Microstructure and pressure-sensitive properties of cement-based composite with Ni nanowires

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HIGHLIGHTS

- We fabricate pressure-sensitive Ni nanowire/cement composite.
- Microstructures of Ni nanowires and Ni nanowires/cement composite are observed.
- Electrical resistivity and piezoresistivity of Ni nanowires/cement composite are examined.

ARTICLE INFO

ABSTRACT

Pressure-sensitive Ni nanowire/cement composites are fabricated using Ni nanowires as conductive filler. The Ni nanowires are obtained using an alternating current electro-deposition method by means of porous alumina template. Polycarboxylate superplasticizer as dispersing agent is applied. The microstructures, electrical resistivity and piezoresistivity of Ni nanowires/cement composites are examined. The results indicate that the Ni nanowires with the mean diameter of about 65nm and aspect ratio of 50 are well dispersed in the cement matrix. The surfaces of Ni nanowires are passivated with the oxide compound of $Ni(OH)_2$ and NiO, influencing their electrical conductivity. The variation in the electrical resistivity of Ni nanowire/cement composite with the increase of Ni nanowire volume fraction displays a typical percolation phenomenon. In addition, the strain sensitivity coefficient of Ni nanowires/cement composite with 0.75 vol% Ni nanowires under uniaxial compression is 2354.6, far higher than those for the other pressure-sensitive cement-based composites.

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1. Introduction

Health monitoring of concrete structure is imperative for the detection of anomalies in the structure's performance, which will help engineers and owners in making a timely decision on its maintenance for preventing the potential accident. For structural health monitoring, pressure-sensitive cement-based composite is one of the most suitable candidate materials as embedded sensor to sense the stress, crack or damage due to the natural compatibility with the concrete. This composite is fabricated by adding some conductive fillers into traditional cement matrix to enhance its sensing ability. When the composite is stressed under external force, the conductive network inside is changed, thus affecting its electrical behaviors. Accordingly, the stress, crack or damage can be detected through measuring the electrical properties of the composite [1,2].

The cement matrix has no or poor sensing ability, so the sensing property of the composite is dominated by the conductive filler. So far, a variety of filler materials have been applied, which can be classified into particle fillers and fibrous fillers according to their shapes[2]. Compared with the particle fillers, the fibrous fillers having high aspect ratios (i.e. ratio of length to diameter) are prone to form the conductive network more easily, which can make the fibers modify the sensing ability of composite at a lower concentration. Such favorable effect is further increased when the size of fibrous filler is decreased from micro-scale to nano-scale. Besides, the application of fibers at the nano-scale as reinforcing materials can improve more obviously the mechanical properties of composite because they can be distributed on a much finer scale than commonly used reinforcing fibers [3]. As a result, the nano-scale fibers are highly desirable for the fabrication of pressure-sensitive cement-based composites with good mechanical properties and high sensitivity.

By now, carbon nanofiber and carbon nanotube are the only available nano-scale fibers that reported in literatures. Many

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efforts have been made on the application of carbon nanofiber and carbon nanotube in the cement matrix due to their excellent mechanical properties and electrical conductivity [4–6]. However, carbon nanofiber and carbon nanotube are extremely difficult to be uniformly dispersed in the cement matrix due to their high hydrophobicity and strong self-attraction. Besides, their chemical stabilities make the surface modification for improving their dispersing effects difficult to be achieved. Such a result leads to the weak homogeneity and repeatability of composite, and the reduction in the mechanical properties and stability of stress sensitivity [7,8]. Contrasted to carbon nanofiber and carbon nanotube, Ni nanowires are hydrophilic, and are easier to carry out the surface modification due to the relatively higher chemical activity. Based on this, a different dispersing behavior for the Ni nanowires in the cement matrix can be anticipated. Moreover, Ni nanowires have good corrosion resistance, high electrical conductivity and mechanical strength [9], which is promising for the application as the conductive filler in cement matrix.

In this paper, we attempt to fabricate the pressure-sensitive Ni nanowire/cement composite using Ni nanowires as conductive filler. The Ni nanowires are obtained using an alternating current electro-deposition method by means of porous alumina template. For improving the dispersion of Ni nanowires in the cement matrix, polycarboxylate superplasticizer as dispersing agent is applied. The microstructures of as-obtained Ni nanowires and Ni nanowires/cement composites are studied by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), energy-dispersed X-ray spectrometry (EDS) and X-ray photoelectron spectroscopy (XPS). Besides, the electrical resistivity and piezoresistivity of Ni nanowires/cement composites are examined.

2. Experimental section

2.1. Materials

Al foils with the purity of 99.999% and thickness of 0.3 mm were used. The cement was No. 42.5 ordinary Portland cement made in China. Its oxide composition was indicated in Table 1. The dispersing agent was PCA®-I polycarboxylate superplasticizer from Subote New Material Co., Ltd, China. Deionized water was employed to prepare the various electrolytic solutions and cement-based composite. Moreover, all chemical reagents in this study were analytically pure.

