



Improvement of performance of ultra-high performance concrete based composite material added with nano materials

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ABSTRACT. Ultra-high performance concrete (UHPC), a kind of composite material characterized by ultra high strength, high toughness and high durability. It has a wide application prospect in engineering practice. But there are some defects in concrete. How to improve strength and toughness of UHPC remains to be the target of researchers. To obtain UHPC with better performance, this study introduced nano-SiO₂ and nano-CaCO₃ into UHPC. Moreover, hydration heat analysis, X-Ray Diffraction (XRD), mercury intrusion porosimetry (MIP) and nanoindentation tests were used to explore hydration process and microstructure. Double-doped nanomaterials can further enhance various mechanical performances of materials. Nano-SiO₂ can promote early progress of cement hydration due to its high reaction activity and C-S-H gel generates when it reacts with cement hydration product Ca(OH)₂. Nano-CaCO₃ mainly plays the role of crystal nucleus effect and filling effect. Under the combined action of the two, the composite structure is denser, which provides a way to improve the performance of UHPC in practical engineering.

KEYWORDS. UHPC; Composite material; Nano material; SiO₂.

INTRODUCTION

With the continuous development of human society, living space of human is constantly narrowed and buildings tend to be high-rise and long-span. Moreover, concrete structure is increasingly threatened by harsh environment such as ocean and salt lake [1, 2]. Therefore, requirement on performance of concrete materials becomes higher and higher. Ultra-high performance concrete composite (UHPCC) featured by high strength, high toughness, high durability and strong deformation resistance is applied more extensively in harsh environment mentioned above and areas which have special requirements on structure; moreover it shows excellent performance in service process [3, 4].

As to research on UHPC, three international conferences concerning UHPC have been held in Kassel University in German, in September 2005, March 2008, and March 2012 respectively. In the first two conferences, participants illustrated their own research achievements and experience, which mainly include composition and ratio of raw materials, preparation condition, performance, characteristics, strength and toughness of microstructure, design and construction as well as application cases of UHPC in practical engineering worldwide [5]. In addition, multiple international technical standards was discussed. In the third international conference, nanotechnology and nanomaterials were proposed to be introduced into UHPC and the latest research progress of UHPC was also discussed.

Nanomaterials as a fine particle between macro substance and cluster possesses small size effect, surface effect, quantum graining effect and macroscopic tunneling effect. How to introduce nanomaterials into concrete has become an issue



constantly explored by concrete material researchers in practice. Ye Q et al. [6, 7] found that, pozzolanic activity of nano-SiO₂ was much stronger than ganister sand and adding 1% ~ 3% nano-SiO₂ could remarkably enhance compressive, rupture and splitting strength of concrete and thus improve microstructure of concrete. Bigley C et al. [8] discovered that, nano-SiO₂ could improve segregation resistance of self-compacting concrete. Chen RS et al. [9] pointed out that, concrete paste mixing with nano-SiO₂ was featured by weaker flowability and shorter setting time; and cement block obtained had high strength in early stage. Nanomaterial can improve microstructure and enhance mechanical performance of material in a certain extent if being applied in ordinary concrete or high-performance concrete. But preparing UHPC using nanomaterials has not been researched yet. Considering the extremely low water-binder ratio of UHPCC, applying nanomaterials with large surface and severe agglomeration into UHPCC will encounter with dispersing and forming difficulty. Thus based on preliminary work, we systematically studied action mechanism of nano-SiO₂ and nano-CaCO₃ adding into UHPCC, aiming to lay a scientific foundation for improvement of UHPC and its promotion..

MATERIALS AND METHOD

Raw Materials

Raw materials used included P·II 52.5R Portland cement (density: 3.1 g/cm³; chemical components: Tab. 1), ultra-fine fly ash (level I from Nanjing thermal power plant; density: 2.1 g/cm³; specific surface area: 400 m²/kg; chemical components: Tab. 1), nano-SiO₂ (Hangzhou Veking New Material Co., Ltd.; superficially porous; average grain diameter: 20 nm; content of SiO₂: over 99%), nano-CaCO₃ (Zhoushan Mingri Nano Material Co., Ltd.; average grain diameter: 30 nm; content of CaCO₃: over 99.9%), fine aggregate (ordinary yellow ground with maximum grain size of 2.5 mm; fineness modulus: 2.26; continuous grading; bulk density: 1.4 g/cm³; apparent density: 2.4 g/cm³) and polycarboxylic high performance water-reducing agent (BASF Aktiengesellschaft; water-reducing rate: over 40%). A previous study [10] suggests that, the best mixing proportion of nano-SiO₂ in UHPCC was 3%. In this study, mixing proportion of nano-SiO₂ was fixed at 3% and mixing proportion of nano-CaCO₃ was adjustable, as shown in Tab. 2.

