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〈研究論文〉

## Effect of Gamma Radiation on Electrochemical Behavior of 9Cr-1Mo Alloy in NaCl Solution

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### ABSTRACT

The electrochemical behaviors of 9Cr-1Mo alloy have been studied in 0.1M NaCl solution (pH: 6.6) at 25°C under  $\gamma$ -radiation ( $Ce^{137}$ ,  $1.5 \times 10^5$  rad/hr) where a variety of radiolytic species, that may change the redox reactions involved in the electrochemical processes, is known to be produced.

It was found that  $\gamma$ -radiation causes the positive shift in the open-circuit potential of 9Cr-1Mo in NaCl solution, generating the additional cathodic reactions by radiolysis of NaCl solution, but the properties of the oxide films formed on 9Cr-1Mo in this solution were not affected by  $\gamma$ -radiation. Among the radiolytic products,  $H_2O_2$  has an important role in determining the corrosion conditions of the irradiated NaCl solution. It provides an additional cathodic reaction, thereby shifting the open-circuit potential of 9Cr-1Mo alloy in the noble direction.

### INTRODUCTION

9Cr-1Mo, ferritic stainless steel, is used (or being considered for use) in geothermal applications, modern power plants, nuclear industry, and nuclear waste package [1, 2]. However, nuclear water reactor systems have experienced corrosion and mechanically induced damage which has significantly affected their reliability and availability [3]. It has been reported that under aggressive water chemistry (high  $O_2$  + acid chloride -  $CaCl_2$ ) 9Cr-1Mo was susceptible to stress corrosion cracking and pitting attack [4], and also previous researcher

has found that the pitting potential depends on the environmental temperatures in geothermal water [5].

In addition to corrosion failure modes normally encountered in corrosion tests, the environment must be understood in light of possible effects on corrosion mechanisms. The interaction of  $\gamma$ -radiation with aqueous environments produces a host transient radicals, ions, and stable molecular species such as H, OH,  $O_2$ ,  $e_{aq}^-$ ,  $H_3O^+$ ,  $OH^-$ ,  $H_2$ ,  $O_2$ ,  $H_2O_2$ , etc. [6]. As a result of the production of such species under radiation, there may be alternation in the

rates or mechanisms of corrosion attack mode. The mechanisms of radiolytic processes of aqueous environments and their effects on the metallic corrosion have been reviewed in detail previously [7, 8].

However, a fundamental understanding of the effect of  $\gamma$ -radiation on the electrochemical mechanisms of 9Cr-1Mo alloy is lacking. In particular, the introduction of new electrochemical reactions by the radiolytically-generated oxidants has received little mechanistic investigation in neutral aqueous environments.

In this paper, the experimental results are reported on the in-situ electrochemical characterization of the response of 9Cr-1Mo to gamma-irradiated NaCl solution. Open-circuit potential measurements and potentiodynamic polarization curves were obtained in 0.1M NaCl solution (pH: 6.6) at 25°C, both with and without  $\gamma$ -radiation at a dose rate of  $1.5 \times 10^5$  rad/hr. Furthermore, the role of  $H_2O_2$  was studied to understand better the radiolytic environment of NaCl solution.

## EXPERIMENTAL PROCEDURE

As-received 9Cr-1Mo, with the chemical composition given in Table 1, used for this work was supplied by the Oak Ridge National Laboratory. The samples, 1.2 cm x 1.2 cm x 0.4 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 silicon carbide paper and further polished with 1.0, 0.3, and 0.05  $\mu$ m gamma alumina slurries on wet polishing wheels. The optical microscopy was also used to obtain the same condition of the polished surfaces. The specimens were

Table 1. Chemical composition of 9Cr-1Mo alloy.

ELEMENT	Cr	Mo	Mn	Ni	Nb	V	Si	C	Fe
wt. %	8.03	0.88	0.4	0.09	0.17	0.2	0.09	0.089	bal.

coated with a thin film of 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 0.1M NaCl solution (pH: 6.6) open to the air, but the electrolyte was not aerated. Also, an analytical reagent chemical (30 %  $H_2O_2$ ) was added to 0.1M NaCl. The corrosion cell consisted of a reference electrode (saturated calomel electrode: SCE), auxiliary electrode (Pt), and working electrode (9Cr-1Mo).

