한국부식학회지
J. Corros. Sci. Soc. of Korea
Vol. 17, No. 1, March, 1988.

〈研究論文〉

Electrochemical Mechanisms for Radiation Corrosion Processess of 316 Austenitic Stainless Steel in Chloride Environment

Young Jin Kim*

Corrosion Research Center, University of Minnesota, Minneapolis, Mn 55455

The effects of gamma radiation (Ce^{137}, 1.5×10^5 rad/hr) on the electrochemical mechanisms of 316 austenitic stainless steel in 1.5M NaCl solution (pH: 2) at 25°C have been investigated. When gamma irradiation is initiated, corrosion potential shifts in the positive direction are observed for 316 SS. These potential shifts are associated with the irradiation-induced production of hydrogen peroxide. The electrochemical mechanisms involved in the corrosion potential shifts, as well as the subsequent effect on pitting resistance, are considered.

(Received October 1, 1987)

INTRODUCTION

The safe disposal of high level nuclear waste materials in geological media represents a current technological challenge. In designing metallic engineered barriers for waste disposal, the susceptibility to potential corrosion failure modes such as uniform corrosion, pitting, crevice attack, hydrogen embrittlement, and stress-corrosion cracking must be evaluated. In addition to these failure modes normally encountered in corrosion studies, the interaction of gamma radiation from the waste with the surrounding chemical environment must be understood in light of possible effects on corrosion mechanisms. The interaction of gamma radiation with aqueous environments produces a host of transient radicals, ions, and stable molecular species including H^+, OH^-, e_{aq}^+, H_3O^+, H_2, H_2O_2, O_2, O_2, etc.[1] As a results of the production of such species under gamma radiation, there may be alternations in the rates or mechanisms of corrosion attack modes. The mechanisms of radiolytic processes of aqueous environments have been reviewed elsewhere.[2]

Previous investigations have found an increased susceptibility of sensitized 304 stainless steel towards intergranular stress corrosion cracking in high temperature water under gamma radition[3] and an increased resistance to crevice corrosion for austenitic stainless steels in aqueous solution under gamma radiation.[4] Furthermore, several reports have shown effects of gamma radiation on the corrosion potentials of austenitic stainless steels[5-7] and titanium alloys[8] in aqueous solutions. Shifts of the corrosion

---

* Current Address: Center for Electrochemical Systems and Hydrogen Research, 238 Engineering Research Center, Texas A & M University, College Station, Tx 77843-3577.

potential in the positive direction have generally been observed under gamma irradiation of oxygenated aqueous media.

However, a fundamental understanding of the effect of gamma radiation on the electrochemical mechanisms of 316 austenitic stainless steel is lacking. In this paper, experimental results are reported on the in-situ electrochemical characterization of 316 SS in gamma-irradiated NaCl solution (pH: 2) at 25°C. Open-circuit potential measurements and polarization curves were obtained under gamma radiation at a dose rate of 1.5×10^5 rad/hr. The major species responsible for the observed electrochemical changes is shown to be radiolytically-generated H_2O_2. The electrochemical mechanisms leading to the observed corrosion potential behavior under gamma irradiation are explored.

EXPERIMENTAL

The samples of 316 austenitic stainless steel, 1.2x1.2x0.4 cm, were welded with copper wire for electrical contact and mounted in polyester embedding material. The specimens were then mechanically ground using 240, 320, 400, and 600 grit SiC and further polished with 1.0μ, 0.3μ, and 0.05μ Al_2O_3 slurries prior to use. The specimens were coated with a thin film microshield lacquer to avoid crevice corrosion between the electrode and the embedding material.

All experiments were carried out at 25°C in a corrosion cell contained 1.5M NaCl (pH: 2) open to air, but the electrolyte was not aerated. When additions of other species were made, analytical reagent chemical (30% H_2O_2) or ultra-high purity gases (H_2 and O_2) were used. The corrosion cell consisted of a reference electrode (saturated calomel electrode: SCE), auxiliary electrode (Pt), and working electrode (316SS). The gamma sources consisted of Ce^{137} pensils in a cylindrical arrangement. The corrosion cell was inserted into the inside of this cylinder, at the center of which the dose rate was 1.5×10^5 rad/hr. This gamma radiation facility has been described in detail elsewhere.[8] Open-circuit potential measurements and polarization curves were obtained with an aid of Princeton Applied Research Model 173 potentiostat and Model 176 current/voltage converter. In order to plot the potentiodynamic polarization curve, after immersion of the specimen into the electrolyte, cathodic reduction was carried out at -0.40V(SCE) for 3 minutes. Then, the potentiostat was turned off until a stable corrosion potential was reached. The potential scanning at 1 mV/sec was started at this potential either in the anodic direction or in the cathodic direction.