Raw material	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	N ₂ O	LOI
Cement	20.40	4.70	3.38	64.7	0.87	1.89	0.49	0.33	3.24
Coal ash	53.98	28.84	6.49	4.77	1.31	1.16	1.61	1.03	0.72

Table 1: Components of cement and coal ash (wt%).

Test specimen	Cement	Coal ash	Nano-SiO ₂	Nano-CaCO ₃	Water-binder ratio	Additive
NSC0	52	35	3	0	0.2	2
NSC1	51	35	3	1	0.2	2
NSC3	49	35	3	3	0.2	2
NSC5	47	35	3	5	0.2	2

Table 2: Mix proportion of different components (wt%).

Test Method - Moulding Technique

UHPCC was prepared using wet mixing technology, i.e., evenly mixing raw materials (coal ash, cement, fine aggregate) in forming process. Detailed procedures are as follows:

(1)Stirring

- ① Add cement mortar into the mixture of quartz sand and silicon ash mixed according to certain mix proportion and then stir for 5 min;
- ② Then add cement, coal ash, quartz powder and nanomaterial and stir for 5 min;
- ③ Add half quantity of water containing water reducing agent and stir for 3 min;
- ④ Add the remaining water and stir for 6 min;
- ⑤ Pour the mixture into a triple mould (40 mm × 40 mm × 160 mm) and then vibrate the mould on vibrating table with a frequency of 50Hz. Manufacturing procedure of concrete mortar matrix is shown in Fig. 1.

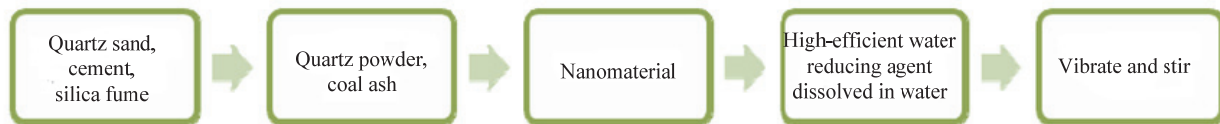


Figure 1: Manufacturing process of concrete mortar matrix.

(2) Maintenance: maintain the test specimen in curing room ($20 \pm 2^\circ\text{C}$) for 24 h, then do:

- ① Standard maintenance (maintain the test specimen in water ($20 \pm 2^\circ\text{C}$) till specified curing age);
- ② Hot water maintenance (maintain the test specimen in 90°C hot water curing box for 48 h and then perform standard maintenance till specified curing age).
- ③ Take specimen for mechanical performance and microscopic performance tests.

Microscopic Test - XRD Quantitative Test

Specimen that had been cured to specified curing age was taken soaked in absolute alcohol for one day [11]. Then it was grinded in agate mortar in an environment of absolute ethyl alcohol until all powder passed through 0.08 mm sieve. Afterwards, all powder was dried in vacuum drying oven (50°C). One hour later, it was put into hermetic bag and cooled to room temperature. Then the powder was mixed with α - Al_2O_3 powder which passed through 80 μm sieve in a ratio of 1 : 9. Absolute ethyl alcohol was also added. After one hour of mixing, all specimen were put into vacuum drier.

Bruker - Axs D8DISCOVER X ray diffractometer equipped with LynxEye array detector was used. Target used was Cu target. Room temperature was $T = 298 \text{ K}$. Operating voltage and operating current were set as 40 kV and 30 mA. Soller slit was 4.0° . Step size was set as 0.02° (2 θ), scanning speed was set as 0.30 s/step, and scanning angle ranged from 5° to 80° (2 θ) or 7° to 80° (2 θ). The power was put on specialized glass-made sample plate of ray diffractometer and moved to sample holder for testing after the parameters were set over.

MIP Test

AutoPoreIV 9510 auto hole test system produced by Micrometrics corporation was used as mercury injection apparatus. Operating parameters were: pressure 0.10 ~ 45000 psia, contact angle 130° , equilibrium time 10s, sampling hole interval 4.3 nm ~ 360 μm . Characteristic parameters of pore structure such as porosity, average pore size and distribution of pore size were analyzed using corresponding analysis software.

