Ni Plating System Design for Repair of Damaged area of RPV

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1. Introduction

A reactor pressure vessel(RPV) consists of carbon/low alloy steel (SA508) as the structural material, and a cladding layer (SS309) as a protective layer. The inner surface of the reactor is very difficult to repair if it is damaged by external forces because of high radiation levels and poor accessibility [1].

Welding, a common repair technique, requires heat treatment because it has high heat input and causes residual stress due to deformation. On the other hand, as a damaged repair technique, nickel plating not only has excellent wear and corrosion resistance, but also has no thermal effect on low carbon steel. In terms of interfacial adhesion strength, a literature has been published that demonstrates adhesion between stainless steel and low carbon steel [2].

The ECD technology used to repair the cladding has been approved in 2013 as the ASME code case N-840 [3].

The purpose of this article is to introduce conditional optimization and physical properties testing of nickel plating, and to introduce the results of successful plating quality using a plating apparatus.

2. Experimental

2.1 Plating principles and concepts

In the plating, the cathode reaction and the anode reaction occur at the same time, and the product is obtained. An object for which ions are usually reduced is called a cathode. Conversely an object that serves to replenish depleted ions through an oxidation reaction is called the anode.
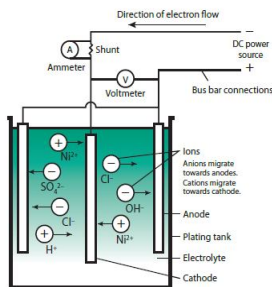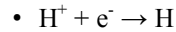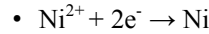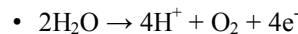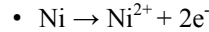

Fig. 1. Schematic showing the movement of ions during a Ni plating reaction

The ionic equation of the nickel plating reaction in Fig. 1 is shown as follows.

Reduction reaction of Cathode
- $Ni^{2+} + 2e^- \rightarrow Ni$
- $H^+ + e^- \rightarrow H$
- $H + H \rightarrow H_2$

Oxidation/Plating reaction of Anode
- $Ni \rightarrow Ni^{2+} + 2e^-$
- $2H_2O \rightarrow 4H^+ + O_2 + 4e^-$

It can be seen from this reaction formula that hydrogen gas is generated in the cathode and oxygen gas is generated in the anode. However, since the gas generation reaction is a side reaction, it is important to increase the efficiency so that the main reaction is dominant in the plating process.

2.2 Plating process and specimen planning

Plating includes a pretreatment process in order to remove the contaminants on the surface of the cathode and to perform 'Strike layer' process for adhesion performance. And there is a process of washing with pure water in every step.
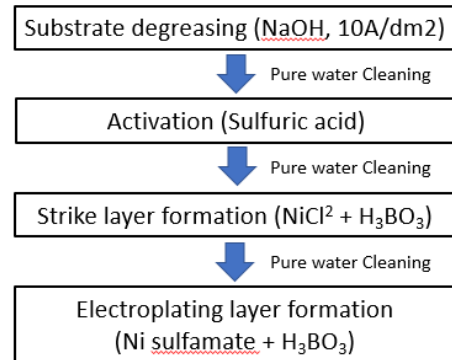

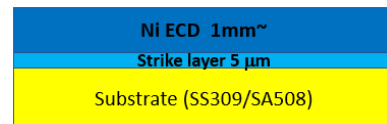Fig. 2. Plating process sequence

Fig. 3. Schematic of the sample according to the process

Fig. 2 shows the plating process sequence, Fig. 3 shows a schematic of a section of the plating specimen to be finally produced according to the process. Plating thickness was aimed at thicknesses exceeding 1 mm, and Type 304 stainless steel was

used as the base material(cathode) in the experimental environment.

2.3 Plating system development

The plating chamber will eventually be used in a mockup specimen that matches the size and shape of the damaged RPV for actual repair. Fig. 4 shows the schematic of the mockup. In the experimental environment, a chamber for plating the surface of Type 304 stainless steel was fabricated.
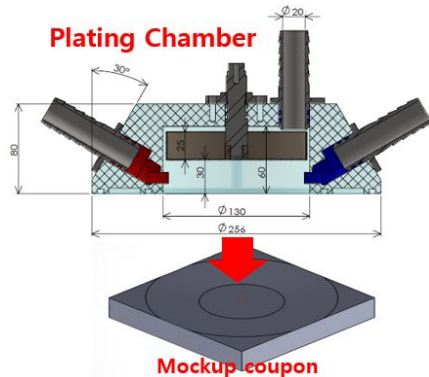

Fig. 4. Schematic of a chamber fabricated for plating

The plating solution circulates thorough the In, Outlets in the chamber. And there is vacuum space between the double O-ring so that they do not leak.

