EFFECTS OF ADSORBATES ON ZIRCALOY OXIDATION IN AIR

Yoonchol Cho, Yun-Goo Kim and Kwangheon Park

Center for Advanced Reactor Research
Institute of Materials Science and Technology,
Department of Nuclear Engineering
Kyunghee University, Suwon, South Korea

ABSTRACT

The air-oxidation of Zry and the effects of adsorbates on the oxidation are found by the intermittent measurement of the weight gain of specimens. NaCl enhances the oxidation, where nonuniform stresses on the surface and Cl ions are the cause. LiOH also enhances the oxidation, where the initial oxide formed by LiOH seems to the reason. The effects of fluorides on oxidation are also measured. NaF is most harmful and KF follows next. LiF does not effect the oxidation of Zry. Diffusion of fluorides in oxide determines the enhancement.

I. INTRODUCTION

Zircaloy(Zry) cladding is the first protective barrier against the release of radioactive fission products from the fuel during normal and accidental conditions. The oxidation of Zry has been of great concern due to its importance on the safety of nuclear reactors. Zry oxidation has been widely investigated in steam and water environments[1-5]; however, relatively little data exist for the oxidation in air[6].

Spent nuclear fuels contain more than 96% of fissionable materials, and are considered as energy resources in the future. Spent fuels are stored in both wet and dry methods. Nowadays, dry storage facilities are more favored because of lower operation cost, improved safety margin in criticality, and easier selection of available sites. However, the spent fuel temperature in the dry storage facility is higher than that in wet storage. So, corrosion and creep of spent fuels are important topics for the safety of dry storage facilities.

The air oxidation of Zry cladding has been an interesting topic, but there exist relatively small amount of the experimental data. And, some adsorbates are possible to stay on the surface of fuel claddings during dry storage. For examples, LiOH, a pH-controller in the coolant of Pressurized Water Reactor(PWR), can be an adsorbate. NaCl also can be adsorbed on the surface of fuels from the permeated air near the sea during storage. And, organic dirt may be on the fuel surface. However, the roles of these adsorbates have not been clarified, so far. In this paper, the effects of these adsorbates on the air-oxidation of Zry are mentioned, and the possible mechanisms of these adsorbates are also discussed.

II. EXPERIMENTALS

The oxidation rates of Zry claddings were determined by the intermittent weight-gain measurements. Zry tubes are as-received Westing House products used in Kori PWR power plants. The tubes were cut and etched to be used as specimens (hight ~ 1cm). Two types of specimens were prepared : specimens with adsorbates on the etched surface and those on the oxide layer. Most probable adsorbates are LiOH and NaCl, the roles of which are observed in both types. Fluorides (LiF, NaF and KF) which represent possible dirt on the fuel surface are tested in the latter case only. Adsorption of these adsorbates is done by drying after the insertion of specimens in 1 M solution for an hour at room temperature. Experiments were done at three temperatures, 400, 450, and 500 ℃. The specimens are oxidized in the air with 80% relative humidity (referenced at room temperature). Figure 1 is a diagram showing the experimental setup and the procedure.

III. RESULTS

3.1. Adsorbates on the etched surface.

Etched Zry specimens without adsorbates on the surface were oxidized intermittently and the results are shown in Fig.2. The results are compared with those of Suzuki and Kawasaki (dashed lines)[6]. The experimental data (points and solid lines) are very close to those of Suzuki and Kawasaki (dashed lines). Transition points at 450 and 500 ℃ are noticeable during the measurement period. While the color of oxide on Zry made in steam or water looks white, most specimens oxidized in air take the color of (bright) yellowish brown. Even the white oxide formed in steam turns into yellowish brown, when Zry is reoxidized in air. The oxide formed in air contains small amount of ZrN, the color of which is yellowish brown.

The oxidation rate can be expressed as follows:

Pre-transition : $(\Delta W)^n = K_n \bullet t$

Post-transition : $(\Delta W - \Delta W_t)^m = k_m \bullet (t - t_t)$

where n, m, K_n, K_m are experimentally measured kinetic constants, ΔW_t is weight gain at the transition point, and t_t is transition time. Table 1 shows the kinetic constants for the oxidation of etched specimens. The unit of weight gain is mg/m^2.

