Research Article

Yang Zhang, Lingling Zhu*, Liugang Chen, Luoqiang Liu, and Guotian Ye

Influence of Magnesia on Demoulding Strength of Colloidal Silica-Bonded Castables

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Abstract: The change in demoulding strength of colloidal silica-bonded castables with and without magnesia is investigated with emphasis on the relationship between the demoulding strength and chemical bond changes. It was confirmed that the demoulding strength was raised with the presence of magnesia in colloidal silica-bonded castables because of the increased chemical bonding between the sol particles. The X-ray photoelectron spectroscopy (XPS) and the Fourier transformation infrared spectroscopy (FTIR) results indicate the formation of new Si–O–Mg chemical bond from the decreased O 1s and Si 2p binding energy, and the appearance of weak vibration peaks at 668 and 419 cm^{-1} in the spectrum of colloidal silica with the addition of MgO after curing at 30°C for 24 hours. The reaction between colloidal silica and magnesia could promote the formation of –Si–O–Mg–O–Si– bonds, which is the primary reason for the demoulding strength improvement.

Keywords: chemical bond change; demoulding strength; colloidal silica-bonded castables; magnesia

1 Introduction

Colloidal silica-bonded castables have advantages over low cement or hydratable alumina-bonded castables in terms of drying performance, sintering properties, low

and intermediate temperature strength and volume stability [1–7]. However, the colloidal silica-bonded castables have not been as widely used as calcium aluminate cement (CAC)-bonded castables because the green mechanical strength of colloidal silica-bonded castables is very low compared to the hydraulic bonded-ones [4]. The strength of the former castables develops sluggishly during curing because the slow condensation reaction of Si–OH between SiO_2 particles ($\text{Si–OH} + \text{HO–Si} = \text{Si–O–Si} + \text{H}_2\text{O}$) lead to very low green strength of the green strength of the castables [2, 4, 8, 10].

In recent years, increasing researches have been done to enhance the green strength of colloidal silica-bonded castables. For example, it was reported that the demoulding strength of colloidal silica-bonded high alumina castables was increased with the reducing curing humidity [2, 9]. In particular, various additives have been introduced into colloidal silica-bonded castables to promote the demoulding strength [5, 6, 8, 10, 11]. CAC and magnesium oxide (MgO) are commonly used as gelling agents to improve the demoulding strength of colloidal silica-bonded castables [5, 6]. However, the presence of CaO from CAC can be deleterious to the high-temperature properties of the alumina-based castables with colloidal silica, because CaO can result in the formation of low-melting temperature phases, such as gehlenite ($2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, melting point (mp) = 1590 °C) or anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, mp = 1550 °C) [12, 13]. It has been proposed that MgO addition is favourable to raise the green strength of colloidal silica-bonded castables because Si–O–Mg bonds will form from the released Mg^{2+} ions and the broken Si–O bonds on the surface of silica particles during the placement and curing processes [7, 14]. However, the cause of the increased demoulding strength through the viewpoint of the new bond formation (–Si–O–Mg–O–Si–) has not been substantiated. This work examines the effect of magnesia on demoulding strength of colloidal silica-bonded castables and on the chemical bond formation of silica particles using XPS and FTIR, with the aim of establishing the relationship between demoulding strength and the change in chemical bonds between SiO_2 particles of colloidal silica caused by the presence of magnesia.

***Corresponding Author: Lingling Zhu:** Henan Key Laboratory of High Temperature Functional Ceramics, School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001; Email: llzhu@zzu.edu.cn; Fax: +86-371-67781590

Yang Zhang, Luoqiang Liu, Guotian Ye: Henan Key Laboratory of High Temperature Functional Ceramics, School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001

Liugang Chen: Henan Key Laboratory of High Temperature Functional Ceramics, School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001; Department of Materials Engineering, KU Leuven, Kasteelpark Arenberg 44, Leuven, 3001, Belgium

Table 1: Formulation of colloidal silica-bonded castables with and without magnesia.

Raw materials		CS0 (wt.%)	CS1 (wt.%)	CS3 (wt.%)	CS5 (wt.%)
Tabular corundum	6-3 mm	20	20	20	20
	3-1 mm	30	30	30	30
	1-0 mm	20	20	20	20
	≤ 0.044 mm	24	24	24	24
Reactive alumina	CL370	6	6	6	6
Dispersant	Sodium hexametaphosphate	0.1	0.1	0.1	0.1
Binder	Colloidal silica	6.6	6.6	6.6	6.6
Gelling agent	Magnesia	-	0.1	0.3	0.5

2 Experimental

The colloidal silica-bonded castables were composed of different-sized aggregates of tabular corundum (Almatix), reactive alumina (CL370, Almatix) and colloidal silica ($\text{SiO}_2 \geq 30$ wt.%, pH = 8.9, Yuda chemical Co.) (Table 1). Sodium tripolyphosphate was used as dispersant for the castable. In order to investigate the effect of magnesia on the demoulding strength of colloidal silica-bonded castables, different amounts (0, 0.1, 0.3 and 0.5 wt.%) of fused magnesia ($\text{MgO} \geq 97.19$ wt.%, ≤ 0.074 mm) were added as gelling agent.

