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Corrosion Behavior of Nickel-Plated Alloy 600 in High Temperature Water

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In this paper, electrochemical and microstructural characteristics of nickel-plated Alloy 600 were investigated in order to identify the performance of electroless Ni-plating on Alloy 600 in high-temperature aqueous condition with the comparison of electrolytic nickel-plating. For high temperature corrosion test of nickel-plated Alloy 600, specimens were exposed for 770 hours to typical PWR primary water condition. During the test, open circuit potentials (OCP's) of all specimens were measured using a reference electrode. Also, resistance to flow accelerated corrosion (FAC) test was examined in order to check the durability of plated layers in high-velocity flow environment at high temperature. After exposures to high flow rate aqueous condition, the integrity of surfaces was confirmed by using both scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). For the field application, a remote process for electroless nickel-plating was demonstrated using a plate specimen with narrow gap on a laboratory scale. Finally, a practical seal design was suggested for more convenient application.

Keywords *: alloy 600, nickel plating, high temperature corrosion, open circuit potential, flow accelerated corrosion*

1. Introduction

Primary water stress corrosion cracking (PWSCC) has been one of major degradation modes that occur in structural materials for steam generators tubes or control rod drive mechanism (CRDM) nozzles in nuclear power plants. Recently, the PWSCC's were found in the inner diameter of penetration nozzles near the weldment of CRDM and reactor pressure vessel upper head in pressurized water reactor (PWR). The safety issue has been raised by crack initiation of nickel-base alloy by combination of high temperature, high residual stress and material properties.[1)]

In order to mitigate PWSCC in nickel base alloys, several techniques have been developed as follows; mechanical surface enhancement (MSE) techniques such as shot-peening and electropolishing which help to reduce surface tensile residual stresses or induce compressive surface stresses, environmental barrier or coating techniques including metal plating and weld deposit overlay which help protect the material surface from an aggressive environment, and open circuit potential (OCP) suppress techniques by chemical addition or dissolved hydrogen concentration.[2)]

Among these mitigation techniques, the electrolytic plating has been successfully developed and applied to nuclear steam generator tubing and pressurizer heater nozzles as a preventive and/or corrective measure against the PWSCC.[3)] Nickel metal is intrinsically suitable for plating on Ni-base alloys, because it can form a non-porous deposit layer with a good adhesion to Ni-base alloys by its composition and thermal expansion close to the base metal (no differential thermal expansion) as well as its high corrosion- and erosion- resistance in primary water condition.

Nickel plating on Ni-base alloys can be achieved electrolytically as well as electrolessly. In the electrolytic Ni-plating, pure nickel solution is used, pure nickel layer is formed on substrate, and separate electrode (anode) is needed for the plating.[4)] In 1994, this technique has been successfully applied to the repair of steam generator tubes in Pickering Unit 5 and pressurizer heater nozzles in Calvert Cliffs Unit 1.[3)] On the other hand, electroless Ni-plating can be applied by autocatalytic surface reaction without external current or separate electrode during the

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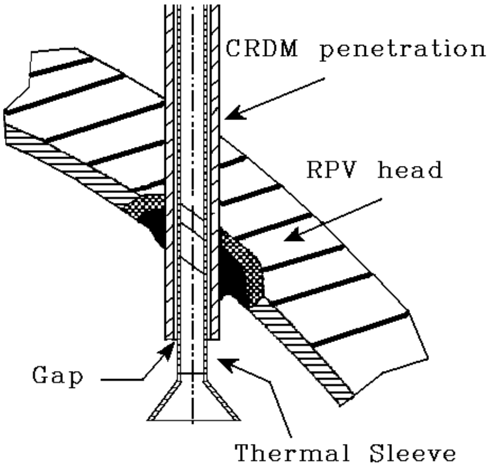


Fig. 1. CRDM nozzle on the reactor pressure vessel head in PWR

process. Because of this advantage, electroless Ni-plating can be applied to the places or mechanical components which cannot be reached by electrode, e.g., gap between CRDM penetration and thermal sleeve in reactor vessel head, as shown in Fig. 1. Even though electroless nickel plating techniques has wider applicability than electrolytic counterpart, there has been few investigation for nuclear power plant applications.

