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Properties and modification mechanisms of nano-zirconia filled reactive powder concrete

Baoguo Han [a,*], Zhu Wang [a], Shuzhu Zeng [a], Daocheng Zhou [a], Xun Yu [b,c], Xia Cui [a], Jinping Ou [a]

[a] School of Civil Engineering, Dalian University of Technology, Dalian 116024, China
[b] Department of Mechanical Engineering, New York Institute of Technology, New York, NY 11568, USA
[c] School of Mechanical Engineering, Wuhan University of Science and Technology, Wuhan 430081, China

HIGHLIGHTS

- Nano-ZrO_2(NZ) are used to modify reactive powder concrete(RPC).
- Flexural, compressive and splitting strengths of RPC with NZ achieve increases of 36.6%, 16.3% and 34.0%, respectively.
- NZ does not accelerate the hydration process of RPC.
- NZ can reduce CH orientation to improve the microstructures of RPC.

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ABSTRACT

The mechanical and electrical properties of reactive powder concrete (RPC) with nano-ZrO_2 (NZ) are investigated in this research. The reinforcing mechanisms of NZ to RPC are studied through thermogravimetry (TG) analysis, scanning electron microscope (SEM) observation and X-ray powder diffraction (XRD) analysis. Research results indicate that the NZ has obvious modifying effect to RPC. The flexural, compressive and splitting strengths of RPC with NZ at curing age of 28 days achieve increases of 36.6%/4.19 MPa, 16.3%/16.18 MPa and 34.0%/1.08 MPa, respectively, compared to plain RPC. The addition of NZ makes a 20% decrease in the electrical conductivity of RPC. The NZ does not accelerate the hydration process of RPC. However, the microstructures of NZ filled RPC are denser than that of plain RPC. This leads to the reduction of the growth space of calcium hydroxide (CH) crystals, thus the size of CH crystals is reduced. Furthermore, NZ can reduce CH crystal orientation to improve the microstructures of the composites.

1. Introduction

With the rapid development of building industry, high-performance concrete materials are in an urgent demand. Properties of concrete have been undergoing changes through technological advancement [1]. Reactive powder concrete (RPC) is known as a type of ultra-high-performance concrete. The primary improvements of RPC include the homogeneity of particle size, porosity and microstructure of matrix [2,3]. Compared to the microstructure of conventional concrete or even high-performance concrete, RPC has a denser microstructure [4,3]. Its compressive strength of RPC can reach up to 800 MPa [5]. However, high-strength concrete is associated with low fracture toughness, low tensile strain and low impact resistance, which limit their applications.

Nano fillers with small size effect and boundary effect can not only fill the pores inside concrete [6], but also improve the interface structure of concrete and aggregate to increase the strength, toughness, impermeability and durability of concrete [7,8]. As a kind of inorganic non-metal oxide, nano-ZrO_2 (NZ) features good wearability and anti-corrosion performance. NZ with high strength, high toughness and good dispersion is an excellent toughening material for ceramics. Because of small size effect and phase transition effect of NZ, the density of ceramics can be increased and the diffusion of micro-cracks of ceramics can be blocked. Therefore, the mechanical strength of ceramics can be significantly enhanced and fracture toughness of ceramics can be increased [9]. Inspired by the research of NZ in the field of ceramics, NZ was used in the field of cement and concrete materials. Soleymani found that the flexural strength of NZ filled ordinary Portland cement paste increased 25%/1.1 MPa at curing age of 28 d [10]. Nazari et al. (2010) observed that the flexural and

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* Corresponding author.
E-mail addresses: hanbaoguo@dlut.edu.cn, hithanbaoguo@163.com (B. Han).

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splitting strengths of NZ filled ordinary Portland cement paste at curing age of 28 d are higher than those of the plain cement paste. The optimal amount of NZ is 1%, which leads to increases in flexural and splitting strength of 31.8%/1.4 MPa and 83.3%/1.5 MPa, respectively [11]. They also studied the compressive strength and workability of NZ filled ordinary Portland cement paste [12,13]. The compressive strength at curing age of 28 d increases first and then decreases with the increase of NZ content. The maximum increase in compressive strength is 18.5%/6.8 MPa. In addition, Soleymani studied the effect of NZ on the pore structure property of cement paste. Experimental results showed that the addition of NZ improves the pore structure of cement paste, and the refined extent of pore structure increases with decreasing NZ content [10].

Based on the above analysis, NZ is a type of promising fillers for developing high-performance cement and concrete materials. However, previous studies mainly focus on the influence of NZ on ordinary Portland cement paste. The research on the effect of NZ on RPC containing aggregate and with high strength characteristics has not been done. Furthermore, previous researchers suggested that reinforcing mechanisms of NZ to ordinary Portland cement paste include filling pores and improving the pore structures [12,13], which are insufficient to fully understanding the effect of NZ to cement and concrete materials. Therefore, RPC with NZ at levels of 0.0%, 0.5%, 1.0%, 3.0% and 5.0% were fabricated in this study. Their flexural, compressive, splitting and electrical properties at curing age of 3 d and 28 d are investigated. Thermogravimetry (TG), scanning electron microscope (SEM) and X-ray powder diffraction (XRD) are used to analyze the reinforcing mechanisms of NZ to RPC.

