

Preparation of the simulated NiFe₂O₄ corrosion oxide by electrodeposition

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1. Introduction

In general, the primary system of the nuclear power plant has a corrosion oxide around the inner surface of the system due to the long-time operation under high temperature and pressure. When oxides are deposited on the surface, radionuclides such as ⁶⁰Co, ⁵⁸Co, etc. activated by neutron flux from the nuclear fuel could be simultaneously embedded by the circulative cooling water of the system [1, 2].

Therefore the removal of those contaminated corrosion oxides is essential for a safe working environment through decontamination to maintenance and decommission of a nuclear facility. Corrosion oxides of the primary system are composed of a magnetite, nickel ferrite, and various chromium oxides such as FeCr₂O₄, and NiCr₂O₄.

In this study, we focused on the manufacture of simulated oxide for the dissolution experiments. The analyses of composition and morphology of oxides were used as indices of similarity of simulated oxides to those found in the nuclear power plant. In addition, decontamination test with reductive solution was performed.

2. Methods and Results

2.1 Preparation of NiFe₂O₄ oxide film

Nickel ferrite oxides were deposited using the electron beam method on the surface of a type 304 stainless steel. The heat treatment under 700 °C and Ar atmosphere was performed to crystallize the oxides. A detailed condition of the oxide preparation is summarized in Table I.

Table I: Oxide film manufacturer description

Process	Manufacturing conditions
Electrodeposition	<ul style="list-style-type: none"> • Equipment : electron beam evaporator • Target material : nickel ferrite (NiFe₂O₄) • Thickness : 500 nm
Crystallization	<ul style="list-style-type: none"> • Equipment : furnace • Temperature : 700 °C in Ar atmosphere • Time : 1hr

2.2 Decontamination solution

The composition of the decontamination solution, which is used for a reductive decontamination, is shown in Table 2. The solution contains N₂H₄ effective for the reduction of Fe(III) to Fe(II) from NiFe₂O₄ and Cu(II) ions to facilitate the reductive dissolution. The optimal acidity was pH 3 adjusted by H₂SO₄ and operating condition was 24 hours at 95 °C.

Table II: Decontamination solution description

Concentration of component and experimental condition	Values
Volume	0.2 L
[N ₂ H ₄]	0.05 M
[Cu(II)]	0.5 mM
Temp.	95 °C
Duration	24 hours
pH	3

2.3 Properties of the corrosion oxide film

Fig. 1 shows the field emission scanning electron microscopy (FE-SEM) image of the surface and cross-section of NiFe₂O₄ film. From the results of Fig. 1 (a) and (b), no observation of faults of oxides during the coating and heat treatment were found. The designated depth of the oxide (~500 nm) was confirmed in Fig. 1(c). Before annealing the sample, the surface of nickel ferrite film was smooth and there is no other film phase after deposition.

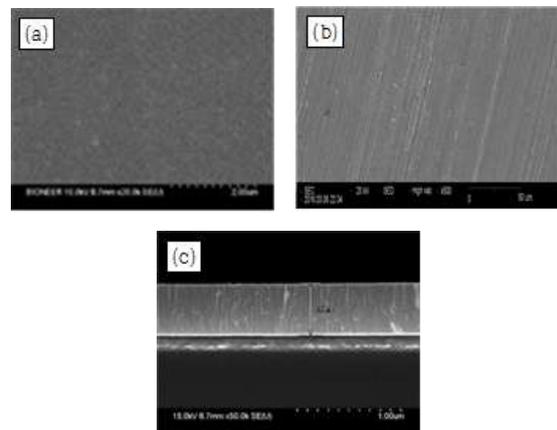


Fig. 1. SEM images of the nickel ferrite film; before (a) and after heat treatment (b), cross-sectional view of nickel ferrite film (c).

The crystallographic structure and phase purity of are examined by X-ray diffraction (XRD). Fig. 2 shows the XRD patterns of target material of nickel ferrite and as-made nickel ferrite film. The characteristic peaks of were found around $2\theta = 220, 311, 222, 400, 422, 511,$ and 440 , which means that nickel ferrite is a soft magnetic material having completely inverse spinel structure [3]. The tendency of peaks of as-deposited NiFe_2O_4 was similar to those characteristic peaks even though there is a little difference on the intensity of peaks. A comparison of the nickel ferrite film and the target can be seen that the peak showing a similar tendency.