Current research activities are focused on the feasibility of electroless Ni-plating as a mitigation method for the cracking in CRDM penetration nozzles, particularly understanding of corrosion behavior at high temperature water. This paper presents initial results on the characterization of corrosion behavior of electroless Ni-plated Alloy 600 in comparison with electrolytic Ni-plated one in high temperature and high pressure aqueous condition. Furthermore, the methodical procedure of remote-controlled electroless Ni-plating applicable for CRDM penetration nozzles with narrow gap has been suggested.

2. Experimentals

2.1 Test specimens

Alloy 600 has been used as substrate for nickel plating in this study. The plate materials have been produced for commercial applications. Chemical composition of Alloy 600 used in this study is given in Table 1.

Table 1. Chemical composition (in weight percent) and mechanical properties of Alloy 600 test materials at room temperature

C	Si	Mn	P	S	Cr	Co	Nb	Ta	Ti	Al	Cu	Fe	Ni
.049	.16	.21	.009	.001	15.37	.1	.01	.01	.26	.16	.02	7.6	Bal.
Yield Strength = 380 Mpa, Young's Modulus = 218 GPa													

Test specimens were prepared by two different plating techniques with two different thickness of plating on the substrate; electrolytic Ni-plating with 15 ㎛ thickness (designated as EC15 hereafter) and 30 ㎛ (EC30), and electroless Ni-plating with 15 ㎛ (ES15) and 30 ㎛ (ES30).

For the electrolytic Ni-plating specimen, following processes were applied in steps; cleaning, surface deoxidation, surface activation, and nickel plating. The cleaning process was achieved by solvent solution containing trichloroethylene, and deionized water was used for rinse, and then electrolytic cleaning in NaCN and NaOM solution was applied to remove oxide layers on the substrate. This was followed by surface activation of substrate by 3% hydrochloric acid solution which resulted in good initiation and adhesion of the coating to the substrate. An electrolyte bath of nickel sulfate, nickel (II) chloride and boric acid solution was used for the plating, and this electrolytic nickel process produced a high purity plating of nickel layer upon alloy 600.

A detail procedure for electroless nickel plating was described in the following section for development of remote process of electroless Ni-plating. While electrolytic nickel plating leads to high purity plating layer, electroless-nickel plating produces a layer containing 7-8 % phosphorous contents. All specimens after plating were heat-treated at 200℃ according to ASTM Method B 689, in order to remove hydrogen absorbed during plating processes.

2.2 Potentiodynamic polarization measurement

To characterize the corrosion behaviors of Ni-plated Alloy 600 in high-temperature aqueous condition, electrochemical and microstructural properties of nickel-plated Alloy 600 were investigated. For high temperature corrosion test of nickel-plated Alloy 600, the specimens were exposed for 770 hours to typical PWR primary water condition with 1,000 ppm boron, 2 ppm lithium and 2.68 ppm dissolved hydrogen gas at a pressure of 18 MPa and a temperature of 290℃.[5] An experimental loop for the potentiodynamic polarization measurement in high temperature aqueous environment was constructed as shown in Fig. 2. EG&G Potentiostat/Galvanostat 273A was used as experimental apparatus for potentiodynamic polarization measurement. During the test, open circuit potentials (OCP's) of all specimens were measured using Ag/AgCl electrode as a reference electrode, 0.5 mmϕ Pt wire with platinization as a counter electrode while $Cu/Cu_2O/ZrO_2$ electrode was employed as a pH electrode. Once OCP was stabilized, which usually took 24 hours after each measurement, the electrodes were first polarized cathodically in order to reduce any oxidized species on the surface. OCP

