New Journal of Glass and Ceramics, 2015, 5, 1-7
Published Online January 2015 in SciRes. http://www.scirp.org/journal/njgc
http://dx.doi.org/10.4236/njgc.2015.51001

Effects of SnO_2 Addition on the Properties of Alumina-Magnesia Refractory Castables

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Received 26 October 2014; revised 16 November 2014; accepted 9 December 2014

Abstract

Alumina-magnesia refractory castables have been widely used in the wall and bottom impact pad of steel ladles. The properties of alumina-magnesia refractory castables with SnO_2 additive in 0 - 5 wt% range were investigated. The phase composition, microstructure, physical and mechanical properties of these refractories were studied. The results showed that the addition of SnO_2 could have a great influence on the properties of alumina-magnesia refractory castables. The expansion, apparent porosity and strength of refractories with SnO_2 were all more prominent than those of reference samples, which were attributed to the formation of CA_6 and enhanced bonding. Meanwhile SnO_2 could react with spinel and CA_6 to form solid solution.

Keywords

Castables, SnO_2, Spinel, Calcium Hexaaluminate

1. Introduction

Alumina-magnesia refractory castables are usually bonded with calcium aluminate cement (CAC) because of its notable advantages including suitable workability and mechanical strength [1]. At high temperatures the free magnesia in the castables' matrix could react with alumina to form spinel, meanwhile calcium dialuminate (CA_2) close to 1100˚C and calcium hexaluminate (CA_6) over 1400˚C formed by the reaction between CAC and alumina in turn [2] [3]. The formation of spinel, CA_2 and CA_6 is associated with the volume expansion of 8%, 13.6% and 3.01% respectively [4] [5]. Therefore, the overall expansion behavior of alumina-magnesia cement-bonded refractory castables depends on the generation of spinel and calcium aluminates. Thermal expansion behavior is one of the most important aspects for a proper refractory lining design and construction. For instance, a con-

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How to cite this paper: Yuan, W.J., Zhu, Q.Y., Deng, C.J. and Zhu, H.X. (2015) Effects of SnO_2 Addition on the Properties of Alumina-Magnesia Refractory Castables. *New Journal of Glass and Ceramics*, **5**, 1-7.
http://dx.doi.org/10.4236/njgc.2015.51001

trolled expansion of the refractory applied at the hot side of the ladle furnace walls can help to close joints and cracks. However, an excessive expansion level can lead to spalling or even damage to the ladle. Due to the volume expansion and ability for stress relaxation attained by composition designing and expansion controlling, alumina-magnesia refractory castables are used in the steelmaking process such as the production of side wall and bottom impact pads of steel ladles [6] [7].

An alternative to master the expansion behavior of alumina-magnesia castables consists in the use of additives (mineralizer/densifier compounds) to attain enhanced properties, including mechanical strength and corrosion resistance under the steelmaking conditions. Researchers tried to use various additives including inorganic salts (such as AlF_3, MgF_2 and $MgCl_2$), oxides (B_2O_3, V_2O_5 and Cr_2O_3), magnesium borate and borosilicate for accelerating spinel-forming reactions [8]-[10]. Moreover, SnO_2 was used as a spinel forming agent in fired magnesia bricks and unfired materials [11].

Based on the above works and considering the absence of comparative studies on different additive amounts of SnO_2, the objective of this work is to evaluate the effects of different SnO_2 amounts (0 - 5 wt%) on the properties of alumina-magnesia refractory castables.

2. Experimental Procedure

Alumina-magnesia castables were prepared according to the Alfred packing model (q = 0.26). The compositions (**Table 1**) comprised tabular aluminas (T60, Almatis) as aggregates, reactive alumina (CL370, Almatis), calcined magnesia (95 wt%) as the main matrix components and calcium aluminate cement as the binder source (Secar 71, Kerneos). Additionally, silica fume (951U, Elkem) was added to all samples. SnO_2 was used as the mineraizing additive. The dispersion was carried out by using 0.2 wt% of an electrosteric dispersant (BASF, Germany). The added water content for the vibratable casting was 4.1 wt%.

