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Effect of fiber content on the thermoelectric behavior of cement

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The effect of discontinuous stainless steel fibers (diameter 60 μm) as an admixture in cement paste on the thermoelectric behavior (the Seebeck effect) was systematically studied as a function of fiber volume fraction from 0 to 0.50 vol%. Without fibers, cement paste has an absolute thermoelectric power of $+3$ μV/°C. A fiber content of up to 0.20 vol% makes the absolute thermoelectric power more negative (down to -63 μV/°C), whereas a fiber content of 0.20–0.50 vol% makes the absolute thermoelectric power more positive (up to $+31$ μV/°C)—even more positive than the positive value for the steel fiber by itself ($+8$ μV/°C). The value is zero at a steel fiber content of 0.27 vol%. The effects are probably due to carrier scattering rather than conduction.

1. Introduction

Fiber addition has been widely used to improve the mechanical properties of materials. Also, the addition of electrically conductive fibers has been used to decrease the electrical resistivity of materials for electronic applications. The science behind these effects is quite well studied. However, little attention has been given to the effect of fiber addition on the thermoelectric behavior [1, 2].

The thermoelectric behavior of cement-based materials [3–8] is relevant to thermoelectric power generation, cement-based thermocouples [9], and thermoelectric heating and cooling. The use of cement-based materials for these functions is attractive, since this allows the functions to be built-in to concrete structures. Due to the large volume of concrete structures and the low cost of concrete, thermoelectric applications using concrete may be viable even if the efficiency is not high. Scientifically, the cement matrix is attractive due to its electrical conductivity, which is in contrast to the non-conductive behavior of most polymers.

The Seebeck effect, which refers to the generation of a voltage due to a temperature gradient, has been observed in cement pastes, such that the effect is largest when short stainless steel fibers (60 μm diameter) in the amount of 0.20 vol% are used as an admixture [6]. The use of carbon fibers in place of steel fibers gives smaller effects [3–5, 8]. The addition of steel fibers (0–0.20 vol%) causes the absolute thermoelectric power to be more negative [6]. The greater the fiber content in this range, the more negative is the absolute thermoelectric power [6].

In this paper, we use the convention in which electrons flowing from the hot point to the cold point corresponds to a negative value of the absolute thermoelectric power, whereas holes flowing from the hot point to the cold point corresponds to a positive value. This convention is opposite to that used in our earlier papers [5, 6, 8, 9], but is more consistent with the convention used in the scientific literature in the thermoelectric field.

In order to study the effect of fiber addition on the thermoelectric behavior of cement paste, this paper investigates the thermoelectric behavior of the steel fiber itself, as well as that of cement pastes with steel fiber content up to 0.50 vol%.

2. Experimental methods

The steel fibers were made of stainless steel No. 434, as obtained from International Steel Wool Corp. (Springfield, OH). The fibers were cut into lengths of 5 mm prior to use in the cement paste. The properties of the steel fibers are shown in Table I. The mechanical properties of mortars containing these fibers are described in Ref. [10]. However, no aggregate, whether coarse or fine, was used in this work. The cement used was portland cement (Type I) from Lafarge Corp. (Southfield, MI). Silica fume, in the amount of 15% by mass of cement and used along with the steel fibers to help the fiber dispersion, was from Elkem Materials Inc. (Pittsburgh, PA, EMS 965).

A rotary mixer with a flat beater was used for mixing. Cement, water, 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

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TABLE I 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}

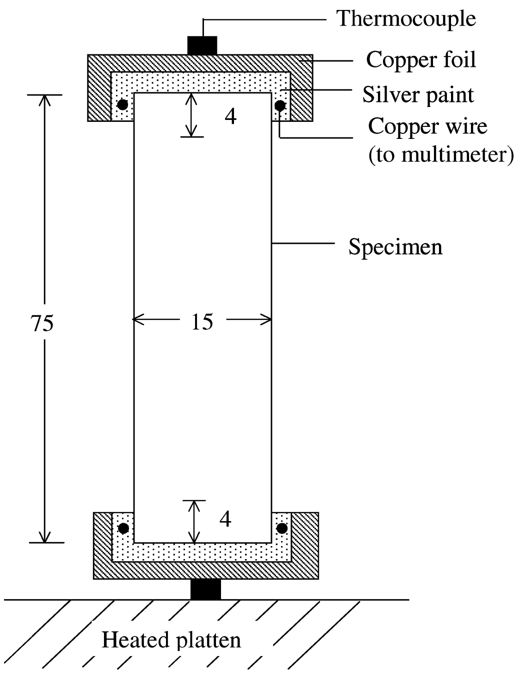

Figure 1 Specimen configuration for thermoelectric testing. All dimensions are in mm. The sizes of the thermocouples, silver paint, copper foils and copper wires are exaggerated for the sake of clarity in the drawing.

air at room temperature (relative humidity = 100%) for 28 days.

