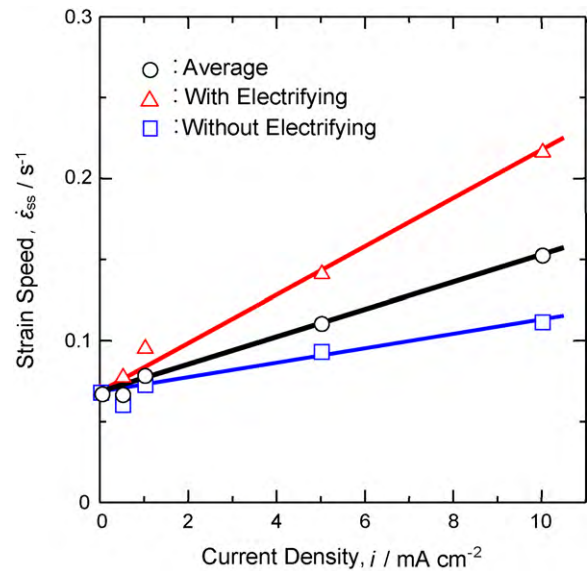
$$E^\circ = 1.69 - 0.1182\text{pH} - 0.0295\text{p}(\text{SO}_4^{2-}) \quad \text{V vs. NHE} \quad (3)$$

### 3.2. Influence of electrifying on creep rate

Fig. 4 shows that the creep rate of pure Pb in a 4.5 kmol m<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution was increased by the electrifying. Therefore, the influence of electrifying to the specimen coupon on the creep strain of pure Pb was investigated using an in situ measurement as shown in Fig. 6. This measurement clarified that the creep rate increased as soon as the current flowed through the specimen electrode, as shown in Fig. 6(a). Moreover, the average creep rate of  $2.17 \times 10^{-4} \text{ s}^{-1}$  during electrifying of 10.0 mA cm<sup>-2</sup> was roughly double that of  $1.12 \times 10^{-4} \text{ s}^{-1}$  during immersion without electrifying (see Fig. 6(b)). A similar behavior had been reported by Revie and Uhlig [14] on the creep of copper in the 1970s.

Fig. 7 shows the creep curves of pure Pb under a 5.0 MPa stress in a 4.50 kmol m<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution at 305 K with electrifying, whose current density was varied from 0 to 10.0 mA cm<sup>-2</sup>. When the current density was 0 mA cm<sup>-2</sup>, namely, the electrode was under natural immersion without electrifying, the specimen coupon was gradually deformed and the final strain was only 8.4%. However, when the current density of the electrifying was raised to 0.5 and 1.0 mA cm<sup>-2</sup>, the final strain increased to 11.2 and 12.4%, respectively. Furthermore, the creep rates with the electrifying of 5.0 and 10.0 mA cm<sup>-2</sup> were particularly accelerated in the latter part of the creep test and both specimen coupons fractured before 86.4 ks. Based on these results, it was confirmed that the creep rate of pure Pb in a 4.50 kmol m<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution rose as the current density of the electrifying increased.

Fig. 8 shows the relationship between the current density of electrifying and steady-state creep rate, which was determined from each part of the steady-state creep in Fig. 7. Whenever the

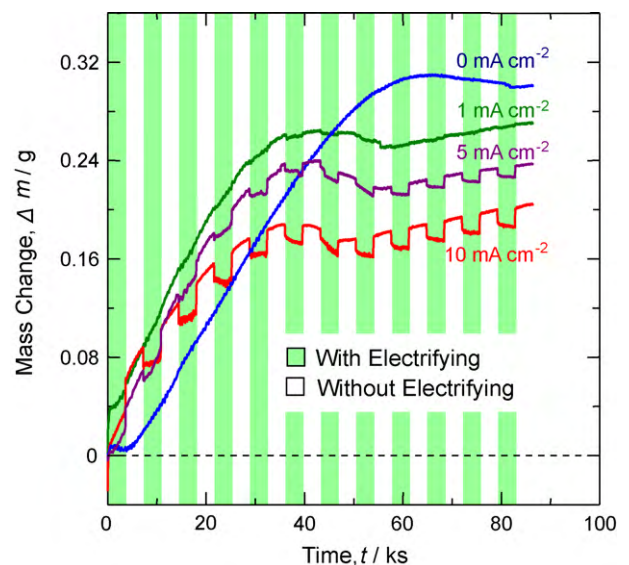


**Fig. 8.** Relationship between current density of electrifying and steady-state creep rate of pure Pb under a 5.0 MPa stress in a 4.50 kmol m<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution at 305 K.

current density of the electrifying increased, the average rate of the steady-state creep almost linearly increased. Moreover, the rate of the steady-state creep with electrifying and that without electrifying were individually calculated. The knowledge that the creep rate with electrifying linearly increased with the applied current density on the electrode coupon was the expected phenomenon. However, it also became clear that the creep rate was slightly dependent on the current density even during natural immersion without electrifying.