After casting, all the prepared samples were cured at 25˚C for 24 h in a climatic chamber with relative humidity of 100%, and dried at 110˚C for 24 h. The expansion curve of the bar sample (40 mm × 40 mm × 160 mm) was measured by heated up to 1450˚C at the rate of 5˚C/min using a self-made dilatometer. The apparent porosity of the castables after drying, thermal expansion measurement and firing at 1450˚C for 5 h was measured using the Archimedes method. Cold modulus of rupture (CMOR) for bar sample (25 mm × 25 mm × 150 mm) after firing at 1450˚C for 5 h was measured by three-point bending test. The phase composition of the castables was analyzed by X-ray diffraction with CuKα radiation (XRD, Philips, X'pert Pro MPD, Netherlands). XRD results were quantitatively evaluated by the RIR method (X'pert Highscore 3.0 Plus, PANalytical, Netherlands). The microstructure and chemical composition of the different samples was observed and measured by scanning electron microscopy (SEM, JEOL JSM-6610, Japan) and energy dispersive spectrometer (EDS, Bruker QUANTAX200-30, Germany).

3. Results and Discussion

Figure 1 shows the expansion curves, the expansion value at 1450˚C (E_{1450}) and permanent linear change (PLC) of alumina-magnesia castables containing different SnO_2 amounts. The expansion curve with the temperature increasing could be divided into two stages: (a) the first stage corresponded to the reversible thermal expansion from raw materials mixes; (b) then the changes in the expansion behavior were attributed to the *in situ* spinel

Table 1. Composition of the alumina-magnesia castables.

Raw materials	Content (wt%)				
	A	AM	Sn1	Sn3	Sn5
Tabular alumina (d ≤ 6 mm)	61	61	63	63	61
Tabular alumina (d ≤ 200 μm)	25	19	16	14	14
Reactive alumina (CL370)	7	7	7	7	7
Magnesia (200 mesh)	-	6	6	6	6
Calcium aluminate cement (Secar 71)	6	6	6	6	6
Silica fume (951U)	1	1	1	1	1
SnO_2	-	-	1	3	5

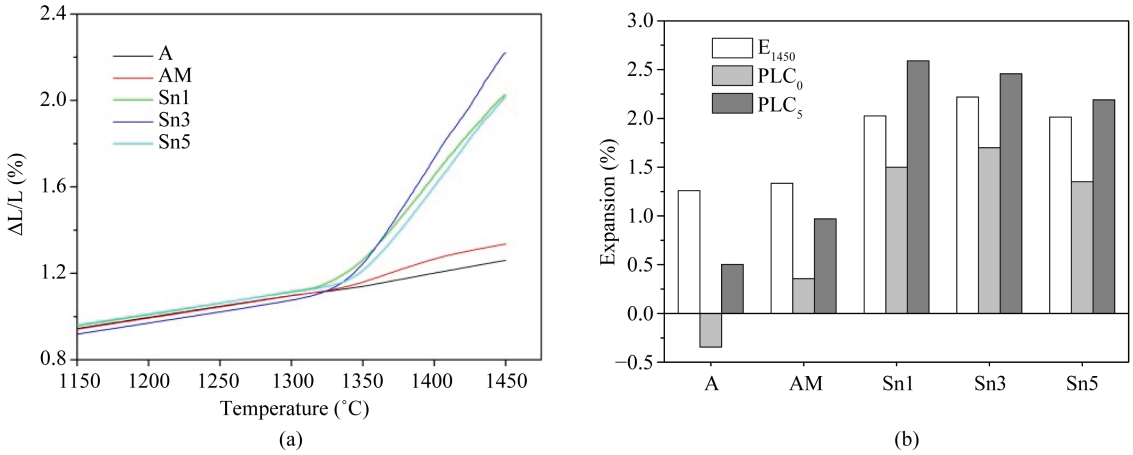

Figure 1. Expansion curves (a), the expansion value at 1450˚C (E_{1450}) and permanent linear change (PLC) (b) of alumina-magnesia castables containing SnO_2.