RESULTS AND DISCUSSION

(1) OPEN-CIRCUIT POTENTIAL BEHAVIOR

That the open-circuit potential, E_{OC}, of 316SS in 1.5M NaCl (pH: 2) at 25°C is significantly affected by gamma radiation due to the generation of new oxidizing species is shown in Figure 1. Upon imposition of the gamma field, E_{OC} shifted in the positive direction, and conversely, when the radiation was removed, E_{OC} became more active.

From this experiment, it seems clear that the positive potential shifts in E_{OC} resulted from the more oxidizing environment produced by gamma irradiation. The initial rapid rise of potential upon imposition of the gamma field

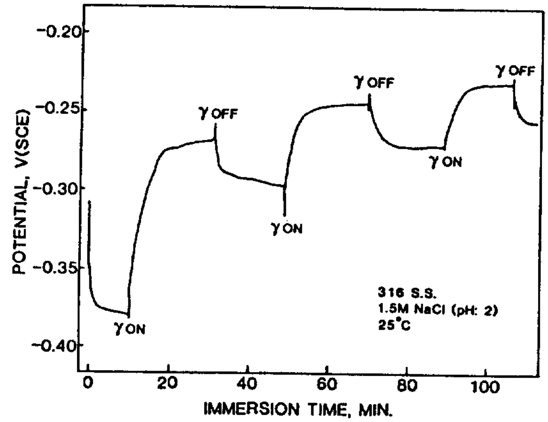

Fig. 1. Open-circuit potential behavior of 316SS in 1.5M NaCl solution at 25℃, both with and without gamma radiation (measured in-situ).

is likely the result of the generation of oxidizing species in the solution layers next to the electrode surface. The subsequent slower rise of potential with time corresponds to the slower buildup of the steady-state bulk concentration of oxidizing products such as H_2O_2. The fall in potential upon removal from the gamma field likely results from the discontinuation of the production of the radiolytic species in the solution layers next to the electrode surface. The potential does not, however, return to the pre-radiolysis values, which indicates either permanent changes in the oxide films on the specimen, or the generation of a stable concentration of oxidizing species in the solution, or both. In order to see whether the observed effects resulted from stable oxidizing species produced in the solution or from permanent changes in the oxide film on the electrode, the following experiment was performed: Following several "on/off" cycles for 316SS in NaCl solution, the cell was removed from the gamma facility and the irradiated solution was replaced by "fresh" non-irradiated NaCl solution. When this was done, E_{oc} immediately shifted in the negative direction (see Figure 2). This indicates that the positive potential shifts observed are due principally to radiolytically-generated stable oxidizing species rather than to oxide film changes. If the latter had been the case, the oxide film would not have been expected to change back to its original state when the solution was replaced, particularly not as rapidly as the observed change in potential occurred.

(2) EFFECT OF H_2O_2

The primary radiolytic products under gamma radiation are known to be H, OH, e_{aq}^-, H_3O^+, OH^-, etc. with the highest concentrations of H_2, O_2, and H_2O_2.[1] It was also found that among the radiolytic products H_2O_2 is an important factor for determining the corrosion conditions in the brine solution.[2] As shown in Figures 1 and 2, it was observed that the changes in E_{oc} were caused by the products of radiolysis of the solution, and not by effect of radiation on the oxide films. It is therefore of interest

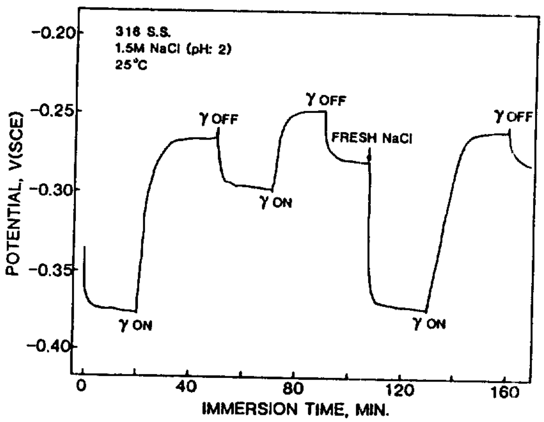

Fig. 2. Passivity of the oxide films produced on 316 SS under gamma radiation in 1.5M NaCl solution at 25℃.

to discover what effect are produced by H_2O_2 when added to NaCl solution.

