

Effect of H_2O_2 on the Corrosion Behavior of 304L Stainless Steel

Taek Ho Song and In Sup Kim
Korea Advanced Institute of Science and Technology

Sung Ki Rho
Korea Atomic Energy Research Institute
(Received September 27, 1994)

H_2O_2 가 304L 스테인리스강의 부식거동에 미치는 영향

송택호 · 김인섭
한국과학기술원

노성기
한국원자력연구소
(1994. 9. 27 접수)

Abstract

In connection with the safe storage of high level nuclear waste, effect of H_2O_2 on the corrosion behavior of 304L stainless steel was examined. Open circuit potentials and polarization curves were measured with and without H_2O_2 . The experimental results show that H_2O_2 increased corrosion potential and decreased pitting potential. The passive range, therefore, decreased as H_2O_2 concentration increased, indicating that pitting resistance was decreased by the existence of H_2O_2 in the electrolyte. These effects of H_2O_2 on corrosion of 304L stainless steel are considered to be similar to those of γ -irradiation. To compare the effects of H_2O_2 with those of O_2 , cathodic and anodic polarization curves were made in three types of electrolyte such as aerated, deaerated, and stirred electrolyte. The experimental results show that the effects of H_2O_2 on the corrosion behavior were very similar to those of O_2 such as increase of corrosion potential, decrease of pitting resistance, and increase of repassivation potential. In acid and alkaline media, the corrosion potential shifts by H_2O_2 were restricted by the large current density of proton reduction and by the le Chatelier's principle respectively.

요 약

사용후 핵연료 저장구조재의 구조적 안정성과 관련해서, 감마선 조사 생성물로 알려져 있는 H_2O_2 를

전해질에 주입시키었을 때, H_2O_2 가 저장구조체인 304L 스테리스강의 부식거동에 어떤 영향을 미치는가를 조사하였다. 실험결과, H_2O_2 는 304L 스테리스강의 부식전위를 상승시키고 pitting 전위를 감소시킴으로써 부동태 영역을 줄이고 pitting 저항성을 감소시키는 것으로 나타났다. 이는 감마선 조사에 의한 부식거동 변화와 유사한 결과라고 볼 수 있으며, 또한 산소농도증가에 의한 부식거동 변화와 유사한 결과로 해석되었다. 채부동태형성전위가 H_2O_2 의 존재로 증가하는데, 이로써 응력부식균열임계전위는 약간 상승할 것으로 추론되었다. 그러나, H_2O_2 농도가 $6.3 \times 10^{-6}M$ 이하로 떨어질 경우, H_2O_2 는 부식거동에 영향을 주지 못했다. 이는 대기압상태에서 용존된 O_2 환원반응속도에 비해 H_2O_2 환원반응속도가 작기 때문이라고 해석되었다. 중성용액보다 산성 및 염기성 용액에서, H_2O_2 가 부식거동에 미치는 영향이 작아졌는데, 이는 산성용액에서는 높은 H^+ 농도 때문에, 염기성용액에서는 le Chatelier의 원리 때문인 것으로 해석되었다.

1. Introduction

The safe disposal of high level nuclear waste materials in geological media requires barrier packages that must be environmentally stable for time periods of 300-1000 years. In connection with this development of barrier package, many studies have been devoted to the corrosion of austenitic stainless steel and titanium.

Glass[1] reported that corrosion potential shift of austenitic stainless steel in the positive direction and decreased pitting resistance were observed under gamma irradiation. He suggested that these results be associated with the radiation-induced production of hydrogen peroxide.

According to Saito's paper[2], IGSCC of 304 stainless steel was accelerated by gamma-ray irradiation under normal water chemistry.

Oriani[3, 4] have studied Grade 12 titanium under gamma-radiation and reported that radiolytically produced hydrogen peroxide plays an important role in determining the corrosion condition in the irradiated solution.

Lin and others[5-7] have studied on the corrosion potential of austenitic stainless steel in connection with SCC of piping materials and referred to H_2O_2 as an important parameter determining corrosion potential of austenitic stainless steel.

The interaction of gamma radiation with aqueous solution produces a host of transient radicals, ion

and stable molecular species including $-H$, $-OH$, e_{aq}^- , H_2O^+ , OH^- , H_2 , H_2O_2 , O_2 , O_2^- and HO_2^- [8-10].

According to the recent paper of Lin[11], H_2O_2 is one of the stable products radiolytically produced in the boiling water reactor(BWR) coolant. And understanding the chemical properties of hydrogen peroxide has become an important factor in dealing with material corrosion problems in the radiation environment.

