Pergamon

Cement and Concrete Research, Vol. 27, No. 1, pp. 23-27, 1997
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0008-8846/97 $17.00 + .00

PII S0008-8846(96)00182-2

FLEXURAL STRENGTH OF CEMENT PASTE COMPOSITES CONTAINING MICRON AND SUB-MICRON NICKEL PARTICULATES

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(Communicated by M. Daimon)
(Received September 30, 1996; in final form October 23, 1996)

ABSTRACT

The effect of nickel particle addition (0.3–5.0 μm diameter) to brittle cement paste matrices on flexural strength was investigated. Strengthening was observed for nickel particle addition up to 15% by volume. This was explained in terms of pore structure modifications and toughening mechanisms using evidence provided by mercury intrusion porosimetry and SEM. *Copyright © 1997 Elsevier Science Ltd*

Introduction

Strengthening of cement matrices through the use of fibre technology has been extensively investigated for several decades [1]. There is a paucity of information on strengthening of cement systems due to particle inclusions as these often weaken these materials.

It has been shown that the fracture energy and strength of ceramics e.g. sodium borosilicate glass, can be increased significantly by incorporating a second-phase dispersion of Al_2O_3 particles [2, 3]. The fracture energy behavior was related to interparticle spacing and the average particle size of the dispersion. The data indicated that the larger particle size dispersions generated higher fracture energies. Conversely flexural strength increased with volume fraction of particulate and decreasing size. A consequence of this was that crack size as determined by the Griffith relation increased from that of the glass matrix by about 1 to 3 times the average particle size of the dispersed phase [2]. A crack bowing model was advanced to explain the fracture energy increase by a pinning of the crack front by the second-phase particles.

A model for composite fracture energy, γ, was expressed in terms of the equation, $\gamma = \gamma_o + F(D) \cdot T/d$ where γ_o = fracture energy of the matrix, T is the line energy at the critical stress level required to propagate the crack, d is the distance between pinning positions and F(D) is a dimensionless function dependent on the pinning particle size D ($0 \leq F(D) \leq 1$). Other toughening theories include induced compression in the crack-front zone, plastic deformation of second phase particles and microfracture in the process zone [3].

It was felt that a dispersion of second phase (micron or sub-micron in size), high modulus of elasticity particulates in a cement paste matrix should have similar strengthening effects to those observed in ceramic glasses. It is therefore argued that there is likely a minium separation of the particles that would increase the energy requirements for crack initiation and propagation. A pilot study using nickel particulates was designed to demonstrate this concept.

TABLE 1

Chemical Composition of Portland Cement and Silica Fume

Mass %	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O	K_2O
Cement	19.83	61.21	4.18	3.20	4.09	3.93	0.45	0.87
SF	95.17	0.23	0.21	0.13	0.15	0.12	0.10	0.27

Experimental

Materials

Cementitious solids. Type 10 portland cement and silica fume (SF) were used in this study. The chemical composition is provided in Table 1.

Nickel particles. Micron and sub-micron nickel (0.3 to 5 μm) 'spherical' particulates were supplied by Alfa Products Thiokol USA. An SEM photomicraph, Figure 1 illustrates the angular nature and rough surface texture of the particles. Figure 2 (a back scatter image–Robinson detector) depicts the uniform distribution of the nickel particles in a cement paste matrix.

Paste binders. A series of cement paste binders was produced using type 10 portland cement and silica fume. The binder mixes were prepared using a conventional Hobart mixer. Each series contained a different volume fraction of Ni particles i.e. 0, 5, 10 and 15%. Samples were cast in the form of thin wafers and cured for one day at 100% relative humidity.

Flexural specimens. Beam specimens, 4 mm × 3 mm × 60 mm, were cut from the wafers and placed in a saturated calcium hydroxide solution for various periods until required. The water-cementitious solid (w/s) ratio of the binders was 0.35 and 0.45. The amount of silica fume used was 15% by mass of cementitious

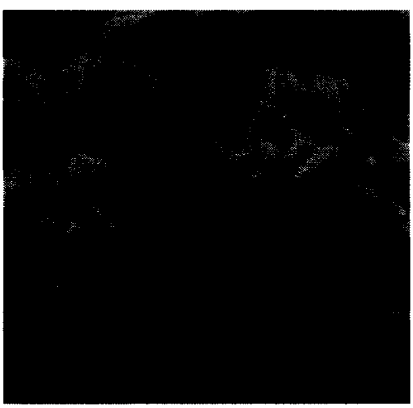

FIG. 1.
SEM photomicrograph of 5 μm nickel particle cluster.

FIG. 2.
Back scatter image of cement paste (w/s = 0.35) containing 10% (by volume) of Ni particles.

TABLE 2

Flexural Strength (Mpa) of Cement Binders (w/s = 0.35, 15% SF) Containing Ni Particulates

Time, days	0% Ni	5% Ni	10% Ni	15% Ni
3	11.73	14.97	12.98	12.26
7	11.93	16.61	17.12	15.12
28	12.83	17.58	18.41	19.00

solids. A sulfonated napthalene formaldehyde superplasticizer was used (0.5% by mass of cement solids).

Flexural tests. Flexural tests (3 point) were carried out using an MTS loading system with a displacement rate of 4.2×10^{-4} mm/s. Reported values are the average of seven determinations.

Porosity measurements. Pore size distribution data was obtained using mercury intrusion porosimetry at pressures up to 408 MPa.

Results and Discussion

Results of flexural strength determinations for w/s = 0.35 (15% SF) are given in Table 2.

The coefficients of variation for the data in Table 2 ranged from 9.8% for 10% nickel at 7 days to 26% for the reference at 7 days.