Thermopower measurement was performed on rectangular cement paste samples of size 75 × 15 × 15 mm, such that heat (up to 65°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 (Fig. 1). 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 and then cooled with the power of the platen turned off. The heating rate was constant, but the cooling rate was not.

DC volume electrical resistivity was measured using the Keithley 2001 multimeter and the four-probe method [11]. 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 in relation to resistivity determination) were 60 mm apart.

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

Thermopower measurement was also performed on single steel fibers of length 75 mm. Copper wires were soldered to the ends of a steel fiber for the measurement.

3. Results and discussion

Table II and Fig. 2 show that the volume electrical resistivity of cement paste is decreased monotonically by steel fiber addition. The higher fiber volume fraction, the lower is the resistivity. The absence of an abrupt drop in resistivity as the fiber content increases suggests that all of the fiber volume fractions used are below the percolation threshold, as expected from the previously reported percolation threshold of 0.5–1.0 vol% for carbon fiber (15 μm diameter) cement paste [12].

TABLE II Absolute thermoelectric power and volume electrical resistivity of cement pastes (with silica fume except for the paste without fiber[d]) and of steel fiber by itself

Fiber content			
% by mass of cement	Vol%	Absolute thermoelectric power (μV/°C)[b]	Resistivity (Ω·cm)
0	0	$+2.69 \pm 0.04$	$(4.7 \pm 0.4) \times 10^5$
0.5	0.10	-52 ± 4	$(5.6 \pm 0.5) \times 10^4$
1.0	0.20	-63 ± 5	$(3.2 \pm 0.3) \times 10^4$
1.1	0.22	-43 ± 5	$(3.0 \pm 0.2) \times 10^4$
1.2	0.24	-20 ± 2	$(2.3 \pm 0.2) \times 10^4$
1.3	0.26	-8 ± 1	$(1.8 \pm 0.1) \times 10^4$
1.4	0.28	$+4.7 \pm 0.2$	$(8.7 \pm 0.1) \times 10^3$
1.5	0.30	$+11.0 \pm 1.2$	$(5.3 \pm 0.4) \times 10^3$
2.0	0.40	$+25 \pm 3$	$(1.7 \pm 0.1) \times 10^3$
2.5	0.50	$+31 \pm 3$	$(1.4 \pm 0.2) \times 10^3$
/	100[a]	$+8.44 \pm 0.15$	6×10^{-5}[c]

[a]Steel fiber by itself.
[b]Measured during heating.
[c]From the manufacturer's data sheet.
[d]For the case without fiber, both the resistivity [11] and the absolute thermoelectric power [12] are essentially unaffected by the addition of silica fume.

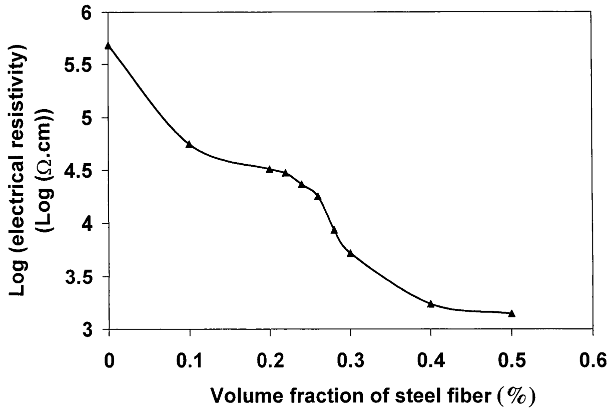

Figure 2 Volume electrical resistivity (log scale) of cement pastes contining various volume fractions of steel fiber. All pastes with fibers contained silica fume.

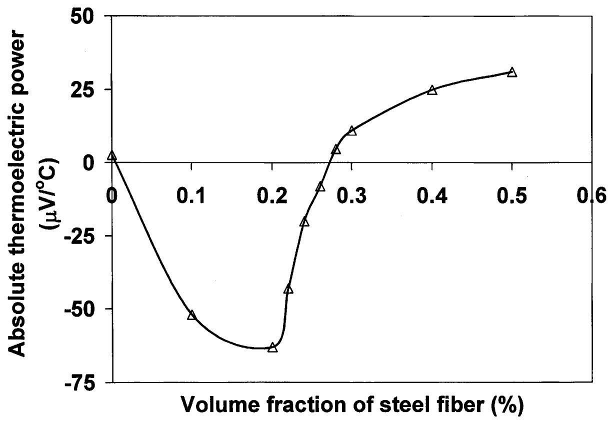

Figure 3 Absolute thermoelectric power of cement pastes contining various volume fractions of steel fiber. All pastes with fibers contained silica fume.

