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Corrosion behavior of magnetic ferrite coating prepared by plasma spraying

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ABSTRACT

In this study, spray dried spinel ferrite powders were deposited on the surface of mild steel substrate through plasma spraying. The structure and morphological studies on the ferrite coatings were carried out using X-ray diffraction, scanning electron microscope and Raman spectroscopy. It was showed that spray dried process was an effective method to prepare thermal spraying powders. The coating showed spinel structure with a second phase of $LaFeO_3$. The magnetic property of the ferrite samples were measured by vibrating sample magnetometer. The saturation magnetization (M_s) of the ferrite coating was 34.417 emu/g. The corrosion behavior of coating samples was examined by electrochemical impedance spectroscopy. EIS diagrams showed three corrosion processes as the coating immersed in 3.5 wt.% NaCl solution. The results suggested that plasma spraying was a promising technology for the production of magnetic ferrite coatings.

1. Introduction

Recent years, the study of radar absorbing materials (RAM) attracts more and more interest because they can absorb energy from microwaves. RAM not only can be used in the field of military technology to enhance equipment stealth ability, but also can be used in civilian technology. Special attention has been focused on the development of new materials and microwave technology. Spinel ferrites exhibit an interesting behavior, absorbing energy from electromagnetic waves, and present the best relation between the absorber's performance and its final thickness [1]. Nature resonance is microwave absorption mechanism of the ferrite materials [2]. Commercial spinel ferrite absorbers are bulk ceramics, these absorbers are fitted to components by bonding or brazing, or paints and polymer composites filled with absorbing powder, which needs a very high thickness in order to be effective [3].

In general, the conventional microwave absorption materials are composed of matrix and absorber, the absorber is blended with organic binders (such as resin), then the mixtures are directly sprayed or brushed onto the surface of components to shield target [4,5]. However, there are some limitations for these RAM because they are easily suffered deterioration with the change of environment due to their low adhesion and thermal shock resistance. Moreover, microwave-absorbing coatings usually serve in harsh environment (i.e., marine environment). The corrosion medium must affect the performance of the coating; nevertheless, the corrosion behavior of RAM has not been studied. A further disadvantage is the cost intensive procedure to fix the small sintered tile onto large-scale devices. Such limitations can be overcome by the application of thermal spraying technology for the preparation of microwave absorbing coatings. Thermal spraying is an important surface modification technique. The principle of the thermal spraying process consists of complete or partial melting of feedstock material (typically in the form of powder or wire) followed by the acceleration of molten particles and their subsequent impact onto a coated part, where the particles rapidly solidify and form a lamellar structure [6–9]. With the advantages of low substrate temperature processing, bulk production capability and cost efficiency, plasma spraying offers a promising route for the synthesis of ferrite coatings using in industry [10]. However, despite the wide industrial application of thermal spraying for the preparation of a large variety of coatings, their uses for the deposition of electromagnetic coatings have been scarce. Since the disadvantage of high deposition, temperatures and thermal stress limit the applicability of ferrite coatings through plasma spraying; only a few studies have been reported up to now [11–14]. Among the few examples, there is a great interest to investigate thermal spraying process for preparing hexagonal ferrite absorbers. Therefore, a further research needs to be done in order to verify the possibility to use plasma spraying for the preparation of spinel ferrite coatings and discuss the corrosion

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behavior of the microwave absorbers. The aim of this research is to investigate the deposition of spinel ferrite coatings by plasma spraying using spray-dried agglomerates of micrometric particles and evaluate the magnetic property as well as corrosion behavior of the ferrite coatings.

2. Experimental

2.1. Powder production

The feedstock powder consisted of spray-dried spherical agglomerates of micrometric spinel ferrite particles with composition of $Ni_{0.5}Zn_{0.4}Mg_{0.1}La_{0.05}Fe_{1.95}O_4$. Stoichiometric amounts of MgO, ZnO, NiO, La_2O_3 and Fe_2O_3 as starting materials were mixed and homogenized in a ball mill. The particles were synthesized by solid-state reaction. These reactants were calcined at 1300 °C for 2 h and then were broken down to powders again, after this process; these powders were calcined at 900 °C for 1 h and cooled down to room temperature naturally. However, the powders were not suitable for plasma spraying due to their poor flow ability. In order to increase the flow ability, spray-drying process was selected to produce the plasma spraying materials. The preparation process was as follows: the ferrite powders were used as raw materials and polyvinyl alcohol as binder. The particles were agglomerated into spherical granules, using a spray-drier attached to a cyclone; the entry and exit temperature were 240 °C and 140 °C, respectively. The spray-dried powders were sieved between 200 screen mesh and 400 mesh and thus, separated from the finer ones.

