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ZIRCONIA STRENGTHENED HIGH PERFORMANCE CONCRETE

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SUMMARY

Based on the mechanisms of the microcracking and the phase transformation, fully stabilized zirconia (FSZ) and partially stabilized zirconia (PSZ) are investigated in high performance concrete without coarse aggregates. The composites containing 2%, 4% and 6% volume fraction of zirconia are examined. According to the experimental data, zirconia can enhance the strength and the toughness of HPC. Adding 4% volume concentration of zirconia to high performance the binder and the mortar is the most effective to strengthen the strength and the elastic moduli. Meanwhile, the microcrack toughening is the better way to enhance the fracture toughness of zirconia/concrete comparing with the transformation toughening.

1. INTRODUCTION

In the high stress field near the tip of a growing crack, the tetragonal zirconia ($t-ZrO_2$) can undergo the stress-induced tetragonal-monoclinic transformation, and the residual stresses around transformed $m-ZrO_2$ particles cause many microcracks. Both mechanisms would give rise to toughening in ZrO_2-toughened ceramics [1].

A class of concrete material belongs to a kind of ceramic materials. For this reason, we are trying to evaluate the strength and the toughness of high performance cementing composites containing zirconia particles. The high performance cementing composite (HPC without coarse aggregates) as a whole is assumed to be a two-phase composite including the binder or the mortar as the matrix, and zirconia with 2%, 4% and 6% volume fraction as the inclusion. In the two-phase composite, we shall refer the matrix as phase 0 and the inclusions as phase 1. The volume concentrations of the matrix and the inclusion are denoted by c_0 and c_1 respectively. Because the zirconia is uniformly dispersed within the high performance binder and the mortar, the cementing composites become isotropic.

2. THEORETICAL ANALYSIS

2.1 Transformation toughening

If PSZ particles (inclusions) are embedded in the binder (matrix), similar to ceramics [2], the stress level near the pre-crack is sufficiently high to induce phase transformation from tetragonal grains to monoclinic grains theoretically. Phase transformation in this process involves a certain amount of volume expansion ε_{kk}^{ph}, producing a compressive residual stress at the crack-tip that helps to reduce the stress-intensity factor.

To calculate the toughness change, we use the weight-function approach and Eshely-Mori-Tanaka method to determine the change of the stress-intensity factor ΔK_t for a transformation problem [3]. The explicit result for spherical inclusions (zirconia) by using mean-stress criterion is shown as follows.

$$\Delta K_t = -0.22 c_1 \frac{E\sqrt{H}}{1-\nu} \frac{\kappa_1(3\kappa_0 + 4\mu_0)}{3\kappa_0\kappa_1 + 4\mu_0(c_0\kappa_0 + c_1\kappa_1)} \varepsilon_{kk}^{ph} \tag{1}$$

where E =the elastic Young modulus of the composite, ν =the Poisson ratio of the composite, κ_r =the bulk modulus of the r-th phase, μ_r =the shear modulus of the *r*-th phase, and H =the half-height of the transformed zone. Here, H can be simplified to

$$H = \frac{3\sqrt{3}}{\pi}\left[\frac{3K_I(1-\nu^2)}{2(1-c_1)E}\right]^2 \tag{2}$$

where K_I = the Mode-I stress intensity factor.

2.2 Microcrack toughening

While the monoclinic zirconia (FSZ) existed within the binder or the mortar of HPC, it is possible to create many microcracks surrounding zirconia particle, and microcracks can reduce the elastic moduli of the composite. However, the elastic moduli of the zirconia are greater than those of the matrix (the binder or the mortar) here. Thereby, the elastic moduli diminution factor to the toughness increase, by considering the effect of microcracks and the moduli differences, needs to be re-evaluated in HPC.