and calcium hexaluminate formation as a result of the reaction between magnesia, calcia and alumina; at the same time the shrinkage behavior was derived from the sintering of the castable samples. According to **Figure 1(a)**, the expansion of all samples presented a linear increase of the expansion values as a function of the temperature (<1300˚C). The expansion of samples A and AM deviated from the baseline to a small extent at higher temperature (>1300˚C). But the thermal expansion curves of the samples containing SnO_2 suddenly rose up to 1450˚C. Normally, permanent linear change (PLC) of refractories was measured after the reheating or cooling, which was an indication of the volume stability of the product. Compared with expansions for different conditions (**Figure 1(b)**), PLC_0 (without soaking) for all samples was less than the expansion value at 1450˚C (E_{1450}) as the result of the shrinkage during the cooling stage. Even the reference composition without magnesia presented PLC_0 with negative value. The accelerated reactions with SnO_2 addition were dominant, which led to the larger expansion (PLC_5) after the soaking stage.

The apparent porosity results of samples (after firing at 110˚C × 24 h, 1450˚C × 0 h and 1450˚C × 5 h) are shown in **Figure 2**. The volume expansion accompanying spinel and CA_6 formation could lead to cracks in the castables, resulting in increased porosity of castables. It was noticed that the variation for the apparent porosity was not absolutely in accordance with the expansion level at different conditions, which was related to the phase composition and microstructure.

The XRD patterns of alumina-magnesia castables after firing at 1450˚C for 0 h and 5 h are shown in **Figure 3(a)** and **Figure 3(c)**. The major phases included corundum, spinel and CA_6, and the minor phases included gehlenite ($Ca_2Al_2SiO_7$, C_2AS), CA_2, unreacted SnO_2 and SiO_2. The bar charts (**Figure 3(b)** and **Figure 3(d)**) present the calculated phase compositions based on RIR method. For the samples after firing at 1450˚C for 0 h, CA_2 only generated in the reference samples, and CA_6 formed in samples containing SnO_2, which indicated that SnO_2 acted as a CA_6 forming agent in the initial stage. According to the phase diagram of CaO-Na_2O-SiO_2-Al_2O_3 quaternary system [12], the melting point of gehlenite was less than 1200˚C, so that gehlenite could enhance the reaction and sintering at high temperatures. Therefore, the less gehlenite and more spinel and CA_6 formation resulted in the higher expansion level for the samples containing SnO_2. Gehlenite and CA_2 were not found in the samples after firing at 1450˚C for 5 h. The addition of 3 wt% of SnO_2 could promote the spinel formation.

The addition of SnO_2 had an influence on not only the spinel and CA_6 formation but also their morphology. **Figure 4** and **Figure 5** show the microstructure of alumina-magnesia castables containing SnO_2 after firing at 1450˚C for 0 h and 5 h respectively. In the samples after continuous heating without soaking, CA_2 presented granular shape in the reference composition AM (**Figure 4(a)**), and CA_6 platelets formed in the samples containing SnO_2 (**Figures 4(b)-(d)**). The grain size of the spinel decreased with the addition of SnO_2 increasing. After soaked for 5 h, CA_6 platelets tended to interlock with each other, and the different phases were jointed tightly (**Figure 5**). The tin element was detected in CA_6 region (EDS spectrums not shown), which indicated SnO_2 dissolved into CA_6. It can be seen that there were hexagonal (Mg, Sn)Al_2O_4 solid solution and spinel grains with octahedron shape in the samples with 5 wt% SnO_2. This mechanism would be investigated in the future.

