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EFFECTS OF MnO ADDITIONS ON THE PROPERTIES OF ALUMINA-MAGNESIA REFRACTORY CASTABLES

VPLIV DODATKA MnO NA LASTNOSTI OGNJEVARNIH MATERIALOV NA OSNOVI Al_2O_3-MgO

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The long life and high efficiency of equipment in the steelmaking industry lead to tougher requirements for the properties of calcium aluminate cement-bonded alumina-magnesia refractory castables. Normally, the properties of castables are modified by adding mineralizing compounds, which are normally used to decrease the reaction temperature and accelerate the densification of castables. In this work, the influence of MnO additions on the properties of calcium aluminate, cement-bonded, alumina-magnesia castables was investigated. The phase composition of the castables with MnO additions after calcining at 1250–1450 °C was identified by X-ray diffraction, and the microstructures of the castables were characterized with a scanning electron microscope. The results showed that MnO accelerated the formation of calcium hexaluminate (CA_6) and spinel ($MgAl_2O_4$). Due to the higher sintering activity of the spinel and the uniform microstructure, the cold modulus of rupture (i.e., the bending strength) of the castables with MnO additions improved from 25 MPa to 34 MPa after being calcined at 1450 °C for 5 h.

Keywords: castables, properties, spinels, MnO

Od opreme (peči) v jeklarski industriji se zahteva visoka učinkovitost in dolga življenjska doba obratovanja, kar postavlja visoke zahteve tudi glede lastnosti s kalcij-aluminatnim cementom vezanih ognjevarnih materialov na osnovi aluminijevega oksida in magnezita. Običajno so lastnosti teh materialov modificirane z dodatki mineraliziranih spojin, ki se navadno uporabljajo za znižanje reakcijske temperature in pospeševanje zgoščevanja. V prispevku avtorji opisujejo raziskavo vpliva dodatka MnO na lastnosti s kalcij-aluminatnim cementom vezanih ognjevarnih materialov na osnovi aluminijevega oksida in magnezita. Fazno sestavo materialov z dodatkom MnO so po kalcinaciji pri 1250–1450 °C določili z rentgensko difrakcijo in mikrostrukturo okarakterizirali z vrstičnim elektronskim mikroskopom (SEM). Rezultati raziskave kažejo, da dodatek MnO pospešuje tvorbo kalcijevega heksa-aluminata (CA_6) in špinela ($MgAl_2O_4$). Zaradi velike aktivnosti sintranja špinela in enovite mikrostrukture se je upogibna trdnost preiskovanega materiala z dodatkom MnO izboljšala s 25 MPa na 34 MPa po 5 h kalcinaciji na 1450 °C.

Ključne besede: ognjevarni materiali, lastnosti, špineli, MnO

1 INTRODUCTION

Calcium aluminate, cement-bonded, alumina-magnesia refractory castables have excellent properties, such as appropriate workability, mechanical strength and thermal shock resistance.[1] So this kind of material is normally used in the steelmaking process for the wall and bottom, and the impact pad of steel ladles.[2] However, the generation of calcium CA_6 and in-situ spinel would cause a volume expansion of 3 % and 8 %, respectively, which seriously affects the integrity of products at high temperatures.[3] Thus, much effort has been made to obtain a suitable volume expansion for alumina-magnesia refractory castables. The addition of mineralizers is regarded as one of most effective methods to design materials' properties. It has been proved that TiO_2 is a multifunctional mineralizer, which can improve the strength and volume stability of alumina-magnesia refractory castables.[4] Moreover, the effects of other compounds such as BaO, B_2O_3, ZrO_2 and rare-earth oxides on the properties of materials have been investigated in the Al_2O_3-MgO-CaO ternary system.[5–8] The results show that additions of even small amounts to materials influence both the chemical and physical properties of castables. Some work was also carried out in recent years that involved choosing MnO as the additive. For example, Yin et al. found the addition of MnO improved the sintering activity as well as the growth of spinel and decreased the amount and aspect ratio of the CA_6 in $MgAl_2O_4$–$CaAl_4O_7$–$CaAl_{12}O_{19}$ composites.[9] Based on the investigation above, MnO was selected as the mineralizer in alumina-magnesia, refractory castables aiming to evaluate its effects on their properties in this work.

2 EXPERIMENTAL PART

The materials used in this investigation include tabular alumina (Almatis, Germany, 99.5 % purity), reactive alumina (CL370, Almatis, Germany, 99.8 % purity), calcined magnesia (Dashiqiao, Liaoning Province,

China, 95 % purity), calsium aluminate cement (Secar71, Kerneos, France), silica fume (951U, Elkem, Norway) and MnO (Aladdin, America, 99.5 purity).