In this paper, H_2O_2 has been chosen as an experimental variable to simulate gamma-irradiation effects on corrosion of as-received 304L stainless steel that was selected as a canister material at Korea Atomic Energy Research Institute. To find out the effect of H_2O_2 on the corrosion behavior of 304L stainless steel, open circuit potential and polarization curve measurements were carried out. Pitting resistance was analyzed in terms of passive range with and without H_2O_2 . These results were compared with those of gamma-irradiation. The comparisons of the effects of H_2O_2 on corrosion with those of O_2 and H^+ were made to compare the degree and direction of corrosion behavior changes with the other oxidants. In various pH conditions, corrosion potential shifts were investigated and discussed with H^+ reduction reaction.

2. Experimental Procedure

Austenitic stainless steel AISI 304L, which is spent

Table 1. Chemical composition of Test Specimens.

Comp.	Fe	C	Fr	Ni	Mo	Mn	Si	P	S	N	Cu
wt.%	Bal.	0.016	18.27	10.05	0.070	1.090	0.650	0.025	0.001	0.041	0.210

fuel storage canister material, was used as a flat specimen, and the composition of the alloy is given in Table 1. The specimen was polished before immersion with 240 grit SiC paper, followed by 320, 400, 600 SiC paper, 1 μ Al₂O₃ paste and 1 μ diamond paste.

Fig. 1 [12] shows that the steady state concentration of hydrogen peroxide has a certain limit. When the radiation intensity is above 1.0×10^{20} eV/cm³, the H₂O₂ concentration becomes a saturation value of 1.0×10^{-3} M/liter approximately.

In regard to Fig. 1, H₂O₂ concentration was selected to be about 10^{-4} M range. In order to find out the minimum concentration of H₂O₂ for making potential shift of 304L stainless steel, 10^{-4} M, 10^{-5} M, 10^{-6} M, and 10^{-7} M range of H₂O₂ concentrations were examined. To compare H₂O₂ reduction reaction with H⁺ reduction reaction, various pH conditions of

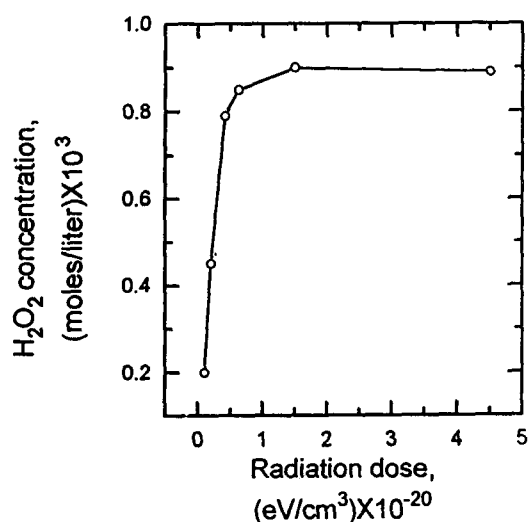


Fig. 1. Accumulation of Hydrogen Peroxide During the Irradiation of Water Saturated with Oxygen. (Ref. 12.)

test solutions were made by using H₂SO₄ and NaOH.

Fig. 2 shows block diagram of the experimental apparatus.

Scanning potentiostat, EG & G Model 362, controls potential between working electrode and reference electrode. And it receives the controlled potential, open circuit potential from the cell, and current between working electrode and counter electrode. All these analog outputs of potentiostat were transformed into digital signals by way of analog digital converter and the transformed digital signals were read in the personal computer screen.

With stirrer and nitrogen gas, three electrode con-

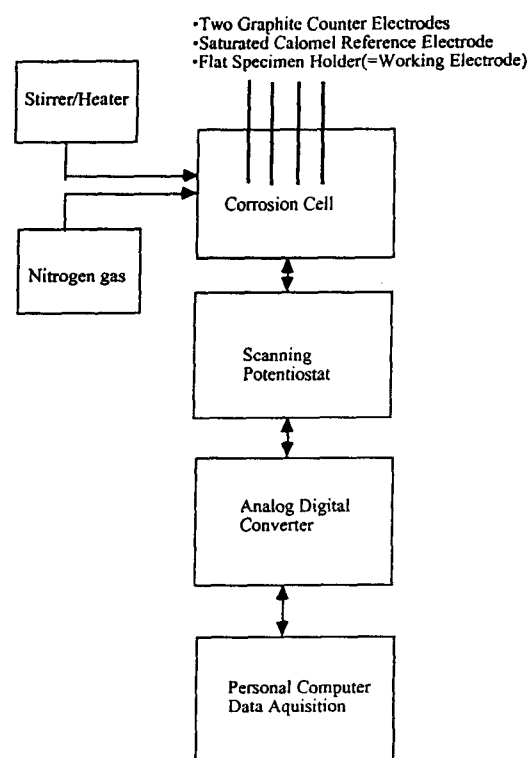


Fig. 2. Block Diagram of the Experimental Apparatus.

ditions were generated such as aerated, deaerated, and stirred condition. Stirred condition was made by stirring electrolyte continuously with magnetic spin bar. Deaerated condition was made by blowing nitrogen gas into the cell with the constant flow rate of 200cc/min.

