JOURNAL OF MATERIALS SCIENCE **40** (2005) 3921 – 3926

Effect of magnesia on strength of hydratable alumina-bonded castable refractories

GUOTIAN YE, TOM TROCZYNSKI
Department of Materials Engineering, University of British Columbia, Vancouver, BC, Canada V6T 1N5

The change in strength of hydratable alumina-bonded castable refractories in the presence of magnesia powder and magnesia aggregate, after heat treatment at 110° and 816°C, and the relationship between the strength and morphology and thermal decomposition behavior of the hydrates in the castables are investigated. The mechanism of bonding facilitated by the presence of magnesite in hydratable alumina-bonded castables after drying is discussed. The contribution of polycondensation process occurring after dehydroxylation of the hydrates in the castables after firing at 816°C is proposed as the principal mechanism for strength development.

1. Introduction

Refractory castables have been increasingly used in steel, foundry and nonferrous industries and calcium aluminate cement has been widely used as a binder in castables [1–5]. In response to the increasing severe service conditions, attempts have been made to reduce CaO content in castables because the presence of CaO is likely to produce relatively low-melting temperature phases, such as gehlenite ($2CaO{\cdot}Al_2O_3{\cdot}SiO_2$, melting point (mp) = 1590°C), anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$, mp = 1550°C) [3], monticellite ($CaO{\cdot}MgO{\cdot}SiO_2$, mp = 1498°C), and merwinite ($3CaO{\cdot}MgO{\cdot}2SiO_2$, mp = 1577°C) [6]. Consequently, ultralow cement and cement-free castables have been developed to enhance thermomechanical resistance and corrosion resistance of the castables. In recent years, hydratable alumina has been used in castables [2, 3, 5, 7] to replace calcium aluminate cement to further reduce lime content. However, hydratable alumina-bonded castables have relatively low strength (1.4–2.0 MPa modulus of rupture) at dehydration temperatures (800–1200°C) when hydraulic bonding is lost while ceramic bonding is not yet significantly formed [3]. It has been proposed that magnesia may influence strength development in these castables because the presence of magnesia accelerates the hydration of hydratable alumina and a hydrotalcite-like compound forms from the hydrated magnesia and the hydratable alumina [8, 9]. Although hydration of hydratable alumina in the presence of magnesia has been studied [8, 9], little is known about the influence of the magnesia on strength of hydratable alumina-bonded castables. The objective of this study is to examine the effect of magnesia on the strength of hydratable alumina-bonded castables after heat treatment at low (110°C) and intermediate (816°C) temperatures. The mechanism of bonding formation between hydratable alumina and magnesite in the castables is proposed.

2. Experimental procedures

The compositions of the castables are shown in Table I. Fused magnesite (Baymag-96, Baymag Inc., Calgary Canada) and fused magnesium aluminate spinel (SP-25, CE Minerals, King of Prussia, USA) were used to compare the strength of the magnesite-aggregate castables (M-0 and M-4) with that of spinel aggregate castables (S-0 and S-4). In order to investigate the effect of magnesite powder on the strength of the castables, one magnesite-aggregate castable (M-4) and one spinel-aggregate castable (S-4) contained 4 wt% deadburnt magnesite powder (P-98, Martin Marietta, <75 μm), while the magnesite powder was not incorporated in the other magnesite-aggregate castable (M-0) and spinel-aggregate castable (S-0). All the castables included 4 wt% hydratable alumina (Alphabond-300, Almatis) as the hydraulic binder and 6 wt% ultrafine alumina powder (RG100, Almatis); the balance was fused magnesium aluminate spinel powder (AR-78, Almatis). Small amounts of sodium polymethacrylate and citric acid were used as dispersants.

The castables were mixed with 5 wt% water and then cast into bars, 2.54 mm wide, 2.54 mm high and 17.78 mm long, under vibration. The samples were cured in molds at ambient temperature for 24 h, and then cured in sealed plastic bags for another 24 h after demolding. Then the samples were dried at 110°C for 24 h and some of the dried samples were fired for 5 h at 816°C. This firing temperature was chosen because the hydrates formed in the castables are decomposed completely [8] and no significant amount of in-situ spinel is formed from magnesia and alumina at that temperature [10]. Flexural 3-point bend strength test (span of 127 mm) was performed using an Instron, at a crosshead speed of 0.127 mm/min. Compressive strength of the castables was determined using a Tinius Olsen press and a head speed of 0.0127 mm/min. Linear change