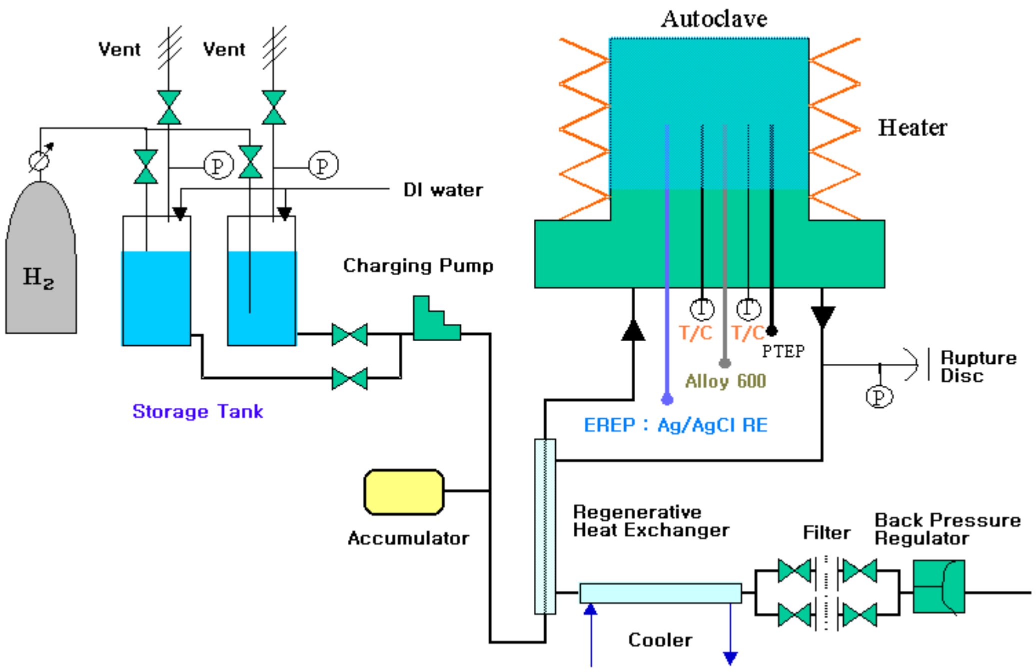


Fig. 2. Schematic of corrosion experimental facility in high temperature aqueous environment.