The compositions of the alumina-magnesia refractory castables are listed in **Table 1**. Tabular alumina (≤6 mm) was used as the aggregate. The matrix of castables included fine tabular alumina, reactive alumina and calcined magnesia. Calcium aluminate cement acted as the binder of castables. Except that, 1 % silica fume was added, aiming to generate liquid phases at high temperatures, which could release thermal stresses caused by the formation of spinel and CA_6. MnO was used as the mineralizer in this system. The electrosteric dispersant FS60 (BASF, Germany) was introduced into the system to accelerate the dispersion and reduce the water content for vibro-casting. About 4.3 % of distilled water was added in the process of molding.

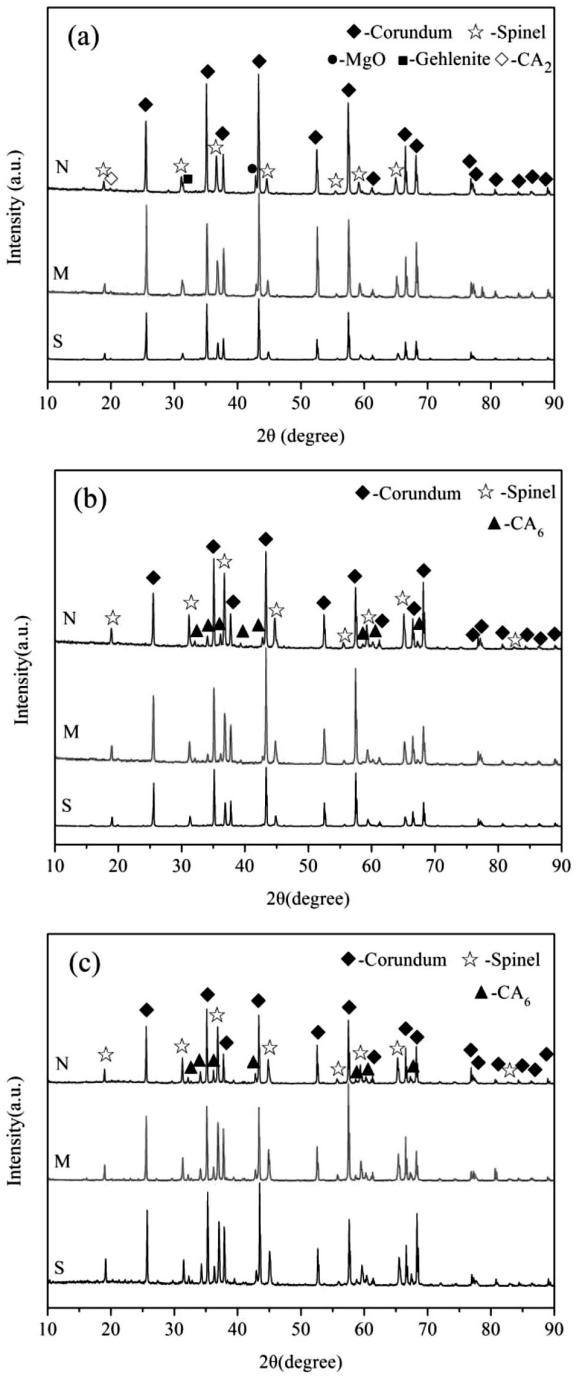

Figure 1: XRD patterns of alumina-magnesia refractory castables calcined at different temperatures: a) 1250 °C, b) 1350 °C and c) 1450 °C

Table 1: Compositions of alumina-magnesia refractory castables with different contents of MnO

Raw materials	Specimens (*w*/%)		
	S	M	N
Tabular alumina (≤6 mm) (Almatis)	61	61	60
Tabular alumina (≤0.2 mm) (Almatis)	19	18	18
Reactive alumina (CL370)	7	7	7
Calcined magnesia (180 mesh)	6	6	6
Calcium aluminate cement (Secar71)	6	6	6
Silica fume (951U)	1	1	1
MnO	0	1	2

