Ni plating technology development for RPV cladding repair

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1. Introduction

Repairing a damaged stainless steel or Ni clad inside the reactor vessel is challenging because of high radiation levels, poor accessibility, and the underwater condition. One promising technology is the electrochemical deposition (ECD) of nickel. The ECD technology used to repair the cladding has been approved in 2013 as the ASME code case N-840 [1]. Some background test results were already reported in the previous work [2].

Based on the code case, some demonstration test by using a Ni plating chamber, which will be used in inside the reactor vessel was carried out. The objectives of the test are (1) to set up Ni plating essential variables in terms of practical application, (2) to support a repair organization with cladding repair tool development. It includes a work supporting the utility with permission from the regulatory organization.

This article aims to address Ni plating system design, some preliminary test results by using Ni plating chamber and beaker test set up.

2. Ni plating system design

In the plating experiment using the plating chamber, the following reasonable plating layer was formed (see Figure 1).

Fig. 1. Feature of plated Ni on type 304 stainless steel.

As shown in this figure, some pit or burning occurred on the surface of the plating. To solve this problem, the plating system was modified as shown in Fig. 2 below.

Removal of impurities generated during plating was solved by installing a filter housing, and a magnetic pump was used instead of the conventional quantitative control pump in order to increase flow rate of the Ni plating solution.

The main reason for the decrease in pH is due to the low solubility of the anode [3]. As the oxygen gas is generated in the anode, sulfamate is converted to sulfate in the solution and acidified. Therefore, S-nickel containing sulfur component was used as the anode. We also solved this problem by using an anode bag, which can remove anode slime.

The anode in the plating chamber is coated with an oxide-coated iridium-insoluble anode, and the anode area of the preliminary plating bath is taken as three times the area of the cathode. The stabilized plating solution was supplied to the chamber with constant stirring.
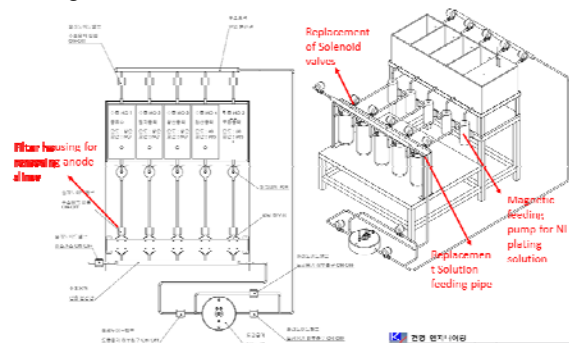

Fig. 2. Modified Ni plating system design.

In the pre-conditioning bath, a reaction to generate sufficient Ni ions is induced, and a part of Ni ions are used for plating in this pre-conditioning bath and most of the Ni ions are transferred to a plating chamber.

Figure 3 shows the improvement of the gas outlet, which facilitates the release of hydrogen gas generated in the plating chamber, which is considered to reduce the generation of pit due to hydrogen gas generated on the surface of the plating.

In addition, the functions installed to smooth the reaction in the plating chamber are summarized as follows.

- Sealing is strengthened by firmly attaching O-ring inside plating chamber.
- Clearance of 12 mm between anode and cathode changed to 22 mm for liquid circulation.
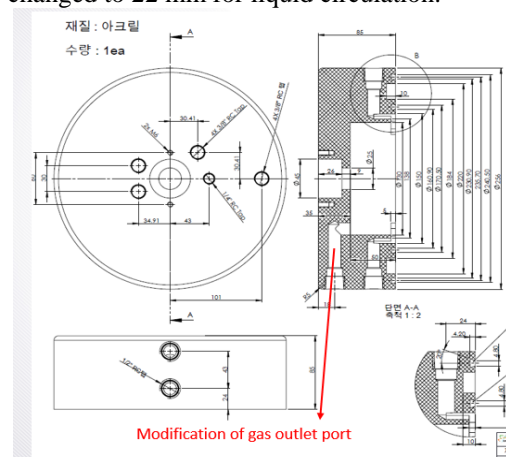

Fig. 3. Modification of gas out port.

- Extend O-ring area of the chamber to broaden the vacuum to make it stronger.
- Installation of a clamp for easy access to the chamber.
- Extend the solution inlet from 1 mm to 5 mm to allow the solution to self-agitate in the chamber.
- The solution outlet and the gas outlet were changed so that they merged into Y when entering the branch pipe.
- The solution piping changed from a hard Teflon to flexible hose.

3. Ni plating conditions setup experiment

The beaker test as shown in Fig. 4 was performed as one of the methods to confirm whether the plating conditions defined in the previous study were well implemented in the plating chamber used in this study. One of the results is shown in Fig. 5.

Fig. 4. Beaker test for setting up the Ni plating conditions.

The specimen was commercially available type 304 stainless steel of which chemical composition is C: 0.0537, Si:0.390, Mn:1.126, P:0.0328, S:0.0042, Cr:18.228, Ni:8.057, N: 332 ppm, Fe: Balance. The composition of Ni plating solution was Nickel sulfamate($Ni(SO_3 \cdot NH_2)_2$) : 1.39 mol/L, Boric acid (H_3BO_3) : 0.65 mol/L. The weight of the specimen before plating is 81.2 g, the weight of the specimen after plating is 166.96 g, and the plating amount is 85.76 g. On the other hand, the anode weight before plating is 893.3 g, the anode weight after plating is 802.8g, and the anode dissolution amount is 90.5 g. The amount of plating can be calculated as described in Faraday's Law as shown in the following.

