Cement-Based Controlled Electrical Resistivity Materials

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Low-cost controlled electrical resistivity materials based on Portland cement and exhibiting low values of the relative dielectric constant have been attained. The materials are cement paste containing short electrically-conducting fibers. With steel fibers (0.1 vol.%), the resistivity and relative dielectric constant (10 kHz) are 8×10^4 Ω·cm and 20, respectively. With carbon fibers (1.0 vol.%) and silica fume, these quantities are 8×10^2 Ω·cm and 49, respectively.

Key words: Cement, electrical resistivity, dielectric constant, composite, steel fiber, carbon fiber

INTRODUCTION

Controlled resistivity materials are used for controlled electrical conduction, static charge dissipation, lightning protection, and electromagnetic interference (EMI) shielding in electronic, mechanical, structural, chemical, and vacuum applications. In particular, controlled resistivity ceramics, such as alumina-matrix composites containing an electrically conducting particulate filler,[1] are used as substrates for handling semiconductor wafers, which require static protection. They are also used in the form of charge-dissipating coatings to improve the breakdown voltage of high-power, high-vacuum devices. In addition, controlled resistivity ceramics in the form of tiles are used for antistatic floors.[2–5]

Controlled electrical resistivity materials are typically in the form of composite materials with an electrically-insulating matrix and an electrically-conductive discontinuous filler, which can be particulate or fibrous. The higher the filler content, the lower the resistivity of the composite. These composites include those with polymer,[6–9] ceramic,[1–5] and cement matrices. Polymers and ceramics are usually insulating electrically, but cement is slightly conductive. Polymers that are electrically conductive exist, but they are expensive. Among all these matrices, cement is the least expensive. In addition, the fabrication of cement-matrix composites is inexpensive and takes place at room temperature. The fabrication of ceramic-matrix composites, such as alumina-matrix composites, is even more expensive than that of polymer-matrix composites, due to the high processing temperatures. Furthermore, cement-matrix composites, like ceramic-matrix composites, are mechanically more rugged and chemically more resistant than polymer-matrix composites. This paper presents a study of these cement-matrix composites.

In addition to providing a range of electrical resistivity, controlled-resistivity materials provide a range of dielectric constant. As the filler content of a ceramic-matrix composite increases, the dielectric constant increases and the resistivity decreases.[1] In the case of an alumina-matrix TiO_2 particulate composite, the relative dielectric constant (1 kHz) is 127,000 (undesirably high) when the resistivity is 5×10^5 Ω·cm and the Al_2O_3 content is >80 wt.%; the relative dielectric constant (1 kHz) is 26.6 when the resistivity is 1×10^9 Ω·cm and the Al_2O_3 content is >94 wt.%.[1] It would be desirable to have the combination of low resistivity (for charge dissipation and related functions) and low dielectric constant (to avoid a capacitive effect). Polymer matrices tend to exhibit lower values of dielectric constant than ceramic or cement matrices, but they tend to be insufficient for mechanical ruggedness and chemical and temperature resistance.

In this work, we provide the combination of low resistivity, low dielectric constant, mechanical ruggedness, and low cost by using cement-matrix composites containing electrically conductive short fibers

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Table I. Effect of Silver Paint at the Electrical Contact on the Measured Relative Dielectric Constant of Cement Paste (i), Which is Described in Table II

	10 kHz	100 kHz	1 MHz
Without silver paint	28.6 ± 3.4	24.8 ± 3.6	23.7 ± 2.8
With silver paint	30.6 ± 3.3	26.1 ± 4.0	24.8 ± 2.7

such as carbon fibers and steel fibers. Short fibers have been used in cement for improving the mechanical properties and decreasing the drying shrinkage.[10] Conductive fibers are known to decrease the electrical resistivity,[11,12] but little attention has been given to the effect of fibers on the dielectric constant of cement.[13] In particular, no prior attention has been given to attaining the combination of low resistivity and low dielectric constant in cement-based materials.

EXPERIMENTAL METHODS

Materials

The cement used was Portland cement (Type I) with no aggregate. The fibers used for controlling the resistivity were in the amount of either 0.5% or 1.0% by mass of cement.

Either silica fume or latex was used as an admixture to enhance fiber dispersion when carbon fibers were used. Silica fume was used in the amount of 15% by mass of cement. The methylcellulose was used along with silica fume in the amount of 0.4% by mass of cement, also for enhancing fiber dispersion. As the methylcellulose generated foam, a defoamer was used along with methylcellulose and it was in the amount of 0.13 vol.%.

The latex, used in the amount of 20% by mass of cement, was a styrene butadiene copolymer with the polymer making up about 48% of the dispersion and with the styrene and butadiene having a mass ratio of 66:34. The latex was used along with an antifoaming agent at 0.5% by mass of latex.

The carbon fibers were isotropic-pitch based, unsized, and ~5 mm in length, 15 μm in diameter, and 1.6 g/cm^3 in density. The fiber resistivity was 3.0×10^{-3} Ω·cm. The ozone treatment of the fibers[14] was performed to improve the fiber-matrix bond. The steel fibers were 434 stainless steel with a diameter of 60 μm, cut into 5 mm lengths, and incorporated in the amount of 0.5% by mass of cement. The fiber resistivity was 6×10^{-5} Ω·cm.

