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Seebeck effect in steel fiber reinforced cement

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Abstract

Cement pastes containing short steel fibers, which contribute to electron conduction, exhibit positive values (up to 68 μV/°C) of the absolute thermoelectric power. A steel fiber content of 1.0% by mass of cement gives a higher value of the absolute thermoelectric power than a content of 0.5% by mass cement, in addition to yielding more reversibility and linearity in the variation of the Seebeck voltage with temperature difference (up to 65°C). In contrast, cement pastes containing short carbon fibers, which contribute to hole conduction, exhibit negative or slightly positive values of the absolute thermoelectric power.

Keywords: Fiber reinforcement; Cement Paste; Electrical properties; Silica fume; Thermoelectric

1. Introduction

The Seebeck effect refers to the thermoelectric effect in which a voltage is generated by a temperature gradient due to the movement of charge carriers from the higher temperature point to the lower temperature point. When the carriers are holes (positive charge), the voltage generated has a polarity which is positive at the lower temperature point relative to the higher temperature point. The thermoelectric power (voltage per unit temperature difference) is then taken as being negative. When the carriers are electrons (negative charge), a voltage with the opposite polarity is generated and the thermoelectric power is positive. The Seebeck effect is the basis for thermocouples. It is attractive to use concrete to measure temperature, as this allows a concrete structure to be able to monitor its own temperature.

The Seebeck effect in carbon fiber reinforced cement paste involves electrons from the cement matrix [1] and holes from the fibers [2,3], such that the two contributions are equal at the percolation threshold, a fiber content between 0.5% and 1.0% by mass of cement [1]. The hole contribution increases monotonically with increasing fiber content below and above the percolation threshold [1].

The Seebeck effect has not been reported in cement with fibers other than carbon fibers. However, due to the free electrons in a metal, cement containing metal fibers is expected to be even more positive in the thermoelectric power than cement without fiber. The attainment of a very positive thermoelectric power is attractive, since a material with a positive thermoelectric power and a material with negative thermoelectric power are two very dissimilar materials, the junction of which is a thermocouple junction. (The greater the dissimilarity, the more sensitive is the thermocouple.) Therefore, this work is focused on the Seebeck effect in steel fiber reinforced cement. Steel fibers are actually more commonly used for cement than carbon fibers, so study of steel fiber reinforced cement is technologically relevant.

In this work, we found that steel fiber reinforced cement is indeed very positive in the thermoelectric power. The magnitude is much higher than that for carbon fiber reinforced cement.

2. Experimental methods

The steel fibers were made of stainless steel No. 434, as obtained from International Steel Wool (Springfield, OH). The fibers were cut into pieces of length 5 mm prior to use in the cement paste. The properties of the steel fibers are shown in Table 1. The mechanical properties of

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Table 1
Properties of steel fibers

Nominal diameter	60 μm
Tensile strength	970 MPa
Tensile modulus	200 GPa
Elongation at break	3.2%
Volume electrical resistivity	6×10^{-5} Ω cm
Specific gravity	7.7 g cm^{-3}

mortars containing these fibers are described in Ref. [4]. However, no aggregate, whether coarse or fine, was used in this work.

The cement used was portland cement (Type I) from Laforge (Southfield, MI). Silica fume (Elkem Materials, Pittsburgh, PA; EMS 965) was used in the amount of 15% by mass of cement. The latex, used in the amount of 20% by mass of cement, was a styrene butadiene copolymer (Dow Chemical, Midland, MI; 460NA) with the polymer making up about 48% for the dispersion and with the styrene and butadiene having a mass ratio of 66:34. The latex was used along with an antifoaming agent (Dow Corning, Midland, MI, No. 2410, 0.5% by mass of latex).

A rotary mixer with a flat beater was used for mixing. Latex (if applicable) was mixed with the antifoam by hand for about 1 min. Then the latex mixture (if applicable), cement, water, silica fume (if applicable), and steel fibers (if applicable) 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.

