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# Localized Corrosion of Pure Zr and Zircaloy-4

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Zirconium based alloys have been extensively used as a cladding material for fuel rods in nuclear reactors, due to their low thermal neutron absorption cross-section, excellent corrosion resistance and good mechanical properties at high temperatures. However, a cladding material for fuel rods in nuclear reactors was contact water during long time at high-temperature, so it is necessary to improve the wear and corrosion resistance of the fuel cladding. At ambient environment, there are few data or paper on the characteristic of corrosion in chloride solution and acidic solution. The specimens used in this work are pure Zr and Zircaloy-4. Zircaloy-4 is a specific zirconium-based alloy containing, on a weight percent basis, 1.4% Sn, 0.2% Fe, 0.1% Cr. Pitting corrosion resistance of two alloys by ASTM G48 is higher than that of electrochemical method. Passive film formed on Zircaloy-4 is mainly composed of $ZrO_2$, metallic Sn, and iron species regardless of formation environments. Also, passive film formed on Zr alloys shows n-type semiconductic property on the base of Mott-Schottky plot.

***Keywords*** : *pure Zr, zircaloy-4, localized corrosion, CPT, Mott-Schottky plot, passive film, XPS*

## 1. Introduction

Zirconium based alloys have been extensively used as a cladding material for fuel rods in nuclear reactors, due to their low thermal neutron absorption cross-section, excellent corrosion resistance and good mechanical properties at high temperatures. However, a cladding material for fuel rods in nuclear reactors was contact water during long time at high-temperature, so it is necessary to improve the wear and corrosion resistance of the fuel cladding.[1)-3)]

At ambient environment, there are few data or paper on the characteristic of corrosion in chloride solution and acidic solution. The specimens used in this work are pure Zr and Zircaloy-4. Zircaloy-4 is a specific zirconium-based alloy containing, on a weight percent basis, 1.4% Sn, 0.2% Fe, 0.1% Cr. Corrosion tests in chloride and acid, and anodic polarization test are performed. Also, XPS analysis and Mott-Schottky plot are measured to elucidate the passive film.

## 2. Experimental

CPT (Critical Pitting Temperature) is measured in 6% $FeCl_3$ and in Green Death Solution (11.5% $H_2SO_4$ + 1.2% HCl + 1% $FeCl_3$ + 1% $CuCl_2$) on the base of ASTM G48 method.[4)] Acid corrosion rate is measured in 80°C, 80% $H_2SO_4$ and boiling 1.5% HCl solutions, and immersion time is 24 hrs.

Anodic polarization tests are performed in deaerated 1N HCl, 1N NaCl + 0.5N HCl, 1% NaCl, 3.5% NaCl, 5% $H_2SO_4$, 6% $FeCl_3$ solutions at room temperature using a Potentiostat (EG&G 273A). SCE is used as a reference electrode and graphite rod is used as a counter electrode.

To elucidate the semiconductic property of passive film, Mott-Schottky plot[5),6)] is measured using an electrochemical impedance system (Gamry, EIS 300). Testing solutions are deaerated 1% NaCl, 1% $H_2SO_4$, 5% $H_2SO_4$, and 0.05M $H_3BO_3$ + 1% $H_2SO_4$ at room temperature.

Also, XPS (X-ray Photoelectron Spectroscopy) analysis is done for the passive film. The passive films are formed by a 24 hrs immersion in 70°C, 6% $FeCl_3$, and a 1 hr passivation in 5% $H_2SO_4$ and 1N NaCl + 0.5N HCl and 6% $FeCl_3$ at room temperature.

## 3. Results and discussion

CPT measurement is mainly used to evaluate pitting corrosion resistance of stainless steels, and therefore high CPT means any material is resistant to chloride containing environments. CPT value is very useful to rate the grade of high corrosion resistant alloys at ambient environment.