TABLE I Formulations (wt%) and properties of castables

Batch		S-0	S-4	M-0	M-4
Aggregate[a]	−4 + 6 mesh	10	10	10	10
	−6 + 14 mesh	25	25	25	25
	−14 + 28 mesh	20	20	20	20
	−28 + 150 mesh	10	10	10	10
SP-25[b]	<75 μm	16	16	16	16
AR-78[c]	<45 μm	4	0	4	0
	<20 μm	5	5	5	5
Alphabond 300[d]		4	4	4	4
P-98[e]	<75 μm	0	4	0	4
RG100[f]	0.5 μm (median)	6	6	6	6
SPMA[g]		0.10	0.10	0.10	0.10
Citric acid		0.02	0.02	0.02	0.02
Linear change (%)	816°C × 5 h	−0.01 ± 0.008	−0.02 ± 0.007	0.10 ± 0.003	0.11 ± 0.005
Modulus of rupture (MPa)	110°C × 24 h	3.66 ± 0.17	5.03 ± 0.13	6.13 ± 0.11	6.42 ± 0.13
	816°C × 5 h	0.61 ± 0.07	0.79 ± 0.08	1.99 ± 0.09	2.27 ± 0.09
Cold crushing strength (MPa)	110°C × 24 h	38.5 ± 1.5	56.6 ± 1.1	71.4 ± 0.6	78.7 ± 1.2
	816°C × 5 h	16.4 ± 0.5	17.5 ± 0.3	33.1 ± 0.4	35.0 ± 0.3
Apparent porosity (%)	110°C × 24 h	16.1 ± 0.3	14.0 ± 0.2	14.6 ± 0.2	13.2 ± 0.1
	816°C × 5 h	18.8 ± 0.3	17.1 ± 0.1	17.4 ± 0.2	16.8 ± 0.1
Increase in apparent porosity (%)	816°C × 5 h	16.8	22.1	19.2	27.3

[a] Baymag-96 (fused magnesite, MgO ≥ 96.0%) in M-0 and M-4, and SP-25 in S-0 and S-4.
[b] SP25: fused magnesium aluminate spinel (MgO 25.0%, Al_2O_3 74.3%).
[c] AR-78: fused magnesium aluminate spinel (MgO 22.0–23.0%, Al_2O_3 76.4–77.6%).
[d] Alphabond 300: hydratable alumina ($Al_2O_3 \geq 88.0\%$, LOI ≤12.0%).
[e] P-98: deadburnt magnesite (MgO 98.0%).
[f] RG100: ultrafine alumina (Al_2O_3 99.8%).
[g] SPMA: sodium polymethacrylate.

was obtained by measuring the length of samples before and after firing. Apparent porosity was measured by immersion method in kerosene under vacuum using the Archimedes' principle. Increase in apparent porosity of the castables after firing was calculated as follows:

$$AP_T^I = \frac{AP_T - AP_D}{AP_D} \times 100(\%)$$

where AP_T^I, Increase in apparent porosity of castables after firing at temperature T (°C); AP_T, Average apparent porosity of castables fired at temperature T (°C); AP_D, Average apparent porosity of castables dried at 110°C. All the physical properties of the castables were determined on three specimens; the average values and standard deviation are reported in Table I.

Pure hydratable alumina Alphabond 300 and a mixture of 16% hydratable alumina Alphabond 300 and 84% deadburnt magnesia P–98 (<75 μm) were hydrated to investigate their morphological features and thermal decomposition behavior. The samples were mixed with distilled water (powder/water weight ratio = 5:4) and hydrated for 48 h at 20°C in sealed polyethylene bags and then for 12 h at 110°C in an autoclave with a pressure of 0.0345 MPa. The hydration in the autoclave step was added to simulate the typical hydration conditions for castables in industrial practice, in particular increased water vapor pressure inside the pores of the castables. All the samples were dried at 110°C for 24 h following the hydration treatment. The hydrated samples were analyzed by thermogravimetric (TG) and differential thermal analysis (DTA) (Setaram, TG-96), at a heating rate of 10°C/min under a flow of helium. The morphology of the hydrated samples was observed by scanning electron microscopy (SEM, S3000N, Hitachi).

