

Mechanical properties of engineering cement-based materials containing modified shape memory alloy fiber

Mengfan Song, Congqi Luan, Jinbang Wang, Lianwang Yuan, Zonghui Zhou

Shandong Provincial Key Laboratory of Preparation and Measurement of Building Materials, Engineering Center of Advanced Building Materials of Ministry of Education, University of Jinan, Jinan 250022, China

ABSTRACT

In this study, a surface modification method for SMA fibers is proposed to improve the interfacial properties of fibers in a cement-based composite. SMA fibers were coated with SiO_2 , which was expected to react with $\text{Ca}(\text{OH})_2$ formed from cement hydration, reducing the possibility of a weak zone and creating a denser microstructure at the fiber-matrix interface. Scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and infrared absorption spectroscopy (IR) were used to characterize the SMA fiber after surface modification. In addition, flexural strength test, compressive strength test and four-point flexural test was carried out to evaluate the enhancement of the mechanical properties of the interface at the macro-scale. The experimental results indicated that the coated SiO_2 , resulting in an increased quantity of C-S-H gel and decreased porosity at the modified SMA fiber-cement interface. The dense adhesion between the modified SMA fibers and cement matrix facilitate the establishment of a stronger interfacial bond, which was benefit to the improvement of flexural strength, compressive strength, four-point flexural strength and deflection. Both the flexural strength, compressive strength, four-point flexural strength and deflection increase significantly at 28d. The results support the conclusion that the proposed surface modification method is suitable for SMA fibers to improve their reinforcement efficiency in engineering cement-based materials.

1. INTRODUCTION

Cement-based materials are the most widely used building materials with excellent strength and durability. However, brittleness and easy cracking limit the improvement of performance. Fiber reinforced cement-based materials [1] have attracted widespread attention for their improvement in toughness. Fibers provide bridging and energy dissipation functions, thereby improving the ductility and toughness of cement-based materials. By adding PVA fiber, polypropylene (PP) fiber and other organic fibers, and based on the principles of microscopic mechanics and fracture mechanics, engineering cement-based materials (ECC) show high toughness [2,3]. With the increasing demand on the life of cement-based materials, it is necessary to control the crack width that affects their durability. Therefore, fracture recovery capability is critical to reduce and control fracture width. SMA fiber is an intelligent material with shape memory effect [4,5,6,7]. Adding SMA fiber into ECC can reduce crack width of specimens after heat treatment [8,9,10,11]. The addition of SMA fiber to ECC can also improve mechanical properties and toughness. Because the interface performance between fiber and cement matrix is relatively poor [12]. Therefore, improving the interface performance

between fiber and cement matrix is very important to improve the performance of SMA fiber reinforced ECC [13,14,15]. Choi et al [16] proposed to use deformed fiber instead of straight fiber to achieve mechanical interlocking between SMA fiber and matrix through irregular fiber shape, thus improving the interface binding force of between fiber and cement matrix.

Many studies have shown that SiO_2 can form hydrated calcium silicate ($\text{CaO}\cdot\text{SiO}_2\cdot n\text{H}_2\text{O}$) with $\text{Ca}(\text{OH})_2$ and fill micropores to improve the microstructure and pore structure, thus improving the mechanical properties of cement-based materials [17,18]. Xiao et al [19] modified carbon fiber by coating its surface with silica, and the results showed that the bonding property of the interface between modified carbon fiber and cement matrix could be improved. Their study confirmed the benefits of surface modification.

SiO_2 has been used for carbon fibers, but no such confirmatory studies have been done with SMA fibers in this way. Therefore, it is necessary to study whether the surface modification method using SiO_2 is suitable for SMA fiber, and whether the characteristics and mechanism of the surface modification are suitable for SMA fiber.

