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Communication

Enhancing the Seebeck effect in carbon fiber-reinforced cement by using intercalated carbon fibers

Sihai Wen, D.D.L. Chung*

Composite Materials Research Laboratory, State University of New York at Buffalo, Box 604400, Furnas Hall, Buffalo, NY 14260-4400, USA

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Abstract

The absolute thermoelectric power of carbon fiber-reinforced cement paste was rendered as negative as -17 μV/°C by using bromine-intercalated carbon fibers, which had a high concentration of holes. The corresponding paste with pristine carbon fibers exhibited absolute thermoelectric power as negative as -0.8 μV/°C only. © 2000 Elsevier Science Ltd. All rights reserved.

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

1. Introduction

The Seebeck effect is a thermoelectric effect that is the basis for thermocouples. Its occurrence in cement-based materials is potentially valuable for the use of concrete as a temperature sensor, which is needed for thermal control. By using a structural material as a sensor, the need for attached or embedded sensors is eliminated, thereby reducing cost, enhancing durability, increasing the sensing volume and avoiding mechanical property degradation, which occurs in the case of embedded sensors.

The Seebeck effect has been reported to occur in carbon fiber-reinforced cement [1–3]. The absolute thermoelectric power is positive (2.0 μV/°C) in the absence of fibers, but becomes negative (as negative as -0.76 μV/°C) in the presence of a sufficient amount of carbon fibers [3]. The higher the carbon fiber content, the more negative is the absolute thermoelectric power. This is because the cement matrix contributes to electron conduction, whereas the carbon fibers contribute to hole conduction, such that the two contributions are equal at the percolation threshold [3].

For practical use of the Seebeck effect, a much larger magnitude of the absolute thermoelectric power is desirable. Attaining this by increasing the fiber content is not practical because the workability and compressive strength decrease with increasing fiber content. In this paper, this has been attained by using bromine-intercalated carbon fibers.

Intercalation is a chemical reaction involving the insertion of a foreign species called the intercalate (bromine in this case) between the graphite layers, thereby forming an intercalation compound. The charge transfer between the intercalate and the carbon host results in a large increase in the carrier concentration and the material becomes metallic. In the case of bromine as the intercalate, a hole metal results, since bromine is an electron acceptor (accepting electrons from the carbon host) [4–14]. Thus, by using bromine-intercalated carbon fibers in cement, the hole conduction is enhanced and the absolute thermoelectric power becomes as negative as -17 μV/°C, as reported here.

2. Experimental methods

2.1. Materials

The carbon fibers (Thornel P-100) were mesophase pitch-based, unsized and of length ~5 mm, as obtained from Amoco Performance Products (Ridgefield, CT). This type of carbon fiber is quite graphitic, thereby allowing intercalation to occur. In contrast, the isotropic pitch-based carbon fiber used in previous work [3] is amorphous and thus cannot be intercalated.

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* Corresponding author. Tel.: +1-716-645-2593 ext. 2243; fax: +1-716-645-3875.

E-mail address: ddlchung@acsu.buffalo.edu (D.D.L. Chung).

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Intercalation of the crystalline carbon fibers was conducted by exposure of the fibers to bromine vapor in air at room temperature for 2 weeks to attain a stage 2 (saturated, with 83% weight uptake) intercalation compound. After this, the fibers were removed from the bromine vapor and allowed to undergo bromine desorption in air at room temperature for 2–3 months in order to attain a stable compound, with about 20% weight uptake relative to the pristine material.

No aggregate (fine or coarse) was used. The cement used was portland cement (Type I) from Lafarge (Southfield, MI). The fibers used were in the amount of 0.5 wt.% of cement (corresponding to 0.5 vol.%). The silica fume (Elkem Materials, Pittsburgh, PA, EMS 965) was used in the amount of 15 wt.% of cement. The methylcellulose, used in the amount of 0.4 wt.% of cement, was Methocel A15-LV (Dow Chemical, Midland, MI). The defoamer (Colloids, Marietta, GA, 1010) used whenever methylcellulose was used was in the amount of 0.13 vol.%. The latex, used in the amount of 20 wt.% of cement, was a styrene butadiene polymer (Dow Chemical, 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, Midland, MI, #2410, 0.5 wt.% of latex).

2.2. Methods

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 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 carbon fiber cement paste were prepared. Four of them contained pristine (not intercalated) carbon fibers; four of them contained intercalated carbon fibers. In each group, two pastes contained fibers in the amount of 0.5 wt.% of cement (one with silica fume and one with latex) and the other two pastes contained fibers in the amount of 1.0 wt.% of cement (one with silica fume and one with latex). The water–cement ratio was 0.35 for all pastes with silica fume and 0.23 for all pastes with latex.