2.4 Application of plating system

In previous beakers experiments, we found that the plating efficiency was close to 100% and the pH of the plating bath remained unchanged to the final state by using Sulfur-containing Ni as an anode. This is because the S-Ni anode was oxidized in proportion to the amount of reduction without forming a passivation film.
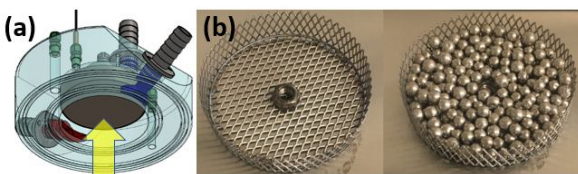

Fig. 5. Design of anode basket for S-Ni anode

S-Ni was also applied to the plating systems. Fig. 5, (a) shows a cylindrical basket attached to the plating chamber. As shown in Fig. 5, (b) S-Ni will need a basket to hold it in the form of a bead. The S-Ni is filled in the basket and wrapped in cloth again, and then it will be positioned inside the chamber and serve as the anode.

The plating chamber experiment was applied with a slope of 28degrees in order to confirm the plating performance by maintaining the tilt angle of the actual repair area. Fig. 6 shows the actual plating with system.
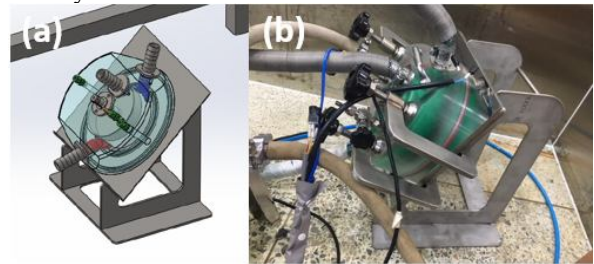

Fig. 6. Chamber plating experiment

3. Result and Discussion

3.1 pH stabilization effect of S-Ni anode

S-Ni is good in solubility and the plating efficiency is close to 100%, and the pH of the plating solution can be maintained. This can be explained by Faraday's equation of plating and some other rules. The formula is as follows.

- $W = (I^* \times T^* \times A^*) / (n^* \times F^*)$

Where :
- W= weight of plated metal in grams.
- I= current in coulombs per second.
- t= time in seconds. (30 h(108,000 s))
- A= atomic weight of the metal in grams per mole.

(1.008 g/mol for H, 58.693 g/mol for Ni)
- n= valence of the dissolved metal in solution in equivalents per mol.(1 for H, 2 for Ni)
- F= Faraday's constant in coulombs per equivalent. F = 96,485.309 coulombs/equivalent.

As the amount of current increases and the time passes, the plating weight or plating thickness increases proportionally. The amount of electricity required for electrolytic plating of 1 g equivalent of material is always 96485.33C regardless of the type of material.

Therefore, the plating time can be obtained by calculating the amount of the current to be inputted to the area of the material to be plated and the amount of the nickel plating of 1 mm in the area.

The plating efficiency is obtained by comparing the theoretical value of W with the actual amount of plated weight. What is important here is the oxidation of the anode. The amount of current is a fixed value, but if the oxidation reaction of the anode is not sufficient enough nickel cations to be reduced, the plating weight will not reach the theoretical value gradually. This will result in side reactions and the pH will gradually decrease.

The criterion for determining the oxidation amount of the anode is as follows. First, it can be known whether the value of W matches the actual plated weight. This is because the amount of oxidation by electric reaction is equal to the amount of plating by

the law. The weight difference between the anode before and after plating can be known by comparing with the plating amount.
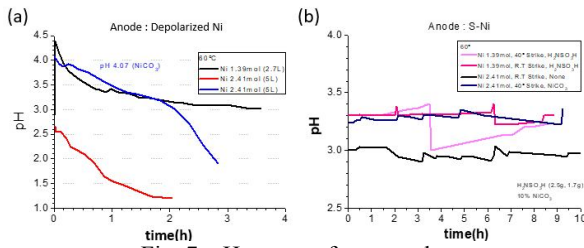

Fig. 7. pH curves of two anodes

Fig. 7, (a) shows the pH curve that declines with time in the plating of depolarized nickel anode. On the other hand, in the plating of the S-Ni anode in Fig. 7 (b), the pH was kept constant even for 10 hours.

3.2 Strike layer adhesion test

In the previous study, the strike layer process condition was set to 2 minutes and 30 seconds, and the thickness of the initial layer was set to 5 μm. The thickness of the strike was used as a parameter to demonstrate the uneven coating or peeling. Therefore, in this study, Ni plating of the same thickness was applied to each specimen with different thickness of strike and bending test was carried out to confirm the integrity of such condition. As a result of bending the thickness 20 μm strike layer specimen, no defect such as peeling was found at the interface between the plated layer and Type 304 stainless steel. We plan to bend the 2 μm thick strike layer plating.