Fig. 1 shows CPT values measured in (a) 6% $FeCl_3$

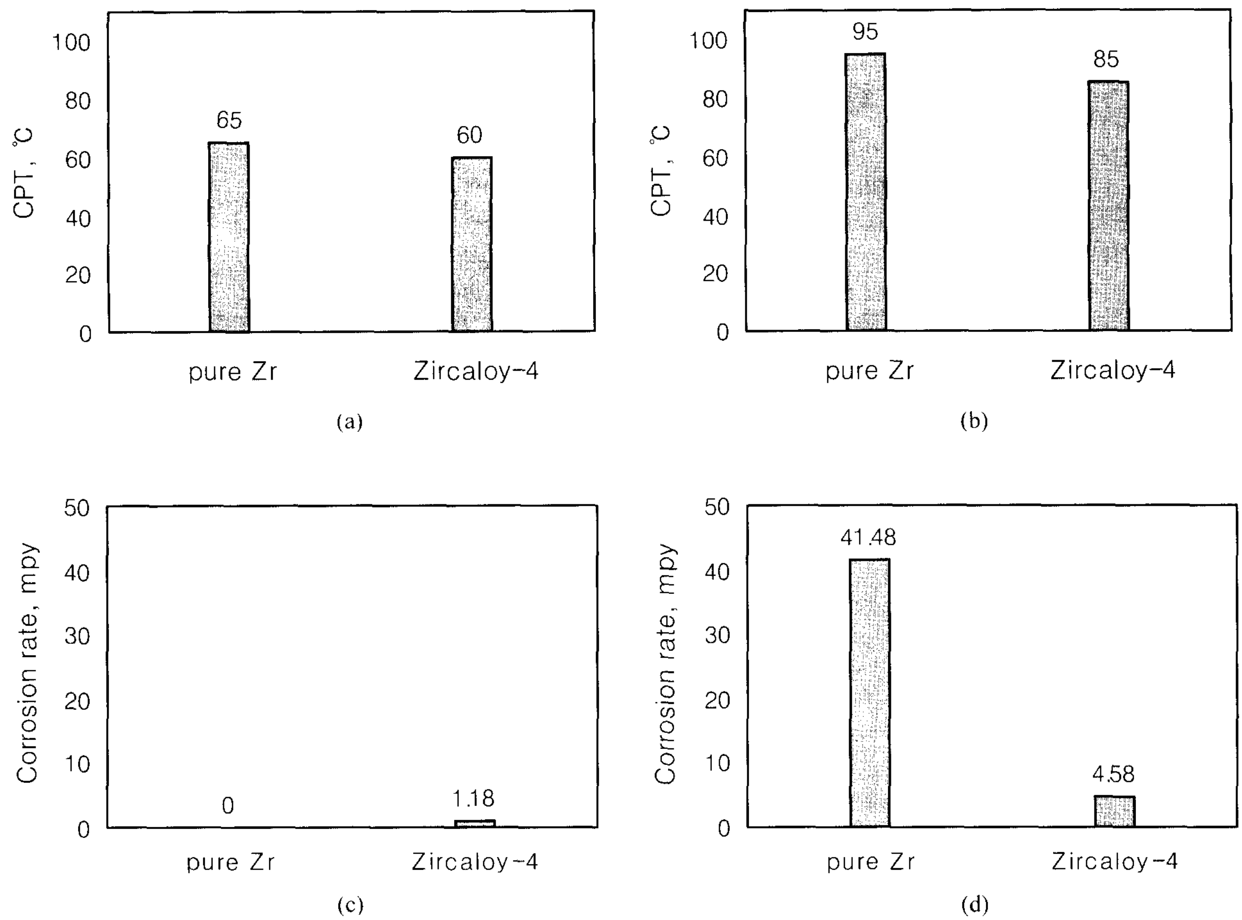


**Fig. 1.** Corrosion rate in (a) 6% $FeCl_3$, (b) Green Death Solution,(c) boiling 1.5% HCl, and (d) 80℃ 80% $H_2SO_4$

and in (b) Green Death Solution (11.5% $H_2SO_4$ + 1.2% HCl + 1% $FeCl_3$ + 1% $CuCl_2$) on the base of ASTM G48 method.[4] In case of pure Zr, CPTs are 95 and 65℃ respectively. In case of Zircaloy-4, CPTs are 85 and 60℃. These CPTs is very high value and then we can imagine these materials will be resistant to chloride environments.

Also, acid corrosion rates are measured in (c) boiling 1.5% HCl and (d) 80℃, 80% $H_2SO_4$. Two alloys show the excellent corrosion resistance to a hydrochloric acid, but reveal relatively high corrosion rate in a sulfuric acid.

Fig. 2 shows anodic polarization curves of pure Zr and Zircaloy-4 in (a) 1.5N HCl, (b) 1N NaCl + 0.5N HCl, (c) 1% NaCl, (d) 3.5% NaCl, (e) 5% $H_2SO_4$, (f) 6% $FeCl_3$ at room temperature. Scanning rate is 1 mV/sec, and test solutions are deaerated using a nitrogen gas before test. In a sulfuric acid, good passivity is obtained and oxygen evolution doesn't occur to 1.5 V(SCE).

However, in the other chloride solutions, pitting corrosion occurs and then passive film breaks and current density sharply increases with potential sweep. In many cases, pitting potential is in the range of +200 ~ +400 mV(SCE).