Thermopower measurement was performed on rectangular 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. 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. 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 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) [15] 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

Table 1
Seebeck coefficient (μV/°C) and absolute thermoelectric power (μV/°C) of eight types of cement paste

Cement paste				
Fiber type	Fiber content (wt.% of cement)	Admixture	Seebeck coefficient	Absolute thermoelectric power
Pristine	0.5	SF	− 1.87 ± 0.11	0.47 ± 0.11
Pristine	1.0	SF	− 3.13 ± 0.16	− 0.79 ± 0.16
Pristine	0.5	L	− 1.56 ± 0.08	0.78 ± 0.08
Pristine	1.0	L	− 2.48 ± 0.12	− 0.14 ± 0.12
Intercalated	0.5	SF	− 13.8 ± 1.13	− 11.5 ± 1.13
Intercalated	1.0	SF	− 18.9 ± 1.32	− 16.6 ± 1.32
Intercalated	0.5	L	− 9.76 ± 1.09	− 7.42 ± 1.09
Intercalated	1.0	L	− 12.5 ± 1.07	− 10.2 ± 1.07

SF: silica fume; L: latex.

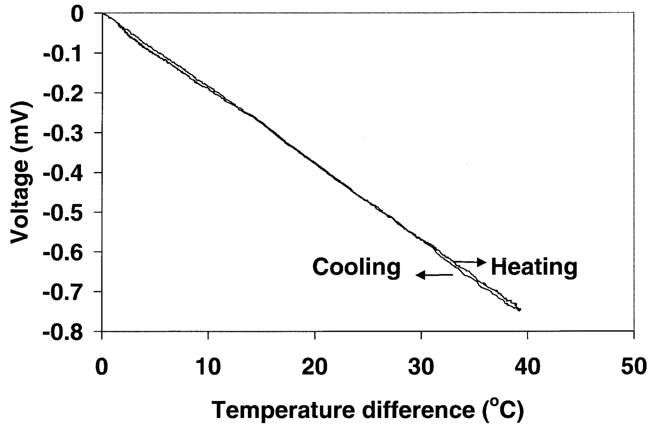

Fig. 1. Variation of the Seebeck voltage (with copper as the reference) vs. the temperature difference during heating and cooling for silica fume cement paste containing bromine-intercalated carbon fibers in the amount of 1.0 wt.% of cement.

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

3. Results and discussion

Table 1 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. The absolute thermoelectric power is negative for all the pastes with intercalated fibers. Among the pastes with pristine fibers, it is negative when the fiber content is 1.0 wt.% of cement and is positive when the fiber content is 0.5 wt.% of cement. Whether with pristine or intercalated fibers, the absolute thermoelectric power becomes more negative as the fiber content increases. At any fiber content and for any fiber type, the use of silica fume as an admixture gives a more negative value of the absolute thermoelectric power than the use of latex as an admixture, as previously reported [3]. This is because silica fume gives a higher degree of fiber dispersion than latex [16].

The curve of Seebeck voltage (with copper as the reference) vs. temperature difference is a straight line with a negative slope for all the eight pastes. The slope is the Seebeck coefficient with copper as the reference. The curves during heating and cooling essentially overlap for each type of paste. Fig. 1 shows the curves for the paste exhibiting the most negative value of the absolute thermoelectric power, i.e., the paste containing silica fume and intercalated fibers in the amount of 1.0 wt.% of cement.

Comparison of the values of the absolute thermoelectric power of the pristine fiber pastes of this work with those of Ref. [3] shows that the values are more negative in this work. This is because of the higher degree of crystallinity of the fibers of this work compared to that of the fibers of Ref. [3] and the consequent lower electrical resistivity of the fibers of this work. The resistivity is 2.2×10^{-4} Ω cm for the pristine fibers of this work and is 3.0×10^{-3} Ω cm for those of Ref. [3].

Due to the high atomic weight of bromine compared to that of carbon, the intercalated carbon fibers have a higher density than the pristine fibers. Thus, at the same fiber content by weight of cement, the fiber volume fraction is lower for the intercalated fiber paste than the corresponding pristine fiber paste. In spite of the lower fiber volume fraction, the absolute thermoelectric power is much more negative for the intercalated fiber paste than the corresponding pristine fiber paste. This is because of the high concentration of holes resulting from bromine intercalation.

4. Conclusion

The use of short bromine-intercalated carbon fibers as an admixture in cement paste gives values of the absolute thermoelectric power as negative as -17 μV/°C, compared to values as negative as -0.8 μV/°C for pastes containing pristine carbon fibers. This is due to the high concentration of holes resulting from bromine intercalation.

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