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Properties of ceramic fiber reinforced cement composites

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Abstract

Mechanical properties and preliminary durability of ceramic fiber reinforced Portland cement composites tested with wet-hot accelerating method were investigated. The results showed that the flexural strength of mortar could be increased obviously by adding ceramic fiber into it, but the effect of the flexural reinforcement was influenced by various factors, including fiber length, fiber content and kinds of matrices; the preliminary durability of ceramic fiber in ordinary Portland cement tested with wet-hot accelerating method was much better than that of alkali-resistant (AR) glass fiber. The mechanism of the durability of ceramic fiber in ordinary Portland cement is also discussed.

Keywords: Ceramic fiber; Cement matrix; Mechanical properties; Durability

1. Introduction

Concrete is one of the widely used building materials in the world, but because its ultimate tensile strain is very small, its tensile strength and impact strength are very low as compared with its compressive strength and it is brittle and prone to crack, etc.; all these limit its use in some special projects that require high strength and high toughness of concrete. Adding fiber into concrete is an effective measure to improve the above shortcomings. Alkali-resistant (AR) glass fiber containing zirconia was developed by Majumdar [1] in 1967 and was used to reinforce ordinary Portland cement matrix. The reinforcing effect was excellent, but the durability of AR glass fiber in ordinary Portland cement was not ideal, as published in 1980 by BRE [2], who stored the AR glass fiber reinforced Portland cement composites in British environment for 10 years. AR glass fiber reinforced low-alkali sulphoaluminate cement composites were studied by Building Materials Research Institute of China. The results showed that AR glass fiber was much more durable in low-alkali sulphoaluminate cement. Because about 95% of cement used in the present world belongs to Portland cement system and the durability of AR glass fiber in this system is not satisfactory, it is necessary to solve the problem of the durability of AR glass fiber in ordinary Portland cement system. The author [3] in this paper found that the durability of AR glass fiber in Portland cement could be improved obviously when the alkalinity of cement was reduced greatly by adding much silica fume into it. Whereas the resource of silica fume is finite and other fibers are not very satisfactory, for example, asbestos fiber is considered to have a bad effect to induce cancer, steel fiber is easy to agglomerate when mixed with other materials and carbon fiber is expensive, etc.; it is also necessary to find some new type of fiber that is durable in ordinary Portland cement, easy to handle and feasible economically. Yon et al. [4] developed calcia/alumina fibers formed by the inviscid melt spinning process. Low and Beaudoin [5] used wollastonite fiber to reinforce cement matrix. They all showed good effects of reinforcement on cement matrix and durability in ordinary Portland cement. Sugama et al. [6] researched ceramic fiber reinforced calcium aluminate/fly ash/polyphosphate cements at a hydrothermal temperature of 280 °C, and found the improving of fracture toughness by adding ceramic fiber to 2.7 times more than that of nonreinforced cements. Ceramic fiber is a new type of inorganic fiber with high elastic modulus. Its raw materials are kaolin and saggar or quartz and alumina. It is formed by melting its raw materials at about 2000 °C in an arc furnace and then centrifuging or blowing. It is mainly used as a thermal insulating material in kiln and stove. Because its main chemical composition is

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Al_2O_3 and SiO_2, its system is simpler than that of AR glass fiber and it will be more resistant to alkali than AR glass fiber theoretically. In this paper, mechanical properties and preliminary durability of ceramic fiber reinforced Portland cement composites were investigated.

2. Experimental

2.1. Materials

Silica fume with specific surface of 20 m^2/g, 32.5# ordinary Portland cement and standard quartz sand were used. Two kinds of ceramic fibers with Al_2O_3 content of 45% and 60%, respectively, filament diameter of 3 μm and tensile strength of about 3×10^4 MPa were used and AR glass fiber with filament diameter of 13 μm and tensile strength of about 1×10^3 MPa was also used for comparison. Methyl cellulose and water-reducing agent SN-2 were used as dispersing agent.

