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Mechanical properties of calcium carbonate whisker-reinforced high-strength cement mortar

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Abstract: In order to improve the brittleness of high-strength cement mortar, calcium carbonate ($CaCO_3$) whiskers are incorporated to strengthen and toughen the high-strength cement mortar. The compressive strength, flexural strength, split tensile strength and work of fracture are measured. Microstructures and micromechanical behaviors are investigated using scanning electron microscopy. The strengthening and toughening mechanisms and the efficiency of whisker-reinforced high-strength cement mortar are discussed. The results show that the addition of $CaCO_3$ whiskers brings positive effects on the high-strength cement mortar. The strengthening and toughening mechanisms are whisker-cement coalition debonding, whisker peeling, whisker impact breakage and whisker bridging. Crack deflection is one efficient mechanism, but it is hard to be achieved in high-strength cement mortar. And the interfacial bonding strength between whiskers and the cement mortar matrix should be appropriately weak to introduce more crack deflection mechanisms to strengthen and toughen the cement mortar efficiently.

Key words: high-strength mortar; $CaCO_3$ whisker; strengthening; toughening

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Cement mortar is the basic component of concrete, which is also usually used for the rehabilitation or repair of reinforced concrete structures. Low tensile strength and high brittleness are the main weaknesses of cement mortar, especially regarding the high-strength one. Usually, steel fiber, synthetic fiber, hybrid fibers[1] or polymer[2] are incorporated to strengthen and toughen cement mortar. However, high cost is one of their common issues.

As one kind of inorganic single crystals, the calcium carbonate($CaCO_3$) whisker obtains a production cost of about 1 500 yuan/t, an aspect ratio of about 20 to 60, an elastic modulus of 410 to 710 GPa, and a tensile strength of no less than 2 GPa. In recent years, it has been added into Portland cement[3]. And the composites with $CaCO_3$ whiskers exhibit excellent mechanical properties. However, there are few researches on whisker-reinforced high-strength cement mortar, and the strengthening and toughening mechanisms need to be discussed deeply.

Therefore, the objective of this study is to investigate the microstructure, mechanical properties and strengthening and toughening mechanisms of $CaCO_3$ whisker-reinforced high-strength cement mortar in order to find another new way to reinforce cement mortar.

1 Experimental Procedure

The materials used in this study are ISO standard sand, Portland cement (P · O 42.5R, Dalian Onoda Cement Co. Ltd., China), $CaCO_3$ whiskers (Sichuan Shuyang Boron Chemical Co. Ltd., China), silica fume and fly ash. Their chemical constituents are shown in Tab. 1.

Tab. 1 Chemical constituent of raw materials %

Composition	Whiskers	Cement	Silica fume	Fly ash
$w(CaO)$	54.93	52.04	0.81	6.61
$w(CO_2)$	42.07	6.00		
$w(MgO)$	2.14	5.15	0.95	0.63
$w(SO_3)$	0.31	4.66	0.84	1.02
$w(SiO_2)$	0.29	23.08	93.47	50.96
$w(Al_2O_3)$	0.11	4.95	0.16	30.61
$w(Fe_2O_3)$	0.07	2.64	0.10	5.61
$w(K_2O)$		0.81	2.89	0.78
$w(Na_2O)$		0.14	0.23	0.17
$w(TiO_2)$		0.31		
$w(P_2O_5)$		0.07	0.40	
$w(MnO)$		0.06	0.06	
$w(SrO)$	0.05	0.09		
$w(Cr_2O_3)$	0.03			

10% silica fume and 20% fly ash are mixed with cement. The water-binder ratio is 0.2, and the sand-binder ratio is 2.3. The group of W0 is obtained as the comparison test, which is without whiskers. Mass percentages of 5%, 10%, 15% and 20% whiskers are incorporated into the matrix to obtain the test groups of W5, W10, W15 and W20. Moreover, the water reducer (Polycarboxylic acid type water reducer with a water reduction ratio of 24.1%) is also incorporated appropriately to assure that

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the cement paste has the same workability and can be cast easily. Afterwards, the mortar is placed into each mold (All the specimens are cast in three lifts) and vibrated on a mortar vibrating table for 120 s. All the specimens are stored in a standard curing box of cement with mold for 24 h; thereafter, they are demoulded and stored at a 100% relative humidity and 20 ℃ for 28 d.

