Communication

Seebeck effect in carbon fiber-reinforced cement

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Abstract

The Seebeck effect in carbon fiber-reinforced cement paste was found to involve electrons from the cement matrix and holes from the fibers. The two contributions were equal at the percolation threshold, with a fiber content between 0.5 and 1.0% by mass of cement. The hole contribution increased monotonically with increasing fiber content below and above the percolation threshold. The fiber addition increased the linearity and reversibility of the Seebeck effect. Silica fume and latex as admixtures had minor influence on the Seebeck effect.   © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The Seebeck effect is a thermoelectric effect that is the basis for thermocouples for temperature measurement. This effect involves charge carriers moving from a hot point to a cold point within a material, thereby resulting in a voltage difference between the two points. The Seebeck coefficient is the voltage difference per unit temperature difference between the two points. Negative carriers (electrons) make it more positive and positive carriers (holes) make it more negative.

The Seebeck effect in concrete is of interest because it gives the concrete the ability to sense its own temperature. No attached or embedded sensor is needed since the concrete itself is the sensor. This means low cost, high durability, large sensing volume, and absence of mechanical property degradation due to embedded sensors. As the temperature affects the performance and reliability of concrete, its detection is valuable.

The Seebeck effect in concrete was first reported by Sun et al. [1,2]. The observation was made on cement paste reinforced with short carbon fibers and containing only a disperser, which was a compound composed of cellulose and chloroform, with no other admixture. Conduction due to the fibers was found to involve holes.

Sun et al. [1,2] reported a Seebeck behavior that corresponds to hole conduction in carbon fiber-reinforced ce-

ment, but they reported the absence of Seebeck effect (i.e., a Seebeck coefficient of zero) for cement with no fiber [2]. However, the nonzero electrical conductivity of cement without fibers [3] suggests that the Seebeck coefficient should not be zero when fibers are absent. Comparing the Seebeck behavior with and without fibers is expected to help understand the effect of carbon fibers on the electrical conduction. Therefore, one objective of this paper is to compare the Seebeck behavior under the presence and absence of carbon fibers.

Sun et al. [1,2] reported the Seebeck coefficient with respect to copper, but did not report the absolute thermoelectric power. The second objective of this paper is to report the absolute thermoelectric power, which gives fundamental information on the electrical conduction.

The electrical conductivity of carbon fiber-reinforced cement depends not only on the fiber content, but also on the admixtures present [3,4]. The use of silica fume as an admixture is particularly effective for enhancing the fiber dispersion, thus resulting in carbon fiber-reinforced cement of increased conductivity. The use of latex as an admixture is less effective and the resulting carbon fiber-reinforced cement is not as conductive as that obtained by using silica fume. The third objective of this paper is to investigate the effect of these admixtures on the Seebeck effect in carbon fiber-reinforced cement. These admixtures are known to enhance the mechanical properties of carbon fiber-reinforced cement [3]. They were absent in the work of Sun et al. [1,2].

Sun et al. reported that the magnitude of the Seebeck coefficient increased with fiber content and abruptly decreased at the percolation threshold for electrical conduc-

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tion [2]. The explanation provided by Sun et al. [2] for the abrupt decrease in the Seebeck coefficient at the percolation threshold is not clear. The fourth objective of this work is to investigate the dependence of the Seebeck coefficient on the fiber content for the case of carbon fiber-reinforced cement containing either silica fume or latex, since the percolation threshold for these cement pastes is known to be at a fiber content between 0.5 and 1.0% by weight of cement [3,4].

Carbon fiber-reinforced concrete is structurally attractive due to its high flexural strength and toughness, high tensile strength, and low drying shrinkage [5].

2. Materials and methods

2.1. Materials

The carbon fibers were isotropic pitch-based, unsized, and approximately 5 mm in length, and obtained from Ashland Petroleum Co. (Ashland, KY, USA). The fiber properties are shown in Table 1. No aggregate (fine or coarse) was used.

The cement used was Portland cement (type I) from Lafarge Corp. (Southfield, MI, USA). The silica fume (Elkem Materials, Inc., Pittsburgh, PA, USA; EMS 965) was used in the amount of 15% by mass of cement. The methylcellulose, used in the amount of 0.4% by mass of cement, was from Dow Chemical Corp., Midland, MI, USA; Methocel A15-LV. The defoamer (Colloids, Inc., Marietta, GA, USA; 1010) used whenever methylcellulose was used was in the amount of 0.13 vol.%. The latex, used in the amount of 20% by mass of cement, was a styrene butadiene polymer (Dow Chemical Co., Midland, MI, USA; 460NA), 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 (Dow Corning Corp., Midland, MI, USA; #2210, 0.5% by mass of latex).

