

# Corrosion Behavior of Cu–Ni Alloy Film Fabricated by Wire-fed Additive Manufacturing in Oxidic Groundwater

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The growing significance of sustainable energy technologies underscores the need for safe and efficient management of spent nuclear fuels (SNFs), particularly via deep geological disposal (DGD). DGD involves the long-term isolation of SNFs from the biosphere to ensure public safety and environmental protection, necessitating materials with high corrosion resistance for DGD canisters. This study investigated the feasibility of a Cu–Ni film, fabricated via additive manufacturing (AM), as a corrosion-resistant layer for DGD canister applications. A wire-fed AM technique was used to deposit a millimeter-scale Cu–Ni film onto a carbon steel (CS) substrate. Electrochemical analyses were conducted using aerated groundwater from the KAERI underground research tunnel (KURT) as an electrolyte with a NaCl additive to characterize the oxidic corrosion behavior of the Cu–Ni film. The results demonstrated that the AM-fabricated Cu–Ni film exhibited enhanced corrosion resistance (manifested as lower corrosion current density and formation of a dense passive layer) in a NaCl-supplemented groundwater solution. Extensive investigations are necessary to elucidate microstructural performance, mechanical properties, and corrosion resistance in the presence of various corroding agents to simplify the implementation of this technology for DGD canisters.

**Keywords:** Copper–nickel film, Additive manufacturing, Corrosion, Deep geological disposal canister

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## 1. Introduction

Managing spent nuclear fuels (SNFs) is crucial to operating nuclear power plants. In this regard, deep geological disposal (DGD) is considered the primary option to manage SNF [1-3]. In DGD, SNFs are sealed in a canister, which is subsequently stored in a deep geological environment (approximately 500 m below the Earth's surface) with an engineered barrier system to isolate the SNFs from the human life zone [4-6]. An SNF canister is exposed to groundwater for an extremely long disposal time; therefore, the canister material should have high corrosion resistance to prevent the release of radioactive nuclides from the SNFs. Typically, Cu is a leading candidate as a canister material due to its excellent stability in DGD repository environments (corrosion rate < a few millimeters per million years) and it also has uniform corrosion behavior [1, 7, 8]. Cu-based alloys are less susceptible to corrosion than Cu because of the incorporation of corrosion-resistant metals such as nickel (Ni) [9]. The Ni in the alloy modifies the structure of the passive barrier films by segregating them into a protective  $\text{Cu}_2\text{O}$  layer, improving corrosion resistance and providing excellent machinability [10]. In this study, the feasibility of using a Cu–Ni alloy film as a corrosion-resistant layer of an SNF DGD canister was investigated in the groundwater solution, because the corrosion behavior of canister is meaningful when examined under conditions similar to the disposal environment. The Cu–Ni film was fabricated using wire-fed additive manufacturing (AM) technique onto a carbon steel (CS) substrate. AM is widely used to build products with complex designs, unique material requirements, specific functionalities, and limited working environments [11, 12]. In the nuclear field, several structural parts, such as pressure vessels, heat exchangers, turbine blades, and spacer grids, are fabricated using 3D printing. Simultaneously, coating and cladding technologies are also being developed to provide additional functions to the existing materials. Therefore, a Cu–Ni film was prepared as mm-scale on CS substrate. Then, naturally aerated groundwater

from the KAERI underground research tunnel (KURT) was used as an electrolyte with NaCl additive to investigate the corrosion behavior of the film to simulate the condition of DGD repository.

## 2. Methods

Fig. 1 shows a schematic of the wire-fed AM used for the Cu–Ni film fabrication. A Cu–Ni wire with a diameter of 1.2 mm (Nikko Yozai MFG, Tokyo, Japan) was used as the starting material for sample preparation. The chemical composition of Cu–Ni wire was 87.71wt% of Cu, 10.31wt% of Ni, and other elements (Mn, Fe, Ti, Si, S, P, and Pb). The gas tungsten arc welding (GTAW) method was used for the film formation process. A CS plate with dimensions of 200 mm × 200 mm was used as the substrate. Subsequently, the wire was supplied to the arc region to form a film surface. The wire was welded onto the substrate in a spiral shape from its origin to a diameter of 150 mm. The welding process was repeated three times to ensure film thickness. The process was performed using a quality assurance procedure assisted by a specialized company (Clad Korea Co., Korea).