Nanoindentation Test

First, specimen which had been cured to specified curing age was cut into small pieces with a side length of 2 cm. Then they were soaked in absolute ethyl alcohol for 48 h. The specimen was cut into slices (5 ~ 10 mm) after cold mounting with epoxy resin. To obtain even and clean surface, the slices were grinded with carborundum paper (180-mesh, 600 mesh, 1200 mesh) on grinding machine and then polished with polishing solution (9 μm , 3 μm , 0.5 μm , 0.05 μm). Finally, the specimen was washed by ultrasonic wave for 15 min to remove particles from polishing solution adhered to the surface.

Nano Test TM produced by Micro Materials Corporation was used for test and pyramidal Berkovich pressure head was equipped. A dot matrix (10 \times 10) was selected in the area next to specimen interface area and the space between two dots was 20 μm . Displacement control mode was applied and the maximum depth of indentation was set as 300 nm. When the pressure head contacts the surface of specimen, the depth of indentation linearly loads to the set value in a speed of 0.25 mN/s, then loads in a constant speed for 30 s, and finally linearly unloads in a speed of 0.25 mN/s. Every test point was processed with loading and unloading. Load - displacement curve was recorded.

RESULTS AND ANALYSIS

Mechanical Performance Test and Analysis

We made tests on static mechanical performance of UHPCC with different curing age. Results are shown in Fig. 2.

It can be seen from Fig. 2 that, different UHPCC material show the same tendency of compressive strength and rupture strength, i.e., strength was higher in material with larger curing age. When curing age was the same, compressive strength and rupture strength improved with the increase of mixing amount of nano- CaCO_3 . But if the



mixing amount was too large, strength improved with a limited amplitude and even decreased slightly. There were two reasons. First, water demand increased, resulting in high water-binder ratio. Secondly, nanomaterial failed to disperse evenly and thus aggregated, lowering evenness of UHPCC [12]. Hence mixing amount of nanomaterial should be controlled within certain scope. We thought the best mixing amount of nano-CaCO₃ was 3% ~ 5%. Compared to test specimen without nano-SiO₂ or with nano-SiO₂ only, test specimen added with nano-SiO₂ and nano-CaCO₃ had significantly improved strength; NSC₃ test specimen with curing age of 90 d could have a compressive strength of 107 MPa and a flexural strength of 20 MPa. Nano-SiO₂ can promote hydration of cement and C-S-H gel generates when nano-SiO₂ reacts with cement hydration products. Though nano-CaCO₃ has low activity, it can be used for filling spaces inside composite material and thus improves density.

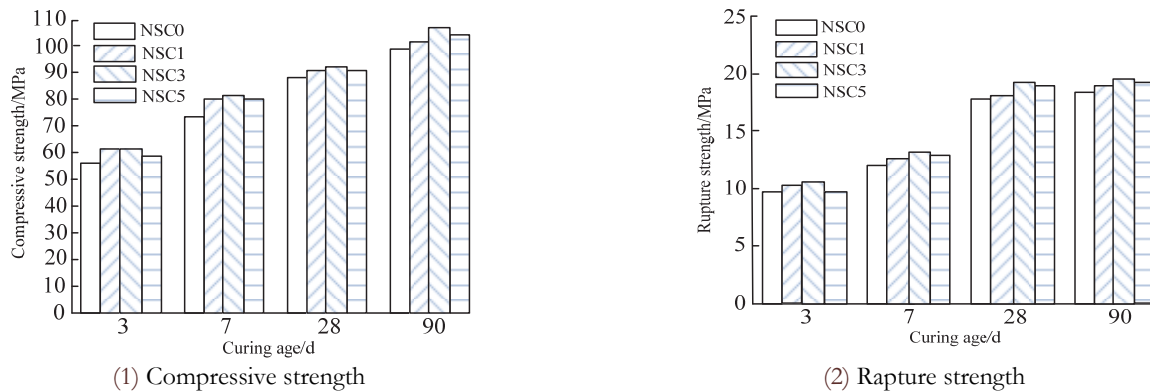


Figure 2: Compressive and rapture strength of UHPCC with different curing age.