All the castables were molded to bar specimens by vibro-casting and then cured at 25 °C for 24 h with a relative humidity of 100 %. After drying at 110 °C for 24 h, all the samples were calcined at 1250–1450 °C for 5 h. The measurements of the permanent linear change (PLC) were carried out in compliance with GB/T 5988-2007. The apparent porosity and the bulk density of the samples were tested according to GB/T 2997-2000. The cold modulus of rupture (CMOR) for the bar specimens (25 mm × 25 mm × 150 mm) was measured by a three-point bending test (E43.504, MTS, China) following GB/T 3001-2007. The phase composition of the castables was analyzed by using X-ray diffraction (XRD, Philips, X'pert Pro MPD, Netherlands). Spectra in the range of 7° and 90° (2θ) were recorded at 40 kV and 40 mA using Cu-K_α radiation (λ = 0.15406 nm) with a step size of 0.033° and a counting time of 15.24 s/step. The phase contents were calculated by the reference intensity ratio (RIR) method (X'pert Highscore 2.0 Plus, PANalytical, Netherlands). The microstructure and the chemical composition of the specimens were observed and measured with a scanning electron microscope (SEM, JEOL JSM-6610, Japan) and an energy-dispersive spectrometer (EDS, Bruker QUANTAX200-30, Germany).

3 RESULTS AND DISCUSSION

To clearly understand the action mechanism of MnO additions on the phase composition of alumina-magnesia refractory castables, XRD patterns of specimens after treatment at different temperatures were detected, as shown in **Figure 1**. Obviously, the main phases were corundum (PDF no. 83-2080), spinel (PDF no. 75-1796) and CA_6 (PDF no. 84-1613). A part of unreacted MgO (PDF no. 75-1525) and little of CA_2 (PDF no. 89-3851) and gehlenite (C_2AS, PDF no. 74-1607) were found in

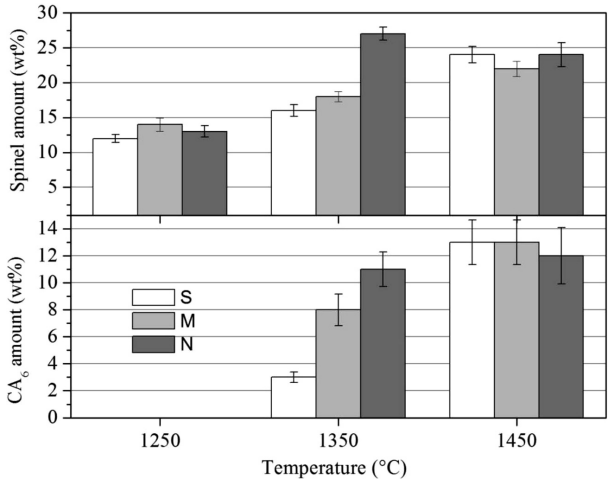

Figure 2: Spinel and CA_6 amounts for specimens calcined at different temperatures

the castables treated at 1250 °C. The CA_6 and spinel contents of the castables calculated by RIR semi-quantitative analysis are shown in **Figure 2**. As the picture presents, the amount of CA_6 and spinel of the castables with MnO additions were evidently more than that of the reference samples at 1350 °C, which demonstrated the in-situ reaction rate for CA_6 and spinel was improved by introducing MnO.

Compared with Al_2O_3 (104) for the reference crystal plane, the change of diffraction position for spinel (311) is shown in **Figure 3**. The rise of the temperature accelerated the Al-rich spinel formation caused by the substitution of Mg^{2+} (0.057 nm) with Al^{3+} (0.039 nm) in the crystal structure of the spinel.[10] Therefore, the diffraction angle of the spinel continuously rose with the firing temperature for all the samples, except for sample S sintered at 1250 °C for 5 h. The larger Mn^{2+} (0.066 nm) dissolved into the spinel grains resulted in the expansion of the spinel's lattice volume. So the diffraction angle of the spinel with MnO addition was obviously lower than that of the reference sample S. More point defects in the spinel grains were formed as the result of Mn^{2+} dissolution, which increased the free energy of the ions surrounding the solute cation due to lattice distortion and consequently decreased the activation energy for ion migration. This lattice distortion greatly enhanced the lattice diffusion, thus promoting the sintering of the spinel.[9]

The variation of the permanent linear changes of the samples with the calcining temperature is shown in **Figure 4**. The slope of the PLC curves for the samples containing MnO with the calcining temperature was significantly higher than that of the reference sample S from 1250 °C to 1350 °C. This phenomenon demonstrated that MnO accelerated the in-situ reaction, including the formation of spinel and CA_6, which was in agreement with the analysis of the XRD. The previous work showed that the PLC value of alumina-magnesia refractory castables with 2 *w*/% TiO_2 addition was less than 1 %.[11] However, the PLC values of all the samples treated at 1450 °C were over 3 % in this study, which indicated that MnO as a mineralizer failed to control the integral expansion behavior of the alumina-magnesia refractory castables.

