

# Characteristics of Oxide Layer of Nickel Alloy in Primary Water Chemistry Environment

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## 1. Introduction

The reactor coolant system of a nuclear power plant transfers the heat which is generated from the fuel to the secondary system through steam generators. This system is operated at high temperatures (about 310°C) under high pressure (about 15.5 MPa), and the integrity of the system and its components is very important in terms of the plant's safety. The failure of pressure boundary material causes loss of coolant accidents; therefore the chemistry of coolant (water) is strictly controlled and corrosion-resistant materials, such as stainless steel and nickel alloy are used as the pressure boundary materials. Also an in-service-inspection program is applied to vulnerable points.

However, corrosion cannot be prevented completely; a small amount of corrosion occurs in high-temperature and high-pressure environments. Usually, an oxide layer is formed on the surface of corrosion-resistant metallic materials when they are exposed to harsh environments. The characteristics of this oxide layer are closely related to general corrosion properties, and to the coolant water chemistry.

In this paper, a water loop system which simulates the reactor coolant environment and the result of a general corrosion experiment are reported.

## 2. Experiment Method

### 2.1 Corrosion Loop

A schematic diagram of the experimental loop system is presented in Fig. 1. One through system loop is used to carefully control impurities. The loop system comprises water chemistry control equipment, pressure/temperature controlling equipment, and an autoclave.

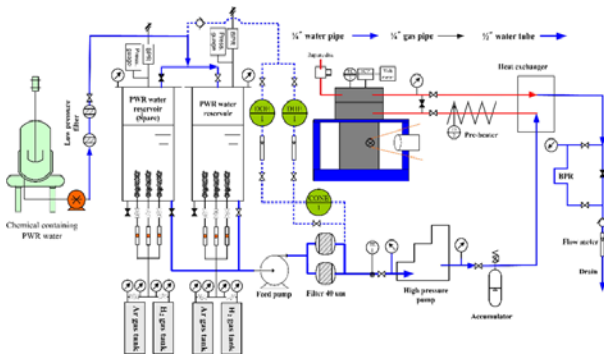


Fig. 1. Schematic diagram of water loop system.

In the water chemistry control equipment, dissolved oxygen, dissolved hydrogen, boric acid, and lithium hydroxide concentrations are controlled. A high pressure pump, a back pressure regulator, and a band-type heater are used to control the pressure and temperature. The autoclave is fabricated with stainless steel, and has 1-liter internal volume. To apply the in-situ laser spectroscopy technique, a diamond/sapphire window is installed. A zirconia membrane pH sensor is used to measure the electro-chemical potential (ECP) in a high-temperature environment.

### 2.2 Material and Environment

The test materials were Alloy 600 and 690 which are used in domestic pressurized water reactor (PWR) steam generator tubing. Coupon type specimens were used for general corrosion test.

The test water chemistry environment is presented in Table 1. The test conditions simulate the normal operation environment of a PWR coolant system. Under the same chemical conditions, the pH value varied with temperature. The pH value was calculated using EPRI ChemWorks[1] program.

The duration of experiment was 1,000 hours; after 100/500/1,000 hours each specimen was taken out and analyzed.

Table 1: Water Chemistry Environment

Test Environment		PWR Primary Environment
Water Temp. & Press.		325 °C, 15.5 MPa
Water Chemistry	pH	pH 6.9 at 311 °C
	DO	< 5 ppb
	DH	25 cc(STP)/kg
	Conductivity	≈ 22 μS/cm (1900 ppm H <sub>3</sub> BO <sub>3</sub> + 2.2 ppm LiOH)

## 3. Result

### 3.1 General Corrosion

To calculate the general corrosion rate and amount, the specimens were weighed before and after experiments with precision balance. However, meaningful mass changes were not found. This seems to be due to the good corrosion resistance of nickel

alloy and the thin passive oxide layer which is supposed to exist in nickel alloy in coolant water chemistry condition [2,3].

### 3.2 Oxide Layer

Scanning electron microscope (SEM) was used to analysis the oxide layer. Fig. 2 shows the surface of the Alloy 600 and Alloy 690 oxide layer.

