The effect of annealing temperature of $NiFe_2O_4$ thin film prepared by E-beam evaporation method for simulated specimen in PWR system

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1. Introduction

Decontamination technology is necessary to reduce radioactive component and contamination of complex equipment during decommissioning of nuclear power plants. There are a number of methods for decontamination process including chemical, electrochemical, foam, and mechanical contamination technologies. Among them, decontamination foam is considered to have potential application for the cleaning of radioactive contaminants from metallic walls, overhead surfaces, and complex components [1]. For the effective decontamination, the understanding of the fundamental mechanisms responsible for corrosion and stress corrosion of austenitic and nickel base alloys is necessary. Austenitic 304L and 316L stainless steel owe their high corrosion resistance in water to the formation of a continuous oxide layer, the passive film, only a few nanometer thick at ambient temperature, strongly enriched in $Cr(3^+)$ and separating and protecting the alloy from the corrosive medium [2,3]. Many researches have been investigated the influences of various parameters such as water chemistry, materials composition and stress, on the initiation and growth of stress corrosion cracking. Most studies reported the observation of a duplex oxide layer with a Fe-rich outer layer and a Cr-rich inner layer. The outer oxide layer is composed of magnetite (Fe_3O_4) or iron-nickel spinel oxide. For the Cr-rich inner layer, composition and phase are subject to controversy.

In this study, we prepared the $NiFe_2O_4$ film on the stainless foil (SUS 304) using E-beam evaporation technique using $NiFe_2O_4$ target. Compared to the other technique, the materials can be simply deposited by E-beam evaporation and is capable of providing advantages such as large area deposition, convenient replacement of source targets, and controllability of precise deposition thickness as low as 1 nm.

2. Experimental

$NiFe_2O_4$ thin film was deposited on stainless foil (SUS 304, thickness 25 μm) by using an electron beam evaporation system at room temperature. $NiFe_2O_4$ pellet (purity 99.9%) was used as a target. Prior to deposition process, the chamber was evacuated down to 3 x 10^{-6} Torr. The deposition rate and thickness of $NiFe_2O_4$ thin film were 0.5 Å/s and about 490 nm monitored by a thickness sensor during the evaporation process. The substrates were sputter-etched with Ar ions for 5 min before deposition in order to remove any oxide layer on the SUS foil surface. For the high crystallinity of $NiFe_2O_4$ thin film, as-deposited sample was annealed at 700 ℃ for 1h in Ar atmosphere.

The morphology of the surface and cross-section of $NiFe_2O_4$ thin film was investigated by a field emission scanning electron microscopy (S-4800, Hitachi) working at 30 kV. A high resolution transmission electron microscope with energy dispersive spectroscopy (JEOL-2100F HRTEM) with a 200 kV operating voltage was also used to capture the morphology and elemental analysis of the $NiFe_2O_4$ sample. The thin film X-ray diffraction (X-pert PRO MRD, Philips) pattern was conducted with Cu Kα radiation (λ = 1.5406 Å) operating at 40 kV and 30 mA between 10° and 90° at a scan rate of 0.01°, 2θ/min. Raman measurement (NTEGRA SPECTRA, NT-MDT) was conducted with a Ar laser excitation source emitting at wavelength of 514 nm. The X-ray photoelectron spectroscopy (K-alpha, Thermo VG Scientific) analysis was performed to evaluate the chemical status of the thin films and the binding energy was referenced to the C 1*s* peak from carbon at 284 eV.