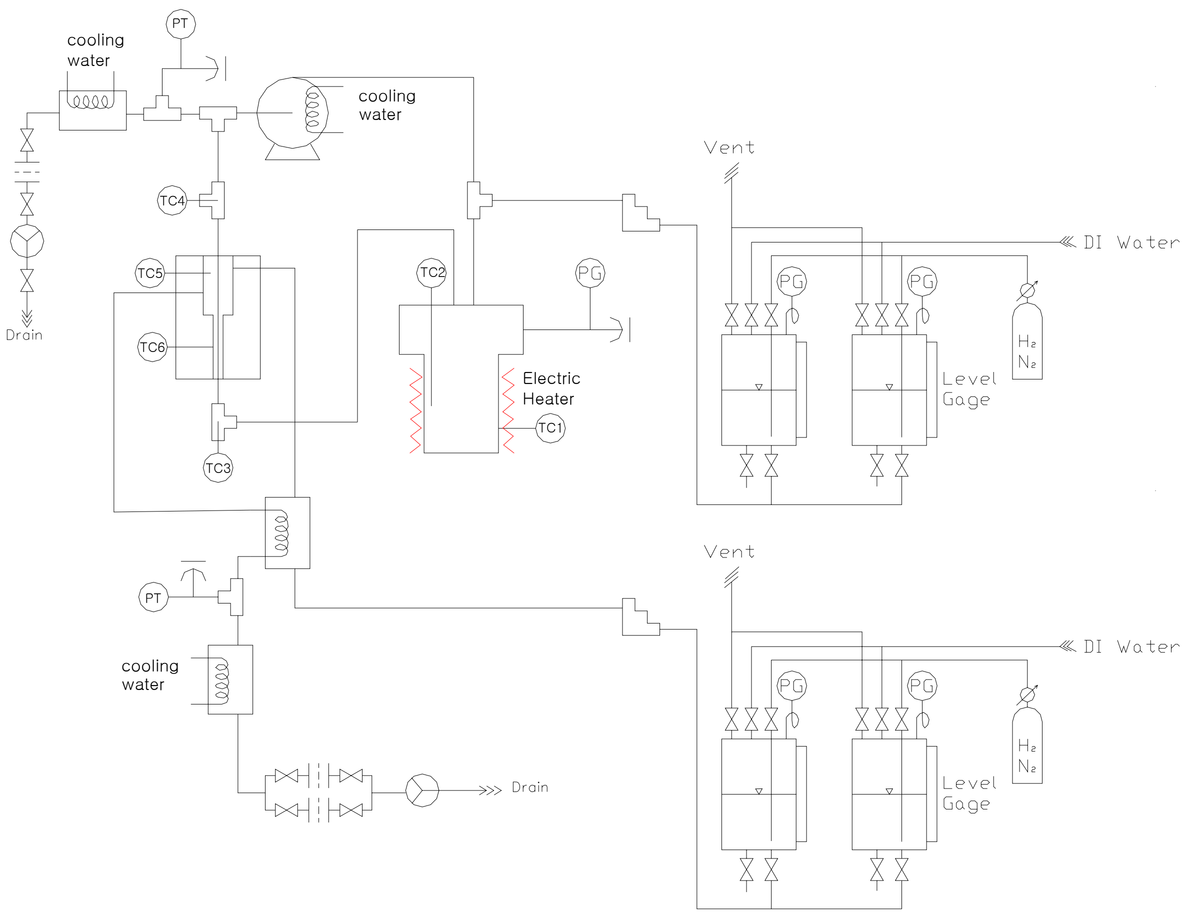
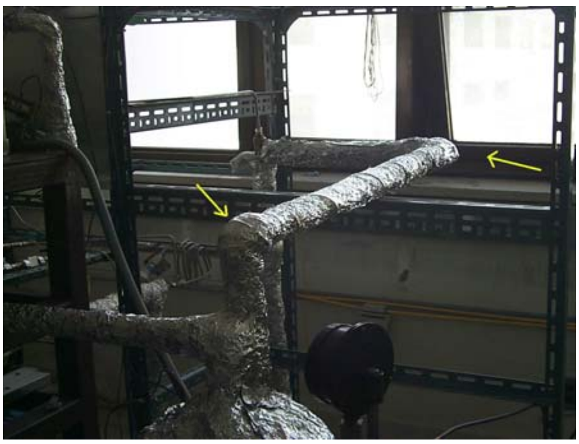


Fig. 3. Schematic of flow accelerated corrosion experimental facility in high temperature aqueous environment.

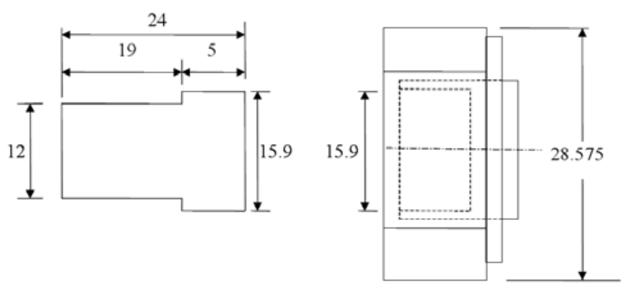
was again stabilized, and potentiostatic polarization began at a rate of 0.5 mV/sec ranging from -0.8 V to 1 V versus the standard hydrogen electrode at temperature (SHE(T)).

2.3 Flow accelerated corrosion test

In order to investigate the structural integrity of Ni-plating layer on substrate, flow accelerated corrosion test has been performed in high flow rate environment. Test specimens were exposed for 20 days at 250℃, 15 MPa and the flow velocity of 2 m/sec. Fig. 3 shows the schematic diagram of an experimental facility used for FAC test in this study. The specimens were T-shaped nickel-plated Alloy 600 specimens with 20 ㎛ thickness, plugged into 3/4” high pressure fitting nuts, and placed in the elbow region of flow system as shown in Fig. 4 (a). After exposures to high flow rate aqueous condition, oxide films formed on the surfaces of specimens were investigated using both scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).