The compressive strength is determined from the portions of prisms (six lifts) broken in the flexural test using a pressure machine at a crosshead speed of 2.4 kN/s according to ISO 679. The three-point flexural test of the specimens (40 mm × 40 mm × 160 mm) are conducted using a computer-controlled electro-hydraulic servo universal tester (WAW-300) at a crosshead speed of 0.05 mm/min to determine the flexural strength and the work of fracture (R_w) of the specimens. And R_w is calculated from the area covered underneath the load-deflection curve divided by twice the fracture surface area of the specimen. The specimens with a size of 40 mm × 40 mm × 40 mm are employed for the determination of the split tensile strength using a computer-controlled electro-hydraulic servo universal tester (WDW-50) at a crosshead speed of 0.1 mm/min. Fracture surfaces and microstructures of the composites are examined using scanning electron microscopy (SEM, QUANTA 450).

2 Results

2.1 Fracture morphology

Multi-cracking is very desirable for high-strength cement mortar owing to the demand of integrality, ductility and safety. As shown in Fig. 1, the integrality of the composites with whiskers is kept well when crushed. Therefore, the addition of $CaCO_3$ whiskers can mend the brittleness of high-strength cement mortar to some extent.

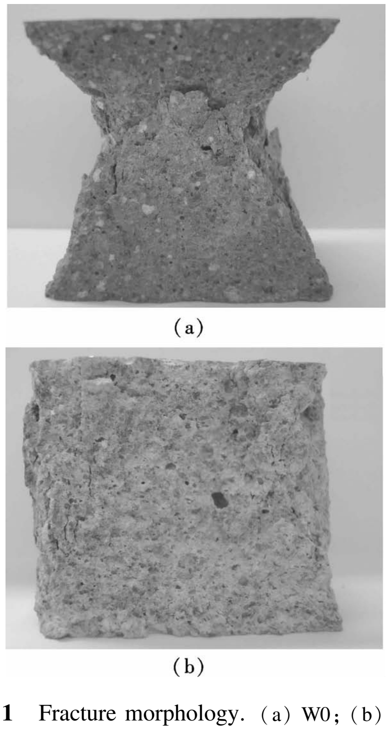

Fig. 1 Fracture morphology. (a) W0; (b) W10

2.2 Mechanical properties

The compressive strength, flexural strength, split tensile strength and work of fracture are measured in this study, as presented in Tab. 2. From Tab. 2, it is concluded that the addition of whiskers provides some positive effects on the mechanical properties of the high-strength mortar when the whisker content is no higher than 10%, whereupon they deteriorate gradually.

For convenience of comparison, the relative increment of each mechanical property is employed, as illustrated in Fig. 2. Here, R_c, R_f, R_s, R_w represent the compressive strength, the flexural strength, the split tensile strength, and the work of fracture, respectively.

Tab. 2 Mechanical properties of reinforced cement mortar

Sample	Specification	Compressive strength/MPa	Flexural strength/MPa	Split tensile strength/MPa	Work of fracture/($J \cdot m^{-2}$)
W0	Pure cement matrix	97.9	15.8	6.4	222.8
W5	+5% whisker	105.7	16.4	7.3	262.4
W10	+10% whisker	98.6	17.3	6.8	346.1
W15	+15% whisker	93.8	16.2	6.1	334.8
W20	+20% whisker	87.8	15.5	5.7	299.4

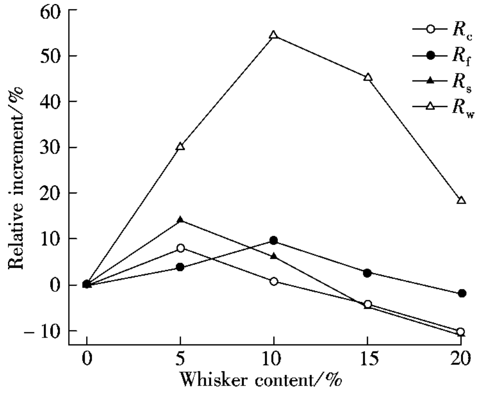

Fig. 2 Relationship between whisker content and relative increment of each mechanical property

From Fig. 2, it can be seen that there are about 8% and 15% increments for compressive strength and split tensile strength, respectively, when the whisker content is 5%; there are nearly 10% and 55% increments for flexural strength and work of fracture, respectively, when the whisker content is 10%. High whisker content is detrimental to the mechanical properties of high-strength cement mortar. The agglomerate of whiskers may be the essential reason which can decrease the density and the compactness of composites[4-5].

