

Research Article

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Effect of nano and micro conductive materials on conductive properties of carbon fiber reinforced concrete

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Abstract: In this study, the pressure sensitivity and temperature sensitivity of the diphasic electric conduction concrete were investigated by measuring the resistivity using the four-electrode method. The diphasic electric conduction concrete was obtained by mixing nano and micro conductive materials (carbon nanofibers, nano carbon black and steel slag powder) into the carbon fiber reinforced concrete (CFRC). The results indicated that, with the increase of conduction time, the resistivity of CFRC decreased slightly at the initial stage and then became steady, while the resistivity of CFRC containing nano carbon black had a sharp decrease at the dosage of 0.6%. With the increase of compression load, the coefficient of resistivity variation of CFRC containing nano carbon black and steel slag powder changed little. The coefficient of resistivity variation increased with the increase of steel slag powder in the dry environment, and CFRC had preferable pressure sensitivity when the mass fractions of carbon fiber and carbon nanofiber were 0.4% and 0.6%, respectively. Besides, in the humid environment, the coefficient of resistivity variation decreased with the increase of steel slag powder, and the diphasic electric conduction concrete containing 0.4% carbon fibers and 20% steel slag powder had the best pressure sensitivity under the damp environment. Moreover, in the dry environment, CFRC containing nano and micro conductive materials presented better temperature sensitivity in the heating stage than in the cooling stage no matter carbon nanofiber, nano carbon black or steel slag powder was used, especially for the CFRC containing steel slag powder.

Keywords: carbon fiber reinforced concrete, carbon nanofibers, pressure sensitivity, temperature sensitivity

1 Introduction

The traditional cement-based materials have many disadvantages due to large shrinkage during cement hydration and low durability [1–4]. In order to make up the disadvantages of traditional concrete, many researchers have conducted a lot of experiments, in which various fibers were added into the matrix to improve the concrete performance. The commonly used fibers are carbon fibers, steel fibers, polypropylene fibers, polyvinyl alcohol fibers and so on [5–9]. Among these fibers, carbon fibers are more suitable than the other fibers in respect of finishability, weatherability, mixability, thermal resistance and long-term chemical stability in unstable environments [10]. Carbon fiber reinforced concrete (CFRC) is a new composite material in which an appropriate amount of carbon fibers were distributed uniformly throughout the ordinary concrete, and CFRC can be used as a kind of smart concrete in health monitoring and intelligent diagnosis of concrete structure [11–14]. CFRC is the perfect combination of traditional construction materials and advanced reinforced materials. On one hand, CFRC possesses excellent compressive strength, and on the other hand, it has better fracture toughness and higher flexural strength than traditional concretes [15,16].

A large number of large-scale civil engineering structures are being constructed each year all over the world. To guarantee the safety, integrality, applicability and durability of these structures, some effective methods must be taken to monitor and evaluate their security status, repair efficiency and damage control. Related study results indicate that some conductive phase materials can be used to prepare conductive concrete composites, the electrical conductivity of which can be applied in the damage intelligent diagnosis of

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structures [17]. According to the conductive phase materials, conductive concretes can be divided into three types, including carbon conductive concretes, metal conductive concretes and polymer conductive concretes [18]. Among these conductive concretes, CFRC is the popular one because CFRC exhibits many other excellent properties besides electrical conductivity. Compared with the ordinary concrete, CFRC is attractive also due to its other excellent characteristics, such as the pressure sensitivity, temperature sensitivity, electromagnetic shielding properties and especially the remarkable conductive properties [19].

Although CFRC has excellent conductive properties, some other conductive phase materials are still needed to improve the pressure sensitivity, temperature sensitivity, electromagnetic shielding properties and other conductive properties of CFRC. During the last several years, with the development of nanoscale materials, more and more researchers not only paid attention to the concrete containing carbon fibers, steel fibers, steel slag and carbon black but also began to explore the concrete composite containing nano and micro conductive materials, such as nano-SiO₂, nano carbon black, carbon nanotubes and carbon nanofibers [20–25]. Among these nanoscale materials, nano carbon black, carbon nanotubes and carbon nanofibers are satisfactory nano conductive phase materials. As a result, carbon nanofibers, nano carbon black and the traditional steel slag powder are used in this study to improve the properties of CFRC.

