

# Electrochemical response of scratched Alloy 600 in simulated primary water and its influence with hydrogen entry

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The effect of scratches on oxidation evolution of Alloy 600 was monitored by EIS in 290°C simulated primary water. EIS result indicates that oxide film reached a stable condition until 7 days' immersion. The scratched Alloy 600 possessed almost the same evolution of oxide film with plain specimens. Anodic polarization was performed to study combined effect of scratches and charged hydrogen. The anodic current changes of scratched Alloy 600 after hydrogen charging were not the simple superimposition between that of scratched and charged plain Alloy 600. Alloy 600 after scratching was supposed to trap more hydrogen because of introduction of cold work. The trapped hydrogen could accelerate the oxidation by enhancing dissolution of chromium oxides. Thus, the oxides became less protective and anodic current increased considerably over more noble potential range.

Keywords: SCC; Cathodic charging; Anodic polarization; EIS

## 1. Introduction

Nickel-based Alloy 600, as a material of steam generator tubing, has been studied for nearly 40 years. This Alloy is known for its susceptibility to intergranular stress corrosion cracking (SCC) in high-temperature PWR water. Recently, field SCC cases indicate that the dominant failure mechanism has been IGA and SCC of free-span surfaces, especially at abnormal surface conditions such as surface dents or scratches which were produced during inserting tubes into the steam generator tube support sheet. Framatome ANP reported that SCC developed in the surface marks/scores of Alloy 600, introduced into the internal surfaces of split tube sections prior to bending [1].

Several tubes in Unit-1 and Unit-2 of Oconee Nuclear Station were removed after eddy current detection and residual compressive stress existed on the scratch. Burst testing indicated that cracking related to surface scratch. SCC initiation which associated with a surface scratch at free span cold leg arose at McGuire-1 and McGuire-2 in Alloy 600MA tube after only several years' service [2-4]. In previous work, the author found scratch-induced SCC initiated in caustic lead containing solution at 330°C [5].

These cases mentioned above implied that local mechanical marks/scratches could be latent sites to initiate SCC. It was reported that the typical scratch surface and outer surface were exposed in the same environment and chemical analyses showed no difference [6]. As with many materials, cold work, similar effect of scratch, increases the rate of SCC and cold worked nickel alloys was supposed to trap more hydrogen in the stress field of dislocations [7]. Hydrogen ingress can occur via corrosion processes and/or dissolved hydrogen in environment, can produce various effects on their properties after entering into matrix.

The presence of scratches is inevitable. In PWR primary water, high concentration of dissolved hydrogen,

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which maintains a lower  $H_2O/H_2$ , and high temperature make hydrogen permeation easier. In order to find a guidance to explain the corrosion behavior of scratched Alloy 600, the combined effect of scratches and hydrogen was studied by performing electrochemical tests.

## 2. Experimental process

### 2.1 Material

Nickel base Alloy 600 was used for this study. This Alloy was heat treated at 606-616°C for 10h 5min and then air cooled. The chemical composition of this Alloy 600 is listed in Table 1.

The specimens were cut from bulk Alloy 600 by  $12 \times 12 \times 3$  mm<sup>3</sup>. The larger faces of sheet specimens were ground with emery paper up to 2400 grit and mechanically polished using 1 $\mu$ m silica paste to get a mirror finish. Some of the specimens were chose to make some scratches (about 120 $\mu$ m in width, 20 $\mu$ m) by using a cone hard alloy head. And then, all the specimens were soldered with high purity Ni wires with diameter of 0.5mm, which covered with two layer shrinkable PTFE tube with aim to increase insulation.

Table 1 Compositions of Alloy 600

Element	C	Si	Mn	P	S	Ni	Cu	Cr	Fe	Nb
wt.%	0.059	0.13	0.21	0.006	0.001	74.19	0.12	15.57	9.41	0.05

The microstructure of this heat after electro-polish was characterized using electron backscatter diffraction (EBSD) as shown in Fig.1. EBSD measurement was conducted on Hitachi S-4300 FE-SEM, which equipped with solutions camera control system made by TSL, Co. Ltd. The data was collected and analyzed by OIM<sup>TM</sup> Software. The grains were about 80 $\mu$ m.