3. Results and discussion

The results of sample characterization (strength and porosity) are compiled in Table I, and plotted in Figs 1 and 2. Fig. 1 shows that Castable S-4 had significantly higher flexural (5.03 ± 0.13 MPa) and crushing strength (56.6 ± 1.1 MPa) than Castable S-0 (3.66 ± 0.17 MPa and 38.5 ± 1.5 MPa respectively) after drying at 110°C. The microstructure of the castables was essentially similar in terms of the maximum flaw size (or pore size). Therefore, the difference in strength of the two castables, i.e. increase by 37% in MOR and 47% in CCS, must be ascribed to the difference in their composition: S-4 contained 4% deadburnt magnesite in the matrix, while no magnesite powder was present in the matrix of the latter.

Our previous work [9] showed that a hydrotalcite-like compound $[(Mg_4Al_2)(OH)_{12}(CO_3)(H_2O)_6]$ was formed in the mixtures of hydratable alumina with deadburnt magnesia and fused magnesia respectively, when the mixtures were hydrated at room temperature for 48 h and at 110°C for 12 h. It is accepted that during drying, hydrogen bonding forms between the neighboring surface hydroxyl groups from hydrotalcite hydrate and $Mg(OH)_2$ surrounding the magnesia particles [11]. We therefore hypothesize that hydrotalcite-$Mg(OH)_2$ hydrogen bonding controlled the strength of the castable after drying. From the above discussion, it is inferred that the hydrogen bonding exists between hydrotalcite and $Mg(OH)_2$ on the surface of magnesia powder in S-4. In contrast, the hydrotalcite-like compound was not formed in the castable without

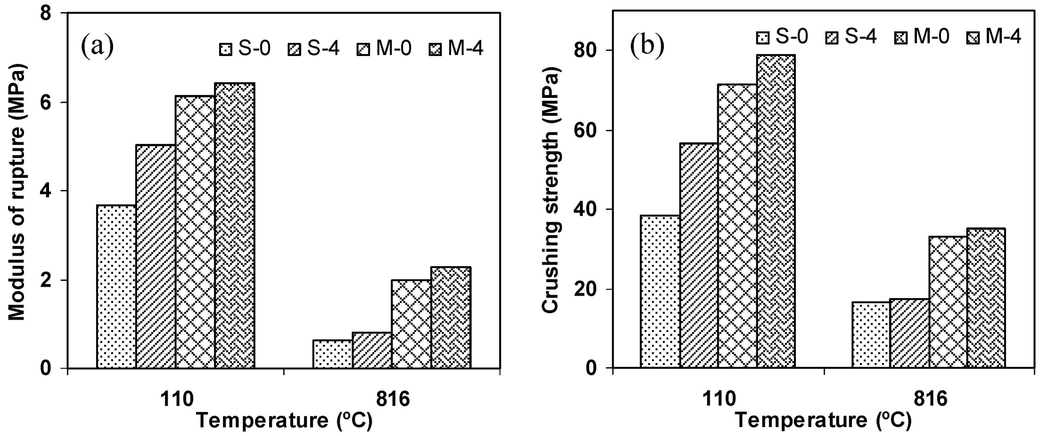

Figure 1 (a) Flexural strength and (b) crushing strength of castables after heat treatment at 110 and 816°C.

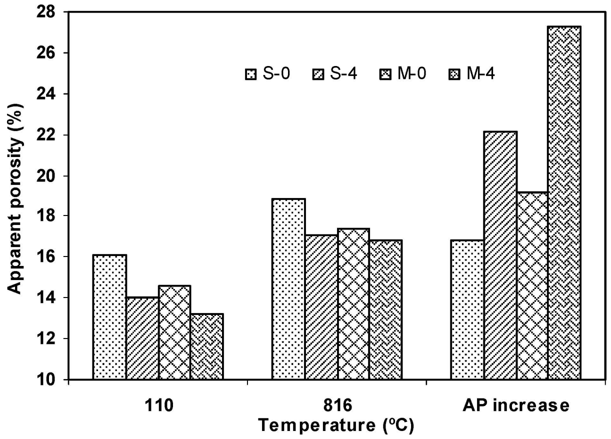

Figure 2 Average values of apparent porosity of castables after heat treatment at 110°C and 816°C and apparent porosity (AP) increase after firing at 816°C over drying at 110°C.

magnesite powder (S-0) as no magnesium hydroxide was available; hence the castable S-0 exhibited lower strength than the castable S-4. These results are in agreement with the finding that addition of 0.25 wt% of co-precipitated magnesium aluminate hydrate ($MgO{\cdot}Al_2O_3{\cdot}16H_2O$) into deadburnt magnesite samples cured at 110°C for 24 h improved their cold crushing strength from 55 to 65 MPa [12, 13]. It has been indicated that high amount of the combined water of magnesium aluminate hydrate ($MgO{\cdot}Al_2O_3{\cdot}16H_2O$) provides a large of number of hydroxyls having active polar groups bonding to $Mg(OH)_2$ on the surface of the MgO particles [12, 13].