In neutral chloride solution (1 ~ 3.5% NaCl), Type 304 and Type 316 show pitting potential of 150 and 300 mV(SCE) and these are similar to those of pure Zr and Zircaloy-4. However, CPT of Type 304 and Type 316 is 20℃ and 30℃ respectively,[7] but pure Zr and Zircaloy-4 show 95℃ and 85℃ respectively. Also, it should be noted that pitting potential of pure Zr and Zircaloy-4 is higher than that of Type 304 and Type 316 in acidic chloride solutions.

Some stainless steels show the higher pitting potential than pure Zr and Zircaloy-4 in a neutral and acidic chloride solution, but CPT of the former is largely low value.[8),9)] How can this behavior arise? Therefore, XPS measurement is analyzed

Passive film for XPS is formed as follows; (a) passivation(+200 mV(SCE)) in 5% $H_2SO_4$ during 1 hr at room temperature, (b) immersion in 6% $FeCl_3$ during 24 hrs at 70℃, (c) passivation(-200 mV(SCE)) in 1 NaCl + 0.5N

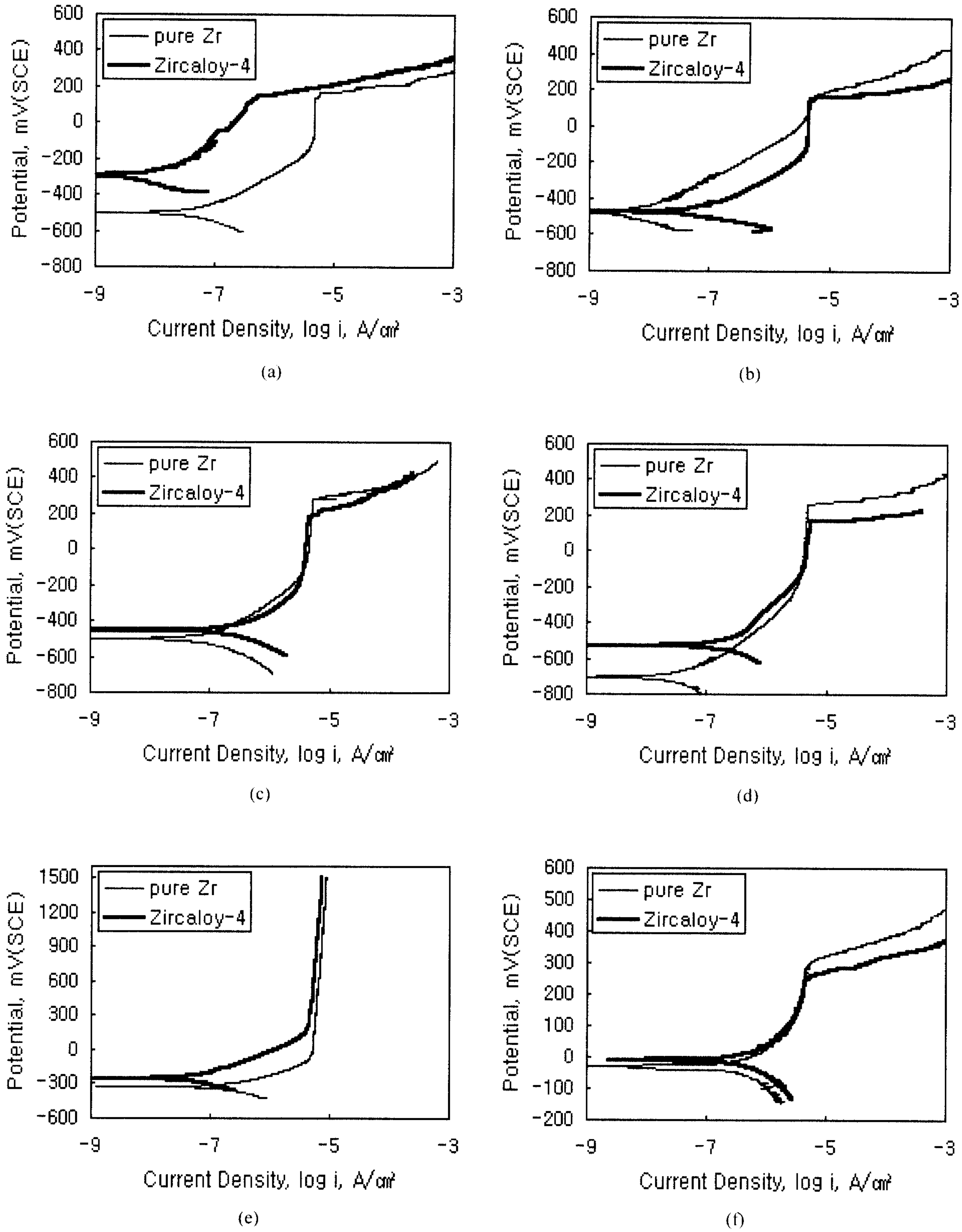


**Fig. 2.** Anodic polarization curves in (a) 1.5N HCl, (b) 1N NaCl + 0.5N HCl, (c) 1% NaCl, (d) 3.5% NaCl, (e) 5% $H_2SO_4$, (f) 6% $FeCl_3$ at room temperature

HCl during 1 hr at room temperature, (d) passivation(+100 mV(SCE)) in 6% $FeCl_3$ during 1 hr at room temperature.

