- Technical Paper -

IMPACT OF NANO-TIO₂ PARTICLES ON DRYING SHRINKAGE OF HARDENED CEMENT UNDER THE FIRST DRYING

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ABSTRACT

This paper reports the influence of nano-TiO₂ given to shrinkage behavior of hardened cement pastes under the first drying process. Cement pastes containing 3% nano-TiO₂ (by external addition) by mass of cement were prepared. During the hydration process, nano-TiO₂ increased the precipitation amount of low density C-S-H. As a result, it was confirmed that the drying shrinkage of the cement paste with nano-TiO₂ in the first drying process was increased, in W/C ratio was 0.55.

Keywords: TiO₂ nanoparticle, calcium silicate hydrate (C-S-H), drying shrinkage, nitrogen sorption, water vapor sorption, BET surface area

1. INTRODUCTION

Titanium dioxide (TiO₂) is relatively cheap and chemically stable, and widely used as a photocatalyst. Also, nanoparticles having a diameter of $1 \sim 100$ nm are simply not only small in size, physical and chemical properties are significantly different than the particle of size several hundred nanometer or more [1]. With the development of nanotechnology in construction and building materials, TiO₂ nanoparticles, which are expected to have an effect of the photocatalyst, have been used as an admixture for concrete in last decades.

Recently, some investigation revealed that the influences of nano-TiO₂ are not only the depollution and self-cleaning performance, but also the improvement of the inherent properties of the hardened cement pastes [2-4]. Chen et al. [2] investigated the effects of blending nano-TiO₂ into cement pastes and mortals on the hydration and properties of the hydrated cement pates. Through their experimental studies, the addition of nano-TiO₂ powders significantly accelerated the hydration rate and promoted the hydration degree of the cementitious materials at early ages. Further, during the hydration process, nano-TiO₂ was inert and stable, so TiO₂ was confirmed to be a non-reactive fine filler that acted as potential nucleation sites for the accumulation of hydration products. Also, the total porosity of TiO₂ blended pastes decrease, mainly within the range of capillary pores. It was suggested that the addition of TiO₂ affects the change in microstructure. Feng et al. [3] revealed that, by the admixing of nano-TiO2 into cement, nano-modification increased the amount of cementitious phase in the paste, decreased the micro-porosity and amount of internal micro-cracks and defects, formed a denser microstructure, and led to the formation of needle-shaped nanoprecipitates.

In addition, the admixing of nano-TiO $_{2}$ into cement enhanced the compressive strength and the

flexural strength at early age [2], [4]. This was due to more formation of hydration products and denser microstructure in presence of nano-TiO₂.

On the contrary, research on the influence of the shrinkage behavior of cement paste or concrete by the addition of nano-TiO₂ is scarce. Hasebe and Edahiro [5] measured drying shrinkage strain of concrete which was mixed nano-TiO₂ at various substitutions proportions, the specimens mixed with nano-TiO₂ tended to shrink overall larger than that of non-miscible. Experimental studies on the effect of TiO₂ on the shrinkage behavior of hardened cement paste, for example [6], was conducted in the range of up to age of 28 days and included the effects of the autogenous shrinkage.

Based on our literature survey, previous studies have focused on the effect of the hydration process and we concluded that little research on the impact of microstructure in mature paste especially for the first drying process has been conducted and such research is needed for applications. We recently reported that nano-TiO₂ particles retarded the belite reaction in mature hydration state, and depress the precipitation of portlandite [7]. In addition, it was confirmed that nano-TiO₂ exist in the vicinity of the low density C-S-H during the hydration process [8].

The aim of this paper is to elucidate the influence of nano-TiO₂ on the shrinkage behavior of hardened cement pastes under the first drying process. Reference samples (plain) and cement/TiO₂ composite samples containing 3% nano-TiO₂ (by extra-addition) by mass of cement were prepared. After the almost fully hydration obtained after curing condition with wet condition for 6 months, short-term length change isotherms for samples dried under different relative humidity at 20 °C, water vapor and nitrogen sorption isotherms were obtained.

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EXPERIMENTAL PROCEDURE 2.

2.1 Materials and sample preparation

TiO₂ nanoparticles (1)

We used nano-TiO₂ provided by the Tayca Corporation. The TiO₂ suspension was dried for one week, the preparation of the test specimen was used as a powder state nano-TiO2. The SEM image of nano-TiO₂ powder was shown in Fig. 1.

Cement paste (2)

White Portland cement was used for the binder of cement paste, because it was planned to conduct nuclear magnetic resonance (NMR) measurements as part of this experiment and it was necessary to use cement with low Fe₂O₃ content. The chemical components, physical properties, and mineral compositions of white cement are shown in Table 1 and 2. The mineral composition was determined by XRD measurements and Rietveld analysis.

