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NOVEL ROUTES OF ADVANCED MATERIALS PROCESSING AND APPLICATIONS

Influence of tobermorite formation on mechanical properties of hydrothermally solidified blast furnace slag

Zhenzi Jing · F. Jin · T. Hashida · N. Yamasaki · Emile H. Ishida

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Abstract A hydrothermal processing method has been used to solidify blast furnace water-cooled slag (BFWS), in which the BFWS could be solidified in an autoclave under saturated steam pressure (1.56 MPa) at 200 °C for 12 h by the additions of quartz or coal fly ash. The experimental results showed that the addition of the quartz or fly ash was favorable to the formation of tobermorite, and the tobermorite formation in turn exerted a signifiant influence on tensile strength. The strength development depended on both tobermorite formation and the density of the tobermorite formed. The excessive addition of quartz appeared to cause strength deterioration due to the fact that the residual quartz affected the formation of tobermorite in the solidified specimens. Fly ash could be used as an additive for the hydrothermal solidification of BFWS, which may offer both energy saving and cost reduction.

Introduction

More than 24 million tons blast furnace slag (BFS) is being generated annually in Japan, and around 65% of it has been utilized for the manufacture of Portland slag cement [1]. The needs for the cement in Japan have been reduced year by year; in addition, large quantities of recycling materials, e.g., coal fly ash, have been also applied to these industries. Hence, the urgent requirement to develop a substitutable and environmental acceptable recycling technology for BFS has created widely concern and attention.

In addition to the utilization of BFS for the manufacture Portland cement and road pavement materials, it is also used to be melted to construction material [2], and to be converted into glass-ceramic material [3]. However, only a small portion of BFS is utilized in these ways.

BFS, of higher lime content, is well known to have a hydraulic activity when mixed with water. Therefore, the BFS may have a potential as a resource for producing building materials directly like Portland slag cement under hydrothermal condition, which will, in turn, offer both energy, resource saving and cost reductions.

The hydrothermal processing method has long been applied to the field of building material manufacture, however, it is recently used to convert concrete waste [4], metals-contaminated soil [5], municipal incineration ash [6], and coal fly ash [7] into building materials.

The hydrothermal processing method is considered to be such an attractive method in that it is capable not only of saving energy and reducing cost, but also of treating or recycling waste on a massive scale. Ishida [8] reported that the energy required for the hydrothermal solidification (at 150 °C) of earth ceramics is only 1/6th that of energy needed for fired ceramic tiles.

In our previous works [6, 7], the wastes could be solidified hydrothermally with tobermorite formation, and the additives, such as cement and slaked lime, were shown to be favorable to the tobermorite formation.

To the best of our knowledge, however, very little has been reported regarding the hydrothermal solidification of

Z. Jing (✉) · F. Jin · N. Yamasaki · E. H. Ishida
Graduate School of Environmental Studies, Tohoku University,
Aoba 6-6-20, Aramaki, Aoba-ku, Sendai 980-8579, Japan
e-mail: zzjing@hotmail.com

T. Hashida
Fracture and Reliability Research Institute, Tohoku University,
Aoba 6-6-20, Aoba-ku, Sendai 980-8579, Japan

Z. Jing · F. Jin
College of Environmental Science and Engineering, Tongji
University, 1239 Siping Road, Shanghai 200092, China

BFS. The objective of the present work is to investigate how to solidify BFS with hydrothermal processing method, and to evaluate the effect of tobermorite formation on the strength development. The results are expected to provide useful information on the manufacture of building materials from BFS by hydrothermal solidification technology.

Experimental

The blast furnace water-cooled slag (BFWS), obtained from Sumitomo Metals Ltd. in Japan, was ground with a ball mill to obtain a BET specific surface area of 370 m^2/kg. The additives of slated lime, fly ash, and quartz were used to solidify BFWS, and their compositions as determined by X-ray fluorescence (XRF; RIX3100, Rigaku) are shown in Table 1. The particle size distributions of the BFWS, ground quartz and fly ash determined by the laser diffraction technology (X100, Microtrac) are shown in Fig. 1. The X-ray diffraction (XRD, MiniFlex, Rigaku) patterns of the BFWS and fly ash used are shown in Fig. 2. The BFWS powder mixed with these additives at different mixing ratio was used as starting materials. The starting material (20 g) was first mixed with 5 mass% distilled water (1 mL) in a mortar manually, and then the mixture was compacted by compaction pressure of 30 MPa in a disc-shaped mould. The demoulded specimens were subsequently autoclaved under saturated steam pressure (1.56 MPa) at 200 °C for 12 h. After autoclaving, all the solidified specimens were dried at 80 °C for 24 h before testing.

