The influence of multi-walled carbon nanotubes (MWCNTs) mixed with silica fume (SF) on the mechanical property of cement-based composites was investigated. Results indicate that SF particles have a favorable dispersion effect on MWCNTs and MWCNTs can be dispersed uniformly in cement matrix when mixed with SF particles. MWCNTs mixed with SF can decrease the sample porosity and the amount of harmful pores and delay the formation process of micro cracks in the cement paste, improving the strength of specimens effectively. The compressive strength of the sample filled with 10% SF reaches maximum when the MWCNT addition is 0.15% and the flexural strength of the sample filled with 0.08% MWCNTs and 10% SF reaches maximum, the increase percent of flexural strength and compressive strength is both above 35%, displaying well reinforcement effect of MWCNTs mixed with SF particles on the mechanical properties of cement-based composites.

Keywords: Multi-walled carbon nanotubes; Silica fume; Cement-based composites; Mechanical properties

1. Introduction

Carbon nanotubes (CNTs), as a one-dimensional nanomaterial, possess a high aspect ratio, large specific surface area and superior electrical conductivity and they have been extensively studied in recent years due to their unusual mechanical, electrical and chemical properties [1,2]. CNTs can be considered as the curling up of graphene layers and they are divided into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) according to the number of graphene sheets. CNTs are suitable for making many excellent composites owing to their extraordinary qualities and MWCNTs have aroused increasing scientific and research interest due to the easier production and lower price compared with SWCNTs [3,4].

There is strong intermolecular Van der Waals force between CNTs, which makes CNTs bundle and agglomerate each other. Therefore, the dispersibility of CNTs in the matrix is one of the key factors that affects the properties of CNTs reinforced composites. Up to now, the dispersion methods of CNTs in the matrix can be classified as mechanical stirring, ultrasonic treatment, surfactant method and surfactant ultrasonic treatment [5-7]. Silica fume (SF), a byproduct of ferrosilicon or industrial silicon production, has small particle size, large specific surface area and high pozzolanic reactivity [8-10]. SF has been widely used as an addition in cement and concrete composites to improve the physical and mechanical properties of cement-based materials. SF particles can act as a lubricant to promote the dispersion of micro-nano fibers in cement matrix and improve the interface bonding between carbon nanomaterials and cement paste [11-14].

The enhancement effect of CNTs/SF on the mechanical properties of cement-based materials was studied and the effect of SF on the dispersion of CNTs in cement-based materials was analyzed in this paper.

2. Experimental

2.1. Raw materials

MWCNTs purchased from Shenzhen NANO-Technology Co., Ltd (Shenzhen, China) were obtained by catalytic decomposition method and their physical parameters are shown in Table 1. The microscopic images of MWCNTs in aqueous solution are shown in Figure 1. The chemical composition and physical properties of Type P-O 42.5R Portland cement produced by Dalian Onoda Cement Co., Ltd (Dalian, China) are shown in Table 2 and Table 3. The microsilica used in the experiment was provided by Shanghai Elkem International Trade Co., Ltd (Shanghai, China) and its physical parameters are shown in Table 4. The polycarboxylate superplasticizer used was provided by Dalian Mingyuanquan Science and Technology Development Co., Ltd. (Dalian, China). The fine aggregate used was China ISO Standard Sand produced by Xiamen ISO Standard Sand Co., Ltd

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(Xiamen, China). Distilled water was chosen as the test water. All the physical data were provided from the manufacturing company’s reports.

![Fig. 1 - Representative TEM images of MWCNTs dispersed using an ultrasonic processing method with anionic gum Arabic: (a) some MWCNTs uniformly; (b) a single MWCNT.]

