A STUDY ON CORROSION RESISTANCE CHANGE THROUGH NI, MO, AND CRO$_X$ COATING OF NI-ALLOY IN CHLORINE-BASED SALT

Jisu Na [a], Unho Lee [a], Mingue Lee [a], and Young Soo Yoon [a]*
[a]Department of Materials Science and Engineering, Gachon University, Gyeonggi-do,13120
[*]Corresponding author: benedicto@gachon.ac.kr

1. Introduction

The 4th generation nuclear power plant MSR (Molten Salt Reactor) is attracting a lot of attention worldwide due to its high thermal efficiency and stability due to low vapor pressure. Structural materials for application to MSR must satisfy various conditions, but the most basic and important characteristic is high temperature corrosion resistance. Therefore, as a structural material for MSR, ORNL (Oak Ridge National Laboratory, Oak Ridge, TN, USA) developed Hastelloy N as a Ni-based superalloy with low Cr content, also called GH3535 in China [1]. However, Hastelloy N also could not avoid the phenomenon of metal ions eluted and brittle during long-term operation. [2] Therefore, various studies are being conducted to supplement this, such as coating through Ni Watt electroplating process after CrN diffusion barrier layer by arc ion plating [3], and Ni or Co coating through laser cladding [4]. In this study, the surface coating of Hastelloy N was performed by RF sputtering, which is the most economical and easy process. The coating material was selected as Ni, Mo, and CrO_x on the corrosion resistance of Hastelloy N. Afterwards, the change of corrosion resistance was confirmed in a high-temperature molten salt through a corrosion immersion test.

2. Methods and Results

2.1 Materials and Coating Method

The material studied was Hastelloy N (UNS N10003) with the chemical composition shown in Table 1.

Table I. The chemical composition of Hastelloy N (UNS N10003) (wt%). [5]

Element	Ni	Mo	Cr	Fe	Si	Mn	V	W	Cu
Mass Fraction	Bal.	16	7	4	1	0.8	0.5	0.5	0.35

Hastelloy N (UNS N10003) substrate was cut to 1cm*1cm thickness 1.5cm. The processed specimen was cleaned through sonication twice in acetone and ethanol before deposition, and then dried. A deposition sample was prepared on a Si wafer using imide tape, and coating was carried out under the conditions shown in Table 2. with RF sputtering.

Table II. Deposition parameters of Ni, Mo, and CrO_x coatings.

Coating materials	Power [W]	Gas flow rate (Ar : O_2)	Deposition Time [s]	Rotation speed [rpm]	Thick ness [um]
Ni	700	100:0	1239	14	1
Mo	700	100:0	1320	14	1
CrO_x	700	90:10	700	14	1

2.2 Corrosion Immersion Test

A corrosion immersion test by providing a Cl-based mixed salt to Hastelloy N was conducted for confirming the effect of surface coating. Binary eutectic NaCl-KCl (50.6-49.4 mol%) was chosen as the experimental molten salt based on its low melting point, low cost, and excellent versatility. The mixed salt was prepared using commercial NaCl, KCl. The tests were performed in a furnace at 800°C, 0.506 NaCl-0.494 KCl eutectic salt, for 48 hours. Through this, it was confirmed whether the corrosion resistance of the uncoated, Ni-coated, Mo-coated, and CrO_x-coated samples was improved before and after the corrosion immersion test.

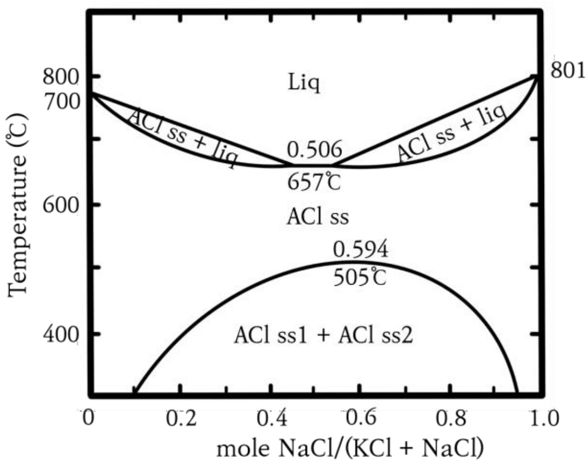

Fig.1. Phase diagram of NaCl-KCl mixed chlorine salt [6]