The specimens adsorbed by NaCl are oxidized faster than the etched ones (Fig.3). There are deviations in weight gain measurements, which may come from the concentration difference of NaCl adsorbed on the surface. The transition points do not appear during the measurement. The oxidation follows approximately the parabolic rate law. The kinetic constants are shown in table 2.

The adsorbate, LiOH enhances the oxidation of Zry in air(Fig.4). The oxidation rate is high initially; but after a transition point, the rate decreases. The kinetic constants for the oxidation of LiOH adsorbed specimens are in Table 3. It is not clear whether the trend of the decreased oxidation rate continues; but, seems to have another transition at 500 ℃ during the measurement period.

3.2. Adsorbates on the oxide surface.

The role of adsorbates staying on the oxide layer was examined by putting adsorbates on the surface after the oxide layer formed. Figure 5 shows the experimental results. Clean Zry specimens are oxidized in air up to 2 mg/m^2(pre-transition region), then pulled out and immersed in the solution containing the adsorbates. After adsorption, the specimens are reoxidized at the same temperature. The temperature was 450 ℃ in the case of figure 5. Adsorbed NaCl enhances the oxidation of Zry, while enhancement of LiOH on oxidation is negligible. Adsorbed LiOH seems to affect only initial oxide formation of Zry. Fluoride except LiF enhances oxidation more than NaCl does. NaF is a most harmful adsorbate, and KF is the next. LiF does not influence Zry oxidation.

IV. DISCUSSION

The oxidation of specimens NaCl-adsorbed on the etched surface approximately follows a parabolic rate law. Figure 6 shows the specimen surface after adsorption(Fig. 6.a) and the surface after 36 hour oxidation at 450 ℃(Fig.6.b). Several size salt crystals form on the etched surface. When oxidation begins, cracks start to show up just nearby salt crystals. Cracks surrounding big salt crystals are frequently observed (Fig.6.b). Based on the observation, the following oxidation mechanism is proposed.

When NaCl crystals adsorbed on Zry surface, strong bonding between Zry and NaCl prevents the oxidation at the sites beneath salt crystals. Compressive stresses exist in the oxide layer due to the high value of Pilling-Bethworth ratio. The oxide adjacent to crystals relieves the compressive stress more easily than the bulk oxide does, since metal or thinner oxide exists beneath the crystal. As oxide thickens, tension comes first on the sites near the salt crystals, where the compressive stress is already relieved. This nonuniform stress-relief mechanism induces many cracks surrounding NaCl crystals.

The crack length is dependent on the size of NaCl crystals. Abnormally porous oxide regions are also observed at the region where tiny NaCl crystals were occupied. The parabolic rate law comes from crack-enhanced oxidation. The cracks formed near salt crystals enhances the oxidation by expanding their length and depth. Cl ion in the oxide layer also helps cracking.

Figure 7 shows NaCl crystals adsorbed on the oxide layer. Large salt crystals are observed on the surface, initially(Fig.7.a). After 146 hour oxidation at 450 ℃, salt crystals become smaller and seem to evaporate and also diffuse into oxide (Fig.7.b). Salt crystals are still seen at 434 hour oxidation; however, they become vague(Fig.7.c). Fast diffusion along grain boundaries and dislocations is dominant in this temperature range. However, the diffusion of NaCl during oxidation needs more study, since dominant point defects of zirconium oxide are mainly oxygen vacancies during oxidation, and cation diffusion is known to be very slow. EDX analysis indicates Na and Cl are almost equally found across the depth of oxide.

