Analysis of Oxide Layer by Simulating $NiFe_2O_4$ Film on Stainless Steel, Incoloy-600 and Carbon Steel

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1. Introduction

Decontamination is one of the important technology that are applied during the decommissioning process of nuclear power reactors to secure the worker's safety and minimization of the secondary waste amount [1]. Thus disolving or removing oxide films can release the radionuclides into solution and decontamination process follows this principle. Stability of oxide layer is mainly caused by the presence of chromium in trivalent state. Even though the reducing water chemistry for operating nuclear power plant, it is found that the oxide consisted of a dual layer, an external thick layer containing mostly iron oxide and a thinner internal layer rich in chromium oxide, is formed on the surface of system. In PWR, typical film thickness of Stainless Steel(SS) surface are 2-3 μm while those Inconel surfaces are closer to 1-2 μm but in CANDU-PHWRs surfaces is about 75 μm due to the presence of carbon steel as the primary system piping. Oxidation behaviour on different metarials depends on their chemical structure and compositions of base metal. It is important to characterize the oxide formed on different kinds of materials for the better understanding of its environmental sustainibility in nuclear reactors.

The main objective of this study is to understand the different composition of oxide layer based on the difference of metal. Other objectives include dissolving the oxide layer by using or developing of different types of decontamination processes based on the chemical composition of oxide layers. In this study, we prepared the $NiFe_2O_4$ on Stainless Steel, Inconel-600 and Carbon Steel using E-beam evaporation technique.

2. Experimental

$NiFe_2O_4$ thin film was deposited on Stainless Steel-SUS 304 (Ni- 9.25Cr- 19.00, Fe- Balance), Inconel-600 (Ni- 72.0, Cr-14.0-17.0, Fe- 6.00-10.00, Carbon- 0.15) and Crabon Steel (Ni- 30.0-35.0, Cr-19.0-23.0, Fe- 39.5) by using an electron beam evaporation system at room temperature [2]. Those three substrates were polished in order to remove the pre-existing oxide layers. $NiFe_2O_4$ pellet (purity 99.9%) was used as a target. The deposition rate and thickness of $NiFe_2O_4$ thin film were 0.7 Å/s and about 0.5 μm 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 metal surfaces. For the high crystallinity of $NiFe_2O_4$ thin film, as-deposited sample was annealed at 600°C for 1 h in Ar atmosphere. The morphology of the different substrates of $NiFe_2O_4$ thin film was investigated by a field emission scanning electron microscopy (SEM, S-4800, Hitachi) working at 30 kV. The thin film X-ray diffraction (XRD, X-pert PRO MRD, Philips) pattern was conducted with Cu, Ka radiation (l ¼ 1.5406 Å) operating at 40 kV and 30 mA between 10° and 90° at a scan rate of 0.01°/min. The XPS, X-ray photoelectron spectroscopy (Kalpha, Thermo VG Scientific) analysis was performed to evaluate the chemical status of each elements of the thin films and the binding energy was referenced to the C 1s peak from carbon at 284 eV.

3. Results and Discussions

The surface morphology of three kinds of substrates was observed by SEM. Fig. 1 shows the SEM images of those substrates, respectively. The crystallographic structure of the $NiFe_2O_4$ thin film on SUS-304, Inconel-600, Carbon Steel after annealing was characterized by X-Ray Diffraction. Fig. 2 shows the XRD patterns of $NiFe_2O_4$ thin film after heat treatment at 600°C for 1h under Ar atmosphere. When the

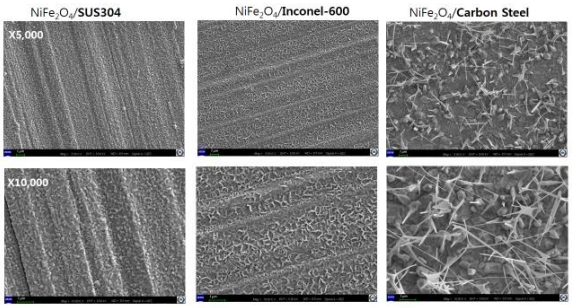

Fig. 1. SEM surface images of SUS304, Inconel-600 and Carbon Steel after $NiFe_2O_4$ deposition and annealing at 600°C.