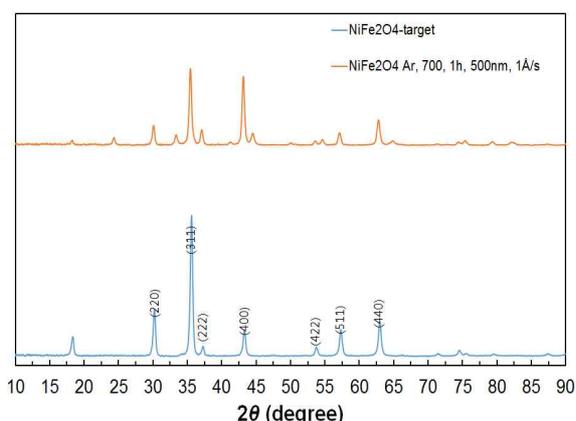


Fig. 2. XRD patterns of target material (blue line on the bottom) and nickel ferrite film on the type 304 stainless steel after heat treatment (red line on the top).

The composition of nickel ferrite film was analyzed with energy dispersive X-ray spectroscopy (EDS) elemental mapping method (see Fig. 3). The compositional fraction of the oxide film was close to the target NiFe_2O_4 while the atomic composition was not exactly same to stoichiometric ratio. We assume that the difference of the composition was due to capture of existence of chrome under the oxide layer. More precise analysis on the composition of oxide will be carried out with thicker ($>1 \mu\text{m}$) oxide in the future.

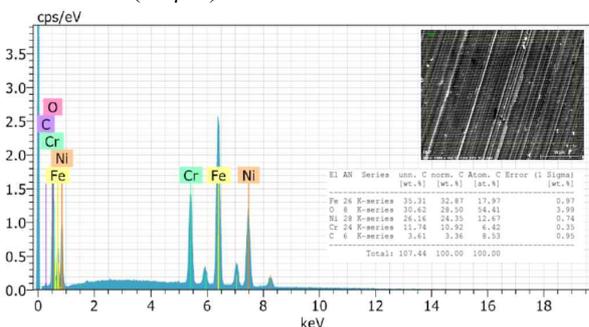
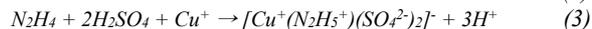


Fig. 3. Elemental analysis of nickel ferrite film (EDS).

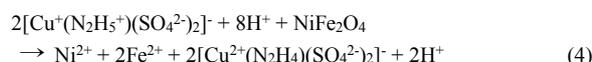
2.4 The evaluation of nickel ferrite dissolution by HYBIRD-D

HYBIRD-D decontamination process uses the hydrazine as a strong reducing agent and copper(I) ion as a catalyst in a coordination complex of $[\text{Cu}^+(\text{N}_2\text{H}_5^+)(\text{SO}_4^{2-})_2]^-$ in which a Cu(I) ions reduce Fe(III) to Fe(II) ions by oxidizing itself to Cu(II) ions. This reductive dissolution continues with generation of Cu(I) ions by hydrazinium ions (N_2H_5^+). The mechanisms of complex formation and decontamination are known as follows [4,5].

Formation of complex



Decontamination



Strong reductive agent dissolves metal oxide under acidic environment. The existence of copper(I) ion critically facilitated the dissolution rate of metal oxide [6]. Fig. 4 is a nickel ferrite film before and after decontamination images by using the reduction decontamination.

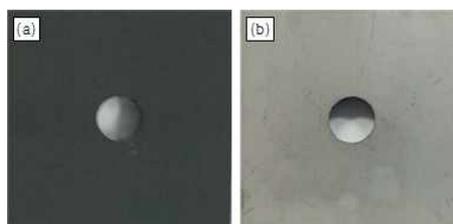


Fig. 4. Decontamination of nickel ferrite film image; before (a) and after decontamination (b).

4. Conclusion

The results of the study have shown that the simulated NiFe_2O_4 oxide is able to be produced by the method of electro-deposition. The formation of NiFe_2O_4 was confirmed by the analyses of morphology and compositions. It would also be possible to manufacture various oxides by electrodeposition, but need in-depth analysis of oxides and decontamination performance in the future study.

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