The resistivity of CFRC is much lower in comparison with traditional concrete. Under the external pressure, the internal structure of CFRC will change, and its resistivity will change in turn, which can be called pressure sensitivity of CFRC. The coefficient of resistivity variation of the concrete is often used to evaluate the pressure sensitivity of CFRC. In general, under the external pressure, the resistivity increases with the increment of pressure, and coefficient of resistivity variation also increases with the increment of pressure. Under the same pressure, CFRC with higher coefficient of resistivity variation exhibits better pressure sensitivity. Numerous related studies have been conducted since 1970s to investigate the effectiveness of carbon fibers on the various properties of concretes. Chen and Chung studied the stress and resistivity changes of CFRC; the results indicated that the safety state of concrete can be reflected by changes in resistivity under the action of load [26]. Zhou *et al.* found that the addition of sodium carboxymethylcellulose can significantly improve the dispersity of carbon fiber in CFRC [27]. Yao and Wang tested the resistivity of CFRC, respectively, using the

two-electrode method and four-electrode method, and they found that the resistivity of CFRC can be accurately reflected by the four-electrode method [28]. Bontea *et al.* studied the resistivity changes of CFRC under constant amplitude cyclic loading, and the result indicated that the small damage inside can be reflected on the change in resistivity [29]. Huang *et al.* studied the resistivity changes of CFRC which they laid on the top and bottom of a beam under different load conditions and found that the resistivity of upper CFRC decreased with the increase of load while the resistivity of lower CFRC increased with the increase of load [30]. The results of Yao *et al.* indicated that the thermoelectric power of the cement mortar can be increased by 2.6 times with the addition of carbon nanotubes (in the rate of 0.5% by weight of cement) and carbon fibers [31]. Based on their test results, Chen and Ding concluded that CFRC presented good electrical conductivity with the addition of nano carbon black [32]. Metaxa *et al.* found that the addition of carbon nanofibers can restrict the generation of micro cracks in cement mortar [33]. The results of Gao *et al.* showed that the self-compacting concrete exhibited good electrical conductivity after adding carbon nanofibers with 1–2% volume dosage [34]. Tang *et al.* concluded that the resistivity of the concrete decreased with the addition of steel slag powder and its stability was improved [35]. Jia *et al.* carried out a series of experiments and they found that the pressure sensitivity of the concrete became more evident when >50% steel slag powder (by weight of cement) was added into the concrete [36].

Though, in the previous studies of the above-mentioned researchers, the resistivity, pressure sensitivity, temperature sensitivity and other properties of CFRC, which make the conductive phases inside the self-induced concrete more understandable, have been discussed, the addition of nano and micro conductive materials may have a certain effect on conductive properties of CFRC, and only a few related research results can be found at present. For this reason, the diphasic electric conduction concrete was prepared by mixing nano and micro conductive materials into CFRC to investigate the effect of carbon nanofibers, nano carbon black and steel slag powder on conductive properties of CFRC. The pressure sensitivity and temperature sensitivity of the diphasic electric conduction concrete were investigated by measuring resistivity using the four-electrode method. It is expected that the synergetic effects of carbon nanofibers, nano carbon black and steel slag powder could significantly improve the conductive properties of concrete composite.

2 Experiments

2.1 Materials

In this study, the carbon fibers used were isotropic pitch-based chopped fibers with the length of 6 mm, and the dosage of fibers was 0.4% by weight of cement. Ordinary Portland cement (P.O42.5 by Chinese standards) was used. The coarse aggregate used in this study was broken rock with the maximum particle size of 10 mm, and the fine aggregate was river sand. In the study of Wang et al., sodium carboxymethylcellulose with the content of 0.3% by weight of cement was used as the dispersant of carbon fibers [37]. In this study, sodium dodecyl sulfate in the same amount as carbon nanofibers was used as the dispersant of carbon nanofibers [38]. Besides, tributyl phosphate in the amount of 0.03% by weight of cement was used as the defoamer. FDN water-reducing agent in the amount of 0.5% by weight of cement was used to adjust the workability of the fresh concrete. The water–binder ratio was set at 0.50. The mix proportion of concrete is shown in Table 1.