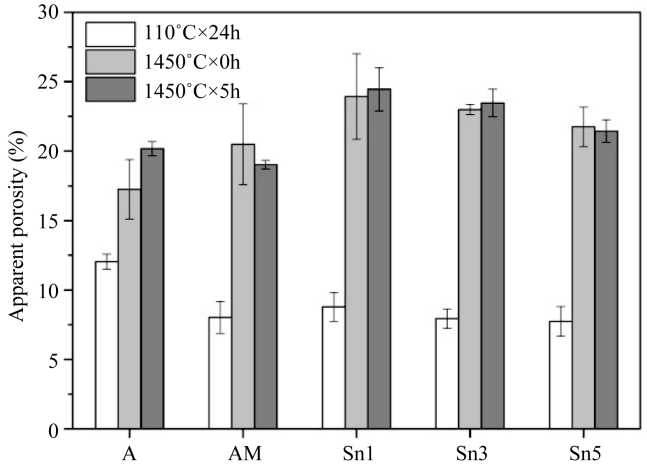

Figure 2. Apparent porosity of the alumina-magnesia refractory castables containing SnO_2 under different conditions.

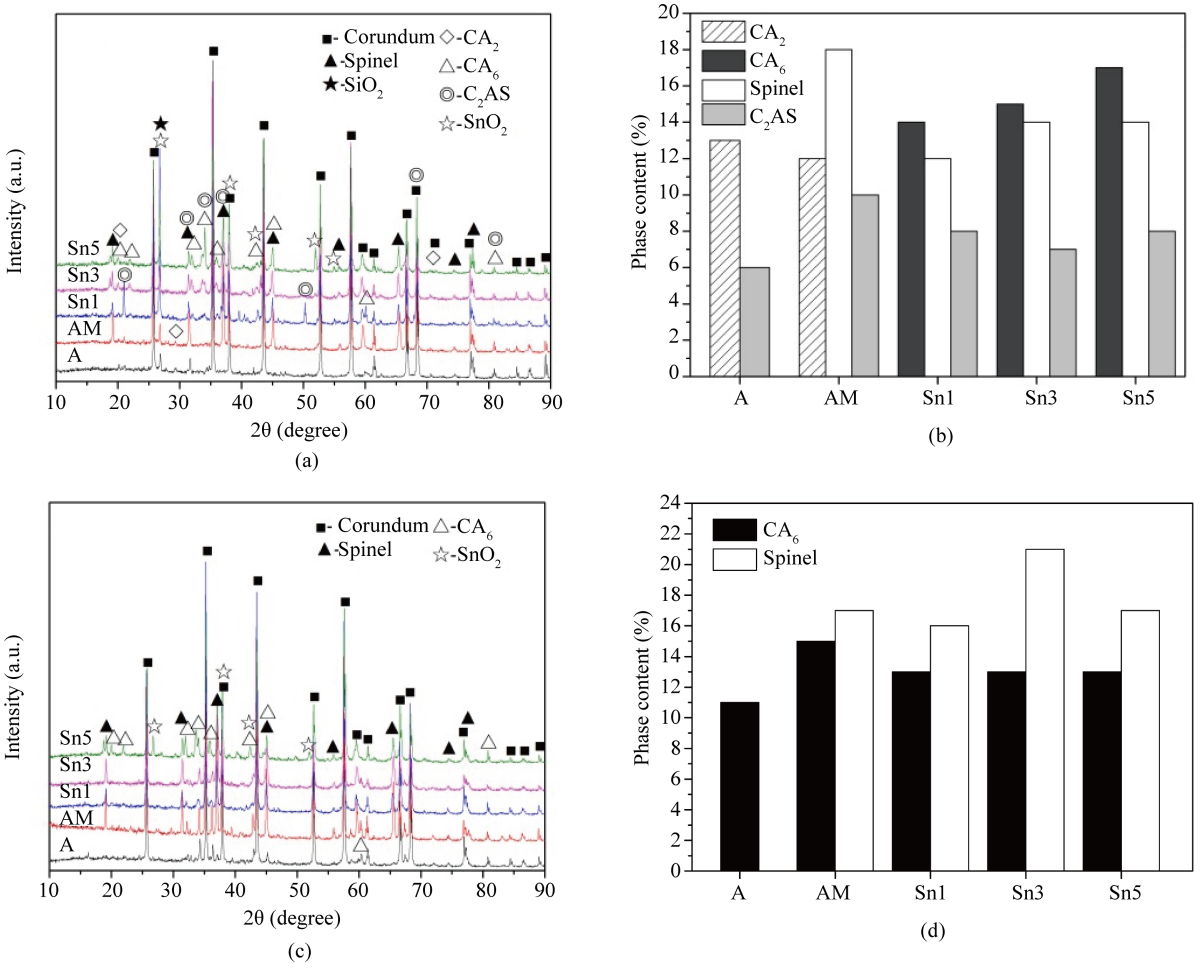

Figure 3. XRD patterns and major phase composition of alumina-magnesia castables containing SnO_2: (a) (b) 1450˚C × 0 h and (c) (d) 1450˚C × 5 h.

