Effect of MnO on Sintering and Microstructure of Al_2O_3-MgO-CaO Refractories

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Abstract

In the current study, Al_2O_3-MgO-CaO refractories were prepared at 1400-1600°C by the addition of MnO micro-powders, and the effect of MnO addition on densification behavior of the refractory was discussed. The results showed that the doped MnO dissolved to $MgAl_2O_4$ phase, and promoted the growth of $MgAl_2O_4$ grains by the formation of $MgAl_2O_4$ solid solution. As a result, the dense microstructure was obtained, with the apparent porosity decreased from 19.2% to 5.4% and the bulk density increased from 2.78g/cm^3 to 3.15g/cm^3 after firing at 1600℃ for 2h by the addition of 4% MnO. In addition, a texture microstructure was observed, which is considered to be favorable to improve mechanical properties and the service life of Al_2O_3-MgO-CaO system refractories.

Introduction

In the Al_2O_3-MgO-CaO ternary phase diagram, the appearance temperature of liquid phase is higher than 1730℃, making use of the thermodynamic information provided by the Al_2O_3-MgO-CaO system, high refractoriness refractories can be designed. Especially when they are located in the subsystem Al_2O_3-$MgAl_2O_4$-$CaAl_4O_7$ area, the appearance temperature of liquid phase is up to 1850 ± 10℃[1,2], and the true density of CaO·$2Al_2O_3$ is smaller in this system[3,4]. Therefore, the high temperature performance can be ensured by adding a small quantity cheap lime (CaO) to replace part of the Al_2O_3 raw materials into the Al_2O_3-MgO system, the lightweight refractory of the Al_2O_3-MgO-CaO system can be prepared, while the lightweight refractory necessarily means energy conservation and emissions reduction [5]. Effects of CaO content on sintering and lightweight of Al_2O_3-MgO-CaO refractories was studied in our previous work[6]. In the synthesis process of the Al_2O_3-MgO-CaO system refractories, sintering and densification is suppressed with the volumetric expansion of multiple reaction between each component, it is difficult to obtain dense refractory. Particularly, spinel has the highest melting point in the phase composition of the Al_2O_3-MgO-CaO system refractories, it is also the most difficult to sinter by using single step sintering method, and general requirements sintering temperature is not lower than 1700℃ even by two-stage sintering method, which is the main reason for restricting its development[7,8].

Based on these aspects described above, in the current study, Al_2O_3-MgO-CaO refractories was prepared by two-stage sintering method, and the effect of MnO addition on sintering and microstructure of Al_2O_3-MgO-CaO refractories were investigated.

Experiment Procedures

The experimental batch compositions are shown in Table 1. The starting raw materials were 82% Al_2O_3 (particle size 8-12 m, 99% purity; Chinalco, Beijing, China), 10% MgO (particle size 2-3 m, 99% purity; Kermel Chemical Reagent, Tianjing, China), $CaCO_3$ (particle size 3-5 m, 99.5% purity; Kishida Chemical, Osaka, Japan) calculated on the ratio of 8% CaO.

Table 1. Batch composition of the samples/ (mass%)

Batchs	$CaCO_3$/%	Conversion CaO/%	MgO/%	Al_2O_3/%	MnO/%
0#	14.29	8	10	82	0
1#	14.29	8	10	82	2
2#	14.29	8	10	82	4
3#	14.29	8	10	82	6

The mixtures according to the preparation of 0 batch were ground in a laboratory-scale attrition milling in isopropanol media for 4h, to obtain homogeneous and highly energetic powder mixtures, and the mixed powder were dried at 120℃, then were isostatically pressed at 25MPa to bars (20mm×20mm×10mm). Pressed shapes were sintered at 1200℃ with a heating rate of 5℃ per min and cooling with furnace after a soaking period of 2h at the peak temperatures, then to grind the first stage sintered samples in a pot mill for 1h, and MnO powder(particle size 3-5 m, 99.5% purity; Xiya Reagent, Shandong, China) was added to the above composite, with external addition of 0, 2, 4 and 6% (shown in Table 1) respectively. Subsequently attrition milled for 4h, mixed powders were then isostatically pressed at 40MPa to briquettes (D20mm×6mm). These prepared samples were sintered secondly in a high temperature electric furnace at 1400, 1500 and 1600℃ in air atmosphere with a heating rate of 5℃ per min and cooling with furnace after a soaking period of 2h at the peak temperatures.

Briquettes were used to characterize the densification, phase compositions, microstructures. The densification was characterized by bulk density and apparent porosity measured in kerosene using Archimedes principle. The phase compositions were examined by X-ray diffraction method(XRD; X'pert PRO, PANalytical, Netherlands) using Cu Kα1 radiation (λ =1.5406 Å) with a step of $0.02°(2\theta)$ and a scanning rate of 2°/min from range of 10° to 90°. The microstructures were analyzed by scanning electron microscopy (SEM; EVO-18, ZEISS, Germany).