Fig. 3. shows Zr 3d spectra. Take-off angle is 15°. As shown in fig., Zr in passive film exists as only $ZrO_2$. In stainless steels, metallic elements as Fe, Cr, Mo, W exist as oxide, metallic, and ionic states.[10),11)]

Fig. 4 shows Sn 3d spectra. Sn in passive film exists mainly as metallic state. Unknown peaks detect near Sn 3d peaks, but tin oxide also exists.

Fig. 5 shows Fe 3p spectra. Binding energies of iron species overlap those of tin species. Iron exists as metallic, oxides, and sulfate states. However, iron species come from two sources as like metallic element and test solution (especially, in ferric chloride solution).

Table 1 summarized iron species and the ratio of [$Fe^{2+}$ + $Fe^{3+}$]/ Fe(M). In case of sulfuric solution, this ratio is very high because of good passivity as shown in Fig. 2e. In case of acidic chloride solution, the ratio is very low among 4 conditions. In case of ferric chloride solution, iron peaks come from the matrix and the solution, and this ratio means the overlapped iron content. When passive film is formed by the immersion in ferric chloride solution, the ratio is 1.28. When passive film is formed by the electrochemical passivation, the ratio is 0.75. Thus, it is considered this ratio may explain the difference between CPT and pitting potential of Zr alloys.