2.2. Test methods

2.2.1. Specimen preparation

The ceramic fibers were cut into 3, 5 and 10 mm in length, respectively, and the AR glass fiber was cut into 10 mm in length. The cement–sand–water ratio of mortar was 1:1:0.4. The specimens with sizes of $2 \times 2 \times 8$ cm and $1 \times 2 \times 8$ cm, respectively, were cast, with the former specimen being used for flexural test and the latter for impact test. The water–cement ratio of paste was 0.4. During mixing of fiber cement mixtures, 0.2% methyl cellulose and 0.5% water-reducing agent SN-2 (by weight of cement) were added to ensure the uniform dispersion of fibers in cement matrices. The above-mentioned specimens used for mechanical properties test were stored in standard curing room for 28 days. The mortar specimens used for durability test were stored in standard curing room for 3 days (demoulded after 1 day) and then were stored in 70 °C wet and hot environment for different ages.

2.2.2. Flexural test

Flexural test was carried out according to Fig. 1 (referring to Chinese Standard GBJ81-85). The value of flexural strength was calculated according to Eq. (1).

$$R = PL/bh^2 \quad (1)$$

where R is flexural strength (MPa), P is failure load (N), L is span between two supports (mm), b is section width of specimen (mm) and h is section height of specimen (mm).

Each group includes six specimens. A maximum and a minimum datum are deleted from the six data, and the remaining four data are used to calculate the average of the group.

The effect of the flexural reinforcement of fiber reinforced cement composites compared with ordinary cement matrix was expressed by the percentage of the ratio of the difference between the flexural strength of specimen with fiber and that of reference specimen to the flexural strength of reference specimen.

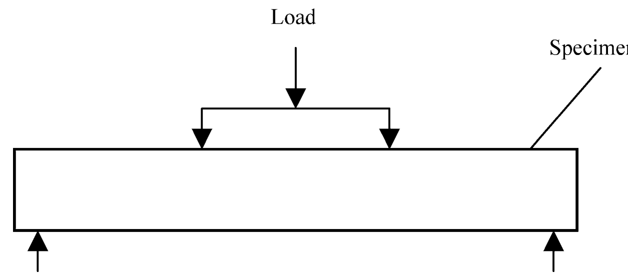

Fig. 1. Sketch map of flexural test.

2.2.3. Impact test

Impact test was carried out by type CHARPY XCJ-50 impact machine. The effect of the impact reinforcement of fiber reinforced cement composites compared with ordinary cement matrix was expressed by the percentage of the ratio of the difference between the impact strength of specimen with fiber and that of reference specimen to the impact strength of reference specimen. Each group includes 10 specimens. Two maximum and two minimum data are deleted from the 10 data, and the remaining six data are used to calculate the average of the group.

2.2.4. Durability test

Durability test of fiber in ordinary Portland cement was carried out by storing specimens with fiber in 70 °C wet and hot environment to accelerate their aging and investigating their changes of the flexural reinforcement or the impact reinforcement during aging time.

3. Results and discussion

3.1. The effect of the flexural reinforcement of ceramic fiber reinforced cement composites

3.1.1. Fiber length

To investigate the effect of different fiber lengths on the flexural reinforcement of mortar, the values of the flexural strength of mortars with ceramic fibers (with Al_2O_3 content of 45%) of different lengths (from 3 to 10 mm) were measured when ceramic fiber content was fixed at 5% (by weight of cement, the same in the following). Fig. 2 shows the effect of fiber length on the flexural reinforcement of mortar. From Fig. 2, it can be seen that the flexural reinforcement of mortar increases gradually at first with the increasing of fiber length due to the increasing of effective bonding area between fiber and cement matrix, but then decreases with the further increasing of fiber length. It was found that the dispersing of fiber in cement matrix was difficult and fiber was easy to curl when it was

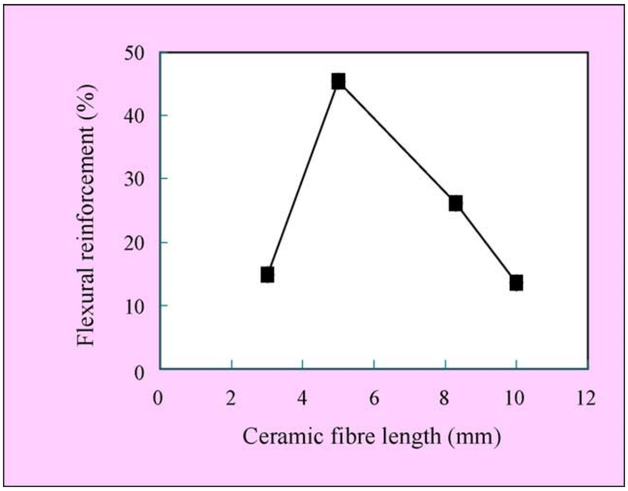

Fig. 2. Effect of ceramic fiber length on the flexural reinforcement of mortar.

