

## Fabrication of Composite Nickel Layers with Nano-sized Ferrites by Using SHS and Electroforming

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### 1. Introduction

Nickel coating is useful for the preparation of nuclear battery, the corrosion/wear protection layers of power plants and the mater sheets for electrons and information display materials. The nickel coating can be formed by various methods like electroplating, electro-less plating and other dry processes. Although each process can make nickel deposits on various substrates, its physical and chemical properties are slightly different due to microstructure and impurity because nucleation and growth behaviors of the nickel layer are dependent upon fabrication environment. That kind of little difference of the properties is so important for the fabrication of high quality products in a leading edge science and industrial field, especially, for preparation of the nano-scale materials. Recently, nickel coating technology is well applied to various industrial fields and replaced to other coating materials like copper and chromium because of its advantage of precise marching and relatively high quality microstructure [1, 2]. Furthermore, neutron scattering methods have been applied to analyze nano-structure to find optimum fabrication of thin and thick films and, to determine non-stoichiometry of materials to control electro-magnetic properties [3]. Although the nickel coating process have been well established, little information and application in industrial fields have been available, especially about composite structures [4]. Hence, composite nickel coating layers with nano-sized ferrites were fabricated and their characteristics were studied. Emphasis are on the analysis of non-stoichiometry and microstructure of the thin nickel layers with nano-sized ferrite particles.

### 2. Experimental Methods and Results

Two kinds of process for the preparation of composite nickel layer with nano-sized ferrite particle were carried. One is self-propagation high temperature synthesis (SHS) for nano-sized ferrite particles and, the other is electroplating of nickel. Starting raw materials for nano-sized ferrites reagent grade iron powders with average particle size of 7  $\mu\text{m}$  and nickel oxide ( $\text{NiO}$ , <120  $\mu\text{m}$ ), zinc oxide ( $\text{ZnO}$ , <150  $\mu\text{m}$ ), and iron oxide ( $\text{Fe}_2\text{O}_3$ , <1  $\mu\text{m}$ ) powders. The reactant powders were ignited at various oxygen pressures of 0.025-0.1 MPa in the SHS chamber. Combustion temperature and combustion velocity were determined using two-thermocouples method. Neutron diffraction measurements have been performed at room

temperature with D-3 diffractometer ( $\lambda=0.243$  nm), installed at IWW-2M reactor (Zarechny, Russia). Program "Fullprof" is applied for calculation of neutron diffraction patterns. Mechanical milling of the SHR products was carried out with a ball mill (SPEX 5000, USA). Inert gas flotation was performed to separate and collect final nano-sized powders. Electroforming was carried out in a Hull-cell containing a modified nickel sulfate bath. The anode and the cathode were titanium electrode and 316 stainless steels, respectively. Ultrasonic agitation at 500W was applied to electro-deposition cell with an ultrasonic generator (BH-50, Korea) during electro-deposition. The electroplating was carried out with a regulator (Jisan-400, Korea) and electroformed nickel strip was separated from cathode by using a doctor blade. The microstructure observation and chemical analysis of the products were performed by using field emission scanning electron microscopy (FESEM, JSM Joel 6400, Japan) and energy dispersive spectroscopy (EDX, Oxford, UK), respectively.

#### 2.1 Nano-sized ferrites particle

The SHS for each powder mixture occurred well in the oxygen pressure range of 0.025 MPa to 0.1 MPa. Average combustion temperature and the combustion velocity are in the ranges of 1050  $^{\circ}\text{C}$  to 1280  $^{\circ}\text{C}$  and 5.7 mm/sec to 14.2 mm/sec, respectively. The combustion temperature and the combustion velocity tend to be increased with increasing addition of lithium oxide and oxygen partial pressure during the SHS. This means that the SHS reaction is competitive reaction between oxidation and reduction reactions. The reason why the combustion temperature and the combustion velocity increase is related to the heat of formation of oxidation and reduction reactants such as -822.2 KJ/mole of  $\text{Fe}_2\text{O}_3$  and enhancement of decomposition of iron oxide by nickel and zinc oxides [5].