On the Alloy 600 surface, a needle-like oxide formed. The thickness of the needles was several nano-meters, and the needle length is seemed to increase as the corrosion time increases. The oxide shape was much different in Alloy 690, where a polyhedron type oxide was formed. The polyhedron size/volume increased with corrosion time. A cross section of the oxide layer was also observed, as shown in Fig. 3. However, it was difficult to analysis the oxide layer because thin oxide layer was blunted during the pre-treatment procedure. The thickness of oxide is supposed to be less than 200 nm.

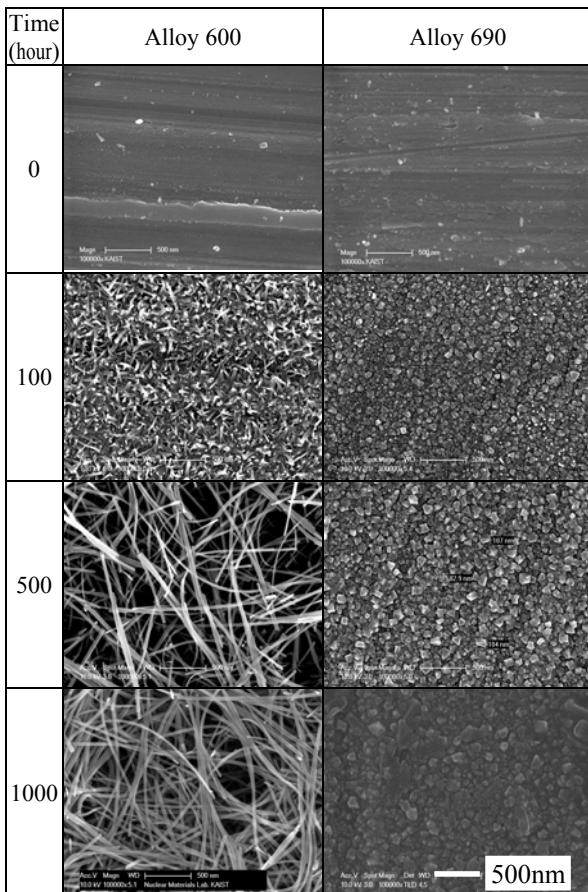


Fig. 2. SEM image of oxide surface (X 10,000)

X-ray diffraction (XRD) was applied to characterize the oxide layer crystal structure. Weak chromite ( $\text{Fe}^{2+}\text{Cr}_2\text{O}_4$ ) and bunsenite ( $\text{NiO}$ ) peaks were observed, due to the thin oxide thickness.

Other analysis methods, such as transmission electron microscopy (TEM), auger electron

spectroscopy (AES), x-ray photoelectron spectroscopy (XPS) are required to identify the oxide layer accurately.

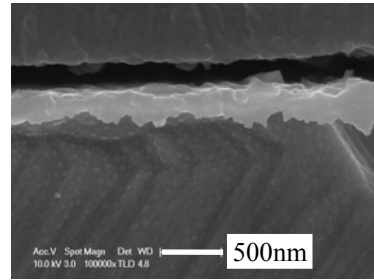


Fig. 3. Cross section image of Alloy 690 oxide layer, after 1,000 hour corrosion test (X 10,000)

### 3.3 Future Plan

Further investigation of the oxide layers will be conducted using more precise analytical tools.

To identify the increased dissolved hydrogen concentration and Zinc (Zn) injection effect, another corrosion test will be performed, a oxide layers will also be investigated. In addition, in-situ oxide analysis using laser spectroscopy will be applied to identify oxide layers under high-temperature water chemistry condition.

## 4. Conclusions

A general corrosion experiment was performed with Alloy 600/690 materials in the simulated environment of PWR reactor coolant system. After a 1,000 hour test, specimens were examined by SEM and XRD. The shapes of the oxide layers are different in Alloy 600 and 690. However, other analysis methods are needed to further characterize the oxide film.

To identify the effect of water chemistry change (dissolved hydrogen concentration, zinc injection), more experiments will be performed.

## REFERENCES

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- [3] J. Deshon, Corrosion Film Characteristics of Fe-Ni-Cr Alloys in PWR Environments, EPRI, 1018721, 2009