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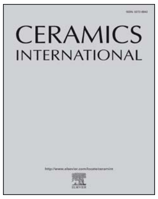

Full length article

Thermoelectric properties of carbon nanotube reinforced cement-based composites fabricated by compression shear

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ABSTRACT

Carbon nanotubes (CNTs) with weight percent of 5.0%, 10.0% and 15.0% were added into the cement matrix to fabricate CNT reinforced cement-based composites (CNTs/CC) by mixing and dry compression shear methods. Seebeck coefficient, electrical conductivity and thermal conductivity of the as-received CNTs/CC were measured and analyzed in detail. The CNTs/CC exhibits the thermoelectric behavior of p-type semiconductor. CNTs were dispersed uniformly in cement matrix by compression shear stress, which promoted a relatively high electrical conductivity (0.818 S/cm) and Seebeck coefficient (57.98 μV/°C) of CNTs/CC. Combining with their lower thermal conductivity ranged from 0.734 to 0.947 $\mathrm{W\,m^{-1}\,K^{-1}}$, the CNTs/CC shows the highest thermoelectric figure of merit (*ZT*) has reached 9.33×10^{-5}, Which is benefit to the applications in large-scale energy harvesting in the buildings and pavements with low cost in the future cities.

1. Introduction

With the continuous development of infrastructure, urban construction has expanded rapidly in recent years. A significant amount of heat energy from solar irradiation and human activity is released into the environment every summer, resulting in an increasingly severe urban heat island effect (UHI) [1]. To alleviate UHI and reduce building energy-consumption, cement-based thermoelectric materials can be widely used for their appropriate energy conversion efficiency, an excellent climate adaptation, convenient for combining with constructions, high mechanical properties and low cost [2–5]. Cement-based thermoelectric materials provide a way to convert thermal energy come from solar radiation in summer and shallow geothermal energy in winter into electrical energy directly, which are expected to play an important role in responding to energy shortages of the society [6].

The Seebeck effect is one of the thermoelectric effects in which the voltage could be generated along the temperature gradient by the charge carrier moving in the materials from a higher temperature part to a lower temperature one [7]. For a certain material, its Seebeck effect can be evaluated by Seebeck coefficient, a rate of thermoelectric potential generated by 1 °C temperature difference, whose value is negative if the main carrier is electronic and is positive if the main carrier is hole conversely [8,9]. Energy conversion efficiency of thermoelectric materials is determined by electrical conductivity, σ, Seebeck coefficient, S, and thermal conductivity, κ, because thermoelectric materials evaluate their performance with a dimensionless figure of merit, $ZT = (\frac{S^2\sigma}{\kappa})T$, where T is absolute temperature [10–13]. Obviously, enhanced thermoelectric conversion efficiency of the materials can be achieved by increasing the electrical conductivity, the Seebeck coefficient and decreasing the thermal conductivity.

At low or room temperature, thermoelectric devices made of traditional thermoelectric materials have characteristics of expensive, brittleness and poor mechanical [14]. For example, Bi_2Te_3 has a high domestic price, making it impractical for large-scale applications, especially in buildings and pavements. However, due to their compatibility with buildings, appropriate thermoelectric property, excellent mechanical property and low cost, cement-based composites are promising for large-scale energy harvesting applications in the future cities.

In 1998, Sun's group reported firstly the Seebeck effect caused by hole-conduction and thermoelectric-percolation phenomena in carbon fiber reinforced cement-based composites [15]. Since then, the Seebeck effect of cement-based composites has been reported extensively. In the composites carbon fibers, bromine intercalated carbon fibers [16], steel fibers [17,18], graphite powder [19], Bi_2Te_3 particles [20,21], metallic oxides particles (such as $Ca_3Co_4O_9$ [22], Bi_2O_3 [23], Fe_2O_3 [23,24], ZnO [25], etc.), were combined with cement matrix. Although the Seebeck coefficient of cement-based composites can be increased greatly by the above-mentioned materials, thermoelectric properties, *ZT* value, does not be improved significantly due to their low electrical conductivity. On the other hand, Waldemar et al. showed that the incorporation of expanded graphite into cement resulted in a high-density

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carbon/cement interfaces and a markedly increase in electrical conductivity of cement-based composites (up to 1.0 S cm^{-1}) [26]. However, *ZT* value was not presented in the study.

In addition, the thermal conductivity of cement-based composites is typically extremely low, which is benefit to achieve a high *ZT* value. Wen reported that the thermal conductivity of cement-based composites with graphite, carbon black, and iron-oxide black dopant, were 0.24, 0.25 and 0.20 W m^{-1} K^{-1}, respectively [27]. Rice-husk cement-based composites also have a lower thermal conductivity of approximately 0.64 W m^{-1} K^{-1} [28]. Thus, the primary approach to producing cement-based composites with high *ZT* and excellent thermoelectric properties, is to improve the Seebeck coefficient and electrical conductivity simultaneously.

