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Letters to the editor

Thermoelectric behavior of carbon–cement composites

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Carbon–cement composites refer to cement–matrix composites that contain carbon (e.g., carbon fibers). Carbon in a discontinuous form is usually used and is the form addressed in this paper, because this form can be added to the cement mix in the mixer (i.e., it can be used as an admixture). In contrast, carbon in continuous form cannot be used as an admixture. Mixing is the most convenient way of incorporating any ingredient in a cement-based material. Not only is mixing inexpensive, it can be done in the field. Another disadvantage of using continuous carbon fibers is the high cost of continuous fibers compared to discontinuous fibers. Low cost is essential for concrete to be practical.

The Seebeck effect is a thermoelectric effect which is the basis for thermocouples for temperature measurement. It also allows the conversion from thermal energy to electrical energy. 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 (hot minus cold) per unit temperature difference (hot minus cold) between the two points. Negative carriers (electrons) make it more negative and positive carriers (holes) make it more positive. This paper is focused on the Seebeck effect of carbon–cement composites.

The Seebeck effect has been previously reported in cement–matrix composites containing short carbon fibers, including pristine [1–5] and intercalated fibers [6]. Using the effect in dissimilar cement–matrix composites, cement-based thermocouples have been made [7].

For the purpose of investigating the Seebeck effect of a larger variety of carbon–cement composites, this paper extends the work to cement–matrix composites containing graphite particles. Graphite particles have been used as an additive in cement-based materials for improving the fracture toughness and plastic behavior [8], for enhancing the electrical conductivity [9,10] and for providing moldable electrochemical electrodes [11]. In contrast to the carbon fibers used in previous work related to cement–matrix composites, graphite particles are crystalline and inexpensive. Associated with the crystallinity is high electrical conductivity. On the other hand, the aspect ratio is low compared to that of carbon fibers. The graphite powder (flakes) was of size <45 μm, as provided by Fisher Chemical (Fair Lawn, NJ). The graphite–cement weight ratio was 1.0. This corresponds to a graphite volume fraction of 37%, as calculated from the densities of the components. The cement used was portland cement (Type I) from Lafarge (Southfield, MI). The water/cement ratio was 0.45.

A rotary mixer with a flat beater was used for mixing, which was conducted for 5 min. After pouring into molds, an external vibrator was used to facilitate compaction and decrease the number 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.

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 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 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

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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 a 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 minus the absolute thermoelectric power of copper (+2.34 μV/°C) [12] is the absolute thermoelectric power of the sample. Each sample was heated at one end at 0.009 °C/s and then cooled with the power of the platen turned off. The heating rate was thus constant, but the cooling rate was not.

DC volume electrical resistivity was measured using 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 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) were 60 mm apart. Six specimens of each composition were tested.

Fig. 1 shows the plot of the Seebeck voltage (relative to copper) versus the temperature difference (relative to 20 °C) for the graphite–cement composite. The effect is linear and reversible.

Table 1 lists the absolute thermoelectric power and resistivity of various carbon–cement composites. The absolute thermoelectric power is negative in the absence of admixture. Addition of carbon fiber or graphite causes the thermopower to be less negative or more positive and decreases the resistivity. The use of a higher fiber content causes the thermopower to be more positive and decreases the resistivity. The use of bromine-intercalated fiber greatly increases the thermopower, while decreasing the resistivity. The use of graphite gives the highest thermopower and the lowest resistivity among all the materials in Table 1, partly because of the high volume fraction of graphite.

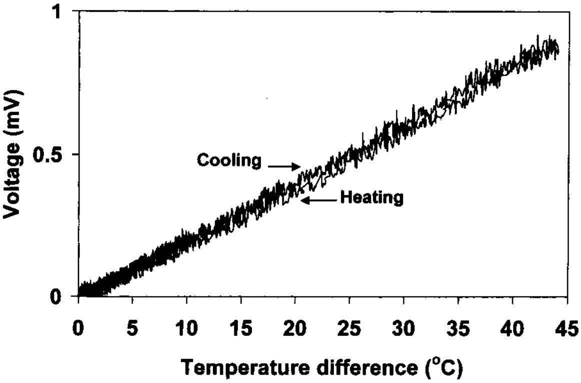

Fig. 1. Seebeck voltage (relative to copper) versus temperature difference (relative to 20 °C) of graphite–cement composite during heating and cooling.

Table 1
Absolute thermoelectric power and electrical resistivity of various carbon–cement composites

Admixture	Absolute thermoelectric power (μV/°C)	Resistivity (Ω·cm)
None [5]	−2.0	$(4.9\pm0.4)\times10^5$
Carbon fiber[b] (0.5 vol.%)[a]	−0.9	$(1.5\pm0.1)\times10^4$
Carbon fiber[b] (1.0 vol.%)[a]	+0.5	$(8.3\pm0.5)\times10^2$
Carbon fiber[c] (0.5 vol.%)[a]	+12	$(6.7\pm0.5)\times10^3$
Carbon fiber[c] (1.0 vol.%)[a]	+17	$(7.1\pm0.6)\times10^2$
Graphite powder (37 vol.%)	+20	$(4.8\pm0.4)\times10^2$

[a] With silica fume (15% by mass of cement).
[b] Amorphous (not intercalated) [5].
[c] Crystalline (intercalated with bromine) [6].

Compared to the thermopower values of carbon materials such as kish graphite (−5 μV/°C [13]) and highly oriented pyrolytic graphite (−3 μV/°C [13]), the values for the carbon–cement composites containing graphite and intercalated carbon fiber are exceptionally large and positive. As the value for plain cement paste (without admixture) is small in magnitude and negative in sign, the large and positive values observed for the composites with graphite and intercalated carbon fiber are attributed, at least partly, to hole conduction in these carbons. The importance of holes is obvious in the case of the bromine-intercalated fiber, as bromine is known to be an electron acceptor. For the case of graphite in cement, carrier scattering may be a factor in causing the high thermopower [14].

From the technological point of view, the attainment of a high thermopower in carbon–cement composites is of interest, particularly since these composites are low in both material and processing costs. From the scientific point of view, the origin of the high thermopower is of interest and is not completely understood.

The absolute thermoelectric powers of carbon–cement composites at room temperature are compared. In summary, addition of carbon fiber or graphite powder to cement paste causes the value to change from −2 to less negative or positive values. The highest value of +20 μV/°C is attained by adding graphite powder (37 vol.%). This value is in contrast to the low values previously reported for graphites [13].

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