

氧化镁掺杂对铝酸盐形成和水化的影响

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摘 要: 为探究方镁石在熟料铝相中的赋存状态, 揭示水化反应机制, 合成了不同 MgO 含量的铝酸盐, 采用扫描电子显微镜, X 射线衍射, 红外光谱等, 研究了 MgO 对合成铝酸盐的形成和水化性质的影响。结果表明: 提高煅烧温度, 增加 MgO 含量有助于 C₄AF 和 C₁₂F₇ 的形成和稳定; 含镁铝酸盐熔体发生分相现象, 黑色相主要由 C₃A 和 MgO 组成, 玻璃体和黄色相中的 MgO 含量较低, 形成了 Ca₂₀Al₂₆Mg₃Si₃O₆₈ 和 Ca₇MgAl₁₀O₂₃ 等含镁化合物; MgO 掺杂降低了铝酸盐相的水化速率; 随着 MgO 含量增加, 铝酸盐相 1 d 的水化热降低。MgO 掺杂的铝酸盐水化产物中存在 Mg:Al 摩尔比约为 2 或 3 的镁铝双金属氢氧化物。

关键词: 铝酸盐; 氧化镁掺杂; 晶体结构; 水化; 镁铝双金属氢氧化物

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Effect of Magnesium Oxide Doping on Formation and Hydration of Aluminate

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Abstract: To investigate the occurrence of periclase in clinker aluminate and reveal the hydration mechanism, aluminates were synthesized *via* MgO doping at various contents. Their structure and hydrates were characterized by scanning electron microscopy, X-ray diffraction and Fourier transform infrared spectroscopy. The results indicate that higher sintering temperature and MgO content improve the formation and stability of C₄AF and C₁₂F₇. A phase separation occurs in molten aluminum phase. The black phase includes the main minerals like C₃A and periclase, while glass and yellow phases both have a low MgO content. The hydration heat of aluminate phase in the first day decreases with the increase of MgO content, indicating that MgO doping decreases the hydration rate of aluminate phase. In addition, the layered double hydroxides with a Mg:Al ratio of 2 or 3 appear in the hydration products of aluminate incorporated with MgO.

Keywords: aluminate; magnesium oxide doping; crystal structure; hydration; magnesium-aluminium layered double hydroxide

1 Introduction

Cement clinker mainly consists of four primary mineral phases, *i.e.*, alite (C₃S), belite (C₂S), aluminate (C₃A), and ferrite (C₄AF); two minor secondary phases, free lime (f-CaO) and periclase (MgO), and a small amount of glass. Among them, periclase is an important component affecting the long-term stability

of concrete, thus requiring a precise control in the clinker production process. Periclase in clinker is typically introduced from limestone as a raw material. No more than 2% MgO, which has a negligible influence on the volume stability of the cement, can be dissolved in the clinker mineral phases and glass^[1]. The approximate solid solubilities of MgO in each clinker phase are 1.3%±0.2% in C₃S, 0.6%±0.2% in C₂S, 2.0%±0.5% in C₃A, and 4.5%±0.5% in C₄AF^[2].

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Pure C_3A has a cubic crystal structure and can form an orthorhombic or a monoclinic crystal structure by ion doping. The aluminate phase is a $3CaO \cdot Al_2O_3$ solid solution doped with ions such as Mg^{2+} , Na^+ , K^+ , Fe^{3+} , and Si^{4+} [3–13]. Fukada *et al.* proposed a generalized formula for ion-doped C_3A , $(Na,K)_{2x}(Ca,Mg)_{3-x-y}[(Al,Fe)_{1-y}Si_y]_2O_6$, but they did not specify the values of x and y [6]. Prodjosantoso *et al.* reported that Mg^{2+} substitutes Ca^{2+} to form a solid solution according to the formula $Ca_{3-x}Mg_xAl_2O_6$ ($0 < x < 0.5$), in which Mg^{2+} has a stabilizing effect on $C_{12}A_7$, and the amount of $C_{12}A_7$ increases with increasing MgO content[14].

Compared with the other three main phases, aluminate phase has the maximum activity and hydration rate. Although the content of aluminate phase in clinkers is relatively low (2%–12%)^[4, 5–16], it has a significant effect on the hydration heat and setting characteristics of cement in the early stages^[9]. In the presence of $CaSO_4$, the second hydration heat peak delays as MgO content in pure C_3A increases. However, MgO content of $>1.5\%$ accelerates the hydration reaction, along with the earlier second heat peak^[9].

Compared with other clinker minerals, aluminate has the maximum activity and its hydration is crucial for the early hydration and rheological properties of cement. Some impurities such as Mg^{2+} ions affect the polymorph and formation of aluminate phase in clinker, thus changing the hydration and hydrates. The main hydration products of magnesium ions in cement paste are $Mg(OH)_2$, $MgCO_3$, $CaMg(CO_3)_2$ and so on. For $Mg(OH)_2$, some of Mg^{2+} ions can be replaced by tripositive ions, forming Mg – Al LDH and Mg – Fe LDH [$Mg_{0.75}Fe_{0.25}(OH)_2(CO_3)_{0.125}(H_2O)_{0.5}$] under a special condition^[17]. To solve the unsoundness caused by the hydration of periclase, a conversion way from magnesium hydroxide to LDH should be proposed. Therefore, aluminates with different MgO contents were synthesized in different calcination regimes to investigate the effect of Mg on the minerals and phases. The hydration characteristics of these minerals and phases were investigated. This paper was to provide an effective approach to solve a problem regarding the stability of high magnesium cement.

2 Experimental

2.1 Material

The laboratory C_3A , aluminates and melten aluminates were synthesized with analytical-grade $CaCO_3$, SiO_2 , $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$, Al_2O_3 , Fe_2O_3 , TiO_2 , Na_2CO_3 , and K_2CO_3 according to typical chemical compositions of the three aluminates^[17]. Table 1 shows the MgO contents in the C_3A , aluminates and melten aluminates. The contents of the other oxides were the same as reported in a reference^[17].

Table 1 Proportions of chemical reagents in the synthesized aluminates and C_3A m/g

Sample No.	Series	MgO	CaO	Al_2O_3	Na_2O	SiO_2	K_2O	TiO_2	Fe_2O_3
C0		0.00							
C1		1.40							
C2		2.80							
C3	C	4.20	62.22	37.78	0.00	0.00	0.00	0.00	0.00
C4		5.60							
C5		10.00							
C6		20.00							
C7		40.00							
A11		1.40							
A12		2.80							
A13		4.20							
A14,	A1	10.00	56.60	31.30	1.00	3.70	0.70	0.20	5.10
MA14*									
A15,		20.00							
MA15*									
A16,	A16*	40.00							
MA16*									
A21		1.20							
A22	A2	2.40	53.90	28.90	0.60	4.30	4.00	0.50	6.60
A23		3.60							
A31		1.00							
A32	A3	2.00	58.10	33.80	0.40	4.60	0.50	0.60	1.00
A33		3.00							

*: Melten.

2.2 Synthesis of C_3A , aluminates and glass

The raw materials were firstly mixed with a appropriate amount of water, and then dried. The dried samples were pressed into a disc with a diameter of 40 mm. In Table 1, a series of samples A1, A2 and A3 were initially heated from room temperature to 1 000 °C at a heating rate of 10 K/min, and then they were heated to 1 280 °C and 1 350 °C at a heating rate of 5 °C/min and calcined for 2 h (B3). The samples calcinated at 1 280 °C and 1 350 °C were named as B1 and B2, respectively. The samples MA14*, MA15*, MA16*, and C1–C6 were heated with the same heating programming as B1 and B2, while they were calcined at 1 400 °C for 2 h (B3). In the experiment, the sample C0 could not react completely at 1 400 °C due to the high content of f-CaO, thus it was calcined at 1 450 °C.

Samples A14*, A15* and A16* were melted with B3 regime and cooled with a fan to obtain the glass. Figure 1 shows the schematic diagram of the preparation of C_3A , aluminates and glass. Figure 2 shows the images of melten aluminates. The black and yellow phases, and glass were carefully striped and their chemical compositions (see Table 2) were measured by a model Bruker S4 Pioneer X-ray fluorescence spectroscopy (XRF, Bruker AXS, Inc., USA). According to the results, the black substance and yellow substance both occur for high MgO and low MgO phases.