Electrochemical characterization of the Cu–Ni film fabricated by wire-fed AM was performed using 1) a three-electrode cell composed of a Cu–Ni film as the working electrode (opening area = 1 cm<sup>2</sup>), 2) a Pt mesh as the counter electrode, and 3) a saturated calomel electrode (SCE) as the reference electrode. Naturally aerated groundwater collected from the KURT was used as the electrolyte. The chemical composition of the KURT groundwater has been described in a previous study [13]. Moreover, 0.1 M sodium chloride (NaCl, 99.5%, Junsei Chemical CO., LTD.) was used as an additive for the chloride ion ( $\text{Cl}^-$ ) source as the amount of  $\text{Cl}^-$  in KURT groundwater is much lower than that in other countries, even though it is an important corrosion-inducing agent. The electrodes were connected to a potentiostat (SP-300, Biologic) for electrochemical measurements. Potentiodynamic measurements (scan rate = 0.167 mV·s<sup>-1</sup>) were

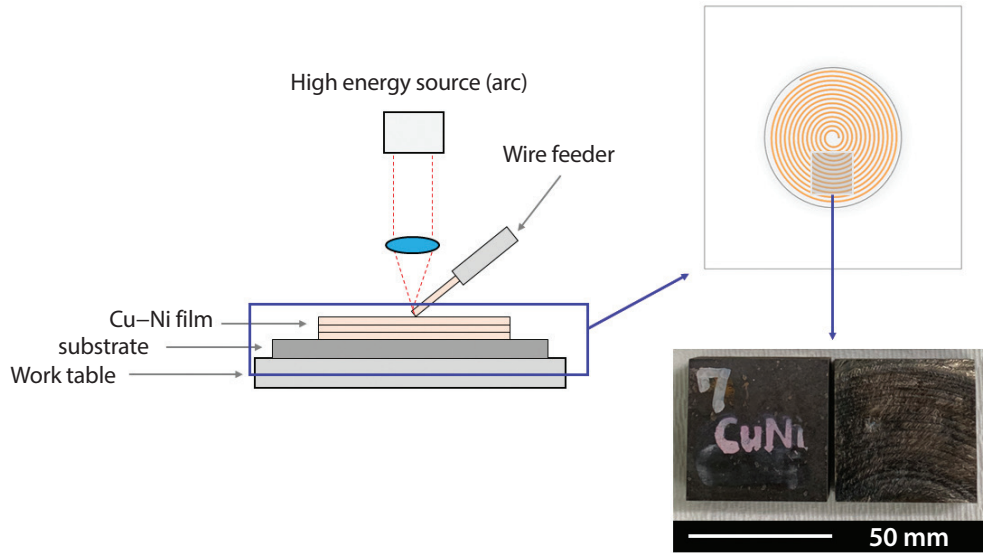


Fig. 1. Wire-fed additive manufacturing of Cu–Ni film.

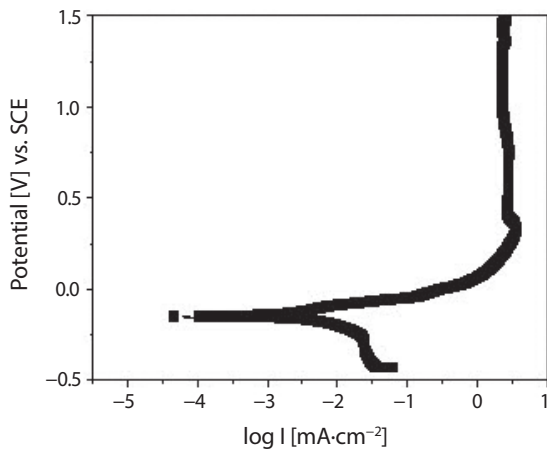


Fig. 2. Potentiodynamic polarization curve of the Cu–Ni film fabricated by wire-fed AM in naturally aerated KURT groundwater with NaCl additive.

