EFFECT OF LOAD AND ANODE/CATHODE AREA RATIO ON WEAR OF Zr-ALLOY IN Na_2SO_4 SOLUTION

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.In this paper we examined the contribution of mechanical and electrochemical factors in corrosive wear for Zr-alloy against Al_2O_3 ball in Na_2SO_4 solution. Normal load and the area of metallic specimen was varied to change the corrosion behavior. At the commence of sliding, the potential drop took place, which increased with load due to the great exposure of fresh surface. Wear volume was linearly proportional to load. The corrosion factor was about 15 %. By increasing the Aa/Ac ratio, corrosion factor to total wear decreases and saturates above Aa/Ac=0.15.
Keywords : Corrosive Wear, Electrochemical, Zr-alloy, Polarization Curve, Potential Pulse Method

1. INTRODUCTION

Zr-alloy (zircaloy-4) is used for fuel rods in nuclear power station due to its high neutron absorption and anti-corrosion properties. Therefore, it is useful to use Zr-alloy for the study on corrosive wear. We have studied the mechanical factor and electrochemical factor in corrosive wear [1-3]. The polarization curve obtained by the potential pulse method was used to the dissolution rate from the fresh surface.

Electrochemical contribution to wear volume is related to the area of the exposed fresh surface by changing normal load, and also to the ratio of anode area to cathode area because the potential drop in corrosive wear is determined by the following equation:

$$AaIa+AcIc=0 \qquad (1)$$

where A is the area and I is the current density. Suffix a and c denotes the anode and cathode. Since we regarded the wear scar area as anodic area, *Aa/Ac* ratio with different size of specimens, i.e., cathodic area, changes *Ic/Ia* ratio [2].

In this paper we investigated the electrochemical contribution by changing normal load and size of specimen.

2. EXPERIMENTAL DETAILS

The experimental apparatus used was a reciprocating tribometer, which was described in the previous paper [3]. The specimen was Zr-alloy (zircaloy-4) plate against an Al_2O_3 ball. We prepared four different exposed area of Zr-alloy specimen with enamel coating, 250, 118, 76, and 42 mm^2. Surface roughness of metallic specimen and alumina ball were 0.10 μ m and 0.07 μ m in Ra, and Vickers hardness were 2,470 MPa and 17,640 MPa, respectively. The metallic specimen acts as working electrode. The reference electrode was a saturated calomel electrode, and the counter electrode was a Pt plate. In this work we defined the areal ratio of anode to cathode (Aa/Ac ratio) by assuming the wear scar area was anodic and unworn area was cathodic.

Experimental conditions are follows: the stroke was 10mm, frequency was 8.33Hz, and the number of cycles was 10^4 cycles. Normal load was varied to 2.45, 4.90, 7.35 and 9.80 N. Electrolyte used was Na_2SO_4 solution with pH 7 and the content of 0.1mol/l. The experiment was carried out under the free potential without any potential control in sliding test. We measured the potential drop in the test. In comparison with the results of Na_2SO_4, pure water was also used.

Wear volume of the metallic specimen was evaluated using 3D-profilometer, and its wear scar was observed with SEM.

3. RESULTS AND DISCUTSSION

3.1 Polarization Curve

Two different polarization curves were measured, dynamic potential method and potential pulse method. Former is the conventional one with a sweep rate of 50 mV/min from –2500mV (vs. SCE) to +2500mV. This property was regarded as that of unworn surface. The latter was obtained by sweeping the potential from –2500mV to certain value with 83.3 V/s. The current was measured with a sampling time of 1 ms. This is the property of the worn surface, where the fresh surface was continuously exposed. Figure 1 shows the results. The corrosion potential is –400 mV for unworn surface, and –1600 mV for the fresh surface. The anodic current density is greater for the fresh surface than the unworn surface by two or three orders of magnitude.

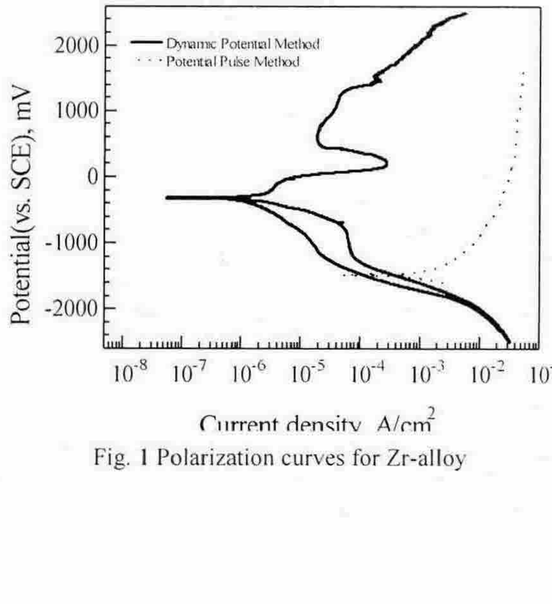

Fig. 1 Polarization curves for Zr-alloy

3.2 Wear Test

The potential decreases at the commence of the sliding, due to the exposure of the fresh surface. Fig.2 shows the potential drop against load at different area ratio. The extent of the drop increases with load. The fresh surface acts as anode, and the unworn area acts as cathode. The current density of the fresh surface is presented by that from PPM and the cathodic current is given by that from DPM. The potential drop occurs to satisfy Eq. 1. Therefore, the increase in the