(a)



(b)

Fig. 4. (a) Photograph showing two locations of specimens installation in the flow accelerated corrosion experimental facility, and (b) drawing of specimen (left) and standard high pressure fitting (right)

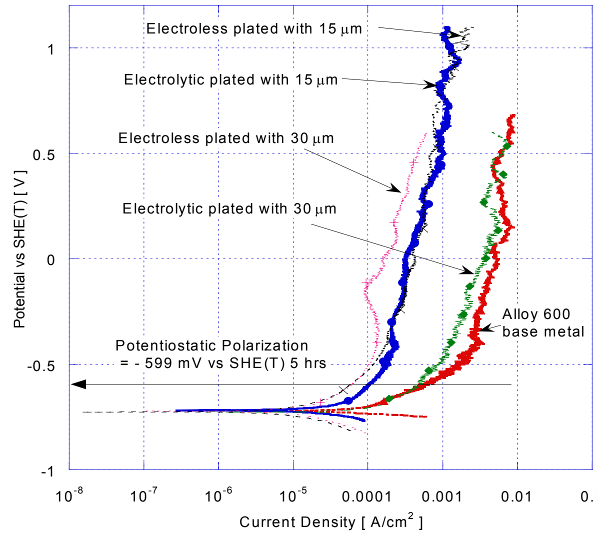


Fig. 5. Potentiodynamic polarization curves of Alloy 600 base metal and Ni-plated Alloy 600 in typical PWR water condition.

Table 2. Electrochemical parameters from potentiodynamic polarization measurements using nickel plated Alloy 600 specimens in high temperature water

Specimen	OCP (mV vs. SHE(T))	i_{corr} (µA/㎠)	β_a (V/decade)
ES15	-734	35	0.235
ES30	-726	35	0.21
EC15	-725	53	0.36
EC30	-722	87	0.36

3. Results and discussion

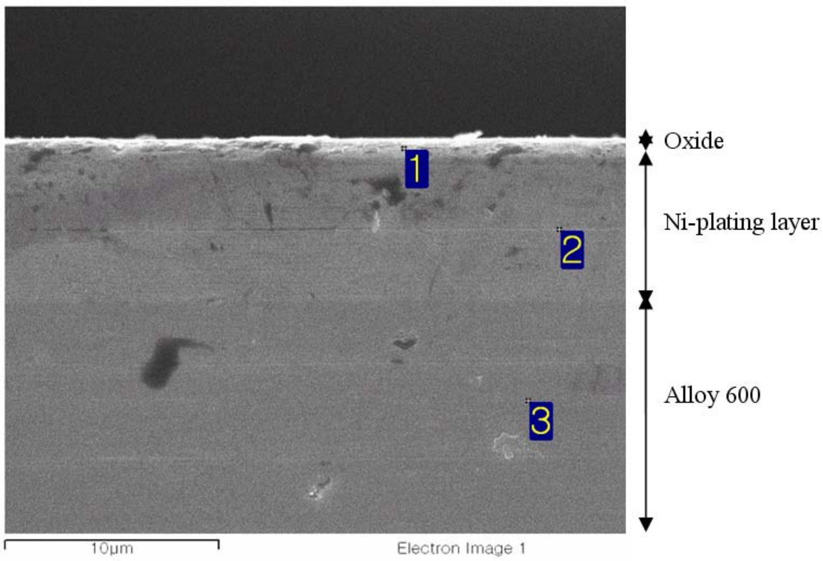
Fig. 5 shows the measured potentiodynamic polarization curves of all specimens including Ni-plated and as-received Alloy 600 specimens exposed to typical PWR primary water condition at 18 Mpa and 290℃. Table 2 summarizes the obtained electrochemical parameters from potentiodynamic polarization measurements. From Table 2, it can be known that the OCP’s are nearly the same for all specimens irrespective of plating method and thickness. But corrosion current density of electroless nickel-plated Alloy 600 specimens is consistently lower than that of electrolytically plated Alloy 600 base metal in this test condition.