$1.3 \times 10^{-4} \text{M}$ H_2O_2 dropping into the cell was made by dropping $10 \mu\text{l}$ of 30% H_2O_2 into the electrolyte composed of 1 liter solution which had been stirred continuously with magnetic spin bar.

3. Results and Discussion

3.1. Potential Shift by H_2O_2

Potential shift: Fig. 3 shows that initial one drop of H_2O_2 makes 120mV potential shift in the noble direction in open circuit potential and that successive equal H_2O_2 additions produce successively smaller potential shifts than the initial addition does, which indicates a tendency toward an eventual saturation effect.

When the temperature increased from room tem-

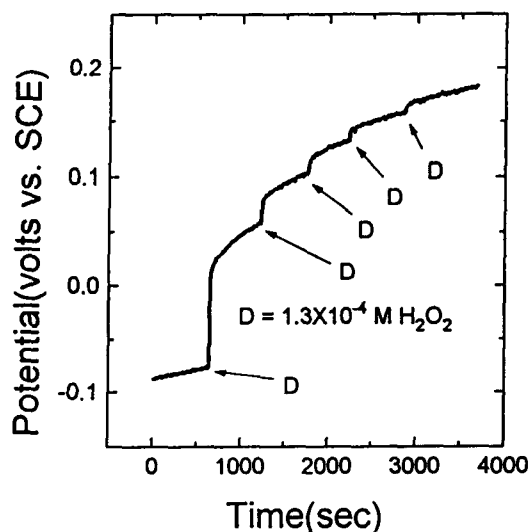


Fig. 3. Effect of H_2O_2 Addition on the Open Circuit Potential in Stirred 0.02M NaCl Solution.

perature to 52°C , the amount of potential shift increased slightly. It is thought to be due to the increased diffusion rate of H_2O_2 .

Permanent change of oxide layer: In order to find out whether these observed potential shifts were passing phenomena with the existence of H_2O_2 or whether permanent change of oxide layer was made with H_2O_2 reduction reaction, subsequent immersion test in Fig. 4 was carried out.

This test showed that H_2O_2 made permanent change in the oxide layer. Specimens that had been immersed in the 0.02M NaCl with various H_2O_2 concentrations for 9000 sec were taken out of the 0.02M NaCl + xM H_2O_2 , cleaned with acetone and distilled water, and then reimmersed in fresh 0.02M NaCl. Fig. 4 shows that with increasing H_2O_2 concentrations in the previous 0.02M NaCl, increasingly noble open circuit potentials are developed on subsequent immersion in 0.02M NaCl. It is clear that H_2O_2 prod-

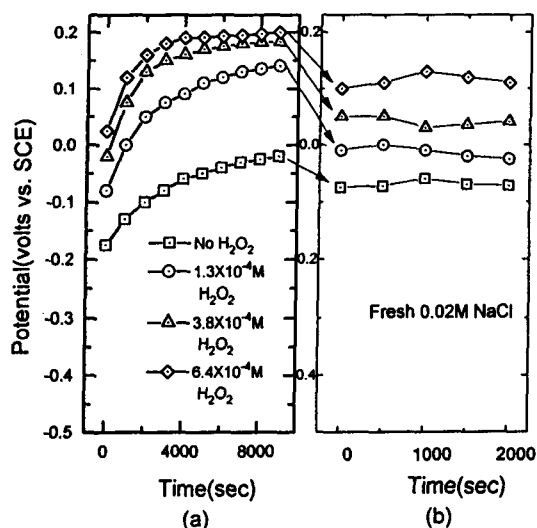
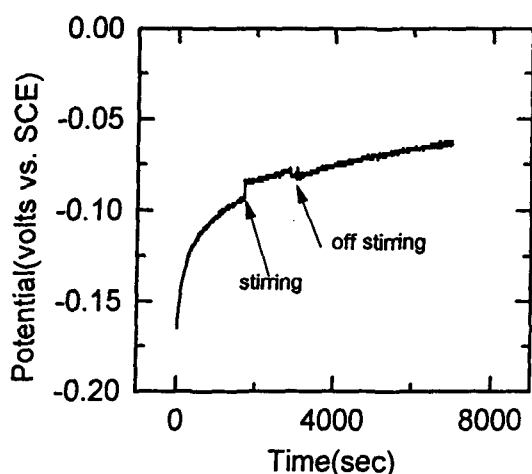


Fig. 4. (a) Open Circuit Potential in 0.02M NaCl with Various Hydrogen Peroxide Concentration. (b) Subsequent Immersion of (a) Specimens into fresh 0.02M NaCl Solution (= Without Hydrogen Peroxide) After 5 Minute Ultrasonic Cleaning of the Specimens in Acetone and Distilled Water.