### Table 1

<table>
<thead>
<tr>
<th>Product</th>
<th>Diameter (nm)</th>
<th>Length (µm)</th>
<th>Purity (%)</th>
<th>Specific surface area (m²·g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNTs</td>
<td>20-40</td>
<td>5-15</td>
<td>&gt;97</td>
<td>90-120</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>SO₃</th>
<th>MgO</th>
<th>Na₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>61.13</td>
<td>21.45</td>
<td>5.24</td>
<td>2.89</td>
<td>2.50</td>
<td>2.08</td>
<td>0.77</td>
</tr>
</tbody>
</table>

### Table 3

<table>
<thead>
<tr>
<th>Loss on ignition (%)</th>
<th>Setting time (min)</th>
<th>Specific surface area (m²·kg⁻¹)</th>
<th>Bending strength (MPa)</th>
<th>Compressive strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.52</td>
<td>187</td>
<td>239</td>
<td>300</td>
<td>28.5</td>
</tr>
</tbody>
</table>

### Table 4

<table>
<thead>
<tr>
<th>Product</th>
<th>SiO₂ content(%)</th>
<th>Specific gravity(g·cm⁻³)</th>
<th>Average particle(µm)</th>
<th>Specific surface area(m²·g⁻¹)</th>
<th>Density(kg·m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF</td>
<td>97.5</td>
<td>1.94</td>
<td>0.15</td>
<td>23</td>
<td>312</td>
</tr>
</tbody>
</table>

### Table 5

<table>
<thead>
<tr>
<th>Number</th>
<th>Water cement ratio</th>
<th>Sand cement ratio</th>
<th>SF (%)</th>
<th>MWCNTs (%)</th>
<th>Polycarboxylate superplasticizer, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1#</td>
<td>0.35</td>
<td>1.5</td>
<td>0</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>2#</td>
<td>0.35</td>
<td>1.5</td>
<td>10</td>
<td>0.05</td>
<td>1.0</td>
</tr>
<tr>
<td>3#</td>
<td>0.35</td>
<td>1.5</td>
<td>10</td>
<td>0.08</td>
<td>1.0</td>
</tr>
<tr>
<td>4#</td>
<td>0.35</td>
<td>1.5</td>
<td>10</td>
<td>0.15</td>
<td>1.0</td>
</tr>
<tr>
<td>5#</td>
<td>0.35</td>
<td>1.5</td>
<td>10</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>6#</td>
<td>0.35</td>
<td>1.5</td>
<td>0</td>
<td>0.08</td>
<td>1.0</td>
</tr>
<tr>
<td>7#</td>
<td>0.35</td>
<td>1.5</td>
<td>0</td>
<td>0</td>
<td>1.0</td>
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</tbody>
</table>
constant temperature (20±1°C). Blank samples, samples only added with SF and samples only added with MWCNTs were prepared at the same time, respectively.

2.3. Test method

The flexure strength of the samples was measured by three point bending test with an electronic hydraulic universal testing machine (WDW-50) at a 0.2 mm/min loading speed and a 100mm span. The compressive strength was measured by a computer control compression testing machine at a stress rate of 0.25 ± 0.05 MPa/s (WHY-300). The micro-morphology of samples was observed using a field emission scanning electron microscope (NOVA NANOSEM450, FEI Co.). In addition, the energy dispersive spectrum (EDS) analysis (Oxford INCA-7260, FEI Co.) and mercury intrusion test (AUTOPORE 9500) were performed as well. After mechanical properties tests, cement/CNFs composites samples were dried in an oven at 100 °C for about 12 hours, and crushed to testing samples - approximately 5×5×1 mm³. Prior to their observation, the testing samples were sputter-coated and a 10 nm thick Au film layer was coated onto enhance surface conductivity.

3. Results and discussion

3.1. The mechanical properties of MWCNTs/SF reinforced cement mortar

Figure 2 demonstrates the strength of SF reinforced cement mortar samples with different MWCNT addition at the age of 28 days. 1# sample is blank mortar sample. In the Figure 2 it can be observed that the mechanical strengths of the samples have been improved greatly when MWCNTs mixed with SF were added into cement composites. When the MWCNT addition is 0.15%, the compressive strength of 5# specimen reaches the maximum of 82.7MPa and increases by 37% compared to that of 1# sample. When the MWCNT addition is 0.08%, the flexural strength of 3# sample reaches the maximum of 13.3MPa and increases by 36%. It shows that the MWCNTs mixed with SF particles have a significant reinforcement effect on the strength of cement-based composites.