The water-cement ratio (W/C) of cement pastes were 0.40 and 0.55. Reference samples which did not contain the TiO₂ nanoparticles named as W40-Plain and W55-Plain. On the other hands, specimens of W/C with 0.40 and 0.55 containing TiO₂ powder were named as W40-TiO₂ and W55-TiO₂ respectively. The amount of nano-TiO₂ powder externally added to the cement was 3% by mass cement of each W/C condition. Cement paste (ca. 300g) was mixed in a 500 cc vacuum mixer for 3 min after the water was added. For dispersion of TiO₂ particles in the cement paste and avoiding the agglomeration, sonication process was applied in case of W55-TiO₂ and W40-TiO₂ for 1.5 min. Then, paste was scraped and mixed for a further 3 min by the mixer. All the materials were stored in a thermostatic chamber at 20 ± 1 °C for 1 day prior to mixing. The mixing was performed at room (ca. 20 °C) temperature and the specimens were then immediately moved to a thermostatic chamber again. To minimize segregation, the paste was remixed every 30 min for 6 hours. The specimens were placed into vial containers with $\phi 15$ mm and 80 mm depth and they were stored in a thermostatic chamber at a temperature of 20 ± 1 °C. They were demolded after 4 days, and the samples were immersed in lime-saturated water for 6 months.

After curing for 6 months, a part of the specimens were dried in a desiccator (controlled with lithium chloride saturated solution and containing carbon dioxide adsorbent) at $20 \pm 1^{\circ}$ C and $11 \pm 2\%$ RH for 2 month.



Fig. 1 SEM image of nano-TiO₂ particles

2.2 Experimental selection

(1) Short-term length change isotherm

For measuring short-term length change isotherms, samples $3 \times 3 \times 1$ mm in size were cut from the saturated hardened cement pastes (hcp) for use with a more rapid experimental technique in which these very small specimens were subjected to forced drying under RH-controlled air flow. Short-term length change for samples dried under different RHs at 20 °C were obtained with a thermomechanical analyzer (TMA) coupled with an RH generator (TMA4000SA and HC9700, Bruker AXS). Length changes were measured with a linear variable differential transfer (LVDT) with a precision of 0.5 µm, a minimum resolution of 0.0025 µm, and a contact load of 0.098 N. The samples were incrementally dried from saturated state to 5% RH, after which they were incrementally re-humidified back up to 90% RH. All the processes were conducted at 20 \pm 0.1 °C. For each step the RH of the flowing atmosphere was kept constant for at 5 hours. In this measurement, all the samples in saturated state were measured.

Water vapor sorption test (2)

Water vapor sorption measurements were conducted by the volumetric method using a water vapor sorption analyzer (Hydrosorb 1000, Quantachrome). A sample (~20 mg) was used for each measurement at 20 °C, with a pressure tolerance of 6.67 Pa and a time tolerance of 120 sec. The measurement

Table 1 Chemical composition of white cement												
Ig.loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na ₂ O	K_2O	Cl			
(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)			
3.18	22.68	4.50	0.19	65.07	1.19	2.75	0.06	0.07	0.004			

Table 2 Mineral composition of white cement determined by XRD and Rietveld analysis											
C ₃ S	C_2S	C ₃ A	Periclase	Bassanite	Gypsum	Calcite					
(%)	(%)	(%)	(%)	(%)	(%)	(%)					
51.6	35.1	5.88	0.61	0.350	2.75	3.76					
0.0.0 0.0.0	A.ALO M.M.	0									

C:CaO, S:SiO₂, A:Al₂O₃, M:MgO

points on the adsorption and desorption branches were at $p/p_0 = 0.05$ intervals up to 0.95, and ended at 0.98 (RH = 98%). The specific surface area (S_{H2O}) of adsorption branch was calculated using BET theory with a water molecule section value of 0.114 nm² [9]. The samples were crushed and particles with diameter of 25 – 75µm was used for this analysis. For pre-treatment, the samples were dried using a vacuum pump (theoretical minimum pressure of 6.7×10^{-2} Pa) and heated to 105 °C with a heating mantle for 30 min. In this measurement, all samples in saturated state were measured.