The solidified disc-shaped specimens (φ30 mm × H20 mm) were used to measure the tensile strength by Brazilian testing [9]. The Brazilian tests were conducted in an instron universal testing machine (M1185) at a crosshead speed of 0.2 mm/min. Three specimens were tested for each hydrothermal processing condition, and the strength results presented in this study are the averaged data. After the Brazilian testing, the crushed specimens were investigated for phase analysis by XRD, for microstructure by a scanning electron microscope (SEM S-4100, Hitachi), and for pore diameter distribution by the mercury intrusion method (Poremaster 33P, Quantachrome).

Table 1 Compositions of the BFWS, quartz, fly ash, and slaked lime used (mass%)

	BFWS	Quartz	Fly ash	Slaked lime
SiO_2	32.6	89.7	53.1	
CaO	44.7	0.91	3.5	>75
Al_2O_3	15.8	7.02	24.0	
MgO	3.5		0.61	
SO_3	1.2		0.08	
Mn_2O_3	0.3			
TiO_2	1.1	0.25	4.58	
Fe_2O_3		0.62	5.1	

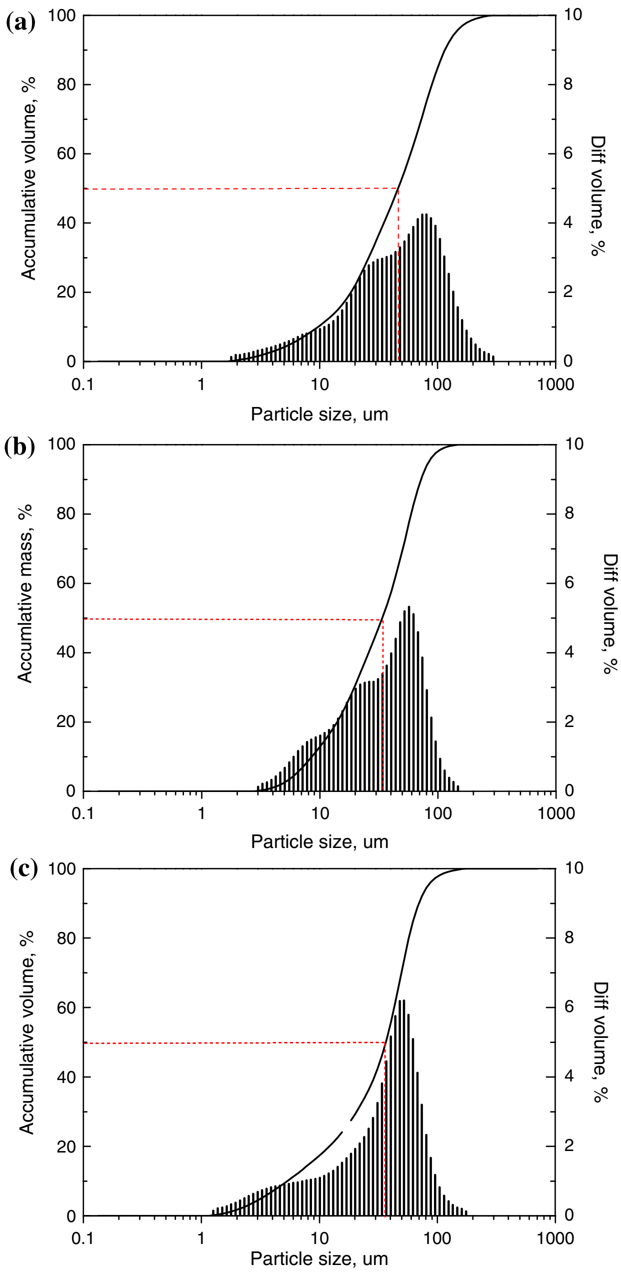

Fig. 1 Integrated particle size distributions of the BFWS, fly ash, and quartz. (**a**) BFWS, (**b**) fly ash, and (**c**) quartz used

Results and discussion

In our previous work [7], the addition of slated lime was shown to be favorable to tobermorite formation for the hydrothermal solidification of coal fly ash; however, the CaO content (Table 1) in the BFWS is higher than the