2.2. Methods

A rotary mixer (Kitchen Aid, St. Joseph, MI, USA) 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 (if applicable) were mixed in the mixer for

5 min. After pouring into molds, an external vibrator was used to facilitate compaction and decrease the amount of air bubbles. The samples were demolded after 24 h and then cured in air at room temperature and a relative humidity of 100% for 28 days.

Eight types of cement paste were prepared, namely (1) plain cement paste (consisting of just cement and water), (2) silica-fume cement paste (consisting of cement, water, and silica fume), (3) carbon-fiber 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), (4) carbon-fiber silica-fume cement paste (same as 3, except having carbon fibers in the amount of 1.0% by mass of cement), (5) carbon-fiber silica-fume cement paste (same as 3, except having carbon fibers in the amount of 1.5% by mass of cement), (6) latex cement paste (consisting of cement, water, latex, and antifoam), (7) carbon-fiber latex cement paste (consisting of cement, water, latex, antifoam, and carbon fibers in the amount of 0.5% by mass of cement, and (8) carbon-fiber latex cement paste (same as 7, except having carbon fibers in the amount of 1.0% by mass of cement). The water/cement ratio was 0.35 for pastes 1 through 5, and 0.23 for pastes 6 through 8.

Thermopower measurement was performed on rectangular samples of $75 \times 15 \times 15$-mm size, so 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 a much larger size 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 approximately 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 that 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 (Keithley Instruments, Inc., Cleveland, OH, USA) 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 temperatures of the two ends. 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) [6] is the absolute thermoelectric power of the sample. Six samples of each of the eight types of cement paste were tested. Each sample was heated at one end at a rate of 0.009°C/s and then cooled with the power of

Table 1
Properties of carbon fibers

Filament diameter	15 ± 3 μm
Tensile strength	690 MPa
Tensile modulus	48 GPa
Elongation at break	1.4%
Electrical resistivity	3.0×10^{-3} Ω · cm
Specific gravity	1.6 g cm^{-3}
Carbon content	98 wt.%

the platen turned off. The heating rate was constant, but the cooling rate was not.

3. Results and discussion

Table 2 shows the Seebeck coefficient (with copper as the reference) and the absolute thermoelectric power. A negative value of the absolute thermoelectric power indicates p-type (hole) behavior; a positive value indicates n-type (electron) behavior. All types of cement paste studied were n-type except pastes 4 and 5, which were p-type. The higher the fiber content, the less n-type (the more p-type) was the paste, whether silica fume or latex was present. Without fibers, the absolute thermoelectric power was 2 μV/°C, whether silica fume and latex were present or not. This is consistent with the similar values of the electrical conductivity for cement pastes with silica fume and with latex, but without fibers [3]. Thus, silica fume or latex addition did not have much influence on the thermoelectric power when fibers were absent, but carbon fiber addition did by enhancing the hole conduction.

As shown in Table 2, the thermopower results obtained during heating and cooling were very close. Fig. 1 shows the variation of the Seebeck voltage vs. the temperature difference during heating and cooling for pastes 1, 2, 3, 6, and 7. With fibers present, the variation was linear and essentially identical during heating and cooling. Without fibers, the variation was nonlinear and hysteretic (i.e., not totally reversible upon cooling subsequent to heating). Thus, although the fiber addition did not increase the magnitude of the absolute thermoelectric power, it enhanced the linearity and reversibility of the Seebeck effect. This enhancement is attributed to the increase in the contribution of holes to the electrical conduction and the association of hole conduction to conduction through the fibers.

The abrupt Seebeck voltage decrease observed by Sun et al. [2] between fiber contents of 1.0 and 1.2% by mass of cement is attributed to the increase in air void content as the fiber content increased, suggested by micrographs [2], which showed a sharp increase in air void content as the fi-

ber content increased from 0.8 to 1.2% by mass of cement. The air void content is known to increase with fiber content and to decrease upon addition of silica fume or latex [3]. Both silica fume and latex were absent in the work of Sun et al. [2].

The increase in the electrical conductivity reported by Sun et al. [2] as the fiber content was increased from 1.0 to 1.2% by mass of cement is attributed to the increase in air void content, the consequent increase in the amount of exposed fibers, and the resulting decrease in the contact resistance, which is a part of the measured resistance due to the two-probe method used. In contrast, Chen et al. [3] and Chen and Chung [4] used the four-probe method to measure the electrical conductivity; the contact resistance is not a part of the measured resistance when the four-probe method is used. Chen and Chung [4] reported that the conductivity increased by more than two orders of magnitude at the percolation threshold (between 0.5 and 1.0% by mass of cement). However, Sun et al. [2] reported that the conductivity increased by one order of magnitude between fiber contents of 1.0 and 1.2% by mass of cement. The relatively small amount of conductivity increase reported by Sun et al. [2] supports the notion that this conductivity increase is not due to the percolation threshold.