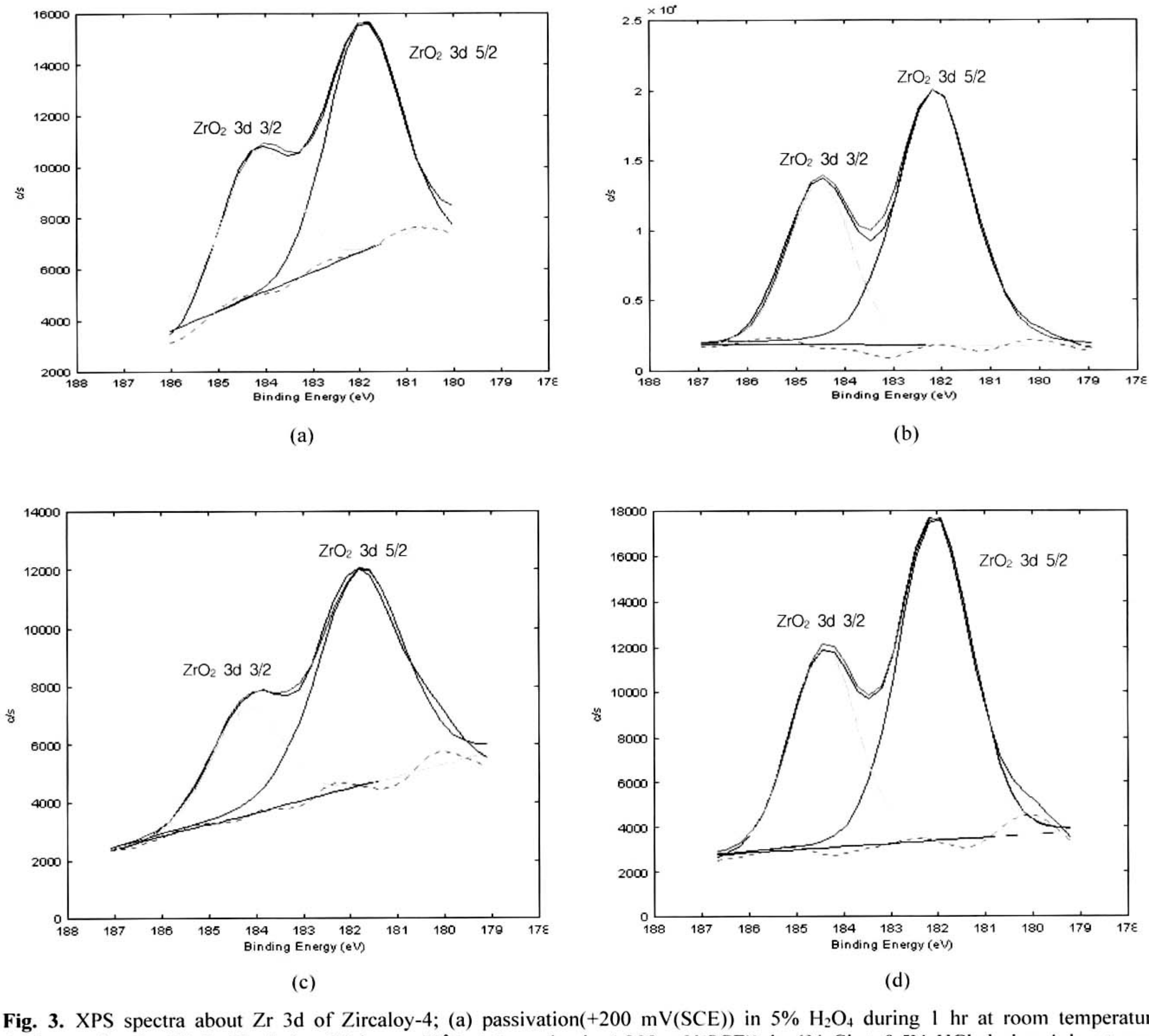


**Fig. 3.** XPS spectra about Zr 3d of Zircaloy-4; (a) passivation(+200 mV(SCE)) in 5% $H_2O_4$ during 1 hr at room temperature, (b) immersion in 6% $FeCl_3$ during 24 hrs at 70°C, (c) passivation(-200 mV(SCE)) in 1NaCl + 0.5N HCl during 1 hr at room temperature, (d) passivation(+100 mV(SCE)) in 6% $FeCl_3$ during 1 hr at room temperature