Based on the weight-function theory and Hutchinson's technique, the analytic form of the toughness change $\Delta K_i = K_{tip} - K_I$ near a pre-crack tip was derived, where K_{tip} =the toughness near the pre-crack, as follows [4].

$$\frac{K_{tip}}{K_I} = f\sqrt{g} \tag{3}$$

where the parameters f and g for circular microcracks are

$$f = \frac{27 + 96k_1(1+\nu_0)^2\eta}{27 + 4(1+\nu_0)^2\eta} \tag{4}$$

$$g = \frac{45(2-\nu_0)[45(2-\nu_0) + 16(1-\nu_0^2)(10-3\nu_0)]}{45(2-\nu_0)^2[45 + 32(5+\nu_0)\eta] + 1024(1-\nu_0^2)(5-\nu_0)(5-2\nu_0)\eta^2} \tag{5}$$

and η=the crack density, the contour factor k_1=1/24 under a stationary condition and k_1=0.0072 under a steady-state propagation condition, respectively.

2.3 Crack density

The crack density η defined by Budiansky and O'Connell is calculated as follows [5].

$$\eta = \frac{8}{\pi^3} M \left\langle l^2 \right\rangle \tag{6}$$

where M =crack numbers per unit area, l =the crack length, and the angle brackets $< \cdot >$ =the orientational average of the said quantity respectively.

3. EXPERIMENTAL PROGRAM

The binder consists of Type I portland cement, fly ash with specific gravity =2.12 and the Blaine 3110 cm^2/g, slag with specific gravity =2.95 and the Blaine 4350 cm^2/g, and Type G superplasticizer. The fine aggregate was river sand from Lao-Lung River, Kaohsiung, Taiwan, with fineness modulus = 3.05, bulk specific gravity = 2.67 and absorption = 1.85 percent. Zirconia with specific gravity = 5.8 is used, where the particle sizes of FSZ and of PSZ are $1 \sim 50\mu m$ and $1 \sim 10\mu m$ respectively.

Mix proportions of high performance cementing composites are shown in Tab.1 ~ 2 with water-binder ratio = 0.32.The mortar was mixed with the binder and the fine aggregate having a binder-sand ratio of 1:1 by weight approximately. Two kinds of test specimens, 10ϕ×20cm for the compressive test and 4╳4╳16cm containing a 0.4cm V-notched pre-crack at the mid-length for the bending test, were prepared respectively. The specimens were loaded at a strain rate $\dot{\varepsilon} = 1\times10^{-5}/\sec$. The measured toughness of the materials is determined by using three-point bending test as follows.

$$K_m = \frac{3FSY}{2W^2B}\sqrt{\pi a} \tag{7}$$

where K_m =fracture toughness, F =bending strength, S =specimen length, B =specimen width, W =specimen height, a =length of pre-crack, and Y =shape factor and equal to 0.97

here. The SEM specimen is prepared for crack measurements, and measurements were taken at a magnification of 1000 here.

Tab.1 Mix proportions of the binder (kgf/m^3)

c_1	cement	slag	fly ash	water	superplasticizer	ZrO_2
0%	1226	68	219	468	16.3	0
2%	1210	67	215	459	15.6	116
4%	1177	66	211	449	15.3	232
6%	1153	65	206	440	15.3	348

Tab.2 Mix proportions of the mortar (kgf/m^3)

c_1	cement	slag	fly ash	sand	water	superplasticizer	ZrO_2
0%	704	39	127	1123	270	9.2	0
2%	690	38	125	1010	265	9.0	116
4%	676	37	122	1078	259	8.8	232
6%	662	37	120	1055	254	8.6	348

4. RESULTS AND DISCUSSION

4.1 Experimental results with FSZ

The material properties of the binder and the mortar depending on c_1 and material ages are shown in Tab. 3 ~ 4. Obviously, the compressive stresses at zirconia $c_1 = 4$ % is the most effective and will decrease for any c_1 after the 90th day of ages. Materials with an overdose of zirconia, for example $c_1 > 4$ %, are a disadvantage to those elastic Young modulus. This is because the number of microcracks increases by increasing c_1 from the SEM observation shown in Tab. 5, where the crack density η is calculated by Eq. (6).

The fracture toughness K_m of the binder and the mortar calculating from Eq. (7) is indicated in Tab. 6, and the toughness continues to increase if c_1 and material ages grow. The toughness change K_m / K_I of the binder is always better than that of the mortar.