Carbon nanofibers in the amount of 0.2%, 0.4% and 0.6% by weight of cement were used. Nano carbon black in the amount of 0.4%, 0.6% and 0.8% by weight of cement was used. Steel slag powder in the amount of 5%, 10% and 20% by weight of cement was used. The properties of carbon nanofibers, nano carbon black and steel slag powder are given in Tables 2, 3 and 4, respectively. The contents of these nano and micro conductive materials of each mix are shown in Table 5.

2.2 Experiment methods

In the resistivity test, direct current (DC) electrical resistivity measurement was established in the stress axis

Table 3: Chemical compositions of steel slag powder

MgO (%)	CaO (%)	SiO ₂ (%)	Fe ₂ O ₃ (%)	Fe (%)	MnO (%)
6	40	10	28	3	6

of the specimen, and the resistivity was measured using the four-electrode method. The four contacts of the electrode were symmetrically positioned with respect to the mid-point along the length of the specimen. The outer contacts (120 mm away from the mid-point) were set for the purpose of passing current. The inner contacts (90 mm away from the mid-point) were set in order to measure the voltage. Figure 1 shows the measuring device of resistivity.

The resistivity of concrete can be calculated as follows:

$$\rho = \frac{US}{IL}, \quad (1)$$

where U is the testing voltage, V; I is the testing current, A; S is the cross-section area of the specimen, cm²; and L is the distance between the two outer contacts, cm.

The coefficient of resistivity variation can be calculated as follows:

$$\eta = \frac{\rho_i}{\rho_0}, \quad (2)$$

where ρ_i is the resistivity of concrete in a certain state and ρ_0 is the resistivity of concrete in the initial state.

The strain-sensitive coefficient can be calculated as follows:

$$\beta = \frac{(\rho_0 - \rho_i)}{\rho_0(u_i - u_0)}, \quad (3)$$

where ρ_i is the resistivity of concrete in a certain state, ρ_0 is the resistivity of concrete in the initial state, u_i is the

Table 1: Basic mix proportion of concrete

Number	Cement (kg/m ³)	Water (kg/m ³)	Fine aggregate (kg/m ³)	Coarse aggregate (kg/m ³)
P	430.88	215.44	698.03	1,055.65

Table 2: Properties of carbon nanofibers

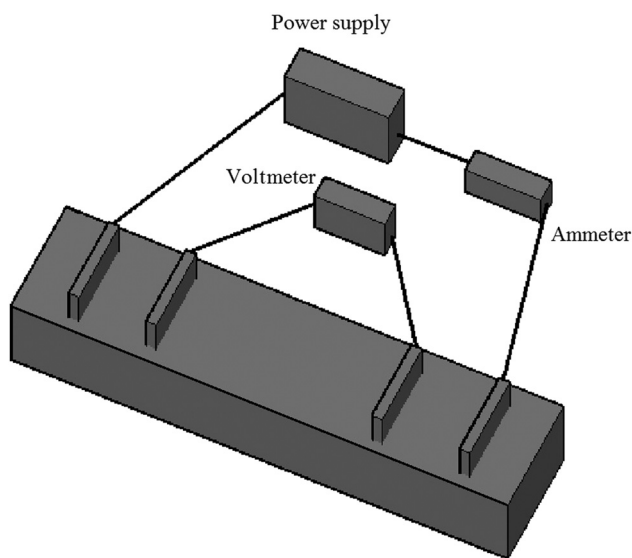
Content (%)	Diameter (nm)	Length (μm)	Specific surface (m ² /g)	Particle morphology	Apparent density (g/cm ³)	Electric conductivity (s/cm)
99.9	150–200	10–0	>20	Threadiness	0.043	150

Table 4: Properties of nano carbon black

Content (%)	Diameter (nm)	Specific surface (m ² /g)	Particle morphology	Density (g/cm ³)
99.9	40	500	Sphere	0.09

Table 5: Contents of nano and micro conductive materials

Mix no.	Carbon nanofiber (%)	Nano carbon black (%)	Steel slag powder (%)
A1	0	0	0
A2	0.2	0	0
A3	0.4	0	0
A4	0.6	0	0
A5	0	0.4	0
A6	0	0.6	0
A7	0	0.8	0
A8	0	0	5
A9	0	0	10
A10	0	0	20

**Figure 1:** Measuring device of resistivity.

stress of concrete in a certain state and u_0 is the stress of concrete in the initial state.

