Jinxia Meng*, Weiqing Chen, Jizeng Zhao and Li Liu

Study of the High-temperature Synthesis of MgAl_2O_4 Spinel Refractory Raw Materials from Chromium Slag

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Abstract: To make use of chromium slag waste, this study examined the technology of the preparation of MgAl_2O_4 spinel refractory raw material by using chromium slag. The results showed that (1) using the traditional sintering process of synthetic spinel, the highest volume density was 3.14 g/cm^3 and the lowest porosity rate was 9.16 %. With the increase of the proportion of MgO powder mixing, bulk density and porosity fluctuations, and which cannot meet the requirements of refractory raw materials. (2) For MgAl_2O_4 spinel prepared by the electric-melting process, the highest volume density was 3.27 g/cm^3 and the lowest porosity rate was 8.78 %. Volume density and the porosity remained stable, and they are affected by MgO powder thus the blending ratio is very small, which can satisfy the requirements of refractory raw materials. (3) MgAl_2O_4 spinel prepared by the electric-melting method is superior to traditional MgAl_2O_4 spinel in terms of slag resistance and thermal shock resistance.

Keywords: chromium slag, MgAl_2O_4 spinel, electric-melting method, sintering method, refractory raw materials

Introduction

Chromium slag is a waste slag produced in the process of metal smelting. At present, most chromium slag is used in chrome corundum bricks for zinc furnaces, zinc volatile kilns, and other non-ferrous metallurgical furnaces. The chromium slag material has been appeared on the low-end market, not only due to low sales volumes but also because it is very inexpensive. In recent years, aluminum costs have increased due to resource shortages,

and refractory manufacturers could consider replacing high-cost aluminum raw materials with low-cost chromium slag. In fact, some ferroalloy companies have begun to test the chromium slag synthesis of magnesium aluminate (MgAl_2O_4) spinel materials with good performance, leading to the production of high-value-added refractory materials.

MgAl_2O_4 spinel is the only compound in the $\text{MgO-Al}_2\text{O}_3$ system with a high melting point (2135°C). It is known for its high refractoriness, low thermal expansion, chemical stability, thermal shock resistance, and corrosion resistance [1, 2, 3, 4, 5]. It has become an important material in refractories and ceramics [6]. Yet, despite these advantages, spinel formation includes a 5–7 % volume expansion [7, 8], which prevents creating of full density magnesium aluminosilicate (MAS) ceramics in a single-stage firing process [9] and, thus, it is difficult to obtain a dense reaction-sintered body [10]. In order to overcome the volume expansion problem, dense MAS ceramics are normally prepared following a two-stage firing process [11, 12]. The two-step process is usually followed by sintering of spinel: the first step for spinel formation ($900\text{--}1200^\circ\text{C}$) and the second step for densification ($1600\text{--}1800^\circ\text{C}$) [4]. The use of two consecutive high-temperature firing cycles significantly increases the production costs of dense MAS ceramics [13]. The electric-melting method entails melting preparation materials in an electric arc furnace. This method can achieve a higher temperature than the sintering method, and thus it can be used to generate a high melting point, at which it would not be easy to sinter refractory materials. The traditional sintering method is normally used in the preparation of MgAl_2O_4 spinel, and there are only a few reports on the preparation of MgAl_2O_4 spinel by the electric-melting method.

Till November 2016, the inventory of chromium slag in a certain plant in China was about 42,000 t and showed an annual increase of 25,000 to 35,000 t. In order to realize the comprehensive utilization of chromium slag waste, one-step sintering and two-step sintering were conducted, as well as electric-melting. Thus, through our research and discussion, we attempt to find the best technology for the preparation of MgAl_2O_4 spinel refractory raw material using chromium slag.

*Corresponding author: Jinxia Meng, State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing 100083, China, E-mail: ustbmjx@163.com

Weiqing Chen, State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing 100083, China
Jizeng Zhao, Li Liu, Beijing Lier High-temperature Materials Co. Ltd., Beijing 102200, China

Materials and methods

Materials

The aluminum thermal metallurgy of chromium chemical reaction is shown in eq. (1). A large amount of chromium slag is produced in the process.

Table 1 shows the composition of chromium slag from different batches, and the measured physical properties are shown in Table 2. It can be seen in Tables 1 and 2: the

Table 1: Chemical composition ranges of different batches of chromium slag.

