Effects of hydrogen peroxide on 304 stainless steel in high temperature water

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Abstract. Hydrogen peroxide (H₂O₂), an oxidizer produced by water radiolysis, is considered one of the main contributors to corrosion of the stainless steel (SS) components in the cooling system of nuclear reactors. The detailed understanding of this chemical system is however still missing. The present research aimed to study the effects of H₂O₂ on 304 SS. The surface morphology and the chemical composition of the SS specimens after experiment were examined using Scanning Electron Microscope – Energy Dispersive X-ray (SEM-EDX). The change in atomic % of Fe, Cr, Ni, and O as a function of temperature will be reported. The corrosion type and possible corrosion products will be proposed and discussed.

1. Introduction
Corrosion is one of the most challenging issues in nuclear industry. This problem occurs mainly to the stainless steel (SS) components of nuclear reactor cooling loop where high temperature water is used as a coolant. The water coolant is constantly exposed to radiation from the reactor core producing radiolytic primary species (\(e_{aq}^{-}, \text{OH}, \text{H}_2\text{O}_2, \text{H}_2\text{O}_2\), H₂ and HO₂/O₂⁻)[1-2]. When the oxidizing species - \(\text{OH} \), \(\text{H}_2\text{O}_2\), and HO₂/O₂⁻ - are in contact with the metal surface, the Electrochemical Corrosion Potential (ECP, \(E_{corr}\)) at the metal/water interface increases. Consequently corrosion takes place, leading to dissolution of free metal ions from the bulk material into water coolant[3-4]. Among the oxidizing species, \(\text{OH}\) is the most powerful oxidizer and it can enhance corrosion on material surface when it is present nearby. \(\text{H}_2\text{O}_2\), however, can contribute to corrosion at the interface from a longer distance. In addition, it has been established that under certain conditions related to nuclear technology, \(\text{H}_2\text{O}_2\) makes the highest impact to corrosion[5-6]. For this reason, effects of \(\text{H}_2\text{O}_2\) on corrosion of nuclear materials have drawn considerable attention to nuclear scientists and engineers.

It has been reported that in steel, such as carbon steel when \(\text{H}_2\text{O}_2\) is added to the chemical system, \(E_{corr}\) at the interface increases and \(E_{corr}\) is found to be a strong function of \(\text{H}_2\text{O}_2\) concentration. Precisely, adding \(\text{H}_2\text{O}_2\) can potentially induce a breakdown of the outer layer protective oxide film on carbon steel surface[4-5]. In the case of stainless steel, it has been shown that with \(\text{H}_2\text{O}_2\) addition after destruction of the outer oxide layer, the chromium-rich inner layer can be also damaged with detectable Cr ions in the solution[6]. In addition, a study under conditions with the presence of ionizing radiation has demonstrated that at \(E_{corr}\) (at the 316 SS/solution interface) around 0.05 V_SCE, a...
rapid growth of a magnetite/maghemite/γ-FeOOH layer is detected[7]. More importantly, $E_{corr}$ of SS (AISI 316 L) has been found to be dependent on temperature/or pressure of the system[8]. Despite a lot of research effort devoted to this topic, the detailed understanding of SS corrosion behavior under nuclear reactor conditions (high temperature - high pressure) is, however, still incomplete.

In the present research, effects of $H_2O_2$ on corrosion of 304 SS were investigated. The surface morphology and the chemical composition of the SS specimens treated with $H_2O_2$ at elevated temperatures up to 80 °C were examined. The change in atomic % of Fe, Cr, Ni, and O as a function of temperature will be reported. The corrosion type and possible corrosion products will be proposed and discussed.

2. Experimental section
304 SS was machined into square-shaped specimens (2 cm x 2 cm x 0.2 cm). A hole of 0.7 cm diameter was drilled at the center of the specimens. For surface preparation, wet polish using polishing paper up to 1200 grit (Buehler MetaServ 250 Twin polisher) was performed. Organic residuals on the specimens were removed by ultrasonic cleaning in acetone, methanol and ethanol, respectively. The cleaned specimens were then air-dried and weighed. Prior to the experiment the chemical composition of the SS prepared was investigated using X-ray Fluorescence (XRF) (Bruker, S8 TIGER).

Deionized water (Thermo Scientific) with 18.2 MΩ-cm resistivity and total organic carbon < 1 ppb was used to prepare 5% and 10% $H_2O_2$ (Merck Millipore) solutions. The solutions were later purged with 99.999% N$_2$ for 2 hours to deaerate and filled into the high pressure pump system of our high temperature setup, the details of which were reported earlier[9]. Subsequently, the solution was flowed at the flow rate of 2 ml/min into the hot cell where the SS specimens were fixed inside with glass hooks. The solution was finally collected in a reservoir at the end of the flow system.