### 3.3. Influence of electrifying on mass of Pb electrode

Fig. 9 shows the influence of electrifying on the mass change of the Pb electrode, which was intermittently electrified with various current densities. Without electrifying, or at the current density of 0 mA cm<sup>-2</sup>, the mass of the Pb electrode almost linearly increased for 40 ks. Its increasing rate then decreased in the latter part of the



**Fig. 9.** Influence of electrifying on the mass change of the Pb electrode, which was intermittently electrified with various current densities.

test and the mass gain was stabilized at about 0.30 g. On the other hand, the last mass gain in the Pb electrode tended to decrease with the increasing current density of the electrifying, while the initial mass gain of the Pb electrode with electrifying was obviously greater than that without electrifying. That is to say, the last mass gains with intermittent electrifying of 0, 1.0, 5.0, and 10.0 mA cm<sup>-2</sup> were 0.30, 0.27, 0.24 and 0.20 g, respectively.

It seems that the dependence of mass gain of the Pb electrode on the current density during electrifying is based on the generated ratio of PbO<sub>2</sub> to PbSO<sub>4</sub>. When the current density is low, the proportion of PbSO<sub>4</sub> → PbO<sub>2</sub> to Pb → PbSO<sub>4</sub> is relatively low so that the last mass gain of the Pb electrode may be increased. On the other hand, it is suggested that high production rate of PbO<sub>2</sub> at a high current density led to a decrease in the final mass gain of the Pb electrode.

Furthermore, it is very important that rapid mass changes were observed at the time of switching during electrifying/natural immersion. As soon as the electrifying started, the mass of the Pb electrode fell in an instant. When the state of the electrode returned to the natural immersion, the mass rapidly recovered to the original state. Moreover, the mass change amounts observed during the switching of electrifying/natural immersion were dependent on the current density applied to the Pb electrode. That is, although an evident mass change was observed by electrifying of 10.0 mA cm<sup>-2</sup>, the amount of the mass change became smaller as the current density decreased. It can be interpreted that the mass loss during switching from a natural immersion to electrifying is related to the dissolution of Pb → Pb<sup>2+</sup> and PbSO<sub>4</sub> → Pb<sup>2+</sup> besides the evolution of oxygen, the oxidation of PbSO<sub>4</sub> → PbO<sub>2</sub> and others. The dissolution reactions by electrifying were confirmed by the polarization measurement using the Pt ring–Pb disk double electrode. However, the proportion of the dissolutions to the oxygen evolution and other reactions is not clear at present. On the other hand, it can be theorized that the recovery of the mass during switching from electrifying to natural immersion is related to the reverse reaction.

### 3.4. Relationship between electrode dissolution and creep rate

Fig. 6 shows that the creep rate of Pb was accelerated by electrifying to the specimen electrode. Moreover, Figs. 7 and 8 clearly showed that the steady-state creep rate linearly rose with the increasing current density during electrifying. On the other hand, an in situ measurement in Fig. 9 showed that the mass of the Pb electrode temporarily decreased by the dissolution incident to electrifying and returned to the original state by the reverse reaction during the natural immersion. The amount of the mass loss by electrifying increased with the increasing applied current density. Therefore, it may be concluded from these results that the creep rate of Pb and the dissolution reaction incident to electrifying were closely related.

The Norton plot of the creep rate in Fig. 4 suggested that the creep of Pb obeyed a dislocation mechanism. The dislocations might

also move toward the surface from the inside and condense near the specimen surface, which was covered with the corrosion products such as PbSO<sub>4</sub> and PbO<sub>2</sub> (see Fig. 5). It can be thought that the reaction of Pb → Pb<sup>2+</sup> or PbSO<sub>4</sub> → Pb<sup>2+</sup> occurred on the specimen surface by electrifying besides PbSO<sub>4</sub> → PbO<sub>2</sub> and the condensed dislocations were released from the surface. Also, the creep rate of the Pb electrode can be accelerated by releasing of the dislocations near the surface. Therefore, it can be concluded that both dissolution of the specimen electrode and the deposition of corrosion products on the surface influenced the creep rate in the 4.5 mol m<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution. Moreover, it can be presumed that the electrifying condition, i.e., the operating conditions have a significant influence on the growth of the Pb-based alloy grid in a lead-acid battery.

## 4. Conclusions

The control of the growth of a Pb-based alloy grid is the most important factor for extending the life of a lead-acid battery. In this study, electrochemical corrosion creep system, which can carry out in situ measurements of the growth of a Pb-based alloy in a concentrated H<sub>2</sub>SO<sub>4</sub> solution, was used. The corrosion creep behavior of pure Pb during electrifying/natural immersion repetitions, which simulated the discharge–charge process of the lead-acid battery, was investigated. The results were consistent with the view that the growth or the creep of pure Pb advanced by a dislocation creep mechanism in the range of stress from 4.0 to 6.0 MPa. Moreover, it was observed by in situ measurement that the creep rate of pure Pb in a 4.50 mol m<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution was accelerated by electrifying to the specimen electrode. This phenomenon can be interpreted as being related to the fact that the release of dislocations near the specimen surface has been promoted by the electrifying.

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