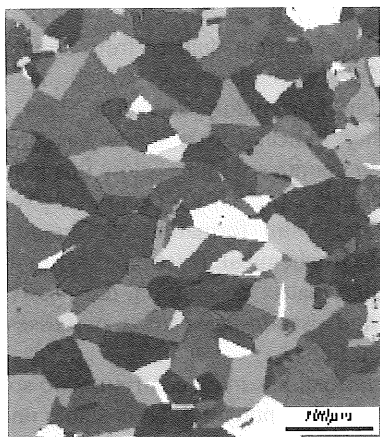


Fig.1. EBSD observation of Alloy 600

### 2.2. Water chemistry control

All the test were performed in the facility of autoclave fabricated by Toshin Kogyo Co., LTD, Japan, with a recirculating water loop to maintain the desired primary water chemistry conditions. The simulated primary water was prepared with 1200ppm B as H<sub>3</sub>BO<sub>4</sub> and 2ppm Li as LiOH. The inlet dissolved hydrogen (DH) was controlled at 30cc/kg and test temperature was 290°C.

### 2.3. Hydrogen charging and electrochemical test

The specimens for electrochemical tests were listed in Table 2.

Table 2 Test detail of Alloy 600

Specimenn	Charging	Test content
Plain	No	EIS, AP <sup>a</sup> ,
Scratched	No	EIS, AP,
Plain	Yes, 86.5h	EIS, AP,
Scratched	Yes, 86.5h	EIS, AP,

<sup>a</sup> AP: Anodic polarization.

A three-electrode system was used, which concluded the external pressure balanced calomel electrode SCE (0.1N) acted as a reference electrode, a platinum wire as a counter electrode and work electrode. All the measured potentials were transferred to potentials referred to standard hydrogen electrode. The potentials of Alloy 600 were monitored with POTENTIOSTAT/GALVANOSTAT HA-151A. EIS was measured by using Solartron Impedance/gain-phase analyzer SI 1260 every two days until the corrosion potential of all the specimens became relatively stable. Some of the specimens were anodic polarized using Solartron electrochemical interface SI 1287.

After this, some specimens were chosen to charge hydrogen cathodically in the simulated primary water. The charged current density was controlled at a small constant of 0.35mA/cm<sup>2</sup> at 290°C, which was in order to minimize the damage of cathodic hydrogen charging to polished and scratched Alloy 600 surface. The total hydrogen charging time was 86.5h for each specimen. Anodic polarization was performed for the charged Alloy 600 after for 4h later.

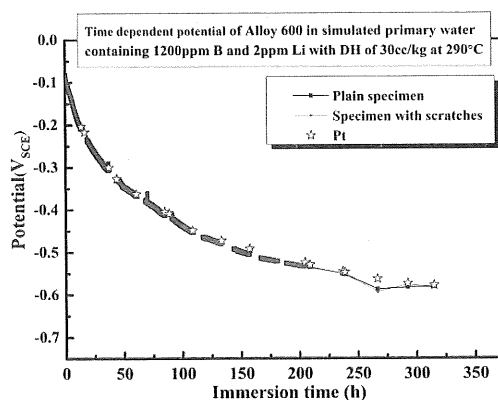


Fig.2. Time dependent potential of Alloy 600 in simulated primary water at room temperature, during heating up and at 290°C

## 3. Results and discussion

### 3.1. The effect of scratches on corrosion of Alloy 600

#### 3.1.1. Oxidation of scratched Alloy 600 by EIS monitoring

The time dependent potentials for plain and scratched Alloy 600 were shown in Fig.2. For these two specimens, the potentials all dropped negatively during the whole monitoring process. At the start of the test, the potentials

shifted negative dramatically. It took about 7 days to reach a stable value in the simulated primary water with a DH 30cc/kg, which means that oxide formation and matrix dissolution needed longer time to get a balance. Measurement of anodic polarization in less than 7 days' immersion may not reflect the electrochemical behavior of long-term service of Alloy 600. However, there seems to be no difference for the corrosion potential between scratched and plain specimens.

During potential monitoring, EISs both for plain (Fig.3a) and scratched (Fig.3b) Alloy 600 were traced every two days. For the low frequencies impedance arc in Fig.3 which stands for the electric double layer, there were no obvious differences between plain and scratched Alloy 600 with increasing immersion time.