A rotary mixer with a flat beater was used for mixing. Methylcellulose (if applicable) was dissolved in water and then the defoamer was added and stirred by hand for about 2 min. Latex (if applicable) was mixed with the antifoam by hand for about 1 min. Then the methylcellulose mixture (if applicable), the latex mixture (if applicable), cement, water, silica fume (if applicable), and fibers were mixed in the mixer for 5 min. After pouring into oiled molds, an external electrical vibrator was used to facilitate compaction and decrease the amount of air bubbles. The samples were demolded after 1 day and cured in air at room temperature (relative humidity = 100%) for 28 days.

Seven types of cement paste were prepared, namely (i) plain cement paste (consisting of just cement and water), (ii) silica-fume cement paste (consisting of cement, water, and silica fume), (iii) latex cement paste (consisting of cement, water, latex, and antifoam), (iv) carbon-fiber (0.5 vol.%) silica-fume cement paste (consisting of cement, water, silica fume, methylcellulose, defoamer, and carbon fibers in the amount of 0.5% by mass of cement, corresponding to 0.5 vol.%), (v) carbon-fiber latex cement paste (consisting of cement, water, latex, antifoam, and carbon fibers in the amount of 0.5% by mass of cement, corresponding to 0.4 vol.%), (vi) carbon-fiber (1.0 vol.%) silica fume cement paste (consisting of cement, water, silica fume, methylcellulose, defoamer, and carbon fibers in the amount of 1.0% by mass of cement, corresponding to 1.0 vol.%), and (vii) steel-fiber cement paste (consisting of cement, water, and steel fibers in the amount of 0.5% by mass of cement, corresponding to 0.1 vol.%). The water/cement ratio was 0.35 for pastes (i), (ii), (iv), (vi), and (vii), and was 0.23 for pastes (iii) and (v).

Testing

Dielectric Constant Measurement

Specimens for dielectric constant measurement were in the form of cylindrical discs of diameter 12.3 mm and thickness 2.0 mm. A specimen, after mechanical polishing on both sides by using alumina particles of size 0.25 mm, was sandwiched by two copper discs (similarly polished) of diameter 12.3 mm at a pressure of 1.68 kPa. The copper discs served as electrical contacts.

The impedance was measured along the thickness of the specimen using the two-probe method and a resistance-inductance-capacitance (RLC) meter at a fixed frequency (10 kHz, 100 kHz, and 1 MHz). The magnitude of voltage applied across the thickness (2 mm) of a specimen was 1.000 V. Hence, the magnitude of the applied electric field was 500 V/m. The resistance (real part of impedance) and reactance (imaginary part of impedance) were obtained from the impedance by assuming that they were in series connection. The capacitance was obtained from the reactance. The dielectric constant was obtained from the capacitance. Six specimens of each type were tested.

The relative dielectric constant was also measured when silver paint had been applied between each copper disc and the specimen for the case of cement paste (i), in order to determine the quality of the electrical contacts. The relative dielectric constant was only slightly higher when silver paint was present,

Table II. Resistivity and Relative Dielectric Constant of Cement Pastes

Paste No.	Fiber Type	Fiber vol.%	Admixture	Resistivity (Ω-cm)	Relative Dielectric Constant 10 kHz	100 kHz	1 MHz
(i)	/	0	/	$(4.9 \pm 0.4) \times 10^5$	28.6 ± 3.4	24.8 ± 3.6	23.7 ± 2.8
(ii)	/	0	SF	$(6.1 \pm 0.2) \times 10^5$	20.8 ± 3.4	19.6 ± 3.2	16.5 ± 0.8
(iii)	/	0	L	$(7.0 \pm 0.1) \times 10^5$	34.9 ± 4.5	31.5 ± 2.9	24.3 ± 2.9
(iv)	Carbon	0.5	SF	$(1.5 \pm 0.1) \times 10^4$	53.7 ± 7.0	38.3 ± 4.8	28.1 ± 2.9
(v)	Carbon	0.4	L	$(9.7 \pm 0.6) \times 10^4$	63.2 ± 5.2	40.4 ± 5.9	33.2 ± 6.8
(vi)	Carbon	1.0	SF	$(8.3 \pm 0.5) \times 10^2$	48.7 ± 4.8	29.6 ± 5.0	25.0 ± 5.0
(vii)	Steel	0.1	/	$(7.8 \pm 0.5) \times 10^4$	19.6 ± 4.8	19.0 ± 1.0	13.7 ± 2.4

Note: SF—silica fume; L—latex

as shown in Table I. Hence, the small amount of air gap at the interface between the copper and specimen in the absence of silver paint contributed little to the measured dielectric constant.

To show that the dielectric constant measurement using the method described above was accurate, measurements were made on a Kapton (a polymer) film. The known dielectric constant of Kapton is 3.9 at 1 kHz. This work had a value of 3.9 also at 1 kHz.