The improved corrosion characteristic of electroless nickel plating can be attributed to about 7-8 % phosphorous contents in the electroless plating.

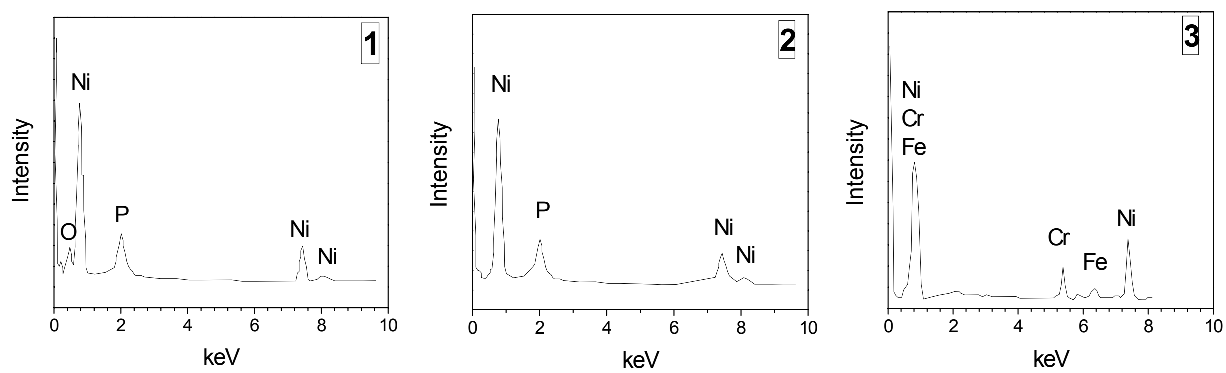
According to Lu and Zangari,[6] they also showed the increase of OCP and the decrease of corrosion current with the increase of phosphorous contents of Ni-plating. While electrolytic Ni-plating leads to mostly crystalline Ni layer, electroless Ni-plating makes a form of Ni-P alloy as a mixture of crystalline and amorphous binary, ternary and quaternary alloys.[7)] Generally, amorphous alloys exhibit higher corrosion resistance than crystalline Ni as the former is characterized by extreme homogeneity and low concentration of defects or preferential corrosion paths, such as grain boundaries in crystalline materials.[8),9)]

From the observed polarization behavior, electroless nickel plating can be considered to have better corrosion resistance than electrolytic nickel-plating in typical PWR primary water condition.

Fig. 6 (a) shows the scanning electron micrograph of cross-sectional area of Ni-plated Alloy 600 specimen exposed to high temperature, high pressure and high flow-rate water with 250℃, 15 MPa and 2 m/sec for 20 days. As seen in Fig. 6(a), there exist three different layers in the specimen cross-section after test; i) Alloy 600 substrate layer, ii) Ni-plating layer and iii) oxide layer. The out layer of nickel oxide is considered to be formed by oxidation of nickel plated layer exposed to high temperature water containing small amount of oxygen. EDS analysis was performed to get the chemical composition of each layer and the results are represented in Fig. 6 (b). From Fig. 6, it can be known that the Ni-plating layer still remains its original thickness after long-term exposure to high temperature and high flow-velocity water. From this result, electroless Ni-plating can play a role of protective layer for structural parts in erosion and/or erosion-corrosion environment with high-velocity water.



(a)



(b)

Fig. 6. (a) Scanning electron micrograph and (b) EDS measurements of nickel plated Alloy 600 specimen exposed to high temperature, high pressure and high flow-rate water with 250℃, 15 MPa and 2 meter per second for 20 days.