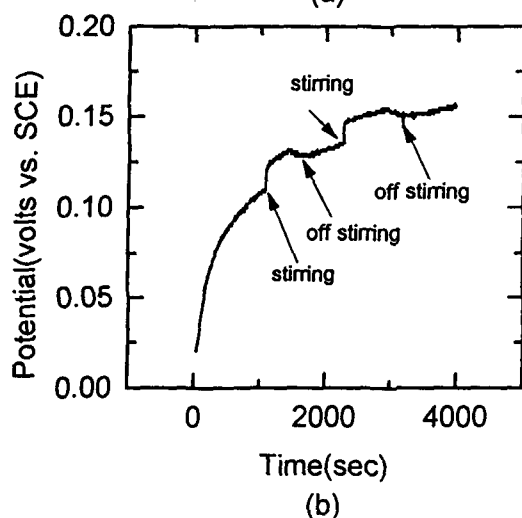
uces a change in the oxide that persists to modify the open circuit potentials in the fresh 0.02M NaCl. This result is in good agreement with the result of gamma-irradiation[1].

Stirring effect: Fig. 5-a shows that when the electrolyte was stirred the potential shift could be generated by increased O_2 concentration on the surface of the specimen.

When $3.8 \times 10^{-4}M$ H_2O_2 was put into the 0.02M



(a)



(b)

Fig. 5. Effect of Stirring on the Corrosion Potential in 0.02M NaCl, (a) Without H_2O_2 , (b) with $3.8 \times 10^{-4}M$ H_2O_2 .

NaCl (Fig. 5-b), the potential shift by stirring was larger than the previous shift in Fig. 5. a. This is thought to be due to H_2O_2 reduction rate increase by stirring.

Minimum concentration for potential shift and the dependence of potential shift on $\log[H_2O_2]$: Potential shifts by H_2O_2 became smaller when the concentration of H_2O_2 was reduced. This is shown in Fig. 6.

The potential shift, ΔE , represents the corrosion potential change by H_2O_2 . In the H_2O_2 concentration range of $10^{-7}M$, there was no shift detected by H_2O_2 addition. The minimum concentration of H_2O_2 for producing potential shift in 0.02M NaCl solution was found to be about $6.3 \times 10^{-6}M$. This is thought to be due to the fact that H_2O_2 reduction rate decreases as H_2O_2 concentration decreases. If the oxygen exceeds H_2O_2 in cathodic reaction rate, H_2O_2 might hardly affect the potential. Above minimum value of H_2O_2 producing potential shift, potential shifts were in proportion to $\log[H_2O_2]$. Lin[5] showed that the electrochemical potential of austenitic stainless steel was in

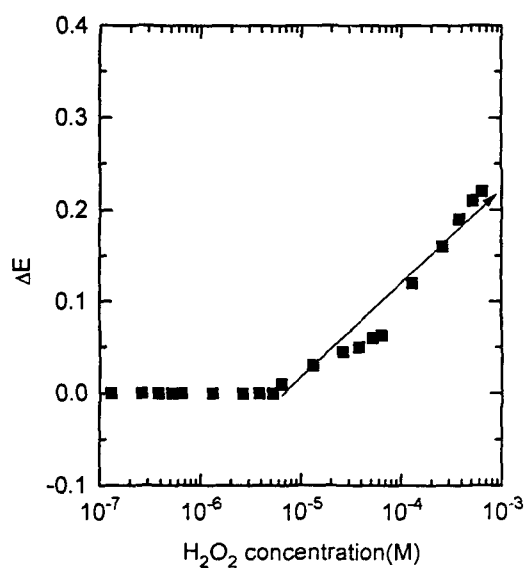


Fig. 6. Dependence of Corrosion Potential Shift on H_2O_2 Concentration.

proportion to $\log[O_2]$, and he proved this with theoretical equations. Like O_2 , the H_2O_2 effects on the corrosion was proved to be a logarithm function of its concentration shown in Fig. 6. Lin's experiment was carried out in high temperature. This experiment was carried out in room temperature. In this point of view, it is not the temperature but the concentration of oxidants that makes the changes of electrochemical potential in proportion to $\log[O_2]$ or $\log[H_2O_2]$

3.2. Polarization Behavior Changes By H_2O_2

Similar effects of H_2O_2 to γ -irradiation : Fig. 7 shows that H_2O_2 shifts corrosion potential in the noble direction by additional cathodic reaction of H_2O_2 and decreases pitting potential.

Fig. 8 shows pitting potential, corrosion potential, repassivation potential, and passive range variations with respect to H_2O_2 concentration.

Approximately, 20mV decrease in pitting potential, 200mV increase in corrosion potential, and 220mV decrease in passive range were made by the existence of $4.0 \times 10^{-4}M$ H_2O_2 in the electrolyte. Simi-

larly, 10mV decrease in pitting potential, 200mV increase in corrosion potential, and 210mV decrease in passive range were made by the existence of gamma-irradiation in the electrolyte as shown in Fig. 9.

It is, therefore, thought that H_2O_2 produces similar effects on corrosion to gamma-irradiation in the H_2O_2 concentration of about $10^{-4}M$.