Hydration Heat Analysis

Hydration heat test was carried out three days after processing the above four kinds of UHPCC with water and the results are shown in Fig. 3. It can be seen from Fig. 3 that, heat curve of four materials were similar; hydration acceleration period of hydration test specimen mixed with nano-SiO₂ was from 10th h to 20th h; double-doped materials which had larger mixing amount of nano-CaCO₃ had hydration acceleration and exothermic peak earlier. It indicates that, double mixture of nanomaterials can accelerate hydration.

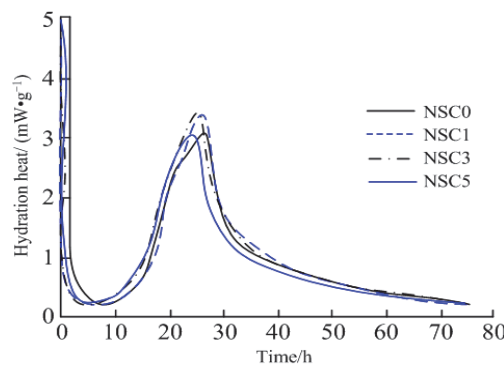


Figure 3: Hydration heat curve for UHPC test specimen.

XRD Quantitative Analysis

Traditional XRD methods usually used for quantitative analysis such as external standard method, internal standard method, K value method, and adiabatic method all aims at analyzing single hkl diffracted ray or hkl diffraction family. Sample of cement based composite material with multiple phases and complex diffraction xrd pattern will bring great difficulty to quantitative analysis due to severely overlapped spectral peak and preferentially orienting effect. Rietveld whole power pattern fitting may transform the status if being applied in XRD pattern analysis. The structure depended method can accurately make an analysis on diffraction peaks and comparison of diffraction strength of different phrase. Specialized cement phase structure database which can be used for analyzing cement clinker and phase of mineral admixtures has been established after years of research works.

We can see a dispersed humpback-like peak at 20 ($25^\circ \sim 35^\circ$) which is caused by mass amorphous C-S-H gel existing in cement hydration product from XRD pattern of hardened cement paste. But as there are lots of sharp crystalline peaks within the scope of diffraction angle, the position of amorphous peak is not obvious. Hence results can be obtained only when phase in a known proportion is added in quantitative analysis of components of cement paste. In quantitative analysis of hydration product of cement based material, $\alpha - Al_2O_3$ which is not contained in original paste, keeps stable at room temperature and cannot react with components of cement paste is used as addition phase. XRD pattern of the power sample obtained was first analyzed with EVA software to find out all and then with TOPAS software which is designed based on Rietveld method.

We made quantitative analysis on hydration products of four kinds of test specimens (curing age of 3, 7, 28 and 90 days). Fig. 4 demonstrates the analysis results of test specimens which was cured for 28 days. Tab. 3 demonstrates quantitative analysis results of main mineral phases.

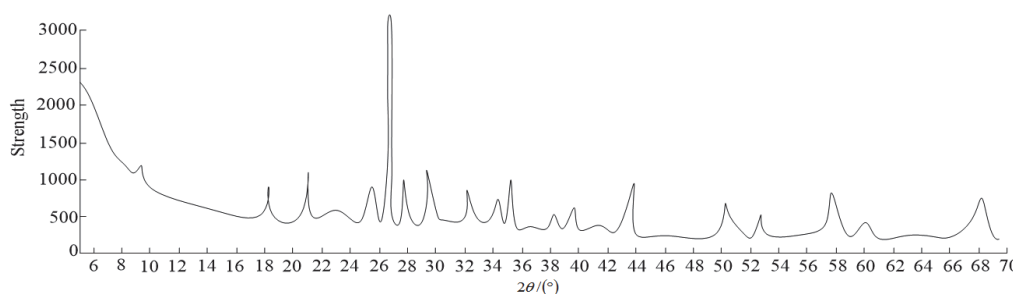


Figure 4: XRD quantitative analysis results of test specimens cured for 28 days.

