The Micro Analysis and Influence of Nano SiO$_2$ on High-Temperature Compressive Performance of Steel Fiber Reinforced Concrete (SFRC)

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Abstract. This paper investigated the compressive strength of the normal concrete (NC), the steel fiber reinforced concrete (SFRC), the Nano normal concrete (NNC) and the Nano-steel fiber reinforced concrete (NSFC) at the high temperature. On the other hand, Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD) were used to analyse Micro-Structure and Matrix phase structure at different temperatures. Results presented that the peak values of compressive strength of four types of concrete under high temperature appeared under 200$^\circ$C. The compressive strength of NSFC was 77.45 Mpa under 200$^\circ$C, respectively being 1.13, 1.21 and 1.34 times of those of SFRC, NNC and NC. Nano SiO$_2$ could go through secondary hydration reaction with cement hydration product Ca(OH)$_2$ so as to reduce Ca(OH)$_2$ content and refine Ca(OH)$_2$ crystals, transform Ca(OH)$_2$ having adverse effect on strength into C-S-H gels and improve structural compactness. Therefore, addition of nano SiO2 could obviously improve high-temperature compressive strengths of the concrete, and it especially played a significantly role in improving compressive strength of SFRC.

1. Introduction

In recent years, the application of nanotechnology in concrete enabled it to develop toward high-performance and multi-functional direction. Nano materials have small-size, quantum, surface, and interface effects, which macro objects do not possess; they have peculiar features that many traditional materials do not have in the aspects of structure, physical properties, and chemical properties [1]. Nowadays, few discussions on high-temperature mechanical properties of nano concrete [2-4] and on micromechanism of the damage of high-temperature mechanical properties of nano concrete are available. Numerous experimental studies and fire field investigations indicated that the concrete strength attenuation under high temperature was unavoidable [5]. Compared with mechanical properties of the concrete under normal temperature and after high-temperature cooling, the mechanical properties under high temperature were more complicated. Three methods are usually used to study the high-temperature mechanical properties of concrete, as follows: (1) load-sustaining test: stress was applied under room temperature, and this stress was sustained during the heating process. Then, the specimen would experience a compression failure after the target temperature was reached. (2) Non load-sustaining test: the specimen was heated under no initial stress, and then a failure after loading at certain heating rate was experienced. (3) Residual non load-sustaining test: the specimen did not bear any stress when it was heated, and it experienced the failure during the loading process after it was cooled to room temperature [6]. Nowadays, the common domestic research on high-
temperature properties is on the residual non load-sustaining test includes research on high-temperature mechanical properties [7-9]. For the first two methods, in view of the great difficulty in equipment and device, relatively fewer studies on high-temperature properties were available [10-11]. Considering that, after the specimen was heated to stipulated test temperature, the specimen was immediately taken out, and loading was implemented. On the one hand, this condition would be appropriate for actual situation of a fire disaster. On the other hand, existing test equipment could be directly used without any requirement for configuration of high-temperature loading equipment. The test scheme of specimen heating → constant temperature → loading and the compressive strength of nano SiO$_2$-adulterated steel fiber reinforced concrete (SFRC) under high temperature were measured. The influences of nano SiO$_2$ on compressive strengths of NC and SFRC were studied. SEM observation of microstructures, after different temperatures, was implemented, and then the mechanical properties after high temperature were analyzed with microstructure change combined.

2. Testing Materials, Preparation and Method

2.1. Raw Materials

The materials used in this test include: 42.5-Class ordinary Portland cement; stones: the grain size ranging from 5 to 20 mm; sands: medium sizes, continuous gradation; steel fiber: arch high strength steel wire with the length of 35 mm, equivalent diameter of 0.6 mm, length diameter ratio of 58 and volume rate of 1.5%. The nano SiO$_2$ used in this paper is from Hangzhou Wanjing New Material Co. Ltd. The content of nano SiO$_2$ is just 2% of cementing materials which substitutes the same amount of cement.

