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# Characterization of soft magnetic spinel ferrite coating prepared by plasma spray

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ABSTRACT

The primary objective of this work is to investigate the microstructure and tribological performance of magnetic nickel–zinc–magnesium ferrite coating prepared through plasma spray. The phase composition, morphology and valence state of the ferrite coating are studied by X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). It is found that the ferrite coating shows a spinel structure. The as-sprayed coating exhibits nanocrystalline with the grain size of 100–200 nm. According to the XPS analysis, the ferrite coating contains both $Fe^{2+}$ and $Fe^{3+}$, a few Ni ions are reduced to metallic Ni. Tribological performance of the ferrite coating is tested in dry friction and 3.5 wt.% NaCl solution using a ball-on-disk test. The wear loss of the ferrite coating is lower than the substrate in both dry friction and NaCl solution under the same wear test conditions. The wear mechanism of the ferrite coating is dominated by delamination and brittle fracture. Microwave absorbing property of the ferrite shows a high value of magnetic loss factor in the frequency range of 1–12 GHz. The results suggest that plasma spray is a promising technology for the production of magnetic ferrite coatings.


## 1. Introduction

The majority applications of thermal spray are in the field of protective coatings and the main functions of the overlay coating are to protect the underlying substrate from heat, wear or corrosion [1]. New opportunities are now emerging in advanced functional materials such as magnetic materials, catalytic materials and bioactive materials. Thermal spray provides advantages in the efficiency for the preparation of such materials. In recent years, thermal spray deposition of microwave absorbing materials has attracted attention because of the relative higher adhesion strength and thinner thickness of the coating compared with the traditional polymer composite method. Among the few examples, Lisjak et al. and Begard et al. focused on the atmosphere plasma spray to prepare barium hexagonal ferrites as electromagnetic absorbers [2, 3]. Other researchers also made correlation studies in this field. Bobzin et al. prepared $SrFe_{12}O_{19}$ coatings through atmospheric plasma spray using two kinds of feedstock powders (type A and type B). The feedstock of type A consisted of spray-dried spherical agglomerates of micrometric $SrFe_{12}O_{19}$ particles while the feedstock of type B was synthesized by reactively sintered agglomerates of $SrCO_3$ and $Fe_2O_3$. They found that type B agglomerates exhibited magnetic properties, which were promising for electromagnetic wave absorption applications [4]. Furthermore, Zhao et al. investigated the microwave absorption properties and the complex permittivity of $Fe/FeAl_2O_4$ coatings deposited by reactive plasma spray using $Al/Fe_2O_3$ powders. They found that the real part and the imaginary part of the complex permittivity increased with Al concentration in the frequency range of 8.2–12.4 GHz [5]. Most of these papers focused on the preparation procedure and give trials for thermal spray in the application of microwave absorption technology.

Nickel—zinc—magnesium (NZM) spinel ferrites are soft magnetic materials and can be used for radar absorbing materials (RAMs) which are mostly applied in the frequency range of 1–18 GHz [6–8]. The NZM ferrites have various forms in products, such as sheet, paints, films and powders. Apart from these products, the ferrite can be blended with organic binders to produce microwave absorbing coatings. Recently much effort has been made to improve the performance of RAMs and simplify the preparation procedure [9]. Plasma spray is a promising technique to meet this need. If NZM ferrites can be fabricated by plasma spray with proper magnetic properties, the preparation efficiency can be improved. However, the deposition of NZM ferrite coating through plasma spray has not been reported so far.

RAMs usually serve in various environments. The RAMs particularly coated on the ships or tanks is often partly scratched by the obstacle in the environment. It can be attributed to the mechanical damage. In addition, the RAMs also can be scratched by the flying glass when a bomb went off [10]. Surface damage generated by abrasive contact will limit the life of RAMs and reduce their reliability. Therefore, tribology performance is also necessary for the RAMs. Unfortunately, the studies on the tribological behavior of RAMs are scarce up to now. The aim of this work is to prepare NZM ferrite coating through plasma spray. Small amounts of lanthanum are added to the NZM ferrite in order to improve the magnetic property and refine the crystal size [11–13]. Tribological tests are

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**Table 1**
Plasma spray parameters of the coating.

| Voltage (V) | Current (A) | Ar ($m^3/h$) | $H_2$ ($m^3/h$) | $N_2$ ($m^3/h$) | Spray distance (mm) | Powder feeding rate (g/min) |
|---|---|---|---|---|---|---|
| 120 | 380 | 3.2 | 0.4 | 0.6 | 100 | 30 |

conducted in dry friction and 3.5 wt.% NaCl solution considering that equipments coated with RAMs sometimes serve in a marine environment. The effect of environmental conditions on the tribological behavior is discussed.

