Ceramics International 42 (2016) 11568–11573

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Enhanced thermoelectric properties of carbon fiber reinforced cement composites

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ARTICLE INFO

Article history:
Received 21 February 2016
Received in revised form
2 April 2016
Accepted 5 April 2016
Available online 6 April 2016

Keywords:
B. Composites
C. Electrical properties
E. Functional applications

ABSTRACT

Thermoelectric properties of carbon fiber reinforced cement composites (CFRCs) have attracted relevant interest in recent years, due to their fascinating ability for harvesting ambient energy in urban areas and roads, and to the widespread use of cement-based materials in modern society. The enhanced effect of the thin pyrolytic carbon layer (formed at the carbon fiber/cement interface) on transport and thermoelectric properties of CFRCs has been studied. It has been demonstrated that it can enhance the electrical conduction and Seebeck coefficient of CFRCs greatly, resulting in higher power factor 2.08 μ W m^{-1} K^{-2} and higher thermoelectric figure of merit 3.11×10^{-3}, compared to those reported in the literature and comparable to oxide thermoelectric materials. All CFRCs with pyrolytic carbon layer, exhibit typical semiconductor behavior with activation energy of electrical conduction of 0.228-0.407 eV together with a high Seebeck coefficient. The calculation through Mott's formula indicates the charge carrier density of CFRCs (10^{14}–10^{16} cm^{-3}) to be much smaller than that of typical thermoelectric materials and to increase with the carbon layer thickness. CFRCs thermal conductivity is dominated by phonon thermal conductivity, which is kept at a low level by high density of micro/nano-sized defects in the cement matrix that scatter phonons and shorten their mean free path. The appropriate carrier density and mobility induced by the amorphous structure of pyrolytic carbon is primarily responsible for the high thermoelectric figure of merit.

1. Introduction

Carbon fiber reinforced cement composites (CFRCs) as a fascinating multifunctional composites, has shown attractive properties of high tensile and flexural properties, low drying shrink-age, low thermal conductivity, high electrical conductivity and thermoelectric behavior, and thus possessed the abilities to facilitate the cathodic protection of concrete, to shield electromagnetic wave, to sense strain, damage and temperature in important structures [1–3]. Especially, the thermoelectric properties of CFRCs has attracted relevant interest in recent years, due to their fascinating ability for harvesting ambient energy, which can capture unused ambient heat energy in urban areas and roads, and convert it into usable electrical energy [4,5]. CFRCs can also be applied in the field of high efficiency pavement deicing with releasing thermal larger than its consumption in winter. Therefore, an approach is provided by CFRCs for saving and harvesting ambient energy economically in civil engineering, since the widespread use of cement-based materials in modern society.

However, improving the thermoelectric properties of CFRCs for above-mentioned applications is still a challenge, much work has been done in the past several years. The dimensionless thermoelectric figure of merit, ZT, ($ZT = S^2\sigma T/\kappa$, where S, σ, T, and κ are Seebeck coefficient, electrical conductivity, absolute temperature and thermal conductivity respectively) is generally used to characterize the thermoelectric performance [6,7]. To optimize ZT, it depends on making electrical conductivity and Seebeck coefficient increase simultaneously while keeping a low thermal conductivity. CFRCs usually exhibits lower thermal conductivity due to the strong phonon scattering by many intrinsic structural defects in the cement matrix that formed by nano/micro-pores, microcrack, carbon fiber/cement interface and interface among hydration products [1]. It is noteworthy that the thermal conductivity of CFRCs can be further decreased by incorporating foam structure, and is insensitive to the mixing proportion of raw materials [8]. Therefore, much effort focuses on enhancing Seebeck coefficient and electrical conductivity, in case of crystalline materials that meaning a favorable electronic dispersion at the Fermi level [7], to

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http://dx.doi.org/10.1016/j.ceramint.2016.04.014
0272-8842/

achieve a higher thermoelectric power factor ($S^2\sigma$).

Wen and Chung improved firstly CFRC Seebeck coefficient from 5.5 to 21.2 μV/°C by using bromine-intercalated carbon fiber that pretreated with intercalating technique and had a larger graphite layer distance than normal carbon fiber [9]. Yao's group indicated that although the Seebeck coefficient had been improved to about 23.7 μV/°C by incorporating micro-sized Bi_2Te_3 particles, a larger Seebeck coefficient of 35.5 μV/°C can be obtained through the alternate layer structure of micro-sized Bi_2Te_3 and CFRCs [10]. Further, tremendous Seebeck coefficient of 92.57 and 100.28 μV/°C was got in our experiment, in which the micro-sized Fe_2O_3 and Bi_2O_3 particles were employed to enhance the thermoelectric properties of CFRCs [11]. Although the Seebeck coefficient increased about 20 times in these reports, *ZT* value of CFRCs still cannot be enhanced greatly for the small electrical conductivity reason.