As seen from Fig. 1, after drying at 110°C, the castable M-0 had higher flexural strength (6.13 ± 0.11 MPa) and compressive strength (71.4 ± 0.6) than castable S-0 (3.66 ± 0.17 MPa and 38.5 ± 1.5 MPa respectively), the castable M-4 had higher flexural strength (6.42 ± 0.13 MPa) and crushing strength (78.7 ± 1.2 MPa) than the castable S-4 (5.03 ± 0.13 MPa and 56.6 ± 1.1 MPa respectively), and the castable M-0 showed lower flexural strength (6.13 ± 0.11 MPa) and compressive strength (71.4 ± 0.6 MPa) than the castable M-4 (6.42 ± 0.13 MPa and 78.7 ± 1.2 MPa respectively). All the above results support the hypothesis that the hydrogen bonding between hydrotalcite and $Mg(OH)_2$ controls strength of the castables.

It is assumed in the above discussion that the fused magnesium aluminate spinel aggregate (SP-25), fused magnesium aluminate spinel powder (AR-78) and ultrafine alumina power (RG100) are inert to water and therefore hydrogen bonding did not form between the hydrotalcite-like compound and the spinel aggregate, spinel powder or the ultrafine alumina powder in the castables. It was reported [11] that ZrO_2 formed in the mechanochemical reaction $ZrCl_4 + 2MgO \rightarrow ZrO_2 + 2MgCl_2$ had appreciable amounts of hydroxyls on the particle surface when the ZrO_2 powder was washed with water. However, when such ZrO_2 was heat treated at 500°C, the surface reactivity of the ZrO_2 powder towards water was decreased and fewer surface hydroxyls were formed. Similarly, it could be inferred that the magnesium aluminate spinel aggregate and powder produced through fusion and the ultrafine alumina powder (RG100) produced through calcination at temperatures above 1200°C are inert to water and hydroxyls formed on their surface is insignificant.

Fig. 1 exhibits that, after firing at 816°C, the flexural strength and compressive strength of the castables are in the following order: M-4 (2.27 ± 0.09 MPa and 35.0 ± 0.3 MPa respectively) > M-0 (1.99 ± 0.09 MPa and 33.1 ± 0.4 MPa respectively) > S-4 (0.79 ± 0.08 MPa and 17.5 ± 0.3 MPa respectively) > S-0 (0.61 ± 0.07 MPa and 16.4 ± 0.7 MPa respectively). It is expected that the hydroxyls leading to formation of hydrogen bonding lose water during heating and the dehydroxylation reaction of the hydrotalcite hydrate and $Mg(OH)_2$ on the surface of magnesite powder and/or magnesite aggregate results in a polycondensation-type reaction [11–13]:

$$\begin{aligned}&\text{HO-Mg-OH} + \text{HO-(Mg, Al)-OH} + \text{HO-Mg-OH}\\&\quad + \cdots\cdots \rightarrow \text{-O-Mg-O-(Mg, Al)-O-Mg-O-} + nH_2O\end{aligned}$$

It is expected that the above condensation process contributes to the strength development of the castables. The condensation reaction during heating of M-4 occurred between the hydrotalcite hydrate and $Mg(OH)_2$ on the surface of both magnesite aggregate and magnesite powder in the matrices. In comparison, the condensation reaction took place between the hydrotalcite hydrate and $Mg(OH)_2$ on the surface of only magnesite aggregate in M-0, between the hydrotalcite hydrate and $Mg(OH)_2$ on the surface of only magnesite powder in the matrices in S-4. And this condensation did not occur in S-0 because neither hydrotalcite hydrate nor $Mg(OH)_2$ was present in the castable. Consequently, after firing at 816°C, the strength of the castable was higher if the extent of the condensation reaction was higher [11], and vice versa.