Open-circuit potential measurements and polarization curves were obtained with an aid of a Princeton Applied Research Model 173 potentiostat and Model 176 current/voltage converter. In order to plot the potentiodynamic polarization curves, after immersion of the specimen into the electrolyte, cathodic reduction was carried out at -0.45 V (vs. SCE) for three minutes. Then, the potentiostat was turned off until a stable open-circuit potential was reached. The potential scanning at 0.2 mV/sec was started at this potential either in the anodic direction or in the cathodic direction.

## RESULTS AND DISCUSSION

### 1. Electrochemical Behavior of 9Cr-1Mo under $\gamma$ -Radiation

The change of the open-circuit potential,  $E_{OC}$ , of 9Cr-1Mo in 0.1M NaCl solution at 25°C both in the presence of  $\gamma$ -radiation and in its absence is shown in Figure 1, which indicates that  $E_{OC}$  is significantly affected by  $\gamma$ -radiation due to the generation of new oxidizing species. 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. This phenomenon shows that the products of the radiolysis of NaCl solution may

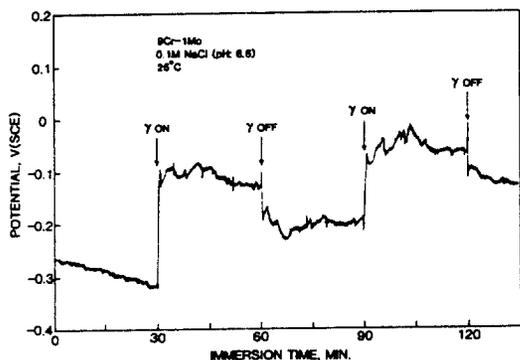


Figure 1. Open-circuit potential of 9Cr-1Mo in 0.1 M NaCl solution at 25°C, both with and without  $\gamma$ -radiation, measured in-situ.

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 2, where we see that under  $\gamma$ -radiation the cathodic current density increases. Several reports have shown the effects of  $\gamma$ -radiation on  $E_{OC}$  of austenitic stainless steel and titanium alloy in aqueous media[9-12].

From these results, it seems clear that the positive potential shifts in  $E_{OC}$  may result from the more oxidizing environment produced by

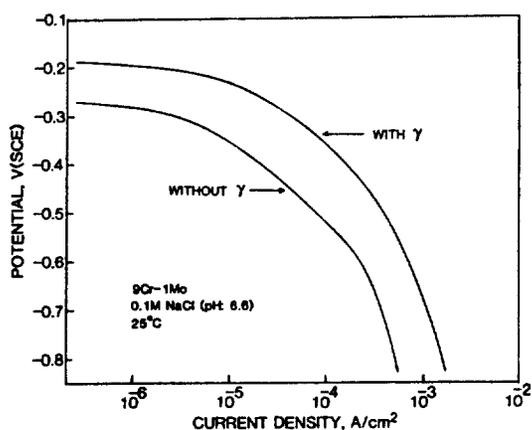


Figure 2. Cathodic polarization curve of 9Cr-1Mo in 0.1M NaCl solution at 25°C, both with and without  $\gamma$ -radiation, measured in-situ.

$\gamma$ -radiation. The initial rapid rise of  $E_{OC}$  upon imposition of the gamma field is likely the result of the generation of oxidizing species in the solution layers next to the electrode surface. The subsequent lower rise of  $E_{OC}$  corresponds to the slower build-up of the steady-state bulk concentration of oxidizing species such as  $H_2O_2$ . The fall in  $E_{OC}$  upon removal of the gamma radiation 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 test whether the observed effects resulted from stable oxidizing species produced in the solution or from permanent changes in the oxide films on the electrode, the following experiment was performed: Following the radiation exposure of the electrode in NaCl solution, the cell was removed from the gamma facility and the irradiated NaCl solution was replaced by fresh non-irradiated NaCl solution. When this was done,  $E_{OC}$  immediately shifted in the negative direction (see Figure 3). 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 layer 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. Furthermore, as shown in Figure 4, there is no significant change on the anodic polarization curves, which means that the properties of the oxide film formed on 9Cr-1Mo alloy in NaCl solution were not affected by  $\gamma$ -radiation.