Because of unique one-dimensional tubular structure, excellent mechanical properties, chemical and thermal stability, Seebeck coefficient of about 100 μV/°C and high electrical conductivity, carbon nanotubes (CNTs) have attracted more attention for enhancing thermoelectric properties of cement-based composites [29–32]. Therefore, CNTs as prime candidates are employed for improving the thermoelectric and mechanical properties of cement-based composites. Zuo showed that the Seebeck effect of cement-based composites can be significantly enhanced by mixing CNTs [33]. In the work, the Seebeck coefficient of the cement-based composites could be increased to 22.6 μV/°C by adding 0.5 wt% CNTs (mass fraction of cement) in the condition of containing 0.4 wt% carbon fiber and 10.0 wt% silica fumes. Meng's work showed that the electrical conductivity of cement-based composites can be enhanced only to 1.59×10^{-5} S/cm despite that 0.1 wt% CNTs (mass fraction of cement) was incorporated into the cement matrix. Although the Seebeck coefficient and electrical conductivity of these CNTs enhanced cement-based composites increased, their *ZT* value was not improved significantly due to the low content and poor dispersion of CNTs in cement matrix [34]. Furthermore, the use of polymer dispersants during CNT ultrasonic dispersion processing in these reports, depressed the electrical conductivity and the final thermoelectric properties of the composites [34,35]. Thermoelectric cement-based composites with high CNT content and without polymer dispersants, would lead to high electrical conductivity and excellent energy conversion efficiency, and have not been reported in previous literature.

In this study, CNT reinforced cement-based composites (CNTs/CC) with high CNT content were fabricated by a special compression shear method, in which CNTs can be uniformly dispersed in dry cement powder without use of the polymer dispersants and water-reducing agents. Low porosity of CNTs/CC was then obtained by the compression process, which is propitious to increase the Seebeck coefficient and electrical conductivity of CNTs/CC. High Specific Surface Area (SSA) of CNTs with high content would result in the high volume fraction of the CNTs/cement interface and high electrical conductivity of cement-based materials. The electrical conductivity, Seebeck coefficient and thermal conductivity of the as-received CNTs/CC was measured, whose thermoelectric properties was then evaluated. The enhanced mechanism of the CNTs/CC's *ZT* value by CNTs was also analyzed in detail.

2. Experimental

2.1. Materials

Sulfate-aluminate early-strength cement (P.O.42.5R), from Zhengzhou Jianwen Special Material Technology Co. Ltd., China, was used in this study. The CNTs used were ordinary multi-walled, and of 10–20 nm diameters and 5–20 μm lengths (purity > 90 wt%, SSA > 120 m^2/g, carbon content > 95 wt%). CNTs with fractions in the composites were 5.0, 10.0, and 15.0 wt% by mass of cement.

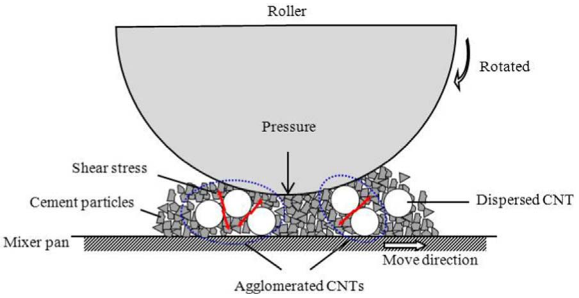

Fig. 1. Schematic of the dry dispersion process, in which bunches and aggregations of CNTs in the cement are sheared and separated into the CNT monofilaments under the compressed stress.

2.2. Specimen fabrication

Firstly, the CNTs and cement were pre-dispersed in a mortar mixer at a mass ratio of 5: 100, or 10: 100 and 15: 100 in a dry dispersion process respectively, stirred for 5–10 min at low speed. The pre-dispersed mixture was then poured into a mill mixer, in which steel heavy rollers were applied to the CNTs and cement mixture. Bunches and aggregation of CNTs in the cement were sheared and separated into the CNT monofilaments under the compressed stress condition as showed in Fig. 1. After about 20 min, a homogeneous mixture was obtained, in which CNT distribute in the cement powder with monofilament status. During this special dry dispersed process, cellulose was not used which was usually as a dispersant in wet dispersed process and could cause a decrease in the electrical conductivity of the cement-based composites. Afterwards, an appropriate amount of the dry mixture was placed into a square steel mold ($10 \times 10 \times 40$ mm^3) to form a bulk specimen at 40 MPa. The molded specimens were then wetted on a water saturated sponge by capillarity. And kept at relative humidity of approximately 95% for 24 h. Finally, the hydration of cement matrix was carried out in water for three days.

2.3. Test methods

The Seebeck coefficient and electrical conductivity of all specimens were measured sequentially from 30 to 100 °C using self-made setups. Silver paste was coated on the two opposite end surfaces (10×10 mm^2) of the specimens and coated in the form of two circles with 1 mm wide which are parallel to the two opposite ends and 20 mm apart. Copper conductive wires were attached to the two opposite ends and two silver circles for measured connection. Next, one square end of each specimen was heated at a rate of 0.01 °C/s in an insulated container using a small ceramic resistance-heater, while maintaining the temperature of the specimen opposite end of the lower approximately 5 °C that of heating end. All temperatures were measured using T-type thermocouples and controlled by two thermostats.

To improve measurement accuracy, electrical conductivity was measured by a four-probe method with two outer and two inner electrodes each couple for current and voltage measurements, respectively. During testing, electrical conductivity and thermoelectric potentials were measured simultaneously, using independent data acquisition channels. Seebeck coefficient is obtained through the rate of the average value of the measured thermoelectric power of the temperature difference of the two specimen opposite ends. The electrical conductivity is calculated from the rate of the measured voltage to current. Data was recorded by data acquisition units.

The thermal conductivity (κ) was measured by a laser flash diffusion method at room temperature using Netzsch LFA 427. A 12.7 mm diameters and 1.0–3.0 mm thick disc specimen were required for the measurements. The thermal conductivity for each was reported the average of three replicates.