7th International Symposium on High-Temperature Metallurgical Processing
Edited by: Jiann-Yang Hwang, Tao Jiang, P. Chris Pistorius, Gerardo R.F. Alvear F., Onuralp Yücel, Liyuan Cai, Baojun Zhao, Dean Gregurek, and Varadarajan Seshadri
TMS (The Minerals, Metals & Materials Society), 2016

EFFECT OF COMPOUND ADDITIVES ON SYNTHETIC MAGNESIUM ALUMINATE SPINEL UNDER LOW TEMPERATURE

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Keywords: composite additives, high temperature solid phase sintering, magnesium aluminate spinel, temperature

Abstract

Magnesium aluminate spinel is widely used in the metallurgical industry as refractory material, however, natural magnesium aluminate spinel is rare and most of the magnesium aluminate spinel is synthetic. The traditional synthesis of magnesium aluminate spinel often needs high temperature, which leads to more energy-consumption. In this article, solid phase sintering process was employed to synthesize magnesium aluminate spinel, in which, magnesium and aluminum oxide were used as raw materials and magnesium and aluminum powder were used as composite additives. The mass ratio of magnesium and aluminum on the effect of synthesis of magnesium aluminate spinel and the characteristic of the synthesis at different temperature and time was discussed. Experiment found that the synthesis temperature was observably lowered when the addition of magnesium and aluminum was 2.0% and 1.0% respectively.

1. Introduction

Because of excellent performance in thermostability and slag corrosion resistance, magnesium aluminate ($MgAl_2O_4$) spinel has attracted much attention in the refractory industry and was widely used in the metallurgical, optical, electrical and chemical industry. For example, it used as refractory in the lining of steel-making furnaces, sidewalls and bottom of the steel ladles, melting tanks, wall lining of intermediate frequency furnace and so on [1]. However, inartificial magnesium

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aluminate spinel is extremely rare, and most of them are synthesized artificially. The inartificial $MgAl_2O_4$ spinel has existed for a long time, and a variety of techniques have been invented to produce $MgAl_2O_4$ spinel powders. Methods including conventional solid-state-reaction [2], hydroxide coprecipitation [3, 4], flame spray paralysis [5], spray-drying [6], freeze-drying [7], Sol-gel [8], and mechanical activation [9, 10]. Compared to other methods, conventional solid-state-reaction is the most utilized one in industrial production and more than 90% of the $MgAl_2O_4$ spinel in China is produced by solid-state-reaction method. However, because of the poor ability of nucleation, the synthesis of $MgAl_2O_4$ spinel by solid-state-reaction method often needs high temperature and complicated process, which lead to high requirement of equipment and high-energy consumption. Therefore, lower the synthesis temperature of $MgAl_2O_4$ spinel become very important in conventional solid-state-reaction method.

The nucleation and grain growth of $MgAl_2O_4$ spinel has been found to be a very strong function of additives either present in the starting materials or incorporated during the sintering process. A variety of additives were studied to enhance the sintering process, AlF_3 and CaF_2 were reported to decrease the temperature of $MgAl_2O_4$ formation by increasing the cation vacancy concentration when fluorine was incorporated in the lattice by replacing oxygen ions [11]. Better sintered properties were also reached with the addition of different rare earth oxides like Y_2O_3, Yb_2O_3 and Dy_2O_3 [12, 13]. Similarly, TiO_2 and MnO_2 were available for densification of magnesium aluminate [14, 15]. Roy et al. [16] proposed that a crystallographic seeding could stabilize a particular phase and lower the crystallization temperature to enhance the densification. According to their research, the ordered lattice of $MgAl_2O_4$ and percentage of spinel at a lower temperature could be increased by adding to 1.69wt% $MgAl_2O_4$ spinel seed during the sintering process. However, impurity ions were also introduced into the product when the above-mentioned additives (except $MgAl_2O_4$ spinel seed) were added, which adversely affects the thermostability and slag corrosion resistance of $MgAl_2O_4$ spinel. This problem was also existed when other additives were employed in the sintering process.