In this study, the surface of SMA fiber was coated with SiO_2 by sol-gel method. The modified SMA fiber

was immersed in $\text{Ca}(\text{OH})_2$ solution to test the reactivity of SiO_2 on the surface of SMA fiber, and the mechanical properties of the modified SMA fiber reinforced SHCC were tested

2. MATERIALS AND EXPERIMENTAL METHODS

2.1 Materials

Sodium hydroxide tablet (analytically pure, Tianjin Damao Chemical Reagent Factory); Ammonia (AR, 25~28%, Shanghai Aladdin Reagent Co., LTD.); TEOS (Reagent grade, 98%, Shanghai Aladdin Reagent Co., LTD.); Anhydrous ethanol (analytically pure, Tianjin Fuyu Fine Chemical Co., LTD.); Cetyltrimethylammonium bromide (CTAB) (Shanghai Aladdin Reagent Co., LTD.); PO42.5 cement (Shandong Shanshui Cement Group Co., LTD.); Fly ash (grade I fly ash, Hebeijing Hang Mineral Products Co., LTD.); Quartz sand (particle size range from 100 μm to 210 μm , average particle size 150 μm , Hebei Yuchuan Mineral Products Co. LTD.); Polycarboxylic acid superplasticizer (Jiangsu Subert Company); Ni-Ti shape memory alloy short cut fibers with curved shape were purchased from Huizhou Zhilian Company; PVA fiber (Japan Kuraray Company).

2.2 METHODS

2.2.1 Preparation of modified shape memory alloy fiber

The Ni-Ti alloy fibers were cleaned with 20% mass fraction NaOH solution to remove the oil and impurities on the surface, cleaned for 6h, then washed with deionized water until the PH value of the final washing was about 7, and the alloy fibers were air-dried. Using 1000 mL anhydrous ethanol as solvent, 80 mL TEOS and cetyltrimethyl ammonium bromide (CTAB) as ionic surfactant were added. 150g cleaned alloy fiber was added to the surface treatment agent and stirred with magnetic force for 6h. 40 ml concentrated ammonia water was added to the final solution and stirred with magnetic force for 6h. After that, the solution was placed in a 45 $^\circ\text{C}$ constant temperature water bath for 12 h, and the solution was aged at room temperature for 24 h. After that, the alloy fibers were washed repeatedly with deionized water. The modified shape memory alloy fibers were dried at 80 $^\circ\text{C}$. Flow chart of fiber modification is shown in Figure 1.



Figure 1. Flow chart of SMA fiber modification

2.2.2 The preparation of ECC

According to relevant literature and through laboratory test, the ECC mixture ratio in this paper adopts cement: fly ash: sand =1:1.5:0.9, and water-binder ratio is 0.34. Superplasticizer mass fraction is 0.8%. PVA fiber volume fraction is 1%. Table 1 is the Mix proportions of ECC. After uniform mixing, the mixed slurry was put into 40 mm \times 40 mm \times 160 mm and 400 mm \times 100 mm \times 15 mm steel molds, and vibrated on the vibration table. After leveling, the slurry was cured for 24 h under standard conditions (20 $^\circ\text{C}$, 95% R.H.), and then released from the mold. A series of tests were carried out after curing to the corresponding age. The average strength of 3 and 6 samples was taken as the test results of flexural and compressive strength, and the corresponding deviations were calculated.

Table 1. Mix proportions of ECC

	Cement (kg/m ³)	Fly ash (kg/m ³)	Silica Sand (kg/m ³)	SMA fiber volume fraction (%)	MSMA fiber volume fraction (%)
C	534.9	802.4	481.4	0	0
S3	534.9	802.4	481.4	0.3%	0
S6	534.9	802.4	481.4	0.6%	0
S9	534.9	802.4	481.4	0.9%	0
M3	534.9	802.4	481.4	0	0.3%
M6	534.9	802.4	481.4	0	0.6%
M9	534.9	802.4	481.4	0	0.9%

3. RESULTS AND DISCUSSION

SEM images of the surface morphology of modified and unmodified SMA fibers are shown in Figure 2 and Figure 3. EDS in point scanning mode was used to determine the type and content of elements on the surface of SMA fibers. It can be clearly observed that the surface of the unmodified SMA fiber is very smooth, as shown in Figure 2. The surface of the modified SMA fiber is covered with granular convex

membrane, as shown in Figure 3. EDS results show that most of the surface elements of unmodified SMA fibers are Ni, Ti, and Si is almost absent. In contrast, the Ni content on the surface of the modified SMA fiber decreases to 10.73% and Si content increases. The results indicate that the substance formed by surface modification is likely to be SiO_2 .