too long, which might decrease effective bonding area between fiber and cement matrix on the contrary and even influence the compacting of the composite. There is an optimum fiber length for the best effect of fiber on the flexural reinforcement of mortar. On this experimental condition, when ceramic fiber length is about 5 mm, the effect of ceramic fiber on the flexural reinforcement of mortar is the best.

3.1.2. Fiber content

When ceramic fiber (with Al_2O_3 content of 45%) length is fixed at 5 mm, the effect of fiber content on the flexural reinforcement of mortar is shown in Fig. 3. From Fig. 3, it can be seen that when ceramic fiber content increases from 3% to 10%, the flexural reinforcement of mortar increases at first, but in the same way as above, then decreases. It was also found that the dispersing of fiber in cement matrix was difficult when fiber content was too much, which influences the flexural reinforcement of mortar on the contrary. On this experimental condition, the optimum ceramic fiber content is about 5%.

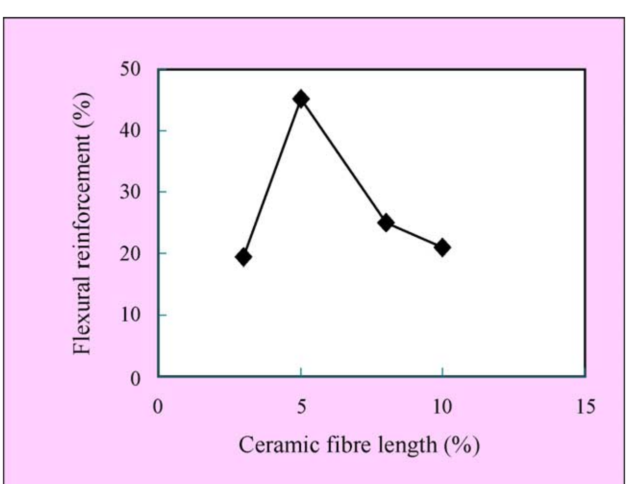

Fig. 3. Effect of ceramic fiber content on the flexural reinforcement of mortar.

Table 1
Effect of Al_2O_3 content of ceramic fiber on the flexural reinforcement of mortar

Al_2O_3 content (%)	Flexural reinforcement (%)
45	41.3
60	44.5

From all results mentioned above, it can be deduced that when ceramic fiber length is about 5 mm and content is about 5%, the effect of ceramic fiber on the flexural reinforcement of mortar is the best. It can reach about 45%.

3.1.3. Al_2O_3 content of ceramic fiber

The effect of different Al_2O_3 contents of ceramic fiber on the flexural reinforcement of mortar is shown in Table 1 (fiber length being 5 mm and content being 5%). Table 1 shows that the flexural reinforcement of mortar increases only slightly when Al_2O_3 content of ceramic fiber increases from 45% to 60%. The higher Al_2O_3 content of ceramic fiber, the higher its refractoriness and the more difficult its manufacture, which makes its cost higher. In practical use, ceramic fiber with lower Al_2O_3 content is more economical. Its cost is about 50% of that of AR glass fiber.