| Table 1. Properties of Nano-SiO$_2$. |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Content | Purity (%) | Average particle size (nm) | Apparent density (g/L) | PH value | Specific surface area (m$^2$/g) | Ignition loss (%) | Appearance |
|------|-------------|-----------------------------|-----------------------------|-------------|-----------------------------|-----------------------------|-------------|
| Properties | 99.5 | 30 | 40-60 | 5-7 | 200±10 | ≤1.0 | Non-crystal White powder |

| Table 2. Mix proportions and compressive strength of different concretes prepared. |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Sample | Cement (kg·m$^{-3}$) | Fly ash | Sand | Coarse aggregate | Water | Nano-SiO$_2$ | Steel fiber | Water Reducing agent | Slump (mm) |
|------|-----------------------------|-------|-------|-----------------------------|-------|-------------|-----------------------------|-----------------------------|-------------|
| NC | 420 | 110 | 668 | 1044 | 165 | 0 | 0 | 17.6 | 225 |
| NNC | 411.6 | 110 | 668 | 1044 | 165 | 8.4 | 0 | 17.6 | 195 |
| SFRC | 420 | 110 | 622 | 973 | 165 | 0 | 117 | 17.6 | 50 |
| NSFC | 411.6 | 110 | 622 | 973 | 165 | 8.4 | 117 | 17.6 | 25 |

2.2. Preparation of the Specimens and Methods of Testing

In this experiment, 32 groups of cubic specimens (100 mm × 100 mm × 100 mm) were prepared. For each group, three specimens were tested. All specimens were stored for 28 d in the laboratory at room temperature. The samples were then kept in the room for 5 d. After the specimen surface moisture had dried, the high-temperature test was carried out.

When compressive strength test under high temperature was implemented, the specimen was heated at 200, 400, 600, and 800 °C. When the set temperature was reached, heat preservation lasted 3 h. Then, the specimen was taken out of the furnace, and 2,000 kN material testing machine was immediately used to perform high-temperature compressive strength test of the specimen with loading rate of 0.5-0.8 MPa/s. Subsequently, the maximum load was recorded, and it was accurate at 0.1 MPa.
S-3400N SEM was used to observe microstructural morphologies of four materials treated at different temperatures, and RigakuDmax 2500 PC X-ray diffractometer was used to analyze the phase structure. The macro-mechanical properties of the materials under high temperature were revealed through analysis of microstructural change.

3. Test Results and Analysis

The residual strength of concrete, after high temperature or fire disaster, is an important basis to evaluate building damage degree after the disaster, and compressive strength is the most important index among mechanical properties. Thus, compressive strength tests under normal and high temperatures of four types of concrete, namely, high-performance normal concrete (NC), steel fiber reinforced concrete (SFRC), nano SiO$_2$-adulterated normal concrete (NNC), and nano SiO$_2$-adulterated steel fiber reinforced high-performance concrete (NSFC) were carried out in this paper.

3.1. Compressive Strengths of NSFC, SFRC, and NC under Normal Temperature

In accordance with the Method Standard of Mechanical Property Test of Normal Concrete (GB/T50081-2002), first, 7-d and 28-d cube compressive strengths of nano SiO$_2$-adulterated normal concrete (NNC) were tested. Results showed that during loading process, crack propagation law and final failure mode of nano SiO$_2$-adulterated normal concrete (NNC) were basically identical with those of normal high-performance concrete (NC) (figure 1). As the load increased, the concrete on specimen surface continuously bulged outward and peeled off. The pressure-bearing area and horizontal constraint force of the specimen continuously reduced, the concrete failure in the middle portion of the specimen was the most serious, and finally two angular conical failure planes with their opposite vertexes connected were formed.

Subsequently, cube compressive strength tests of residual groups of steel fiber reinforced concrete were similarly conducted. Figure 2 shows the comparison of compressive failure modes between nano SiO$_2$–adulterated steel fiber reinforced concrete (NSFC) and steel fiber reinforced concrete (SFRC) when loading was conducted until specimen failure. The steel fiber existed inside the concrete, which inhibited generation and development of cracks, and then swelling was not evidently exerted in the aspect of lateral deformation. Thus, angular conical failure planes were not observed on NSFC or SFRC as NC. After compression, SFRC damage area was large with wide and deep cracks at large quantities. A crack appeared at the position approximately 1-1.5 cm away from the surface. However, the damage area of NSFC specimen after compression was small without evident crack on the surface, and the generated cracks after compressive failure were small in quantity. Evidently, adulteration of nano SiO$_2$ improved compressive strength of concrete. Therefore, after adulteration of nano SiO$_2$, compressive failure degree of concrete was lighter than that of concrete, which was not adulterated with SiO$_2$. Compressive strength results of several types of concrete are presented in table 3. Table 3 shows that among the four types of concrete, the 7 d and 28-d compressive strengths of nano SiO$_2$–adulterated concrete were improved to different degrees when compared with those of non nano SiO$_2$–adulterated concrete. For normal concrete, after adulteration of nano SiO$_2$, 7-d compressive strength was improved by 2.64%, but adulteration of nano SiO$_2$ had little influence on the 28-d compressive strength given that it was improved only by 0.22%. For steel fiber reinforced concrete, 7-d compressive strength was increased by 24.56%, and the 28-d compressive strength was increased by 13.55%. Evidently, addition of nano SiO$_2$ could significantly improve the early-stage compressive strength of concrete and more evidently improve the compressive strength of steel fiber reinforced concrete. Compressive failure degree of nano SiO$_2$–adulterated concrete was lower than that of non nano SiO$_2$–adulterated concrete, as shown in figure 2.
Figure 1. Compressive strength failure form of NNC and NC specimen.