2.2. Preparation of Ni nanowire/cement composite

A two-step aluminum anodic oxidation technique, which had been described elsewhere [10], was applied to prepare the porous alumina template. The anodization was carried out in 0.3 M oxalic acid solution at 40 V and 0–5 °C. Subsequently, the as-prepared alumina template was placed into the electrolytic solution of 110 g·L^{-1} NiSO$_4$·6H$_2$O and 40 g·L^{-1} H$_3$BO$_4$ at 30 °C to carry out the alternating current electro-deposition. During this process of electro-deposition, the pH value of the solution was maintained at 4.0–5.0. Besides, the applied voltage and AC frequency were kept constant at 20 V and of 200 Hz, respectively. The duration of electro-deposition was 25 min. After this, the electrodeposited alumina template was taken out, and soaked in 1 mol·L^{-1} NaOH to remove the alumina. The Ni nanowires liberated from alumina template were dipped into 0.25 mol·L^{-1} H$_2$SO$_4$ for 5 min to remove the oxide layer on their surfaces. A manual mixing was gently applied for preventing mechanical damage of Ni nanowires. Then, the nanowires were cleaned and dried at 60 °C in a vacuum of about 10^{-3} Pa.

The as-obtained Ni nanowires were used as the conductive filler to fabricate the pressure-sensitive Ni nanowire/cement composite. The polycarboxylate superplasticizer was served as dispersing agent to disperse the Ni nanowires in the composite. The composition of cement matrix had the mass ratio of 1:0.5:0.008 for cement: water: superplasticizer. The Ni nanowires with the volume fractions of 0.25%, 0.5%, 0.75%, 1.0% and 1.25% were added, respectively. Besides, the control sample without the addition of Ni nanowires was also prepared. Initially, the dispersing agent and

water were thoroughly mixed. Subsequent to this, the Ni nanowires were added into the mixed solution. After the mixture was submitted to a pulse of sonication for 15 min, it was mixed with the cement by mechanically stirring at an initial slow speed for 2 min and then a fast speed for 2 min. Then, the slurry was poured into a plastic mould, and four stainless meshes were embedded along the length of mould at identical intervals (see Fig. 1). After the waiting time of 1 d, all the Ni nanowire/cement composite specimens (1 cm × 1 cm × 4 cm) were demoulded and then cured in a 95% humidity chamber at 20 ± 2 °C for 27 d.

2.3. Characterization

The morphologies of as-obtained nanowire array and Ni nanowire/cement composite were observed by scanning electron microscopy (SEM: SU8010 operating at 15 kV). Transmission electron microscopy (TEM: Hitachi800 working at 200 kV) was employed to survey the Ni nanowires liberated from the porous alumina template. The X-ray diffraction instrument (XRD: DX-2700 diffractometer with Cu Ka radiation) was applied to measure the crystalline structure of prepared Ni nanowires. The surface composition of Ni nanowire in the composite was decided by energy-dispersed X-ray spectrometry (EDS) attached to the SEM. Besides, X-ray photoelectron spectroscopy (XPS) (ESCALASB 250Xi, ThermoScientific, USA) measurements were performed to analyze the chemical states of elements on the surface of Ni nanowires. The deconvolution and spectral line fitting were carried out using the software of XPSPeak 41.

The electrical resistivity of Ni nanowire/cement composite was measured by a four-probe method as shown in Fig. 1. DC-stabilized power source was applied to supply the current in the circuit. Voltage V and current I in the circuit were measured with multimeters Keithley 2100. Electrical resistivity ρ was calculated from the measured voltage V and current I by the following equation:

$$\rho = \frac{V \cdot S}{A \cdot L} \tag{1}$$

where S, L were the cross-sectional area of Ni nanowire/cement composite specimen and distance between the two inner stainless meshes, respectively.

A compressive experiment was performed with load control using a hydraulic mechanical testing system (MTS) with a loading capacity of 100 kN maximum (see Fig. 2). The applied cyclic compressive loading was ranged from 0.5 MPa to 8.0 MPa, and the loading rate was 0.05 kN/s. All the results were automatically collected through a data logger. All the experiments were carried out at room temperature.

3. Results and discussion

3.1. Microstructures of prepared Ni nanowire and composite

Fig. 3(a) indicates the SEM image of porous alumina template prepared by two-step anodic oxidation technique. It can be seen that pores with high density are regularly arrayed throughout the template. The diameters of pores are ranged from 45 nm to 80 nm, and have a mean value of about 65 nm, which is clearly indicated by the corresponding statistical distribution of pore diameters (see Fig. 3(b)). Due to the restricted growth of Ni nanowires in the pores, it is assumed that the prepared Ni nanowires have the same diameters. The SEM image of prepared Ni nanowires is presented in Fig. 4. It can be found that a large amount of Ni nanowires have been successfully prepared using the alternating current electro-deposition method by means of the porous alumina template. For the SEM observation of Ni nanowires, the electrodeposited alumina template has been dissolved partly by chemical etching in 5 wt% NaOH solution to expose the Ni nanowires in the pores. Due to the loss of support from the alumina, the Ni nanowires are prone to be tilted and gathered into bundles. Furthermore, the TEM images clearly show that the prepared Ni nanowires have a smooth surface, and exhibit continuously uniform diameters along their lengths (see Fig. 5). Besides, the length of Ni nanowires is more than 3.0 μm, and thus the aspect ratio is about 50. The XRD pattern of prepared Ni nanowires is indicated

Table 1
Oxide composition of cement used in this study (% w/w).

Oxide	CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	K$_2$O	Na$_2$O	SO$_3$	Ignition loss
Composition (wt.%)	56.87	25.19	9.52	3.11	0.86	1.03	1.08	0.98	1.96