To see whether H_2O_2 could produce the potential shifts of the magnitude observed under irradiation, one drop of 30% H_2O_2 solution was added to the fresh NaCl solution in the cell from the experiment above, producing a concentration of $0.7x10^{-4}$M. The potential was observed to shift in the positive direction immediately (see Figure 3). The observed change when H_2O_2 was added to the solution, coupled with the knowledge that H_2O_2 is the most concentrated radiolytic species present in an irradiated solution, provides strong evidence that it is reponsible for the potential shift observed upon irradiation in NaCl solution. Also, it can be seen that the potential shift observed following the addition of the first drop is within the range of potential shifts observed under radiolysis. Successive additions of H_2O_2 yield smaller potential jumps than the initial addition on a per-drop basis, indicating a tendency toward an eventual saturation point. These results add further support to the interpretation that the production of H_2O_2 under radiolysis leads to the long-term potential shifts.

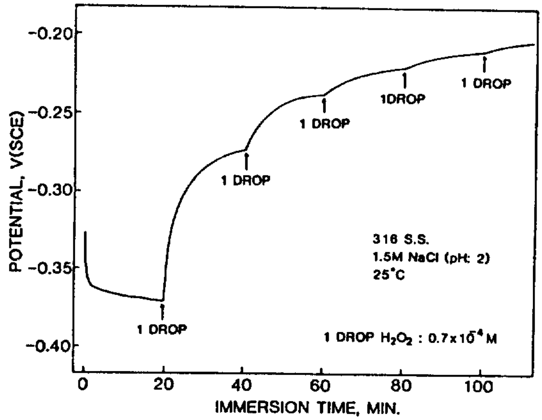

Fig. 3. Effect of H_2O_2 on the open-circuit potential of 316SS in 1.5M NaCl solution at 25℃.

(3) PITTING RESISTANCE

As described previously, it is important to know what the effect of the positive corrosion potential shifts will be on the corrosion mechanisms. In particular, it would be of interest to find out whether the positive potential shifts increase the susceptibility of the material to pitting.

That the pitting susceptibility of 316SS is not increased under gamma radiation is shown by comparison of the potentiodynamic polarization curves in Figure 4 obtained with the gamma field and without it, measured in-situ. For the non-irradiated case, the corrosion potential, E_{corr}, was -360mV(SCE). Upon scanning anodically, the pitting potential, E_{pit}, was found to be 160mV. The value of $E_{pit} - E_{corr}$ is therefore 520mV. For the gamma irradiation case, the corresponding values for E_{corr} and E_{pit} are -280mV and 260mV, respectively. This represents a seperation of $E_{pit} - E_{corr}$ of 540mV.

It therefore appears that both the corrosion potential and the pitting potential are shifted positively in the presence of gamma radiation, and by roughly the same amount. These results indicate that the products of the radiolysis of NaCl solution may increase the possible cathodic reactions so that the mixed potential moves in the anodic direction. This point of view was confirmed by the cathodic polarization curves shown in Figure 4, where we see that under gamma radiation the cathodic current density increases. In addition, since under gamma radiation the seperation value of E_{corr} and E_{pit}

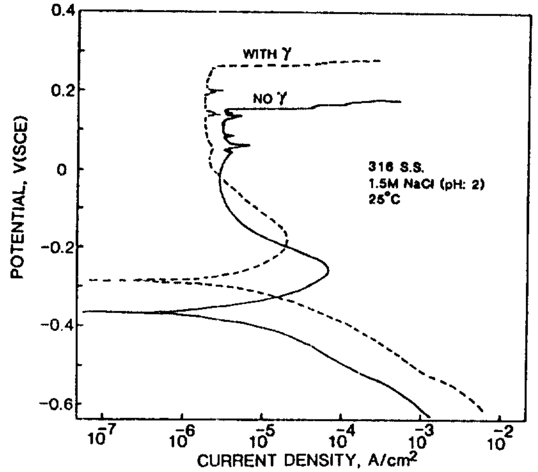

Fig. 4. Effect of gamma radiation on the polarization behavior of 316SS in 1.5M NaCl solution at 25℃.

remains essentially the same as it is without gamma radiation, there appears to be no increase in susceptibility to pitting with gamma radiation.