3. Result and discussion

The structure of $NiFe_2O_4$ film according to the heat temperature was determined by X-ray diffraction (XRD). Fig.1 shows the XRD patterns of $NiFe_2O_4$ film after heat treatment at 600, 700, and 800 ℃ for 1 h. It is clearly found that sharp diffraction peaks appeared after heat treatment, which means high crystallinity and purity of $NiFe_2O_4$ materials. As shown in Fig. 1, all samples have showed diffraction peaks at similar 2θ degree compared with $NiFe_2O_4$ target peak which is corresponding to the (220), (311), (222), (400), (511), and (440) crystal planes of the $NiFe_2O_4$ (JCPDS No. 54-0964). These diffraction peaks confirmed the presence of single-phase $NiFe_2O_4$ with face centred cubic and Fd3m space group. The peak intensity become more strong according to the heat temperature. The peaks annealed at 800 ℃ revealed the highest sharp peak, indicating improvement of crystallinity compared to that of lower temperature.

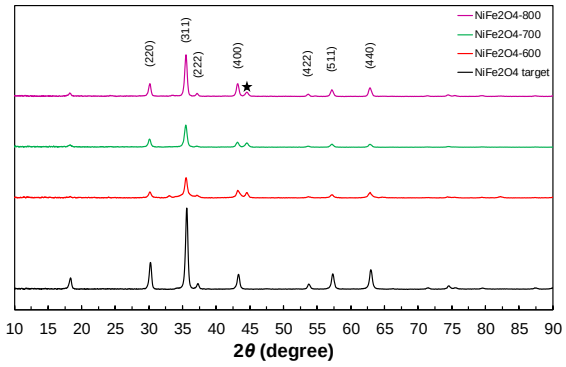

Fig. 1. XRD patterns of $NiFe_2O_4$ according to the annealing temperature.

The morphology of the $NiFe_2O_4$ film was observed through the FE-SEM and HR-TEM. Fig. 2a-c shows surface morphologies of the $NiFe_2O_4$ electrode annealed at 600 °C, 700°C, and 800 °C. As can be seen in Fig. 2a and 2b, the **$NiFe_2O_4$** film shows numerous streaks along based on mother substrate without any cracking and a few droplets is observed. These particles are ascribed to the incomplete elimination of target splashing during deposition. After heat treatment at 800 °C, however, the surface morphology is much different with electrode heated at lower temperature. The roughness and porosity of the surface is observed, evidencing the effect of annealing temperature. This observation of roughened surface is suggesting that the film might be undergoing change of orientation. It is reported that the heat treatment of stainless steel changes their chemical composition and the thickness of the passive film. Thus, the surface morphologies are depending on the heat temperature. It is anticipated that the roughened surface of $NiFe_2O_4$ electrode could lead to obtain low resistance interface of electrode. Besides, the thickness of electrode on glass was about 500 nm(Fig 2d) and the conformal $NiFe_2O_4$ film was clearly observed.

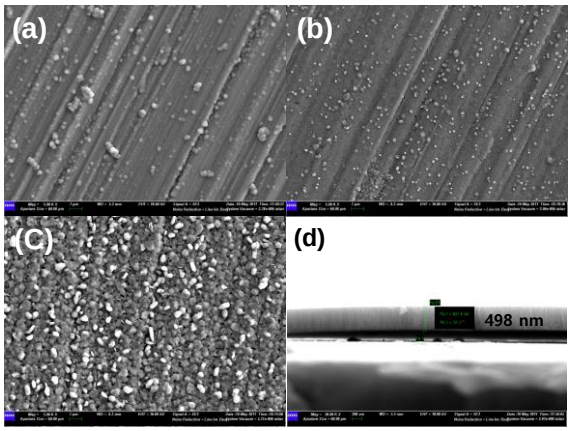

Fig. 2. SEM images of the $NiFe_2O_4$ thin film annealed at 600(a), 700(b), 800(c) **℃,** (d) cross-sectional view of $NiFe_2O_4$ thin film.

4. Conclusion

The $NiFe_2O_4$ thin film electrode has been prepared by using an electron beam evaporation system at room temperature. The phase, structure and morphology of materials were confirmed by XRD, SEM, and HR-TEM analysis.

REFERENCES

[1] L. Nunez, L. Kaminski, Foam and gel methods for the decontamination of metallic surface, US patent,166, 758 (2007).