2.3 Analysis before/after corrosion immersion test

After the corrosion immersion test, the change of the actual sample was visually confirmed, and the weight loss was checked. After that, the change of the coating surface and the interface due to corrosion was observed with OM (Optical Microscope) and SEM (Scanning Electron Microscope). XRD (X-Ray Diffraction) investigated the microstructure of the coating layer before and after corrosion to confirm structural stability. Then, the amount of metal eluted from the substrates to the molten salt was determined through ICP-MS (Inductively Coupled Plasma-Mass Spectrometry).

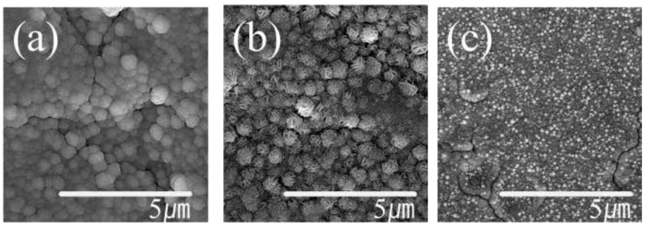

Fig.2. Sputtering deposition for anti-corrosion alloy of Hastelloy N10003 on (a) CrO_x, (b) Mo, and (c) Ni Thin film

2.4 Results and discussion

As a result of SEM-EDS, only Ni, Mo, and CrO_x, which are coating materials, were confirmed, so it was confirmed that there was no problem in the material deposition process. After the corrosion immersion test, because of comparing the three coating materials, original shape was best maintained in the order of CrO_x < Mo < Ni. These tendencies are the similar when compared with the thermodynamic Gibbs free energy theory. NaCl and KCl are stable because they have a high negative Gibbs Free energy value. However, corrosion occurs in a high-temperature NaCl- KCl molten mixed salt environment. This corrosion is mostly due to moisture and impurities in the salt, as well as the metal oxides and metal chlorides formed further. In fact, according to the Gibbs free energy results at 800°C, the order of the oxidation and chlorination reaction rates of alloying elements proceeds as Cr > Fe > Mo > Ni >> Cr_2O_3. Compared with the experimental results, this theoretically explains that surface property modification through Ni coating helped to improve corrosion resistance.

Table III. Gibbs free energy of formation per molecule Cl_2 for various chlorides at 800°C.

Reaction	800°C ΔG (kJ/mol)
$Cr_2O_3 + 3\ Cl_2 \rightarrow 2\ CrCl_3 + 3/2\ O_2$	232.683
$Mo + 3\ Cl_2 \rightarrow MoCl_6$	-4.116
$Mo + 5/2\ Cl_2 \rightarrow MoCl_5$	-119.496
$Ni + Cl_2 \rightarrow NiCl_2$	-123.300
$Fe + 3/2\ Cl_2 \rightarrow FeCl_3$	-142.048
$Mo + 3/2\ Cl2 \rightarrow MoCl_3$	-183.626
$Fe + Cl_2 \rightarrow FeCl_2$	-186.605
$Cr + Cl_2 \rightarrow CrCl_2$	-241.405
$Cr + 3/2\ Cl_2 \rightarrow CrCl_3$	-280.750

3. Conclusions

We conducted coating for three candidates and corrosion immersion tests to find the most suitable material to improve the corrosion resistance properties of structural materials for MSR. As a result of confirming the change after corrosion of the coated alloy compared to the non-coated sample, it could be determined that Ni on the surface prevents metal elution and improves corrosion resistance. However, it cannot be said that complete corrosion protection has been realized due to the Ni coating. Therefore, it is necessary to precede the salt purification process to completely control corrosion caused by impurities and moisture in the salt in future research. In addition, it is necessary to find a way to maintain a continuous and dense coating layer through supplementation such as barrier layer deposition or additional surface modification during the coating process. Nevertheless, the corrosion resistance improvement of Ni is judged to be excellent as a coating material applicable to chlorine-based salt MSR, so we propose Ni as a surface coating material for structural materials.

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