Figure 2. Compressive strength failure form of NSFC and SFRC specimen.

Table 3. Compressive strength of four kinds of concrete at 7d and 28d (MPa).

|       | NC   | NNC  | Strength growth | SFRC | NSFC | Strength growth |
|-------|------|------|-----------------|------|------|-----------------|
| 7Day  | 38.32| 39.33| 2.64%           | 44.22| 55.08| 24.56%          |
| 28Day | 49.27| 49.38| 0.22%           | 55.14| 62.61| 13.55%          |

3.2. Compressive Strengths of NSFC, SFRC, NNC and NC under High Temperature

Figure 3 shows the cube compressive strength values of NSFC, SFRC, NNC, and NC under normal temperatures of 200, 400, 600, and 800 °C. Among the four types of concrete, NSFC under high temperature was the highest, followed by SFRC and NC. However, as shown in figure 3, the variation trend of concrete compressive strength under high temperature was not identical with that of cube compressive strength after high temperature. At the moment, the compressive strength peak values of the four types of concrete did not appear under 400 °C but under 200 °C. Table 4 shows that at 200 °C, the compressive strength of NSFC was 77.45 MPa, which was 1.13, 1.21, and 1.34 times of SFRC, NNC and NC at the same temperature, respectively.

Table 4. Compressive strength of NSFC, SFRC, NNC and NC at different temperatures.

|       | NC   | NNC  | Strength growth | SFRC | NSFC | Strength growth |
|-------|------|------|-----------------|------|------|-----------------|
| 200°C | 57.64| 64.15| 11.29%          | 68.72| 77.45| 12.70%          |
| 400°C | 51.81| 54.97| 6.10%           | 60.61| 76.89| 26.86%          |
| 600°C | 42.69| 46.63| 9.23%           | 44.08| 47.37| 7.46%           |
| 800°C | 16.39| 16.09| -1.83%          | 18.97| 25.27| 33.21%          |

When the temperature rises to 400 °C, the compressive strength of NNC was 6.10% higher than that of NC under high temperature, and the compressive strength of NSFC was 76.89 MPa under high temperature, which was 26.86% higher than that of SFRC. Evidently, the addition of nano SiO₂ could improve concrete compressive strength under high temperature. It especially played a significant role in improving compressive strength of SFRC under high temperature. Table 4 shows that the compressive strength of NSFC at 400 °C almost did not decrease. When the temperature exceeded 400 °C, the compressive strengths of the four types of concrete suddenly decreased, but NSFC still maintained high bearing capacity before 600 °C, and up to 800 °C. The residual compressive strength of NSFC was 33.21% higher than that of SFRC.

Evidently, the increase in temperature accelerated hydration reaction. At about 200 °C, given that concrete matrix was reduced because of loss of free water, the material structure gradually became compact [12] to enhance the occlusal force between C–S–H gel and aggregate that partially counteracted the strength loss caused by heating failure of aggregate and the adhesive failure between set cement and aggregate. Consequently, the concrete compressive strength slightly increased again within this temperature interval, similar to concrete “steam curing”.
4. Influence of Nano SiO$_2$ on Matrix Structure and its Action Mechanism