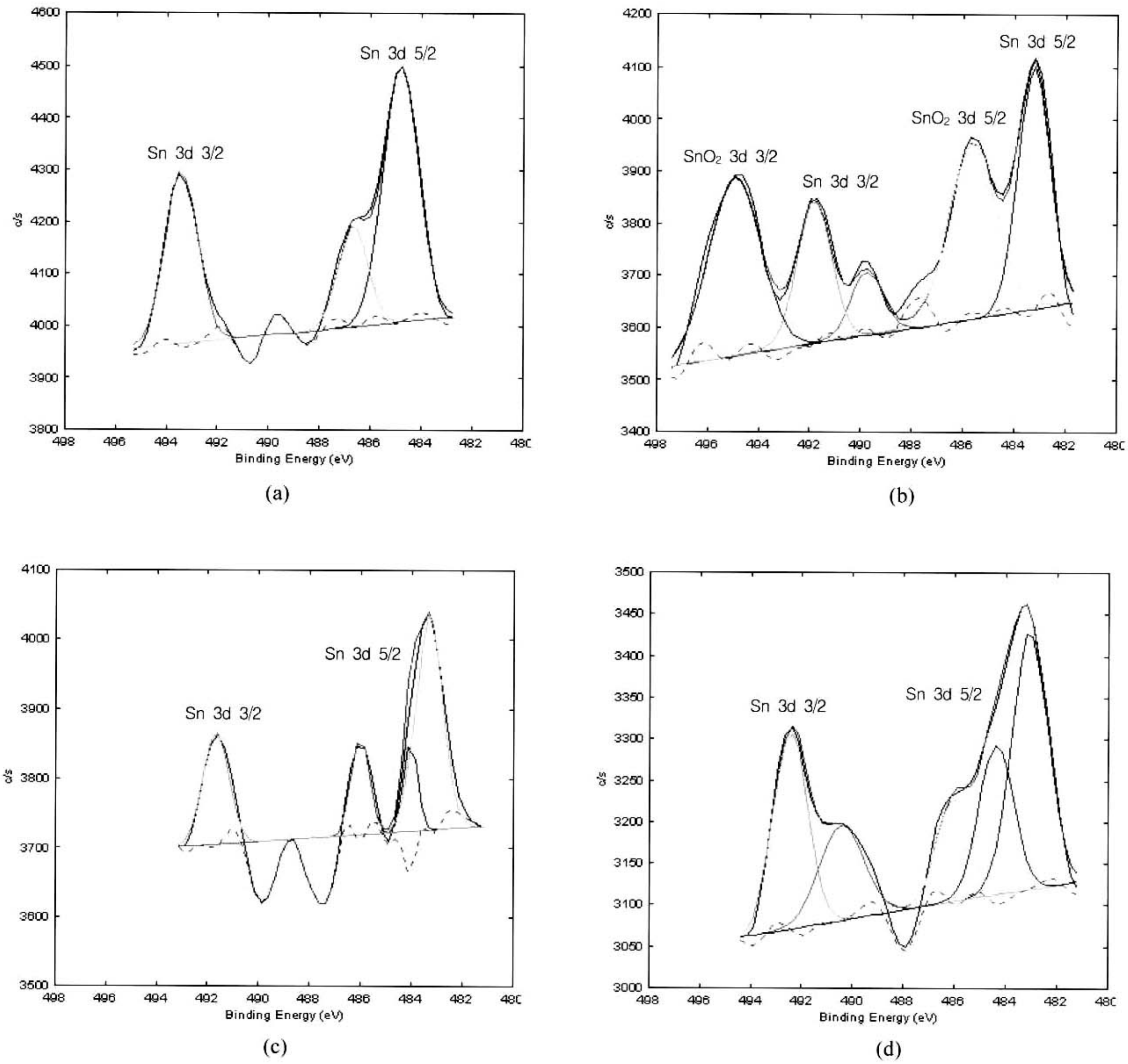


**Fig. 4.** XPS spectra about Sn 3d of Zircaloy-4; (a) passivation(+200 mV(SCE)) in 5% $H_2SO_4$ during 1 hr at room temperature, (b) immersion in 6% $FeCl_3$ during 24 hrs at 70°C, (c) passivation(-200 mV(SCE)) in 1NaCl + 0.5N HCl during 1 hr at room temperature, (d) passivation(+100 mV(SCE)) in 6% $FeCl_3$ during 1 hr at room temperature

**Table 1. Effect of Testing Condition on Area Ratio between ionic Fe and metallic Fe**

| | $Fe^{2+}$+$Fe^{3+}$ | Fe (M) | [$Fe^{2+}$ + $Fe^{3+}$]/ Fe(M) |
|---|---|---|---|
| Passivation in 5% $H_2SO_4$ | 251 | 115 | 2.18 |
| Immersion in 6% $FeCl_3$ | 451 | 353 | **1.28** |
| Passivation in 1N NaCl + 0.5N HCl | 28 | 49 | 0.57 |
| Passivation in 6% $FeCl_3$ | 1026 | 1369 | **0.75** |

Fig. 6 shows Mott-Schottky plot for passive state in (a) 1% NaCl (-100 mV(SCE)), (b) 5% $H_2SO_4$ (+500 mV(SCE)), (c) 1% $H_2SO_4$ (+500 mV(SCE)), (d) 0.05M $H_3BO_3$ + 1% $H_2SO_4$ (+200 mV(SCE)) at room temperature and passivation time is 1 hr. In all environments, passive film has a n-type semiconductic properties, and the slope is changed with the solutions and flat band potential also is changed with the solutions.

According to the result of N. E. Hakiki et al.[6], the slope is changed with the passivation conditions but flat band potential is constant in case of AISI 304 in pH 9.2, (0.05 M) $H_3BO_3$ + $Na_2B_4O_7$, 10 $H_2O$ (0.075 M). When iron adds to pure chromium, donor and acceptor concentration, and flat band potential also are changed. Many researches are