In order to determine a structure state of the SHS product, neutron diffraction analysis was carried out. Fig. 1 shows the neutron powder diffraction patterns of  $\text{Ni}_x\text{Zn}_{x-y}\text{Fe}_2\text{O}_4$  samples for the initial molar composition of ( $\text{NiO} : \text{ZnO} = 1 : 1$ ) at the different oxygen pressures of 0.1 MPa, respectively. Rietveld refinement showed that  $\text{Ni}_{0.46}\text{Zn}_{0.54}\text{Fe}_2\text{O}_4$  and  $\text{Ni}_{0.44}\text{Zn}_{0.56}\text{Fe}_2\text{O}_4$  ferrites with  $Fd\bar{3}m$  crystal structure were formed at the oxygen pressures of 0.025 and 0.1 MPa, respectively. The lattice parameter of them are  $a=0.8412(1)$  nm and  $a=0.8413(1)$  nm, respectively. Besides the phase with the spinel structure both diffraction patterns show a phase  $M'M''_2\text{O}_4$  (where  $M'$  and  $M''$  are the Ni, Zn, Fe)

with orthorhombic structure, described by  $Pnma$  space group and starting materials.

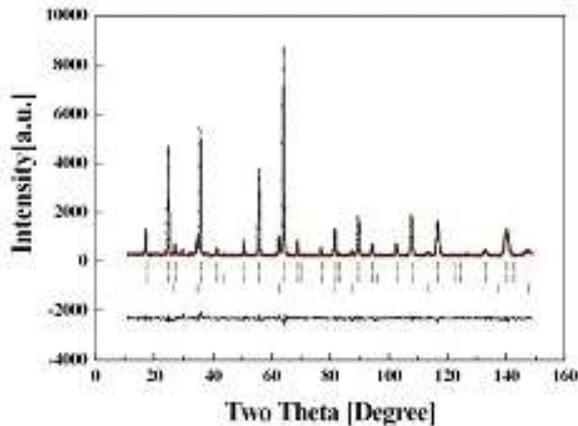


Fig. 1. Typical neutron diffraction spectra of copper-nickel-zinc ferrites formed by SHS

Fig. 2. is typical morphology of nano-sized  $Ni_xZn_{x-y}Fe_2O_4$  ferrites formed by SHS followed by mechanical milling for 2 hours observed by field emission electron microscopy. The SHS products are so porous as to be well pulverized by mechanical milling. As shown in Fig. 1, the SHS product is agglomerated nano-sized powders with about 150 nm in size.

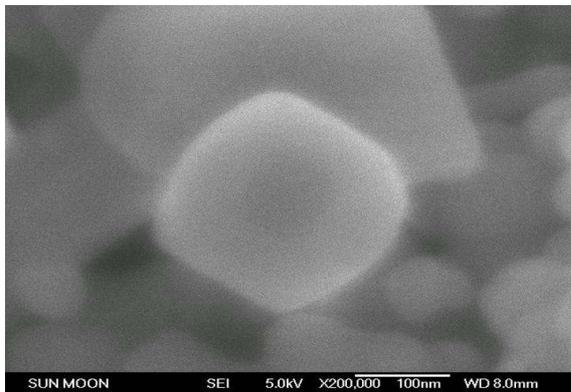


Fig. 2. Typical FESEM image of copper-nickel-zinc ferrites formed by SHS

### 2.2 Nickel layers with nano-sized ferrites particles

Table 1 is EDX data of the nickel layers with nano-sized nickel-zinc ferrites with different plating bath. As shown in Table 1, chemical composition depended on the plating bath. It is clear that bath-a is only for single nickel layers, whereas, bath-b and bath-c are suitable for the fabrication of composite layers with nano-sized ferrites because the nickel exists both of substrate and nano-particles. The ferrite contents of the composite layers were estimated by about 5 at% in this study. Maximum content of the nano-sized ferrites were obtained by using Bath-c in this study. Additional study

should be carried out to find an optimum condition based on industrial requirements.

Table 1. Composition of nickel layers with electroplating bath s

Ele.	Bath-a		Bath-b		Bath-c	
	wt%	at%	wt%	at%	wt%	at%
Ni	100	100	96.43	96.54	93.00	2.26
Fe	0	0	1.65	1.74	2.14	93.36
Zn	0	0	1.92	1.72	4.86	4.33
Total	100	100	100	100	100	100

### 3. Conclusions

In this study, composite nickel layers applicable to the nuclear battery and the protection layer of nuclear power plants were fabricated. The nano-sized ferrite particle were prepared by SHS reaction combined by mechanical milling, whereas, the thin composites nickel layer containing nano-sized ferrites were well prepared by electroforming process. Additional study to find an optimum process of the SHS and the electroforming for industrial production are under study.

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