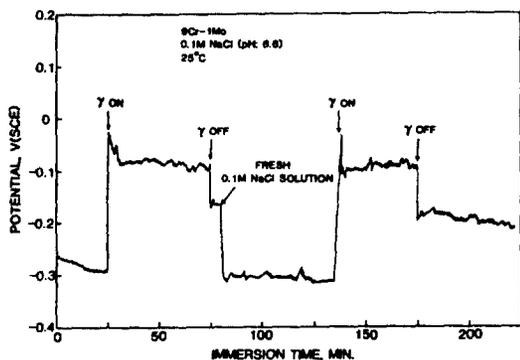


Figure 3. Effect of  $\gamma$ -radiation on the open-circuit potential and the oxide films produced on 9Cr-1Mo in 0.1M NaCl solution at 25°C.

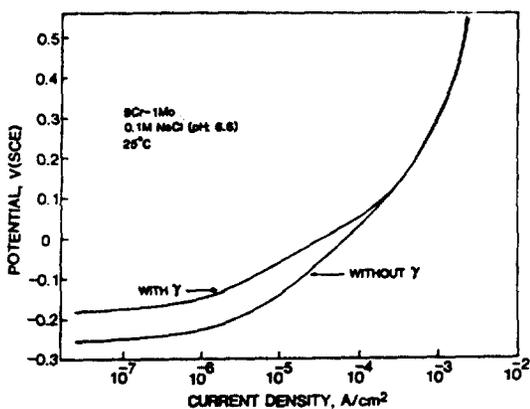


Figure 4. Anodic polarization curve of 9Cr-1Mo in 0.1M NaCl solution at 25°C, both with and without  $\gamma$ -radiation, measured in-situ.

Therefore, the positive shift of the corrosion potential under  $\gamma$ -radiation may result from reaction of the radiolytic species rather than from the oxide film changes.

## 2. Effect of $H_2O_2$ on Electrochemical Behavior of 9Cr-1Mo

A large number of electrochemical reactions involving oxidizing species are possible in gamma-irradiated aqueous solution. The primary radiolytic products under  $\gamma$ -radiation are known to be  $H$ ,  $OH$ ,  $e_{aq}^-$ ,  $H_3O^+$ ,  $OH^-$ , and  $HO_2$  with the highest concentrations of  $H_2$ ,  $O_2$ , and  $H_2O_2$ [6], and the predominant species are

$O_2$  and  $H_2O_2$  in the region of pH 4 to 10. It was also found that among the radiolytic products  $H_2O_2$  is an important factor for determining the corrosion conditions in the neutral brine solution[12]. Of course, the 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.

Under the gamma radiolysis where  $O_2$  and  $H_2O_2$  are generated in the neutral NaCl solution and may directly adsorb or decompose on the surface, the electrochemical processes of these species could be important in determining the corrosion potential of the electrode. In the bulk, only the generation of  $H_2O_2$  will be important as other products have too short a lifetime to diffuse appreciably[6, 13]. But, the real 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 on such factors as dose rate, pH, electron transfer rate constants, temperature, relative concentrations of scavenger species, etc.

As shown in Figures 1-4, it was observed that the changes in  $E_{oc}$  of 9Cr-1Mo alloy in NaCl solution 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 to discover what effects are produced by  $H_2O_2$  when added to NaCl solution. To see whether  $H_2O_2$  could produce the potential shifts observed under  $\gamma$ -radiation, a small amount of 30%  $H_2O_2$  was added to the fresh 0.1M NaCl solution; a concentration of one drop  $H_2O_2$  is approximately  $0.7 \times 10^{-4} M$ , that was chosen from pure water irradiated with  $\gamma$ -radiation at a dose rate similar to this experiment[14]. These results may then be compared with the effects of  $\gamma$ -radiation.

As shown in Figure 5, the potential was observed to shift in the positive direction immediately. This 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 responsible for the potential shift observed under 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 addition of  $H_2O_2$  yield smaller potential jumps than the initial addition on a per-drop basis, indicating a tendency toward an eventual saturation concentration.

To shed further light on the electrochemical effects of  $\gamma$ -radiation, the NaCl- $H_2O_2$  solution was used to measure  $E_{OC}$  and polarization curves. Figure 6 shows that increasing the concentration of  $H_2O_2$  in NaCl solution increases  $E_{OC}$ . The positive shift of  $E_{OC}$  upon the addition of  $H_2O_2$  is due to the availability of other cathodic reaction; the reduction of  $H_2O_2$ . This point of view was confirmed by the cathodic polarization curves shown in Figure 7, where with increasing amounts of  $H_2O_2$  the cathodic current density increases. These cathodic polarization curves