We observed that the absolute thermoelectric power monotonically became less positive (more negative) as the fiber content increased through the percolation threshold, which was at a fiber content between 0.5 and 1.0% by mass of cement [3,4]. This observation is in sharp contrast to the report [2] that the Seebeck effect abruptly diminished at the percolation threshold. Since the conductivity increases monotonically with increasing fiber content through the percolation threshold [2–4], it is reasonable for the Seebeck effect associated with the holes to increasingly become more pronounced as the fiber content increases through the percolation threshold, as observed in this work.

The change of the absolute thermoelectric power from positive to negative values occurred at a fiber content between 0.5 and 1.0% by mass of cement when silica fume was present. This means that at this fiber content, which happened to be the percolation threshold [3,4], compensation took place between the electron contribution from the

Table 2
Seebeck coefficient (μV/°C) and absolute thermoelectric power (μV/°C) of eight types of cement paste

| Cement paste	Heating		Cooling	
	Seebeck coefficient[a]	Absolute thermoelectric power	Seebeck coefficient[a]	Absolute thermoelectric power
(1) Plain	−(0.35 ± 0.03)	1.99 ± 0.03	−(0.38 ± 0.05)	1.96 ± 0.05
(2) Silica fume	−(0.31 ± 0.02)	2.03 ± 0.02	−(0.36 ± 0.03)	1.98 ± 0.03
(3) 0.5% fibers + silica fume	−(1.45 ± 0.09)	0.89 ± 0.09	−(1.45 ± 0.09)	0.89 ± 0.09
(4) 1.0% fibers + silica fume	−(2.82 ± 0.11)	−0.48 ± 0.11	−(2.82 ± 0.11)	−0.48 ± 0.11
(5) 1.5% fibers + silica fume	−(3.10 ± 0.14)	−0.76 ± 0.14	−(3.10 ± 0.14)	−0.76 ± 0.14
(6) Latex	−(0.28 ± 0.02)	2.06 ± 0.02	−(0.30 ± 0.02)	2.04 ± 0.02
(7) 0.5% fibers + latex	−(1.20 ± 0.05)	1.14 ± 0.05	−(1.20 ± 0.05)	1.14 ± 0.05
(8) 1.0% fibers + latex	−(2.10 ± 0.08)	0.24 ± 0.08	−(2.10 ± 0.08)	0.24 ± 0.08