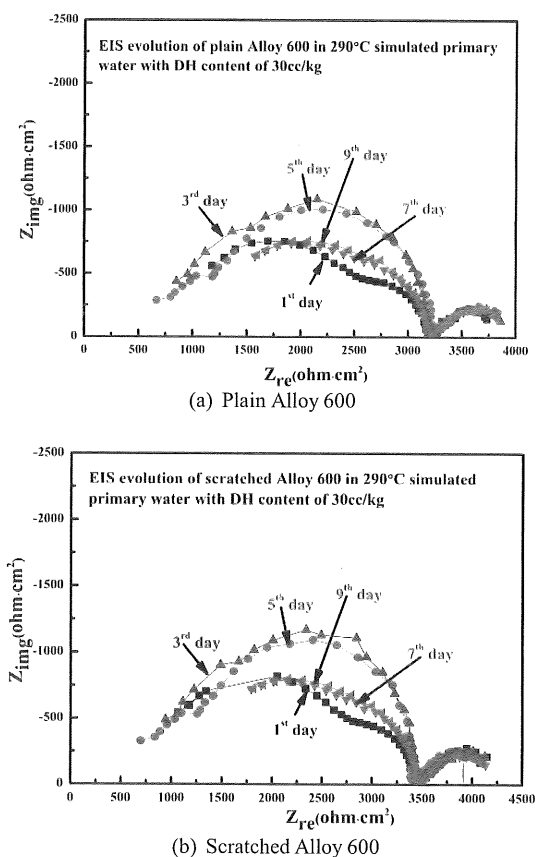


Fig.3. Evolution of Nyquist diagrams for plain and scratched Alloy 600 in simulated primary water

However, significant difference can be found in the high and intermediate frequencies impedance arc as shown in Figs.3a and 3b. This part of impedance arc can reflect characters of oxide film. It is noteworthy that there is no persistent increase of imaginary part during the evolution of oxide film in the simulated primary water. The imaginary part in high and intermediate frequencies dropped after 5 days' immersion. Oxides became more stable from 7th day and Nyquist diagram did not change a lot from that time on. This is consistent with the result of potential monitoring.

### 3.1.2. Anodic behavior of scratched Alloy 600

The polarization curves for plain and scratched Alloy 600 were shown in Fig.4. Even though Alloy 600 was scratched, there was no apparent effect on anodic behavior compared to plain Alloy 600. The identical character may be caused by dissolved hydrogen. The dissolved hydrogen can easily enter into the alloy 600 matrix [7]. Because of the uniform hydrogen in the aqueous environment, surface distribution of hydrogen permeated into the oxide film and matrix was supposed to be homogeneous in both kinds of specimens. At corrosion potential, dissolved hydrogen can partly reduce the surface film and the film toward corrosion for both scratched and plain Alloy 600. The high anodic current also suggests that matrix dissolution was not restrained even though there covered oxide film on the surface. Scratching brought about a heavy plastic deformation to the surface, but dissolved hydrogen as the leading role, suppressed the effect of scratches on the surface.

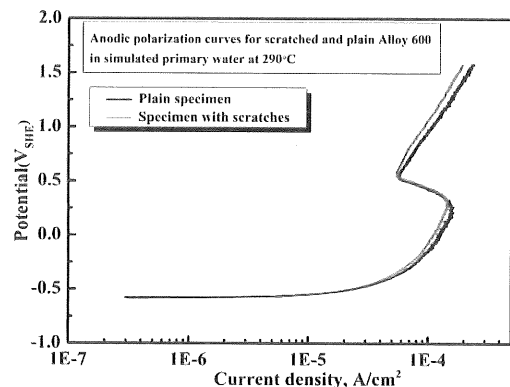


Fig.4. Anodic polarization curves for plain and scratched Alloy 600 in simulated water containing 1200 ppm B and 2 ppm Li at 290°C.

A decrease of current density from about +0.2V/SHE to +0.6V/SHE was observed, which is not a real passivation but a pseudo-passivation. This decrease of current density indicates that there was pre-passivation process during anodic scanning below this potential range. The competition probably occurs between matrix dissolution and film formation at anodic potentials. When the electrochemical reaction of film formation is more rapid than matrix dissolution, pre-passivation below +0.2V/SHE and pseudo-passivation processes take place as presented in Fig.4.