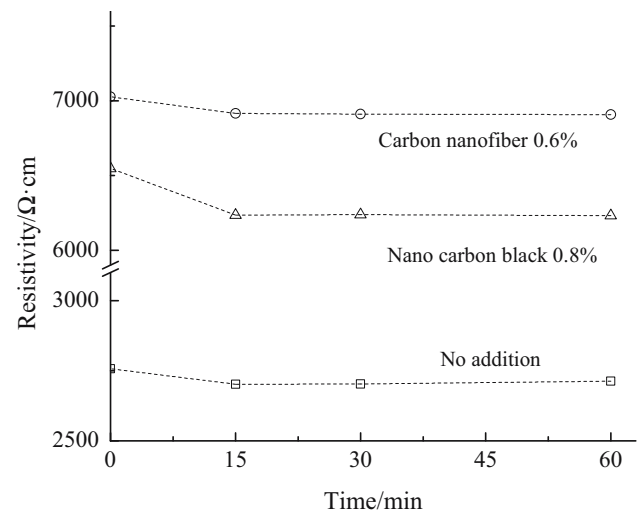
To obtain the pressure sensitivity of the diphasic electric conduction concrete, the measurement of coefficient of resistivity variation was carried out in the dry environment and humid environment. In this study, the specimens were placed in a thermostatic drying oven at 30°C for 1 d, and then at 20°C for 1 d to simulate the dry environment. The specimens were cured for 1 d in the curing room at the temperature of 20°C and humidity of 98% to simulate the humid environment. The loading range was 0–50 kN, with the loading rate of 2 kN/s.

The temperature sensitivity tests were measured in the dry environment with the temperature process of 20°C to 50°C and 20°C to –20°C, which was achieved by a thermostatic drying oven. The relationship between coefficient of resistivity variation and temperature can be obtained by this method. When the temperature was adjusted to a certain value, the coefficient of resistivity variation was obtained after keeping this temperature unchanged for 30 min.

3 Results and discussion

3.1 Effect of conduction time on resistivity of diphasic electric conduction concrete

Figure 2 shows the variation in resistivity of the CFRC containing conductive materials with the extension of conduction time. As shown in Figure 2, no matter carbon nanofiber, nano carbon black or steel slag powder was used, the resistivity of the concrete decreases slightly at the initial stage with the increase of conduction time. However, when the conduction time is >15 min, the resistivity of the concrete becomes steady, which may be because of the polarization effect with the extension of

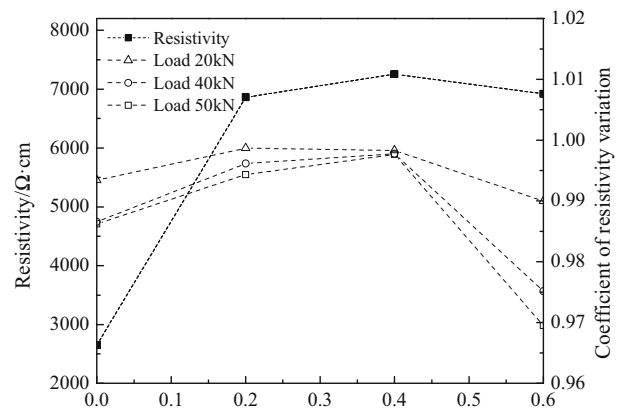
**Figure 2:** Relationship between conduction time and resistivity of CFRC.

conduction time. During the course of resistivity measurement of CFRC, after the electrode was charged with electricity, the electric current decreased little by little. At this moment, the electrode was reversed, and the reversed electric current increased rapidly. With the extension of charging time, the electric current decreased little by little again. The repeating change in electric current can be called the polarization effect. Therefore, the specimens were kept power on for 30 min to avoid unfavorable effect on resistivity of the concrete before testing.