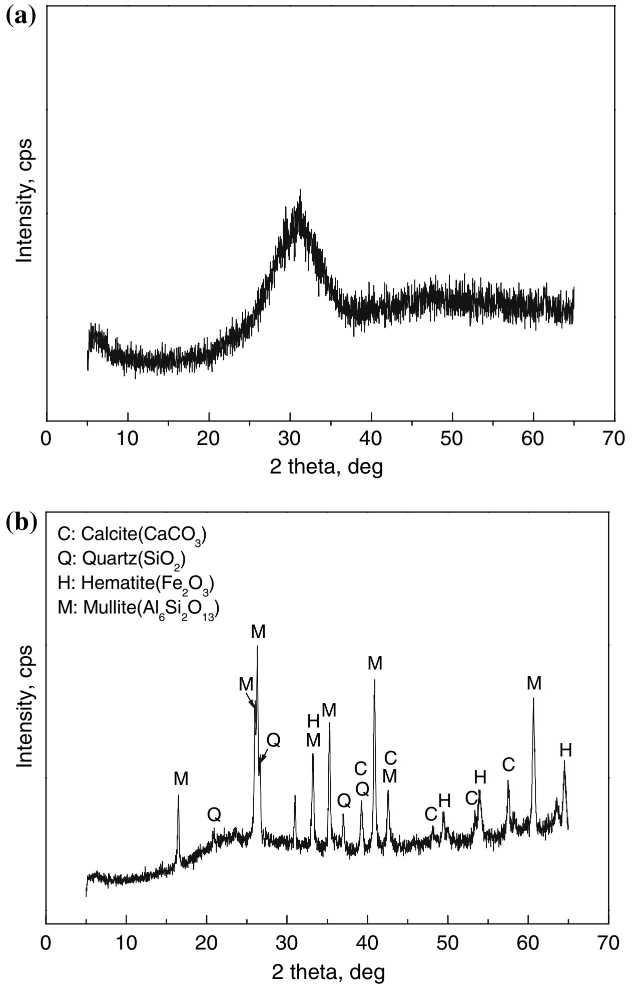

Fig. 2 XRD patterns of BFWS and fly ash used. (**a**) BFWS and (**b**) fly ash

SiO_2, which indicates that the addition of slated lime may be unfavorable to tobermorite formation. In contrast, addition of SiO_2 or some materials containing higher CaO content (e.g., fly ash in this study) should improve the tobermorite formation.

Effect of the additions of the slaked lime, fly ash, and quartz on tensile strength was investigated first. The results (Fig. 3), as expected, show that effects on the strength development is very different, e.g., the additions of the quartz and fly ash exert a significant influence, but the influence of the addition of slaked lime has few effects on the strength development. For the fly ash and quartz added, the strengths increase first, and then decrease, suggesting that an optimum fly ash or quartz exists for the hydrothermal solidification of BFWS.

Figure 4 shows XRD patterns for the specimens synthesized with the slaked lime 20 mass%, fly ash 20 mass%, quartz 20 mass%, and only BFWS, respectively. The BFWS is XRD amorphous (Fig. 2), and after autoclaving a new phase corresponding to hibschite ($Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x(x=0.2–1.5)}$) is superimposed on the broad amorphous background feature. With the addition of slaked lime, main phase of portlandite ($Ca(OH_2)$) is distinct, while the additions of the fly ash and quartz confirm the phases of mullite ($3Al_2O_3 \cdot 2SiO_2$), calcite ($CaCO_3$), quartz (SiO_2), and 1.1 nm tobermorite ($5CaO \cdot 6 SiO_2 \cdot 5H_2O$). A significant difference, clearly, is that the additions of the fly ash and quartz result in the tobermorite formation, suggesting the tobermorite formation may cause the strength increases shown in Fig. 3.