Curing period/d	Test specimen	Phase						Amorphous phase
		C ₃ S	C ₂ S	C ₃ A	C ₄ AF	Ca(OH) ₂	CaCO ₃	
3	NSC0	10.65	7.93	3.65	2.02	4.89	2.67	43.63
	NSC1	8.76	7.74	2.88	2.14	5.04	4.16	41.52
	NSC3	8.32	8.97	3.45	2.05	3.65	7.68	43.29
	NSC5	8.40	9.21	3.18	2.30	4.26	8.97	40.77
7	NSC0	7.56	7.66	2.33	1.85	4.08	3.30	47.31
	NSC1	6.22	5.54	2.64	2.31	3.38	4.23	40.61
	NSC3	6.35	5.09	3.34	1.82	3.34	7.32	39.81
	NSC5	6.07	5.83	3.01	1.94	3.36	8.01	40.83
28	NSC0	6.09	7.02	2.16	1.50	3.57	3.07	49.14
	NSC1	7.06	7.90	2.28	2.18	3.42	4.81	43.98
	NSC3	5.89	6.34	2.14	1.67	2.76	6.54	48.02
	NSC5	6.68	5.79	3.23	1.84	3.68	8.50	47.96
90	NSC0	7.46	7.40	2.13	0.96	3.56	2.99	48.88
	NSC1	7.05	6.76	2.64	1.94	3.12	4.36	43.37
	NSC3	5.90	6.20	2.35	1.59	3.08	6.08	46.84
	NSC5	6.33	5.58	3.09	1.32	3.37	9.01	47.71

Table 3: XRD quantitative analysis results of UHPCC with different curing age (%).



It can be seen from Tab. 3 that, as curing period prolonged, unhydrated cement phase (C_3S , C_2S , C_3A , C_4AF) gradually reduced, amorphous phase of hydration products (C-S-H gel, etc) increased, $Ca(OH)_2$ generated from hydration decreased, and $CaCO_3$ had no obvious change; moreover, in early period (before 7 d), amorphous phase of double-doped test specimen was less than single-doped test specimen, suggesting some nano- $CaCO_3$ involves in hydration of cement and plays a supplement role in cement based composite material. In addition, we can know from the table that, when curing exceeded 28 d, variation tendency of hydration product content slowed down; in early period (before 7 d), addition of nanomaterials had an obvious promotion effect on hydration of UHPCC. The accelerated hydration of cement is attributable to high reaction activity of nano- SiO_2 . Nano- $CaCO_3$ acting as a supplement role increases the density of UHPCC and also improves its mechanical performance.

MIP Result and Analysis

Preparation of test sample: cement block which has finished test of strength of concrete was crashed and put into absolute ethyl alcohol for stopping hydration. Before test, the broken concrete was moved into a vacuum drier (50°C). 24 h later, it was taken out and packed with closed bag.

We made test on pore structure of four test specimens with different curing age. Tab. 4 shows data of pore structure of cement paste test block. Fig. 5 demonstrates MIP results of four materials after 28 d-standard maintenance.

Sample	NSCO	NSC1	NSC3	NSC5
Average pore size(nm)	38.1	25.1	27.3	30.9
Critical poresize (nm)	427	171	223	249
Total pore space (ml/g)	0.2226	0.2043	0.2137	0.2184

Table 4: Statistics of pore structure of test block.

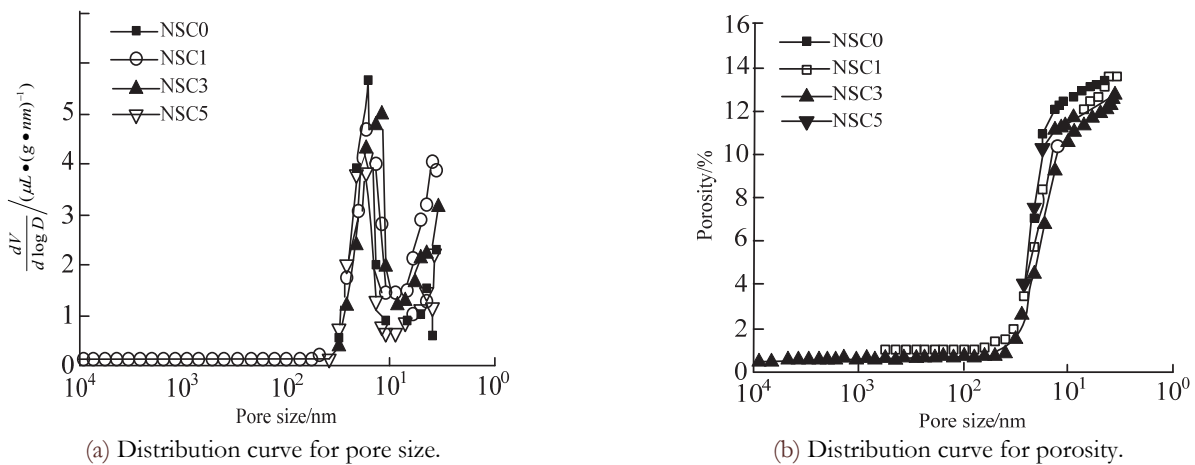


Figure 5: MIP analysis results of UHPC.