When LiOH is adsorbed on the etched surface of Zry, the oxidation rate increases at the initial stage. After a transition point, the oxidation rate decreases. However, in the case of LiOH on the oxide layer, the oxidation rate does not change. Figure 8 shows the surface of specimens just after LiOH adsorption on the etched surface (Fig.8.a), 30 hour oxidation (Fig.8.b), and 736 hour oxidation(Fig.8.c) at 450 ℃ in air. On the surface of the specimens oxidized for 30 hours, spherical particles (or crystals) are observed. This structure seems to do an important role in enhancing oxidation, that needs more detail analyses. The composition and structure of these particles are under examination. These particles totally disappear after a certain period of oxidation(Fig.7.c). LiOH are known to work as a mineralizer during corrosion in high temperature water[7]. LiOH makes the initial oxide layer very fine structure enough to oxidize abnormally fast. The fine grain of the oxide gives many fast paths for oxygen diffusion. As oxidation continues, columnar oxides start show up, and the oxidation rate decreases.

When LiOH is adsorbed on the oxide surface, the oxidation rate is rarely affected. LiOH crystals are observed on the surface of the specimen oxidized for 144 hours after adsorption (Fig.9.a). LiOH barely penetrates the oxide layer and stays on the surface, and evaporates. After 720 hour oxidation, LiOH particles are still observable (Fig.9.b). Hence, LiOH affects the oxidation of Zry only when it is adsorbed on the etched surface, and the enhanced oxidation is mainly due to the oxide structure initially formed.

NaF is the most powerful oxidation-enhancer among the adsorbates tested in the experiment. Fluorides were adsorbed on the oxide surface and reoxidized. There appear many cracks (and even spalling) on the surface of NaF-adsorbed specimen oxidized up to 108 hour(Fig.10.a). KF adsorbed specimen shows spalling at the oxide surface, but crack density seems lower than NaF-adsorbed one(Fig.10.b). Cl and F ions are known to make oxide very brittle. The diffusion of F in oxide is interrelated with cation movement. Assuming that only fluorine ion changes the oxide property, the diffusion rate of fluoride in oxide is the important factor controlling the oxidation rate of Zry. NaF seems diffuse faster in oxide than KF does. LiF on the oxide surface barely diffuses into oxide. Most LiF on the surface stays after enough time of oxidation (Fig.10.c), and LiF does not affect the oxidation of Zry.

V. CONCLUSION

The air-oxidation of Zry and the effects of adsorbates on the oxidation are found by the intermittent measurements of the weight gain of specimens. Pure Zircaloy air-oxidation results are almost identical to those of Suzuki and Kawasaki. NaCl enhances the oxidation of Zry, where nonuniform stresses on the oxide surface and Cl ions are the cause of cracks that make the enhancement of oxidation. LiOH also enhances the oxidation, where initial oxide structure formed by LiOH seems to the reason. Hence, LiOH adsorbed on the oxide layer does not affect the oxidation of Zry. The role of fluorides on the oxidation of Zircaloy is studied to see the effect of harmful dirt. NaF turned out to be most harmful adsorbate tested in the experiment, and KF follows after. LiF does not enhance the oxidation. F ion changes the oxide to be brittle. So, the diffusion of fluoride in oxide decides the degree of enhancement.

REFERENCES

1. A. B. Johnson, E.R.Gilbert, PNL-4835 (1983)
2. B. Cox, 'Oxidation of Zirconium and Its Alloy', in Advaces in Corrosion Science and Technology, Plenum Press (1976)
3. J. K. Dawson, G. Long, W. E. Seddonand and J. F. White, J. Nucl. Mater. 25, 179 (1968)
4. R.A.Ploc, J. Nucl. Mater. 82, 316 (1975)
5. F.Gazarolli, H.Seidel, R.Tricot and J.P.Gros, ASTM STP 1132, 395 (1991)
6. M. Suzuki and S. Kawasaki, J. Nucl. Mater. 140, 32 (1986)
7. N. Ramasubramanian, N. Precoanin, and V.C.Ling, ASTM STP 1023, 187 (1989)

Tabel 1. Kinetic constants for the oxidation of etched specimens

Temp(C)	n	K_n	t_t	ΔW_t	m	K_m
500	2.36	0.657	44.9	4.195	1.07	0.092
450	2.38	0.153	245.6	4.606	1.01	0.017
400	2.95	0.0321	-	-	-	-

Table 2. Kinetic constants for the oxidation of NaCl adsorbed specimens.

