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Effect of MnO_2 additive on the dielectric and electromagnetic interference shielding properties of sintered cement-based ceramics

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Abstract

Cement-based ceramic pellets were prepared and their properties were studied for electromagnetic interference (EMI) shielding applications. The shielding materials were made of Portland cement with the addition of different concentrations of manganese oxide (MnO_2) up to 10 wt%. The pellets were sintered at 850 °C for 5 h and then polished prior to characterizations of density, porosity, microstructures, dielectric properties, and EMI shielding effectiveness (SE). Results show that the MnO_2–cement pellets have good dielectric properties, i.e. high dielectric constant (~300) and low dielectric loss (<0.3). The dielectric constant increased with increasing MnO_2 content in the cement matrix. The SE values of the MnO_2–cements fluctuated between 2 dB and 9 dB in the frequency range of 8–13 GHz. The sample with 10 wt% MnO_2 additive had SE values of up to 9 dB. Most of the samples with high additive concentrations produced SE exceeding 7 dB.

Keywords: A. Sintering; B. Composites; C. Dielectric properties; E. Functional applications; Electromagnetic interference shielding; Manganese oxide

1. Introduction

An electromagnetic interference (EMI) is created by electromagnetic energy which is transmitted from one electronic device to another via radiated or conducted paths or both [1,2]. For example, the power systems of laptops and computers generate broadband EMI energy. This radiated energy is propagated and picked up by television antenna, wireless remote control units, and any other power units that might cause irregular performance. In general, EMI problems can be caused by electromagnetic energy at any frequency in the electromagnetic spectrum. The electromagnetic (EM) spectrum is the range of all potential electromagnetic radiation frequencies, and generally, the electromagnetic spectrum of an object is the quality distribution of electromagnetic radiation from that particular object. Most problems are caused by energy in the radio frequency range, which extends from about 100 kHz to 1 GHz. Undesired energies which come from cellular phones are a specific form of EMI known as radio frequency interference (RFI) [1]. Besides that, researchers also report the importance of EMI shielding in relation to the high demand of the technology industry today, especially on the reliability of electronics and the rapid growth of radio frequency radiation sources. EMI prevention is in critical demand due to the interference of these radio frequency devices with digital devices and also the increasing sensitivity and importance of electronic devices [1–3].

The main mechanism for EMI shielding using conductive materials is reflection [4]. The loss (attenuation) due to reflection increases with decreasing frequency. Shielding effectiveness (SE) can be broken into three terms: reflection loss (R_{dB}), absorption loss (A_{dB}), and multi-reflections (M_{dB}). The SE of an EMI shielding material is defined in decibels (dB) and its magnitude can be written as follows [5]:

$$\mathrm{SE}\ (\mathrm{dB}) = 20\ \log\left|\frac{E_i}{E_t}\right| = R_{dB} + A_{dB} + M_{dB} \qquad (1)$$

where E_i is electric fields that are incident on the shielding material and E_t is electric fields that are transmitted through the

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shielding material

$$R_{\mathrm{dB}} = 106 + \log\left(\frac{\sigma_r}{f\mu_r}\right) \tag{2}$$

is the reflection loss caused by the reflection at the surface of the shielding material,

$$A_{\mathrm{dB}} = 20\ \log\left(\exp\left(\frac{-t}{\delta}\right)\right) \tag{3}$$

is the absorption loss of the waves as it proceeds through the shielding material,

$$M_{\mathrm{dB}} = 20\ \log\left(1 - \exp\left(\frac{-2t}{\delta}\right)\right) \tag{4}$$

is the additional effect of multiple reflections and transmissions in the interior of the shield material,

$$\delta = \frac{1}{\sqrt{\pi\mu\sigma f}} \tag{5}$$

is the skin depth of the shielding material, a distance into the shield that the incident wave propagates when the wave amplitude decays by a factor of e^{-1}; where f = frequency, μ = magnetic permeability = $\mu_o\mu_r$, μ_r = relative magnetic permeability, $\mu_o = 4\pi \times 10^{-7}$ H m^{-1}, and σ = electrical conductivity in Ω^{-1} m^{-1} [6,7].