Composition	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	SiO ₂	Na ₂ O	Cr ₂ O ₃
Content (mass %)	72~82	0.2	0.5	1.4~2.4	0.3	1.5~2.0	13~18

Table 2: The physical properties of chromium slag.

Bulk density (g/cm ³)	Porosity (%)	Water absorption (%)	Mohs hardness	Refractoriness (°C)	Load softening temperature of T 0.6 (°C)
3.68	5.24	1.48	9	≥ 1950	≥ 1750

Table 3: Chemical composition of the two raw materials used in the experiment.

	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	SiO ₂	Na ₂ O	Cr ₂ O ₃	Burning reduction
Chromium slag (mass %)	81.07	0.18	0.65	1.56	0.33	1.99	13.86	0.00
Light burned magnesium (mass %)	0.01	0.43	95.41	1.19	0.78	–	–	1.93

Table 4: Size and proportion of the two materials used in the experiment.

	Specifications/mesh	A	B	C	D	E
Chromium slag (mass %)	200	90.00	80.00	70.00	60.00	50.00
Light burned magnesium (mass %)	200	10.00	20.00	30.00	40.00	50.00

Figure 1: Flowchart of the preparation of MgAl₂O₄ spinel by the sintering process.

chromium slag Al₂O₃ content is higher; Fe₂O₃, CaO, SiO₂, and other contents are low; and the degree of resistance and other physical properties are good. Therefore, the slag has the characteristics of high-quality refractory raw material. The composition of chromium slag used in this study is shown in Table 3, and the ratio of two raw materials required for the synthesis of MgAl₂O₄ spinel is shown in Table 4.

Methods

Sintering experiments

The sintering process is a method of synthesizing MgAl₂O₄ spinel by calcination at a high temperature in the sintering equipment. The calcination equipment used in China mainly consists of rotary kilns. The sintering process is outlined in Figure 1. The sintering experiments in this study were carried out in a sintering furnace, as described below.

- (1) The one-step sintering method experimental process: The sintering temperature was 1500 °C, 1600 °C,

1700 °C, and 1750 °C, and the heat preservation was 3 h, according to the technological process of Figure 1.

- (2) The two-step sintering method experimental process: According to the process of Figure 1, the samples were firstly held at 1350 °C for 3 h then finely ground and shaped, and finally held at 1500 °C, 1600 °C, 1700 °C, and 1750 °C for 3 h.

Electric-melting experiment

The electric-melting method melts good raw materials in the electric arc furnace until the raw materials can be fully reacted. The process is outlined in Figure 2.

Results and discussion

Compactness

Bulk density and porosity are the main indicators to measure the compactness of the material. Therefore, the volume density and the porosity of the spinel prepared from chromium slag were tested. The bulk density (ρ_b) is calculated according to eq. (2):

$$\rho_b = \frac{m_1}{m_3 - m_2} \times \rho_{\text{ing}} \quad (2)$$

where ρ_{ing} is the density of the liquid at the test temperature.

The apparent porosity (π_a) is calculated according to eq. (3):

$$\pi_a(\%) = \frac{m_3 - m_1}{m_3 - m_2} \times 100 \quad (3)$$

In eqs (2) and (3), m_1 is the mass of the dried sample, m_2 is the mass of the saturated sample suspended in the liquid, and m_3 is the mass of the saturated sample.

According to the test results for both the one-step sintering method and the two-step sintering method, the bulk density of the sample increased gradually with the increase of sintering temperature, whereas the porosity decreased

gradually. Therefore, only the experimental data that show the highest sintering temperature – the bulk density and porosity at 1750 °C (see Figures 3 and 4) – are listed. Analysis of the results includes the following: (1) the best data from the one-step sintering method are a volume density of 2.56 g/cm³ and a porosity of 25.96 %. The best data from the two-step sintering method are a volume density of

Figure 3: Bulk density data of MgAl_2O_4 spinel refractory materials prepared by the sintering method and electric-melting method.

Figure 4: Porosity ratio data of MgAl_2O_4 spinel refractory materials prepared by the sintering method and electric-melting method.

Figure 2: Flowchart of the preparation of MgAl_2O_4 spinel by the electric-melting process.