Plating amount $W = I \times t \times A / n \times F$ (1)

$W = 7.87 \times (3600 \times 10) \times 58.693 / 2 \times 96485 = 86.17$ g

As a result, the plating efficiency was evaluated as 99.5%, the anodic dissolution efficiency was evaluated as almost 100%, and the plating surface was also evaluated as a condition for producing a good quality plating layer without pit and burning.

The conditions to be established by the beaker experiment were to suppress the pH decrease and to reduce pit and burning. Figure 6 shows the case where the pH decrease is abruptly occurred when the conventional electrolytic nickel anode is used.

As discussed earlier in Section 2, the sulfamate anion slowly hydrolyzes in the electrolyte, ammonia forms, pH decreases. And the rate of decomposition increases as the temperature increases. Therefore, the temperature of the plating bath should not exceed 70°C and the pH should not fall below 3.0 [3].
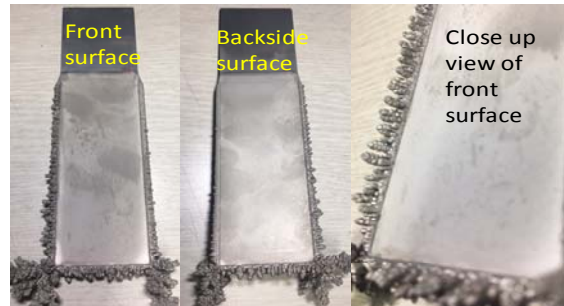
Strike formation at 40℃, Ni conc. : 2.41 mol, Anode: S-Ni, Ni plating temp.: 60℃, pH 3.06, Ni plating for 10 hrs, Wetting agent: SNAP 5ml

Fig. 5. Surface features of plated Ni by using S-Ni

In general, the cathode efficiency is not as high as the cathode efficiency. That is, slightly more nickel than plated on cathode is dissolved from the anode.

A greater amount of hydrogen is released from the cathode than the oxygen released from the anode and consequently the OH^- ions in the solution rises and the pH increases to maintain charge balance. However, if the anode is not well dissolved and the anode efficiency is low, oxygen may be released from the anode and the pH may drop.

When the electrolytic nickel was used as in this study, the anodic dissolution was not smooth and the pH was decreased.
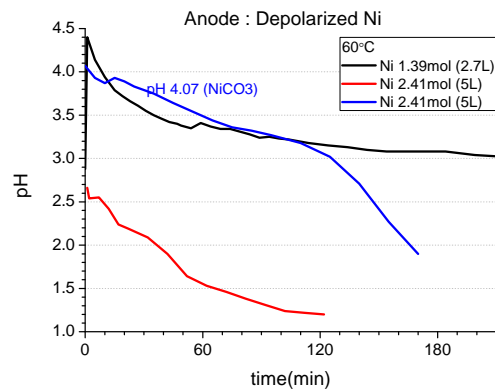

Fig. 6. pH change with time when electrolytic depolarized Ni anode was used.

In the case of Fig. 7 using the newly applied S-Ni anode, only a slight amount of the additive sulfamic acid and $NiCO_3$ is used, it can be seen that the decrease of pH was much less.

Overall, judging from the use of S-Ni and the improved device, the variation of pH was very small, so it is expected that successful experiments for 10 hours to produce 1 mm of plating will be conducted.
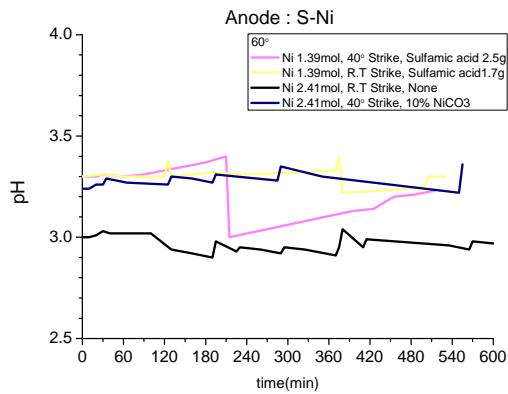
Fig. 7. pH change with time when Sulfur containing Ni anode(S-Ni) was used.

4. Conclusions

- A plating system was modified to solve the pit or burning on the surface
- Anodic dissolution was not smooth and the pH decreased when the electrolytic nickel is used.
- Sulfur contained Ni anode(S-Nickel) showed relatively constant pH value with only a slight amount of the additive sulfamic acid and $NiCO_3$

REFERENCES

[1] ASME code case N 840, Cladding Repair by Underwater Electrochemical Deposition in Class 1 and 2 Applications Section XI, Division 1.
[2] Myong-Jin Kim, Dong Jin Kim, Joung Soo Kim, Hong Pyo Kim, Seong Sik Hwang, TECHNICAL BASIS FOR PROPOSED CODE CASE OF ALTERNATIVE RULES FOR CLADDING REPAIR BY UNDERWATER ELECTROCHEMICAL DEPOSITION IN CLASS 1 AND 2 APPLICATIONS, Proceedings of PVP2013, PVP2013-97857, July 14-18, 2013, Paris, France.
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