(3) Nitrogen sorption test

Nitrogen sorption tests were performed by the volumetric method using a nitrogen sorption analyzer (BELSORP-mini II, MicrotracBEL Corp.). A sample (~ 100 mg) was used for each measurement at -196 °C, with a sorption tolerance of 5.0 cm^3 /g and a time tolerance of 180 sec. The measurement points on the adsorption and desorption branches were ended at p/p_0 = 0.99. The specific surface area (S_{N2}) of adsorption branch was calculated using the BET theory with a nitrogen molecule section value of 0.162 nm² [10]. For pre-treatment, all the specimens were crushed into pieces of 2 mm or less with a hammer and immersed in isopropanol for 6 hours. After the immersion, the sample and isopropanol were separated by suction filtration using an aspirator. After the hydration reaction was stopped by isopropanol, in order to remove isopropanol remaining in the sample, vacuum degassing was carried out for 1 h with an aspirator (minimum pressure of about 3.17×10^2 Pa at 20 °C). Then, the samples which were crushed and classified to particle size of 25 to 75 µm which were dried using a vacuum pump (theoretical minimum pressure of $6.7 \times$ 10⁻² Pa) and heated to 105 °C with a heating mantle for 30 min. In this measurement, all samples in saturated state and after dried at 11% RH were measured.

3. RESULTS AND DISCUSSIONS

(1) Short-term length change isotherms

The short-term length change isotherms were shown in Fig. 2. For drying shrinkage under the first desorption branches shown in Fig. 2, the difference of the shrinkage value between cement paste with and without nano-TiO₂ occurred largely in the range of saturated state to 40% RH for each W/C ratio. The shrinkage of hcp during the first desorption process is normally accompanied by microstructural changes [11]. But the shrinkage strain of short-term length change is less affected by the microstructural changes caused by a short drying time, while some impact of C-S-H colloidal alteration under the first desorption process is inevitable [12].

At 5% RH, the shrinkage strain of W55-TiO₂ was larger than that of W55-Plain, while the shrinkage strain of W40-TiO₂ was smaller than that of W40-Plain. Therefore, the impact of the addition of TiO₂ on drying shrinkage differed with W/C ratio. But it was clarified that TiO₂ influences on the C-S-H colloidal alteration



Fig. 2 Short-term length change isotherms

which occurs in the range from 100% to 40% RH under first drying process.

(2) Water vapor sorption isotherms

Water vapor sorption isotherms are shown in Fig. 3 and Fig. 4. In case of W/C = 0.40, water sorption amount of W40-TiO₂ sample was slightly more than W40-Plain in adsorption branch, but the shapes of both isotherms were nearly the same. In case of W/C = 0.55, sorption amount of W55-TiO₂ sample obviously decreased above 60% RH of adsorption branch and over 40% RH of desorption branch. This indicates that the mesoscale pore structures (i.e. pore diameters of 2 -50 nm in the Kelvin equation at 20 °C) of cement paste were modified by nano-TiO₂ in case of W/C = 0.55. But in the W/C =0.40, nano-TiO₂ had less impact on the change of mesoscale pore structure. The BET surface area (S_{H2O}) measured by water vapor adsorption branch was shown in Fig. 5. For each W/C ratio, S_{H2O} of TiO₂ added cement paste was slightly larger, so nano-TiO₂ addition was found to increase the surface area of the hydration products.

(3) Nitrogen sorption isotherms

Fig. 6 shows the BET surface area (S_{N2}) based on nitrogen sorption isotherms. It should be noted that, in nitrogen sorption test, nitrogen molecules can adsorb only up to low density C-S-H and not access high density C-S-H inside the originally cement particles, while water molecules can access both of them [13]. So the BET surface area of nitrogen sorption is related to the amount of low density C-S-H.

As shown in Fig. 6, S_{N2} of W55-TiO₂ was larger than that of W55-Plain, and S_{N2} of W40-TiO₂ was slightly larger than W40-Plain in the saturated conditions. After drying at 11% RH, S_{N2} of W55-TiO₂ was still larger than that of W55-Plain, but S_{N2} of W40-TiO₂ was smaller than W40-Plain. In this measurement, it was clarified that nano-TiO₂ increased the amount of low density C-S-H precipitated during the hydration process particularly in case of W/C = 0.55. Nitrogen sorption isotherms are shown in Fig. 7 and Fig. 8. Comparing isotherms of the saturated state samples, the difference in the shapes of isotherm of cement paste with and without TiO₂ showed the similar trend as the water vapor sorption isotherms (shown in Fig. 3 and Fig. 4). After drying at 11% RH, The shape of isotherm of W40-TiO₂ was clearly different from W40-Plain, and sorption volume of W40-TiO₂ was decreased.

It has been reported that the stepwise desorption isotherm due to the cavitation (from $p/p_0 \sim 0.49$ to ~ 0.47 for nitrogen at -196 °C, so-called as "kink") occurs in materials, which have the bottle neck shaped pore network structures [14].