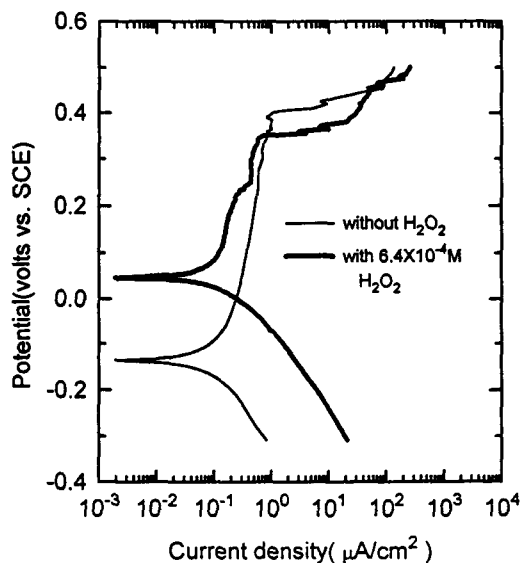
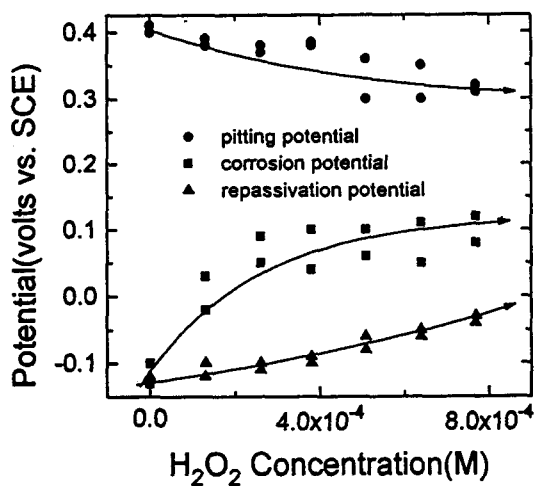
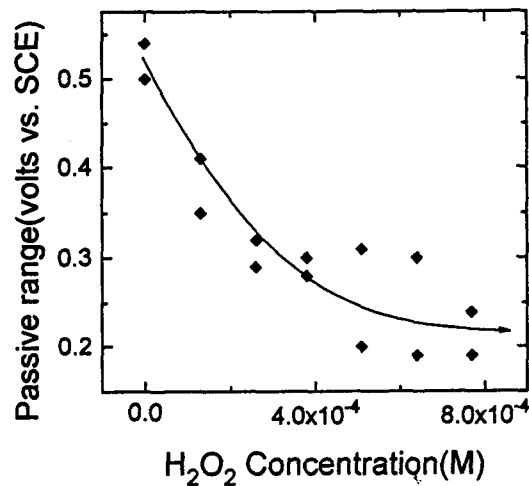


Fig. 7. Potentiodynamic Polarization Curves in Aerated 0.02M NaCl.



(a)



(b)

Fig. 8. Electrochemical Potential(a) and Passive Range (B) in Aerated 0.02M NaCl with Various H_2O_2 Concentrations.

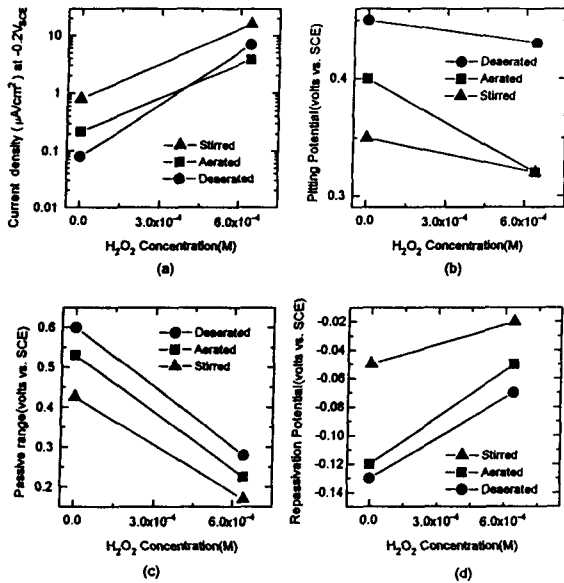
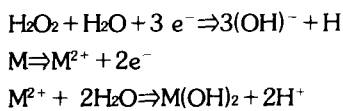


Fig. 9. Comparison of H₂O₂ Effect with O₂ Effect on the Cathodic Reaction Rate(a), Pitting Potential(b), Passive Range(c), and Repassivation Potential (d).

Pitting resistance: To observe pitting potentials, specimens were polished again, and pitting potentials were measured with different H₂O₂ concentrations. As shown in Fig. 8, the decreased pitting potential by H₂O₂ can be thought to be due to the promotion of depassivation and suppression of repassivation by the increase in hydrolysis reaction by cation and can be summarized in the following reaction. [8, 9, 10, 15, 16]



The increased reduction reaction by H₂O₂ will increase metal dissolution reaction and the increased metal cation will increase hydrolysis reaction. The increased proton on the metal surface will promote depassivation and suppress repassivation of the oxide film in 304L stainless steel.