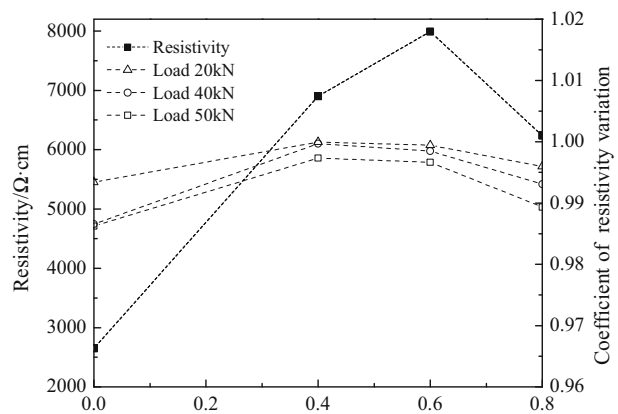
3.2 Pressure sensitivity of diphasic electric conduction concrete under compression loading

Figure 3 illustrates the resistivity and coefficient of resistivity of CFRC containing different nano and micro conductive materials with different dosages under compression loading. It can be seen from Figure 3 that the resistivity of CFRC containing lower content of nano and micro conductive materials varies little with the increase of nano and micro conductive material content. That is because in the dry environment, when carbon fiber content is low, the main electric conduction form inside the CFRC is tunneling effect electric conduction, and CFRC will be more compacted with the addition of nano and micro conductive materials, hence it is more difficult for internal carriers to go through the potential barrier of the diphasic electric conduction concrete. As a result, the resistivity of the CFRC containing nano and micro conductive materials is higher than that of the CFRC without nano and micro conductive materials in it. However, with the continuous increase of nano and micro conductive materials, the space occupied by nano and micro conductive materials inside the concrete is enlarged and meanwhile more internal overlapping conduction paths come into being, which causes the reduction of resistivity.

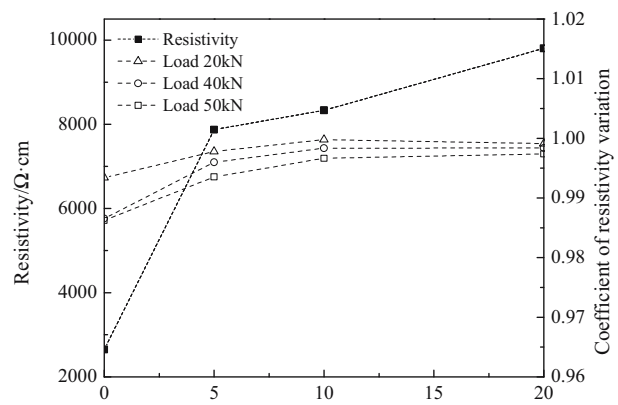
From Figure 3, it can be seen that the resistivity of CFRC containing carbon nanofiber and steel slag powder increases gradually with the increase of addition dosage except that there is a slight decline for the CFRC containing carbon nanofiber at the dosage of 0.4%. However, the resistivity of CFRC containing nano carbon black has a sharp decrease at the dosage of 0.6%. It can also be observed from Figure 3 that, when the ratio of nano and micro conductive materials is set at a certain value, the coefficient of resistivity variation varies, though not always quite obvious, with the increase of compression load, except for CFRC with carbon



(a)



(b)



(c)

Figure 3: Resistivity and coefficient of resistivity of CFRC under compression loading: (a) carbon nanofiber, (b) nano carbon black, (c) steel slag powder.

nanofibers that account for 0.6% by weight of cement. With the increase of compression load, the coefficient of resistivity variation of CFRC containing nano carbon black and steel slag powder changes little. The possible

reason is as follows: it is prone to form the overlapping mode between carbon fibers and carbon nanofibers inside the CFRC containing carbon nanofibers under the load, because carbon nanofiber has the greatest length–diameter ratio among the three types of nano and micro conductive materials. Therefore, the tunneling effect electric conduction was transformed to the overlapping electric conduction, which leads to an obvious variation of coefficient of resistivity. So according to the results in Figure 3, in the dry environment, with addition of carbon nanofibers (accounted for 0.6% by weight of cement) into the CFRC, the pressure sensitivity of CFRC is more significant than that with addition of nano carbon black or steel slag powder.

with the increase of steel slag powder. On the contrary, in the humid environment, the coefficient of resistivity variation decreased with the increase of steel slag powder. As can be seen from the relation curves in Figure 4, the pressure sensitivity of CFRC with the addition of steel slag powder accounted for 20% by weight of cement is the best in the damp environment. In the humid environment, the main electric conduction forms of CFRC are the tunneling effect electric conduction and ionic conduction. The concentration of the ions performing ionic conduction is enhanced with the addition of steel slag powder so that CFRC containing steel slag powder presents better pressure sensitivity than CFRC with no steel slag powder in it.