Here, the bottle neck shaped pore network refers the structure consisting of large mesopores (pore body) connected by smaller mesopores (neck pore) which exposed to the surface. Desorption via cavitation occurs regardless of the pore shape and size and also on the size of connecting pores, if neck diameters is smaller than 4-5 nm [14]. Therefore, desorption volume of this kink has related to the presence of these bottle neck pore structures in cement paste.

In Fig. 7 and Fig. 8, a kink due to cavitation was confirmed in all isotherms. In 11% RH, the kink of W40-TiO₂ is clearly smaller than W40-Plain. This suggested that in case of W40-TiO₂, during drying period at 11% RH, narrow mesopores spread or large mesopores disappeared.

(4) Impact on drying shrinkage

Drying shrinkage behavior under the first drying process showed different trend in respect to the W/C ratio. In case W/C = 0.55, drying shrinkage strain became larger by the addition of nano-TiO₂, while in case W/C = 0.40, drying shrinkage strain of nano-TiO₂ added cement paste became smaller than reference sample. This can be explained by increasing amount of low density C-S-H by the addition of nano-TiO₂ in case W/C = 0.55. Generally, during the first drying process, morphological alteration of low density C-S-H occurs dramatically and influences shrinkage behavior of cement paste [15]. Nano-TiO₂ acts as nucleus of hydration products to promote the hydration reaction at early age and form a denser microstructure. As a result, the strength increases at the early hydration stage, while the drying shrinkage of the first drying process increases as the precipitation amount of low density C-S-H increases.

But in case of W/C = 0.40, it cannot explain about the shrinkage behavior only by the impact on low density C-S-H amount. S_{H2O} of W40-TiO₂ was larger than W40-Plain, while S_{N2} of W40-TiO₂ was almost the same as W40-Plain. It indicates an increase in the amount of hydration products (such as high density C-S-H) in the area where nitrogen molecules cannot access. Namely, W40-TiO₂ had a denser and less shrinkable microstructure than W40-Plain.

This phenomenon is thought to be due to the difference in the location where TiO_2 nanoparticle works in cement paste. When TiO_2 acts as a nucleus for hydration products between two cement particles (which may produce large amount of low density C-S-H), drying shrinkage increases, but if it works between cement particles and pores, it is considered that it does not significantly affect drying shrinkage. Therefore, as a result of the different places where TiO_2 works effectively for each W/C ratio, it is considered



Fig. 3 Water vapor sorption isotherms (W/C =0.40)



Fig. 4 Water vapor sorption isotherms (W/C=0.55)



Fig. 5 BET surface area (S_{H2O}) calculated from water vapor adsorption branches.

that a difference in shrinkage behavior occurred.

However, further investigations are required, for this behavior.

In addition, although this study used white

Portland cement, the effect of nano-TiO₂ addition was manifested in the outer C-S-H precipitated from the hydration reaction of alite or belite. Therefore, it is thought that similar results can be obtained even when experiments are performed with different cement types.

4. CONCLUSIONS

The impact of the addition of nano-TiO₂ particles on drying shrinkage of hardened cement paste was investigated through comparison of a white Portland cement paste, used as a reference sample, with a cement paste containing 3% of nano-TiO₂ particles with respect to mass of cement. The followings were newly obtained by the experiment:

- (1) Short-term length change isotherms showed that the drying shrinkage strain of nano-TiO₂ added to cement paste is larger than that of reference paste in case W/C = 0.55, while it obtained the opposite result in W/C = 0.40. However, it was clarified that the influence of nano-TiO₂ on the shrinkage behavior appeared largely in the first drying process from saturated condition to 40% RH at 20 °C.
- (2) Water vapor sorption measurements showed that BET surface area of cement paste with nano-TiO₂ was larger for each W/C ratio. In case W/C = 0.55, nano-TiO₂ reduces mesoscale pores.
- (3) Based on nitrogen sorption measurements, during the hydration process, nano-TiO₂ increase the precipitation amount of low density C-S-H. This results were less apparent in W/C = 0.40, but clearly confirmed in W/C = 0.55.
- (4) At a water-cement ratio of 0.55, it was revealed that the addition of nano-TiO₂ increased the low density C-S-H during the hydration process, resulting in larger shrinkage than reference cement paste during the first drying process.

ACKNOWLEDGEMENT

A part of the present experiments are sponsored by JSPS KAKENHI Grant Number 26630254, 16H06363, and 15H04077. Experiment using FE-SEM was conducted in Nagoya University, supported by Nanotechnology Platform Program (Molecule and Material Synthesis) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

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Fig. 6 BET surface area (S_{N2}) calculated from nitrogen adsorption branches.



Fig. 7 Nitrogen sorption isotherms (W/C = 0.40)



Fig. 8 Nitrogen sorption isotherms (W/C = 0.55)

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