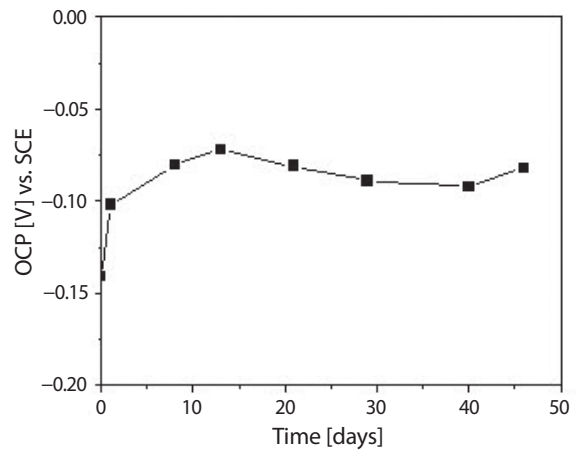


Fig. 3. Open-circuit potential (OCP) profile of the Cu–Ni film fabricated by wire-fed AM during the exposure.

performed to determine the corrosion parameters. An electrochemical impedance spectroscopy (EIS) measurement was performed at open circuit potential ( $E_{ocp}$ ), applying an AC signal of  $\pm 10$  mV rms amplitude, in a frequency range from 100 kHz to 10 mHz. The sampling size considered six data points per decade. Surface morphology and elemental composition of the corroded Cu–Ni film was observed by scanning electron microscope (SEM, JSM IT-8000, JEOL) with an energy-dispersive X-ray spectroscope (EDS). All

surface analyses were performed at the KAIST Analysis Center for Research Advancement (KARA).

### 3. Results and Discussion

Potentiodynamic measurements were conducted in naturally aerated KURT groundwater with an NaCl additive as a preliminary step in applying the Cu–Ni film as a