3.3 Pressure sensitivity of diphasic electric conduction concrete under different environments

The results of coefficient of resistivity variation with compressive loading under different environments are presented in Figure 4. It can be seen from the figure that the pressure sensitivity of multiphase conductive concrete in the humid environment is better than that of the concrete in the dry environment. In the dry environment, the coefficient of resistivity variation increased

3.4 Pressure sensitivity of diphasic electric conduction concrete under cyclic loading

Figure 5 presents the varying rules of the coefficient of resistivity variation and strain of CFRC containing carbon nanofibers and CFRC with no addition, respectively, under the repeat compressive loading in the dry environment. As shown in Figure 5, the CFRC containing carbon nanofibers presents good sensitivity and regularity under the loading effect. The strain-sensitive coefficient of

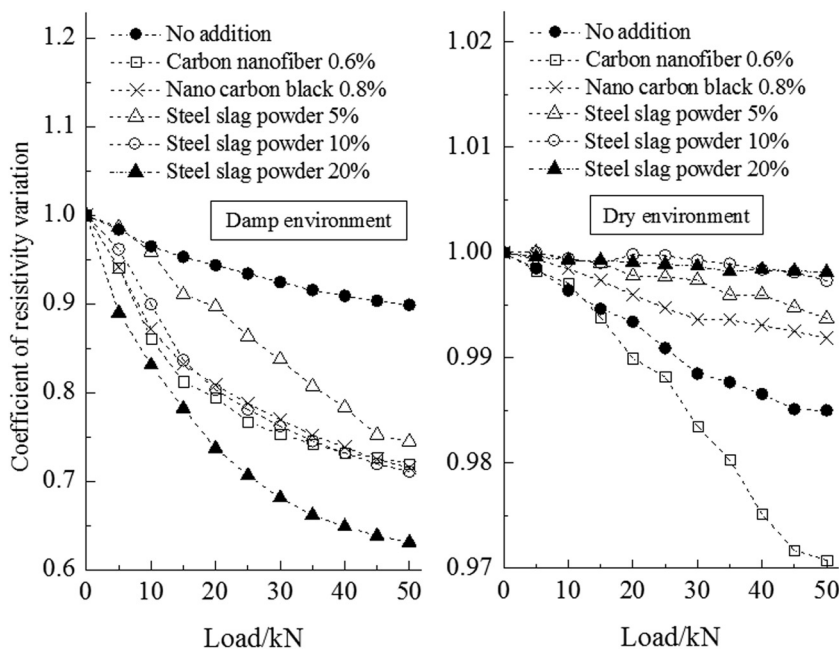


Figure 4: Relationship of load and coefficient of resistivity variation of CFRC.

CFRC containing carbon nanofibers accounted for 0.6% by weight of cement in the dry environment is 0.135, which is twice of the strain-sensitive coefficient of common CFRC in the dry environment.

