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Characterisation of plasma-sprayed $SrFe_{12}O_{19}$ coatings for electromagnetic wave absorption

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Abstract

$SrFe_{12}O_{19}$ coatings, intended as electromagnetic wave absorbers, were produced by atmospheric plasma spraying (APS) using two different kinds of feedstock powders: spray-dried agglomerates of micrometric $SrFe_{12}O_{19}$ particles (type-A) or spray-dried agglomerates of raw materials ($SrCO_3$, Fe_2O_3), reactively sintered at 1100 °C (type-B).

During spraying, type-A agglomerates either remain unmelted, producing porous coating regions where crystalline hexaferrite is retained, or are disrupted into smaller granules which melt completely, resulting in dense coating regions with no crystalline hexaferrite.

The sintered type-B agglomerates possess higher cohesive strength and do not fall apart: the finer ones melt completely, whereas, in the larger ones, the outer region melts and infiltrates the porous unmelted core which retains crystalline hexaferrite. Dense coatings can therefore be obtained while preserving high amounts of crystalline hexaferrite even inside the dense areas. Such coatings show magnetic properties that are promising for electromagnetic wave absorption applications.

Keywords: Ferrites; Atmospheric plasma spraying; Magnetic properties; Functional applications; Hard magnets

1. Introduction

The demand for absorbers of electromagnetic waves has recently increased, because of the need to suppress electromagnetic noise and to prevent electromagnetic interference phenomena, caused by an extensive exploitation of electromagnetic waves in modern technology (electronics, wireless communication, telecommunications...).[1–4] Suitable materials for the production of microwave and mm-wave absorbers are hexaferrites. These are ferrimagnetic Fe-containing oxides based on the $MFe_{12}O_{19}$ (M = Ba, Sr, etc.) compound, which has a complex magnetoplumbite structure[5] where Fe ions occupy five different interstitial positions between closely packed M^{2+} and O^{2-} ions. The anisotropic structure and the specific site occupancy of the Fe ions produce very high magnetocrystalline anisotropy. These materials behave as ferrimagnets and possess considerable magnetic permeability (μ) also at high frequencies (up to 50 GHz). The magnetic losses (described by the imaginary part of the magnetic permeability μ'') attain a maximum at the ferromagnetic resonance (FMR) frequency where a strong absorption of electromagnetic waves occurs. This makes the basic $MFe_{12}O_{19}$ suitable for mm-wave applications; for microwave absorption, the frequency of ferromagnetic resonance has to be reduced by decreasing the magnetocrystalline anisotropy through a partial substitution of Fe ions with $Me^{II}M^{IV}$, where Me = Mn, Co, Ni, Zn and M = Ti, Sn, Ir, Rh.[6–11]

Pure hexaferrite-based ceramics are commercially available as sintered tiles or plates; therefore, there are obvious limitations in the possibility to adjust them to the wide variety of shapes of real components requiring electromagnetic protection. Higher flexibility could be attained by applying hexaferrite layers directly onto such components using thermal spraying

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processes. Despite the wide industrial diffusion of thermal spraying for the preparation of a large variety of coatings,[12,13] their use for the deposition of electromagnetically active layers has, up to now, been scarce. Among the few examples, Bartuli et al.[14] prepared absorbing coatings based on lossy conductors, dielectrics and spinel ferrites by thermal spraying. Other studies considered the preparation of spinel ferrite coatings,[15–18] but the crystalline structure of the material was altered by the spraying process, so that annealing was necessary for the crystallisation of ferrite phases. The crystallisation of $BaFe_{12}O_{19}$ coatings prepared from Ba- and Fe-nitrate solutions by inductively coupled plasma technique was achieved only when the substrates were kept at 600–900 °C.[19]

Since the use of high deposition temperatures and/or of post-process heat treatments limits the applicability of thermally sprayed ferrite layers, a further research has been undertaken in order to verify the possibility to use thermal spraying for the direct deposition of hexaferrite layers with suitable phase composition and magnetic properties.

The results obtained so far were mainly focused on Ba-hexaferrites. They have shown that, when processing $BaFe_{12}O_{19}$ and $BaCoTiFe_{10}O_{19}$ compounds by atmospheric plasma spraying (APS) or HVOF-spraying, excessively "hot" process parameters result in the formation of undesirable secondary phases[20,21]; therefore, the retention of large amounts of crystalline hexaferrite requires special adjustments.