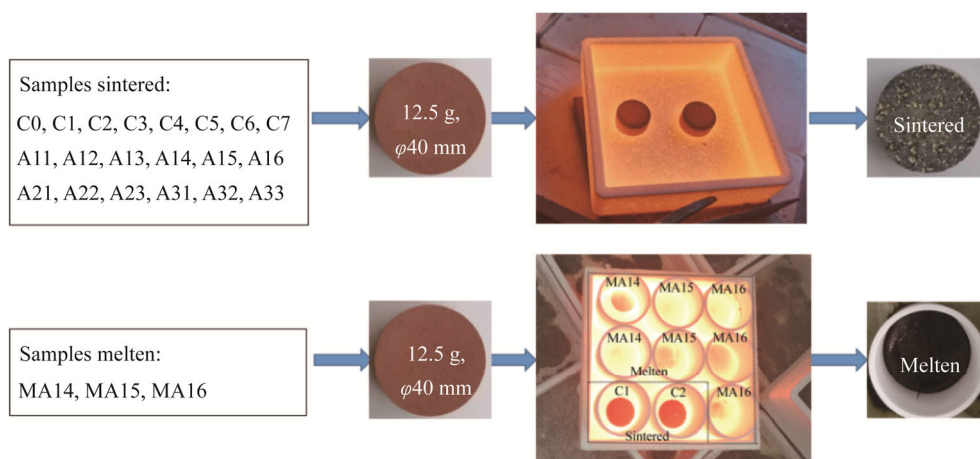
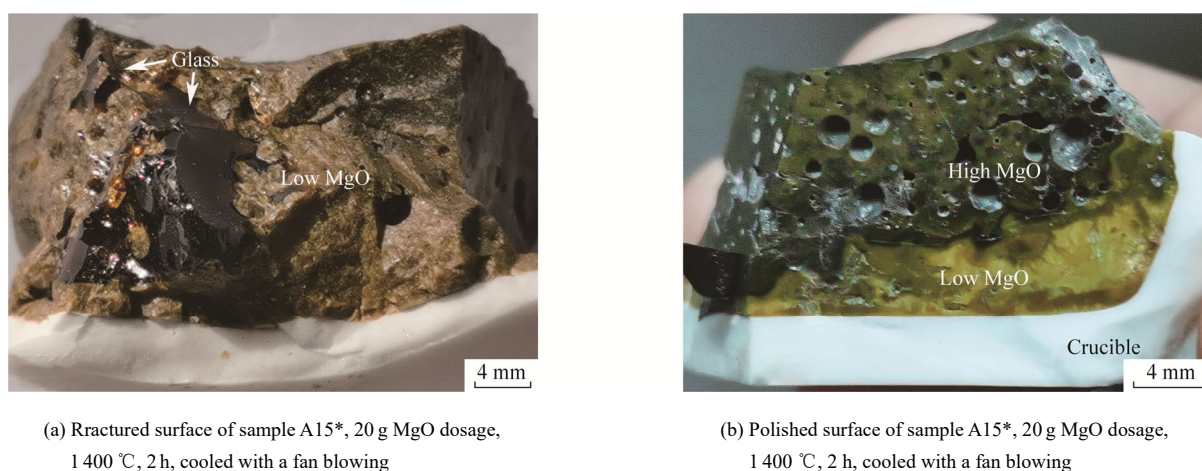
Fig. 1 Schematic diagram of synthesis of C_3A , aluminates and glass

Fig. 2 Images of the polished and fractured surfaces of samples

Table 2 Chemical compositions of different phases in Figure 2, sample A15* with 20 g MgO

w/%

Sample	Phase	CaO	Al ₂ O ₃	MgO	Fe ₂ O ₃	SiO ₂	Na ₂ O	K ₂ O	TiO ₂	SO ₃
A15*	High MgO, black	41.72	21.47	26.67	5.16	3.22	0.70	0.624	0.19	0.12
A15*	Low MgO, yellow	46.88	35.76	5.77	5.06	4.69	0.77	0.50	0.23	0.13
A15*	Glass	52.42	34.17	2.29	5.70	3.57	0.92	0.52	0.21	0.05

w—Mass fraction.

The resultant aluminate, glass and C_3A samples were ground and screened by a sieve with mesh 200 (*i.e.*, 75 μm). The heat release process was analyzed with a model TAM-air (8-channel) hydration calorimeter from TA instruments, USA. A model Rigaku X-ray diffractometer (D/MAX2200 PC, Rigaku, Japan) was used to determine the mineral phases of aluminate and hydration products of cement paste. In the XRD analysis, a Cu target was used and K_{α} line was selected. The tube voltage and tube current were 40 kV and 30 mA, respectively, the scanning range was 10° – 70° , and the continuous scanning mode was used with a scanning rate of $2^{\circ}/\text{min}$. A model Mettler-Toledo TGA/DSC1/1600 simultaneous thermal analyzer (Mettler Toledo Corp., Switzerland) with a temperature accuracy of $\pm 0.5^{\circ}\text{C}$ was used to perform the TGA. A model FEI Quanta 200 SEM (FEI

Company, USA) with EDS was used to determine the cross-sectional morphology and the elemental compositions of the specimens. The FTIR spectra of the samples were measured using a model Nicolet IS50 Fourier transform infrared spectroscope (Thermo Fisher Scientific, USA), and the measurement range was set between 400 and $1\,000\text{ cm}^{-1}$.

3 Results and Discussion

3.1 Effect of MgO on C_3A

Figure 3 shows the XRD patterns of the samples C0–C7. In Fig. 3, clearly, the main reaction products are C_3A and $C_{12}A_7$. The diffraction peak of $C_{12}A_7$ decreases with the increase of MgO content. When the MgO content reaches 10 g, the diffraction peak of $C_{12}A_7$ disappears, and correspondingly the diffraction

peak of C_3A increases. When the MgO content reaches 20 g, the diffraction peak of C_3A decreases, which is attributed to a relatively lower content of C_3A due to the MgO content.

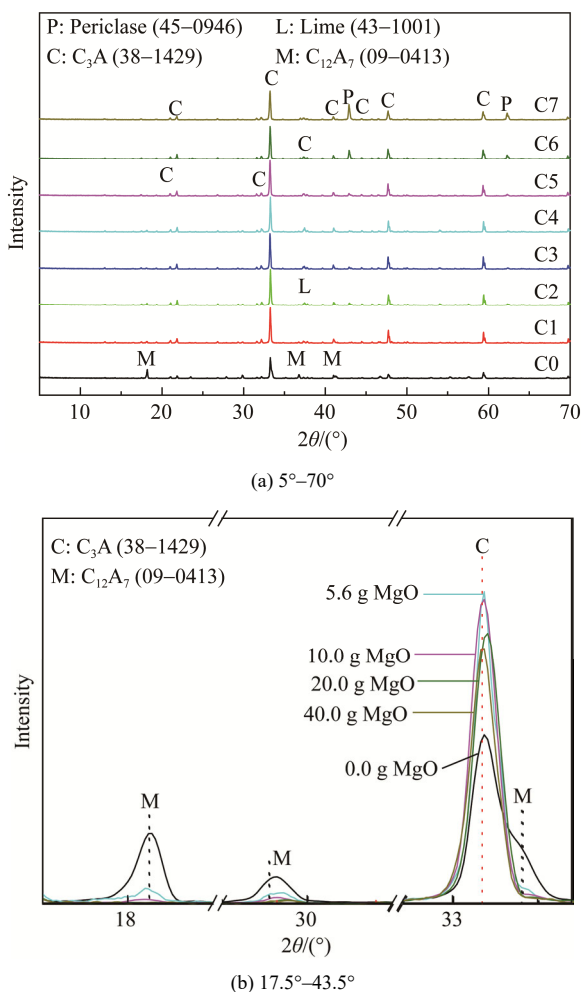


Fig. 3 XRD patterns of a series of samples C

3.2 Effect of MgO on aluminates

Figure 4 shows the XRD patterns of the samples A11, A21 and A31 with identical MgO contents for typical aluminates^[17], and calcined under conditions for samples B1 and B2. Clearly, the diffraction peak corresponding to f-CaO for all the samples is not pronounced, indicating that CaO in the samples mostly forms other compounds. The intensity of the diffraction peak of periclase is too low to observe. This is due to a fact that the MgO contents in these typical aluminates are significantly lower than those for the solid solubility of MgO in aluminate (*i.e.*, $2\% \pm 0.5\%$ ^[2]), thus resulting in insignificant or rather low-intensity diffraction peaks. Each of three series of samples has a cubic crystal structure^[16]. The samples series A1 and A2 contain 5.1 g and 6.6 g Fe_2O_3 , respectively, and C_4AF forms. The intensities of the diffraction peaks of C_4AF sintered at 1350 °C (B2) are lower than those of the samples sintered at 1280 °C

(B1), indicating that a higher sintering temperature enables Fe_2O_3 to dissolve in aluminates. Since a molar ratio of Ca to Al for the sample series A3 (3.13) is lower than that for sample series A2 (3.40) and sample series A1 (3.29), the diffraction peak of $C_{12}A_7$ is higher in sample series A3. A higher reaction temperature significantly reduces the intensity of diffraction peak of $C_{12}A_7$, especially for the samples A1 and A2, indicating that an increase of reaction temperature promotes the combination of $C_{12}A_7$ and CaO.

