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Origin of the thermoelectric behavior of steel fiber cement paste

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Abstract

Carrier scattering dominates the origin of the Seebeck effect in steel fiber cement. The scattering sites include the fiber–matrix interface, which is like a pn junction, since the fiber and cement paste have opposite signs of the absolute thermoelectric power. The scattering results in positive and negative values of the absolute thermoelectric power, depending on the fiber content. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The thermoelectric behavior of cement-based materials [1–5] is relevant to thermoelectric power generation, cement-based thermocouples [6], 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.

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 [3]. The use of carbon fibers in place of steel fibers gives smaller effects [1–3,5]. The addition of steel fibers (0–0.20 vol.%) causes the absolute thermoelectric power to be more negative. The greater the fiber content in this range, the more negative is the absolute thermoelectric power.

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 [3–6].

In order to understand the origin of the thermoelectric effect in steel fiber cement paste, this paper investigates the thermoelectric behavior of the steel fiber itself, as well as that of cement pastes with a larger range of steel fiber content.

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 mortars containing these fibers are described in Ref. [7]. However, no aggregate, whether coarse or fine, was used in this work. The cement used was portland cement (Type I) from Lafarge (Southfield, MI).

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 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

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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}

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 minus 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. 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 midpoint 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 2 shows that the volume resistivity of cement paste is decreased by steel fiber addition. The higher fiber volume fraction, the lower is the resistivity. It appears 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 [8].

Table 2 gives 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, whereas cement paste without fiber has a negative value. The addition of fibers up to 0.20 vol.% makes the value more negative, as previously reported [4]. However, increase of the fiber content to 0.50% makes the value positive—even more positive than the value of the fiber by itself. In other words, a change in sign occurs between 0.20 and 0.50 vol.%.

It was previously assumed that the steel fiber provides free electrons which would make the absolute thermoelectric power more negative [4]. However, this work shows that this assumption is incorrect, as the steel fiber itself has a positive value of the absolute thermoelectric power (due to scattering of electrons from lattice vibrations within the fiber).

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. Both the negative and positive values of the absolute thermoelectric power of cement pastes containing 0.5–2.5 vol.% steel fibers are attributed to the scattering. A quantitative understanding of the scattering effect requires detailed information on the mean free path and mean free time of the carriers and is beyond the scope of this paper.

The situation is quite different in the case of carbon fiber cement paste. The carbon fiber contributes to hole conduction [1,2], thus, making the absolute thermoelectric power of the

Table 2
Absolute thermoelectric power and volume electrical resistivity of cement pastes and of steel fiber by itself

Fiber content			
Percent by mass of cement	Vol.%	Absolute thermoelectric power (μV/°C)[a]	Resistivity (Ω cm)
0	0	-1.99 ± 0.04	$(4.7 \pm 0.4) \times 10^5$
0.5	0.10	-53 ± 5	$(7.8 \pm 0.5) \times 10^4$
1.0	0.20	-59 ± 5	$(4.8 \pm 0.4) \times 10^4$
2.5	0.50	$+26 \pm 3$	$(1.4 \pm 0.2) \times 10^3$
/	100[b]	$+3.76 \pm 0.15$	6×10^{-5}[c]

[a] Measured during heating.
[b] Steel fiber by itself.
[c] From the manufacturer's data sheet.

cement–matrix composite more positive [3]. By using intercalated carbon fiber which provides even more holes, the absolute thermoelectric power becomes even more positive [5]. Thus, hole conduction, rather than scattering, dominates the origin of the Seebeck effect in carbon fiber cement paste. In contrast, scattering, rather than electron conduction, dominates the Seebeck effect in steel fiber cement paste.

4. Conclusions

Carrier scattering dominates the origin of the Seebeck effect in steel fiber cement paste. 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. The scattering results in highly positive (+26 μV/°C) and highly negative (−59 μV/°C) values of the absolute thermoelectric power, depending on the fiber content in the composite. The absolute thermoelectric power changes from being negative (akin to the cement paste) to being positive (akin to the steel fiber itself) at a fiber content between 0.2 and 0.5 vol.%.

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