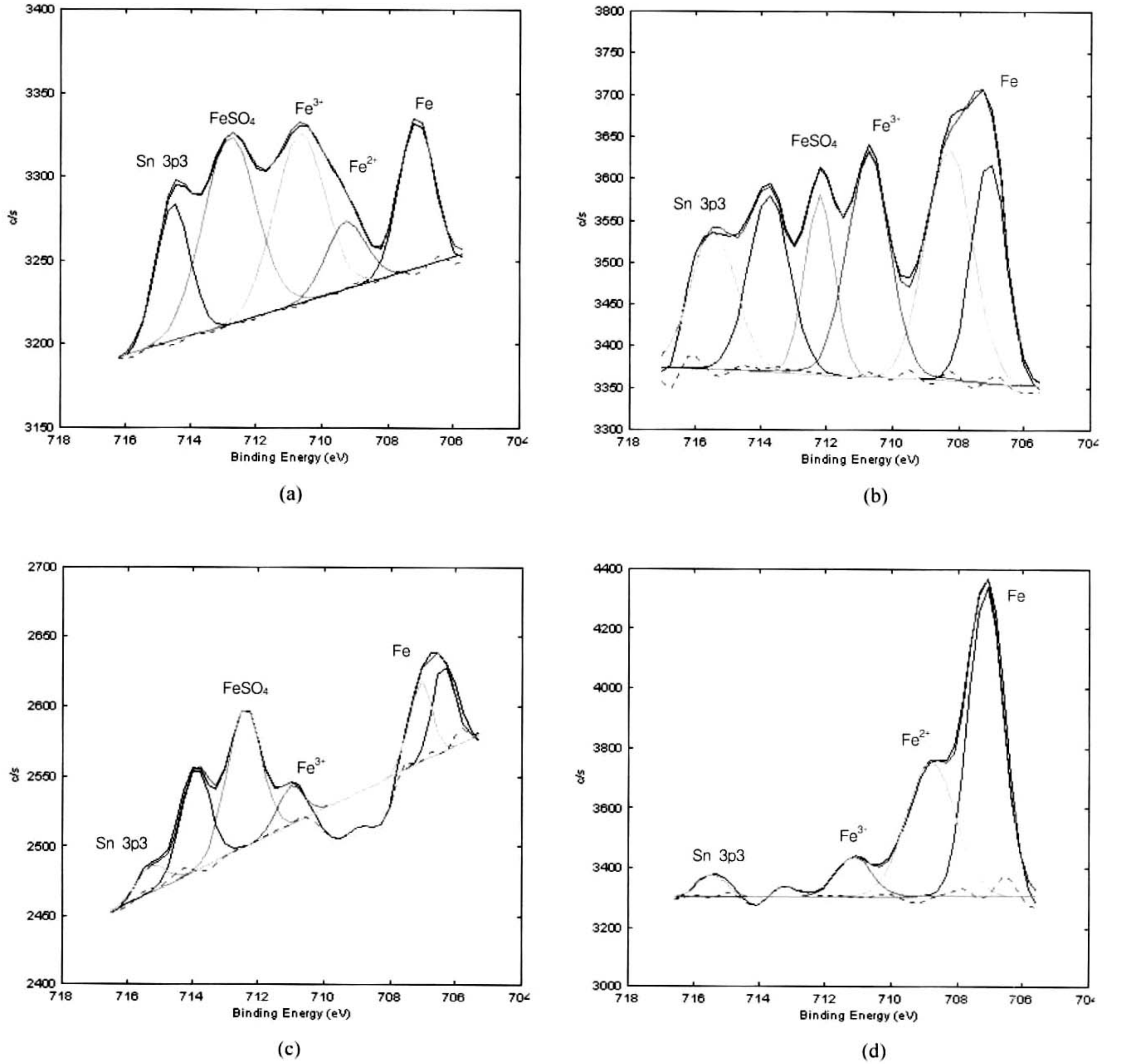


**Fig. 5.** XPS spectra about of Zircaloy-4; (a) passivation(+200 mV(SCE)) in 5% $H_2SO_4$ during 1 hr at room temperature, (b) immersion in 6% $FeCl_3$ during 24 hrs at 70℃, (c) passivation(-200 mV(SCE)) in 1NaCl + 0.5N HCl during 1 hr at room temperature, (d) passivation(+100 mV(SCE)) in 6% $FeCl_3$ during 1 hr at room temperature

done in boric solutions and the relationship between Mott-Schottky parameters and corrosion resistance is not clear. Therefore, further study should be proceeded.

## 4. Conclusions

Pitting corrosion resistance of pure Zr and Zircaloy-4 in 6% $FeCl_3$ and in Green Death on the base of ASTM G48 method is high, but electrochemical pitting resistance is relatively not high in anodic polarization tests.

In passive film, zirconium exists as only $ZrO_2$ state, tin exists as mainly metallic state, and iron exists as metallic and oxide states.

Passive film formed on Zircaloy-4 in 4 kinds of solutions shows an n-type semiconductic property, and the slope is changed and flat band potential is changed with the solutions.