In our present work, magnesium and aluminum powders were used as composite additives to prepare $MgAl_2O_4$ spinel. The effect of mass ratio of Mg and Al in additives, sintering temperature and time were investigated at a different level. Finally, the sinter was analyzed using an X-ray diffractometer.

2. Experimental Procedure

The magnesium oxide, aluminum oxide, magnesium and aluminum powder used in the experiment were of analytical grade. The magnesium oxide and aluminum oxide were premixed with a molar ratio of 1.2:1, and then additives with different mass ratio of Mg and Al were added accompanying with sufficient mixing. The total mass of additives was 3.0wt% of the magnesium oxide and aluminum oxide. The sintering of the mixed powders was carried out at different temperatures with 100℃ temperature interval ranging from1000℃ to 1400℃ for 4~7h soaking at peak temperature. The powders were mixed-milled with help of high dense ZrO_2 balls in acetone media. The phases in sintered samples were analyzed using an X-ray diffractometer (Rigaku Miniflex diffractometer with Cu Kα X-ray radiation). The spinel content in sintered samples was calculated from the XRD analysis using the following equation [17]:

vol. % of $MgAl_2O_4$

$$= \left\{\frac{\text{height counts of } MgAl_2O_{4(311)}}{\sum \text{height counts}\left[MgAl_2O_{4(311)}+MgO_{(200)}+Al_2O_{3(104)}\right]}\right\} \times 100 \quad (1)$$

Finally, the optimal parameters in sintering process were determined according to the experimental results.

3. Results and discussion

3.1 Effect of additives

Fig. 1 represents the XRD pattern of sintered powders with or without additives. It can be observed that the diffraction intensity of $MgAl_2O_4$ was obviously enhanced when additives were added. This may be attributed to the increase of $MgAl_2O_4$ content and the increased crystallinity of $MgAl_2O_4$ in sintered powders. Fig. 1 also reveals the trend of unreacted magnesium oxide and aluminum oxide, which are less in the sintered powders with additives. Table 1 shows the calculated volume percent of $MgAl_2O_4$ in the sintered powders according to Fig. 1. The phase analysis demonstrates ~11 and 24 vol. % spinel phase at 1300℃ without and with additives respectively, which indicated an obvious increase of spinel formation with additives

comparing to without additives. The results also proved that the compound additives containing aluminum and magnesium were conducive for the formation of $MgAl_2O_4$ spinel. The reason could be explained as follows. In the sintering process, compound additives melted first due to the low melting point of aluminum (660℃) and magnesium (648℃). Then, melted additives would induce the nucleation of $MgAl_2O_4$ spinel and accelerate the growth of the crystals.

Table I. The calculated vol. % of spinel content of sintered powders obtained from sintering with or without additives

	Sintering temperature	Sintering time	Content of spinel
With additives	1300℃	4h	24.1%
Without additives			11.4%

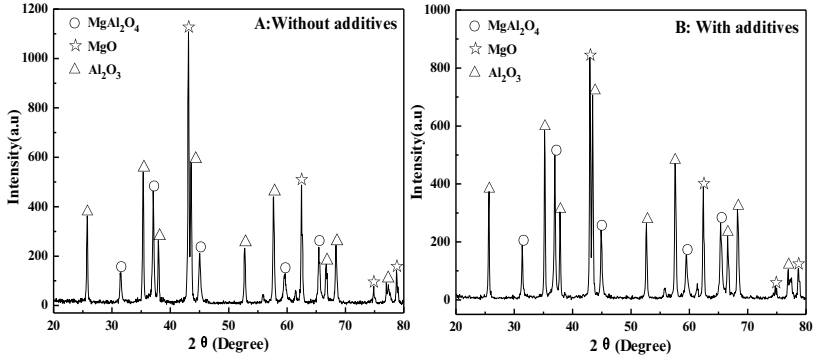

Figure 1 XRD pattern of MgO and Al_2O_3 powder sintered with or without additives (Sintering temperature 1300℃, time 4h)