In this study, remote process for electroless nickel-plating has been also simulated in order to apply to CRDM nozzles in laboratory scale. For field application of nickel-plating to actual degraded components such as CRDM nozzles in nuclear power plants, electroless nickel-plating technique has significant advantage over electrolytic counterpart because electroless Ni-plating needs no separate electrodes which are essential for electrolytic Ni-plating. Such provisions cannot be readily installed within the narrow gap between the inner diameter of nozzle and thermal sleeve. Schematic diagram of nickel plating process and procedure are shown in Fig. 7. As shown in Fig. 7, all process was controlled by electric motors and valves which make circulation of each solution at each step. Fig. 8 shows a specimen design to simulate remote Ni-plating process in the CRDM nozzles with narrow gap.

During the electroless nickel plating process, four primary processes were applied in steps; chemical cleaning, surface deoxidation, surface activation, and nickel plating. The cleaning process consisted of solvent pre-cleaning, water rinse, alkaline soak and water rinse over the entire inner surface of nozzle specimens. This was followed by surface deoxidation which removed surface oxides in order to obtain good bonding of nickel to the substrate. Then, surface activation of substrate by 10% hydrochloric acid solution was applied to obtain good initiation and adhesion of the coating to the substrate. During the surface activation, the temperature of activation solution was maintained from 40 to 60℃. Finally, nickel-phosphorous layer deposited nickel on the substrate surface by autocatalytic reaction in the bath containing hypophosphorus acid solution.

The temperature of nickel plating solution was maintained in the range of 60~80℃ by using immersion heaters

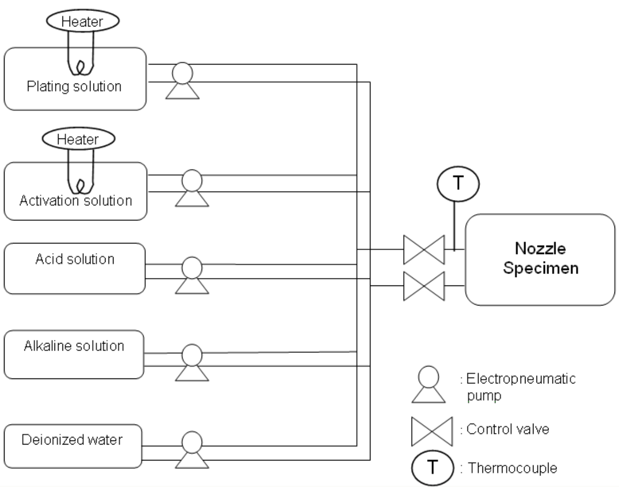


Fig. 7. Schematic of remote electroless nickel plating process.

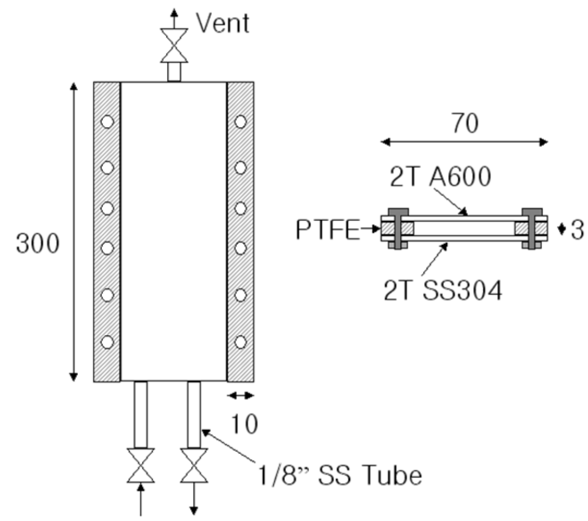


Fig. 8. A schematic design of plate specimen for remote electroless nickel-plating process to simulate the narrow gap between CRDM penetration and thermal sleeve