Figure 5 presents the variation of the bulk density and the apparent porosity for castables with different temperatures. It can be seen that the castables with MnO additions had a higher apparent porosity and a lower bulk density than that of the reference sample at 1350 °C, which demonstrated that MnO accelerated the expansive reaction including CA_6 and spinel formation at this temperature. However, the differences in the apparent porosity and the bulk density for all the samples were rather small when the temperature reached 1450 °C. As a comparison, the apparent porosity of the alumina-magnesia refractory castables with a 2 *w*/% TiO_2 addition decreased from 23 % to 15 % after being calcined at 1450 °C for 5 h as a function of the lower viscosity liquid phase.[12] It was confirmed that MnO had

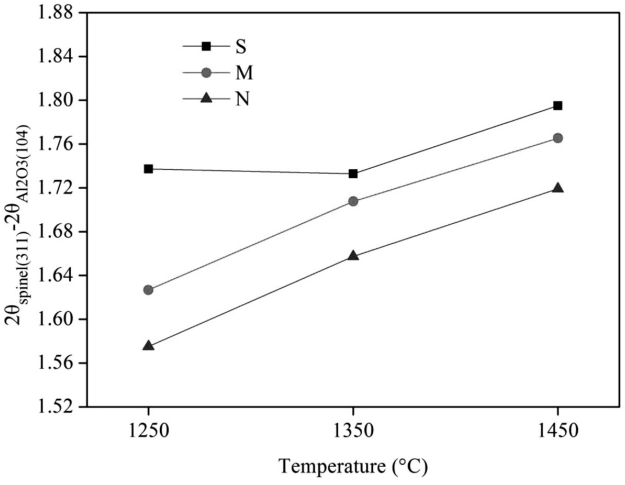

Figure 3: The diffraction peak shift for the spinel with the firing temperature

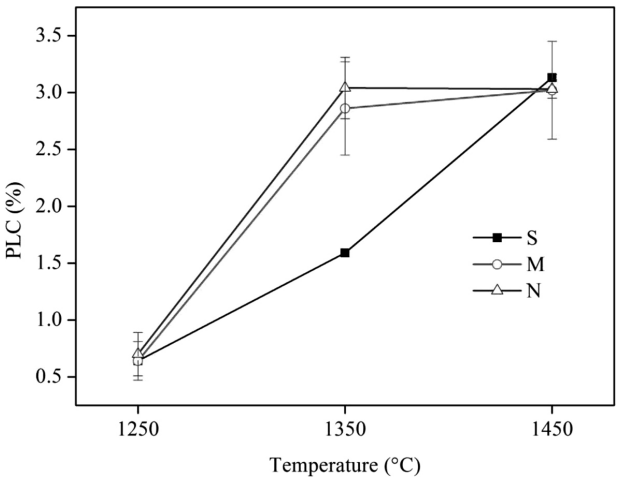

Figure 4: Permanent linear change of samples calcined at different temperatures

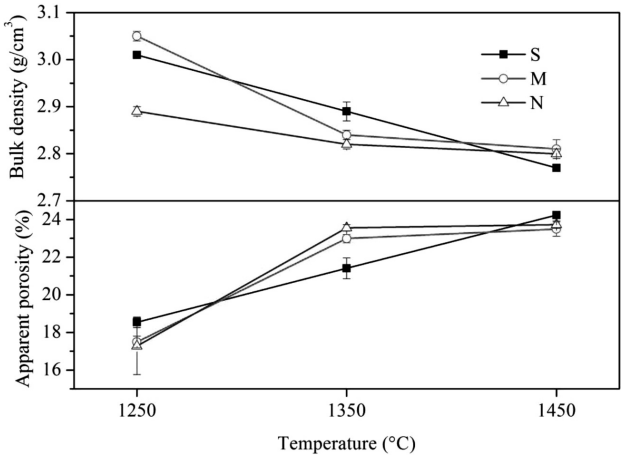

Figure 5: Bulk density and apparent porosity of castables treated at different temperatures

little influence on the formation of the low-melting-point liquid phase, which had a great impact on the densification of the materials.