3.2 Effect of Mg and Al ratio in additives

The mass ratio of Mg and Al in additives also affected the synthesis of $MgAl_2O_4$ spinel and the experimental result was shown in Fig. 2. According to Fig. 2, the initiation of spinel phase was presented with broad lines, which could be ascribed to the low crystallinity of $MgAl_2O_4$ spinel at this temperature. Similarly, the volume percent of $MgAl_2O_4$ in the sintered powders was calculated, and the results were listed in Table 2. It could be seen that the content of $MgAl_2O_4$ spinel increased slowly with the increase of the mass ratio of Mg and Al, the $MgAl_2O_4$ content reached the

maximum when the mass ratio of Mg and Al was 2.0. However, further increasing in the mass ratio of Mg and Al led to the decrease of $MgAl_2O_4$ content. Therefore, the mass ratio of Mg and Al in additives was determined to 2.0 in subsequent experiment.

Table Ⅱ. The calculated vol. % of spinel content according to Fig. 2

Mass ratio of Mg and Al	Sintering temperature	Sintering time	Content of spinel
0.2(A)			3.3%
0.5(B)			3.5%
1.0(C)	1000℃	4h	3.6%
2.0(D)			3.8%
5.0(E)			2.9%

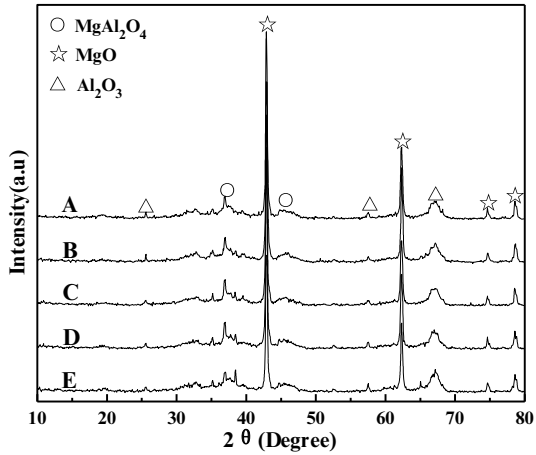

Figure 2 XRD pattern of MgO and Al_2O_3 powder sintered with different mass ratio of Mg and Al (sintering temperature 1000℃, time 4h)

3.3 Effect of sintering temperature and time

The effect of sintering temperature on the formation of $MgAl_2O_4$ spinel was shown in Fig. 3. As can be seen from Fig. 3, the diffraction intensity of MgO became to weakened as the temperature rose, while the diffraction intensity of $MgAl_2O_4$ spinel enhanced at the same time. This could be attributed to the accelerated formation of $MgAl_2O_4$ spinel caused by elevated temperature, which also reduced the MgO content in sintered powders. After a sintering at 1000℃ and 1100℃, only weak diffraction peaks of $MgAl_2O_4$ spinel phase appeared. This indicated few $MgAl_2O_4$ spinels were

synthesized at 1000℃ and 1100℃. When the temperature rose to 1200℃, strong and broad diffraction peaks of $MgAl_2O_4$ spinel phase emerged, as the temperature continued to rise, the increase in the diffraction peak height accompanied by sharpening of the diffraction peaks was observed. This indicated that the crystallite size of the $MgAl_2O_4$ spinel increased with elevated sintering temperature. The volume percent of $MgAl_2O_4$ with or without additives was also displayed in Fig. 3, and the results were agreed with the XRD patterns of sintered powders: the content of $MgAl_2O_4$ spinel increased quickly with the increase of sintering temperature.

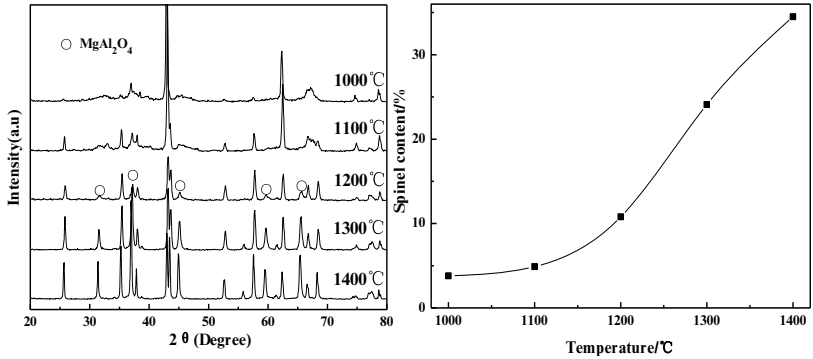

Figure 3 Effect of sintering temperature on the formation of $MgAl_2O_4$ spinel (Sintering time 4h, mass ratio of Mg and Al in additives is 2.0)