On the one hand, the spray parameters and the size distribution of the feedstock powder have to be optimised in order to embed a controlled fraction of unmelted material in the sprayed layer while retaining sufficient deposition efficiency[22,23]; specifically, the best results were obtained using the APS technique.[22]

On the other hand, the production route of the feedstock powder also plays a crucial role. APS-processing of spray-dried agglomerates of fine Ba-hexaferrite particles gave rise to coatings with "bimodal" microstructure, where dense regions, produced by molten agglomerates and containing no crystalline hexaferrite, surround unmelted regions containing the original micron-sized hexaferrite particles.[22] On the contrary, reactively sintered hexaferrite agglomerates gave different results. Reactively sintered agglomerates were produced by spray-drying a stoichiometric mixture of micrometric reagent particles ($BaCO_3 + Fe_2O_3$ in the case of Ba-hexaferrite) and by heat-treating the resulting agglomerates in order to promote reaction and develop crystalline hexaferrite. The resulting APS coatings contained crystalline hexaferrite both in the porous unmelted regions and in the dense ones.[23]

The aim of the present research is therefore to study the deposition of $SrFe_{12}O_{19}$ (Sr-hexaferrite) coatings by APS using both spray-dried agglomerates of micrometric Sr-hexaferrite particles and reactively sintered agglomerates. Particularly, the paper focuses on the different microstructures and phase distributions within the coatings obtained by using these two kinds of feedstock, investigated by SEM, XRD and micro-Raman spectroscopy. Moreover, the magnetic properties of the coatings were also examined and electromagnetic absorption was estimated.

2. Materials and methods

2.1. Powder production

Two different kinds of feedstock powders suitable for thermal spray use, both having $SrFe_{12}O_{19}$ composition, were produced.

The first kind of feedstock powder (type-A) consisted of spray-dried spherical agglomerates of micrometric $SrFe_{12}O_{19}$ particles. These latter were synthesized by solid-state reaction from $SrCO_3$ (Merck, Darmstadt, Germany, 98.5% pure) and Fe_2O_3 (NK-α SEW, IROX-NKK Co. Ltd., Tokyo, Japan, 99.65% pure) in 1–2 kg batches. The reagents were homogenized in stoichiometric amounts in a water/ethanol slurry for 1 h using a Turbula homogenizer (System Schatz Type T2F, Willy A. Bachofen AG, Maschinenfabrik, Basel, Switzerland). After drying at 80 °C, the powders were calcined at 1100 °C for 3 h and then attrition-milled for 2 h at 200 rpm speed. The resulting particles, whose size was of 1–2 μm, were agglomerated into spherical granules, using a spray-drier attached to a cyclone (Niro pilot P6.3, GEA Niro Inc., Columbia, USA): the coarser agglomerates, with sizes approximately >20 μm (Fig. 1A), suitable for APS, were collected at the bottom of the spray-drying chamber and were separated from the finer ones collected into the cyclone.

Using the calcined and attrition-milled micrometric particles, a bulk sample was also produced in order to assess the intrinsic permeability and permittivity of the $SrFe_{12}O_{19}$ compound (see Section 2.3). For this purpose, the particles were uniaxially pressed and sintered at 1300 °C for 1 h.

The second kind of feedstock powder (type-B) consisted of reactively sintered agglomerates of reagent particles. This powder was therefore based on a stoichiometric blend of the above-mentioned $SrCO_3$ and Fe_2O_3 reagents. These reagent particles were first homogenized in a water/ethanol slurry for 1 h using the Turbula homogenizer; then, this powder mixture was dispersed in water with the aid of a dispersing agent and was spray-dried to achieve spherical agglomerations (Niro pilot P6.3) and the finer agglomerates (approximately <20 μm), unsuitable for APS processing, were separated through the cyclone as mentioned previously. The spherical agglomerates were then heat-treated at 1150 °C for 4 h to achieve reactive sintering, so that all of the original reagents were converted to Sr-hexaferrite phase. Since part of the agglomerates collapsed during this treatment, the sintered feedstock was classified using a 20 μm sieve to separate the finer particles.

2.2. Coating deposition

Type-A (spray-dried hexaferrite particles) and type-B (reactively sintered agglomerates) powders were processed by the APS system F4-HBS from Sulzer Metco (Hattersheim, Germany). All of the coatings were deposited onto a glass–ceramic substrate, grit-blasted before spraying. The glass–ceramic substrate was chosen because of its non-magnetic characteristics, which make it suitable for the measurement of the magnetic properties of the coatings. Based on some preliminary testing, it was decided that slightly different process