The film formation can be contributed to some possible reasons. At corrosion potential, Ni is stable under a DH of 30cc/kg at 290°C [8] and the oxide film formed on Alloy 600 was rich in Fe and Cr [9]. According to potential-pH diagram of Ni, Cr, Fe in high temperature [10], at anodic potentials in studied environment (pH≈7), only Ni can be oxidized as NiO and Cr and Fe are stable oxides as Cr<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, respectively. Oxides such as NiCr<sub>2</sub>O<sub>4</sub> and NiFe<sub>2</sub>O<sub>4</sub> may form on the surface during anodic scanning. With increasing anodic potential, the protective of film become more compact, which induced a pseudo-passivation zone. Over +0.6V/SHE, oxides dissolution or

oxygen evolution may start.

### 3.2. The electrochemical response of Alloy 600 to charged hydrogen

After hydrogen charged in simulated primary water, Fig.5 shows the anodic polarization curves obtained from plain Alloy 600. To some extent, the current density at pseudo-passivation zone for the charged specimen increased, i.e., the formation of compact oxide film, which has been discussed in Section 3.1.2, was retarded.

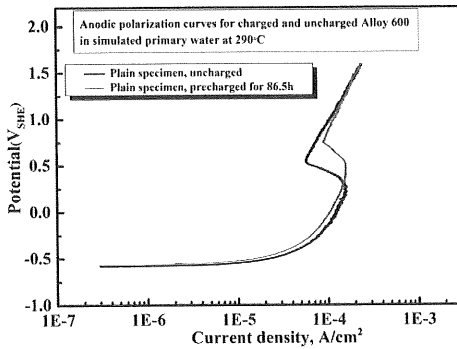


Fig.5. Anodic polarization curves for plain Alloy 600 after charging in simulated water containing 1200 ppm B and 2 ppm Li at 290°C.

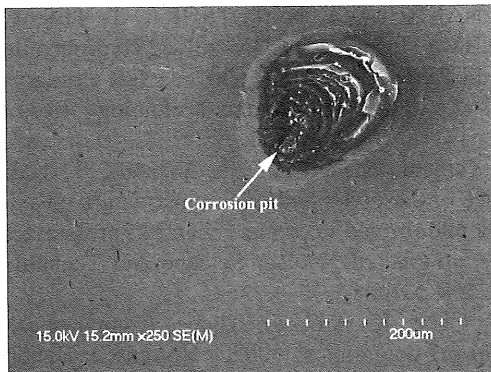


Fig.6. SEM micrograph revealing the surface corrosion pit of 86.5h hydrogen charged plain Alloy 600 after anodic polarization

This phenomenon can be explained by the permeated hydrogen during charging process in the oxide and Alloy 600 matrix. The hydrogen entered into the matrix is divided into two parts: the reversible hydrogen and irreversible hydrogen. According to M.Uhlemann [7], carbide/carbonitride precipitates were principal irreversible traps and hydrogen reversibly trapped in the interstitial atoms could release at a temperature higher than 250°C. There are chromium carbides or titanium nitrides existed in nickel alloys. Hydrogen can be trapped in these precipitates even at 290°C, which results in local higher hydrogen concentration than that of uncharged Alloy 600.

Fig.6 depicts the optical micrograph of hydrogen charged Alloy 600 after anodic polarization in simulated high temperature primary water. It was found that a corrosion pit appeared on the surface. This extra

irreversible hydrogen could slow down the formation of oxide film and accelerate matrix dissolution.

### 3.3. The combined effect of scratches and charged hydrogen

Anodic polarization curve for scratched Alloy 600 (Fig.7) was measured after hydrogen charging for 86.5h in simulated primary water, too. The pseudo-passivation zone over +0.3V/SHE after hydrogen charging, compared to the uncharged but scratched one, disappeared.