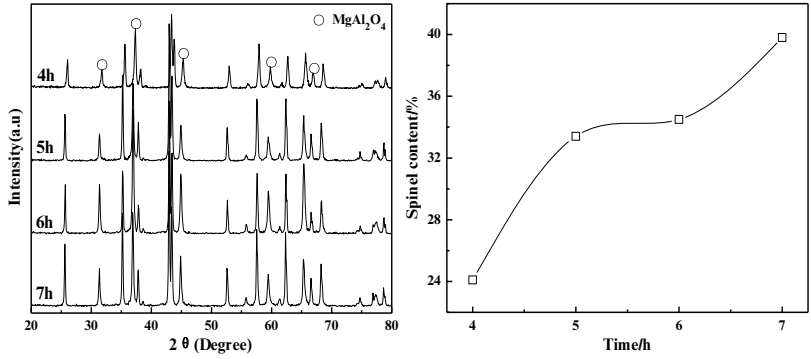

Figure 4 Effect of sintering time on the formation of $MgAl_2O_4$ spinel with additives (Sintering temperature 1300℃, mass ratio of Mg and Al in additives is 2.0)

Fig. 4 revealed the effect of sintering time on the formation of $MgAl_2O_4$ spinel with

additives. It can be summarized from Fig. 4 that the diffraction intensity of $MgAl_2O_4$ spinel and the volume percent of $MgAl_2O_4$ were increased with sintering time extending. After a sintering at 1400℃ for 7h, there were still diffraction peaks of MgO and Al_2O_3 appeared. This indicated that the unreacted MgO and Al_2O_3 were existed in sintered powders, and the sintering time was deficient. However, compared to sintered powders without additives as showed in Fig. 5, the diffraction intensity of $MgAl_2O_4$ spinel and volume percent of $MgAl_2O_4$ in sintered powders with additives was increased much more. When the mixed powders were sintered at 1300℃ for 7h, the volume percent of $MgAl_2O_4$ was 39.8% with additives and 22.3% without additives. This meant a shorter time to reach same volume percent of $MgAl_2O_4$ in the sintering process. Therefore, sintering time could be shorted when additives were added in formation of $MgAl_2O_4$ spinel.

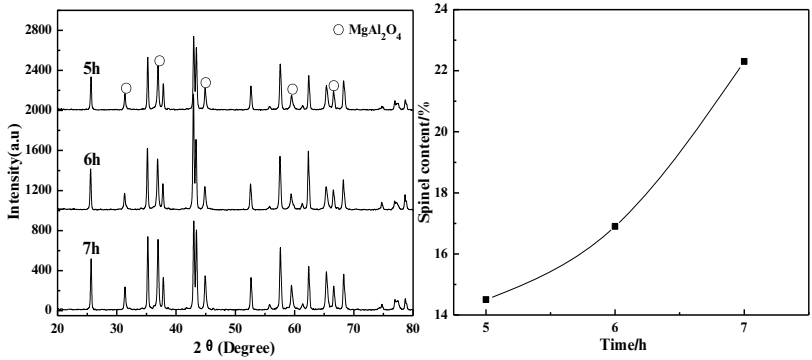

Figure 5 Effect of sintering time on the formation of $MgAl_2O_4$ spinel without additives (Sintering temperature 1300℃)

4. Conclusions

A new additive containing magnesium and aluminum powder was used to prepare $MgAl_2O_4$ spinel. The experimental results showed that the compound additives were beneficial for the formation of $MgAl_2O_4$ spinel and the optimal mass ratio of Mg and Al in additives was 2.0. The results also indicated the possibility to synthesize $MgAl_2O_4$ spinel at a lower temperature with shorter sintering time. When the mixed powders were sintered at 1300℃ for 7h, the volume percent of $MgAl_2O_4$ was 39.8% with additives, while the content was 22.3% without additives.

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