Tab.3 Material properties of the binder with FSZ

ZrO_2 (c_1)	peak stress (MPa)			peak strain ($\times 10^{-3}$)			Young's modulus (GPa)		
	14 days	28 days	90 days	14 days	28 days	90 days	14 days	28 days	90 days
0%	52.70	57.00	71.11	6.3	5.7	4.9	13.30	16.98	19.30
2%	54.58	62.59	72.72	6.3	5.8	5.1	14.22	17.20	19.55
4%	58.13	65.66	75.34	6.9	6.8	5.4	15.73	17.94	20.27
6%	54.39	63.45	70.47	6.8	6.0	4.1	15.89	18.29	20.87

Tab.4 Material properties of the mortar with FSZ

ZrO_2 (c_1)	peak stress (MPa)			peak strain ($\times 10^{-3}$)			Young's modulus (GPa)		
	14 days	28 days	90 days	14 days	28 days	90 days	14 days	28 days	90 days
0%	48.17	56.24	65.27	4.3	3.2	4.8	21.18	23.90	25.14
2%	50.33	59.50	69.63	3.5	3.3	4.0	22.57	25.77	25.96
4%	53.00	61.27	71.10	3.2	3.2	3.8	22.74	25.95	26.22
6%	51.55	57.74	69.70	3.3	3.2	4.2	20.96	23.18	23.58

Tab. 5 Crack density of the binder and the mortar with FSZ

c_1	2%	4%	6%
binders (η)	0.143	0.155	0.160
mortars (η)	0.139	0.142	0.146

Tab. 6 Fracture toughness of the binder and the mortar with FSZ

ZrO_2 (c_1)	binders $K_m\left(MPa\sqrt{m}\right)$			mortars $K_m\left(MPa\sqrt{m}\right)$		
	14 days	28 days	90 days	14 days	28 days	90 days
0%	0.419	0.522	0.576	0.801	0.886	0.935
2%	0.435	0.544	0.591	0.851	0.912	0.968
4%	0.441	0.552	0.612	0.872	0.938	0.992
6%	0.445	0.555	0.622	0.874	0.950	0.999

4.2 Experimental results with PSZ

The trends of the compressive stresses and the elastic Young modulus for materials with PSZ are similar to materials with FSZ. The fracture toughness of the binder at the 90th day of the age is shown in Tab. 7. The fracture toughness continues to increase as PSZ particles increase. By comparing Tab. 6 with Tab. 7, one finds that the toughening effect of the cementing material with FSZ is greater that that with PSZ.

Tab. 7 Fracture toughness of the binder with PSZ at 90 days

c_1	0%	2%	4%	6%
K_m $MPa\sqrt{m}$	0.557	0.567	0.584	0.587

4.3 Theoretical calculations to material toughening

From the experimental results shown in Tab. 6, the binder and the mortar having the toughening are always observed if FSZ particles are added. We calculate the toughness change due to the effect of microcracks and the moduli differences from Eq. (3), and, after summing those two toughness change, the theoretical results for cementing material with FSZ are obtained. The theoretical calculations shown zirconia toughened cementing materials in evidence coincide with the experimental results. From Tab. 7 or the theoretical calculations by Eq. (1), one finds that the values of the toughness increase for the binder containing PSZ are small, for example 5% toughness enhancement at c_1 =6 %.

5. CONCLUSIONS

The following conclusions are drawn from the test results and the theoretical analysis.

1. Zirconia particles can strengthen the compressive strength and the elastic moduli of the binder and the mortar, and the optimum volume fraction of zirconia $c_1 = 4\%$.
2. The material properties of the HPC without coarse aggregates continue to increase until volume fraction of zirconia $c_1 > 4\%$. This is because the material microcracking becomes a particular factor and affects the behavior of the materials.
3. The micro-FSZ and PSZ particles continue to enhance the toughness of the binder and the mortar as c_1 increases. The toughness increment is less 10% if $c_1 = 6\%$, that is, unlike zirconia toughened ceramics, micro-FSZ and PSZ particles can toughen the cementing materials but the effect is not effective. This result also obtains from the theoretical calculations because the elastic Young modulus of zirconia is almost 10 times greater than that of the matrix (binder and mortar).
4. Microcrack toughening is the better way to enhance the fracture toughness of zirconia/concrete comparing with the transformation toughening.

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