(4) ELECTROCHEMICAL MECHANISMS

A large number of electrochemical reactions involving oxidizing species are possible in gamma-irradiated aqueous solution.[1] During the electrochemical reactions, the corrosion potential will be a mixed potential resulting from the superposition of the kinetics of all the anodic and cathodic reactions occurring on the electrode surface. The situation is so complex that the relative contributions of reactions of secondary importance are difficult to ascertain. The relative importance of the reactions will depend upon such factors as dose rate, pH, relative concentrations, electron transfer rate constants, temperature, etc.

In considering the electrochemical behavior of Pt in non-irradiated aqueous solutions of H_2O_2, previous researchers[10] have proposed the following reaction as determining the open-circuit potentials:

$$(\cdot OH)_{ads} + e^- \longleftrightarrow OH^- \qquad (1)$$

In this equation, absorbed hydroxyl radcals on the Pt surface participate in an electrochemical equlibrium with hydroxide ions in solution. The adsorbed hydroxyls originate from a surface-catalyzed decomposition of H_2O_2, i.e.,

$$H_2O_2 \rightarrow 2(\cdot OH)_{ads} \qquad (2)$$

In addition to the above explanation, a more complicated scheme has been proposed to explain the electrochemical behavior of Pt in aqueous solutions of H_2O_2.[11] In their scheme, H_2O_2 was conceived to be electrochemically discharged on Pt into either adsorbed hydroxyl or perhydroxyl (HO_2) radicals in cathodic or anodic reactions, respectively. With a relative importance depending on pH, the adsorbed hydroxyls could then participate in a cathodic process to liberate OH^-, whereas the adsorbed HO_2 species could liberate O_2 by an anodic process. In addition, and concurrently, these adsorbed speci OH and HO_2 could participate in a cyclical catalytic mechanism to decompose H_2O_2 on the surface, liberate H_2O and O_2, and regenerate the original adsorbed species. This catalytic scheme would be more important at higher pH. The balance of anodic and cathodic reactions in this cyclical catalytic scheme would then determine the open-circuit potential of Pt.

In this case of gamma radiolysis where both ·OH and H_2O_2 are generated in solution and may directly adsorb or decompose on the surface, respectively, either of the above mechanisms could be important in determining the corrosion potential of 316SS. These species, generated in the solution layers next of the electrode, would be important in this regard.

In the bulk, only the generation of H_2O_2 will be important as the $\cdot OH$ radicals have too short a lifetime to diffuse appreciably[1,9]. As stated previously, the generations of both $\cdot OH$ and H_2O_2, particularly $\cdot OH$, in the solution layers next to the electrode are probably important for the initial rapid rise in potential observed upon imposition of the gamma field. The subsequent slower rise of potential is probably due to the bulk generation of H_2O_2 and its diffusion to the electrode surface. If the above mechanism for H_2O_2 decomposition can be applied to the corrosion behavior of 316SS in aqueous solutions under gamma radiation, another oxidizing species, O_2, could also be present at the electrode surface. The corrosion potential would then be established by a balance of the anodic and cathodic processes occurring in the cyclical catalytic decomposition of H_2O_2.

Although reactions such as (1) and (2), or, alternatively, the catalytic mechanism[10], may be very important in determining the corrosion potential of 316SS in aqueous solution under gamma radiolysis, the situation is complex in that other reactions (e.g., metal dissolution) will also certainly play a role. Stainless steel forms a much more complex electrochemical interface with aqueous solutions than does Pt and may not have a surface saturation coverage of adsorbed hydroxyl species. A lower rate constant for the decomposition of H_2O_2, or other reactions with the oxide film may account for this. In any case, one would not expect the open-circuit potential behavior for 316SS under gamma radiation as that for Pt in non-irradiated aqueous solution of H_2O_2. The mechanisms leading to the positive corrosion potential shifts for 316SS under gamma radiation, although clearly associated with the production of $\cdot OH$ and H_2O_2, need further clarification.

The anodic and cathodic reactions which are believed to be of major importance in determining the corrosion potentials of 316SS under gamma radiation are listed below. Based upon the results presented above, the following reactions will probably predominate under gamma radiation in aqueous solution.