samples were heated at 600°C, the film began to be crystalized as indicated by the $NiFe_2O_4$ peak. Three XRD peaks for SUS-304, Inconel-600, Carbon Steel have showed similar peak index. This is assigned to those of the $NiFe_2O_4$ cubic spinel, which could be indexed to the inverse spinel. The peak at 33° has showed higher intensity in Carbon Steel. After the heat treatment, the reflections become narrower with an increase of crystallite size. Later, we will find why the carbon steel sample shows different XRD peaks regarding crystal structure. More study will be conducted in the future.

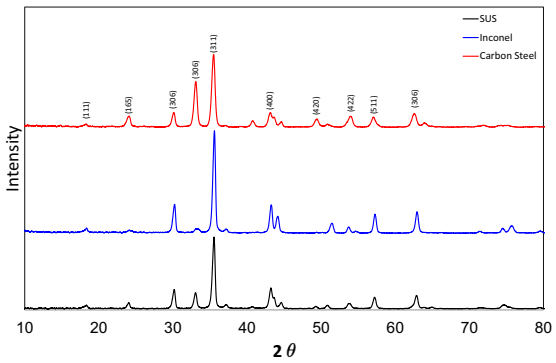

Fig. 2. XRD profiles of SUS304, Inconel-600, Carbon Steel.

XPS has been studied to observe the chemical state of each element and also for understanding the depth profile. Fig. 3 shows the XPS graph of SUS304, Inconel-600, Carbon Steel, respectively. In SUS304, Nickel was observed at 846.22 eV with a satellite peak, which is characteristic of material Ni $2p_{3/2}$. Due to spin orbit coupling Fe 2p peak always split into two (709.68 eV, 2 $p_{3/2}$ and 722.92 eV, 2 $p_{1/2}$) and describe the presence of Fe^{2+} and Fe^{3+}. This is indicating the different oxidation state of iron in SUS304 material. Both in Incoloy-600 and Carbon Steel Fe is present in Fe^{2+} state. Chromium presents in Cr^{3+} state in all three materials. In the case of $NiFe_2O_4$ deposition on Incoloy-600 the concentration iron has increased with the etch time but presence of nickel goes down. The presence of chromium found high wirh etch time in SUS304. Nickel has deposited in the uppermost layer on SUS304.

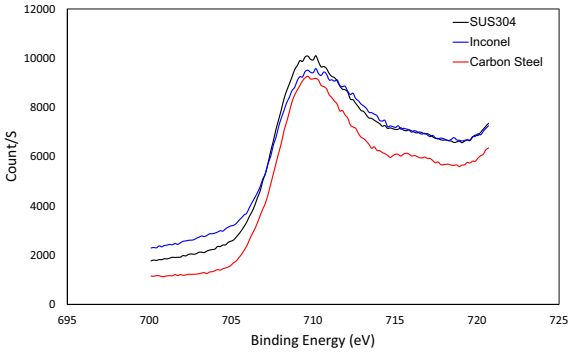

Fig. 3. XPS Spectra for Fe on SUS304, Inconel-600, Carbon Steel respectively.

4. Conclusion

The $NiFe_2O_4$ thin film has been deposited on substrates of Stainless Steel, Inconel and Carbon Steel by using an electron beam evaporation system. The reaction between Nickel Ferrite with different metal ions makes different composition of oxide layers. The phase, structure and morphology of materials were confirmed by SEM, XRD and XPS analysis. By analyzing these oxide layers it can be possible to determine the decontamination procedure for these metals, in future.

REFERENCES

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