Temp(C)	n	K_n
500	2.32	0.123
450	2.14	1.78
400	2.04	13.9

Table 3. Kinetic constants for the oxidation of LiOH adsorbed specimens

Temp(C)	n	K_n	t_t	ΔW_t	m	K_m
500	1.42	2.59	9.2	9.2	4.1	963
400	1.44	0.56	32.8	8.0	5.1	1316

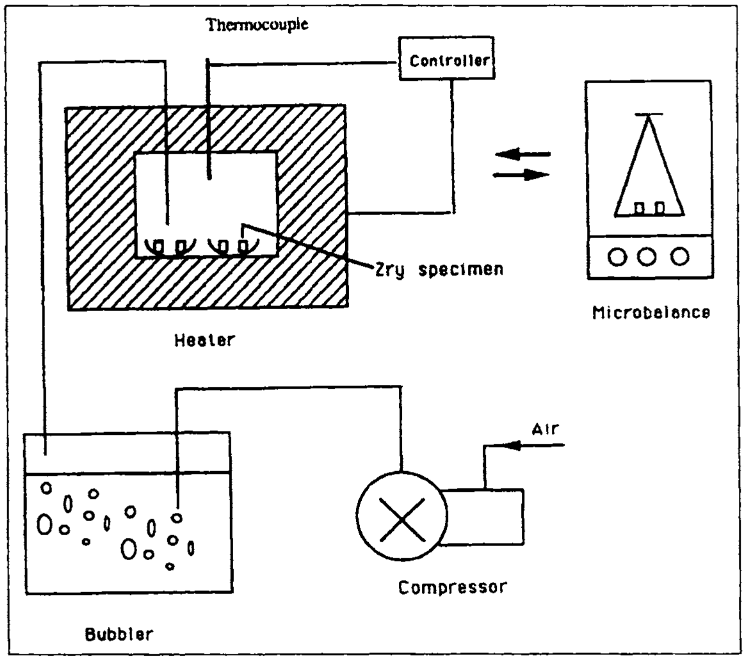

Figure 1. Expromental Diagram.

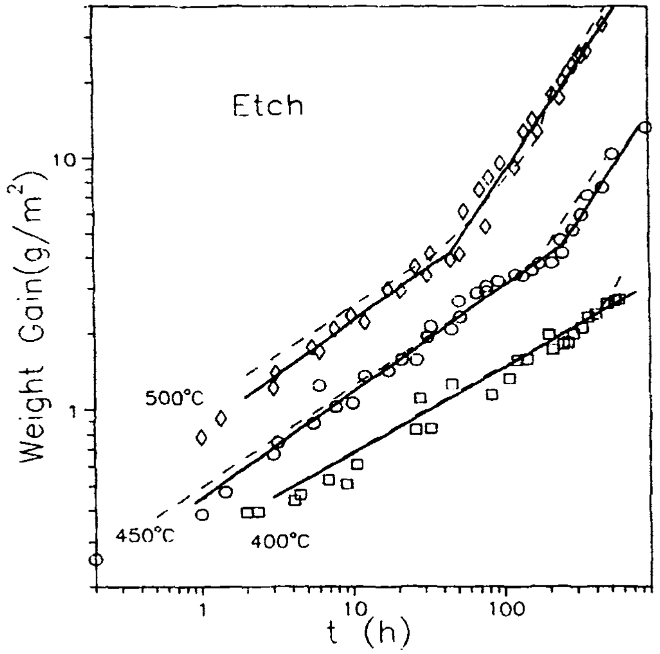

Figure 2. The weight gain of etched specimens.