As presented in Table I, M-0 and S-0 contained the same matrix (without magnesite powder), but magnesite and spinel aggregates respectively; and S-4 and S-0 included the same spinel aggregate, but different matrixes with and without magnesite powder respectively. It is interesting to note in Fig. 1 that the difference in strength between the castables M-0 and S-0 is larger than that between the castables S-4 and S-0, indicating that the presence of magnesite aggregate contributed to higher strength than the presence of magnesite powder. This is confirmed by comparing the strength difference between M-4 (with magnesite aggregate) and S-4 (with spinel aggregates) with the strength difference between M-0 (without magnesite powder) and S-4 (with magnesite powder). Moreover, the castable M-0 with magnesite aggregate, but without magnesite powder, had higher strength than the castable S-4 with magnesite powder, but without magnesite aggregate. The above results suggest that bonding and condensation reaction between hydrotalcite and $Mg(OH)_2$ on the surfaces of magnesite aggregate contribute to the strength of the castables to a higher extent than those between hydrotalcite and $Mg(OH)_2$ on the surfaces of the magnesite powder.

It is accepted that powders, compared with aggregates, have more significant effect on the strength of castables after drying and firing [8, 14]. The results of this work suggest that the bonding between the binder (hydratable alumina) and the magnesite aggregate contribute significantly to the strength after heat treatment at 110 and 816°C. Accordingly, use of magnesite aggregate in hydratable alumina-bonded castables is beneficial to the strength of the castable after drying and firing at intermediate temperatures.

Fig. 2 shows that, after drying at 110°C, the castable M-4 had the lowest apparent porosity, the castable S-0 the highest apparent porosity and the apparent porosity of the castables S-4 and M-0 was intermediate. The difference in apparent porosity of the castables should be related to the amount of the hydrates formed during curing and drying. As discussed before, $Mg(OH)_2$ was expected to form on the surfaces of both magnesite the aggregate and the magnesite powder in the castable M-4 during curing and drying; in comparison, $Mg(OH)_2$ was formed on the surfaces of the magnesite aggregate in M-0, and on the surfaces of the magnesite powder in S-4. On the other hand, $Mg(OH)_2$ is not expected to form on the spinel aggregate and the matrix in S-0. As a result, during curing and drying, the hydrotalcite compound formed from hydratable alumina and $Mg(OH)_2$ [9] on magnesite aggregate and magnesite powder in M-4, only on magnesite aggregate in M-0, only on magnesite powder in S-4, and neither on the aggregate nor on the matrix in S-0. Therefore, it could be inferred that the apparent porosity of the castables is inversely proportional to the amount of the hydrotalcite compound formed during curing and drying.

One factor influencing the porosity of the castables after drying is the hydration extent of hydratable alumina and magnesia. For example, it was reported that transition alumina was not completely hydrated in 24 h at 15 and 55°C [15], and hydratable alumina Alphabond 300 was not completely hydrated even after 46 h at 20°C and after 25 h at 110°C [9]. However, hydratable alumina in the presence of reactive magnesia was almost completely consumed to form the hydrotalcite compound when hydrated for 24 h at 20°C [8]. The presence of magnesite, either in the form of aggregate or in the form of powder in the castable, is expected to accelerate hydration of the hydratable alumina and generation of the hydrotalcite phase. However, compared with magnesite aggregate, magnesite powder could be more effective in accelerating hydration of hydratable alumina because the magnesite powder has much higher specific surface area than magnesite aggregate. Consequently, the amount of the hydrotalcite compound would be higher in the castable with magnesite powder than in the castable with magnesite aggregate, and a higher amount of the hydrotalcite compound results in lower porosity of the castable after curing and drying. As presented in Table I, the castable S-4 has almost the same particle size composition as the castable M-0, indicating that the particle packing would not lead to variation in apparent porosity between the two castables. However, the castable S-4 had lower apparent porosity than the castable M-0 (see Fig. 2) after drying. This must be attributed to the difference in composition between the two castables: the castable S-4 with 4% magnesite powder would contain a relatively higher amount of the hydrotalcite and consequently exhibited lower apparent porosity; and the castable M-0 with 65% magnesite aggregate (but without magnesite powder) would contain a relatively lower amount of hydrotalcite and accordingly displayed higher apparent porosity.

The apparent porosity variation after heat treatment at 816°C is also show in Fig. 2. Refractory castables are composed of aggregates (the "skeleton") and fine powders which fill in the space between the larger aggregate particles. When hydrates (such as magnesium hydroxide and hydrotalcite-like compound) in the matrix dissociate, voids are produced because the oxides have higher density than their corresponding hydrate parents. Accordingly, as seen in Fig. 2, castables after firing at 816°C have higher apparent porosity than their corresponding samples after drying because hydrates were decomposed during the firing.