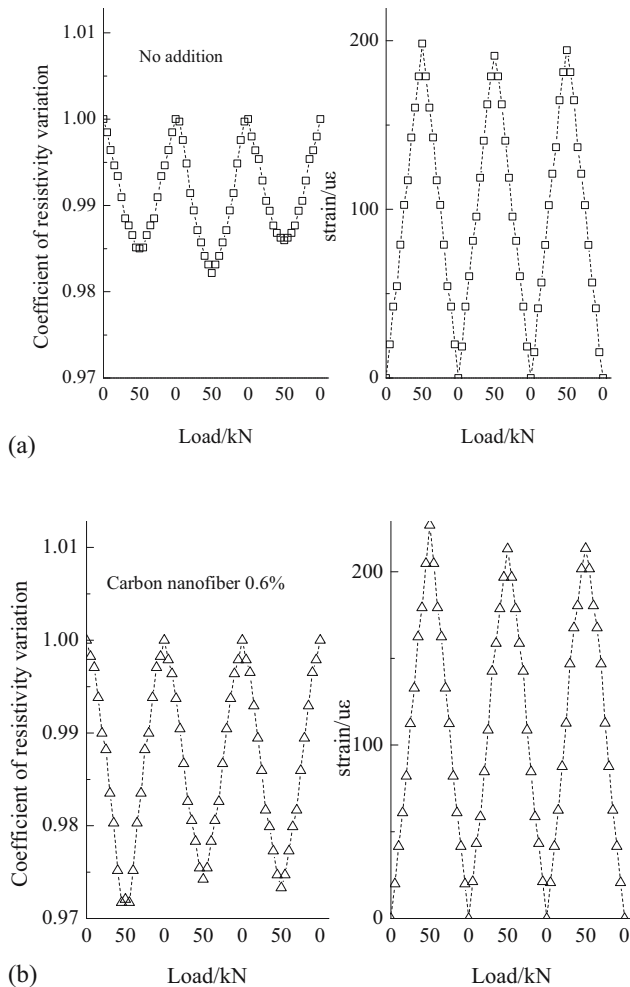


Figure 5: Relationship of coefficient of resistivity variation, strain and load: (a) no addition, (b) carbon nanofiber.

After moderate content of carbon nanofibers was added into CFRC, the resistivity of CFRC increased first and then decreased gradually with the increment in dosage. A large number of carbon nanofibers dispersing inside the concrete improve the degree of density of CFRC due to the small volume of tiny nanofibers, which increase the migration difficulty for the electrons among the carbon fibers. Some nanofibers were dispersing among the carbon fibers in large distance, and they formed the new migration channels for the electrons, which increased the resistivity of CFRC. However, with the further increase in dosage used, carbon nanofibers occupied larger scope and space inside the CFRC, and they formed electrical pathways with carbon fibers,

which decreased the resistivity of CFRC in turn. Compared with carbon nanofibers, nano carbon black is in micro powders and the particle size is much smaller than the length of nanofiber. As a result, it needs a larger amount of nano carbon black to form excellent electrical pathways with carbon fibers. Therefore, there is a sharp decrease in resistivity of CFRC after the dosage of nano carbon black is beyond 0.6%. With the addition of steel slag powder in CFRC, the resistivity of CFRC increased gradually as the content of steel slag powder was increasing continuously, which may be due to the difference in conductive mechanism of steel slag powder in CFRC compared with carbon nanofibers and nano carbon black.

3.5 Temperature sensitivity of diphasic electric conduction concrete

The relationship between temperature and coefficient of resistivity variation of CFRC containing different nano and micro conductive materials is shown in Figure 6. There are eight curves in Figure 6 for the four mixes (no addition, 0.6% carbon nanofiber, 0.8% nano carbon black and 5% steel slag powder), and each mix has two curves. The contents of nano and micro conductive materials in CFRC are controlled at 1%, approximately. According to the chemical composition of steel slag powder, the conductive material in steel slag powder accounts for only 20% of the total weight; therefore, steel slag powder in the amount of 5% by weight of cement should be added in CFRC. As can be seen from Figure 6, the effect of nano and micro conductive materials on coefficient of resistivity variation in the process of temperature decreasing under freezing point is different from that in the process of temperature increasing above freezing point. The coefficient of resistivity variation of diphasic electric conduction concrete is decreasing gradually when the temperature increases from -20°C to 50°C after the specimens were kept power on for 30 min. During the course of rise in temperature, the temperature sensitivity of the diphasic electric conduction concrete seems to be steady, which can be observed from the curves' tending to be linear. The diphasic electric conduction concrete presents better temperature sensitivity than the common CFRC with no addition. As can be seen from Figure 6, relation curves of steel slag powder are the steepest ones, which means that the CFRC added with steel slag powder (in the amount of 5% by weight of cement) shows the best

temperature sensitivity. CFRC containing nano and micro conductive materials presents better temperature sensitivity in the heating stage than in the cooling stage, especially for the CFRC containing steel slag powder.