Results and Discussions

XRD patterns of the first stage samples sintered at 1200℃ for 2h is shown in Fig.1. It is observed that the presence of reaction products CA_2, MA and unreacted periclase, corundum phases. It may be explained that the solid reaction is not thoroughly during the sintering of the first stage samples.

XRD patterns of the second stage sintered samples for both with 2%, 4%, 6% and without additives at 1600℃ for 2h (Fig.2a) shows the phase of the samples are MA, CA_2 and CA_6, no diffraction lines for MnO were detected for the case of 2%, 4% and 6% MnO added. Further analysis shows that only the diffraction peak of MA took place shift among the three kinds of peak position. This implies that the added MnO might have formed $MgAl_2O_4$-MnO solid solution. By reason of $R_{Mn}^{2+}(0.067nm)＞R_{Mg}^{2+}(0.049nm)$, Mn^{2+} having similar characteristics

can substitute the Mg^{2+} in spinel, Mn^{2+} will causes the lattice distortion of the Mg^{2+} crystal cell, which is considered , it can result in fast diffusion within the single grains during the sintering process, which is favorable to improve the reaction speed. Meanwhile, the lattice parameters and the interplanar spacing of Mg^{2+} crystal cell will increase during the process of the lattice distortion. In combination with bragg equation $\lambda = 2d\sin\theta$, Mn^{2+} will prompt the diffraction peak of MA moving to a lower angle. Fig.2b is the slow-scan patterns of (400) of MA solid solution, reproducing an enlarged section of Fig.2a, it shows that the peak of (400) shifted to a lower angle with increased amount of MnO to 6%[9]. This result precisely proved the above analysis and identified the formation of the $MgAl_2O_4$-MnO solid solution.
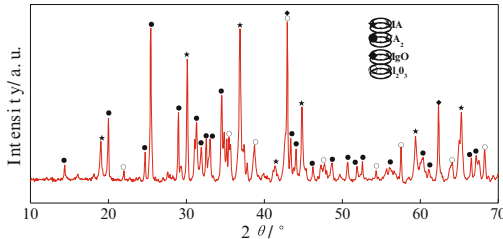

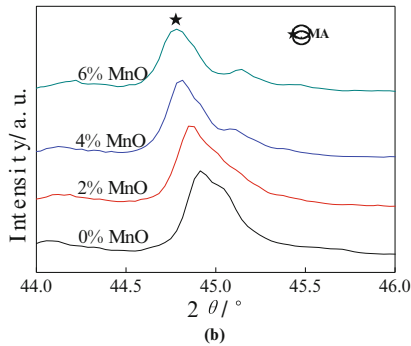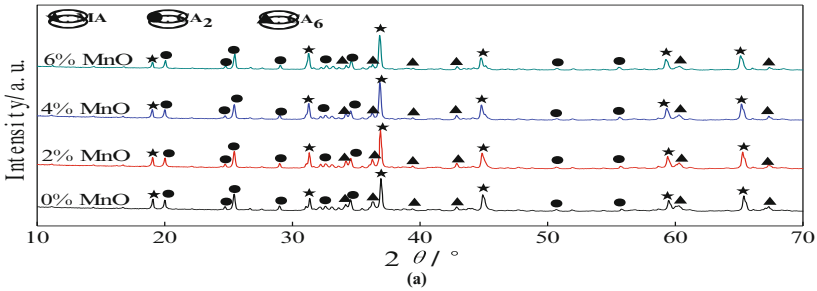Fig. 1. XRD patterns of the first stage samples sintered at 1200℃ for 2 h.

(a)

(b)

Fig. 2. XRD patterns of different MnO content second stage samples sintered at 1600℃ for 2h.(a) normal XRD patterns,(b) XRD pattern of (400) of MA crystal.