XRD patterns with the different fly ash and quartz content are shown in Fig. 5. Without the fly ash after curing at 200 °C for 12 h (Fig. 5a), a phase corresponding to hibschite is confirmed. With the 20 mass% fly ash added, main phases of mullite, quartz, calcite, and 1.1 nm tobermorite become distinct, however, the tobermorite phase disappears at 40 mass%. Compassion of the XRD results with the strength increase shown in Fig. 3 shows that the strength increase depends on the tobermorite formation, e.g., with the addition of fly ash 20 mass%, the strength increases nearly two times as large as the one with the fly ash addition 0 mass%, and with the disappearance of tobermorite, the strength decreases. The similar trend for the addition of the quartz is observed (Fig. 5b). Example, at 20 mass% quartz, a new phase corresponding to 1.1 nm tobermorite is distinct, thus leading to the highest strength increase (Fig. 3), however, the addition of the 40 mass% quartz lowers the strength, showing the excessive quartz added could cause a reduction in strength.

SEM photographs of the specimens synthesized with quartz 20 mass% and fly ash 20, 40 mass% are shown in Fig. 6. Many fibrous crystals (tobermorite) form, surrounding particles and filling the spaces between these particles, which is believed to enhance the strength of solidified body for the specimens synthesized with quartz

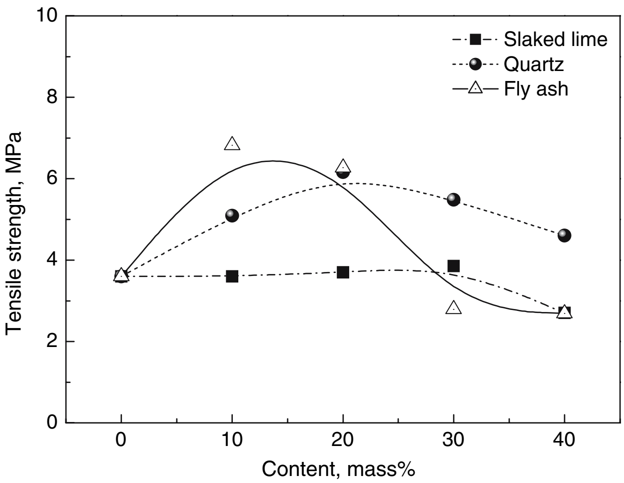

Fig. 3 Effects of the additions of the slaked lime, quartz, and fly ash on the tensile strength of the specimens cured at 200 °C for 12 h

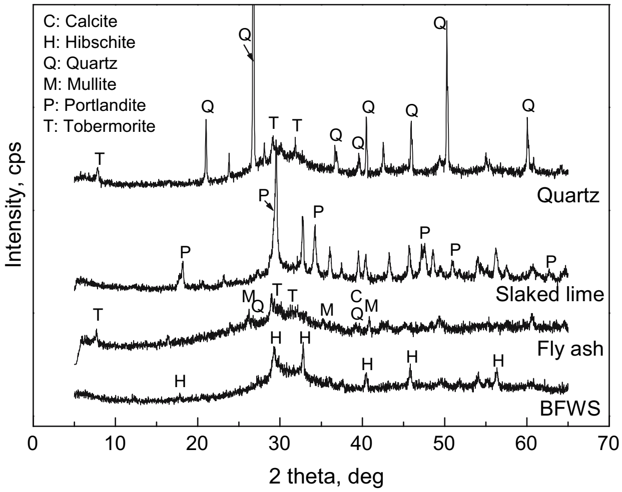

Fig. 4 XRD patterns for the specimens synthesized with the slaked line 20 mass%, quartz 20 mass%, fly ash 20 mass%, and only BFWS, respectively