In addition to this model, multiple oxidants effect

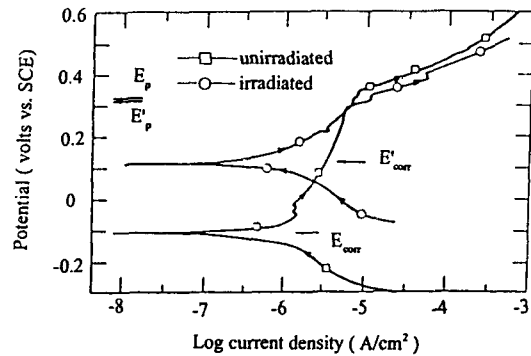


Fig. 10. Comparison of the Potentiodynamic Anodic Polarization Behavior for 316L Stainless Steel in 0.018M NaCl Solution in Deionized water with and Without Gamma Irradiation. [Obtained from Ref. 1]

can be thought. The electrolyte with multiple oxidants is likely to promote pit initiation by producing more defects in the oxide layer than the electrolyte with only a single oxidant. Fig. 10 proves this explanation.

In this figure, the pitting potential in the electrolyte containing H₂O₂, H⁺, and H₂O₂ (stirred with 6.4 × 10⁻⁴ M H₂O₂) is lowest. But the pitting potential in the electrolyte containing only H⁺ (deaerated with no H₂O₂) is highest. It is thought that this pitting potential change is closely related to the permanent change of oxide layer, as shown in Fig. 4.

Passive range, the difference between pitting potential and corrosion potential, represents pitting resistance. This passive range decreases as H₂O₂ concentration increases, which is shown in Fig. 8-b. Therefore, it is thought that the pitting resistance of 304L stainless steel decreases in the H₂O₂ bearing environment.

Repassivation potential: As shown in Fig. 8-a, the repassivation potential increases as H₂O₂ concentration increases, and the corrosion potential increases also. In spite of the increase of repassivation potential, the corrosion potential is still higher than the

repassivation potential. Therefore, if the pit is formed on the surface of 304L stainless steel, the pit will propagate in open circuit state. The repassivation potential represents the critical potential for SCC in the case of austenitic stainless steel. It is, therefore, inferred that the critical potential for SCC may increase in the H_2O_2 bearing environment.

Similar effects of H_2O_2 to O_2 : Fig. 10 shows the comparison of H_2O_2 effect with O_2 effect on the cathodic reaction rate, pitting potential, passive range, and repassivation potential. O_2 concentration on the metal surface in aerated electrolyte must be higher than in deaerated electrolyte. Similarly, O_2 concentration on the metal surface in stirred electrolyte must be higher than in aerated electrolyte. Deaerated, aerated, and stirred condition, therefore, represents O_2 concentration on the metal surface. As shown in Fig. 10, the pitting potentials are in proportion to O_2 concentration and H_2O_2 concentration. In this table, the passive range and repassivation potential are inversely proportional to H_2O_2 and O_2 concentration. From the above observations, it is clear that H_2O_2 effects on corrosion behavior of 304L stainless steel are similar to O_2 effects.

3.3. The Effect of H_2O_2 in Acid and Alkaline Media

The pH was hardly changed with $6.3 \times 10^{-4} \text{M}$ H_2O_2 addition in all test solutions. The pH which is going to be mentioned from now on means the initial pH measured before addition of the H_2O_2 .

In acid media: Fig. 11 shows that the more acid the solution becomes, the smaller the potential shift by H_2O_2 becomes.

At $\text{pH} = 0.7$, no potential shift could be produced by H_2O_2 . This is thought to be due to the fact that H^+ exceeds H_2O_2 in cathodic reaction rate and that the relatively smaller cathodic reaction rate of H_2O_2 can hardly affect the corrosion potential.

As shown in Fig. 12, cathodic reaction lines of H^+

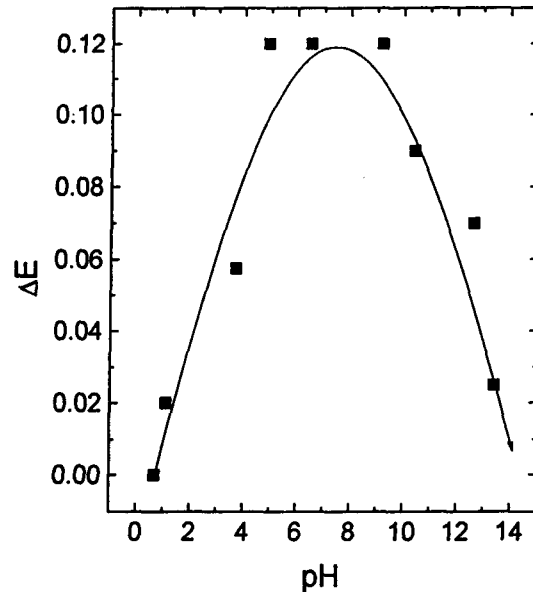


Fig. 11. Corrosion Potential Shift Produced by $1.3 \times 10^{-4} \text{M}$ H_2O_2 Addition in Various pH Conditions.