Before characterization, the SS specimens were left to dry and weighed. The surface morphology and chemical composition of the specimens were then examined using SEM-EDX (TESCAN VEGA 3) at 20 keV. For each feature on the specimen surface, the EDX spectra of 4 major elements: Fe, Cr, Ni and O were acquired from 5 different locations using point analysis.

3. Results and discussion
XRF analysis shows that the 304 SS received is composed of 70.20% Fe, 18.75% Cr, 7.75% Ni and 1.80% Mn with trace levels of Cu, Si, Mo, Co and C. The difference between the weight of the post-treatment specimens and the initial weight is found to be not statistically significant. Figure 1 shows the surface morphology of the 304 SS specimens exposed to $H_2O_2$ for 100 hrs at temperatures up to 80 °C.

![Figure 1. SEM images of the 304 SS exposed to $H_2O_2$ for 100 hrs: (a) DI water, 25 °C, (b) 5% $H_2O_2$, 25 °C, (c) 10% $H_2O_2$, 25 °C, (d) 10% $H_2O_2$, 50 °C and (e) 10% $H_2O_2$, 80 °C.](image-url)
The SEM images reveal the formation of pitting corrosion on the specimen surface in the temperature range studied. As seen in figure 1, in all cases distinct features found on the surface are smooth area, corrosion products and pits. Increasing of H$_2$O$_2$ concentration from 0 to 5% (figures 1(a) and 1(b)) at room temperature seems to increase the pit density. However, the effect on pit density is unnoticeable when the H$_2$O$_2$ concentration changes from 5 to 10%. At H$_2$O$_2$ concentration of 10%, raising the temperature to 50°C and 80°C shows no effect on deposition of corrosion product and pit density, whereas an increase of pit size with temperature is observed.

The characterization of chemical composition was focused on 3 different features: smooth area, corrosion product and pit. For all cases, in the smooth area of the specimens, Fe and Ni were found to decrease within 1% and Cr was found to increase 1.6% in comparison with the blank sample. No O was detected, and effects of H$_2$O$_2$ concentration and temperature were not seen. Therefore, it can be stated that almost no corrosion occurred in this smooth area. For analysis of the corrosion products which appeared in lighter color under SEM, in all cases O was observed suggesting oxide formation. Increasing concentration of H$_2$O$_2$ was found to result in decreasing of Fe and Ni contents with increases of Cr and O. This suggests that H$_2$O$_2$ induces dissolution of Fe and Ni contained in the oxide, hence, exposing the remained inner layer oxide to the environments. Based on this information, therefore, the possible stable corrosion products in the system must contain Cr and O. In addition, the composition of corrosion products remained unchanged with temperature.

The results from EDX study of the treated specimen surface in the pit area are presented in figure 2. It is clear that in the pit area at room temperature, decreases of Fe and Ni, and increase of O are seen with increasing of H$_2$O$_2$ concentration. The content of Cr, however, seems to be unaffected. The results imply that at this temperature, the pits are still covered with the chromium-rich inner oxide layer. At 50°C and 80°C, adding 5% H$_2$O$_2$ shows a small effect on Fe and Cr. For Ni content, a large effect of H$_2$O$_2$ is seen in the 80°C case. Nevertheless, at these temperatures with 10% H$_2$O$_2$, there are a sharp drop of Fe and a dramatic enhancement of Cr content with no Ni detected. It should be also noted that at the 2 elevated temperatures, O is undetectable. These results indicate that under these conditions the protective oxides in the pits are fully removed; therefore, the bulk material is exposed to the solution. Moreover, it is evident that H$_2$O$_2$ has a harsh effect towards Fe and Ni.

**Figure 2.** Chemical composition in the pit area on the 304 SS surface exposed to different concentrations of H$_2$O$_2$ for 100 hrs: (a) Fe, (b) Cr, (c) Ni and (d) O.
4. Conclusion

The effects of H$_2$O$_2$ on corrosion of SS 304 at temperatures up to 80 °C have been investigated. The results obtained from SEM-EDX show that pitting is the main corrosion formed under the experimental conditions. Increasing H$_2$O$_2$ concentration has a larger effect on depletion of Fe and Ni in comparison with Cr. The possible stable corrosion products are chromium oxides. The results obviously indicate that the effects of temperature in this chemical system is complicated. Increasing of H$_2$O$_2$ and temperature can highly accelerate pitting corrosion of the SS surface.

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