The castables were firstly dry-mixed for 1 minute, and then followed by 2 minutes wet mixing with colloidal silica in a laboratory mixer. After that, the mixtures were cast in 40 mm $\times$ 40 mm $\times$ 160 mm molds under vibration. After curing in the molds for 24 hours at 30°C, the samples were de-molded, and the cold crushing strength (CCS) and cold modulus of rupture (CMOR) of the castable samples were tested.

In order to study the influence of magnesia on the chemical bond changes between colloidal silica, the samples of colloidal silica with and without magnesia were prepared. Both colloidal silica and magnesia were separately kept at 30°C for 24 hours in advance, and then colloidal silica and the mixture of colloidal silica with of 0.5 wt.% magnesia were agitated with a magnetic stirrer for 2 minutes. After curing at 30°C for 24 hours, the as-prepared samples were rapidly frozen at -50°C for 1.5 hours, and then dried in a vacuum box under a pressure of 60 Pa at 20°C for 24 hours to remove the water. The microstructure differences of the samples were observed by FESEM (JSM-7500F, JEOL, Tokyo, Japan), and the chemical bonding change was detected by XPS (Amicus, Kratos, Manchester, UK) through the shift of O 1s and Si 2p binding energy, and FTIR (Nicolet iS 50, Thermo Fisher, USA) through the presence of Si–O–Mg vibration and shift of Si–O–Si vi-

bration. Furthermore, the FTIR analysis has been carried out over the frequency range of 4000–400 cm^{-1} .

3 Results and Discussion

Figure 1 shows the demoulding strength of colloidal silica-bonded castables with and without magnesia after curing at 30°C for 24 hours. As shown in Figure 1, both CMOR and CCS of the colloidal silica-bonded castables are improved by the increase of magnesia addition. For example, the CMOR of the castable with 0.5 wt.% magnesia (CS5, 1.7 MPa) is significantly higher in comparison with that of the castable without magnesia (CS0, 0.8 MPa). Similarly, the CCS of the castable with magnesia (CS5, 10.2 MPa) is considerably higher than that of the castable without magnesia (CS0, 6.1 MPa). The above results demonstrate that the addition of magnesia favors the demoulding strength of the colloidal silica-bonded castables.

Figure 2 presents the microstructure of colloidal silica with and without magnesia after curing for 24 hours at 30°C. The morphology of the silica sol significantly changed with the addition of 0.5 wt.% magnesia after curing for 24 hours at 30°C. It is seen that pure colloidal silica is composed of mono-dispersed SiO_2 particles with the size of 20 nm (Figure 2a); while SiO_2 colloidal particles are partially agglomerated together with the addition of 0.5 wt.% magnesia (Figure 2b). The above results indicate that the addition of magnesia promotes the adhesion of SiO_2 colloidal particles, which may help accelerate the condensation of colloidal silica.

Referring to the promoted adhesion of SiO_2 colloidal particles (as shown in Figure 2b) in colloidal silica with addition of magnesia after curing at 30°C for 24 hours, the influence of magnesia on the condensation of colloidal silica was examined by XPS to detect if any new chemical bonds could be formed in colloidal silica with MgO. According to

Figure 1: CMOR and CCS of colloidal silica-bonded castables with and without magnesia cured at 30 °C for 24 hours.

the XPS spectra of colloidal silica with and without magnesia shown in Figure 3, characteristic peaks corresponding to Mg 1s (1302 eV), Mg 2p (74 eV) and Mg KLL auger are present in the XPS spectrum of colloidal silica with the addition of 0.5 wt.% magnesia after curing at 30 °C for 24 hours. In order to figure out the O 1s and Si 2p binding energy (BE) changes in colloidal silica with the addition of 0.5 wt.% magnesia, O 1s and Si 2p XPS spectra for colloidal silica with and without magnesia, and the peak fitting of O 1s spectrum for colloidal silica with 0.5 wt.% MgO are analyzed.

As shown in Figure 4 (a) and (b), the O 1s BE (532.60 eV) and Si 2p BE (103.20 eV) in colloidal silica with 0.5 wt.% magnesia are lower than the O 1s BE (532.85 eV) and Si 2p BE (103.65 eV) in colloidal silica, indicating the formation of Si–O–Mg bonds in colloidal silica with magnesia. Because Mg is less electronegative than H, and consequently, the substitution of H (2.1) in Si–OH by Mg (1.2) would decrease the O1s BE in Si–O–Mg bonds, due to the increase of

Figure 2: SEM photograph of colloidal silica without (a) and with MgO (b) after curing for 24 hours at 30 °C.