In Figure 3, the strengths of samples containing MWCNTs mixed with SF, of theirs added with MWCNTs and with SF respectively, were compared and analyzed. It can be observed in Figure 2 and Figure 3 that the strength of 6# sample filled with only 10% SF is slightly higher.

Fig. 2 - Mechanical properties of MWCNTs/SF reinforced cement mortar: (a) Compressive strength (b) Flexural strength.

Fig. 3 - Mechanical properties of MWCNTs reinforced cement mortars: (a) Compressive strength (b) Flexural strength.
than that of 1# sample. And the strength of 7# sample containing only MWCNTs is closely to that of 1# sample, indicating that the effect of MWCNTs added directly into cement composites on the strength is little owing to the agglomeration of MWCNTs in the cement samples. Figure 3 displays that the strengths of 3# sample containing MWCNTs mixed with SF are significantly higher than those of 6# and 7# samples. So it can be presumable that MWCNTs can be dispersed uniformly in cement-based materials when it is mixed with SF particles. So, MWCNTs mixed with SF particles can present superior reinforcement effect on the strength of cement composites.

3.2. The micro measurements results of MWCNTs/SF reinforced cement mortar samples

The EDS test results of SF reinforced cement mortar sample mixed with 0.08% MWCNTs are shown in Figure 4. Figure 4(a) is the test scanning area and the distribution of silicon, carbon and oxygen elements of the sample are shown in Figure 4(b), (c) and (d), respectively. As Figure 4(b) and (c) show, silicon element and carbon element both show a uniform distribution in the matrix. As is well known, there is Van der Waals force between MWCNTs, making it difficult for MWCNTs to be dispersed evenly in the cement matrix. SF particles which have micro-nano size and lubrication can destroy the intermolecular attraction between MWCNTs and make the most of MWCNTs be independently distributed. As a result, the interface bonding between MWCNTs mixed with SF particles and cement composites can be enhanced greatly. The uniform distribution of carbon elements in the cement matrix indicates that the dispersion of MWCNTs in cement material can be promoted by SF particles. The test result of element content in the scanning area is shown in Figure 4(e), of which carbon content is 9.06%, oxygen content is 52.19%, aluminum content is 0.94%, silicon content is 9.05%, calcium content is 25.64%. Thus the existence and distribution of MWCNTs in the scanning area are proved in the qualitative and quantitative aspects.

The mercury intrusion test results of MWCNTs/SF reinforced cement mortar samples are shown in Table 6. The data show that MWCNTs mixed with SF decrease the porosity of cement composites effectively and the total injected mercury volume and porosity of mortar samples decrease with the increase of MWCNTs content. The porosity of 5# cement mortar sample with 0.15% MWCNTs reaches the minimum of 8.43%, decreasing by 37.9% compared to that of 1# sample. Moreover, compared to the relative stable change of mesopore diameter (area) of the samples, we can see that the mesopore diameter (volume) decreases significantly, which varies from 2000 nm to 18 nm. This is mainly attributed to the addition of MWCNTs and SF, which reduce the amount of harmful pores and increase the amount