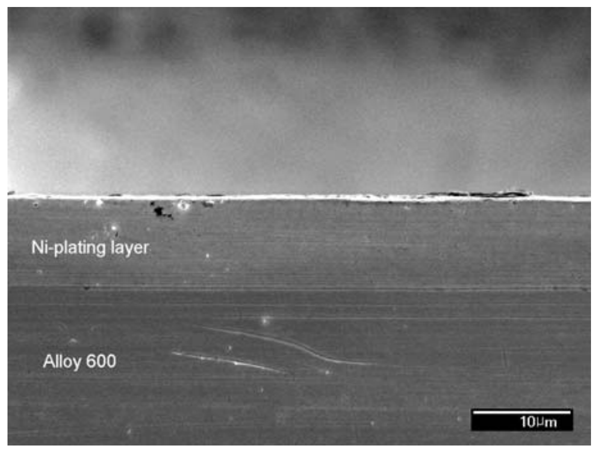


Fig. 9. Scanning electron micrograph of cross section of plate specimen after remote electroless Ni-plating

in the solution bath. The target thickness of plating on the substrate is about 10 um. It took about 30 minutes for each step and the whole process was sequentially carried out.

After electroless nickel plating was completed, CRDM nozzle specimens were disassembled and cut to small section in order to examine the plating quality as well as thickness. Fig. 9 shows the cross section of a nickel plated Alloy 600 specimen cut from CRDM nozzle specimen after remote electroless nickel plating. It can be seen that the plating layer is very uniform and the thickness is very close to the target thickness. From this result, it is shown that the electroless nickel plating can be applied by the

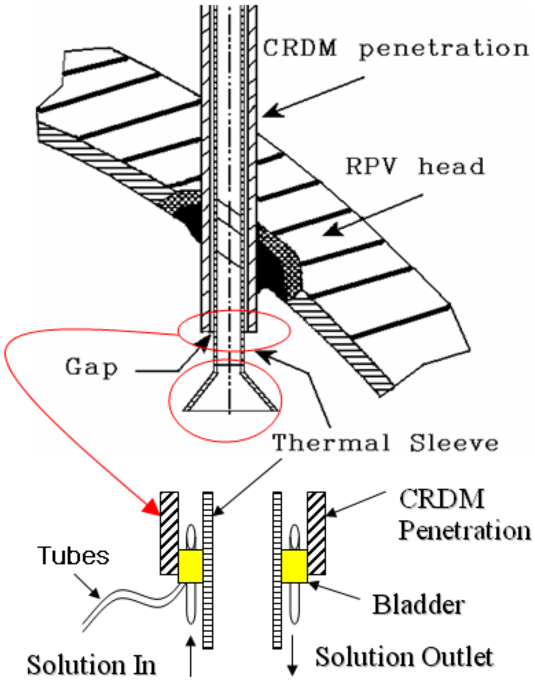


Fig. 10. Special end-effector using hydraulic bladder for remote electroless Ni-plating process in CRDM nozzles

remote process on a lab scale, at least, to the very narrow gap of CRDM nozzle.

For the more convenient application with upright annulus of CRDM nozzles, special end seals using hydraulic bladder can be utilized during the plating process between nozzle inner and sleeve outer surfaces, as shown in Fig. 10. This O-ring type bladder can be inserted into the gap, to establish leak-tight expansion seals with hydraulic pressure supplied from external pump. After sealing, this bladder can also be used as penetrations for the solution transfer within the nozzle and interested region for the plating. Chemical and demineralized water containers with electropneumatic pump and heater, electropneumatic controller and temperature controller can be used for the remote operation of nickel plating in plant condition.

4. Conclusions

In order to develop a preventive and corrective measure to mitigate environment assisted cracking of Ni-base structural alloy components in nuclear power plants, Ni-plating techniques is explored in this paper. Corrosion behavior of electroless Ni-plated Alloy 600 has been investigated in high temperature aqueous condition. From this study, following conclusions are made:

1) Corrosion rate of electroless nickel-plated Alloy 600 is lower than that of electrolytic plating in simulated primary water condition at 290℃. The lower corrosion rate is attributed to phosphorus that is included in the plated layer.

2) Electroless Ni-plating can be as effective as electrolytic plating for PWSCC mitigation, provided mechanical properties are acceptable. Electroless Ni-plating can play a role of protective layer for structural parts in erosion and/or erosion-corrosion environment with high-velocity water.

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