Construction and Building Materials 158 (2018) 755–760

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

The effect of nano-γAl_2O_3 additive on early hydration of calcium aluminate cement

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HIGHLIGHTS

- The early-age hydration heat of cement was increased with nano-γAl_2O_3 introduction.
- Nano-γAl_2O_3 additive could promote the formation of the amount of main hydrates.
- Nano-γAl_2O_3 additive contributed to the denser microstructure of CAC.

ARTICLE INFO

Article history:
Received 1 July 2017
Received in revised form 13 October 2017
Accepted 16 October 2017
Available online 20 October 2017

Keywords:
Nano-γAl_2O_3
Calcium aluminate cement
Hydration
Microstructure

ABSTRACT

Aiming to solve the decrease of the mechanical strength of calcium aluminate cement (CAC) at high temperature, nano-γAl_2O_3 additive ranging from 0.5 to 1.5 mass% was added in CAC with water to cement ratio (w/c) of 0.36 respectively. The influence of nano-γAl_2O_3 additive on hydration heat was studied by isothermal calorimetry. It shows that nano-γAl_2O_3 additive increases heat release rate and shortens the induction period of hydration. X-ray diffraction (XRD) and thermal analysis (TG-DTA) demonstrate that the main hydrate products are $CaAl_2O_4{\cdot}10H_2O$ (CAH_{10}) and $Ca_2Al_2O_6{\cdot}8H_2O$ (C_2AH_8) and their amounts increase obviously with nano-γAl_2O_3 additive. Besides these, no other new phases are formed. The microstructure development of the hydrates was characterized by scanning electron microscopy (SEM). Due to the formation of smaller hydrate crystals together with amorphous aluminum gel, the microstructure of CAC with 1 mass% nano-γAl_2O_3 additive becomes much denser, which contributes to enhance the mechanical strength at high temperature during the CAC hardening process.

1. Introduction

CAC is a kind of special high-performance cements and usually used in the refractory concretes as a hydraulic binder due to its high early strength, high refractoriness and good resistance to chemical attack [1]. The cement anhydrous phases can produce a variety of hydration products, which interlace with each other to form a crystal-gel network structure and obtain excellent mechanical strength during the hardening of castable. However, the mechanical strength decreases obviously with the heating temperature increasing, which greatly restricts its practical application [2]. It is well known that the mechanical strength of castable is closely related to the hydration degree and the microstructure evolution during the cement hardening process [3]. Therefore the hydration behavior of CAC is a key factor of affecting the mechanical strength of castable.

It has been reported that such factors as the curing temperature, w/c and additives [4–14] have great influences on the hydration process in CAC. This in turn affects the mechanical strength of CAC at high temperature. In view of the additives, alkali metals [7,8], polycarboxylate superplasticizer [9] and silica fume [12–14] are usually adopted because they can participate in the cement hydration process to modify the hydration degree and microstructure evolution. However, there are still some problems that cannot be ignored. For instance, alkali-aggregate reaction can occur in alkali metals leading to the internal expansion in concrete, which is harmful to their properties. Besides, the organic anions can react with Ca to form organic acid salts. This process will prevent cement hydration. In addition, researchers pointed out that silica fume always acted as filler rather than entered the katoite host structure. By comparison, the nano-scale additives can dramatically improve the mechanical strength of cement by

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https://doi.org/10.1016/j.conbuildmat.2017.10.071
0950-0618/

promoting the hydration process due to the high surface area and reactivity [15–17]. Herein various nano-additives such as nano-TiO_2 [18], nano-Fe_2O_3 [19], nano-SiO_2 [20,21] and nano-Al_2O_3 [22,23] have been used to improve the mechanical strength of ordinary Portland cement (OPC). For example, Zhang et al. [18] pointed out that the nano-TiO_2 increased the compressive strength of OPC mortar through its acceleration on cement hydration. Li et al. [20] investigated OPC mortars with 3, 5 and 10 mass% nano-SiO_2 or nano-Fe_2O_3 to explore the significant mechanical properties at the 7th day and 28th day. It proved that nano-SiO_2 behaved not only as filler but also as a promoter of pozzolanic reaction to improve cement mortar compressive strength. Recently, Ali and Shadi [22] found that 2.0 mass% nano-Al_2O_3 additive in the OPC could increase mechanical properties significantly and accelerate the appearance of the first peak by conducting calorimetry tests. This provides a hint that the identical element can be used as potential additives in CAC to improve the mechanical properties. This has not been reported up to now.

