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Development of an electroplating method using the emulsion under supercritical CO_2

Jeongmin Choi[a], Kwangheon Park*, Sungwoo Ha[b]
Department of Nuclear Engineering, Kyunghee University, Kyunggi -do 776-701, Korea
west0476@khu.ac.kr

1. INTRODUCTION

Recently, pressurized-water reactor nuclear fuel has been developed as high burn up nuclear fuel that can be operated for a long time. To this end, the nuclear fuel aggregate adding neutron absorber (Burnable absorber-BA) is required. Burnable poison has been mainly produced in the form of adding BA to pellet. However, burnable poison which is easier to be manufactured and evenly distributed is required because it is complicated to make pellet burnable poison and nuclear calculation for location and behavior while burning of burnable poison is complicated. To this end, a new technology to replace burnable poison in the form of pellet is required. If BA coating is made inside the nuclear fuel cladding, it is possible to produce burnable poison that improved performance more than that of burnable poison in the form of existing pellet. Generally, coating using plating can be simply manufactured at a low temperature compared to the complex process of making pellet and can also distribute burnable poison overall evenly. The problem in the behavior of high burn up nuclear fuel is pellet-cladding interaction (PCI) shown while burning. Several methods to reduce it have been devised and recently, research on nuclear fuel that can reduce PCI by making Ni coating inside the cladding has been carried out in Korea Atomic Energy Research Institute.

To this end, a technology of plating a metal evenly inside the cladding is required. The plating technology includes wet plating and dry plating. Dry plating has been applied only to a part because plating time is long and it costs a lot to build a system and plating possible area is limited. Although the most common and well known method, wet plating has a problem that coating is made unevenly due to bubbles (hydrogen) generated during electroplating. In order to solve this problem, this study developed the emulsion coating method using supercritical CO_2. Supercritical CO_2 is a solvent with low surface tension and excellent penetration and replaces existing harmful solvents because it can move the solute even to the fine part. A small amount of plating solution is used when making the emulsion of supercritical CO_2 and plating solution so waste water generated from the process can be reduced innovatively and very even coating can be created because hydrogen generated during electroplating is dissolved in supercritical CO_2 [1].

2. EXPERIMENTAL

2.1 Method

The composition of nickel plating solution (electrolyte) used in general electroplating and emulsion plating using supercritical CO_2 is as shown in Table 1.

Table 1. Nickel electrolyte composition

Nickel Sulfate(NiSO4·6H2O)	260 g/L
Nickel Chloride(NiCl2·6H2O)	50 g/L
Boric Acid(H3BO3)	45 g/L

The plating specimen is placed at the negative pole (-) and two types of sheet specimen (copper and Zry-4) were used. And the nickel plate (Purity 99.9%) was placed at the positive pole (+). A specimen was made in size of 1cm in width, 2cm in length and grinding was carried out step-by-step (No.180, 220, 600, 2000) by using a grinder to remove debris and organic matter remaining on the surface.

For supercritical CO_2 emulsion plating, the schematic diagram of high pressure system and general electroplating was shown in Figure 1. The experimental method of the supercritical emulsion was to put plating solution (15~95%, 50ml) in a high pressure vessel (50ml) and maintain constant pressure (150bar) and temperature(50℃ or higher) by using a pressurized metering pump and then, supply supercritical CO_2 in the high pressure vessel. In order to form an emulsion, plating was carried out by supplying constant current (0.21A) for 15 minutes in the emulsion state formed after fully stirred for 5 minutes by using ultrasonic waves. For general electroplating, constant current (0.21A) was supplied for 15 minutes while maintaining the temperature (50℃) after fully stirring the plating solution (100%, 100ml) by using a magnetic bar. After plating, the coating of the specimen was analyzed. In order to observe the plating thickness and surface condition of general electroplating and emulsion plating using supercritical CO_2, a scanning electron microscope(SEM) and optical microscope (OM) were used.

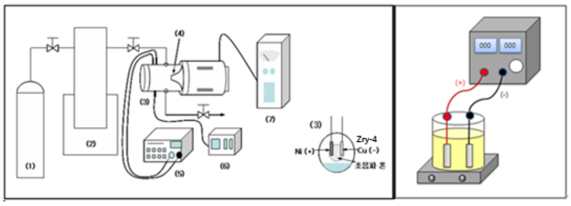

Fig 1. Plating experimental apparatus schematic diagram– supercritical emulsion plating ((1) CO_2 cylinder (2) Syringe pump (3) High-pressure reaction vessel (4) ultrasonic horn (5) Current supply device (6) Temperature regulator (7) Ultrasonic generator) and general electroplating

3. RESULTS AND DISCUSSION

The emulsion in supercritical CO_2 was checked by using the sapphire window mounted high pressure vessel. After putting plating solution (10~95%, 50ml) and nonionic surfactant (NP-10, 1ml), it was stirred with ultrasonic waves while maintaining constant pressure and temperature. After stirring for 30 seconds, the emulsion began to form. The effectively formed emulsion was observed as shown in Figure 2 because a plating solution was finely pulverized due to ultrasonic agitation and surface tension between CO_2 and water was lowered.

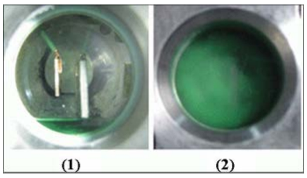

Fig 2. Emulsion formation using ultrasonic agitation– emulsion state (1) before agitation (2) after agitation

Figure 3 is the specimen after nickel plating. In Ni coating manufactured in emulsion plating (10~95%, 50ml), in the case of Cu specimen (purity 99.9%), the plating surface showed more smooth glossy compared to general electroplating(100ml). In the case of Zry-4specimen, however, the plating film thickness of emulsion plating was not constant compared to general electroplating. Unlike pure Cu specimen, Zry-4 specimen is estimated to have an uneven thin film on the surface due to the nature of the alloy.