## 2. Material and methods

### 2.1. Powder production

The feedstock powder consisted of spray-dried spherical agglomerates of micrometric spinel ferrite particles with a 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 a solid state reaction. These starting materials were sintered at 1300 °C for 2 h to achieve reactive sintering, so as to make the original reagents convert to a spinel phase. During this process, the size of reagents got bigger and distributed inhomogeneously. In order to achieve fine products, the sintering products were broken down to powders again. The powders were heat-treated at 900 °C for 1 h after the shattering process, which is used to reduce the internal stress and defects. At last, the powders were cooled down to room temperature naturally. However, these powders were not suitable for plasma spray due to their poor flowability. In order to prepare spherical agglomerates and improve their flowability, spray-drying process was selected to produce plasma spray materials. The preparation procedure was as follows: the ferrite powders were used as raw materials and polyvinyl alcohol as the binder. The particles were agglomerated into spherical granules, using a spray-drier attached to a cyclone; the entry and exit temperatures were 240 °C and 140 °C, respectively. The spray dried powders were sieved between 200 mesh and 400 mesh to separate the bigger and finer ones, so that the size of agglomerates fell within the scope of plasma spray. The size distribution of the particles finally used in plasma spray was in the range of 200 mesh to 400 mesh.

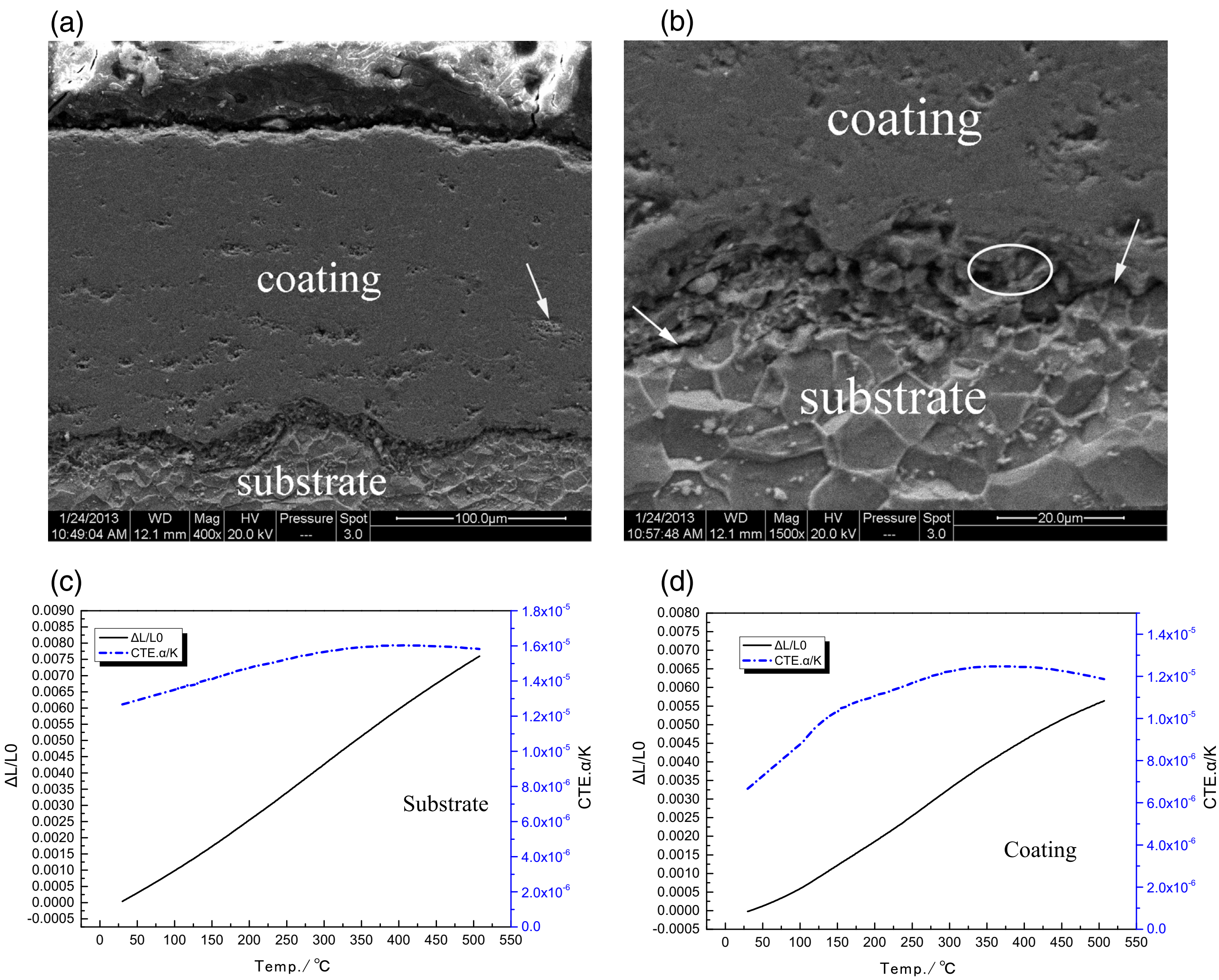


**Fig. 1.** SEM image of the ferrite coating: (a) Cross-section morphology, (b) image of the interface, (c) CTE of the substrate and (d) CTE of the coating.

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