Moreover, as shown in Fig. 2, the increase in apparent porosity of M-4 (27.3%) and S-4 (22.1%) is higher than that of M-0 (19.2%) and S-0 (16.8%), respectively, after firing at 816°C. As described before, M-4 and S-4 contained higher amounts of hydrates than M-0 and S-0 respectively after curing and drying. Consequently, castables with higher contents of hydrates are expected to have higher increase in apparent porosity after firing at 816°C because decomposition of the hydrates would leave voids in the materials (sintering is negligible at the temperature).

As shown in [9], bayerite and boehmite were formed from hydratable alumina after hydration at 20°C for 48 h and 110°C for 12 h. It could be inferred that the hydroxyls of bayerite and boehmite also form hydrogen bonding with $Mg(OH)_2$ on the surfaces of magnesite, which could contribute to the strength of the castables after drying. However, hydratable alumina had a granular shape (Fig. 3a) after hydration at 20°C for 48 h and 110°C for 12 h. This morphology was also observed after the hydratable alumina was hydrated at 25°C for 100 h [16]. The granular shape of bayerite and boehmite makes the hydrates less accessible to $Mg(OH)_2$ on the surfaces of magnesite and limited their contribution to the strength of castables.

The morphology of hydrotalcite formed from the mixture of hydratable alumina and magnesite at 20°C for 48 h and 110°C for 12 h is presented in Fig. 3b. Comparison of the morphologies of pure hydratable alumina and the mixture reveals that hydrotalcite formed in castables bonded well with $Mg(OH)_2$ on the surfaces of magnesite. It appears that the morphological features of hydrotalcite promote its bonding with $Mg(OH)_2$ on the surfaces of magnesite.

The increased strength of hydratable alumina-bonded castables in the presence of magnesite is also related to the thermal decomposition behavior of the hydrates in the castables. For pure hydratable alumina after hydration (Fig. 4a), the formed bayerite and boehmite decomposed around 280°C [17] and 426°C [18] respectively. Fig. 4b exhibits the thermal decomposition behavior of the mixture of hydratable alumina and magnesite powder; the endothermic peaks in the temperature range of 150–220°C represented the dissociation of interlayer water in hydrotalcite and those of 300–400°C were due to loss of the (OH) and (CO_3) groups in hydrotalcite [7, 19, 20].

Comparison of the TG results in Figs 4a and b reveals that the weight loss in hydratable alumina sample after hydration occurred in a narrower temperature range and with fewer steps than in the mixture of hydratable alumina and magnesia after hydration. In hydratable alumina-bonded castable after curing and drying, rapid decomposition of bayerite and boehmite could create local "explosion spalling", because significant water vapor pressure from the dissociation of hydrates inside the castables could built up in closed pores during heating [5]. The pressure buildup in the closed pores could lead to local cracks or even explosion of the whole block [2, 21]. We expect that decomposition of hydrotalcite in the lower temperature range (150–220°C) generated a micro-porous microstructure [8], which provided escape channels for the water vapor at the higher temperature range (300–400°C). Consequently, decrease

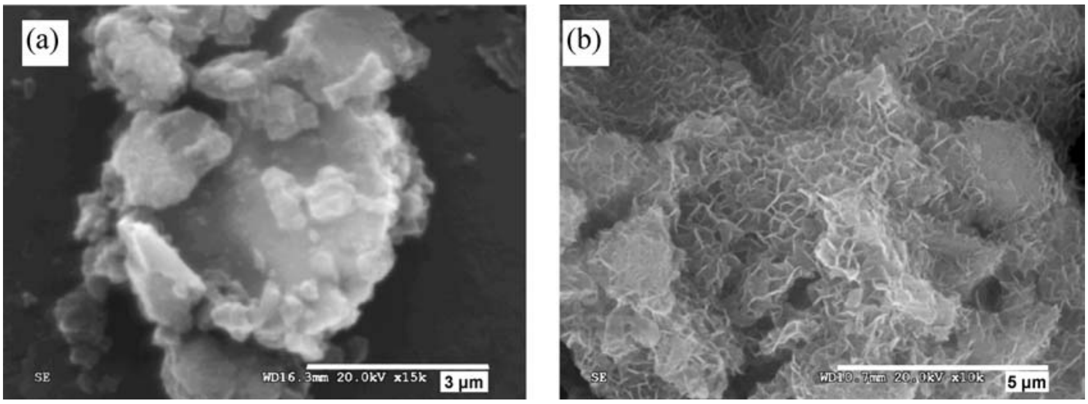

Figure 3 SEM images of (a) pure hydratable alumina and (b) the mixture of hydratable alumina and magnesite after hydration at 20°C for 48 h and 110°C for 12 h.