2. Experiment

2.1. Materials

The NZ with an average particle size of 20 nm provided by Nanjing Haitai Nano-materials Co. Ltd. in China is used as the filler. Its SEM image is shown in Fig. 1. The Portland cement (P•O 42.5R) provided by Dalian Onoda Cement Co. Ltd. in China was used as the binder. Silica fume is a commercially available product by Elkem Materials Ltd. The fly ash provided by Dalian Daokete Building Materials Co. Ltd. in China was used as the mineral admixture. Quartz sand with a size range of 0.12–0.83 mm was used as aggregate. RHEOPLUS 411 (BASF) superplasticizer was used to adjust the workability of the concrete mixture and to assist NZ dispersion. Stainless steel gauzes with opening of 40 mm × 60 mm were used to make electrodes.

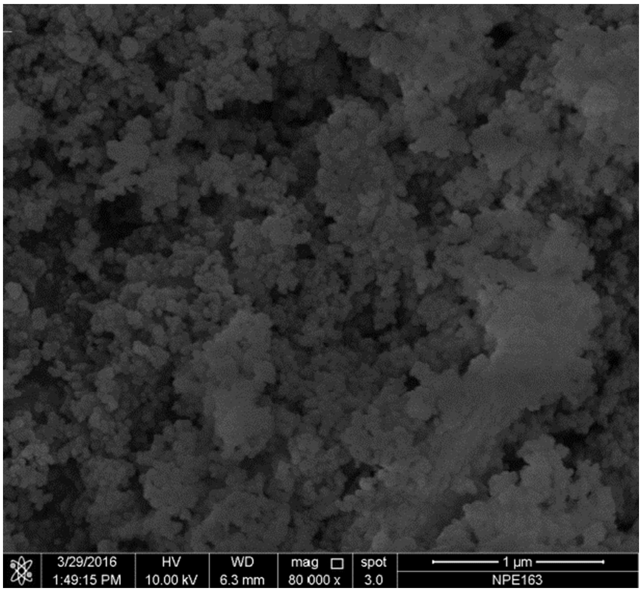

Fig. 1. SEM image of NZ.

2.2. Preparation

The content levels of NZ are 0.5%, 1.0%, 3.0%, 5.0% by weight of cement, respectively. The water to binder ratio was fixed at 0.24 for all the mixtures. The detail mix proportions are shown in Table 1. In order to mix NZ uniformly and keep good workability of the mixture, water reducer was first put into the water containing NZ. The progress of fabricating NZ filled RPC is presented in Fig. 2. The details are as following: (1) Water, water reducer, NZ, cement, silica fume, fly ash and sand were weighted as mix proportions. (2) Water, NZ and water reducer were mixed by a Constant Speed Stirrer (DW-2 DC, provided by Chinese Yu Hua Instrument Ltd.) at low speed (relation and revolution of mixing blade is 140 ± 5 r/min and 62 ± 5 r/min) for 10 s. (3) The silica fume was put into the suspension slowly and mixed at low speed for 60 s. (4) The cement and fly ash were put into the mixing pot and mixed at low speed firstly for 120 s and then at fast speed (relation and revolution of mixing blade is 258 ± 10 r/min and 125 ± 10 r/min) for 120 s. (5) The sand was put into the suspension and mixed at low speed firstly for 60 s and at fast speed for 240 s. (6) The mixture was poured into the oiled mould (40 mm × 40 mm × 40 mm and 40 mm × 40 mm × 160 mm) and the mould was put on the electric vibrator to eliminate bubbles. (7) Two electrodes were embedded in the mixture whose size is 40 mm × 40 mm × 160 mm (as shown in Fig. 3(a))[14]. (8) The composites were cured at temperature of 20.0 °C in 95% relative humidity for 24 h before demold. Then half of specimens were cured for 2 d and others were cured for 27 d in water at 20 ± 1 °C.

The preparation process of plain RPC is same as that of NZ filled RPC except he steps (1) and (2), in which NZ was not added.

The samples for TG and XRD test were cement paste (its mix proportions as shown in Table 2) because the addition of sand may affect the test accuracy. One reason is that the weight of dry sand does not decrease with increasing temperatures and that the amount of sand in samples for TG is random. The other reason is that the XRD characteristic peaks of sand are too strong to make the XRD peaks of hydration products of cement observable. The manufacture process of cement paste was the same with the cement mortar except the process of adding sand. After hydration for 3 d and 28 d, the cement pastes was crushed, milled and sieved at 80 μm for TG and XRD test. In addition, samples were dried at 50 °C for 24 h to avoid the effect of absorbed water.

The samples for SEM selected from the composites after testing flexural and compressive strength at age of 28 d.

2.3. Measurement

The tested properties of the specimens include flexural strength, compressive strength, splitting strength, and electrical resistivity. The flexural strength was measured by a mortar folding meter DKZ-5000 at age of 3 d and 28 d. All the specimens were loaded to failure at constant loading rate of 0.5 mm/min. The average value of flexural strengths of 3 specimens in each group was recorded as the final flexural strength if the maximum or the minimum value was 10% less than the average value. The compressive strength was also measured according to GB/T17671-1999 of China (Method of testing cements-determination of strength-ISO). The specimens of 40 mm × 40 mm × 160 mm were broken in two near the middle after flexural test. The two pieces were measured by a