4.1. Influence of Nano SiO$_2$ on Hydration Characteristics of Ordinary Portland Cement

Hydrates of Portland cement are mainly calcium silicate (C–S–H), Ca(OH)$_2$, Aft phase (ettringite and C$_3$A·3CaSO$_4$·32H$_2$O), and AFm phase (mono-sulfur ettringite and C$_3$A·CaSO$_4$·12H$_2$O). Ca(OH)$_2$ has adverse effect on cement strength, and highly-dispersed nano SiO$_2$ can react with Ca(OH)$_2$ to generate the C–S–H gel, which is called pozzolanic effect. The specific reaction formula is as follows:

$$XCa(OH)_2 + SiO_2 + (n-x)H_2O \rightarrow xCaO \cdot SiO_2 \cdot nH_2O$$

When nano SiO$_2$ was added into the cement, the large amount of Ca(OH)$_2$ in the early-stage hydration products became less as the cement hydration period lengthened [13]. When the nano SiO$_2$ contacted the mixing water, “rich silica gel” was initially formed, moisture was absorbed, gel aggregated between non-hydrated cement grains, and gradually wrapped the cement grains. Ca(OH)$_2$ reacted with surface of silica gel to generate C–S–H gel, which originated from nano SiO$_2$ and Ca(OH)$_2$ were generated in C–S–H gel pores under cement hydration, which greatly improved structural compactness. Therefore, the pozzolanic effect of nano SiO$_2$ could transform Ca(OH)$_2$ with adverse effect on strength into C–S–H gels, which are filled between cement hydration products to powerfully boost growth of high-performance concrete. Meanwhile, nano SiO$_2$ reacted with Ca(OH)$_2$ to continuously consume Ca(OH)$_2$, which would then accelerate cement hydration to improve early-stage concrete strength. XRD test was conducted as specimens were taken out after NNC and NC were put under standard curing for 28 d. The analysis results are shown in figure 4 C–S–H gel had poor degree of crystallinity with extremely wide and low characteristic peak. It could almost not be identified [14]. Therefore, the effect of nano SiO$_2$ on cement hydration reaction could be judged by observing the change in diffraction peak intensity of Ca(OH)$_2$. Figure 4 shows that the diffraction peak value of Ca(OH)$_2$ in nano SiO$_2$-adulterated concrete evidently decreased because nano SiO$_2$ replaced some cement to decrease Ca(OH)$_2$, which was generated by cement hydration. Moreover, Equations (1) indicate that nano SiO$_2$ continuously reacted with Ca(OH)$_2$ and part of Ca(OH)$_2$ was consumed. Intensities of diffraction peaks (d=0.263 nm, d=0.490 nm, d=0.193 nm and d=0.169 nm) on Ca(OH)$_2$ crystal faces (101), (001), (102), and (111) in NNC were weaker than those in NC.

![Figure 3. Compressive strength of NSFC, SFRC, NNC and NC at different high temperatures.](image1)

![Figure 4. XRD patterns of the nano-SiO$_2$ normal concrete and normal concrete.](image2)

4.2. Influence of Nano SiO$_2$ on Concrete Microstructure

The number of surface atoms increased with many unsaturated bonds of high surface energy and chemical activity because of surface effect and small-size effect of nano SiO$_2$ grains. These atoms would easily bond with other atoms to be stable. Hence, nano SiO$_2$ grains could form bonding effect...
on nanograin surface with hydration product Ca(OH)$_2$ to generate secondary reaction and new C–S–H gels, which would be filled in concrete matrix pores to reduce Ca(OH)$_2$ content and refine Ca(OH)$_2$ crystals. Figure 5(a) presents the SEM analysis chart of NC matrix structure under normal temperature, and figure 5(b) presents the SEM analysis chart of the matrix structure of nano SiO$_2$-adulterated concrete (NNC). Their comparison shows that NC was not added with nano SiO$_2$ grains; thus, its matrix structure had poor compactness with many large holes and large hydration product grains. The typical grain size is about 5.64μm. Figure 5 (b) shows that after addition of nano SiO$_2$ grains, the concrete has favorable uniformity and few small holes, and the fine hydration product grains were arranged on the matrix. The grain size is about 2.82μm or less. Evidently, the addition of nano SiO$_2$ grains could improve concrete matrix structure, reduce matrix porosity, improve compactness, reduce Ca(OH)$_2$ content and strengthen grain refinement.

(a) SEM micrograph of NC
(b) SEM micrograph of NNC

Figure 5. Matrix organization of NC without adding nano SiO$_2$ and NNC with nano SiO$_2$.