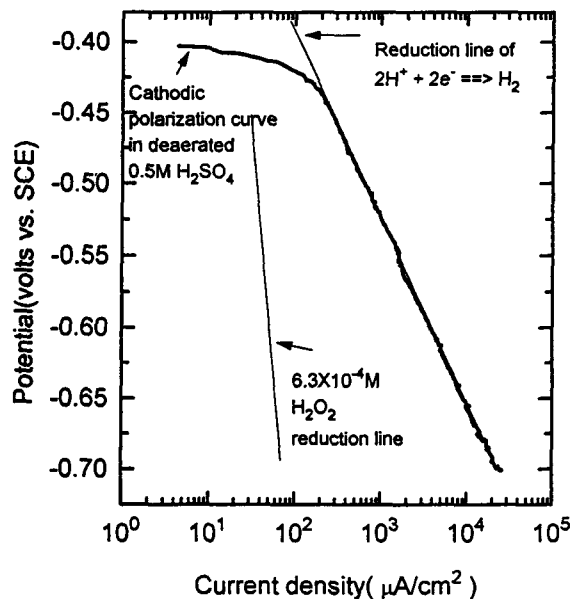


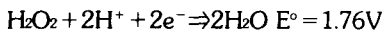
Fig. 12. Comparison of H_2O_2 Reduction Line with H^+ Reduction Line.

and H₂O₂ obtained from Tafel extrapolation method [13, 14] confirm the above explanation. In this Figure, H⁺ line exceeds H₂O₂ in current density.

In alkaline media : As shown in Fig. 11, the extent of potential shift by H₂O₂ decreased as pH of the solution was increased. It is thought that by the le Chatelier's principle H₂O₂ reduction reaction is likely to be hindered by high concentration of OH⁻ in alkaline media[15]. As shown in Fig. 11, the higher the OH⁻ concentration was, the smaller potential shift was produced by H₂O₂.

Theoretical consideration : Potential dependence of H₂O₂ reduction on pH was calculated thermodynamically in the following manner[16, 17]

(i) In acid solution.



$$\Delta G = \Delta G^\circ + RT \ln \frac{1}{[\text{H}_2\text{O}_2][\text{H}^+]^2}$$

$$= \Delta G^\circ + RT \ln [\text{H}_2\text{O}_2] + 4.606 RT \text{pH}$$

where $\Delta G^\circ = 339634$ joules/mole

$R = 8.3144$ joules/mole

$T = 298$ K

$\text{pH} = -\log[\text{H}^+]$

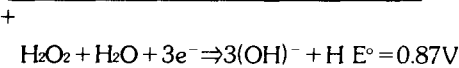
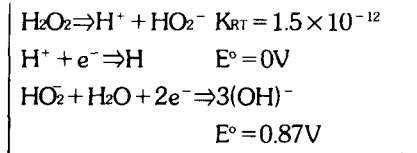
$$\Delta G = -2FE$$

Where $F = 96487$ coulomb/mole

When $[\text{H}_2\text{O}_2] = 0.00013\text{M}$, $E = 1.66 - 0.059 \text{ pH}$ (1)

When $[\text{H}_2\text{O}_2] = 0.00064\text{M}$, $E = 1.64 - 0.059 \text{ pH}$ (2)

(ii) In neutral and basic solution.



The driving force of above reduction reaction, that is the Gibbs free energy change, is

$$\Delta G = \Delta G^\circ + RT \ln \left\{ \frac{[(\text{OH})^-]^3}{[\text{H}_2\text{O}_2]} \right\}$$

$$K_{RT} = \frac{[\text{H}^+][\text{HO}_2^-]}{[\text{H}_2\text{O}_2]}$$

$$K_w = 1.0 \times 10^{-14} = [\text{H}^+][(\text{OH})^-]$$

$$\Delta G = \Delta G^\circ - 96.7RT + 6.9\text{pH} RT - RT \ln [\text{H}_2\text{O}_2]$$

where $\Delta G^\circ = -251831$ joules/mole

$$\Delta G = -3FE$$

When $[\text{H}_2\text{O}_2] = 0.00013\text{M}$, $E = 1.62 - 0.059 \text{ pH}$ (3)

When $[\text{H}_2\text{O}_2] = 0.00064\text{M}$, $E = 1.63 - 0.059 \text{ pH}$ (4)

Reduction potential of H₂O₂, which is over the calculated value, is higher than O₂ and H⁺. Equations (1), (2), (3), and (4) were put into Pourbaix diagram [17], and Fig. 13 was made with the above calculations.