It is apparent that the nickel particulate inclusions can strengthen the cement-silica fume binders. A 48% increase in flexural strength at 28 days was observed for the binder containing 15% Ni particulates. Strengthening occurred at every level of nickel addition.

Similar trends were observed for w/s = 0.45 preparations. For example the composite containing ten percent Ni particulates had a flexural strength of 17 MPa relative to a value of 11.5 MPa for the reference paste containing no nickel inclusions.

It is apparent that the micron size nickel inclusions can 'reinforce' brittle cement paste matrices. Results of the mercury intrusion porosimetry investigation for the portland cement/silica fume paste (w/s = 0.45) hydrated 28 days are given in Table 3. The results for the portland cement/silica fume paste (w/s = 0.35) show similar trends and are not presented.

The increase in flexural strength with addition of nickel particulates can be partially explained by the reduced porosity particularly at the 10 and 15% level. Pore volume in the

TABLE 3

Pore Descriptors—Portland Cement/Silica Fume Paste (w/s = 0.45)

Pore Structure Descriptor	Volume Percentage of Nickel Particles			
	0	5	10	15
Total porosity, %	26.8	26.6	22.7	22.2
Threshold pore diameter, µm	0.020	0.022	0.021	0.020
Pore volume (0.004-0.005 µm), %	7.5	9.3	10.3	8.0
Pore volume (0.009-0.017 µm), %	8.3	5.1	2.8	5.3

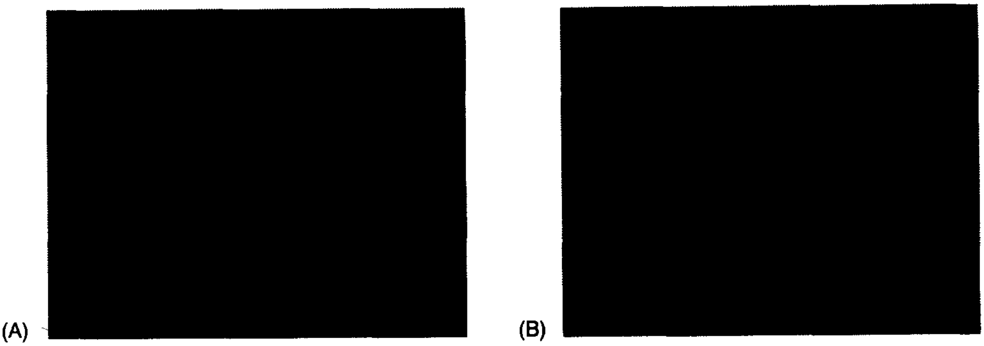

FIG. 3.
(A) SEM photomicrograph of cement paste (w/s = 0.45, 5% Ni) showing bifurcation. (B) SEM photomicrograph (w/s = 0.45, 5% Ni) showing 'crack-pinning' by Ni particle.

finest pore range measured (0.004–0.005 μm) is largest for the 5 and 10% nickel composites. The use of superplasticizer alone does not account for differences between pastes containing different amounts of nickel particles. The total porosity of the paste containing 5% nickel is similar to the reference where superplasticizer was not used. Further, the largest pore volume in the range (0.009–0.017 μm) is contained by the reference paste which is consistent with lower observed strength [4].

It is also apparent through SEM examination that toughening mechanisms are operative in these composites. Processes resulting in bifurcation and crack pinning are illustrated in Figure 3a and 3b for the paste (w/s = 0.45) containing 5% nickel. Nickel particle clusters (about 2 μm in diameter) clearly influence crack growth. Crack growth on both sides of a nickel particle cluster and cracks impeded by nickel clusters are illustrated in Figure 4a and 4b for a paste containing 15% nickel. Increased energy requirements for crack initiation and propagation may correspond to an increase in flexural strength.

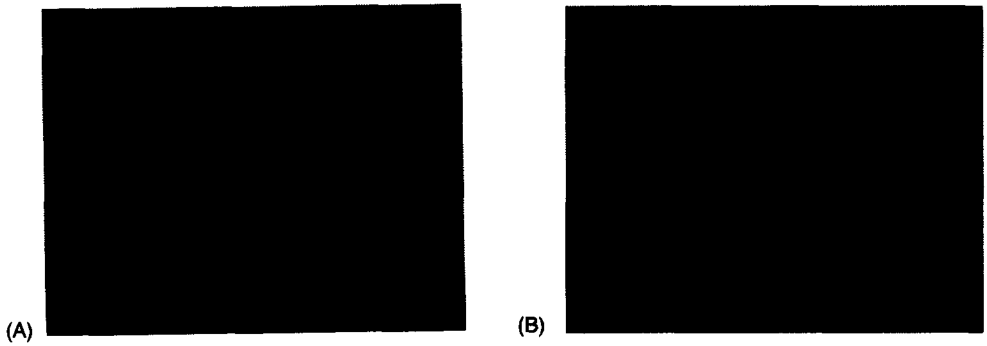

FIG. 4.
(A) SEM photomicrograph of cement paste (w/s = 0.35, 15% Ni) showing crack growth on both sides of a Ni particle cluster. (B) SEM photomicrograph of cement paste (w/s = 0.35, 15% Ni) showing cracks impeded by Ni clusters.

Conclusions

1. Addition of micron and sub-micron size nickel particulates to brittle cement paste matrices can increase flexural strength.
2. Porosity is reduced by approximately 15% with the addition of 10 percent (by volume) of nickel particles. The volume of large pores (0.009–0.017 μm) is reduced and the volume of fine pores (0.004–0.005 μm) is increased.
3. Reduced porosity and toughening mechanisms e.g. crack pinning and bifurcation would appear to result in strengthening of brittle cement matrices.

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