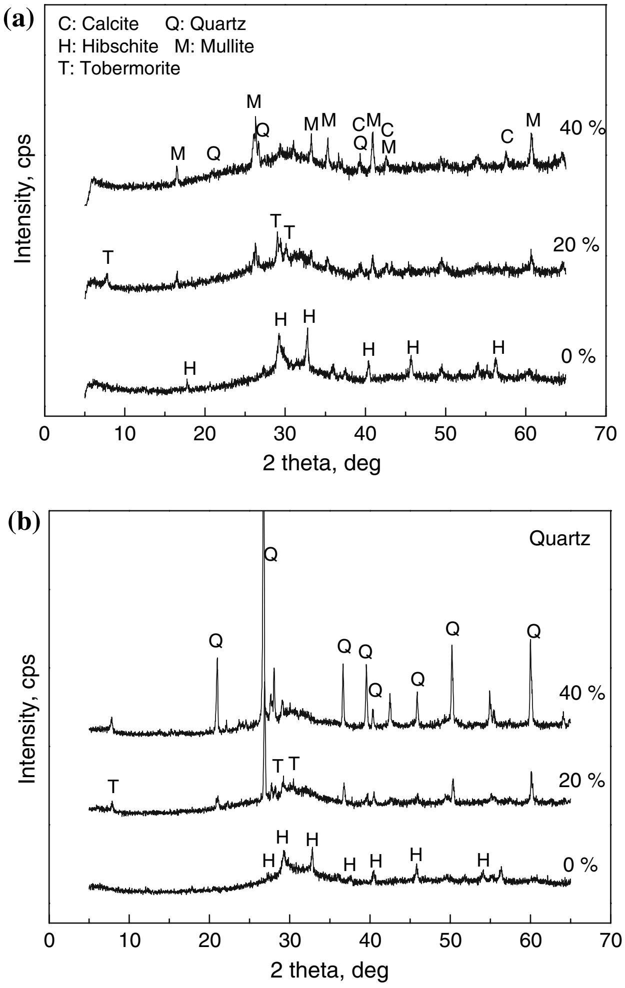

Fig. 5 Evolution of the XRD patterns with increasing fly ash and quartz content. (**a**) Fly ash and (**b**) quartz

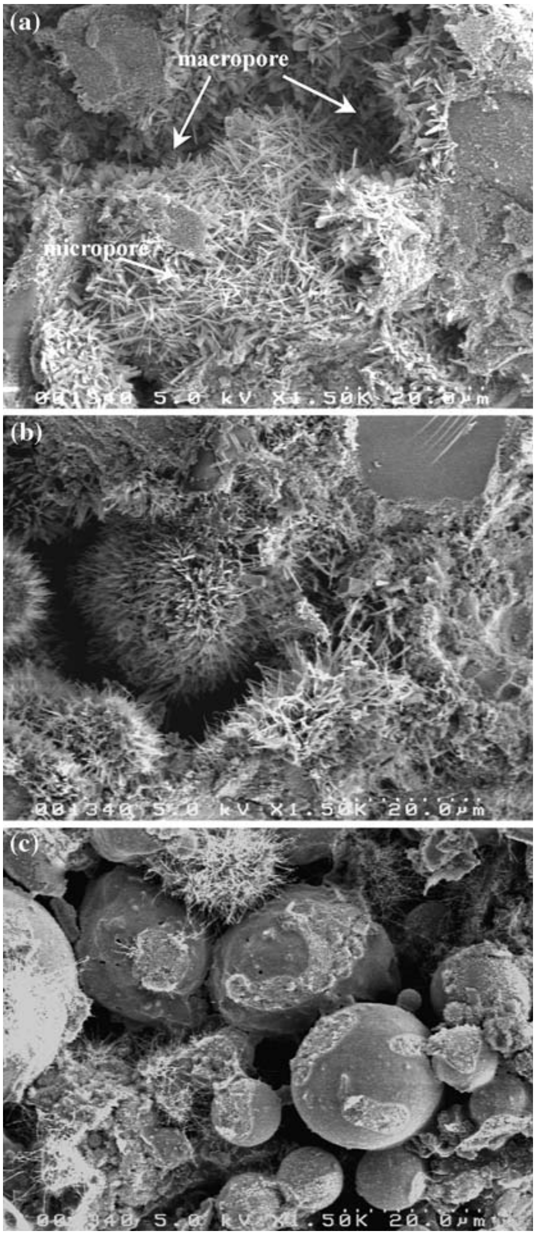

Fig. 6 SEM photographs of the solidified specimens with addition of 20 mass% quartz, 20 mass% fly ash, 40 mass% fly ash, respectively. (**a**) 20 mass% quartz, (**b**) 20 mass% fly ash, and (**c**) 40 mass% fly ash

and fly ash 20 mass%. In contrast, at the fly ash 40 mass%, few crystals form, leading to the lower strength shown in Fig. 3. From these SEM photographs, the microstructure within the solidified body affects its mechanical property significantly.