As shown in Fig. 13, H₂O₂ reduction potential is higher than O₂ and H⁺ regardless of pH.

The dependence of H₂O₂ effect on pH : As shown in Fig. 13, the reduction potential of H₂O₂ is higher than H⁺ regardless of pH. But, it turned out to be that in acid and alkaline media H₂O₂ effects on corrosion become smaller than in neutral water environment as shown in Fig. 11.

4. Conclusions

The conclusions are :

- 1) In neutral water environment, above $6.3 \times$

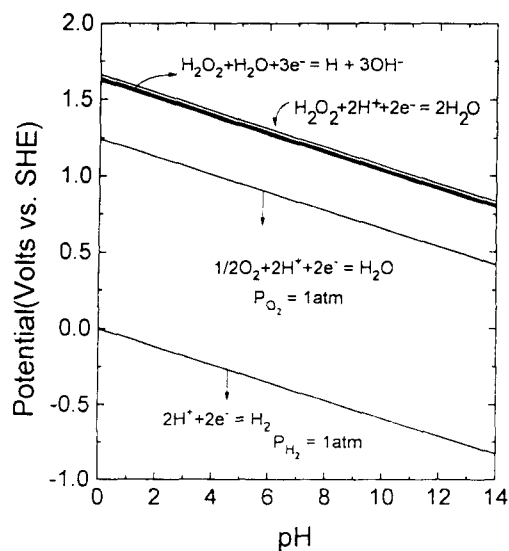


Fig. 13. Calculated Potential Dependence Upon pH.

10^{-6} M H_2O_2 , H_2O_2 shifted corrosion potential in proportion to $\log[\text{H}_2\text{O}_2]$. Below 6.3×10^{-6} M H_2O_2 , H_2O_2 hardly affected potential, which was due to the fact that O_2 exceeds H_2O_2 in cathodic reaction rate. It is, therefore, inferred that only the concentration of H_2O_2 more than this critical value can affect the corrosion behavior of 304L stainless steel.

2) By the existence of H_2O_2 , pitting potential was decreased and passive range was decreased, which represented the decrease of pitting resistance. It is closely related to the permanent change of oxide layer, and these effects of H_2O_2 are considered to be similar to those of O_2 .

3) By the existence of H_2O_2 , repassivation potential was increased. From this, it is inferred that the critical potential for SCC will increase in the H_2O_2 bearing environment.

4) The effects of H_2O_2 were observed to be similar to those of gamma-irradiation. Therefore, it may be possible to simulate gamma-irradiation effect with H_2O_2 .

5) In acid and alkaline media, the corrosion potential shifts by H_2O_2 were restricted by the large current density of proton and by the le Chatelier's principle respectively.

Acknowledgement

The authors would like to thank Kun-Sik Kim and Eun-Ka Kim at the Korea Atomic Energy Research Institute for their help for the present research.

References

1. Robert S. Glass, *Corrosion Science*, 26, p. 577–590 (1986)
2. N. Saito, *Corrosion-July*, p. 531–536 (1990)
3. Y.J. Kim and R.A. Oriani, *Corrosion-NACE*, 43, p. 85-91 (1987)
4. Y.J. Kim and R.A. Oriani, *Corrosion-NACE*, 43, p. 92–97 (1987)
5. C.C. Lin, F. R. Smith, *Corrosion-January*, p. 16–28 (1992)
6. C.C. Lin, F.R. Smith, *EPRI NP-6733*, (1990)
7. M.E. Indig, J.E. Weber, *EPRI NP-3362*, (1988)
8. C.J. Hochanadel, *J. phys. Chem*, 56, p. 587 (1952)
9. A.O. Allen, *The Radiation Chemistry of Water and Aqueous Solutions*, D. Van Nostrand and Co Princeton (1961)
10. J.W.T. Spinks and R.J. Woods, *An Introduction to Radiation Chemistry*. 2nd edition. John Wiley. New York (1976)
11. Chien C. Lin, *Nuclear Technology*, 103, p. 257–261, (1993)
12. Val'kov, V.D. and A.V. Byalobzheskii. — In: *Sbornik, Korroziya metallov i splavov*, P. 298, Moskva, Metallurgizdat (1958)
13. L.L. Shreir, *Corrosion*, 1, Tien Wah Press Ltd., Singapore (1979)
14. Mars G. Fontana, *Corrosion Engineering*, United Publishing and Promotion Co. LTD (1978)
15. Clyde R. Dillard, *Chemistry*, p. 154–56, Macmillan Publishing Co Inc., New York (1978)
16. F. Albert Cotton, *Basic Inorganic Chemistry*, John Wiley. New York, (1976)
17. M. Pourbaix, *The Thermodynamics of Aqueous Solutions*, trans. J.N. Agar, London (1949)