Six types of cement paste were prepared, namely (i) steel-fiber cement paste (consisting of cement, water and steel fibers in the amount of 0.5% by mass of cement, i.e., 0.10 vol.% of composite), (ii) steel-fiber cement paste (same as (i) except for having steel fibers in the amount of 1.0% by mass of cement, i.e., 0.20 vol.% of composite), (iii) steel-fiber silica-fume cement paste (consisting of cement, water, silica fume and steel fibers in the amount of 0.5% by mass of cement, i.e., 0.10 vol.% of composite), (iv) steel-fiber silica-fume cement paste (same as (iii) except for having steel fibers in the amount of 1.0% by mass of cement, i.e., 0.20 vol.% of composite), (v) steel-fiber latex cement paste (consisting of cement, water, latex, antifoam and steel fibers in the amount of 0.5% by mass of cement, i.e., 0.085 vol.% of composite), and (vi) steel-fiber latex cement paste (same as (v) except for having steel fibers in the amount of 1.0% by mass of cement, i.e., 0.17 vol.% of composite). The water/cement ratio was 0.35 for pastes (i), (ii), (iii), and (iv), and was 0.23 for pastes (v) and (vi).

Thermopower measurement was performed on rectangular samples of size 75 × 15 × 15 mm, such that heat (up to 85°C) was applied at one of the 15 × 15 mm ends of a sample by contacting this end with a resistance heated platen of size much larger than 15 × 15 mm. The other end of the sample was near room temperature. The thermal contact between the platen and the sample end was enhanced by using a copper foil covering the 15 × 15 mm end surface of the sample as well as the four side surfaces for a length of ~ 4 mm from the end surface. Silver paint was applied between the foil and the sample surface covered by the foil to further enhance the thermal contact. Underneath the copper foil was a copper wire, which had been wrapped around the perimeter of the sample for the purpose of voltage measurement. Silver paint was present between the copper wire and the sample surface under the wire. The other end of the rectangular sample was similarly wrapped with copper wire and then covered with copper foil. The copper wires from the two ends were fed to a Keithley 2001 multimeter for voltage measurement. A T-type thermocouple was attached to the copper foil at each of the two ends of the sample for measuring the temperature of each end. Voltage and temperature measurements were done simultaneously using the multimeter. The voltage difference divided by the temperature difference yielded the Seebeck coefficient with copper as the reference, since the copper wires at the two ends of a sample were at different temperatures. This Seebeck coefficient plus the absolute thermoelectric power of copper (+2.34 μV/°C) is the absolute thermoelectric power of the sample. Samples were heated at one end at a rate of 0.009°C/s for pastes (i), (iii), and (v), and a rate of 0.012°C/s for pastes (ii), (iv) and (vi), and then cooled with the power of the platen turned off. The heating rate was constant, but the cooling rate was not.

After conducting thermopower testing, the DC volume electrical resistivity was measured using the Keithley 2001 multimeter and 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. The four planes were symmetrical around the mid-point along the length of the specimen, such that the outer contacts (for passing current) were the same as the wires for Seebeck voltage and the inner contacts (for measuring the voltage in relation to resistivity determination) were 45 mm apart.

Six samples of each composition were tested. Each sample was tested in terms of both the thermopower and the resistivity.

3. Results and discussion

Table 2, as well as Figs. 1 and 2, show the thermopower results. The absolute thermoelectric power is much more positive for all the steel-fiber cement pastes compared to all the carbon-fiber cement pastes. An increase of the steel fiber content from 0.5% to 1.0% by mass of cement increases the absolute thermoelectric power, whether silica fume (or latex) is present or not. An increase of the steel fiber content also increases the reversibility and linearity of the change in Seebeck voltage with the temperature difference between

Table 2
Volume electical resistivity, Seebeck coefficient (μV/°C) with copper as the reference, and the absolute thermoelectric power (μV/°C) of various cement pastes with steel fibers (S_f) or carbon fibers (C_f); SF: Silica fume; L: latex.