Cathodic reactions:

$$(\cdot OH)_{ads} + e^- \leftrightarrow OH^- \qquad (3)$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (4)$$

$$O_2^- + H_2O + e^- \rightarrow HO_2^- + OH^- \qquad (5)$$

$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^- \qquad (6)$$

Anodic reactions:

$$Fe \rightarrow Fe^{+2} + 2e^- \qquad (7)$$

$$Cr \rightarrow Cr^{+3} + 3e^- \qquad (8)$$

$$Ni \rightarrow Ni^{+2} + 2e^- \qquad (9)$$

$$2OH^- + H_2O_2 \rightarrow O_2 + 2H_2O + 2e^- \qquad (10)$$

$$HO_2^- + OH^- \rightarrow O^2 + H_2O + 2e^- \qquad (11)$$

The last two reactions for both the cathodic and anodic sets are expected to be of lesser importance at low pH. The coupling of the cathodic processes with metal dissolution reactions will results in the observed mixed corrosion potential. Again, the equlibrium described in equation (1) may be one of the most important reactions pinning the corrosion potential.

Along with the surface reactions, the radiolytically generated species can also participate in a series of bulk oxidation reactions such as those given in reactions (12) through (17).

$$\cdot OH + Fe^{+2} \rightarrow Fe^{+3} + OH^- \qquad (12)$$

$$HO_2 + Fe^{+2} \rightarrow Fe^{+3} + HO_2^- \qquad (13)$$

$$H_2O_2 + Fe^{+2} \rightarrow Fe^{+3} + OH^- + \cdot OH \qquad (14)$$

$$H\cdot + Fe^{+2} \rightarrow Fe^{+3}H^- \quad (15)$$

$$Fe^{+3}H^- + H^+ \rightarrow Fe^{+3} + H_2 \quad (16)$$

$$2Fe(OH)_2 + H_2O_2 \rightarrow 2FeOOH + 2H_2O \quad (17)$$

Processes such as the oxidation of ferrous ion under gamma radiolysis have been proposed previously to explain an observed inhibition of crevice corrosion of stainless steel.[4]

CONCLUSIONS

Gamma irradiation increases the oxidizing nature of NaCl solution which may account for the observed positive corrosion potential shifts of 316SS. The generation of oxidizing species in the solution layers adjacent to the electrode surface is responsible for the rapid potential shifts observed upon imposition of gamma field. Upon continued radiolysis, a rise in concentration of oxidizing species, particularly H_2O_2, in the bulk solution also gradually increases the steady-state corrosion potential of the 316 stainless steel. The electrochemical equilibrium between adsorbed hydroxyl species and hydroxide ions may be important in determining the corrosion potentials of 316SS in irradiated NaCl solution. In addition, experimental results suggest that the susceptibility of 316SS to pitting is not increased under gamma radiation. It appears that both the corrosion potential and pitting potentials are shifted positively by approximately the same amount.

ACKNOWLEDGEMENT

The author thanks D.B. Le for an aid with the operation of the gamma facility of the University of Minnesota.

REFERENCES

1. A.O. Allen, *"The Radiation Chemistry of Water and Aqueous Solutions,"* D. Van Nostrand and Co., Inc., Princeton, NJ, 1961.
2. Y.J. Kim, This Journal, **15(4)**, 19, 26 (1986).
3. N. Fujita, M. Akiyama, and T. Tamura, Corrosion, **37**, 335 (1981).
4. A.V. Byalobzheskii, *"Radiation Chemistry ,"* Israel Program for Scientific Translations, Jerusalem, 1970.
5. S. Uchida, E. Ibe, and R. Katsura, Rad. Phys. Chem., **22**, 515 (1983).
6. W.E. Clark, J. Electrochem. Soc., **105**, 483 (1958).
7. W.G. Burns, W.R. Marsh, and W.S. Walters, Rad. Phys. Chem., **21**, 259 (1983).
8. Y.J. Kim and R.A. Oriani, Corrosion, **43** **(2)**, 85 (1987).
9. W.G. Burns and P.B. Moore, Radiation Effects, **30**, 233 (1976).
10. J.O'M. Bockris and L.F. Oldfield, Trans. Faraday Soc., **51**, 249(1955).
11. R. Gerischer and H. Gerischer, Z. Phys. Chem., **6**, 178 (1956).