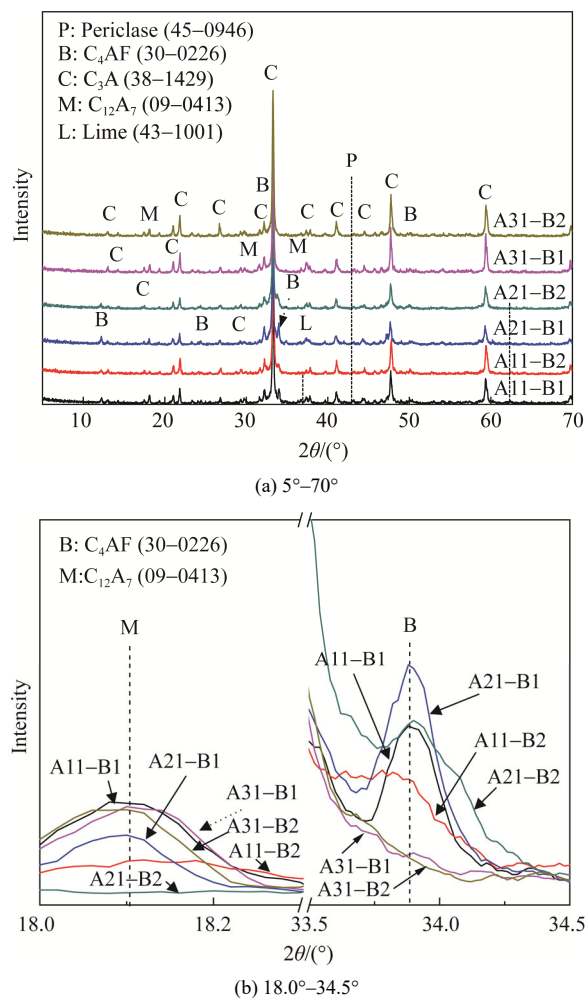


Fig. 4 XRD patterns of aluminates with typical chemical compositions

Figures 5–7 show the XRD patterns of the sample series A1, A2, and A3 with different MgO contents, respectively. The most intense peak of periclase at 2θ of 42.916° increases slightly, while the diffraction peaks of $C_{12}A_7$ and C_4AF increase greatly with the increase of MgO content, indicating that MgO has a stabilizing effect on $C_{12}A_7$, and facilitates the formation of C_4AF . Since a molar ratio of Ca to Al for the sample series A3 is relatively low, the samples contain a larger amount of $C_{12}A_7$. As a result, the diffraction peak of $C_{12}A_7$ negligibly shifts with increasing the MgO content. The Fe_2O_3 contents in the

samples A1 and A2 are higher. In Figures 5 and 6, increasing MgO content increases the C_4AF formation, which is attributed to higher Fe^{3+} occupation of

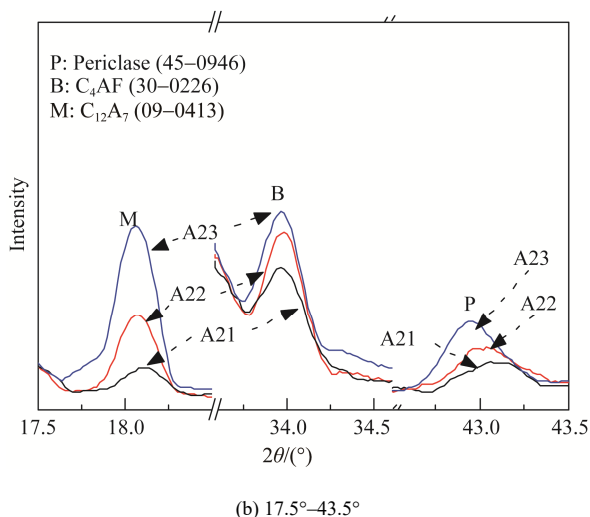
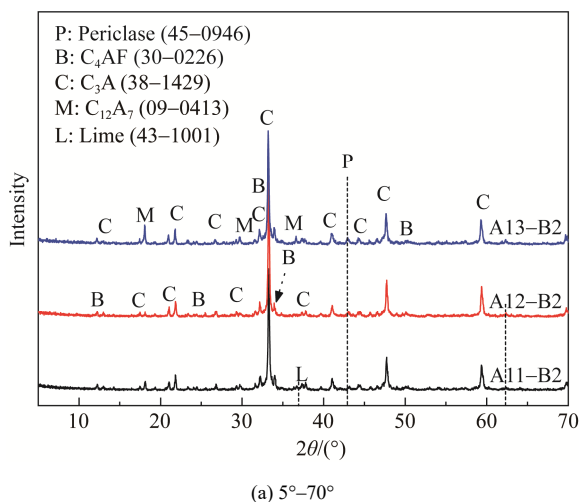


Fig. 5 XRD patterns of sample series A1 aluminates with different MgO contents

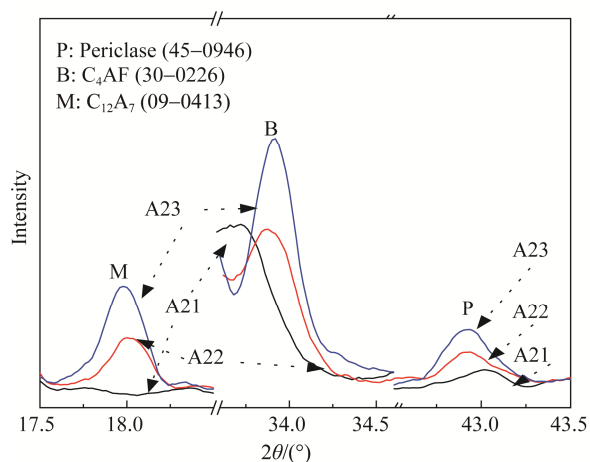


Fig. 6 XRD patterns of sample series A2 aluminates with different MgO contents

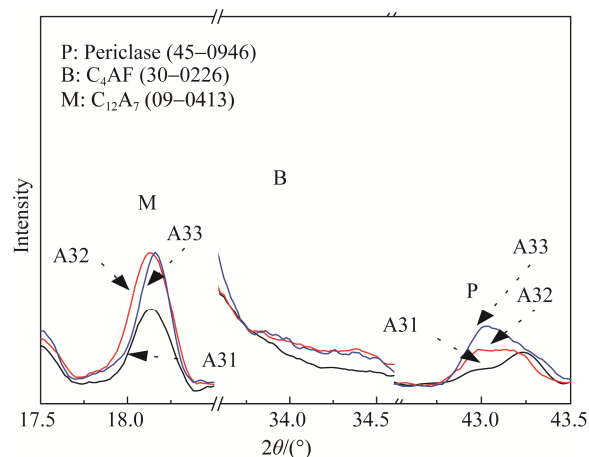


Fig. 7 XRD patterns of series A3 aluminates with different MgO contents

tetrahedral sites promoted by Mg^{2+} ^[18–19] and the Mg^{2+} solid solubility in C_4AF ^[20]. The Fe_2O_3 content in the sample series A3 is significantly low, and this series contains little C_4AF .