Electrical Resistivity Measurement

DC volume electrical resistivity was measured using the four-probe method. In this method, four electrical contacts were applied by silver paint around the whole perimeter at four planes perpendicular to the length of the specimen (150 × 15 × 15 mm). The four planes were symmetrical around the mid-point along the length of the specimen, such that the outer contacts (for passing current) were 80 mm apart and the inner contacts (for measuring the voltage) were 60 mm apart. Six specimens of each composition were tested.

RESULTS AND DISCUSSION

Table II shows the DC resistivity and the relative dielectric constant of seven types of cement paste, each at three frequencies. The resistivity slightly increases with the addition of silica fume or latex, but is significantly decreased with the addition of carbon or steel fibers. The resistivity decreases with increasing fiber volume fraction, as shown for the case of carbon fibers with silica fume as an admixture to help fiber dispersion. The resistivity is higher when latex rather than silica fume is used as an admixture along with carbon fibers. The percolation threshold is between 0.5 and 1.0 vol.% carbon fibers in the presence of silica fume, as also shown in Ref. 12. The lowest resistivity is attained by using carbon fibers (1.0 vol.%) along with silica fume. Steel fibers do not give a composite with as low a resistivity, due to the low volume fraction and large diameter of the fibers.

For any type of cement paste, the relative dielectric constant decreases with increasing frequency, as expected. At any of the frequencies, the addition of silica fume decreases the relative dielectric constant, and the addition of latex increases the relative dielectric constant. The further addition of carbon fibers to a paste containing either silica fume or latex increases the relative dielectric constant. However, an increase in fiber content from 0.5 to 1.0% by mass of cement slightly decreases the relative dielectric constant. All three pastes containing carbon fibers exhibit significantly higher values of relative dielectric constant compared to the three pastes which contain no fiber. In contrast, the addition of steel fibers decreases the relative dielectric constant.

Reference 15 reported that, at frequencies from 1 MHz to 1.5 GHz, silica fume appears to have a small effect on the dielectric constant of cement paste. However, at a low frequency (10 kHz – 1 MHz), silica fume decreases the dielectric constant of cement paste. Since the dielectric constant decreases with increasing frequency, the effect of silica fume is harder to observe when the frequency is higher. The effect of silica fume cannot be due to the air voids (which are generally present in cement-based materials), as silica fume is known to decrease the air-void content, and air voids tend to decrease the dielectric constant. In other words, a decrease in air-void content is expected to increase the dielectric constant. The decrease of the dielectric constant by the silica fume addition is attributed to the low dielectric constant of silica fume (SiO_2) compared to cement; the moisture and ions in cement cause the dielectric constant to be relatively high.

Latex addition increases the dielectric constant of cement paste. This effect is partly attributed to the decrease in air-void content (a well-known effect of latex addition). However, the air-void content cannot explain the large (up to 27%) increase in the dielectric constant. Latex itself is relatively low in dielectric constant because it is a polymer. The observed effect is attributed to the large amount of interface between latex and cement and the electric dipoles at the interface.

The addition of carbon fiber increases the dielectric constant of cement paste. This effect is attributed to the functional groups on the fiber surface (which had been ozone treated) and the resulting dipoles at the fiber-matrix interface. The dielectric constant decreases when the fiber volume fraction is increased from 0.48 to 0.95 vol.%, because of percolation. As shown by the resistivity data in Table II, the percolation threshold is between 0.5 and 1.0 vol.% fibers.

For cement paste containing short steel fibers in the amount of 0.5% by mass of cement (0.1 vol.%, which is much below the percolation threshold) in the absence of silica fume or latex, the relative dielectric constant is lower than that of the paste without any admixture (first entry in Table II), and is comparable to that of the paste with silica fume (second entry in Table II). Hence, steel fiber additions decrease the relative dielectric constant, in sharp contrast to the effect of carbon fiber additions. The effect of steel fiber additions is attributed to the volume occupied by the fibers in place of cement, and the air-void content increase (a well-known effect of fiber addition). The contribution of the fiber-matrix interface to the dipole moment is apparently small, due to the oxide on the fiber surface. Hence, the effects on the dielectric constant are very different for the different types of fiber.

Of the seven types of paste listed in Table II, the use of carbon fibers plus latex gives the highest value of the relative dielectric constant, whereas the use of either steel fibers or silica fume gives the lowest value of the relative dielectric constant. On the other hand, the use of carbon fibers (1.0 vol.%) plus silica fume gives the lowest value of the resistivity. To attain a combination of low resistivity and low value of the relative dielectric constant, pastes (vi) and (vii) of Table II are recommended. Paste (vi) is advantageous for its low resistivity; paste (vii) is advantageous for its low dielectric constant.

CONCLUSION

Cement pastes containing short carbon fibers result in low-cost-controlled electrical resistivity materials exhibiting the combination of low resistivity and low dielectric constant have been achieved. With steel fibers (0.1 vol.%), the resistivity attained is 8×10^4 Ω·cm and the relative dielectric constant (10 kHz) is 20. With carbon fibers (1.0 vol.%) and silica fume, the resistivity is 8×10^2 Ω·cm and the relative dielectric constant is 49.

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