Cement paste	Volume fraction fibers (%)	Resistivity (Ω cm)	Heating: Seebeck coefficient	Heating: Absolute thermoelectric power	Cooling: Seebeck coefficient	Cooling: Absolute thermoelectric power
(i) S_f (0.5[a])	0.10	$(7.8\pm0.5)\times10^4$	51.0±4.8	53.3±4.8	45.3±4.4	47.6±4.4
(ii) S_f (1.0[a])	0.20	$(4.8\pm0.4)\times10^4$	56.8±5.2	59.1±5.2	53.7±4.9	56.0±4.9
(iii) S_f (0.5[a])+SF	0.10	$(5.6\pm0.5)\times10^4$	54.8±3.9	57.1±3.9	52.9±4.1	55.2±4.1
(iv) S_f (1.0[a])+SF	0.20	$(3.2\pm0.3)\times10^4$	66.2±4.5	68.5±4.5	65.6±4.4	67.9±4.4
(v) S_f (0.5[a])+L	0.085	$(1.4\pm0.1)\times10^5$	48.1±3.2	50.4±3.2	45.4±2.9	47.7±2.9
(vi) S_f (1.0[a])+L	0.17	$(1.1\pm0.1)\times10^5$	55.4±5.0	57.7±5.0	54.2±4.5	56.5±4.5
[b]C_f (0.5[a])+SF	0.48	$(1.5\pm0.1)\times10^4$	−1.45±0.09[b]	0.89±0.09[b]	−1.45±0.09[b]	0.89±0.09[b]
[b]C_f (1.0[a])+SF	0.95	$(8.3\pm0.5)\times10^2$	−2.82±0.11[b]	−0.48±0.11[b]	−2.82±0.11[b]	−0.48±0.11[b]
[b]C_f (0.5[a])+L	0.41	$(9.7\pm0.6)\times10^4$	−1.20±0.05[b]	1.14±0.05[b]	−1.20±0.05[b]	1.14±0.05[b]
[b]C_f (1.0[a])+L	0.82	$(1.8\pm0.2)\times10^3$	−2.10±0.08[b]	0.24±0.08[b]	−2.10±0.08[b]	0.24±0.08[b]

[a] % By mass of cement.
[b] From Ref. [1].

the hot and cold ends, as shown by comparing Fig. 1 (steel fibers in the amount of 1.0% by mass of cement) and Fig. 2 (steel fibers in the amount of 0.5% by mass of cement), and by comparing the values of the Seebeck coefficient obtained during heating and cooling in Table 2. The values obtained during heating and cooling are close for the pastes with the higher steel fiber content, but are not so close for the pastes with the lower steel fiber content. In contrast, for pastes with carbon fibers in place of steel fibers, the change in Seebeck voltage with the temperature difference is highly reversible for both carbon fiber contents of 0.5% and 1.0% by mass of cement [1], as shown also in Table 2 by comparing the values of the Seebeck coefficient obtained during heating and cooling.

Table 2 shows that the volume electrical resistivity is much higher for the steel-fiber cement pastes than the corresponding carbon fiber cement pastes. This is attributed to the much lower volume fraction of fibers in the former (Table 2). An increase in the steel or carbon fiber content from 0.5% to 1.0% by mass of cement decreases the resistivity, though the decrease is more significant for the carbon fiber case than the steel fiber case. That the resistivity decrease is not large when the steel fiber content is increased from 0.5% to 1.0% by mass of cement and that the resistivity is still high at a steel fiber content of 1.0% by mass of cement suggest that a steel fiber content of 1.0% by mass of cement is below the percolation threshold.

Among the steel fiber cement pastes at the same fiber content in percentage by mass of cement, the absolute thermoelectric power increases in the following order: steel-fiber latex cement paste, steel-fiber cement paste (without latex or silica fume) and steel-fiber silica-fume cement paste. The resistivity decreases in the above order as well. The correlation between the absolute thermoelectric power