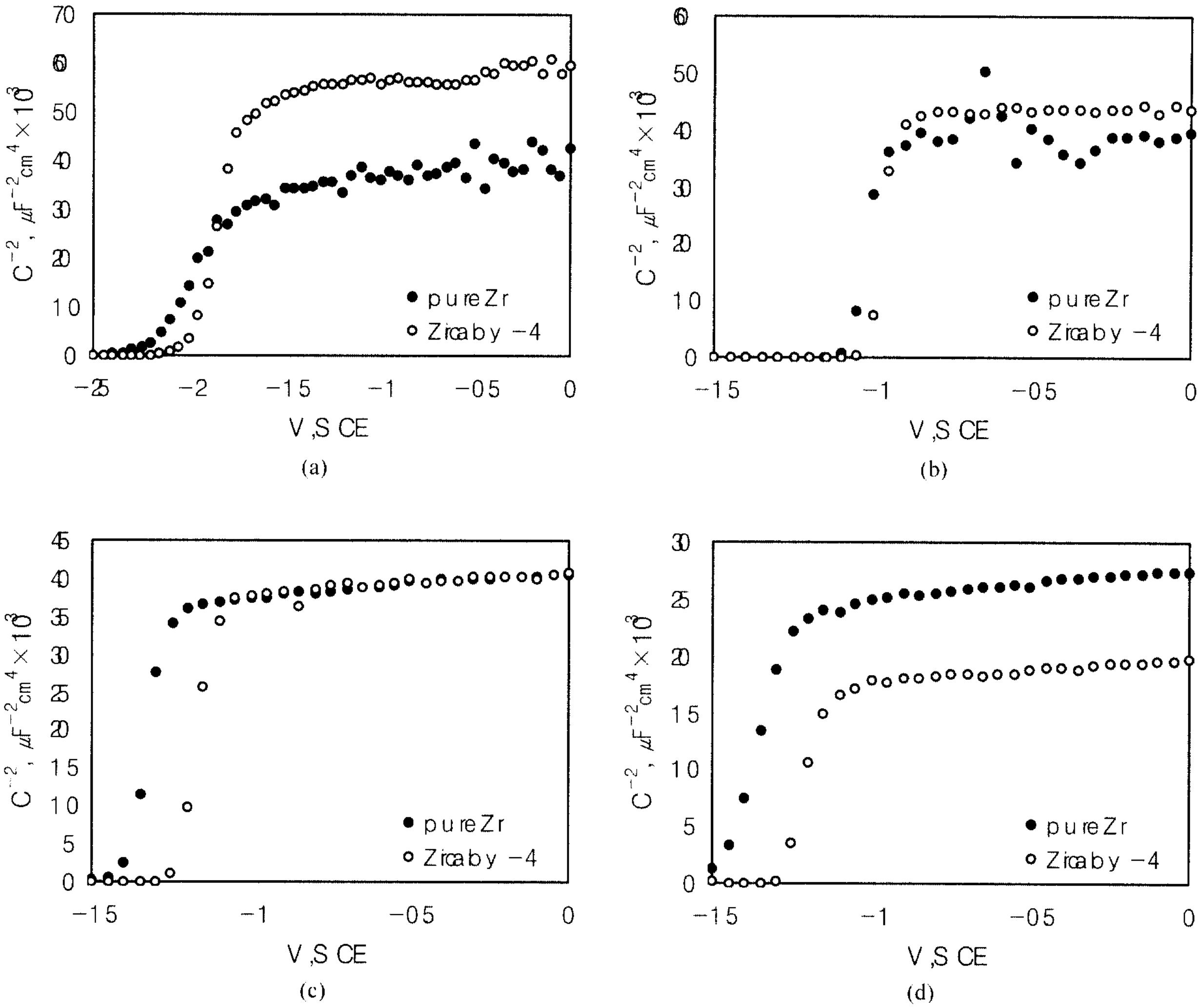


**Fig. 6.** Mott-Schottky plot for passive state in (a) 1% NaCl (-100 mV(SCE)), (b) 5% $H_2SO_4$ (+500 mV(SCE)), (c) 1% $H_2SO_4$ (+500 mV(SCE)), (d) 0.05M $H_3BO_3$ + 1% $H_2SO_4$ (+200 mV(SCE)) at room temperature (passivation time; 1 hr)

## References


1. Y. H. Jeong, in Study on Phase Transformation Behavior and Nodular Corrosion Characteristics of Zircaloy-4 Alloy, Ph. D. Dissertation, The Graduate School, Yonsei University, (1991).
2. H. G. Kim, M. H. Lee, S. Y. Park, Y. H. Jeong, and M. Y. Wey, *The Korean Institute of Metals and Materials*, **37**, 11, 1399 (1999).
3. S. J. Lee, H. S. Kwon, and J. S. Kim, *Metals and Materials*, **6**, 2, 145 (2000).
4. ASTM G 48, 'Standard Test Methods for Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloy by the Use of Ferric Chloride Solution', Annual Book of ASTM Standards Vol. 03.02, Philadelphia, PA, USA, 1992
5. N. E. Hakiki and M. Da Cunha Belo, *J. Electrochemical Society*, **143**, 10, 3088 (1996).
6. N. E. Hakiki, S. Boudin, B. Rondot, and M, Da Cunha Belo, *Corrosion Science*, **37**, 11, 1809 (1995).
7. Product Catalog, URANUS® 45N, A 22Cr 3Mo Duplex stainless Steel with PREN≥33 or 34, Crensot-Liore Industrie, France
8. Y. S. Kim and J. Kim, 'Synergistic effect of W and Mo addition on the pitting resistance of super ferritic stainless steels', *1998 Gordon Research Conference on Aqueous Corrosion*, **I-23**, Colby-Sawyer College, New London, NH, USA (1998).
9. Y. S. Kim, Y. S. Park, B. Mitton and R. Latanision, *Proceedings of the symposium on critical factors in localized corrosion III*, R.G. Kelly, G.S. Frankel, P.M. Natishan, and R.C. Newman (eds.), p.89 (1998).
10. Y. S. Kim, B. Mitton and R. Latanision, *Proceeding of The Korean Electrochemical Society Spring Meeting*, p.35 (1999).
11. Y. S. Kim and H. Y. Jang, *Proceeding of 196th Meeting of The Electrochemical Society*, Hawaii, p.513 (1999).