Fig.3 shows an increase in the bulk density and a reduction in the apparent porosity with the increase in the sintering temperature and additive amount of the two stage sintered samples. Sintering below 1500℃ is not sufficient to obtain high densification in samples with and without additive. Composition without additive results in a very poor density and a very high apparent porosity on sintering even at 1600℃. Again MnO too improves the density and reduces the apparent porosity sharply, which was associated with the grain growth and pore coalescence. For the batch sintered at 1600℃ the beneficial effect of additive of 4% and 6% MnO was most prominent. The apparent porosity decreased from 19.2% to 5.4% and the bulk density increased from 2.78g/cm^3 to 3.15g/cm^3 after firing at 1600℃ for 2h by addition of 4% MnO, it has reached more than 90% of the theoretical density. Addition of MnO between 0% and 4% enhances the densification and reduces the apparent porosity at 1600℃, but for higher additive amount the scope of further increase in sintered density and apparent porosity is limited.
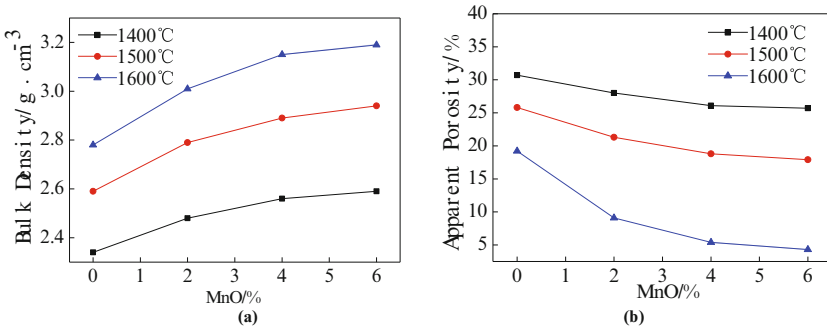

Fig. 3. Variation of bulk density and apparent porosity of the samples after two-stage sintering.

The typical back-scattered electron (BSE) images of microstructures on the polished surfaces of the with and without MnO content second stage samples at 1600℃ are given in Fig.4a, it shows that the microstructure of sintered samples without MnO content samples is not uniform, a porous structure was observed, with limited grain growth. However, the intergranular pores amount of the 4% MnO content samples sintered at 1600℃(Fig.4b) shows an obviously reduce, and the grain size shows an obviously increase in the MA of octahedrons structure and quadruple prisms structure of CA$_2$ with the increase of the MnO additive, but it shows a obviously reduce in the plates structure of CA$_6$ grain size. Analysis the above reason is that the doped MnO dissolved to MgAl$_2$O$_4$ phase, and the sintering activity of MgAl$_2$O$_4$ phase was obviously improved by the formation of MgAl$_2$O$_4$-MnO solid solution. So it mainly promote the spinel grain growth and occupy a certain space, therefore it limit the growth space of CA$_6$, thereby it inhibit the growth of CA$_6$ grain[10]. On the contrary, it promote the growth of the CA$_2$ grain because of it experience the formation and growth ($CaO \cdot 2Al_2O_3 + 4Al_2O_3 = CaO \cdot 6Al_2O_3$) during the CA$_6$ grain formation process within the system. In addition, a texture microstructure of the crystal phase, which includes MA, CA$_2$ and CA$_6$, was observed in the typical back-scattered electron (BSE) images of microstructures with 4% MnO content samples sintered at 1600℃ for 2h. Which is considered to be favorable to improve the mechanical properties and the service life
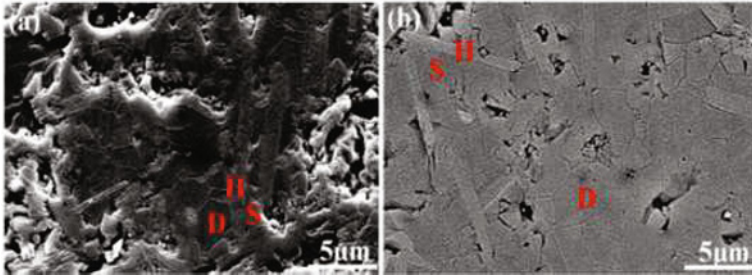
of the Al_2O_3-MgO-CaO system refractories[11,12].

Fig. 4. BSE images of samples sintered at 1600℃ for 2h.(D:CA$_2$, H:CA$_6$, S:MA):(a) without MnO. (b) 4% MnO

Conclusions

Al_2O_3-MgO-CaO refractories was prepared by two-stage sintering method, and the effect of MnO addition on sintering and microstructure were investigated. Based on the above results, the following conclusions have been drawn:

1) The phase compositions of Al_2O_3-MgO-CaO refractories after firing at 1600℃ for 2h are MA, CA$_2$ and CA$_6$.
2) The added MnO causes the lattice distortion of MA crystal, which is considered , it can result in fast diffusion within the single grains during the sintering process, which is favorable to improve the reaction speed.
3) The added MnO dissolved to $MgAl_2O_4$ phase, and promoted the growth of $MgAl_2O_4$ grains by the formation of $MgAl_2O_4$ solid solution. As a result, the dense microstructure was obtained, with the apparent porosity decreased from 19.2% to 5.4% and the bulk density increased from 2.78g/cm^3 to 3.15g/cm^3 after firing at 1600℃ for 2h by addition of 4% MnO.

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