It can be seen from Fig. 5(a) that, pore volume of test specimen added with nano- SiO_2 only and maintained for 28 d was the largest when pore size was between 0.003 and 0.03 μm , and the peak value appeared when pore size was 11 or 4 nm; for double-doped test specimen, distribution curve of pore size deviated to the right slightly and the peak pore size was relatively smaller.

Fig. 5(b) shows distribution curve for porosity of four test specimens. It can be seen from the figure that, adding two nanomaterials had an obvious influence on lowering porosity of composite material, about 2%. Thus it is concluded that, reasonable selection and optimization of UHPCC, hydration promotion effect of nano- SiO_2 and supplement effect of nano- $CaCO_3$ can greatly improve density of UHPCC, reduce microscale and microscopic scale defects, and thus enhance performance of material.

Nanoindentation Test Results and Analysis

XRD quantitative analysis results suggested that, UHPCC hardened cement paste contained hydrated gel phase, Ca(OH)_2 phase, CaCO_3 phase and unhydrated cement particles. C-S-H gel phase of ordinary concrete is mainly composed of high and low density hydrated calcium silicate gel (LD C-S-H and HD C-S-H) whose elasticity modulus are 14 ~ 24 GPa and 24 ~ 35 GPa. Results of previous researches [13, 14] demonstrated that, UHPCC contains a large amount of higher-density C-S-H gel (UHD C-S-H) which has stronger mechanical performance and an elastic modulus of 35 ~ 50 GPa that is close to Ca(OH)_2 phase. We made nanoindentation test on single-doped and double-doped test specimens which were processed by standard maintenance for 90 days. As Ca(OH)_2 phase accounted for a small proportion in the material, it was ignored during analysis. Distribution of mechanical performance parameters of single-doped and double-doped test specimens maintained for 90 days is shown in Fig. 6. We can find that, test specimens contain a large amount of unhydrated cement particles and UHD C-S-H phase; HD C-S-H phase is surrounded by hydration product UHD C-S-H; LD C-S-H phase has disappeared; a distinct interfacial transition zone could not be seen.

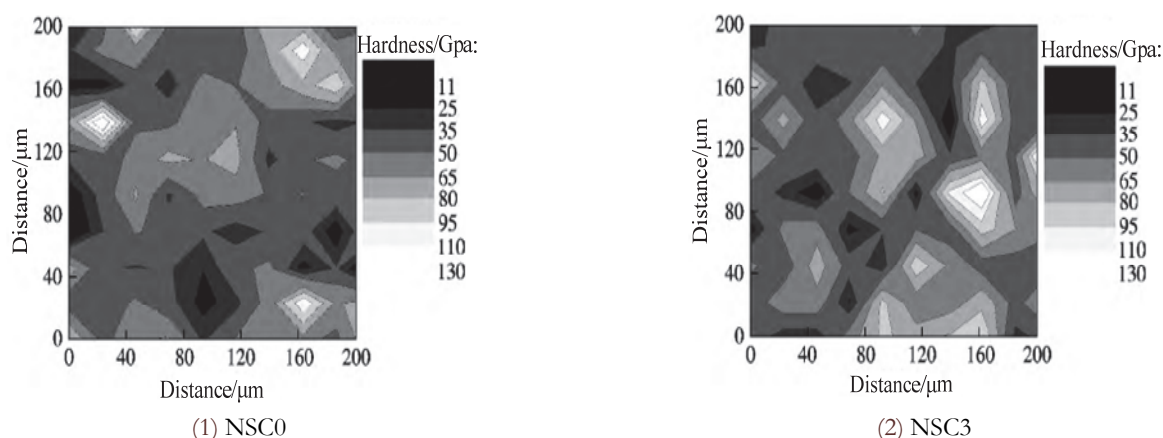


Figure 6: Distribution of elasticity modulus on the surface of single-doped and double-doped test specimen.