Figure 7 shows the pore diameter distributions of the solidified specimens with different quartz and fly ash contents. Without the addition of quartz, the highest frequency of pore distribution is of 7 μm in diameter (Fig. 7a). With the addition of quartz, however, the main pore distribution peak shifts and some new peaks form. As

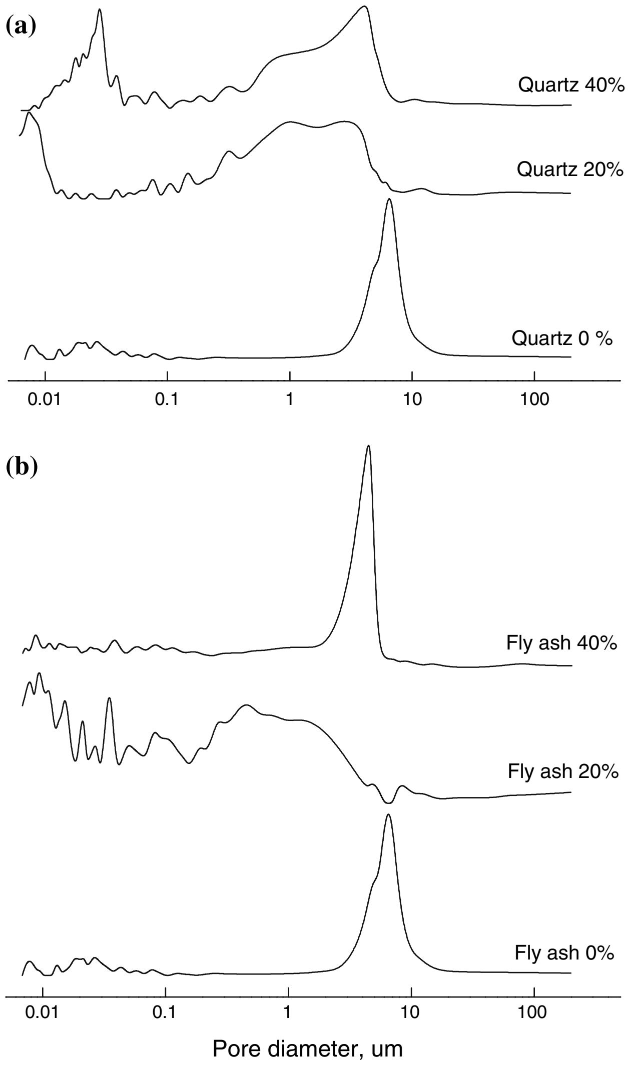

Fig. 7 Evolutions of the pore size distributions of the solidified specimens with increasing quartz and fly ash content. (**a**) quartz and (**b**) fly ash

shown in the figure, the main peak shifted is in the range of macropore (>0.1 μm), while the new-formed peak in the range of micropore (<0.1 μm). The peak of pore distribution reflects the space between the particles within specimen at the time of its formation. The peak shift corresponds to some crystals which have filled in these spaces; while new formed peak in the range of micropore suggests the new space of formed intercrystalline, and usually the finer pore size the peaks shift to, the denser the intercrystalline forms. With increasing the quartz content, the both pore distribution peaks (micropore and macropore) appear to shift to a large pore diameter. This suggests that at the addition of quartz 40 mass%, the microstructure of solidified body has been changed, i.e., the new-formed intercrystalline spaces become larger (the filling degree of the formed crystals become sparser), smaller number of crystals have been filled in the space between particles within the solidified specimen. This behavior may cause the strength deduction shown in Fig. 3, which suggests that strength development depends on both tobermorite formation and formation density of tobermorite.

The evolution of pore distribution with increasing the fly ash content was also carried out. Figure 7b shows that at 20 mass% fly ash, the pore distribution changes thoroughly, suggesting a lot of crystals have been formed in the spaces between particles, thus, in turn, leading to a higher strength shown in Fig. 3. However, at 40 mass% fly ash, there seems no changes occurred in the pore distribution, only a small peak shift appears to move toward a fine pore diameter (compare with fly ash 0 mass%). This result corresponds to the strength decrease (Fig. 3), and the small peak shift may be affected by the addition of the fly ash whose particles are smaller than that of BFWS.

The strength evolution for BFWS solidified specimens synthesized with the fly ash 20 mass% and quartz 20 mass% was also investigated. As show in Fig. 8, the tensile strengths increase with the curing time. It is notable that the developments increase slowly during the first 3 h, and then become rapid afterward. The strength evolution was also investigated by XRD analysis (Fig. 9). For the first 3 h of hydrothermal processing, few crystals form, suggesting that little reaction occurred in such a short time. Above 6 h, a trace of phase corresponding to 1.1 nm tobermorite becomes distinct, and the mount of 1.1 nm tobermorite increases with increasing the curing time for both cases of the additions of the fly ash and quartz added. Comparison of the evolution of XRD patterns with the strength results shown in Fig. 8 reveals that the strength increase depend on the formation of tobermorite.