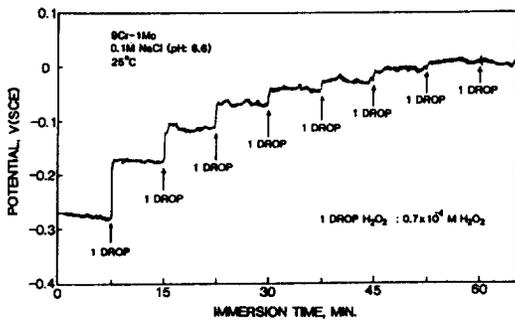


Figure 5. Effect of the successive addition of  $H_2O_2$  to 0.1M NaCl solution at 25°C on the open-circuit potential of 9Cr-1Mo.

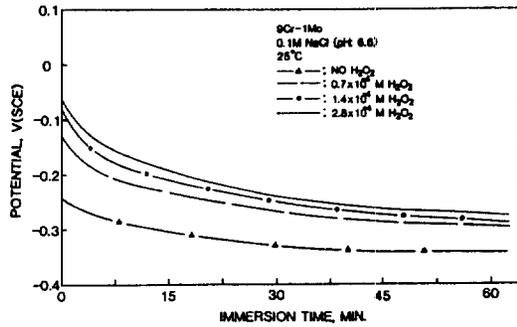


Figure 6. Effect of  $H_2O_2$  addition to 0.1M NaCl solution at 25°C on the open-circuit potential of 9Cr-1Mo.

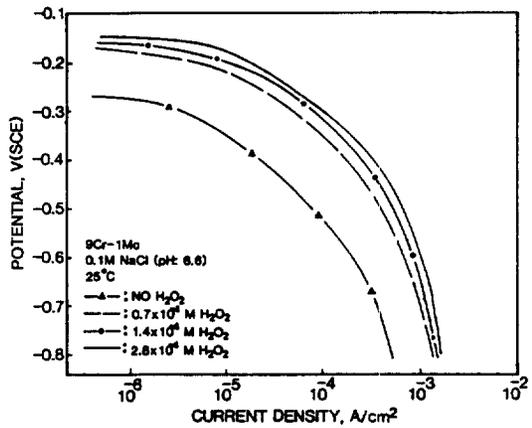


Figure 7. Effect of  $H_2O_2$  addition to 0.1M NaCl solution at 25°C on the cathodic polarization curve of 9Cr-1Mo.

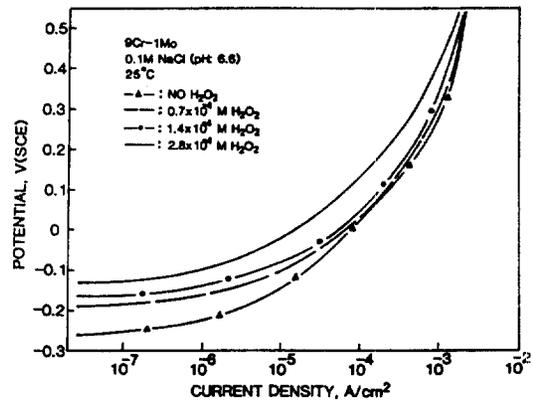


Figure 8. Effect of  $H_2O_2$  addition to 0.1M NaCl solution at 25°C on the anodic polarization curve of 9Cr-1Mo.

with  $H_2O_2$  additions display a similarity to the polarization curve under  $\gamma$ -radiation (see Figure 2). Furthermore, as shown in Figure 8,  $H_2O_2$  did not cause changes in the oxide properties formed on 9Cr-1Mo in NaCl solution, and the positive shifts of the corrosion potential can be understood by an additional cathodic reaction of  $H_2O_2$ .

### CONCLUSIONS

Gamma radiation increases the oxidizing nature of NaCl solution through production of radiolytic species. The generation of oxidizing products in the solution layers adjacent to 9Cr-1Mo alloy is responsible for the rapid potential shifts observed upon imposition of the 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 9Cr-1Mo. But, it was found that  $\gamma$ -radiation did not cause changes in the oxide properties formed on 9Cr-1Mo in 0.1M NaCl solution.

The beneficial effects of radiation are similar to those produced by addition of  $H_2O_2$  to NaCl solution, which indicated that  $H_2O_2$  is the most important product generated by radiolysis of NaCl solution in determining the corrosion potential of 9Cr-1Mo alloy, providing another cathodic reaction (reduction of  $H_2O_2$ ).

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