5. Conclusions
Nano SiO$_2$ has small grain size and huge specific surface area; thus, it would easily agglomerate with strong water-absorbing ability. The addition of nano SiO$_2$ could evidently reduce concrete slumps. Therefore, in practical application, appropriate amount of superplasticizer should be added to adjust its working characteristic according to concrete use.

The addition of nano SiO$_2$ could evidently improve high-temperature compressive strengths of the concrete, and it especially played a significant role in improving compressive strength of SFRC. Crack propagation law under compressive and final failure modes of NNC was basically identical with those of NC, and the final specimen failure modes were two upright-inverse conjoint angular conical failure planes. The addition of nano SiO$_2$ could evidently improve normal- and high-temperature compressive strengths of the concrete, and it especially played a significant role in improving compressive strength of SFRC.

XRD analyses showed that: Nano SiO$_2$ could go through secondary hydration reaction with cement hydration product Ca(OH)$_2$ to reduce Ca(OH)$_2$ content, refine Ca(OH)$_2$ crystals, transform Ca(OH)$_2$ with adverse effect on strength into C–S–H gels, improve structural compactness, improve concrete matrix structure, and powerfully boost NSFC strength growth. In the meantime, nano SiO$_2$ reacted with Ca(OH)$_2$ to continuously consume Ca(OH)$_2$, which would accelerate cement hydration to improve concrete strength.

The addition of nano SiO$_2$ significantly improved the high-temperature cube compressive strengths of concretes. Among the four types of concrete, the high-temperature compressive strength of NSFC remained the highest, followed by SFRC, NNC, and NC. The compressive strength peak values of the four types of concrete appear at about 200 °C. At 200 °C, the compressive strength of NSFC was 77.45 MPa, that is, 1.13, 1.21, and 1.34 times those of SFRC, NNC, and NC, respectively.
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References
[1] Xu B 2004 The Application Technology of Nano-Materials Beijing: Chemical Industry Press.
[2] Zhang M H and Islam J 2012 Use of nano-silica to reduce setting time and increase early strength of concretes with high volumes of fly ash or slag Construction and Building Materials 29 573-580
[3] Luciano S, Dachamir H, et al. 2010 Mortars with nano-SiO$_2$ and micro-SiO$_2$ investigated by experimental design Construction and Building Materials 24 (3)19-21
[4] Peng G F, I Y, Wen W, Zhao J, et al. 2006 Explosive spalling and residual mechanical properties of fiber-toughened high-performance concrete subjected to high temperatures Cement and Concrete Research 36(4) 723-727.
[5] Yan L, Xing Y M and Li J J 2013 High-temperature Mechanical Properties and Microscopic Analysis of Hybrid-fiber-reinforced High-performance Concrete Magazine of Concrete Research 65(3),
[6] Phanlt and Carino N J 2003 Code provisions for high strength concrete strength-temperature relationship at elevated temperatures Material and Structure 36(2) 91-98.
[7] Poon C S, Shui Z H and Lam L 2004 Compressive behavior of fiber reinforced high-performance concrete subjected to elevated temperatures Cement and Concrete Research 34(12):2215-2222.
[8] Chen B and Liu J 2004 Residual strength of hybrid-fiber-reinforced high-strength concrete after exposure to high temperatures Cement and Concrete Research 34(6) 1065-1069.
[9] Xiao J and Falkner H 2006 On residual strength of high-performance concrete with and without polypropylene fibers at elevated temperatures Fire Safety Journal 41(2) 115-121.
[10] Hu H T and Dong Y L 2002 Experimental Research on Strength and Deformation of High-Strength Concrete at Elevated Temperature China Civil Engineering Journal 35(6) 44-47.
[11] Li W and Guo Z H 1993 Experimental investigation of strength and deformation of concrete at elevated temperature Journal Of Building Structures 14(1) 8-16.
[12] Dias W P S, Khoury G A and Sullivan P J E 1990 Mechanical prosperities of hardened cement paste exposed to temperature up to 700e ACI Materials Journal 87(2) 160.
[13] Ye Q, Zhang Z N, Kong D Y and Chen R S 2007 Influence of nano-SiO2 addition on properties of hardened cement paste as compared with silica fume Construction and Building Materials (21) 539–545.
[14] Lian H Z, Tong L and Chen E Y 1996 Building Materials Phase Research Base Beijing: Qinghua University Press 25.