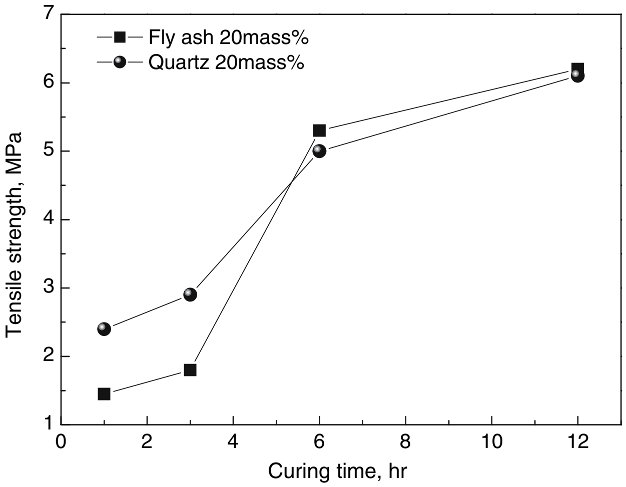

Fig. 8 Influence of curing time on the tensile strength of the specimens synthesized with the fly ash 20 mass% and quartz 20 mass%

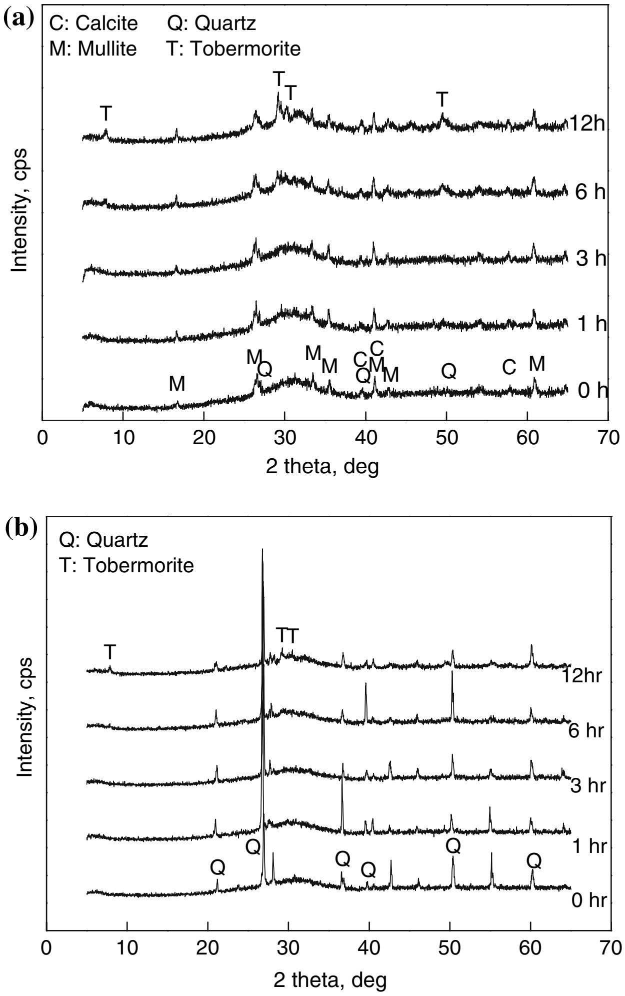

Fig. 9 Evolution of the XRD patterns with curing time for the specimens synthesized with the fly ash 20 mass% and quartz 20 mass%. (**a**) fly ash (**b**) quartz

Conclusions

(1) BFWS could be hydrothermally solidified at 200 °C for 12 h by the additions of quartz or coal fly ash. With the additions of quartz 20 mass%, or coal fly ash 10–20 mass%, the tensile strengths of the solidified specimens researched more than 6 MPa, which is higher than that of ordinary concrete.

(2) The development in tensile strength depended on both tobermorite formation and the density of the tobermorite formed in the solidified blocks.

(3) With excessive quartz addition, the residual quartz left in the specimen appeared to affect the tobermorite formation, and the filling degree of formed crystals seem to become sparser within the solidified body, thus resulting in the deterioration in strength.

(4) Fly ash could be used as an additive to solidify BFWS, which will offer both resource saving and cost reduction.

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