Cold modulus of rupture values for alumina-magnesia castables after firing at 1450˚C × 5 h are shown in **Figure 6**. CMOR for sample A was more than that for sample AM due to its lower expansion. In contrast, the

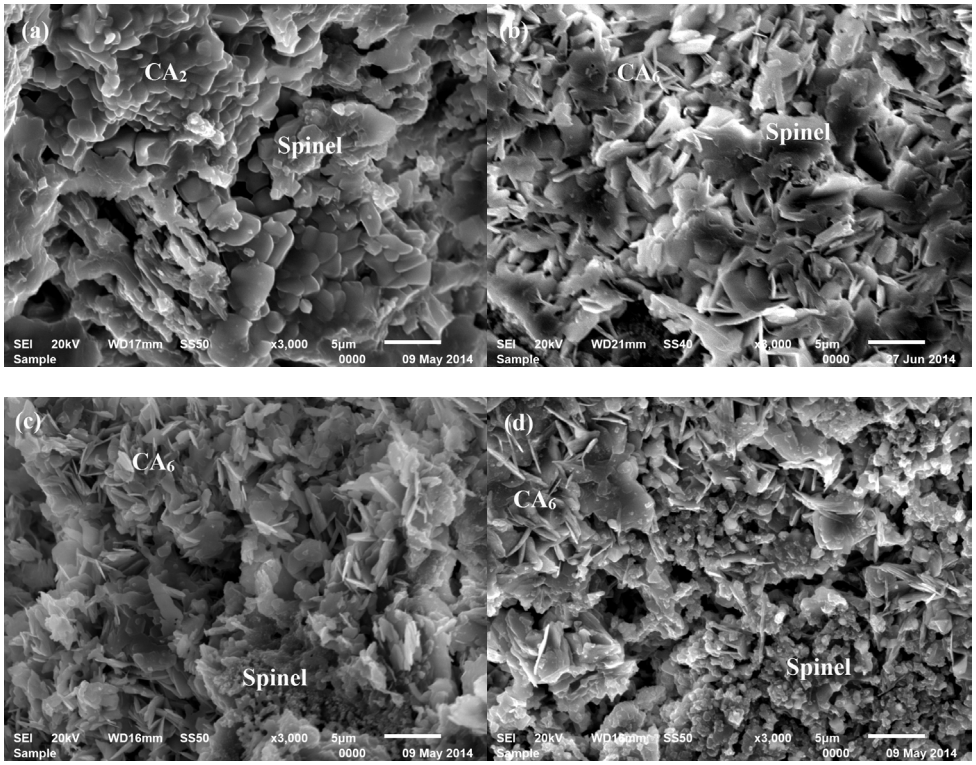

Figure 4. SEM images of alumina-magnesia castables containing SnO_2 after firing at 1450˚C × 0 h: (a) AM, (b) Sn1, (c) Sn3 and (d) Sn5.