Figure 8 shows the Rietveld structurally refined XRD patterns of sample A12. Table 3 lists the corresponding calculation results. Clearly, the results have a good reliability with an R_{WP} of 8.6. In addition, the primary phase of the synthesized aluminates is C_3A . The C_4AF content is the second maximum amount in these samples due to the higher Fe contents in both samples series A1 and A2. Furthermore, the sample series A3 contains more $C_{12}A_7$ than the other series. These results indicate that the f-CaO content in the samples also increases with the increase of MgO content. When the MgO content increases by 2 to 3 times on the typical composition, the f-CaO in the sample A23 reaches 3.97%. Since the MgO content in the sample series A1 is higher than that in the sample series A2, the periclase content in the sample series A1 aluminates is correspondingly higher than that in the sample series A2. C_4AF and $C_{12}A_7$ contents both increase with the increase of MgO content.

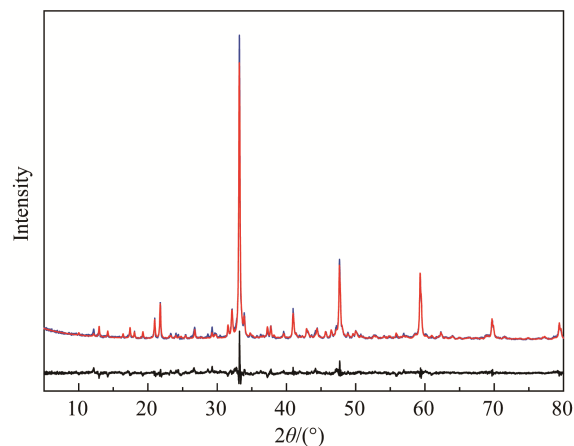


Fig. 8 Structurally refined XRD patterns of sample A12

Table 3 Mineral phase contents calculated with Rietveld refinement

Samples	C ₃ A	C ₁₂ A ₇	C ₄ AF	Periclase	f-CaO
A11	89.12	1.71	8.33	0.76	0.08
A12	86.27	2.72	8.13	2.59	0.29
A13	67.08	13.53	13.16	4.85	1.39
A21	83.69	1.11	15.00	0.09	0.11
A22	83.3	1.52	13.1	2.07	0.01
A23	63.54	9.36	19.22	3.91	3.97
A31	92.82	5.97	0.58	0.37	0.27
A32	81.47	11.43	4.39	1.66	1.06
A33	82.55	9.67	3.81	3.04	0.93

3.3 Effect of MgO on aluminates melted

Figure 9 shows the XRD patterns of the glass stripped from sample A15* melted at 1 400 °C. The diffraction patterns for the glass show a wide diffraction peak ranging from 20° to 35°. An asymmetric diffraction peak, for the typical lamellar and turbostratic structure decreases rapidly when the 2θ increases from 5° to 15°. Such a disordered structure is defined as the absence of three-dimensional periodicity^[21]. In addition, the diffraction peaks of C₃A and C₁₂A₇ are rather distinct. This may be due to the fact that C₃A and C₁₂A₇ crystals both are wrapped in the glass, or the crystals both are mixed when stripping the glass.

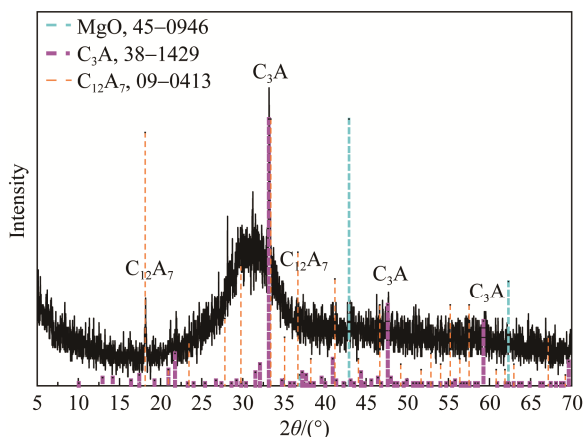


Fig. 9 XRD patterns of glass stripped from sample A15* with 20 g MgO

Figure 10 shows the XRD patterns of the glass stripped from sample A16* melted at 1 400 °C. Little diffraction peak of periclase appears in the diffraction patterns. The higher sharp peaks at the 2θ of 28° and 31° are a combined peak of Ca₇MgAl₁₀O₂₃ (JCPDS No. 140448), Ca₂₅Mg₈Al₃₄O₈₄ (JCPDS No. 140416), and Ca₃MgAl₄O₁₀ (JCPDS No. 170137). In addition, Mg-bearing compound includes Ca₂₀Mg₃Al₂₆Si₃O₆₈ (JCPDS No. 350133). These results indicate that part of MgO can be combined, thus forming the compounds under the condition of rapid cooling.

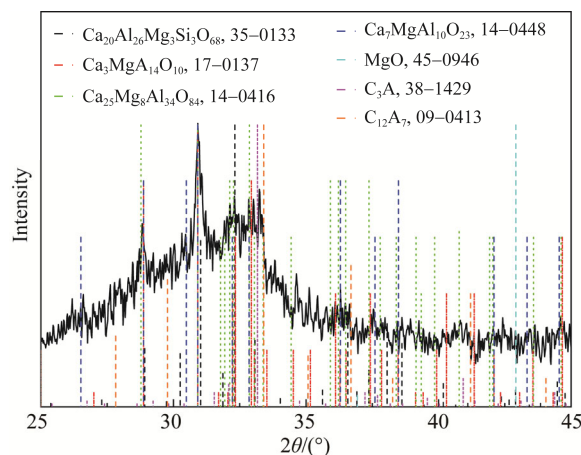


Fig. 10 XRD patterns of glass from sample A16* with 40 g MgO

Figure 11 shows the XRD patterns of the low Mg phase (*i.e.* yellow substance in Fig. 2) of molten aluminates incorporated with 20 g (sample A15*) and 40 g MgO (sample A16*), respectively. In Figure 11, clearly, a broad diffraction peak from 32.0° to 34.0° appears, indicating that there is a certain amount of glass in the low magnesium yellow substance. Such a peak also causes the most intense diffraction peak (2θ=33.168°) of C₃A, while the second intense peak (*i.e.*, as 2θ=47.625°) and the third intense peak (*i.e.*, as 2θ=59.270°) are not obvious. This indicates that the content of C₃A is low in the low Mg phase. In the sample A15* with 20 g MgO content, the main crystal phase is C₁₂A₇, while the diffraction peaks of Ca₂₀Al₂₆Mg₃Si₃O₆₈ (Q phase, C₂₀Al₁₃M₃S₃, JCPDS No. 350315)^[22–25] and Ca₃MgAl₄O₁₀ (C₃MA₂, JCPDS No. 170737)^[26] also appear.

The samples with 20 g MgO and 40 g MgO have no difference in mineral phase types, but their contents are different. The sample A15* with 20 g MgO contains the more C₁₂A₇, while the diffraction peaks of Ca₂₀Al₂₆Mg₃Si₃O₆₈ and Ca₃MgAl₄O₁₀ samples with 40 g MgO are higher than those of the sample with 20 g MgO.

Figure 12 shows the XRD patterns of the high Mg phase (*i.e.* black substance in Figure 2) of melted aluminates incorporated with 20 g and 40 g MgO, respectively. Clearly, the main minerals of the two samples are C₃A, C₁₂A₇, periclase and C₄AF, and a small amount of lime as well. The sample with 20 g MgO has a slightly higher C₁₂A₇ content than the sample with 40 g MgO.

Figure 13 shows the FTIR spectra of molten aluminates A15* and A16*. The first region (400–550 cm⁻¹) corresponds to the deformation of tetrahedron and octahedron^[27] and the maximum absorption band at 850–700 cm⁻¹ corresponds to the asymmetric stretching vibration of [AlO₄]⁻ tetrahedron^[1,28]. Huang *et al.* investigated the infrared spectrum of aluminosilicate glass and divided the infrared spectrum into three

regions of 400–550 (green area), 550–850, and 850–1 300 cm^{-1} [29]. The third region gradually redshifts and merges with the second region (blue area), and a

shoulder band at near 700 cm^{-1} forms as SiO_2 content decreases[29], which is similar to the infrared spectra of the two glasses, as shown in Fig. 13.