Fig. 4 - Sample surface scanning and energy spectrum measurement of MWCNTs/SF reinforced cement mortar sample; (a) scanning area; (b) silicon element distribution; (c) carbon element distribution; (d) oxygen element distribution; (e) EDS analysis
of pores smaller than 50 nm. The pore size distribution of the samples is shown in Figure 5. It is observed that the pore size of 1# sample ranges from 100nm to 100µm. When the MWCNTs mixed with SF are added, the pore amount of the samples in the range of 100nm and 100µm was reduced gradually with the increase of MWCNT addition and the amount of pores smaller than 50nm increases significantly compared to that of 1# sample. Thus the specimens can have compacting structure and high strength when added with MWCNTs mixed with SF.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Total injected mercury volume (mLg⁻¹)</th>
<th>Total pore surface area (m²g⁻¹)</th>
<th>Mesopore diameter (volume) (nm)</th>
<th>Mesopore diameter (area) (nm)</th>
<th>Average pore diameter (nm)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1#</td>
<td>0.0638</td>
<td>5.223</td>
<td>2050.6</td>
<td>9.7</td>
<td>48.8</td>
<td>13.58</td>
</tr>
<tr>
<td>2#</td>
<td>0.0625</td>
<td>11.284</td>
<td>49.1</td>
<td>10.3</td>
<td>23.2</td>
<td>12.03</td>
</tr>
<tr>
<td>3#</td>
<td>0.0475</td>
<td>9.116</td>
<td>29.4</td>
<td>10.4</td>
<td>20.9</td>
<td>10.42</td>
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<tr>
<td>4#</td>
<td>0.0454</td>
<td>10.234</td>
<td>17.8</td>
<td>10.5</td>
<td>17.8</td>
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<tr>
<td>5#</td>
<td>0.0365</td>
<td>8.245</td>
<td>18.6</td>
<td>10.0</td>
<td>17.7</td>
<td>8.43</td>
</tr>
</tbody>
</table>

Based on the above analysis, it is concluded that MWCNTs mixed with SF can enhance the strength of samples effectively by improving the pore structure of cement composites. The SF particles which have micro-nano size can promote the dispersion of MWCNTs in cement matrix. As shown in Figure 6(a) and (b), MWCNTs can be found anchored in the cement hydration products when mixed with SF particles, the MWCNTs distributed evenly fill the harmful pores of the cement composites and the separate MWCNTs connect the micro cracks existing in the cement paste. The embedded MWCNTs dispersed uniformly in matrix in Figure 6(a) and the MWCNTs in Figure 6(b) have been bridged and pulled out from the formed crack [15]. When the addition of MWCNTs reaches optimum in cement material, the forming processof micro-cracks in cement paste can be delayed by pulling-out and bridging effect of MWCNTs and large number of harmful pores of the sample can be filled by MWCNTs. Consequently, the strength of cement composites will be improved by MWCNTS mixed with SF particles [16,17]. However, it could become difficult for MWCNTs to be dispersed uniformly if the addition of MWCNTs keeps increasing, and the amount of harmful pores in cement composites can increase because of the agglomeration of MWCNTs in the cement composites, affecting the sustainable growth of sample strength [18].

4. Conclusions

In this study, MWCNTs/SF reinforced cement mortar samples were prepared and the influence of MWCNTs mixed with SF on mechanical properties of cement-based composites is discussed by strength test and electron microscopy analysis. Experiment results indicate that SF particles have a favorable dispersion effect on MWCNTs. Therefore, MWCNTs mixed with SF can decrease the sample porosity and the amount of harmful pores effectively and increase the amount of pores smaller than 50nm. Consequently, the pore structure of cement composites can be improved significantly and therefore the samples develop higher strength compared to that of blank samples. When the MWCNT addition is 0.15% and 0.08%, the compressive strength and flexural strength of sample with 10% SF reaches maximum and their increases are both above 35%, displaying well reinforcement effect of MWCNTs mixed with SF particles on the mechanical property of cement-based composites.
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REFERENCES

MANIFESTĂRI ŞTIINŢIFICE / SCIENTIFIC EVENTS

RCCS - International conference on the regeneration and conservation of concrete structures, Nagasaki, Japan - From 01 June 2015 to 03 June 2015

This symposium aims to bring together researchers, practicing engineers, scientists, and others from around the world to share knowledge and experiences related to the regeneration and conservation of existing reinforced concrete structures which have been in long-term service. Regeneration includes condition assessment, maintenance, repair, retrofitting and environmentally-conscious renewal and renovation.

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- Deterioration simulation models
- Durability design
- Facility management
- Regeneration approaches
- Condition assessment
- Nondestructive methods and approaches
- Monitoring methods
- Repair and retrofitting
- Modern materials technology
- Conservation of structures

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