3.1.4. Flexural reinforcement of ceramic fibers in different cement matrices

The flexural reinforcements of ceramic fibers in different cement matrices, such as cement mortar, cement paste and cement paste added with 40% silica fume (by weight of cement) are investigated. The results are shown in Table 2 (fiber length being 5 mm and content being 5%). From Table 2, it can be seen that the effect of ceramic fiber (with Al_2O_3 content of 45%) on the flexural reinforcement of paste is better than that of mortar. When large amount of silica fume is added into paste, the effect of ceramic fiber on the flexural reinforcement of paste can be increased to about 100%. The authors consider that the reasons may be due to the following two aspects: (1) because ceramic fiber is very fine but cement and sand particles are coarse relatively, with the decreasing of coarse particles, the large cracks in the cement matrices may decrease, which will be of benefit to the crack-bridging effect of ceramic fiber; (2)

Table 2
Effect of different cement matrices on the flexural reinforcement of ceramic fiber reinforced cement matrix

Type of cement matrix	Flexural reinforcement (%)
Mortar	41.3
Paste	47.8
Paste with 40% silica fume	102.4

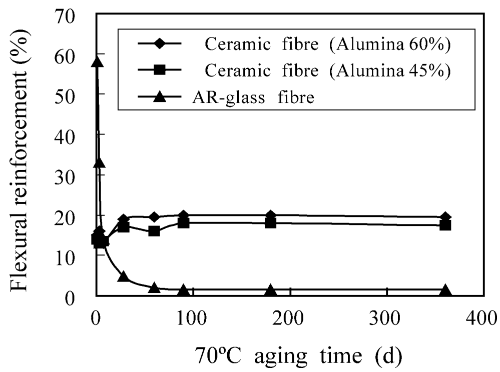

Fig. 4. Change of the flexural reinforcement of fiber reinforced mortar with aging time.

with the decreasing of coarse particles, the cement hydrates may increase, which will be of benefit to the improving of contact situation between ceramic fibers and cement matrices.

3.2. Durability of ceramic fiber in ordinary Portland cement

The durability of ceramic fiber in ordinary Portland cement is assessed by the changes of the flexural reinforcement and the impact reinforcement of ceramic fiber reinforced mortar with aging time in 70 °C wet and hot environment. Fig. 4 shows the change of the flexural reinforcement of fiber reinforced mortar with aging time, in which ceramic fiber and AR glass fiber lengths are 3 and 10 mm, respectively, and their contents are 5%. Fig. 5 shows the change of the impact reinforcement of ceramic fiber reinforced mortar with aging time, in which ceramic fiber length is 3 mm and contents are 1% and 3%, respectively (by volume of cement).

From Fig. 4, it can be seen that the effect of AR fiber on the flexural reinforcement of mortar is much better at early age, although it has smaller fiber aspect ratio and lower tensile strength of filament than those of ceramic fiber. But it decreases sharply with aging time and almost loses at 60 days because of the attacking of alkali irons on AR fiber and the destroying of crystalline in microcracks at AR fiber surface in the interfacial area. The effect of ceramic fiber on the flexural reinforcement of mortar does not decrease with aging time, which indicates that ceramic fiber is much more durable in ordinary Portland cement than AR fiber at present wet-hot environment. From Fig. 5, it can be seen that, similarly, the effect of ceramic fiber on the impact reinforcement of mortar does not decrease with aging time, although the values are more discrete.

4. Discussion on the mechanism of the durability of ceramic fiber in ordinary Portland cement

Because the main chemical composition of ceramic fiber is Al_2O_3 and SiO_2, and there is little CaO, MgO and R_2O in it, when it is exposed in high alkaline environment of ordinary Portland cement, soluble eroding of Na^+, K^+, Ca^{2+} and Mg^{2+} ions does not take place. It is one of the reasons that ceramic fiber is more stable in cement matrix than AR glass fiber. On the other hand, thermodynamic stability of ceramic fiber is better than AR glass fiber.

The author in this paper found that the zirconium hydroxide protective coat of AR glass fiber was not stable in alkaline environment in which the pH value was higher than 10.5. Some cracking would appear on the coat and through the cracking, alkali liquor would attack the glass fiber. Zhang [7] supposed the chemical reaction of glass fiber with OH^- ion as following:

$$SiO_2\ (\text{glass}) + 2OH^-_{aq} \rightarrow H_2SiO_4^{2-}$$

According to Γ ecc law:

$$\begin{aligned} G^0_{\text{reaction}} &= G_{H_2SiO_4^{2-}} - (2G^0_{OH^-} + G^0_{SiO_2}) \\ &= -283.19 - (-2 \times 37.60 - 202.83) = -5.16 < 0 \end{aligned}$$