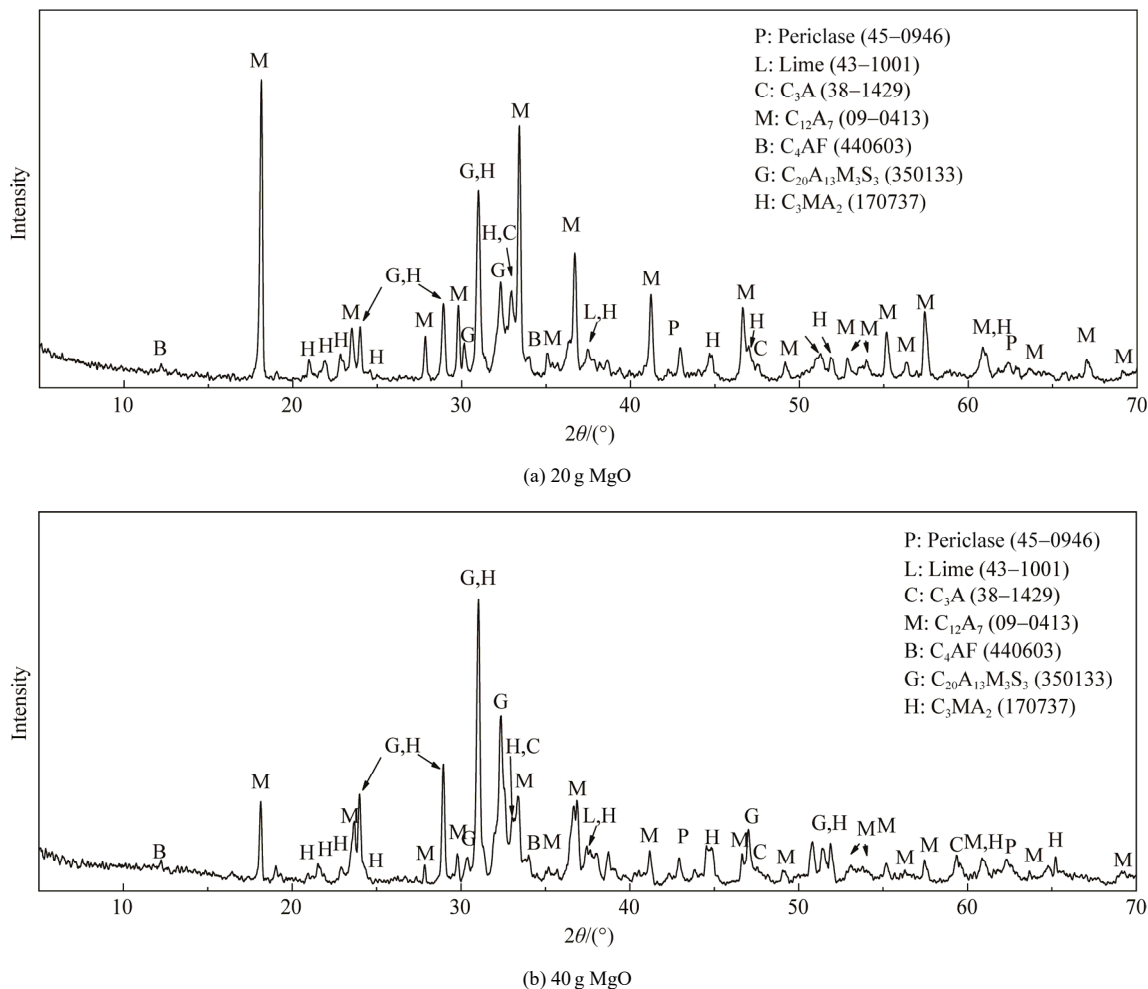


Fig. 11 XRD patterns of the low Mg phase of melted aluminate samples

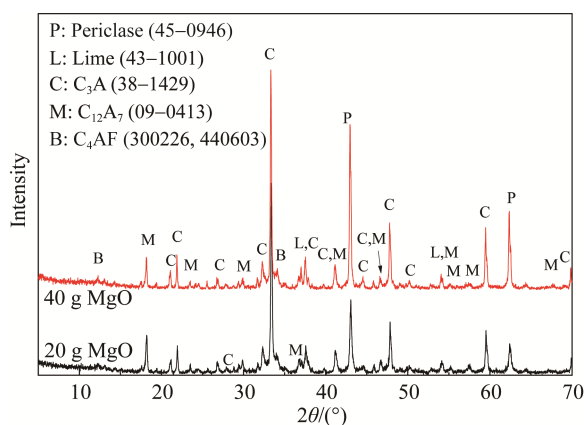


Fig. 12 XRD patterns of the high Mg phase of melted aluminate samples

Figure 14 shows the BSE images of molten aluminate samples A15* and A16*. Clearly, a clear boundary appears between the high and the low MgO areas

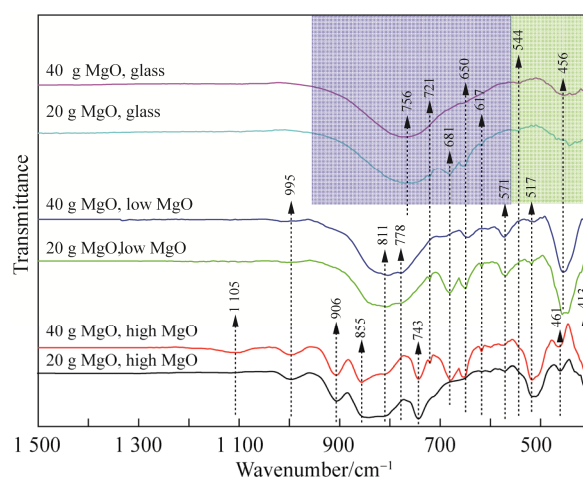
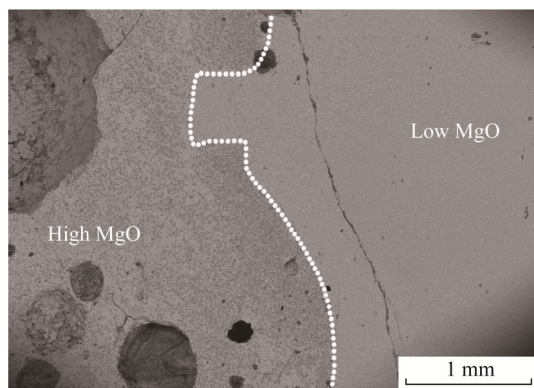


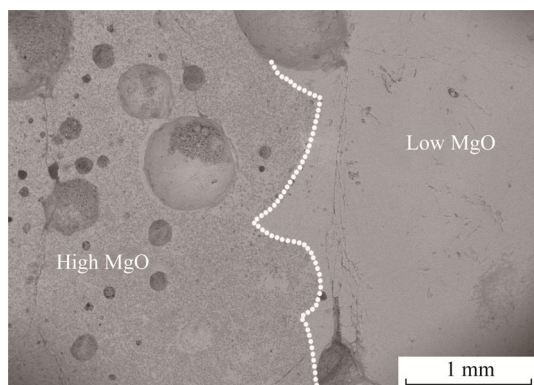
Fig. 13 FTIR spectra of molten aluminates A15* and A16*

of the melted samples. In the high MgO region, most of periclase occupies the field of view, while in the low magnesium region, only a small amount of

periclase appears. It is puzzled that the densities of the main phases including $C_{20}Al_{13}M_3S_3$ (2.983 g/m^3), C_3MA_2 (2.960 g/m^3), and $C_{12}A_7$ (2.676 g/m^3) in the low MgO region are lower than those of the main phases of C_3A (3.023 kg/m^3) and periclase (3.584 kg/m^3)^[30] in the high MgO region. However, periclase does not precipitate at the bottom of the crucible. Meanwhile, there are numerous big pores in the high MgO region, while little or no pores occur in the low MgO region.