In this work, we put forward adding nano-particle additive in CAC hydration such as nano-Al_2O_3 which can react with $Ca(OH)_2$ and have high hydration activity to promote the cement hydration. Compared with the ordinary nano-Al_2O_3 material, the γ phase of nano-Al_2O_3 crystalline additive has the lowest surface energy and higher reactivity [24], which can deeply participate in CAC curing process. It has great potential to promote the nucleation of hydrates by reducing the nucleation barrier. Especially there are no other foreign ions in the system that may affect the hydration of CAC paste. Therefore the nano-γAl_2O_3 additive was selected in this work. The exothermic phenomenon of CAC hydration process was observed by isothermal calorimetry and TG-DTA. XRD and SEM analyses were applied to describe the cement hydration process with nano-γAl_2O_3 additive. Based on this, the acceleration mechanism of hydration process with nano-γAl_2O_3 additive was discussed.

2. Materials and methods

2.1. Materials

The nano-γAl_2O_3 additive with average particle size of 20 nm was supplied. CAC was used in this work. The oxides composition and the quantification of crystalline phases of CAC were characterized by X-ray fluorescence (XRF) (Table 1) and XRD Rietveld analysis (Table 2) respectively. It can be seen that the major phases of the cement are $CaO{\cdot}Al_2O_3$ (CA) and $CaO{\cdot}2Al_2O_3$ (CA_2) with the amount of 80.6 and 15.5 mass% respectively.

2.2. Sample preparation

CAC pastes were prepared by adding nano-γAl_2O_3 additive with the amount of 0 mass%, 0.5 mass%, 1.0 mass% and 1.5 mass% respectively. For simplification, the obtained CAC paste samples are marked as 0%. 0.5%, 1.0% and 1.5%. The nano-additive was mixed with cement in dry condition. Then distilled water was added into the above mixture with the w/c to be 0.36. The samples were poured into forms with the dimensions of 40 × 40×160 mm. Finally, the CAC pastes were cured at 20 °C and 95% relative humidity for 24 h.

2.3. Test methods

2.3.1. Phase characterization

The phases of samples were characterized by XRD (D8 Advance, USA) at the scanning range of 5°–50°. Due to lack of accurate knowledge on the detailed structures of crystalline aluminate hydroxides especially about CAH_{10} and C_2AH_8, a semi-quantitative analysis with reference intensity ratio (RIR) method was adopted. The appropriate crystalline structure should be chosen to match the specimen as close as possible. Then, the specific RIR of different phases obtained in database can be used to calculate the relative percentage of phase compositions in CAC pastes, indicating the changing tendency of different phases. The microstructure development was analyzed using SEM (nova™ nano 450, USA) equipped with an energy dispersive spectrometer (EDS, EDAX-TEAM™, USA).

2.3.2. Hydration characterization

Isothermal calorimetry is an important method to study the exothermic reaction occurring in controlled conditions. It can measure the heat flow rate and the cumulative heat of CAC paste hydration at an early stage. The measurement was carried out at 20 °C using a TAM Air calorimeter. During the experiments, the w/c was fixed at 0.36 and different amounts of nano-γAl_2O_3 addition were added. The heat flow curves were recorded for 24 h.

The thermogravimetric analysis (TG) and differential thermal analysis (DTA) were utilized to characterize the reaction process of cement hydrates with temperature increasing. The experiment was heated from ambient temperature up to 1000 °C at the heating rate of 10 °C min^{-1}. The samples were placed in the high purity alumina crucible (99.99%) and the tests were carried out in flowing nitrogen.

3. Results and discussion

3.1. Isothermal calorimetry

The heat flow rate and cumulative heat curves for CAC pastes with different amount of nano-γAl_2O_3 additive are shown in Figs. 1 and 2, respectively. The first exothermic signal, related to the initial dissolution of cement, declines rapidly leading to a steady condition that is termed as "induction period". During this period, the ions concentration reaches a maximum level in the solution [2,5]. Then a single sharp peak corresponding to the massive precipitation of hydrates occurs after certain time of hydration. Compared with the sample without nano-γAl_2O_3 additive, the induction period is apparently shortened and calorimetric peak occurs earlier in the case of the sample with nano-γAl_2O_3 additive as shown in Fig. 1. The occurrence of calorimetric peak is shortened from 7 h (without additive) to 4 h (with 1.5% nano-γAl_2O_3 additive). With the amount of nano-γAl_2O_3 addition increasing, the induction periods become shorter and the maximum values of calorimetric peak gradually increase. From the cumulative heat curves (Fig. 2), it is shown that when nano-γAl_2O_3 is added, the total heat does not change. The possible reason is that nano-γAl_2O_3 provides base sites for nucleation to form hydration product, during which a small amount of heat can be released. The above results demonstrate that nano-γAl_2O_3 additive clearly shortens the induction period and accelerates the cement hydration process.

Table 1
XRF analysis of the composition of CAC.

Oxides	Al_2O_3	CaO	SiO_2	MnO	Fe_2O_3	SO_3	TiO_2	LOI
mass%	66.22	33.04	0.10	0.28	0.04	0.04	0.05	0.37