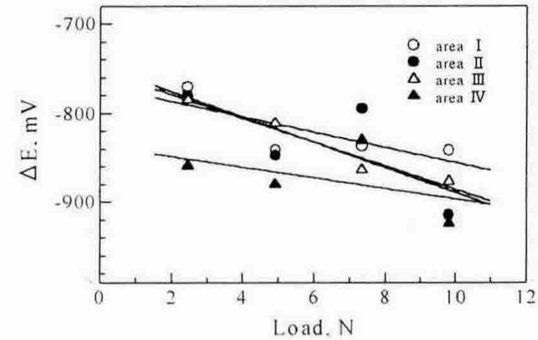

Fig. 2 Potential drop ΔE during sliding against load.

drop means the increase in the fresh surface exposed.

The wear volume is shown in Fig. 3, where the result in pure water is also shown. Wear volume is linearly proportional to normal load, and the gradient of the volume in Na_2SO_4 solution became steep with the decrease in Aa/Ac ratio. This means the electrochemical factor becomes great as the ratio becomes small. The wear volume in Na_2SO_4 solution is more than in pure water, because the electrochemical contribution is added in corrosive wear.

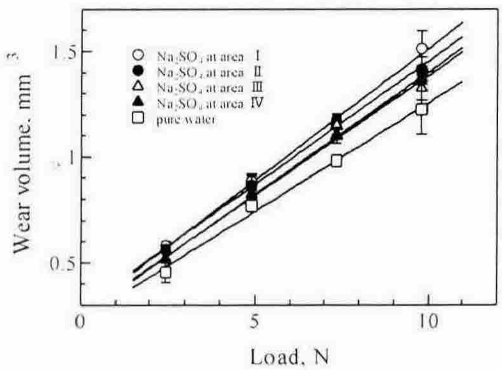

Fig.3 Wear volume after 10^4 cycles against load

As the index of wear property the dimensionless wear coefficient k is defined as

$$k=VH/PL=KH \qquad (2)$$

where V is wear volume, H is Vickers hardness, P is normal load, and L is sliding distance. K is referred as specific wear rate. From the data of Fig. 3 wear coefficient was obtained. In corrosive wear the wear volume is the summation of those of mechanical and electrochemical factor. Therefore, Eq. 2 can be written as

$$k=k_m+k_c \qquad (3)$$

where k_m is the wear coefficient due to mechanical action and k_c electrochemical action. The wear in pure water represents the mechanical factor in this work. The ratio, kc/k, means the contribution of electrochemical factor, and it is 15.7 % for Aa/Ac=0.11. This value is not great, compared with type-304 stainless steel [2]. As the result, the mechanical factor significantly governs the wear property for Zr-alloy.

Fig. 4 shows the electrochemical wear coefficient kc against Aa/Ac ratio. The coefficient decreases steeply to Aa/Ac ratio of 0.1 and becomes saturates around 1.4×10^{-4}. This result revels that the smaller the Aa/Ac ratio, the greater the electrochemical factor is. As the cathodic area is relatively small, *i.e.*, Aa/Ac increases, the electrochemical factor becomes constant.

SEM observation of wear scar was carried out for both specimen. Worn surface was very roughened in Na_2SO_4 and in pure water. Severe transfer of metallic debris on Al_2O_3 ball was observed.

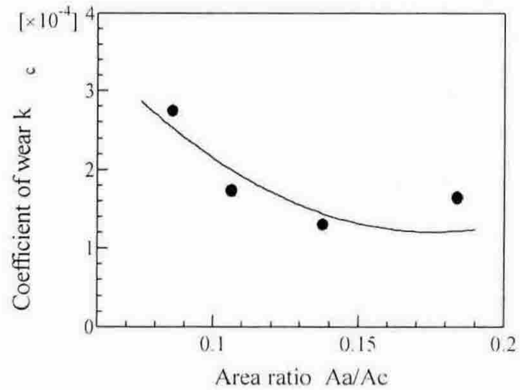

Fig.4 Electrochemical wear coefficient against area ratio

4. CONCLUSION

The following conclusion are drown in the present work:

1) The potential drop is proportional to normal load in Na_2SO_4 solution.
2) Wear volume increase with normal load, linearly. Compared with the wear in pure water, the electrochemical contribution is about 15 % for Zr-alloy, and the mechanical factor is significant.
3) The electrochemical contribution depends on the area ration of anode to cathode, and the contribution becomes great as the ratio becomes small, and it becomes saturated as the ratio increases.

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