(a) Sample A15* with 20 g MgO



(b) Sample A16* with 40 g MgO

Fig. 14 BSE images of melted samples A15* and A16*

3.4 Effect of MgO on hydration of aluminates

Figure 15 shows the heat evolution curves of samples C5, C6 and C7 in the first day. Clearly, a lower heat of samples with MgO doping releases. The heat release curves are similar among the three samples before 0.2 h. After 1 day, the hydration heat of samples C5, C6, and C7 are 461, 431, and 387 J/g, respectively. the hydration heat is decreased by 6.5% and 16.1% when the MgO content is increased from 10 g to 20 g and 40 g, respectively. The increased ratio of MgO content is higher than the decreased ratio of hydration heat, indicating that in addition to C_3A hydration, MgO also hydrates and releases the heat (see Fig. 16).

Figure 17 shows the hydration heat flow curves of series A1. In Figure 17, the first heat flow peaks of the samples appear at 0.05 h, and the second heat flow

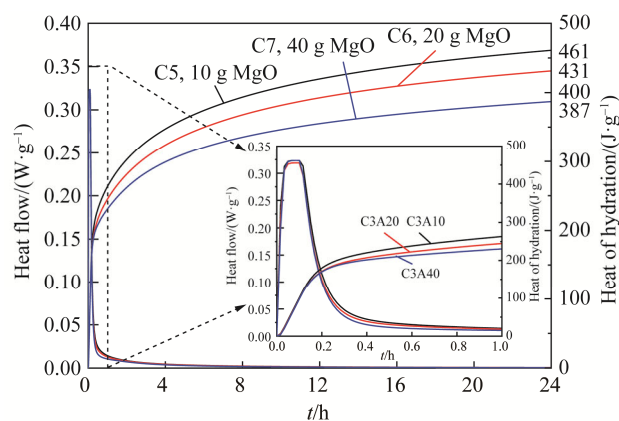


Fig. 15 Heat flow and total heat of the samples C5, C6, and C7

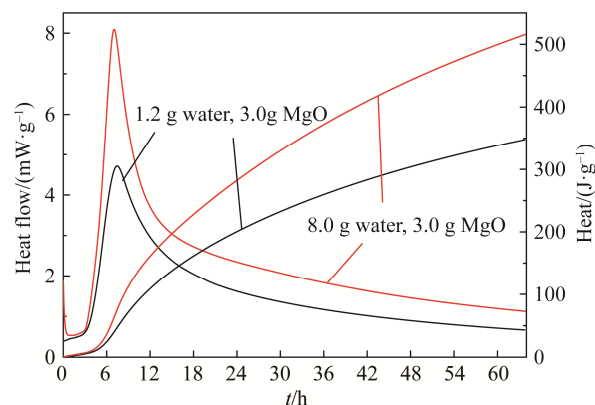
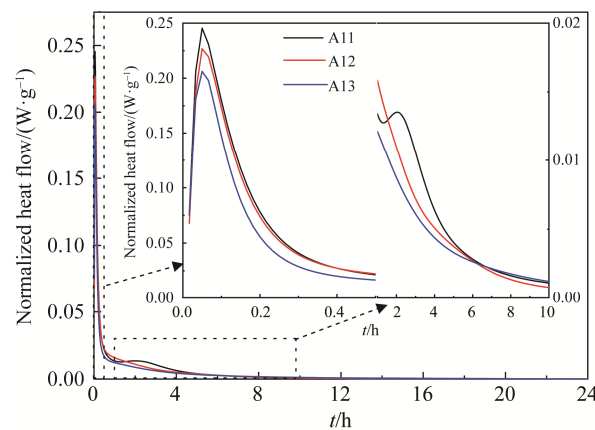
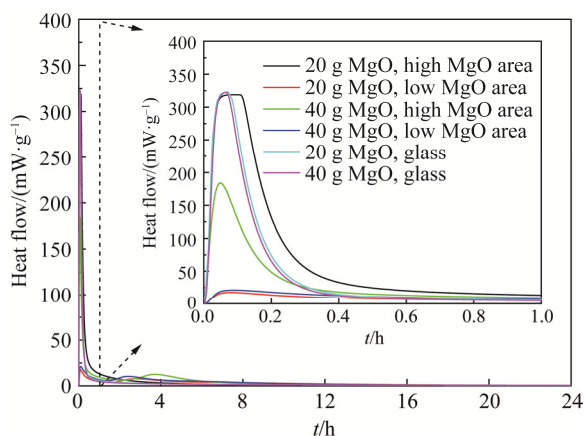
Fig. 16 Heat flow and total heat of MgO calcined from $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$ at $1400^\circ C$ for 2 h

Fig. 17 Heat flow curves of the samples A11, A12 and A13

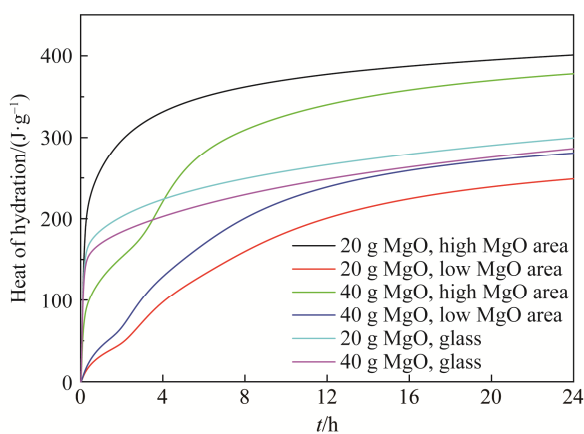
peak of the A11 appear at approximately 2 h. The samples A12 and A13 both do not show the second heat peak with increasing the MgO content. The cumulative heat of the samples A11, A12, and A13 are 379, 337, and 294 J/g, respectively. The hydration heat decreases as the MgO content increases. Before 6 h, the heat flow rate of the sample A13 is lower than that of the other two samples, whereas the opposite trend appears after 6 h. This may be due to the relatively high $C_{12}A_7$ content in the sample A13. Furthermore,

the hydration rate of C_3A is much higher than that of C_4AF ^[31]. And $C_{12}A_7$ hydrated at 20 °C has a second heat peak at approximately 8 h^[32–33].

Figure 18 shows the heat flow and hydration heat curves for high MgO, low MgO substance and glass stripped from samples with the addition of 20 g (sample A15*) and 40 g (sample A16*) MgO. Clearly, the heat flow peak of the high MgO substance becomes smaller and narrower as the MgO content increases from 20 g to 40 g. The heat flow peak of the low MgO substance is much lower than that of the high MgO substance. This is because the main mineral phase of high MgO material is C_3A , while the main mineral phase of low magnesium material is $C_{20}Al_{13}M_3S_3$ and $C_{12}A_7$ (see Fig. 11). The reactivities of $C_{12}A_7$ and $C_{20}Al_{13}M_3S_3$ are lower than those of C_3A ^[9,34].



(a) Heat flow



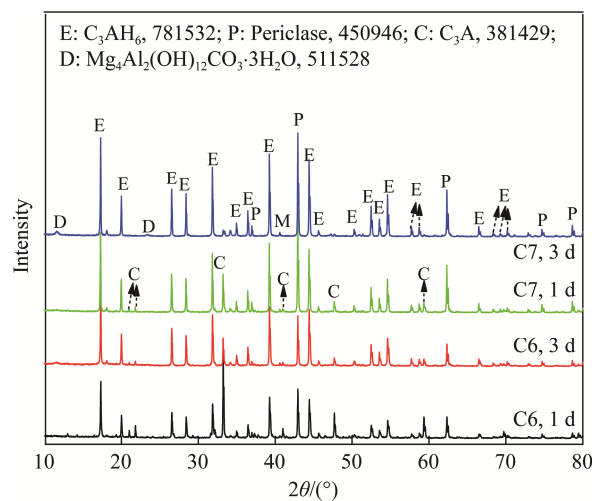
(b) Total heat

Fig. 18 Heat flow and total heat curves of the high MgO and low MgO substances stripped from the samples A15 and A16

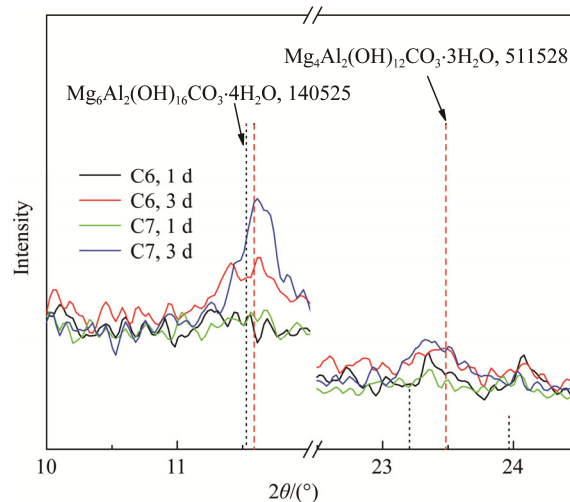
3.5 Effect of MgO on hydrates

Figure 19 shows the XRD patterns of the samples C6 and C7 after 3 d of hydration. In Figure 19, the main phases are C_3AH_6 , anhydrate periclase, $C_{12}A_7$, and C_3A . Also, there exist Mg-bearing hydrates. The

diffraction peaks at 2θ of 11.5° and 23.5 °C correspond to Mg-Al LDHs, such as $Mg_4Al_2(OH)_{12}CO_3 \cdot 3H_2O$ (JCPDS No. 51–1528) or $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ (JCPDS No. 14–0525), while no diffraction peak of brucite appears.