[a] With copper as the reference.
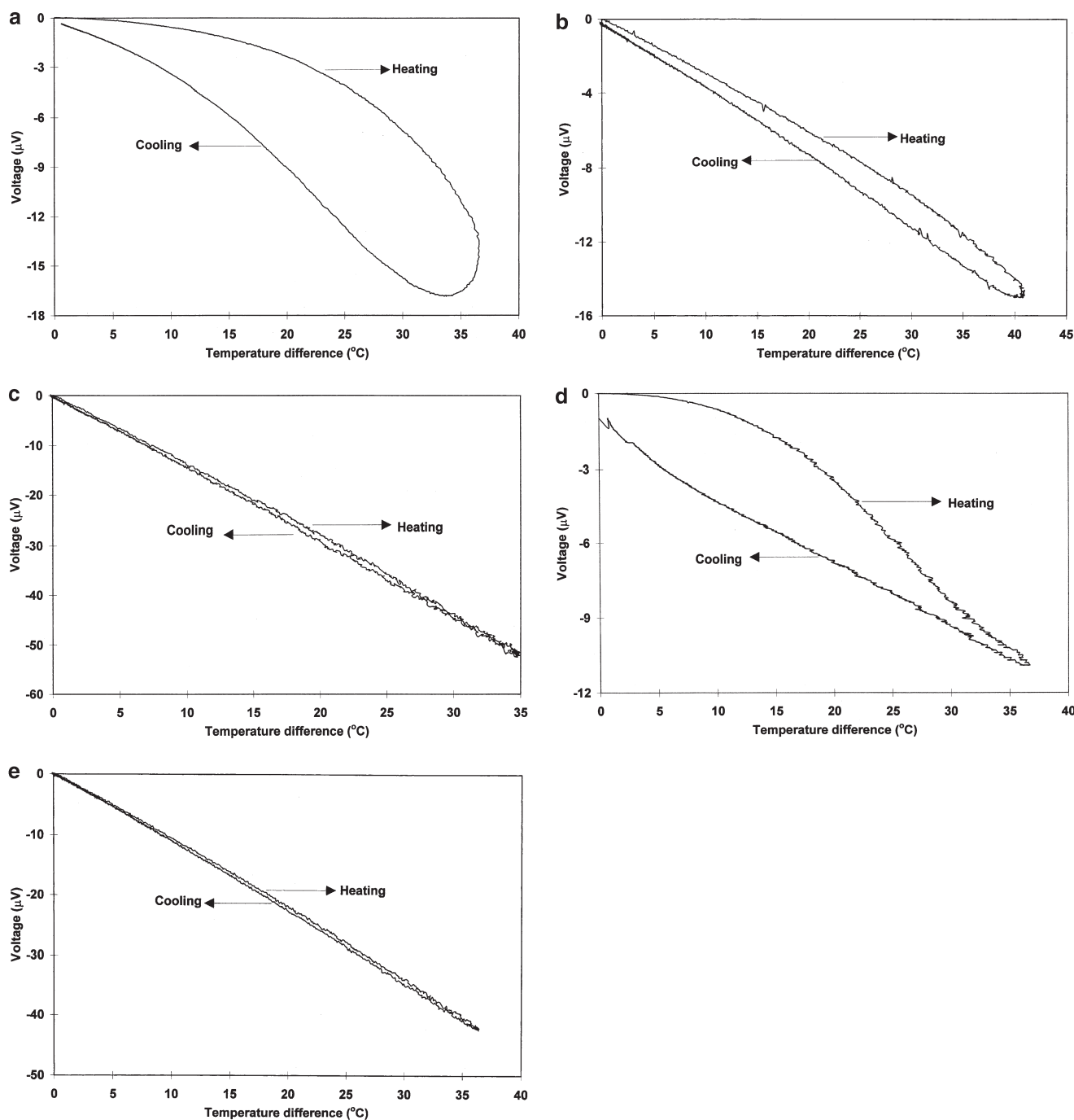
Fig. 1. Variation of the Seebeck voltage (with copper as the reference) vs. the temperature difference during heating and cooling for (a) paste 1, (b) paste 2, (c) paste 3, (d) paste 6, and (e) paste 7.

cement matrix and the hole contribution from the fibers. It should be noted that at any fiber content, electrons and holes contributed additively to the electrical conductivity, but subtractively to the thermopower. The correlation between the percolation threshold and change in sign of the absolute thermoelectric power is reasonable since the fibers dominated the conduction by means of holes above the percolation threshold and the cement matrix dominated the conduction by means of electrons below the percolation threshold.

In the presence of latex instead of silica fume, the highest fiber content investigated was 1.0% by mass of cement and a change in sign of the absolute thermoelectric power was not observed, even though the percolation threshold was also between fiber contents of 0.5 and 1.0% by mass of cement for the case of latex. Although a change in sign of the absolute thermoelectric power was not observed for the case of latex, the absolute thermoelectric power was a very small positive value at a fiber content of 1.0% by mass of cement

and the absolute thermoelectric power decreased monotonically with increasing fiber content. Based on this trend, it is highly probable that a change in sign would occur just above 1.0% by mass of cement for the case of latex. That a change in sign of the absolute thermoelectric power did not occur at the percolation threshold (but probably just above the threshold) is attributed to the low conductivity of carbon-fiber latex cement paste compared to carbon-fiber silica-fume cement paste at the same fiber content [3] and the associated weaker hole conduction in the latex case. This is consistent with the observation that at the same fiber content (whether 0.5 or 1.0% by mass of cement), the absolute thermoelectric power was more positive for the latex case than the silica fume case (Table 2).

The values of thermoelectric power reported by Sun et al. [1,2] are actually the magnitudes of the Seebeck coefficient with copper as the reference. Their values are as high as 17 μV/°C—much higher than our values. The origin of this difference is not clear, but it may be due to difference in carbon fiber type (PAN-based fibers in Sun et al. [1,2] and pitch-based fibers in this work).

4. Conclusion

The addition of short carbon fibers to cement paste increased the linearity and reversibility of the Seebeck effect, in addition to decreasing the absolute thermoelectric power from +2 μV/°C to less positive (more negative) values. At the percolation threshold (a fiber content between 0.5 and 1.0% by mass of cement), the absolute thermoelectric power changed from being positive to being negative, indicating compensation of the carriers, which were electrons from the cement matrix and holes from the fibers. The Seebeck effect due to the holes became increasingly pronounced as the fiber content increased beyond the percolation threshold. Admixtures such as silica fume and latex had minor influence on the Seebeck effect.

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