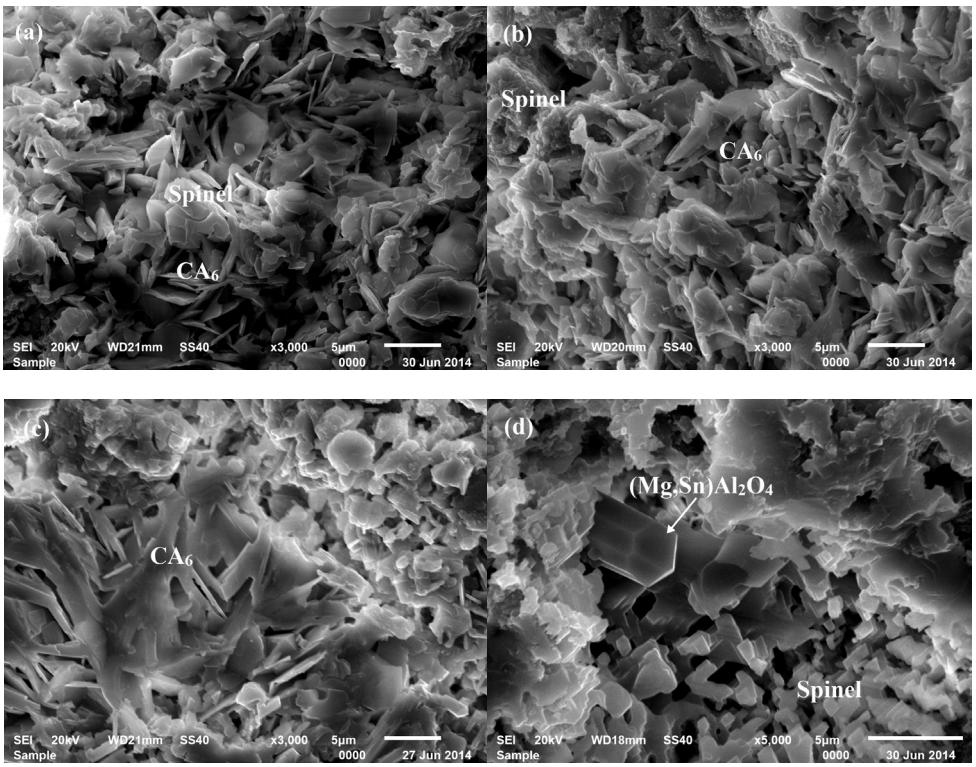

Figure 5. SEM images of alumina-magnesia castables containing SnO_2 after firing at 1450˚C × 5 h: (a) Sn1, (b) Sn3 and (c) (d) Sn5.

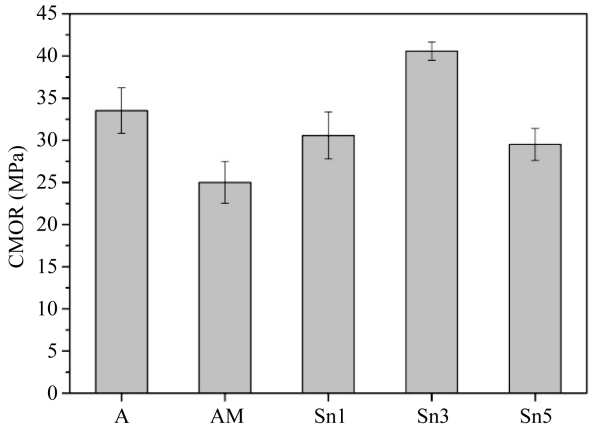

Figure 6. CMOR of alumina-magnesia refractory castables after firing at 1450˚C × 5 h.

higher porosity of the samples containing SnO_2 did not lead to lower CMOR due to the influence of SnO_2 addition, where CMOR for sample Sn3 with higher spinel content reached a maximum value. It can be deduced that the phase composition and bonding between different phases were essential factors for the strength.

4. Conclusion

Alumina-magnesia refractory castables were prepared by the interaction between tabular alumina, reactive alumina and calcined magnesia with calcium aluminate cement. SnO_2 as an additive could accelerate the formation of spinel and CA_6 in this system. The bonding between different phases was enhanced by the formation of spinel and CA_6 solid solution containing SnO_2. The addition of SnO_2 resulted in higher expansion and apparent porosity as well as cold modulus of rupture. The correct regulation of additives was a key issue to attain castables with desirable properties according to their application.

Acknowledgements

The authors are grateful to National Key Basic Research Program of China (973) (No. 2012CB722702), Almatis (Qingdao), Kerneos (Tianjin) and Elkem (Shanghai) Co. Ltd. for supporting this work.

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