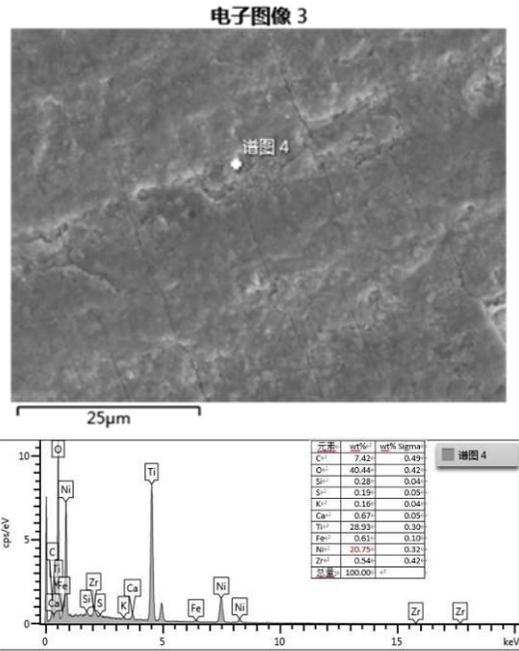


Figure 2. SEM picture of unmodified SMA fiber

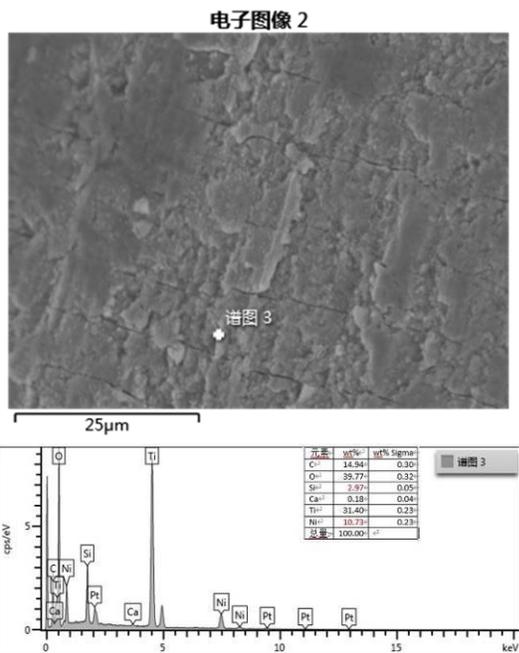


Figure 3. SEM picture of modified SMA fiber

Figure 4 shows the IR results of the modified SMA fiber products. When considering the range of the

characteristic absorption peak of the product, the observation range between 300 cm^{-1} and 2300 cm^{-1} was selected. The type of substance can be determined by determining the type of specific chemical bonds or functional groups based on the location of characteristic absorption peaks. It can be seen that the peak at 465 cm^{-1} corresponds to the Si-O bending vibration peak. The peak at 799 cm^{-1} corresponds to the symmetrical stretching vibration peak of Si-O. The peak at 960 cm^{-1} corresponds to the bending vibration peak of Si-O-Ti. The peak at 1093 cm^{-1} corresponds to Si-O-Si antisymmetric bending vibration peak. The peak at 1062 cm^{-1} corresponds to HOH bending vibration peak. These absorption peaks are basically consistent with the characteristic absorption peaks of industrially prepared SiO_2 [20]. Therefore, the modified product is likely to contain SiO_2 .