Table 1 : Strike layer thickness variable

Anode	mol	Strike layer form.			Current A/dm2	Temp.	hr	Current A/dm2	Vol. (Liter)	additive	(+).(-) distance (mm)	pH (i/f)	plating efficiency	Anode Oxidation
		Temp.	min	T(μm)										
S-Ni	2.41mol	40	10	20.5	10	60	5	10	5	X	70	3.3/3.43	100.03%	104.36%
S-Ni	2.41mol	상온	10	20.5	10	60	5	10	5	X	70	3.53/3.5	99.63%	100.12%
S-Ni	2.41mol	상온	5	10.2	10	60	5	10	5	X	70	3.5/3.5	101.23%	101.51%
S-Ni	2.41mol	상온	2.5	5.1	10	60	5	10	5	X	70	3.53/3.58	100.75%	97.40%
S-Ni	2.41mol	상온	1	2.0	10	60	5	10	5	X	70	3.6/3.6	100.84%	98.00%

Table 1 shows the experimental history and the different plating times at the same current density to make the strike layer thicknesses different.

3.3 Control of current density and pH

The plating conditions were optimized in the beaker experiment. In order to evaluate the efficiency and to make uniform electrodeposit of Ni plating, the current density was used as a variable, and the pH was used as a variable for the purpose of changing the hardness and removing the pits on the surface of the plating. Other conditions were kept the same.

Table. 2 : pH and current density variable test

Anode	mol	Strike layer form.		Temp.	Plating form.			additive	(+).(-) distance (mm)	pH (i/f)	Weight	plating efficiency
		min	T(μm)		hr	Current A/dm2	Vol. (Liter)					
S-Ni	1.976mol	2.5	5.1	60	10	10	5	X	70	4.23/4.23	x	x
S-Ni	1.976mol	2.5	5.1	60	10	10	5	X	70	4.42/4.48	86.45	100.27%
S-Ni	1.976mol	2.5	5.1	60	20	5	5	X	70	4.42/4.42	86.4	100.21%
S-Ni	1.976mol	2.5	5.1	60	33.337	3	5	X	70	4.42/4.45	85.9	99.62%
S-Ni	1.976mol	2.5	5.1	60	10	10	5	X	70	3.08/3.1	86.16	99.93%
S-Ni	1.976mol	2.5	5.1	60	20	5	5	X	70	3.18/3.24	85.75	99.46%
S-Ni	1.976mol	2.5	5.1	60	33.337	3	5	X	70	3.02/3.13	85.74	99.44%
S-Ni	1.976mol	2.5	5.1	60	33.337	3	5	X	70	2/2.4	83.73	97.10%
S-Ni	1.976mol	2.5	5.1	60	20	5	5	X	70	2/2.3	83.47	96.81%
S-Ni	1.976mol	2.5	5.1	60	10	10	5	X	70	2/2.3	85.18	98.80%

Because of the good oxidation effect of the S-nickel anode in the previous experiments, the plating efficiency was close to 100% regardless of the high current density or the low current density. However, even at the same current density, uniform electrodeposition was significantly reduced at high current density. In the beaker experiment, all of the corners of the specimen are exposed in the plating solution, so that the plating begins to rise along the corners as electrodeposited. This was more pronounced when the current density was high. However, lowering the current density to 2 A/dm^2 solves this non-uniform electrodeposition problem.

The pH range was varied from 2 to 4.5 to find the optimum pH, and the results are ongoing. For another purpose, the pH was changed to remove the pits generated on the surface of the plated layer, but as a result of plating, the pits appeared randomly in all pH ranges. This is because hydrogen gas, which is a product of 1% side reaction, is generated on the surface of the cathode. If this is not removed, pits will be created because the plating proceeds with covering the bubble. Sufficient agitation is required in order to remove the gas bubbles.

Table. 2 shows the experimental history of changing the current density and pH conditions. Plating time was increased with decreasing current density to make the same thickness of plating.

3.4 Side bend test

The side bend test is to bend the section of the plated specimen with a force. For this purpose, the manufactured fixture follows ASME section IX, QW-160 (GUIDED-BEND TESTS). As an alternative to the condition that the width of the specimen is 10 mm or less, the fixture followed the ASTM E 290, QW-462.2.