O outer electron density [15–17]. And then the outer electron density of Si would increase [15, 16] because of the covalence of Si–O bond, resulting in the decrease of Si 2p BE in Si–O–Mg bonds. These results are consistent with the result shown in Figure 4(c). As new chemical bond of Si–O–Mg forms through the condensation reaction between colloidal silica (with Si–OH on its surface) and magnesia after curing at 30 °C for 24 hours, the demoulding strength of colloidal silica-bonded refractory castables increases with the addition of magnesia (shown in Figure 1)

The change in chemical bond of colloidal silica with and without magnesia was further investigated by FTIR. The FTIR spectra of colloidal silica with and without magnesia after curing at 30 °C for 24 hours are shown in Figure 5. It can be seen in the figure that the most intense peak at about 1115 cm^{-1} is assigned to the asymmetric Si–O–Si stretching vibration [18]; peaks at 1219 and 1068 cm^{-1} are attributed to the Si–O stretching vibration [18, 19], a peak at 799 cm^{-1} results from the symmetric Si–O stretching vibration, and peaks at 557 and 475 cm^{-1} are corresponding to the internal deformation of Si–O [18, 20–22], while the

Figure 3: XPS spectra of colloidal silica with and without MgO after curing for 24 hours at 30 °C (a), and (b) is a local amplification spectrum of (a).

Si–O stretch of Si–OH groups at the silica surface can be seen at 970 cm^{-1} [23]. As the the magnesia addition increased from 0.1 wt.% to 0.5 wt.%, the spontaneous condensation of silanol groups has been enhanced through the incorporation of magnesia, because the intensity of the peak at 970 cm^{-1} (assigned to Si–OH) gradually decreases and eventually disappears in the FTIR spectrum of colloidal silica with 0.5 wt.% magnesia (CS5). Similar trend can also be found in terms of peaks at 799 and 557 cm^{-1} , which become weaker and even vanish as the magnesia addition increased from 0 to 0.5 wt.%, revealing that Si–O bonds have been partially broken by the introduction of magnesia [23].

Furthermore, the red-shift of characteristic Si–O vibration from 475 cm^{-1} to 467 cm^{-1} suggests interaction between the MgO and silica [20, 24]. Because the binding force of Mg–O is weaker than that of Si–O and the Mg–O bond is longer than the Si–O bond [25, 26], the partial replacement of Si^{4+} in Si–O–Si linkages by Mg^{2+} would lower the frequency around 475 cm^{-1} . Therefore, the decreased wavenumber of 467 cm^{-1} (as shown in Figure 5b)

Figure 4: O 1s (a) and Si 2p (b) XPS spectra for colloidal silica with and without magnesia, and the peak fitting of O 1s spectrum for colloidal silica with 0.5 wt.% MgO (c).

in the colloidal silica with 0.5 wt.% magnesia is possibly caused by the incorporation of Mg^{2+} into the Si–O–Si linkages.

In particular, new peaks at 668 and 419 cm^{-1} , which are attributed to the formation of Si–O–Mg bonds [27–29] in colloidal silica with 0.3 wt.% (CS3) and 0.5 wt.%

Figure 5: FTIR spectra of colloidal silica without and with 0.1–0.5 wt.% MgO after curing for 24 hours at 30°C (a), and the magnification of FTIR spectra in the 520–400 cm^{-1} region (b).

(CS5) magnesia, can be observed in Figure 5(a). This phenomenon confirms that more amounts of Si–O–Mg bonds appear with the increase of magnesia addition. As described above, the enhanced condensation of colloidal silica with magnesia and the formation of Si–O–Mg bonds would provide higher demoulding strength of colloidal silica-bonded castables with magnesia after curing at 30°C for 24 hours.

4 Conclusions

The addition of magnesia enhanced the demoulding strength of colloidal silica-bonded castables with magnesia after curing at 30°C for 24 hours, due to the formation of Si–O–Mg bonds caused by the condensation reaction of

colloidal silica with magnesia during the curing process. The formation of Si–O–Mg bonds in the mixture was verified by the decreased O 1s BE (532.60 eV) and Si 2p BE (103.20 eV) in Si–O–Mg in colloidal silica with 0.5 wt.% magnesia, compared with O 1s BE (532.85 eV) and Si 2p BE (103.65 eV) in Si–OH after curing. Moreover, the formation of Si–O–Mg bonds in the mixture (CS5) was confirmed by new vibration peaks at 668 and 419 cm^{-1} corresponding to Si–O–Mg bonds after curing at 30°C for 24 hours.

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