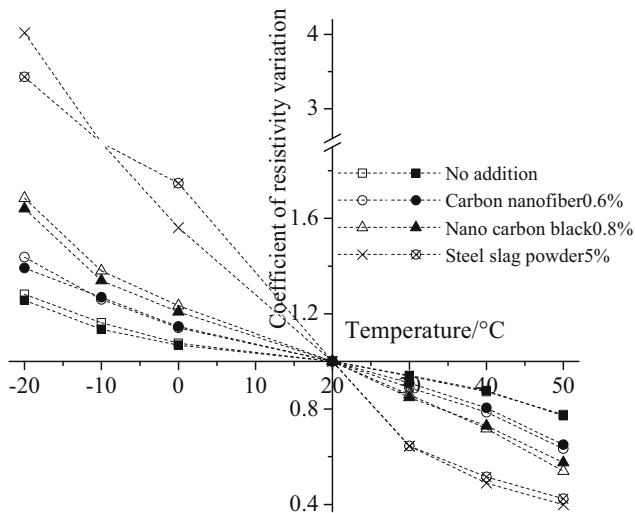


Figure 6: Relationship between temperature and coefficient of resistivity variation.

The testing results of the temperature sensitivity of the CFRC containing steel slag powder (accounted for 5% by weight of cement in dry environment) can be analyzed by the method of least squares to obtain the curves of relationship between temperature (x) and coefficient of resistivity variation (y).

During the heating stage, the relationship can be expressed as follows:

$$y = 66.87 - 295 \exp(-x/13) \quad (20 \leq x \leq 50). \quad (4)$$

During the cooling stage, the relationship can be expressed as follows:

$$y = 0.685 - 0.97 \exp(-0.061x) \quad (-20 \leq x \leq 20). \quad (5)$$

During the heating stage, the number of the internal carriers inside CFRC changes with the change of temperature. When the temperature is rising, the internal carriers inside the CFRC can go through the barrier more easily because of more energy absorbed, which caused the decrease in coefficient of resistivity variation. For diphasic electric conduction concrete, the addition of nano and micro conductive materials leads to the increase in number of internal carriers and then forms some new conductive channels. Therefore, the diphasic electric conduction concrete has better temperature sensitivity in the process

of temperature change. Due to the presence of the conductive ions, there is scattering effect in the diphasic electric conduction concrete. With the scattering effect being more significant at low temperature, the change rate of the coefficient of resistivity variation is higher during the cooling stage compared with that during the heating stage. For CFRC containing steel slag powder, the addition of steel slag powder increases the amount of internal carriers and the scattering effect becomes more evident. Therefore, CFRC can obtain the preferable temperature sensitivity with the addition of the steel slag powder (in amount of 5% by weight of cement). The coefficient of resistivity variation of CFRC containing steel slag powder (accounted for 5% by weight of cement) reaches 4, which is 10 times higher than that of the common CFRC.

4 Conclusions

This study concerns the experimental results of the conductive properties of CFRC containing nano and micro conductive materials (i.e., the carbon nanofibers, nano carbon black and steel slag powder). The following conclusions can be drawn from the analysis results presented in this paper:

1. With the increase of conduction time, the resistivity of the CFRC decreased slightly at the initial stage and then became steady no matter carbon nanofiber, nano carbon black or steel slag powder was used. The resistivity of CFRC containing nano carbon black had a sharp decrement at the dosage of 0.6%. With the increase of compression load, the coefficient of resistivity variation of CFRC containing nano carbon black and steel slag powder changed little.
2. In the dry environment, the coefficient of resistivity variation increased with the increase of steel slag powder, and CFRC had preferable pressure sensitivity when the mass fraction of carbon fiber and carbon nanofiber was 0.4% and 0.6%, respectively. In the humid environment, the coefficient of resistivity variation decreased with the increase of steel slag powder, and the diphasic electric conduction concrete containing 0.4% carbon fibers and 20% steel slag powder had the best pressure sensitivity.
3. In the dry environment, CFRC containing nano and micro conductive materials presented better temperature sensitivity in the heating stage than in the cooling stage no matter carbon nanofiber, nano carbon black or steel slag powder was used, especially for the CFRC containing steel slag powder.

Conflict of interest: The authors declare no conflict of interest regarding the publication of this paper.

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