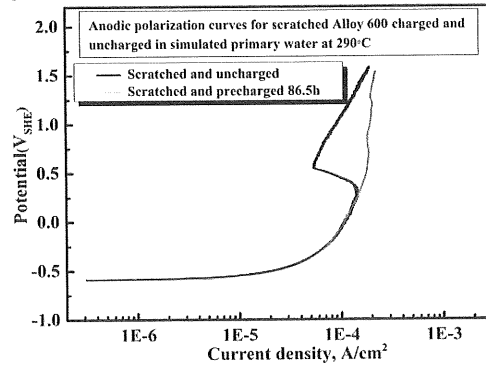
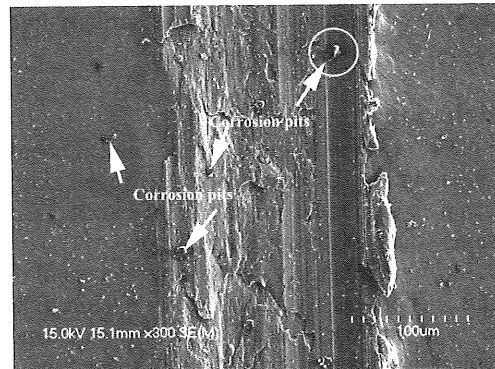
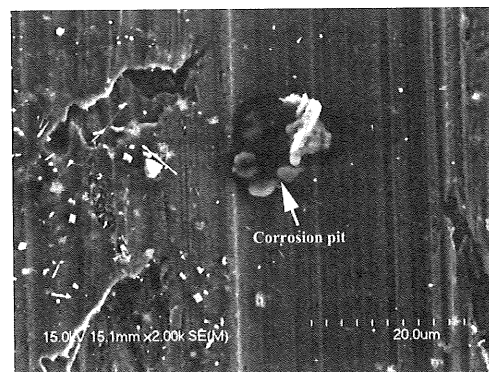


Fig.7. Anodic polarization curves for scratched Alloy 600 after hydrogen charging in simulated water containing 1200 ppm B and 2 ppm Li at 290°C.



(a) Top view of a scratch



(b) Marked area in (a) with a high magnification

Fig.8. Surface observation of 86.5h hydrogen charged Alloy 600 with scratches after anodic polarization

In the test condition, charged hydrogen in the interstitial atoms or the stress field of dislocation already released at 290°C. Cold worked Alloy 600 can trap more hydrogen in the matrix since the existence of microvoids

as irreversible traps [7, 11]. Scratches have a similar effect. For nickel based alloy, scratching the surface introduced many micro-voids and caused a heavy deformational layer at the scratch groove which has been investigated by F. Meng et al. [5]. Amounts of irreversible hydrogen were trapped in the deformed layer around the scratch groove.

The anodic current over +0.2V/SHE for scratched Alloy 600 was not related to increased potential, which implies that anodic dissolution was controlled by diffusion. The irreversibly trapped hydrogen in cold worked Alloy 600 can be as high as 6ppm at this test temperature [7], which was higher than the dissolved hydrogen (about 2.67ppm) in the simulated primary water. The irreversible hydrogen was sufficient to inhibit formation of oxide film such as  $\text{NiCr}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4$  and quickened anodic dissolution by oxidizing  $(\text{Fe,Cr})_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$ . As displayed in Fig.8, a lot of corrosion pits appeared at two banks of scratch and the scratch groove. The pits illuminate that the protective chromium oxide was also dissolved.

According to B.T. Lu et al. [12], the synergistic effect due to the interaction of charged hydrogen and local stress field is negligible. In present test, the superimposition of dissolved hydrogen in the primary water and scratch-induced local stress field can be ignored as indicated in Fig.4. However, the charged irreversible hydrogen caused by scratching have a strongly interaction with active dissolution of Alloy 600.

#### 4. Conclusion

The effect of scratches on electrochemical behavior of Alloy 600 and its influence with hydrogen entry was investigated in simulated primary water at 290°C. Some conclusions could be drawn as following:

I. Oxide film reached a stable condition until 7 days' immersion according evolution of corrosion potentials and EIS. The scratched Alloy 600 possessed almost the same evolution of oxide film with plain specimens.

II. Scratched Alloy 600 did not change the anodic behavior at all. Uniform dissolved hydrogen plays a leading role in matrix dissolution in simulated primary water and may suppress effect of scratches.

III. The anodic current changes of scratched Alloy 600 after hydrogen charging were not the simple superimposition between that of scratched and charged plain Alloy 600. The irreversibly trapped hydrogen could accelerate the oxidation by enhancing dissolution of chromium oxides at more noble potentials.

However, additional studies are needed for a deeper and more quantitative analysis of the structure of corrosion scale for charged and uncharged Alloy 600.

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