Fig. 3 and Tab. 3 give the results of load-deflection curves of the flexural tests. It can be concluded that the addition of $CaCO_3$ whiskers is advantageous to improve the deformability and ductility of high-strength mortar. At a low load level, the mortar with whiskers exhibits a higher deformability. With the increase in the whisker content (no higher than 10%), the peak load and peak deflection of the mortar are both enhanced. Although the deformability is still increased along with the whisker content (higher than 10%), the peak area of the curve is decreased. Thus, the work of fracture of the high-strength mortar is also decreased, which means that the energy required to create a unit surface area by crack propagation is decreased as well[6].

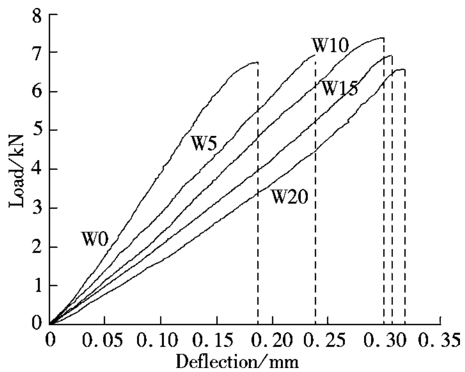

Fig. 3 Load-deflection curves of high strength mortar with 0 to 20% $CaCO_3$ whisker

Tab. 3 Details of load-deflection curves

Sample	W0	W5	W10	W15	W20
Peak load/N	6 741.3	6 997.5	7 381.4	6 912.1	6 613.7
Peak area/(N · mm)	713.1	839.7	1 107.2	1 071.4	958.2

3 Discussion

3.1 Strengthening and toughening mechanisms

3.1.1 Microstructures

Fig. 4 shows the fracture surface of the high-strength mortar without $CaCO_3$ whiskers and with 10% $CaCO_3$ whiskers. It is apparent that the mortar without whiskers has a relatively loosened microstructure, which presents a large number of cracks and holes. In comparison, the mortar containing whiskers has a compact microstructure, and it can be seen that the whiskers are well-distributed. Meanwhile, from the regions *A* and *B* in Fig. 4(b), some visible whiskers can be found, which cross the cracks and impede the crack propagation. Therefore, it is believed that the addition of whiskers can bring positive impacts on resisting the cracks caused by matrix shrinkage and applied load, on the microstructural level.

3.1.2 Micromechanics

Four micromechanical strengthening and toughening mechanisms are observed in this study, as shown in Fig. 5.

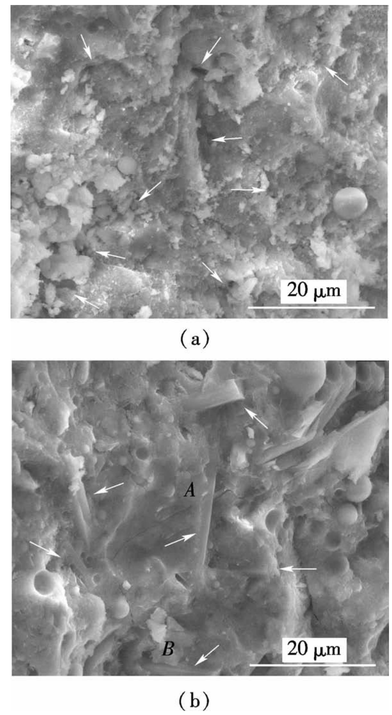

Fig. 4 Typical microstructures of high-strength mortar. (a) Without $CaCO_3$ whiskers; (b) With 10% $CaCO_3$ whiskers

To the whisker-reinforced high-strength mortar, an equation can be achieved when we only take the contribution of one whisker that is perpendicular to the fracture surface into consideration[7], namely, $l_c/d = f_w/2f_i$, where l_c is the critical whisker length, d is the diameter of the whisker, f_w is the ultimate strength of the whisker, f_i is the interfacial bonding strength between the whisker and the matrix. If the ratio of f_i/f_w is beyond 1/2, then whisker tensile breakage will take place. However, theoretically, the ultimate strength of the whiskers is nearly 10^5 fold higher than the ultimate shear strength of Portland cement. Therefore, when the interfacial bonding strength is higher than the ultimate shear strength of the cement, the cement encased around the whisker surface will debond from the cement matrix, which means that even though the maximum of the interfacial bonding strength is high enough, the maximal effective value is just the same as the ultimate shear strength of the cement when the whisker-cement coalition is pulled out (see Fig. 5(a)). In this case, the load-bearing capacity of the mortar can be enhanced, and the energy consumption can be caused by the friction between the cement matrices. In this study, an interesting phenomenon is also found, namely, whisker peeling (see Fig. 5(b)), which seems to occur when the whisker is parallel to the fracture surface. Nevertheless, this mechanism can strengthen and toughen the high-strength mortar during the whisker peeling process.