With the rise of more problems associated with electromagnetic environment pollution, the study on cement materials capable of preventing EMI has attracted great attention. This is due to the fact that a cement-based building material is not only a structural material, but may also possess EMI shielding effectiveness properties. The composites can absorb or reflect the electromagnetic waves to decrease interference phenomenon.

Cement is a material of rich resource and good environmental flexibility and is one of the most common structural materials used in engineering constructions. Cement is slightly conductive, but its EMI shielding effectiveness and wave absorbing properties are very low. Thus, a simple and practical method that can increase its EMI shielding effectiveness is by adding conductive fillings and loadings into the cement [6]. Eq. (1) shows that the shielding effectiveness of a material is linked closely to the electric conductivity and the electromagnetic parameters of the material. In contrast to a polymer matrix which is electrically insulating, the cement matrix is slightly conductive and its shielding effectiveness is closely related to its conductivity [6]. Due to its special performance properties, Portland cement was used as the cementation starting material in this study.

The cement matrix is only slightly conductive with an electrical resistivity of 10^5–10^6 Ω cm [4]. With the use of electrically conductive admixtures in the form of particles or short fibres, the resistivity of a cement-based material can be greatly decreased. Continuous fibres can also be used to reduce the resistivity but they cannot be integrated in a cement mix. Thus, the making of a continuous fibre cement-based material is much more complicated than that of a short fibre cement-based material.

Based on previous research, the ratio of water to the total cementation material was 0.35 [8]. A water-reducing agent such as sodium salt of a condensed naphthalenesulfonic acid can be used in the amount of 1.00% by mass of cement without aggregate.

Due to the high demand for low cost EMI shielding material and long-term compatibility with the chemical environment in a cement-based material, the electrically conductive admixtures used are mainly either steel or carbon. Previously, steel was used because it is more conductive than carbon. However, it is less available in the form of fine particles or fibres thus contributing to uneasy processing [4]. Generally, three main kinds of conductive fillers have been used in cement matrix materials: conductive polymers, carbon materials and metal materials. The most commonly used fillings are carbon materials (including graphite, carbon black and carbon fibre) which have relatively high conductivity and EMI shielding effectiveness [6]. It is desirable for EMI shielding materials to attain a low resistivity at just a low volume fraction of an admixture. This is because the workability and compressive strength decreases with increasing volume fraction of the admixture (due to the increase in air void content) and the cost increases with the admixture volume fraction. As a consequence, a small particle size, a small fibre diameter and a large aspect ratio are usually attractive properties of the admixture. However, an admixture unit size that is too small can be a disadvantage for the conductivity [4]. This may be due to the electrical contact resistance at the interface between the adjacent admixture units and the large number of such interfaces when the filler unit size is small.

In order for a conductive filler to be highly effective for shielding, it should preferably have a small unit size, high conductivity and a high aspect ratio. As to improving the conductive ability and shielding effectiveness of cement matrix composites, carbon fibres are more effective than particles such as carbon black and coke due to their large aspect ratio which can help to make more conductive networks through intercalating [9,10]. With the decrease in carbon fibre cost and the increase of demand for cement-based composites with high structure and multiple functions, carbon fibre cement matrix composites are gaining importance quite rapidly [6].

Many other conductive fillers such as nickel-plated carbon fibres, nickel coated mica and conductive papers have been used in EMI shielding applications [11–13]. However, these fillers are considered expensive and complicated to process as well so they are not commonly used in cement matrix composites. Metal powder has a disadvantage of high density, which produces lower shielding effectiveness with a small introduction. When the loading is increased to improve the shielding effectiveness, the density of the EMI shielding material is increased, resulting in a decrease of the mechanical strength of the composite material [6]. On the other hand, a material which is superior in conductivity is not necessarily superior in shielding, as proven by comparing carbon nanofibre cement and coke cement. The conductivity of carbon nanofibre