3.14 g/cm³ and a porosity of 9.16 %. Clearly, by comparing the two sintering methods, the two-step sintered MgAl₂O₄ spinel refractory raw materials had better compactness. (2) The volume density of the samples showed a trend of falling and then rising, and the porosity of the samples showed a trend of rising and then falling. This may be due to the highest ratio of MgAl₂O₄ spinel forming in the middle of the process and the maximum volume expansion. (3) The best volume density and porosity in the sintering method appeared in run E, which had the highest amount of magnesium and lowest amount of chromium slag (already below 50 %). In a word, the chromium slag is more complex than the traditional materials in the composition, and the structure is also different from the traditional materials, so it is more difficult to sinter than the traditional materials. Therefore, the sintering method cannot achieve the expected results of this study.

The electric-melting experiment was carried out in an electric furnace (husking furnace). The bulk density and porosity of the MgAl₂O₄ spinel refractory raw material prepared by the electric-melting method are shown in Figures 3 and 4. Analysis of the results includes the following: (1) the maximum bulk density of the refractory was 3.27 g/cm³ and the minimum value was 3.20 g/cm³; the minimum porosity was 8.78% and the maximum value was 11.96%. The bulk density and porosity of MgAl₂O₄ spinel refractory raw materials prepared by the electric-melting method are greatly improved compared with the sintering method. (2) The small volume density and the porosity change of the samples indicate that the compactness of the material is affected by the amount of magnesium, which is very small. It implied that the electric-melting method can achieve compactness of the

refractory raw material with little magnesium. On this basis, we used scanning electron microscopy (SEM) and X-ray diffraction (XRD) (Figure 5) to detect the refractory raw materials. The results show that the synthesis of electric-melting MgAl₂O₄ spinel refractory raw material exhibits a typical spinel phase. Thus, the electric-melting method meets the requirements of the densification of refractory materials, and the use of a low ratio of magnesium to consume a large amount of chromium slag achieves an efficient use of chromium slag.

Slag resistance

Slag resistance was tested using the static crucible method. The matrix of the crucible was prepared from the electric-melting MgAl₂O₄ spinel refractory raw material and the traditional MgAl₂O₄ spinel refractory raw material, respectively, and the aggregate of the crucible is corundum. There were two types of slag used in the test (see Table 5), of which slag No. 1 is a common slag, and slag No. 2 is a strong oxidizing slag. The test slags were added to the crucibles and maintained at a high temperature of 1600 °C for 1 h.

Table 5: Composition and content of the slag in the slag resistance experiment.

Composition	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	SiO ₂	MnO
No. 1 slag (mass %)	5.65	1.08	12.2	45.7	30.82	2.86
No. 2 slag (mass %)	3.25	18.11	9.16	32.64	29.34	3.86

Figure 5: XRD phase of electric-melting refractory material and a typical MgAl₂O₄ spinel photograph of SEM.

The results of the slag resistance test are shown in Figure 6; the crucible of (a) and (c) were made by electric-melting MgAl_2O_4 spinel refractory raw material and (b) and (d) were made by the traditional MgAl_2O_4 spinel refractory raw material. In addition, (a) and (b) used slag No. 1 and (c) and (d) used slag No. 2. Analysis of the results includes the following: (1) in a comparison of (a) and (b) crucible erosion results, the lower part of the (b) crucible wall had an obvious depression, while the (a) crucible wall was smaller, indicating that the ability of the (a) crucible to resist slag No. 1 is better than that of the (b) crucible. (2) In a comparison of (c) and (d) crucible erosion results, due to the strong oxidation of slag No. 2, the (d) crucible wall and bottom had a deep scum intrusion, with a more pronounced erosion channel, while the (c) crucible had a shallow intrusive scum and less of an erosion channel. The result indicates that the oxidation resistance of (c) crucible is better than that of (d) crucible.

Thus, the slag resistance of MgAl_2O_4 spinel refractory raw material made from chrome slag is superior to that of traditional MgAl_2O_4 spinel refractory raw material.

Thermal shock resistance

In this study, the thermal shock test was performed using the most commonly used test method: allow the sample to repeatedly undergo the heating-cooling process, and assess the degree of damage to the material to evaluate the thermal shock resistance. The aggregate of the crucible is corundum, and the matrix was prepared by electric-melting MgAl_2O_4 spinel fine powder and traditional MgAl_2O_4 spinel powder, respectively. The process employed to test the thermal shock resistance was as follows: heat at 1100°C for 0.5 h, water cool (25°C) for 0.5 h, then repeated the heating and water cooling steps.