In the other reports, the electrical conductivity of CFRCs was increased considerably through another approach, but the Seebeck coefficient was even smaller than primary CFRCs. Waldemar and his coworker enhanced the electrical conductivity of cement-based materials up to 1.0 S cm^{-1} through high density carbon/cement interface by incorporating expanded graphite [12]. However, they reported Seebeck coefficient was only 3.0 μV/°C. The highest electrical conductivity of 76.9 S cm^{-1} has been got in the cement-based composites containing 12.5 vol% exfoliated graphite, that was fabricated by compressing dry raw mixture at uniaxial pressure of 5.6 MPa before curing in water [13]. Further, the electrical conductivity of 10.0 S cm^{-1} was also observed in graphene oxide-ferrofluid-cement nanocomposites with a weight ratio of graphene oxide to cement of 0.30 [14]. Because of the use of high specific area carbon materials (exfoliated graphite and graphene), high density of carbon/cement interface can be formed under well dispersive condition in these reported in above-mention literatures [12–14]. Therefore, not only metal oxide/cement (including Bi_2Te_3/cement) interface has an important effect on the thermoelectric properties of cement-based composites [10,11], but also carbon/cement interface as well [12–14]. To our best knowledge, until now no effort has been taken to improve the thermoelectric properties of CFRCs by incorporating metal oxide/cement interface and carbon/cement interface. Interface engineering probably provides a potential approach to break through the relevance of the three transport coefficients (S, σ and κ), especially for CFRCs with high density structural defects.

In this work, a series of pyrolytic carbon layer was fabricated at the carbon fiber/cement interface by pyrolyzing phenolic resin, based on iron oxide modified CFRCs [11]. Then, the effect of pyrolytic carbon layer on transport and thermoelectric properties of CFRCs was investigated in detail. The activation energy of electrical conduction, energy gap and charge carrier density were calculated and analyzed. A higher power factor and *ZT* value, compared to those reported in the literature and comparable to oxide thermoelectric materials near room temperature, were finally got for cement-based materials.

2. Experimental

2.1. Materials

The carbon fiber is polyacrylonitrile (PAN) based and unsized from Jiyan Carbon Co., Ltd (Jilin, China). Its diameter is seven micrometers, length about five to seven millimeters and the electrical resistivity 16–25 × 10^{-3} Ω cm. Its tensile strength and modulus are 2.6–2.9 GPa and 210–230 GPa respectively. Carbon fiber was employed in amounts of 1.0 wt% by mass of cement in the composites. Commercial high-purity Fe_2O_3 particles with 325 meshes, were introduced into the cement matrix in amount of 5.0 wt% by mass of cement. No aggregate was used. The cement used was sulfate–aluminate cement (P.O.42.5R) from Qinling Cement Plant of China. The water/cement ratio was maintained at 0.23. Meanwhile, same amount of polyocarboxy acid super-plasticizer, 0.50 wt% by mass of cement, and 0.05 wt% defoamer (tributyl phosphate) were employed in the composites. Sodium citrate was used as a set retarder in amount of 0.10 wt% by mass of cement.

2.2. Preparation of pyrolytic carbon layer

Pyrolytic carbon layer was prepared on the surface of carbon fiber by pyrolyzing phenolic resin. Firstly, carbon fiber was immersed absolutely into the ethanol solution of phenolic resin with weight percent of 0.5, 1.0, 3.0 and 5.0 wt%. The larger the phenolic concentration was, the thicker the final pyrolytic carbon layer. After completely drying in a vacuum chamber, the carbon fiber was subsequently heat treated at 700 °C for 1h in argon atmosphere, to convert the residual phenolic resin into carbon. Finally, the carbon fiber was cooled down to room temperature naturally. Scanning electron microscopy (SEM, JEOL JSM-6390A) was employed to characterize the microstructure of the carbon layer.

2.3. CFRCs fabrication

A dry dispersive process was utilized to make the carbon fiber homogenous in the cement for avoiding the use of cellulose. Pretreated carbon fiber and dry cement powder were firstly added into a pan mixusageer to blend for about 20 min, until the dispersive uniform condition was achieved. The obtained mixture, Fe_2O_3 microparticles, polyocarboxy acid super-plasticizer, sodium citrate, defoamer and water were then subsequently put into a bowl of JJ-5 mortar mixer orderly and mixed for 3–5 min for acquiring a good workability. Afterwards, mixture paste was got, which was poured into an oiled mould (40 × 40 × 160 mm^3) and compacted by a GZ-85 electric vibrator to diminish air bubbles. Finally, the as-received sample was demoulded after 24 h and cured in air at room temperature and relative humidity of about 95% for three days.

During above fabrication, proportions of the raw materials were fixed for all CFRCs sample, except for the carbon fiber with different thickness of pyrolytic carbon layer. The samples were labeled respectively with CFRC-0PR, CFRC-0.5PR, CFRC-1.0PR, CFRC-3.0PR and CFRC-5.0PR, to represent control sample (with original carbon fiber) and CFRCs with carbon fiber pretreated by phenolic solution with weight percent of 0.5, 1.0, 3.0 and 5.0 wt%.

2.4. Seebeck coefficient and electrical conductivity measurement

In this work, Seebeck coefficient and electrical conductivity measurement were performed simultaneously by a home-made apparatus. A temperature range from 35 to 80 °C was adopted in these measurements because the energy harvesting application of CFRCs are focused on road surfaces which temperature increased quickly and can approach above 60 °C under strong solar radiation in summer. The as-received CFRCs specimens were cut into smaller ones with size of 10 × 10 × 40 mm^3, whose two opposite end surfaces (10 × 10 mm^2) were polished by sand paper and coated by silver paste. The samples were subsequently placed into an insulation container. Heat was applied on one of the square ends of each sample by a small platelet resistance heater. The ambient temperature of the sample was also heated in succession to follow the square end temperature, and held a difference of about 5 °C. All the temperatures were actively controlled by two thermostats (Shimaden FP-93, Shimaden Co., Ltd) and increased at a rate of 0.01 °C/s for achieving thermal equilibrium of the system