Because the free energy of the above reaction is negative, the reaction of OH^- ion attack on glass fiber will happen spontaneously at normal temperature and atmospheric pressure. Because Al_2O_3 and SiO_2 in ceramic fiber will be crystallized out to form mullite in the cooling process, and $G_{298\text{k, mulite}}$ ($G_{298\text{k, mulite}} = -1649.4$ kcal/mol) is much less than $G_{298\text{k, SiO2}}$ ($G_{298\text{k, SiO2}} = -220.66$ kcal/mol) [8], suppose that SiO_2 in ceramic fiber reacts with OH^- ion in the form of mullite, the $G_{\text{reaction,298K}}$ will be more than zero, which means the reaction of OH^- ion attack on ceramic fiber nonspontaneous at normal temperature and atmospheric pressure, that is, ceramic fibers will be stable in cement matrices.

All the above analyses indicate that ceramic fiber is more durable than AR glass fiber in the high-alkaline environment of ordinary Portland cement, at least in the wet-hot environment. Of course, the durability of ceramic fiber in cement matrices should be investigated in nature environment in the future.

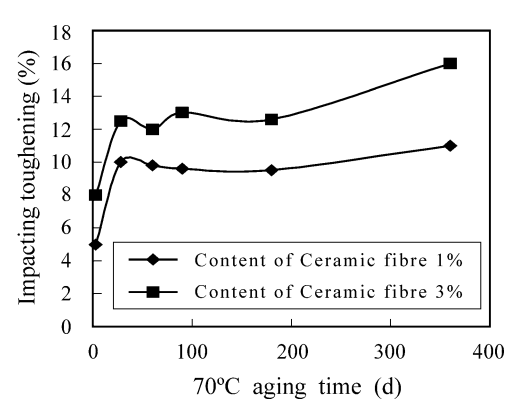

Fig. 5. Change of the impact reinforcement of ceramic fiber reinforced mortar with aging time.

5. Conclusions

There is an optimum ceramic fiber length and content for the best effect of ceramic fiber on the flexural reinforcement of mortar. The effect of Al_2O_3 content of ceramic fiber on the flexural reinforcement of mortar is not obvious. The effect of ceramic fiber on the flexural reinforcement of cement matrix is different in different cement matrices.

When ceramic fiber length is about 5 mm and content is about 5%, the effect of ceramic fiber on the flexural reinforcement of mortar is the best. It can reach about 45%. For paste with 40% silica fume, the effect of ceramic fiber on the flexural reinforcement can reach about 100%.

Preliminary durability of ceramic fiber in ordinary Portland cement tested with wet-hot accelerating method is much better than that of AR glass fiber.

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References

[1] R. Shen, On the new trend in fiber reinforced cement composites, Proceedings of the Chinese Ceramic Society, Beijing, Chinese Ceramic Society, 1984, pp. 4–7 (in Chinese).
[2] R. BRE, Information Paper, IP, vol. 36, Building Research Establishment, London, 1979.
[3] Y. Ma, Master Paper of Building Materials Research Institute of China, 1986 (in Chinese).
[4] K.-Y. Yon, B.S. Mitchell, S.A. Dunn, J.A. Koutsky, Introduction of new reinforcement for cementitious materials calcia/alumina (CA) fibers formed by the inviscid melt spinning (IMS) process, Cem. Concr. Compos. 15 (3).
[5] N.M.P. Low, J.J. Beaudoin, Flexural strength and microstructure of cement binders reinforced with wollastonite microfibers, Cem. Concr. Res. 23 (4) (1993) 905–916.
[6] T. Sugama, L. Weber, L.E. Brothers, Ceramic fibre-reinforced calcium aluminate/fly ash/polyphosphate cements at a hydrothermal temperature of 280 °C, Adv. Cem. Res. 14 (1) (2002) 25–34.
[7] X. Zhang, Research on attack of hydroxide on medium alkali glass fiber, J. Build. Mater. Res. Inst. China 31 (2) (1985) 31–33 (in Chinese).
[8] H. Salmang, Translated by X. Huang, Ceramics: Part, Light Industry Press, Beijing, 1989 (in Chinese).