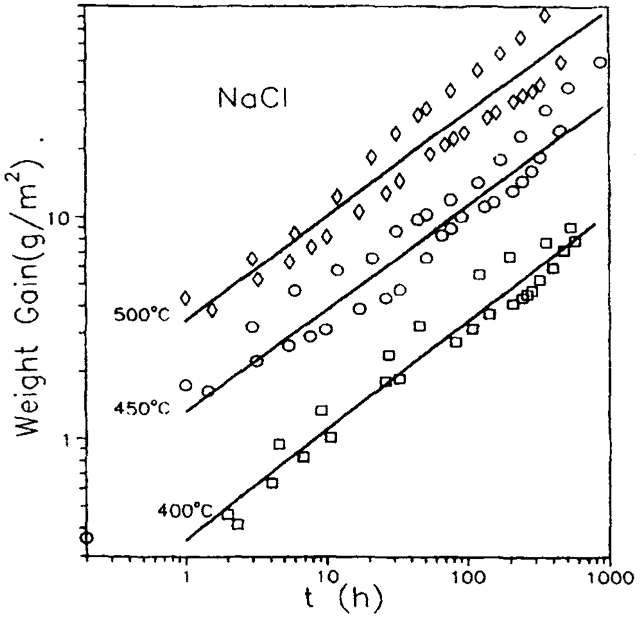

Figure 3. The weight gain of NaCl adsorbated specimens (adsorbed on the etched surface.)

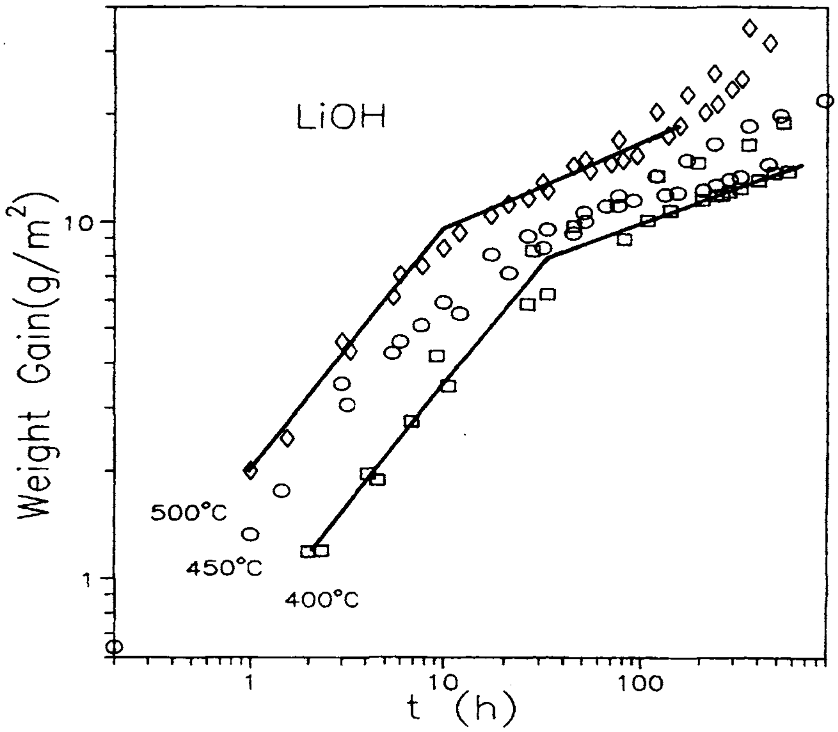

Figure 4. Weight gain of LiOH adsorbed specimens (adsorbed on the etched surface).