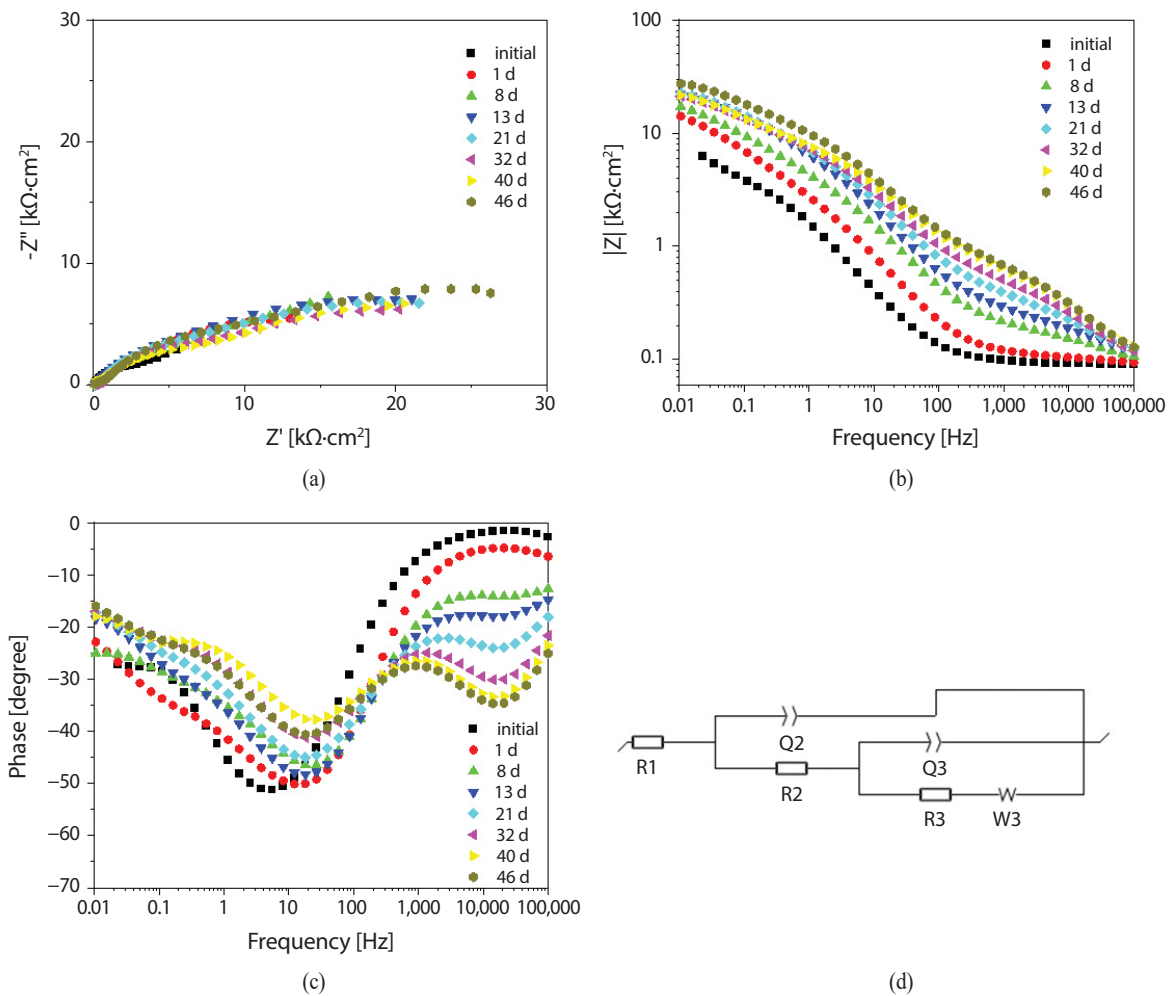


Fig. 4. (a-c) EIS responses of the Cu–Ni film fabricated by wire-fed AM during the exposure to the naturally aerated KURT groundwater with NaCl additive and (d) its equivalent circuit for fitting (Note that the initial measurement of Cu–Ni was stopped unexpectedly after 0.02 Hz).

corrosion-resistant layer in the DGD canister. Fig. 2 shows  $E_{\text{corr}} \sim -0.151$  V vs. SCE and  $I_{\text{corr}} \sim 0.981 \mu\text{A}\cdot\text{cm}^{-2}$  for the Cu–Ni film. For comparison, a Cu film fabricated by the same technique exhibits  $-0.170$  V vs. SCE of  $E_{\text{corr}}$  and  $5.214 \mu\text{A}\cdot\text{cm}^{-2}$  of  $I_{\text{corr}}$  (data not shown). This indicates that Cu–Ni exhibits enhanced corrosion resistance compared to Cu in the chloride-containing oxidic KURT groundwater.

To investigate the surface evolution of the Cu–Ni film induced by oxidic corrosion, the film was immersed in naturally aerated KURT groundwater with an NaCl additive for 46 days. The  $E_{\text{ocp}}$  and EIS responses were measured at

regular time intervals during the exposure. Fig. 3 shows that the initial  $E_{\text{ocp}}$  is  $-0.14$  V vs. SCE and increases and stabilizes to  $-0.08$  V vs. SCE. This indicates that a passivation layer was formed on the Cu–Ni film during the immersion period.

The EIS spectra of the Cu–Ni films fabricated by wire-fed AM during exposure were measured. Fig. 4(a) shows that the initial impedance response of Cu–Ni is a semicircle, followed by a slash in the low-frequency region. As the exposure time increased, it transitioned into a state exhibiting the characteristics of a system undergoing corrosion

Table 1. EIS fitted results of the Cu–Ni film fabricated by wire-fed AM in KURT groundwater with NaCl additive

Time (days)	1	46
$R_1$ ( $\Omega \cdot \text{cm}^2$ )	91.6	54.7
$Q_2$ ( $F \cdot s^{(n_2-1)} \cdot \text{cm}^{-2}$ )	$1.09 \times 10^{-4}$	$3.47 \times 10^{-5}$
$n_2$	0.61	0.43
$R_2$ ( $\Omega \cdot \text{cm}^2$ )	$1.08 \times 10^4$	$1.57 \times 10^4$
$Q_3$ ( $F \cdot s^{(n_3-1)} \cdot \text{cm}^{-2}$ )	$2.94 \times 10^{-4}$	$7.06 \times 10^{-7}$
$n_3$	0.84	1.0
$R_3$ ( $\Omega \cdot \text{cm}^2$ )	$6.09 \times 10^3$	$2.52 \times 10^4$
$W_3$ ( $\Omega \cdot s^{-0.5} \cdot \text{cm}^2$ )	$6.65 \times 10^2$	$8.46 \times 10^2$