Table II and Fig. 3 give the absolute thermoelectric power of cement pastes and of the steel fiber by itself. The steel fiber itself has a positive value of the absolute thermoelectric power. Cement paste without fiber has a slightly positive value. The addition of fibers up to 0.20 vol% makes the value more negative, as previously reported [6]. At the same fiber volume fraction of 0.10%, the use of silica fume changes the absolute thermoelectric power from -49 ± 5 μV/°C[6] to -52 ± 4 μV/°C, due to a higher degree of fiber dispersion [13], as shown by the decrease in electrical resistivity from 8×10^4 to 6×10^4 Ω·cm [6]. Increase of the fiber volume fraction from 0.10 to 0.20% causes the absolute thermoelectric power to become even more negative, reaching -63 ± 5 μV/°C, which is the highest in magnitude among all cement pastes studied. However, increase of the fiber content beyond 0.20 vol% makes the value less negative and more positive (as high as $+31 \pm 3$ μV/°C)—even more positive than the value of the fiber by itself ($+8.44 \pm 0.15$ μV/°C). A change in sign occurs at 0.27 vol%.

It was previously assumed that the steel fiber provides free electrons which would make the absolute thermoelectric power more negative [6]. However, this work shows that this assumption is incorrect, as the steel fiber itself has a positive value of the absolute thermoelectric power.

As the steel fiber and the cement paste without fiber have opposite signs of the absolute thermoelectric power, the interface between steel fiber and cement paste is a junction of electrically dissimilar materials, like a *pn*-junction. Carrier scattering at this junction, which is distributed throughout the composite, affects the flow of carriers (electrons and ions) between the hot point and the cold point. In addition, carrier scattering can occur due to lattice vibrations. Both the negative and positive values of the absolute thermoelectric power of cement pastes containing 0.1–0.5 vol% steel fibers are probably due to the scattering. A quantitative understanding of the scattering requires detailed information on the mean free path and mean free time of the carriers and is beyond the scope of this paper.

When stainless steel fiber of diameter 8 μm is used in place of the fiber of diameter 60 μm of this work, the absolute thermoelectric is much smaller in magnitude. At the same fiber volume fraction of 0.2 vol%, the steel fiber of diameter 8 μm gave a value of $+7$ μV/°C [14], compared to a value of -63 μV/°C for the case of steel fiber of diameter 60 μm (Table II). On the other hand, the fiber of diameter 8 μm gave much lower resistivity in the cement paste. At the same fiber volume fraction of 0.2 vol%, the fiber of diameter 8 μm gave resistivity 1.4×10^3 Ω·cm [14], compared to a value of 3.2×10^4 Ω·cm in the case of the fiber of diameter 60 μm (Table II). The low resistivity attained by the 8 μm diameter fiber is attributed to the large aspect ratio, which is favorable for percolation. The origin for the weak thermoelectric behavior attained by the 8 μm diameter fiber is not clear presently. Nevertheless, the combination of high conductivity and weak thermoelectricity in the case of 8 μm diameter fiber and the combination of low conductivity and strong thermoelectricity in the case of the 60 μm diameter fiber suggest that carrier conduction does not dominate the Seebeck effect in steel fiber cement pastes. That the electrical resistivity of steel fiber (60 μm diameter) cement decreases monotonically with increasing fiber content whereas the absolute thermoelectric power decreases and then increases as the fiber content increases further supports this notion.

The situation is also quite different in the case of carbon fiber cement paste. The carbon fiber contributes to hole conduction [3, 4], thus making the absolute thermoelectric power of the cement-matrix composite more positive [5]. By using intercalated carbon fiber which provides even more holes, the absolute thermoelectric power becomes even more positive [8]. Thus, hole conduction dominates the origin of the Seebeck effect in carbon fiber cement paste.

The change in sign of the absolute thermoelectric power of steel fiber cement paste at 0.27 vol% steel fiber may be related to a change in carrier scattering mechanism resulting from the increasing proximity between the fibers. An oxide layer is present on the surface of the stainless steel fibers. The role of the oxide layer may become more important as the fibers become closer to one another.

This work shows that the science of the electrical behavior of cement containing discontinuous steel fibers is quite complex. This science is relevant to the design of electrically conductive cement-based materials. Much more work is needed to understand this science.

4. Conclusion

Without fibers, cement paste has an absolute thermoelectric power of $+3\ \mu$V/°C. A steel fiber content of up to 0.20 vol% makes the absolute thermoelectric power more negative (down to $-63\ \mu$V/°C), whereas a steel fiber content of 0.20–0.50 vol% makes the absolute thermoelectric power more positive (up to $+31\ \mu$V/°C)—even more positive than the positive value for the steel fiber by itself ($+8\ \mu$V/°C). The value is zero at a steel fiber content of 0.27 vol%.

Carrier conduction fails to explain the Seebeck effect in steel fiber cement paste. Carrier scattering probably contributes considerably to the Seebeck effect. The scattering sites include the fiber-matrix interface, which is like a *pn*-junction, since the fiber and cement matrix have opposite signs of the absolute thermoelectric power.

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