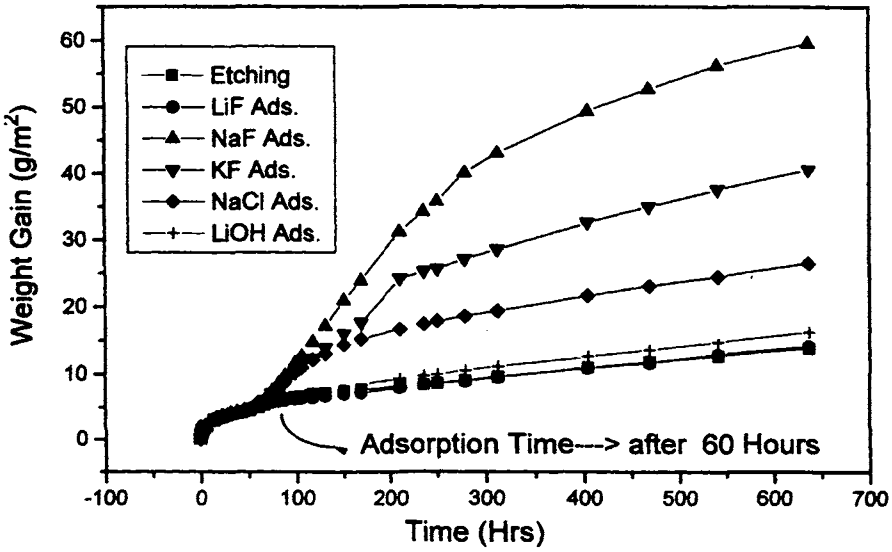

Figure 5. The effects of adsorbates on the oxidation of Zry (adsorbed on the oxide).

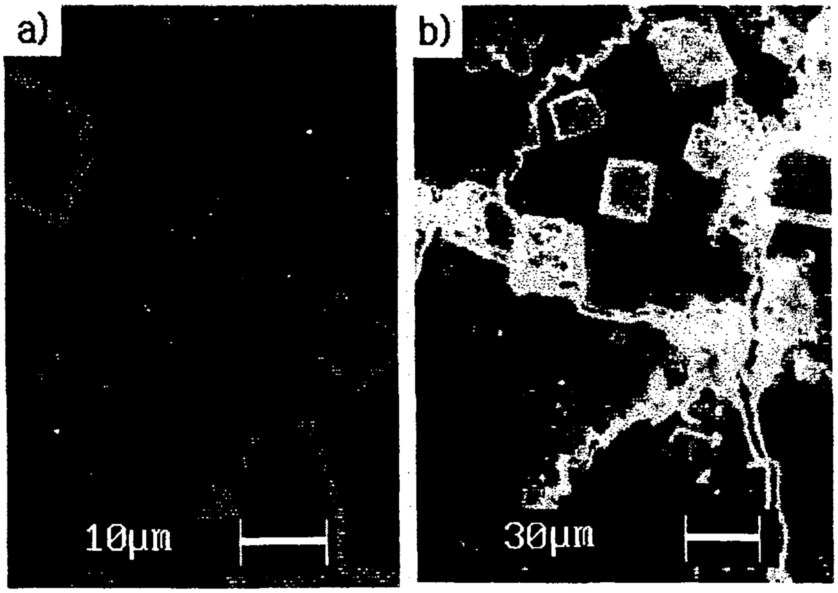

Figure 6. NaCl adsorbed Zry surface
a) just after adsorption
b) oxidized for 36 hours at 450℃