or dissolution, marked by the precipitation of a corrosion film at the interface [14]. The impedance increased with the immersion time because of the formation and thickening of the passive film (Fig. 4(b)). The initial maximum phase angle moved slightly towards the higher-frequency region with the appearance of another maximum phase angle at 15k Hz (Fig. 4(c)). The phase peak in the high-frequency band was attributed to the formation of a  $\text{Cu}_2\text{O}$  film on the metal surface [15]. The impedance responses were fitted to an equivalent circuit (Fig. 4(d)) representing a two-time constant model, where  $R$  refers to the resistance element, and  $Q$  refers to the constant phase element (CPE). CPE was adopted to represent the nonideal capacitive behavior due to surface roughness and heterogeneity, electrode porosity, nonuniform potential and current distribution, and slow adsorption [16]. That is,  $Z_{CPE} = [Q(j\omega)^n]^{-1}$  ( $j^2 = -1$ ), where  $Q$  is the CPE amplitude,  $\omega$  the angular frequency, and  $n$  the CPE exponent. The parameters  $Q$  and  $n$  are independent of frequency. CPE represents pure resistance when  $n = 0$  and pure capacitance when  $n = 1$  [17]. The equivalent circuit of Cu–Ni for fitting analysis is shown in Fig. 4(d) [18].  $R_1$  is the electrolyte solution resistance,  $R_2$  and  $Q_2$  correspond to the passive layer, and  $R_3$  and  $Q_3$  are the charge transfer resistance and double-layer capacitance, respectively [19]. The other element,  $W_3$ , accounts for diffusion, which may indicate that a diffusion process and charge-transfer step control the corrosion mechanism [18]. The results of the

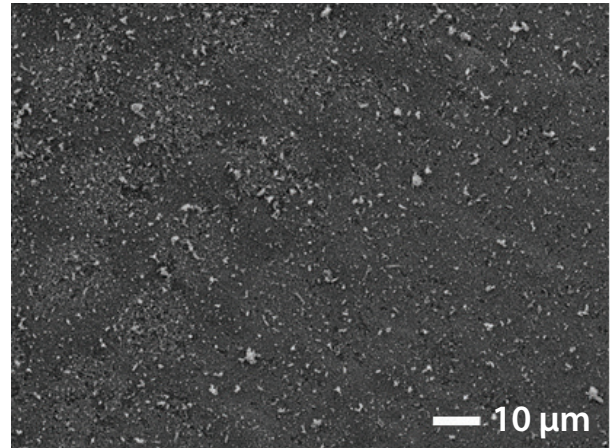


Fig. 5. SEM analysis of the Cu–Ni film after 46 days of exposure to the naturally aerated KURT groundwater with NaCl additive.

fitting analyses are listed in Table 1.  $R_2$  of Cu–Ni increases with increasing exposure time to the chloride-containing oxidic environment, indicating that the surface layer becomes more protective with increasing time. The passive film thickness, which is directly proportional to  $1/Q_2$ , increased with increasing immersion time.

Fig. 5 shows the surface morphology of Cu–Ni after 46 days of exposure to the oxidic KURT groundwater solution with 0.1 M NaCl additive. It was completely covered by copper oxide particles, which were identified by EDS analysis (Cu 41.78, O 57.81, Ni 0.41 atom%). This uniformly dense surface film enhances the corrosion resistance in a NaCl-added groundwater solution.

## 4. Conclusions

In this study, a Cu–Ni film was fabricated using wire-fed AM, and its electrochemical corrosion behavior was investigated as a corrosion-resistant layer for a DGD canister. The potentiodynamic polarization curve shows that the corrosion current density of Cu–Ni was lower than that of Cu in oxidic groundwater with NaCl additive. EIS measurements revealed the formation of a dense passive layer on the Cu–Ni surface during 46 days of exposure to the NaCl-added

groundwater solution, as observed by SEM-EDS analysis. Comprehensive mechanical and electrochemical characterizations with further improved film quality and scalability will be performed to identify its feasibility as a DGD canister and realize an AM-coated canister.

## Author Contributions

Kim, G.Y. designed experiments. Jung, Y.I. and Lee, Y.H. fabricated Cu–Ni film. Kim, G.Y., Woo, J.H., and Jang, J. performed the electrochemical experiments. All authors participated in the data analysis and discussion. The manuscript was written with contributions from all authors. All the authors approved the final version of the manuscript.

## Conflict of Interest

The authors declare that they have no competing financial interests or personal relationships that could have influenced the work reported in this study.

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