The elastic modulus and CMOR were analyzed to explore the effects of MnO additions on the mechanical properties of castables, as presented in **Figure 6**. The decrease of the elastic modulus and CMOR of samples M and N after calcining at 1350 °C was accounted for by the expansion effect. Although the difference in the PLC value between the reference sample (S) and the specimens (M and N) with MnO additions was obvious at 1350 °C, as presented in **Figure 4**, the CMOR of the samples calcined at this temperature was fairly close. Besides that, the strength of samples M and N was obviously higher than that of the reference at 1450 °C in the case of a similar PLC value, apparent porosity and bulk density for each sample, as described in **Figures 4** and **5**. The mechanism causing the improvement in the strength will be discussed in the next section.

SEM images of the samples (S, M and N) calcined at 1450 °C for 5 h are shown in **Figure 7**. The matrix of

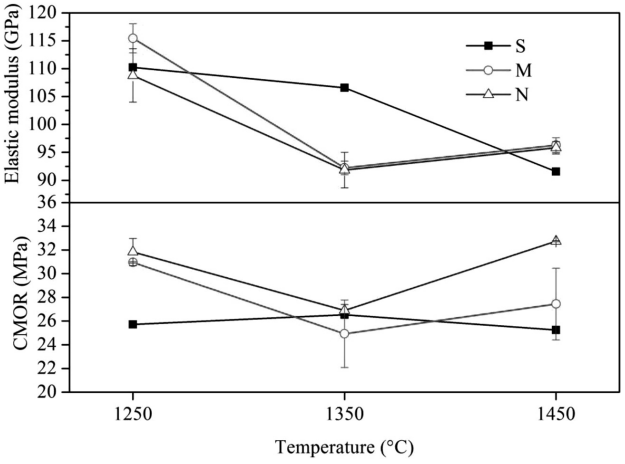

Figure 6: The elastic modulus and CMOR of alumina-magnesia refractory castables

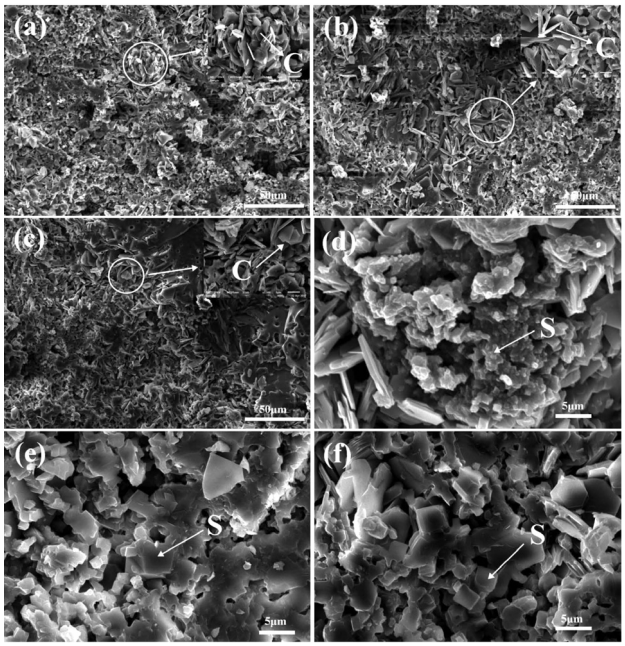

Figure 7: SEM images of alumina-magnesia refractory castables after treating at 1450 °C for 5 h: a)-d) S, b)-e) M, and c)-f) N (C indicates CA_6 and S indicates Spinel)

alumina-magnesia refractory castables comprised flaky CA_6 and granular spinel. Compared with the reference sample (seen in **Figure 7a**), the microstructures of the castables containing MnO were more uniform and the pore size was smaller, as shown in **Figures 7b** and **7c**. Besides, the addition of MnO improved the sintering activity of the spinel, thus better connections between the spinel particles and the larger spinel particles were achieved in the matrix, as presented in **Figures 7d, 7e** and **7f**. These factors led to an improvement in the strength for the samples containing MnO.

4 CONCLUSIONS

The effects of MnO additions on the properties of alumina-magnesia refractory castables were investigated in this study. Based on the results above, the following conclusions were drawn. The addition of MnO accelerated the formation of spinel and CA_6, which speeded up the expansion effect of castables at high temperatures. The densification of alumina-magnesia refractory castables was not accelerated due to the limited effect of the MnO mineralizer on the formation of a liquid. In spite of this, MnO can be selected as an additive to modify the properties of alumina-magnesia refractory castables, especially the bending strength. The enhancement mechanism was that Mn^{2+} doping into the spinel grains resulted in a lattice distortion and an improvement in the sintering activity of the spinel. Finally, a more uniform microstructure and a better connection of the matrix were obtained.

Acknowledgment

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