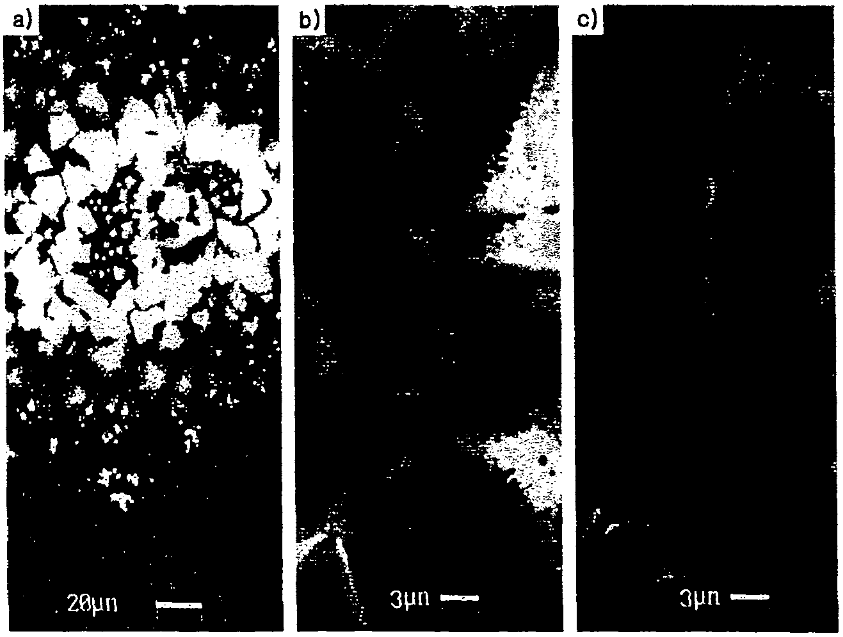

Figure 7. NaCl adsorbe on the oxide layer
a) 1 hour oxidation
b) 146 hour oxidation
c) 434 hour oxidation after adsorption.
Temperature is 450℃.

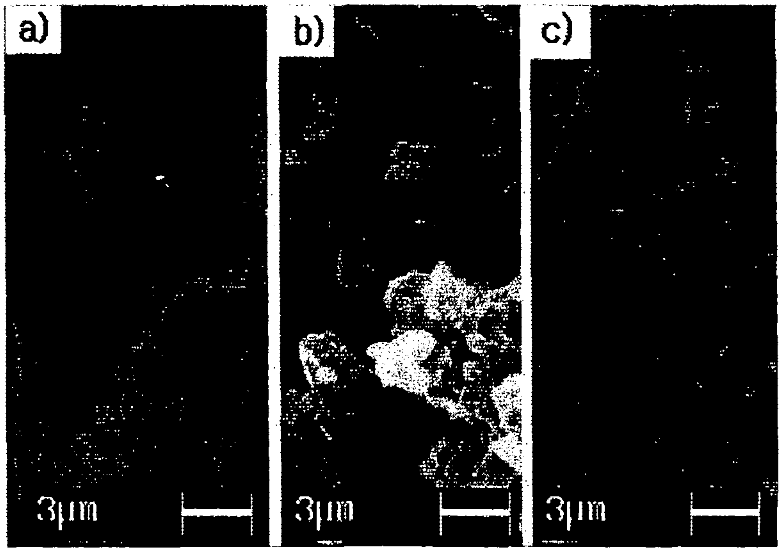

Figure 8. LiOH adsorbed Zry surface

a) just after adsorption

b) oxidized for 30 hours

c) oxidized for 736 hours. Temperature is 450℃.

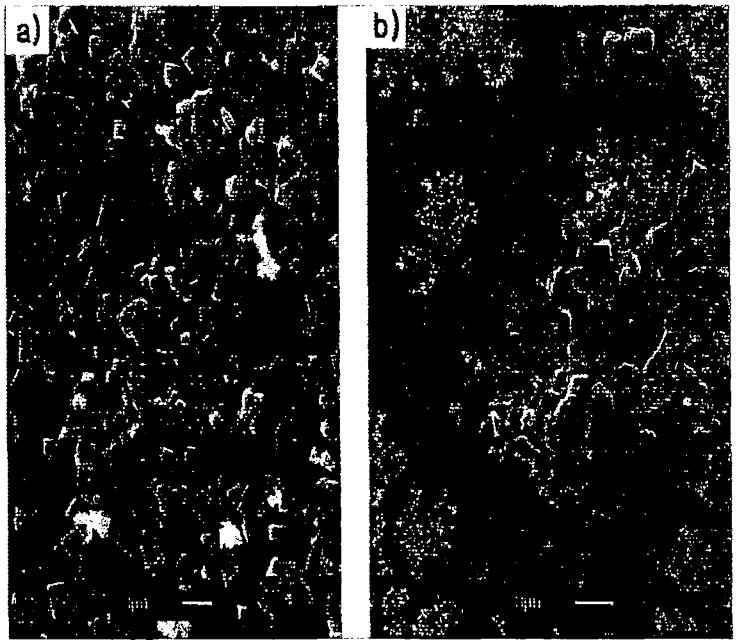

Figure 9. LiOH adsorbed on the oxide

a) 144 hour oxidized

b) 720 hour oxidized.

Temperature is 450℃