(a) 10°–80°



(b) 10.0°–24.5°

Fig. 19 XRD patterns of the samples C6 and C7 after 3 d hydration

Besides, a LDH diffraction peak appears after hydration for 3 d when pure C_3A sample is mixed with 40 g MgO. For the aluminate sintered with 40 g MgO (A16), the LDH diffraction peak is more prominent in the hydration product after hydration for 3 d (see Fig. 20). The C_3A in aluminate has higher crystal defects and higher activity rather than the pure C_3A , resulting in a higher LDH content in hydrates. Even if the sample contains only 1.4 or 1.2 g MgO (samples A11 and A21), LDH will be formed (see Fig. 21). The partial Mg in the LDH may originate from the Mg-bearing solid solution because the MgO content in the samples A11 and A21 is rather low. The diffraction peak of the Mg-Al LDHs also gradually enhances with

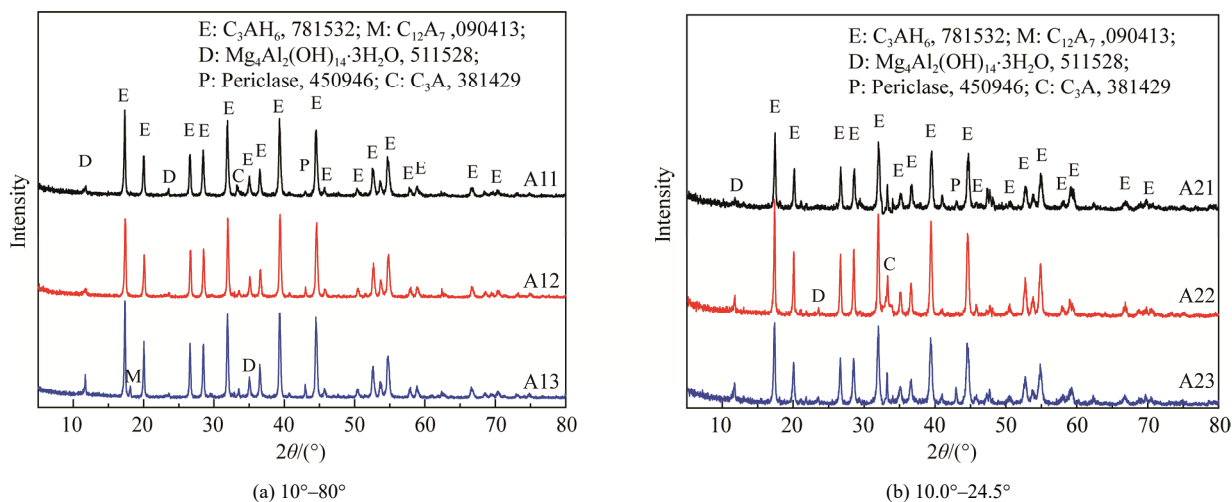


Fig. 20 XRD pattern of hydrates of the sample A16 with 40 g MgO for 3 d hydration

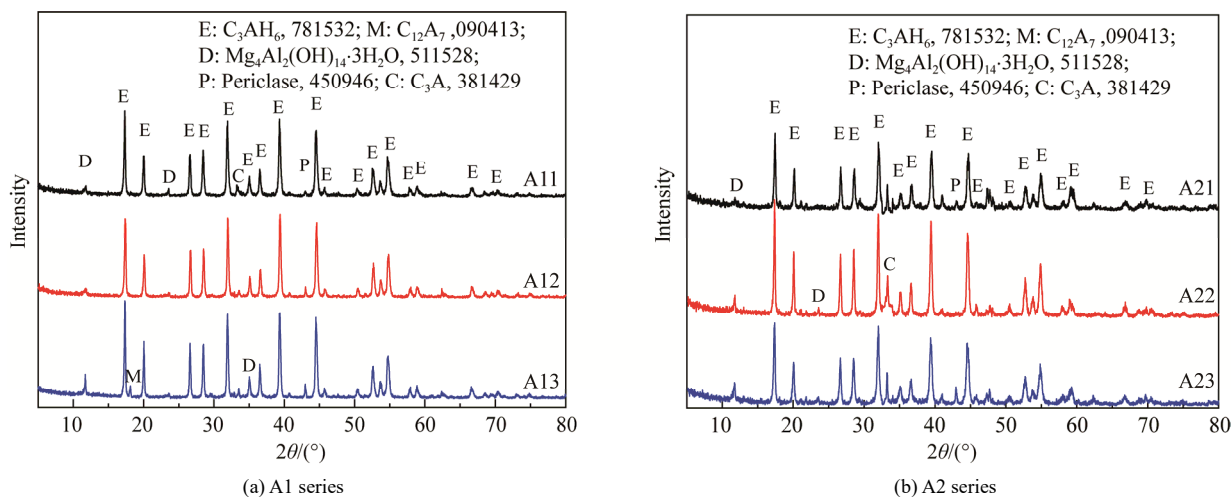


Fig. 21 XRD patterns of aluminates after 3 d of hydration

increasing the MgO content in the sample series A1 and A2.

Figure 22 shows the XRD patterns of hydrates of the black substance and glass stripped from the molten

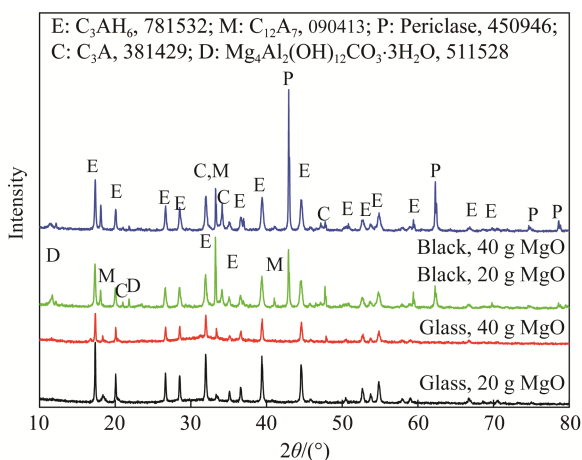


Fig. 22 XRD patterns of the glass and high-MgO substance of the samples A15* and A16* after 1 d hydration

samples A15* and A16* after hydration for one day. In Figure 22, almost no LDH appears since the MgO content in the glass is rather low. However, there is an obvious LDH diffraction peak in the reaction product of black substance.

Figure 23 shows the TG and differential TG (DTG) curves of the aluminates after 1 d hydration. The thermal decomposition at approximately 300 °C is caused by the dehydroxylation of C_3AH_6 ^[15]. The sample series A1 display the maximum hydration degree, followed by the sample series A3 and the sample series A2. The hydration degree of the aluminates decreases with increasing the MgO content, which can be explained by the decrease of the C_3A contents in the samples (see Table 3).

Figure 24 shows the TG and DTG curves of the hydrates of the glass and high MgO substance of the A15* and A16* samples after 1 d hydration. The weight loss between 100 °C and 200 °C refers to the dehydration of $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$, while the weight loss at 400 °C is caused by decarbonation of $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ ^[35].