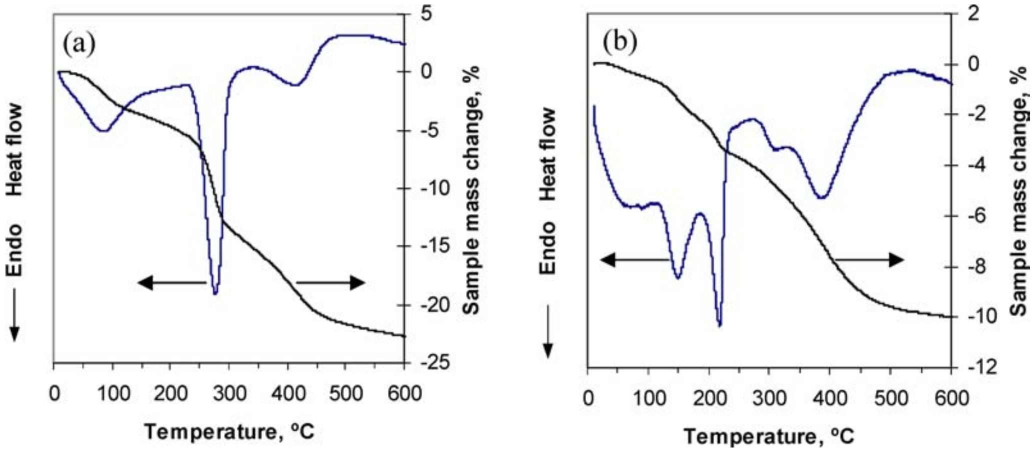

Figure 4 TG-DTA curves for the thermal decomposition of (a) hydratable alumina and (b) the mixture of 16% hydratable alumina and 84% magnesia powder after hydration at 20°C for 48 h and 110°C for 12 h.

in the local vapor pressure mitigated the local spalling, and therefore also prevented the strength decrease of the castables after heat treatment at the intermediate temperatures.

Generally, hydration of MgO is detrimental to the volume stability and, accordingly, the strength of the castables because formation of brucite from MgO is accompanied by a large volume expansion ($\sim$120%). However, as reported in our previous work [9], only hydrotalcite was identified in the mixtures of hydratable alumina and deadburnt/fused magnesite powder after hydration at 48 h at 20°C and then for 12 h at 110°C, and brucite was not detected in the hydrated products, suggesting that the hydrated MgO in the castables existed in hydrotalcite, rather than brucite. The volume change accompanying hydrotalcite formation from hydratable alumina and magnesia during hydration is not clear yet. However, no expansion was observed during curing and drying of the castables, indicating the castables did not incur harmful volume increase due to the formation of hydrotalcite.

4. Conclusions

1. The presence of magnesite aggregate and powder in hydratable alumina-bonded castables improved the strength of the castables after drying at 110°C. It is hypothesized that the principal contribution to strength increase is development of the hydrogen bonding between hydrotalcite and $Mg(OH)_2$ on the surface of magnesite particles.

2. The polycondensation accompanying dehydroxylation of hydrotalcite and $Mg(OH)_2$ at 816°C contributed to the strength of hydratable alumina-bonded castables containing magnesite.

3. The morphological features of hydrotalcite facilitated bonding formation of hydrotalcite with $Mg(OH)_2$ on the surfaces of magnesite and contributed the strength of the magnesite-containing castables after drying.

4. It is proposed that decomposition of hydrotalcite at the lower temperatures (150–220°C) provides escape channels for the vapor released at higher temperatures (300–400°C) and, accordingly alleviate local explosion spalling during heating-up and benefit the strength of castables after firing at intermediate temperatures.

Acknowledgments

The authors acknowledge NSERC for financial support. We are grateful to Dr. George Oprea for invaluable input and comments. We would like to thank Almatis, Baymag Inc., CE Minerals and Martin Marietta Materials for supplying raw materials.

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Received 22 November 2004
and accepted 28 February 2005