Whisker impact breakage and whisker bridging mechanisms are very easily observed in this study, as illustrated

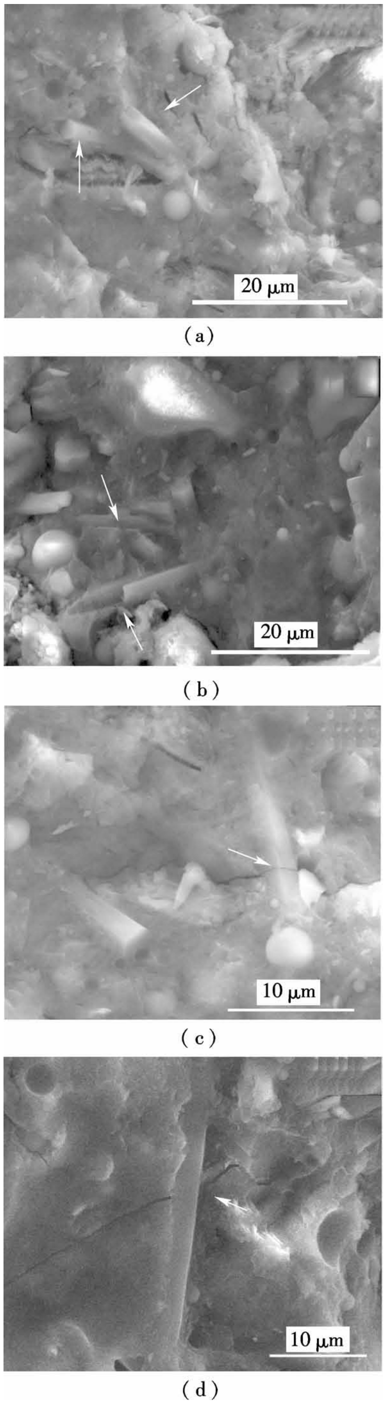

Fig. 5 Micromechanical mechanisms. (a) Whisker-cement coalition debonding; (b) Whisker peeling; (c) Whisker impact breakage; (d) Whisker bridging

in Figs. 5(c) and (d). They all resist or blunt crack tip and crack propagation processes when cracks try to cross the whiskers. As shown in Fig. 5(c), the stress concentration created by crack tip can lead to the impact breakage of whiskers, and then the cracks keep on propagating. Likewise, the process of whisker impact breakage can also increase load bearing capacity and absorb energy. But unlike whisker impact breakage, whisker bridging can blunt crack tip by forming closure stress. This resistance to crack development and propagation is advantageous to strengthen and toughen the high-strength mortar.

3.2 Strengthening and toughening efficiency

An interesting phenomenon is found when compared with previous work. Ref. [8] presented some research on $CaCO_3$ whisker-reinforced ordinary-strength cement mortar when whiskers and salt fiber hybrid cement mortar are discussed. It is shown that the maximal increment of flexural tensile strength is only about 7% when the whisker content is 10% at 28 d of age. However, a nearly 30% increment of flexural tensile strength is obtained at 3 d of age when the compressive strength is only 40 MPa. Therefore, the composites which have the same mix proportion and manufacturing procedure as W0 and W10 in this study, are employed to observe their microstructures and flexural tensile strengths at 3 d of age. The results show that the compressive strength of W0 is 43 MPa, and the flexural tensile strengths of W0 and W10 at 3 d of age reach 10.7 and 12.8 MPa, respectively. And a nearly 20% increment for the flexural strength is obtained when W10 is compared with W0.

Thus, it seems that the whiskers can bring better effects to the low-strength and high-strength cement mortar matrices than moderate-strength ones. To the whisker-reinforced high-strength cement mortar, the increase in the interfacial bonding strength between the whiskers and the cement mortar matrix can strengthen the effects contributed by the various strengthening and toughening mechanisms mentioned in section 3.1.2. So the reinforcing effects are better than those in moderate-strength ones. However, as for the low-strength cement mortar, the crack deflection mechanism is found in W10 at 3 d of age, as illustrated in Fig. 6. And the crack deflection mechanism is the essential reason accounting for the best strengthening and toughening efficiency found in the low-strength cement mortar, as explained below.