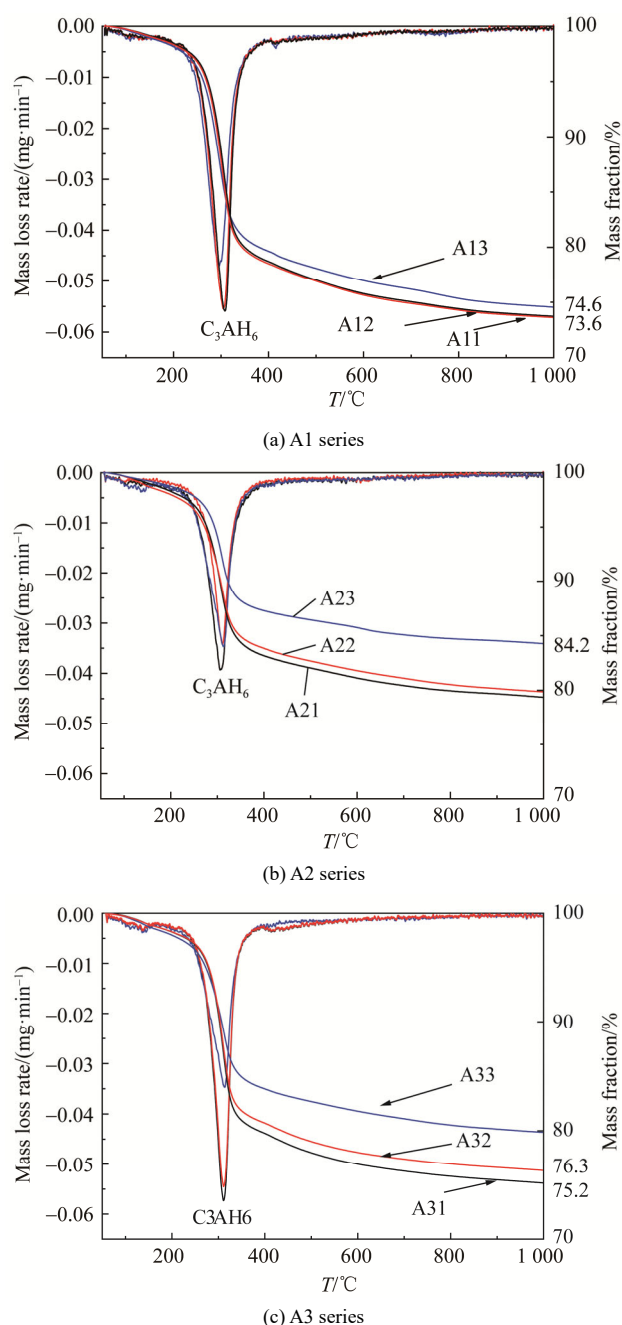


Fig. 23 TG and DTG curves of the aluminates after 1 d hydration

Fig. 25 shows the SEM images of aluminates after 3 d hydration. For the samples A12, A22, and A32 sintered at 1350 °C, the hexagonal lamellar clusters of the C_3AH_6 have clear edges and are composed of mostly euhedral or subhedral crystals (see Figs 25 (a) and (b)). In addition, a flocculent surface appears at high magnification (see Fig. 25 (c)). In Figure 25 (d), hydrated Mg^{2+} can form a flocculent phase. Based on the EDS data (see Table 4), the Mg/Al ratio of the magnesium-containing phase is ~ 2 . A small amount of C in the sample may originate from the adsorption of CO_2 from air during the sample preparation.

Figure 26 shows the SEM images of the high-MgO substance of the molten sample A15* (20 g MgO) after

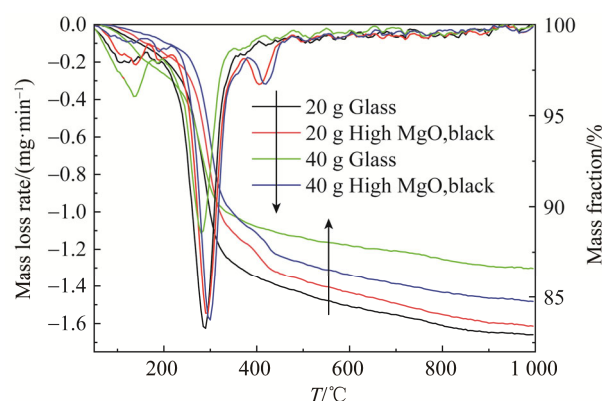


Fig. 24 TG and DTG curves of the hydrates of the glass and high MgO substance of the samples A15* and A16* after 1 d hydration

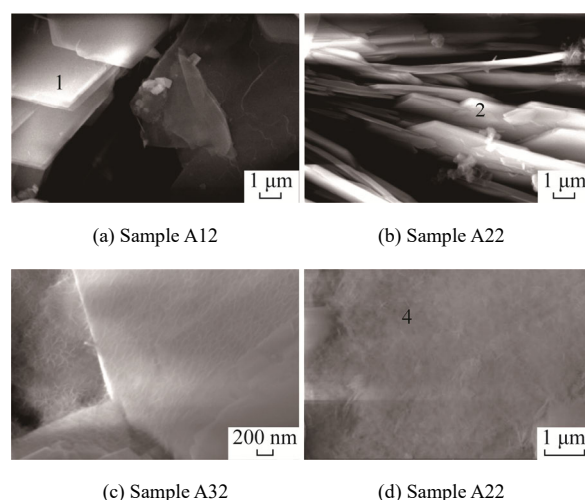


Fig. 25 SEM images of aluminates after 3 d hydration

Table 4 EDS elemental analysis of sample points in Fig. 25

Point	Mole fraction/%						
	C	O	Mg	Al	Si	Ca	Ti
1	2.36	72.5	1.53	8.38	1.22	12.11	0.05
2	3.24	72.03	1.57	8.05	2.02	11.06	0.19
3	2.08	71.78	1.08	8.93	1.67	12.29	0.33
4	7.07	67.21	12.43	6.71	1.01	3.51	0.18

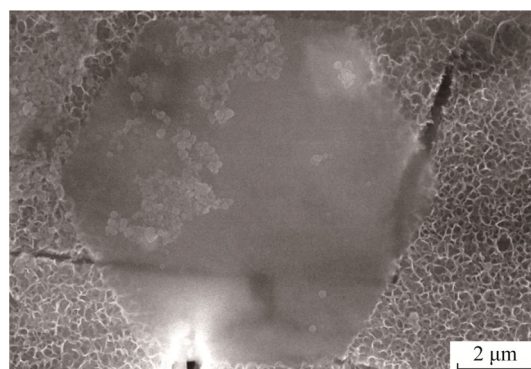


Fig. 26 SEM image of the high-MgO substance of the sample A15* (20 g MgO) after 12 h hydration

12 h hydration. A crystal containing Mg occurs. According to the EDS analysis, the contents of Ca, Mg, Al, Si, Fe, and C of the crystal are 9.09%, 4.95%, 8.23%, 3.27%, 4.05%, and 13.73%, and therefore the formula of this crystal is calculated as $\text{MgCa}_{1.84}\text{Al}_{1.66}\text{Fe}_{0.82}[\text{SiO}_4^{2-}]_{0.66}(\text{CO}_3^{2-})_{2.77}(\text{OH})_{6.25}$ from the charge balance.

4 Conclusion

1) The MgO content had a significant effect on the mineral phase content of the aluminate. Increasing the MgO doping content increased the contents of the periclase, f-CaO, C_4AF , and C_{12}A_7 .

2) A phase separation appeared in molten aluminate. The main minerals in the black phase were the C_3A and periclase, and MgO in the glass and yellow phase was rather low. $\text{Ca}_{20}\text{Al}_{26}\text{Mg}_3\text{Si}_3\text{O}_{68}$ and $\text{Ca}_3\text{MgAl}_4\text{O}_{10}$ occurred in the yellow phase, while $\text{Ca}_7\text{MgAl}_{10}\text{O}_{23}$, $\text{Ca}_{25}\text{Mg}_8\text{Al}_{34}\text{O}_{84}$, and $\text{Ca}_3\text{MgAl}_4\text{O}_{10}$ appeared in the glass.

3) The hydration heat of the aluminate gradually decreased with increasing the MgO doping content. The hydration rate of the black phase in the molten aluminate was higher than that of the glass and yellow phase. The hydration degree of the aluminate decreased with increasing the MgO content. The hydrated Mg^{2+} could form Mg-Al LDHs with a Mg/Al mole ratio of 2 or 3.

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