Two groups were tested for thermal shock resistance, and the results of the test are shown in Figure 7. One test group consisted of (a) and (b), and one consisted of (c) and (d); the samples of (a) and (d) were MgAl_2O_4 spinel

Figure 7: Comparison of thermal shock resistance tests: (a) and (d) are MgAl_2O_4 spinel prepared from chromium slag and (b) and (c) are traditional MgAl_2O_4 spinel.

prepared by the chrome slag, and the (b) and (c) samples were traditional MgAl_2O_4 spinel. Analysis of the results includes the following: (1) In a comparison of (a) and (b), the damage to (b) after eight heat shocks was more serious than (a) after 22 thermal shocks, so the thermal shock resistance of (a) was significantly better than (b); and (2) in a comparison of (c) and (d), the damage to (c) after 21 heat shocks was more serious than (d) after 30 thermal shocks, so the thermal shock resistance of (d) was significantly better than (c).

Therefore, the thermal shock resistance of the MgAl_2O_4 spinel refractory raw materials prepared by chromium slag is better than that of the traditional MgAl_2O_4 spinel refractory raw materials.

Conclusions

- (1) In the experiment synthesizing MgAl_2O_4 spinel refractory raw materials from chromium slag waste by sintering, the volume density of the product is low and the porosity is too high. Thus, the material cannot meet the requirement of MgAl_2O_4 spinel refractory materials

Figure 6: Comparison of slag resistance tests: (a) and (c) are MgAl_2O_4 spinel prepared from chromium slag and (b) and (d) are traditional MgAl_2O_4 spinel.

preparation, either by the one-step or by two-step sintering method.

- (2) With the electric-melting method, high-quality MgAl_2O_4 spinel refractory raw materials with high bulk density and low porosity can be prepared by using chromium slag waste.
- (3) MgAl_2O_4 spinel material made from chromium slag is better than traditional MgAl_2O_4 spinel material in slag resistance and thermal shock resistance.

References

- [1] J.L. Huang, S.Y. Sun and Y.C. Ko, *J. Am. Ceram. Soc.*, 80(12) (2010) 3237–3241.
- [2] T. Yamamura, T. Hamazaki and H. Kato, *Taikabutsu Overseas*, 12 (1992) 21–27.
- [3] J.E. Sheehan, J. Sigalovsty, J.S. Haggerty and J.R. Porter, *Ceram. Eng. Sci. Proc.*, 14(7/8) (1993) 660–670.
- [4] H.S. Tripathi, B. Mukherjee, S. Das, M.K. Haldar, S.K. Das and A. Ghosh, *Ceram. Int.*, 29(8) (2003) 915–918.
- [5] G. Baudin, R. Martinez and P. Pena, *J. Am. Ceram. Soc.*, 78(7) (1995) 1857–1862.
- [6] W. Bakkar and J.G. Lindsay, *Am. Ceram. Soc. Bull.*, 46(11) (1967) 1094–1097.
- [7] H.C. Park, Y.B. Lee, K.D. Oh and F.L. Riley, *J. Mater. Sci. Lett.*, 16(22) (1997) 1841–1844.
- [8] D.O. McCreight and R.E. Birch, US patent no. 2,805,167 (1952).
- [9] Z.E. Nakagawa, N. Enomoto, I.S. Yi and K. Asano, *Proceedings of the UNITESR'95, Congress, Effect of corundum/periclase sizes on the expansion behavior during synthesis of spinel*, Tokyo, (1995), pp. 379–386.
- [10] E. Ryshkewitch, *Oxide Ceramics*, Academic Press, New York (1960), pp. 257–274.
- [11] I. Ganesh, K.A. Teja, N. Thiyagarajan, R. Johnson and B.M. Reddy, *J. Am. Ceram. Soc.*, 88(10) (2005) 2752–2761.
- [12] I. Ganesh, S.M. Olhero, A.H. Rebelo and J.M.F. Ferreira, *J. Am. Ceram. Soc.*, 91(6) (2008) 1905–1911.
- [13] I. Ganesh, G.J. Reddy, G. Sundararajan, S.M. Olhero, P.M. Torres and J.M. Ferreira, *Ceram. Int.*, 36(2) (2010) 473–482.