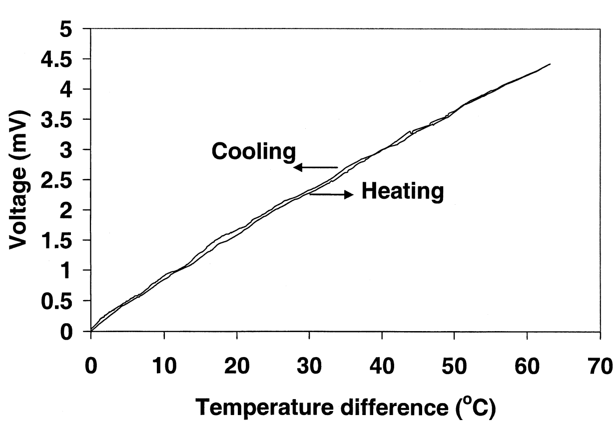

Fig. 1. Variation of the Seebeck voltage (with copper as the reference) vs. the temperature difference during heating and cooling for steel-fiber silica fume cement paste containing steel fibers in the amount of 1.0% by mass of cement.

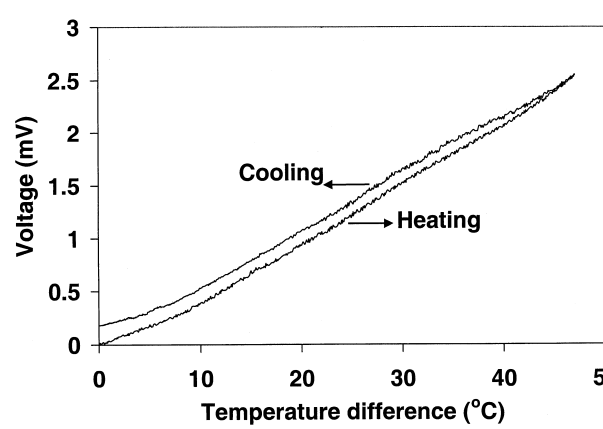

Fig. 2. Variation of the Seebeck voltage (with copper as the reference) vs. the temperature difference during heating and cooling for steel-fiber silica fume cement paste containing steel fibers in the amount of 0.5% by mass of cement.

and the resistivity is due to the fact that both thermopower and conductivity are enhanced by a higher degree of fiber dispersion. Silica fume is known to be particularly effective in enhancing the degree of fiber dispersion [5]. Similarly for carbon-fiber cement pastes, silica fume yields a more negative value of the absolute thermoelectric power and a lower value of the resistivity than latex.

The highly positive values of the absolute thermoelectric power of steel-fiber cement pastes is attributed to the metallic nature of steel, which conducts by electron movement. In contrast, carbon fibers contribute to hole conduction [1–3]. As a result, the absolute thermoelectric power of carbon-fiber cement pastes is either negative or slightly positive.

Whether with or without silica fume (or latex), the change of the Seebeck voltage with temperature is more reversible and linear at a steel fiber content of 1.0% by mass of cement than at a steel fiber content of 0.5% by mass of cement. This is attributed to the larger role of the cement matrix at the lower steel fiber content and the contribution of the cement matrix to the irreversibility and non-linearity. As shown in Ref. [1], irreversibility and non-linearity are particularly significant when the cement paste contains no fiber.

From the practical point of view, the steel-fiber silica-fume cement paste containing steel fibers in the amount of 1.0% by mass of cement is particularly attractive for use in temperature sensing, as the absolute thermoelectric power is the highest (68 μV/°C) and the variation of the Seebeck voltage with the temperature difference between the hot and cold ends is reversible and linear. The absolute thermoelectric power is as high as those of commercial thermocouple materials.

4. Conclusion

Steel-fiber cement pastes exhibit positive values (up to 68 μV/°C) of the absolute thermoelectric power. A steel fiber content of 1.0% by mass of cement gives a higher value of the absolute thermoelectric power than a content of 0.5% by mass of cement, and also yields more reversibility and linearity in the variation of the Seebeck voltage with temperature difference (up to 65°C). The use of silica fume in combination with steel fibers yields a particularly high value of the absolute thermoelectric power. The use of carbon fibers in place of steel fibers gives negative or slightly positive values of the absolute thermoelectric power, due to the contribution of carbon fibers to hole conduction. In contrast, steel fibers contribute to electron conduction.

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