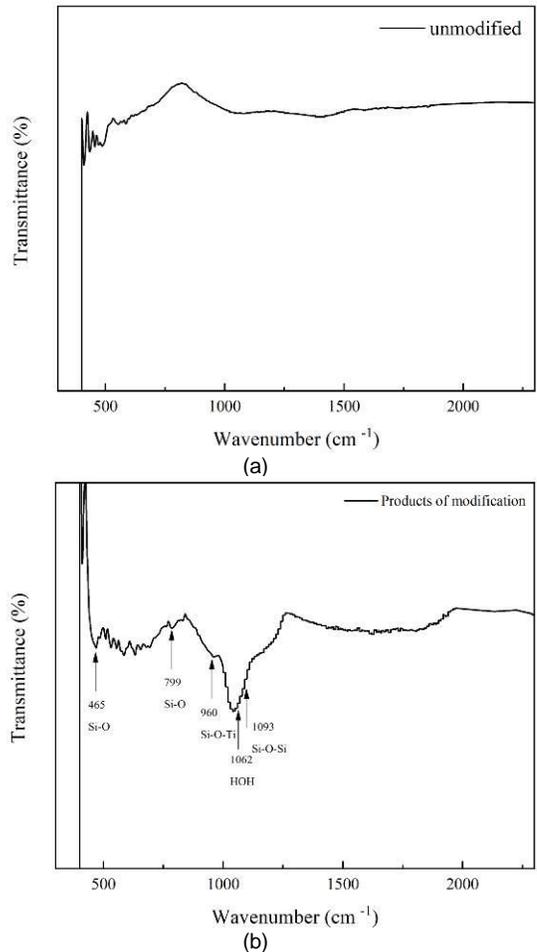


Figure 4. IR results (a) Unmodified SMA fiber (b) Modified SMA fiber

In order to verify the reactivity of SiO_2 formed on the surface of modified SMA fiber. The fibers are immersed in saturated $\text{Ca}(\text{OH})_2$ solution to simulate cement hydration. Thus, whether SiO_2 can react with $\text{Ca}(\text{OH})_2$ is detected. IR analysis of surface products

of modified SMA fibers soaked in Ca(OH)_2 solution saturated at $(20\pm 2)^\circ\text{C}$ for 7 days and 28 days was shown in Figure 5 (a) and (b). Compared with the surface absorption spectrum of modified SMA fiber. Two new characteristic absorption peaks, 872 cm^{-1} and 1428 cm^{-1} , appeared in the absorption spectra of the modified SMA fibers immersed in saturated Ca(OH)_2 solution. These correspond to the characteristic absorption peaks of synthetic calcium silicate hydrate $\text{CaO}\cdot\text{SiO}_2\cdot n\text{H}_2\text{O}$ [21]. It can be determined that the SiO_2 on the surface of the modified SMA fiber has chemical reactivity and reacts with Ca(OH)_2 to form $\text{CaO}\cdot\text{SiO}_2\cdot n\text{H}_2\text{O}$.

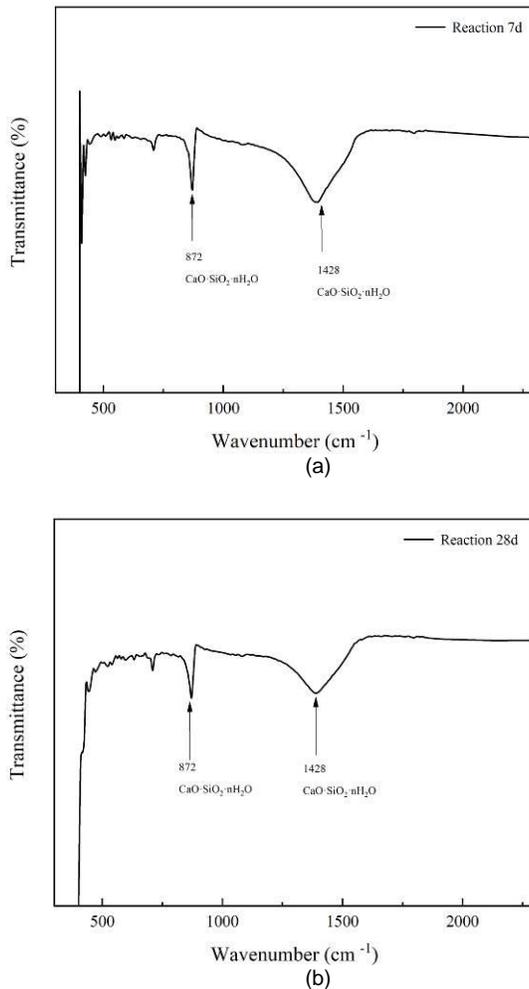


Figure 5 IR results of modified SMA fiber soaked in Ca(OH)_2 saturated solution (a) for 7d (b) for 28d

The flexural strength and compressive strength of ECC enhanced by modified SMA fiber are shown in Figure 6 and Figure 7. It can be seen from the figure that the mechanical ability of ECC enhanced by modified SMA fiber is improved compared with that enhanced by unmodified SMA fiber. When the volume fraction of Ni-Ti alloy fiber is 0.3%, 0.6% and 0.9%. The flexural strength of SHCC reinforced by modified SMA fiber is increased by 13.24%, 17.61%

and 16.55% compared to ECC reinforced by unmodified SMA fiber. The compressive strength of SHCC reinforced by modified SMA fiber is increased by 8.57%, 11.20% and 8.00% compared to SHCC reinforced by unmodified SMA fiber. Four-point flexural strength-deflection curves of ECC reinforced by modified SMA fiber is shown in Figure 8. According to the figure, when the SMA fiber content is 0.3%, the four-point flexural strength and deflection of the modified SMA fiber reinforced ECC sample are increased by 37.57% and 83.47% compared to the unmodified SMA fiber reinforced ECC sample. Therefore, the modified SMA fiber is of great help to improve the bending strength and ductility of ECC. The results show that the mechanical properties of ECC can be further improved by modifying SMA fibers.