Fig. 8, (a) shows the cross section of the machined specimen. (b) shows the production size of the fixture and (c) shows the actual fixture.
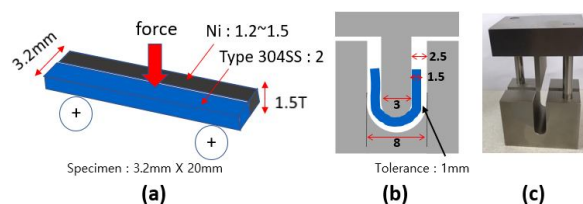

Fig. 8. Drawings of specimen and fixture

Fig. 9. (a) shows a cross section of a clean polished plating specimen. After bending as in (b), OM observations revealed no defects at the interface between the plated layer and Type 304 stainless steel. No other specimens had the same result after the bending.
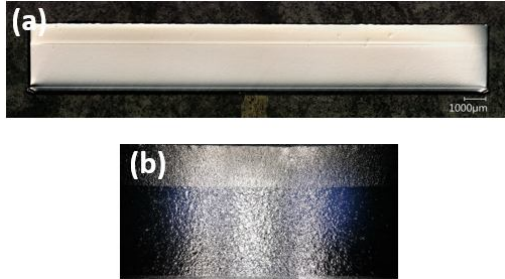

Fig. 9. Result of side bend test

3.5 Plating result with chamber system

The plating process using the apparatus was conducted by compromising the optimal conditions through the beaker experiment. Therefore, the strike layer was plated with 5 μm by the pretreatment process. The plating current density was 5 A/dm^2, which was plated for 20 hours to make a thickness of 1 mm. the pH of the plating solution was fixed at 4.0. The plating solution was 1.976 mol, 20 L was prepared and maintained at 60 degrees.

The total Ni cation in the plating solution is about 2297.2 g, and the area of 132.665 cm^2 consumes 145 g for 1mm plating thickness. Therefore, the bath load is 6.3% as compared with the ion amount, and the amount of ions in the plating solution will not change because the nickel anode is supplemented by oxidation.

Fig. 10. Plating result with chamber system

As shown in Fig. 10, no pits were found on the surface of the plating layer, and the plating efficiency was close to 100% as a result of weighing and the pH of the solution was maintained at 4.0 during the plating.

3.6 Chemical analysis

The composition of the plating layer was analyzed according to the chemical qualification requirement of code case N-840. Table 3 shows the composition of the specimens under most conditions in the beaker experiment. The code case is specified as follows. Nickel 99.0% minimum, Silicon 0.01% maximum, Sulfur 0.01% maximum. As a result of the analysis, there were no components exceeding the respective allowable values.

Table. 3 : Chemical analysis of Ni plating

시편 번호	분석 위치	Si	P	S	Ni
NIP BP-4*	center	0.000	0.000	0.006	99.994
NIP BP-4*	side	0.000	0.000	0.006	99.994
NIP BP-10*	center	0.002	0.000	0.016	99.982
NIP BP-10*	side	0.004	0.000	0.039	99.957
NIP BP-13*	center	0.000	0.000	0.003	99.997
NIP BP-13*	side	0.000	0.000	0.008	99.992
NIP BP-15*	center	0.000	0.000	0.007	99.993
NIP BP-15*	side	0.000	0.000	0.007	99.993
NIP BP-16*	center	0.000	0.000	0.006	99.994
NIP BP-16*	side	0.000	0.000	0.005	99.995
NIP BP-17*	center	0.000	0.000	0.005	99.995
NIP BP-17*	side	0.000	0.000	0.006	99.994
NIP BP-18*	center	0.000	0.000	0.007	99.993
NIP BP-18*	side	0.000	0.000	0.006	99.994
NIP BP-19*	center	0.000	0.000	0.004	99.996
NIP BP-19*	side	0.000	0.000	0.004	99.996
NIP BP-20*	center	0.001	0.000	0.004	99.995
NIP BP-20*	side	0.001	0.000	0.005	99.994
NIP BP-23*	center	0.000	0.000	0.007	99.993
NIP BP-23*	side	0.000	0.000	0.007	99.993
NIP BP-27*	center	0.000	0.000	0.017	99.983
NIP BP-27*	side	0.000	0.000	0.015	99.985
NIP BP-28*	center	0.000	0.000	0.006	99.994
NIP BP-28*	side	0.001	0.000	0.006	99.993

4. Conclusions

- S-Ni oxidized and replenished the depleted nickel cations in the plating solution. The resulting plating efficiency is up to 100% and there was no pH change due to side reaction.
- Adhesion performance of the plated layer was sufficient even though the thickness variable of the strike is in the range of 5 to 20 μm.
- The low current density condition made a great contribution to uniform electrodeposition plating. The plating efficiency was not affected by the current density fluctuation due to the S-Ni anode.
- The pit can be controlled with sufficient agitation.
- As a result of bending, there was no interfacial defect of nickel plating.
- As a result of analyzing the components of the plating layer, the content of Ni was 99% or more, and the content of impurities was 0.01% or less.

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[2] D. J. Kim, M. J. Kim, J. S. Kim, H. P. Kim, Material characteristics of Ni-P-B electrodeposits obtained from a sulfamate solution, Surface & Coatings Technology, Vol. 202, p. 2519, 2008.

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