After making a statistical analysis on the data, distribution of probability of elasticity modulus of measured points on test specimen was obtained (Fig. 7). It can be seen from the figure that, peak value of elasticity modulus of the test specimens was between 30 and 70 GPa; a large amount of UHD-C-S-H phase and a small amount of unhydrated cement particle phase existed in the test specimens; as to hydration products of double-doped test specimens, UHD C-S-H phase accounted for a larger proportion, HD C-S-H phase was in a small amount and LD C-S-H was not found. Thus we conclude that, hydration products of UHPCC are significantly different with ordinary concrete; UHD C-S-H phase is the major hydration product; and the above difference is more obvious in double-doped material. Because of generation of a large amount of high-strength and high-elasticity hydration products, interface of composite material is fully strengthened and structure tends to be tighter.

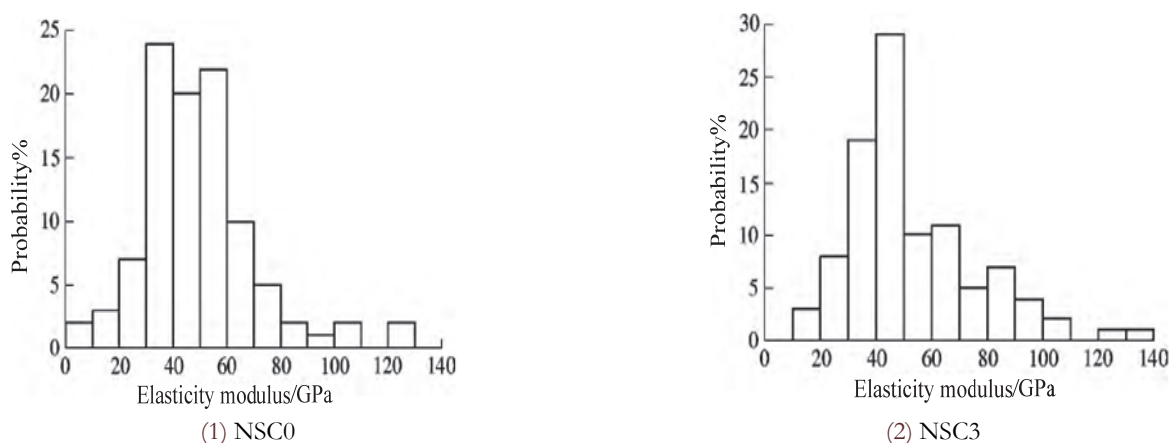


Figure 7: Distribution of probability of elasticity modulus of single-doped and double-doped test specimen



CONCLUSIONS

Nano materials with outstanding performance have been applied in many fields. Li H et al. [15] once researched the influence of nano-SiO₂ and nano-Fe₂O₃ on mechanical performance and microstructure of cement mortar and found nano-SiO₂ and nano-Fe₂O₃ could improve compressive strength of cement mortar for 20% over. Ltifi M et al. [16] found that, cement mortar tended to have poorer flowability and faster hydration after nano-SiO₂ was added. They thought compressive and bending strength of cement mortar strengthen if nano-SiO₂ was added. That is because nano-SiO₂ as an activator promotes hydration of cement and moreover nanoparticles dispersing in a high degree could improve microstructure of mortar.

It is seldom applied in UHPC field and moreover few studies focus on influence of nanomaterials on performance of UHPC, though ordinary cementing material in combination with nanomaterials has been reported frequently. Based on the current research achievements of UHPC [17, 18], this paper discussed over the enhancement effect of nanomaterials on performance of UHPC in aspects of tightness and chemical reaction. We made systematic test and analysis on doped UHPCC and concluded that:

- 1) UHPCC with excellent performance can be prepared through adopting reasonable mix proportion of raw materials and adding nanomaterials; mechanical performance of material can be significantly improved if nano-SiO₂ and nano-CaCO₃ are added, and the optimal mixing proportion is 3% ~ 5%.
- 2) adding nano-SiO₂ can accelerate hydration progress of cement; as to double-doped UHPCC, hydration acceleration period of cement starts earlier and exothermic peak appears earlier; mutual action of nano-SiO₂ and nano-CaCO₃ further accelerates hydration progress.
- 3) hydration of cement can be promoted by nano-SiO₂ due to its high reaction activity; C-S-H gel generates when nano-CaCO₃ reacts with Ca(OH)₂ which is the hydration product of cement; benefitting from the supplement effect of nano-CaCO₃ added, UHPCC becomes tighter and microscopic defects dramatically reduces.
- 4) UHPCC added with both nano-SiO₂ and nano-CaCO₃ is found with significantly lowered porosity, a large amount of UHD C-S-H gel with higher performance, fully strengthened interface region, tighter microstructure and excellent mechanical performance.

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