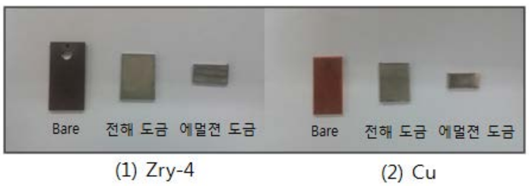

Fig 3. Nickel plated specimens

The thickness of the plating specimen was measured with an optical microscope. In the case of Zry-4specimen, nickel of about 23um thickness was plated in general electroplating and emulsion was plated in about 15um thickness. Cu specimen was plated in about 20um, 7um in general electroplating and emulsion plating, respectively. Given that electroplating solution used in emulsion plating was reduced 40% of general electroplating solution condition, the thickness of plating is considered relatively good. And side effect of pinholes were diminished.

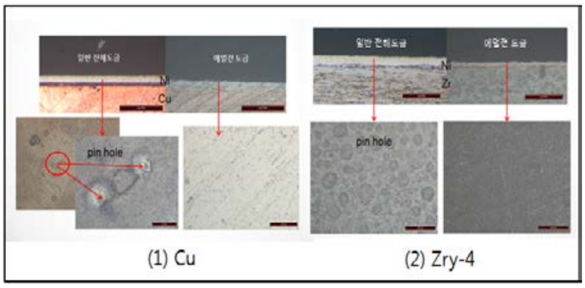

Fig 4. Comparison of nickel plating thickness of Zry-4 and Cu specimens (OM)

The surface of nickel plated specimens was observed by using the scanning electron microscope (SEM).
In Cu specimen using the emulsion, nickel particles were pulverized at 50~95% planting solution used and compact form was observed compared to general electroplating. And Pinholes were not observed at 50~95% planting solution used of emulsion planting.

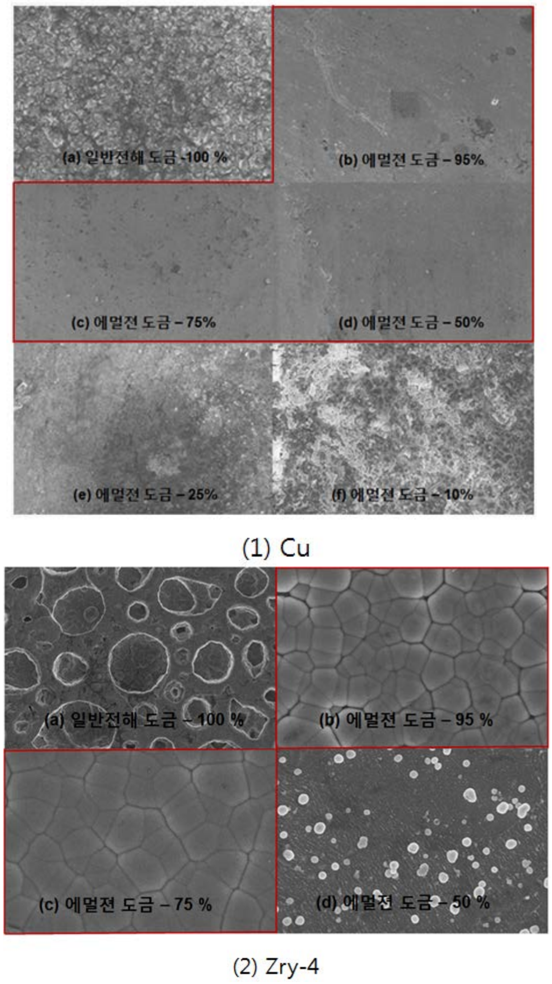

Fig 5. Comparison of nickel plating surface of Zry-4 and Cu specimens (SEM)

In the case of Zry-4 specimen, nickel particles were not completely stuck to the metal surface compared to general electroplating but given 75~90% of the amount of plating solution used, the plated nickel particle layer was relatively uniform and showed a compact form compared to general electroplating. And side effect of pinholes were diminished. Currently, research is being carried out in order to obtain a smooth and uniform nickel film of Tube type of Zr specimen and optimized conditions of emulsion plating using supercritical $CO_{2.}$

4. CONCLUSIONS

The development of an internal cladding metal coating technology is required as a measure for manufacturing homogeneous burnable poison and preventing PCI. This study applied nickel plating obtaining a film on the metal surface by making the emulsion of supercritical CO_2 and plating solution. It is an eco-friendly process that reduced an electrolyte used in the electroplating process to 40% and a method that can inhibit the effect of bubbles generated during plating. According to the experimental results, it was found that emulsion can be formed through agitation by using ultrasonic horn. And the nickel plating film in the relatively uniform and dense from was formed in Zry-4 and Cu specimens with the formed emulsion. Additionally, the side effects of pinhole in existing electroplating were diminished through the emulsion electroplating. Process development research is underway in order to secure a plating layer with the smoother and generally even specimen surface and find optimized plating conditions and this study can be used as the basic data for new plating process development.

ACKNOWLEDGMENT

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REFERENCE

[1] J.Y. Park. W. Lee. D. Kim, C. H. Lee, and J. S. Lim, Electroplating of nickel on copper substrates in super-critical CO2, Theories and Applications of Chem. Eng., 8(1), 172 (2002).