First, the fracture toughness of brittle material is given in Griffith's brittle fracture theory. Namely, $K_{1c} = \sqrt{E\gamma}$, where E is the Young modulus and γ is the fracture energy. Increasing E and/or γ will increase the fracture toughness. However, as for cement mortar, it is hard to increase its Young modulus via the addition of $CaCO_3$ whiskers, and thus the only way is to increase γ. As is known, $\gamma = \alpha \sum \gamma_i$, where α is the coefficient depending on the fracture surface; γ_i represents the energy consumption styles, such as light, heat, sound, creating new surface and causing plastic deformation, and so on. The energy consumption by whisker pull-out may be not large enough due to the very short lengths of the whiskers and the low interfacial bonding strength in the low-strength

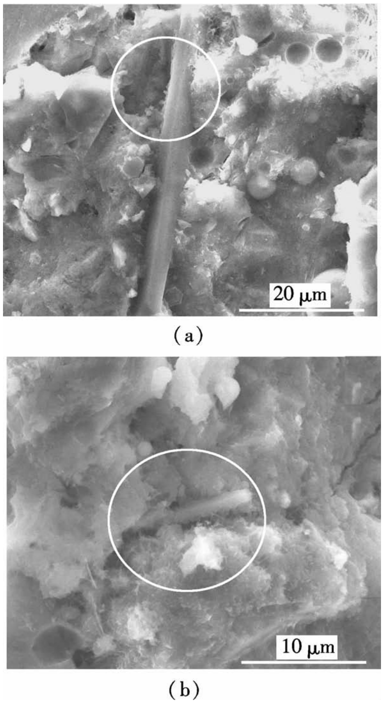

Fig. 6 Crack deflection mechanism found in the composites of W10 at 3 d of age

cement mortar. Furthermore, the contribution by the plastic deformation of cement mortar is also very limited due to its ability to endure strain, which is about 0.002. Consequently, maybe creating a new surface is an efficient and feasible way. And crack deflection is taken into consideration, since it can create more surfaces and prolong the length of cracking to consume energy.

Secondly, according to the Faber-Evans model[9-10], when rod-shaped particles exist in the composite, the toughness increment caused by the crack deflection mechanism shows an asymptotic limit. The reason is that in the theoretical model, cracks are assumed to be diverted along the whole of the whiskers. However, in practice, this can scarcely be achieved due to strong interfacial bonding between whiskers and the matrix so that only a small portion of the whiskers can take part in crack deflection. Therefore, a weak enough interfacial bonding is necessary for the crack deflection mechanism. Namely, in low-strength cement mortar, more crack deflection can be introduced to increase the strengthening and toughening efficiency caused by whisker loading.

4 Conclusions

1) Calcium carbonate whiskers are incorporated into high-strength cement mortar. The deformability and ductility of high-strength cement mortar are improved to some extent.

2) Compressive strength, flexural strength, split tensile strength and work of fracture are measured, and 8%, 10%, 15% and 55% maximal increments are obtained, respectively.

3) The mortar with whiskers obtains a compact microstructure, but the mortar without whiskers does not. Whiskers resist and blunt micro-cracks, and, therefore, they increase the propagation resistance of the cracks.

4) Four main micromechanical strengthening and toughening mechanisms are observed in this study, namely, whisker-cement coalition debonding, whisker peeling, whisker impact breakage and whisker bridging.

5) Although the high-strength cement mortar matrix is advantageous to the strengthening and toughening efficiency contributed by whisker loading, the low-strength matrix is more compatible. Crack deflection mechanism is found in low-strength cement mortar composites, which can efficiently strengthen and toughen the composites. And low strength interfacial bonding strength is beneficial for the crack deflection mechanism in cement mortar composites.

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碳酸钙晶须增强高强水泥砂浆的力学性能

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摘要：为改善高强砂浆的脆性，将碳酸钙晶须引入高强砂浆中以实现增强与增韧的目的．研究了抗压强度、抗折强度、劈拉强度以及断裂功等基本力学性能，采用扫描电子显微镜观察材料的微观结构和微观力学行为，讨论了碳酸钙晶须增强增韧高强水泥砂浆的机理和效率．研究表明：碳酸钙晶须的引入对高强砂浆的力学性能产生了较为积极的影响；碳酸钙晶须增强增韧高强砂浆的机理为晶须-水泥石脱黏、晶须剥离、晶须冲断以及裂纹桥联；裂纹偏转机制是比较高效的一种增强增韧机制，但并不容易在高强水泥砂浆基质中出现．研究认为，晶须与水泥砂浆基质间的界面黏结强度应该适当弱一些，这样有利于通过引入更多的裂纹偏转来增强增韧水泥砂浆复合材料．

关键词：高强砂浆；碳酸钙晶须；增强；增韧

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