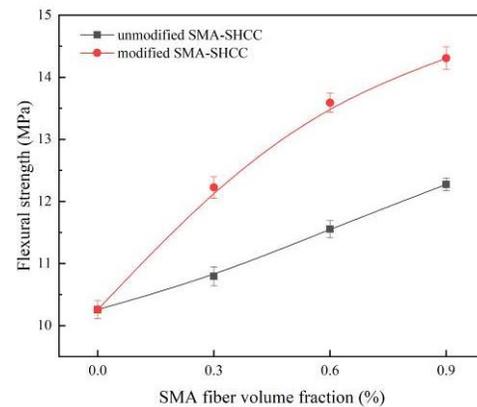


Figure 6. Flexural strength of ECC enhanced by modified and unmodified SMA fibers

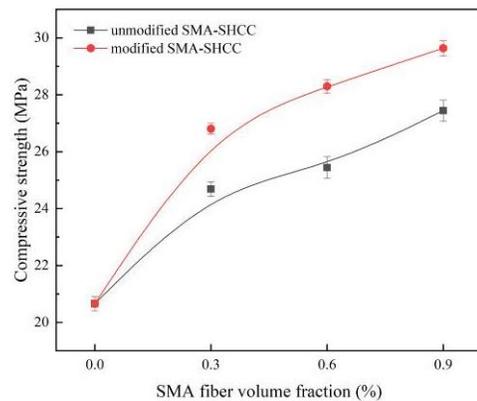


Figure7. Compressive strength strength of ECC enhanced by modified and unmodified SMA fibers

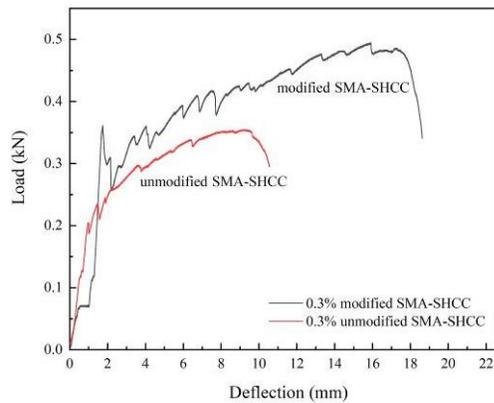


Figure 8. Four-point flexural strength-deflection curves of ECC enhanced by modified and unmodified SMA fibers

After modification by TEOS, the modified SMA fiber was prepared by attaching SiO_2 on the surface of SMA fiber. The hydration reaction between SiO_2 on the surface of modified SMA fibers and hydration products such as CH in cement continued to occur, thus enhancing the bonding force between SMA fiber and cement-based materials, making the modified SMA fiber wrapped by hydration products. Cement-based material has a tighter internal structure, and the modified SMA fiber can further play a role in toughening and cracking resistance.

4. CONCLUSION

In this study, a method to modify the surface of shape memory alloy fiber was proposed. Its benefit was evaluated by characterization methods. SiO_2 uniformly grows on the surface of shape memory alloy fiber. SiO_2 prepared by surface modification has high chemical reactivity and can react with $\text{Ca}(\text{OH})_2$ to produce $(\text{CaO}\cdot\text{SiO}_2\cdot n\text{H}_2\text{O})$ rapidly. SiO_2 reacts with $\text{Ca}(\text{OH})_2$ in the cement matrix, reducing the content of CH and porosity, and increasing the content of $\text{CaO}\cdot\text{SiO}_2\cdot n\text{H}_2\text{O}$. In this way, it increases the density of the microstructure and reduces the possibility of weak regions at the fiber-matrix interface. When the SMA fiber volume content is 0.6%, the bending strength, compressive strength, four-point bending strength and deflection of modified SMA fiber reinforced ECC are increased by 17.61%, 11.20%, 77.5%, 37.57% and 83.47% at 28d compared to unmodified SMA fiber reinforced ECC. Surface modification of SMA fiber not only increases the interfacial bonding between SMA fiber and ECC matrix, but also improves the mechanical properties of SMA fiber reinforced ECC.

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Conflict of interest

There are no conflicts to declare.