2.2. Coating samples preparation

Mild steel substrate was used in this study. The substrate was ground with abrasive papers up to 600 grit, cleaned with acetone, and then sandblasted using emery grit prior to plasma spraying. Ultrasonic plasma spraying equipment was applied to prepare the ferrite coatings [15]. Detailed operating parameters are listed in Table 1. Besides, in order to measure the magnetic properties of the ferrite coating, aluminum foil was selected as a substrate because it allowed simple preparation and had a small paramagnetic moment that had no significantly interfere with the magnetic signal of the ferrite coating.

2.3. Characterization

The phase structure of the ferrite powder and coating were studied by D8 advance X-ray diffraction (XRD) with λ = 0.154 nm Cu-Kα radiation. The cross sectional samples were prepared by metallographic cutting, hot-mounting in resin, grinding with abrasive papers (up to 2000 mesh) and polishing with diamond slurry. The morphology patterns of ferrite powders and the coating surface were observed using a scanning electron microscope (SEM, Quanta 200, FEI). The cross section morphology of the ferrite coating was analyzed using field emission scanning electron microscope (FEI, Navo NanoSEM 450). The composition analysis of the ferrite coating was performed by energy dispersive spectra (EDS, OXFORD Feature Max). The microstructure of the ferrite coating nanocrystalline is studied by a JEOL JEM 2000FX transmission electron microscope (TEM). The polished cross-section of the coating was also studied by micro-Raman spectroscopy (HR800, Jobin-Yvon, France; laser wavelength: 532 nm). The magnetic properties of the ferrite samples were measured under a static magnetic field using a Lake Shore 7410 vibrating sample magnetometer (VSM) with a maximum applied magnetic field of 20 kOe. In order to accurately access the magnetic property of the ferrite feedstock, the ferrite powders were compacted into a block with a dimension of 3 mm × 3 mm × 4 mm for the magnetic measurement. For accurately measuring magnetic property of the ferrite coating, the coating was prepared on aluminum substrate with the same plasma spraying parameter. Then the ferrite coating foil was cut from the aluminum substrate with a linear cutting machine. The foil was ground to 1000 mesh for the magnetic measurement.

Table 1
Plasma spraying parameters.

Current (A)	Voltage (V)	Ar (m^3/h)	H_2 (m^3/h)	Powder feeding rate (g/min)	Spray distance (mm)
380	120	3.2	0.4	30	100

2.4. Electrochemical experiments

The electrochemical impedance spectroscopy (EIS) was used to measure the corrosion behavior of the ferrite coatings immersed in 3.5 wt.% NaCl solution for 24 h, 96 h, 168 h, 264 h and 408 h. The tests started by recording the electrode potential with time. When the corrosion potential remained stable, a sinusoidal AC signal of 5 mV (rms) amplitude at the open circuit potential (OCP) was applied to the electrode over the frequency ranged from 100 kHz to 10 mHz. The measurements were carried out using a ZAHNER IM6 electrochemical working station. The impedance data were displayed as Nyquist and Bode plots. The acquired data were fitted and analyzed using Zsimpwin software. All electrochemical measurements were conducted in a conventional three-electrode electrolyte cell with the coated sample as the working electrode, a platinum plate as the counter electrode and a saturated calomel electrode (SCE) as the reference one. All experiments were carried out at room temperature. The specimens for electrochemical measurements were ground up to 1000 grit by SiC papers and mounted in epoxy resin with only a square area about 1 cm^2 exposed to NaCl solution. The experiments were monitored using the software of Thales.

3. Results and discussion

3.1. Characterization of the feedstock powders

The various plasma spraying process parameters and the properties of powders influences the characteristics of deposited coatings strongly. Fig. 1(a) shows the micrographs of sintered ferrite. It can be seen that the particles are agglomerate together with a size of 4–10 μm. These particles are not suitable for plasma spraying due to poor flow ability and small particle size. The SEM images of spray dried ferrite powder are shown in Fig. 1(b). It can be seen that the rough shape of the spray-dried particles is nearly spherical with the particles size ranging from 50 to 85 μm. The spray-dried powders have excellent flow ability, which is appropriate for plasma spraying. Moreover, the spray-dried processes do not alter the original phase structure and the magnetic properties of the powders.

3.2. Characterization of the ferrite coating

The XRD patterns of the sintered ferrite powder and the ferrite coatings samples are presented in Fig. 2. The sharp and strong peak around 35° and the well resolved broad diffraction peaks corresponding to (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) reflections planes confirm the formation of cubic spinel phase structure in the prepared samples. The XRD patterns prove the success of preparing spinel ferrite coating through plasma