Effect of Y_2O_3 doping on the high-temperature properties of magnesia aluminate spinel refractories

Jiangbo Liu¹ · Zhoufu Wang¹ · Hao Liu¹ · Xitang Wang¹ · Yan Ma¹

Received: 16 July 2018 / Revised: 21 January 2019 / Accepted: 5 March 2019 / Published online: 13 March 2019
© The Author(s) 2019

Abstract

A series of low-creep magnesium aluminate spinel refractories doped with 0–3 wt% Y_2O_3 were prepared by sintering at 1750 °C. The physical properties, especially the high-temperature properties of the refractories, were investigated. X-ray diffractometry (XRD) and scanning electron microscopy (SEM) were applied to characterize the phases and microstructure of the refractories. The results indicated that yttrium aluminum garnet (YAG) could be in situ formed with the addition of Y_2O_3 in the spinel refractories. This stabilized the grain boundary of the spinel. The mechanical properties and high-temperature creep resistance of the spinel refractory could significantly be improved by the addition of Y_2O_3 .

Keywords Magnesium aluminate spinel · Y_2O_3 · YAG · High-temperature resistance

Introduction

Magnesium aluminate spinel refractories are widely used as important materials for heat equipment that requires long-term resistance to high temperature and chemical corrosion [1, 2]. However, as modern high-temperature industrial production technology proceeds, there is a need for higher requirements including good mechanical properties and especially good high-temperature creep resistance. This results in a shortage of magnesium aluminate spinel. The dissolution of corundum and the secondary spinelization reaction in a saturated spinel structure under a long-term high temperature and load changes the microstructure of the materials [3, 4]. There is then an increasing high-temperature creep of materials [5] and a decrease in the structural stability of the equipment. Therefore, the production safety was reduced.

Researchers have done many works to regulate the grain boundary of spinel. The addition of additives (such as SiO_2 , Fe_2O_3 , and TiO_2) can improve the sintering process and reduce the porosity and the pore size. This can increase the effective area of creep resistance and then improve the creep resistance of the materials at a high temperature. However, the

resulting low melting point phase will reduce the high-temperature strength and service life of the materials [6–11]. If a high-temperature oxide containing a large-radius metal ion was incorporated in situ formation into the spinel matrix structure at a high temperature, the grain boundary diffusion can be inhibited and the spinel solid solution structure can be stabilized. Then, the breakthrough improvements in the high-temperature creep behavior of spinel refractories can be expected.

It is worth to note that the yttrium aluminum garnet (YAG) has been a good choice because of its high melting point, interesting mechanical properties, good high-temperature chemical stability, and what's more, a low high-temperature creep rate (lowest of all known oxides 2.5×10^{-9} /s at 1700 °C, 100 MPa) [12–18]. YAG was in situ synthesized in the spinel refractory matrix by using a fused spinel as the raw material and an Y_2O_3 micropowder as the additive in this work. The effect of Y_2O_3 addition on the microstructure and sinterability and the creep behavior of the spinel refractories were investigated.

Experimental

Material preparation

Fused spinel (Kaifeng Special Refractory Co., Ltd., China) was used as the raw material. Y_2O_3 micropowder (purity $\geq 99.9\%$, Hongde New Technology Development Co., Ltd.,

✉ Zhoufu Wang
whwangzf@126.com; whwangzf@163.com

¹ The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan 430081, People's Republic of China

Table 1 The physical properties of the samples

Sample no.	BD (g/cm ³)	AP (%)	CMOR (MPa)	CCS (MPa)	HMOR (MPa)
A	2.99 ± 0.01	16.7 ± 0.2	23.3 ± 1.2	89 ± 3.2	5.0
AY1	3.03 ± 0.02	14.4 ± 0.3	24.6 ± 2.1	102 ± 2.8	8.6
AY2	3.05 ± 0.01	13.3 ± 0.2	25.3 ± 1.2	112 ± 1.7	10.0
AY3	3.03 ± 0.02	15.6 ± 0.2	21.3 ± 1.8	93 ± 2.6	10.9

China) was used as the additive. The MgCl₂ liquor (density is 1.25 g/cm³) was employed as the binder. The chemical compositions (wt%) that resulted from the fused spinel are Al₂O₃ (75.34), MgO (23.56), SiO₂ (0.13), Fe₂O₃ (0.27), and CaO (0.52). Recipes were prepared by incorporating 0, 1, 2, and 3% Y₂O₃ micropowders by weight into fused spinel-based compositions that contained 45 wt%, 15 wt%, and 40 wt% with spinel grain sizes of 1–3 mm, 0–1 mm, and ≤ 0.088 mm, respectively. The added Y₂O₃ micropowders were to replace the spinel with a grain size of ≤ 0.088 mm. The recipes were marked as A, AY1, AY2, and AY3, respectively.

First, all the raw materials were weighed per the desired composition. Then, the additives and the different spinel materials were mixed using a ball mill for 6 h, respectively. Second, this mixture was grounded with fused spinel aggregates using an Eirich sand mixer for 10 min; the MgCl₂ liquor was used as the binder. The ground mixture was then kneaded for 12 h and pressed at 150 MPa into molds (230 mm × 114 mm × 65 mm). All of these specimens were dried at 110 °C for 24 h and heated to 1750 °C and held for 6 h. The burned bricks were cut into bars (25 mm × 25 mm × 140 mm), cubes (40 mm × 40 mm × 40 mm), and cylinders with an inner hole (diameter 50 mm, height 50 mm, and inner hole diameter 12 mm) according to the test requirements, respectively.

Fig. 1 The fitted creep curves

Characterization

The bulk density and apparent porosity values were carried out in water using the Archimedes principle. The cold modulus of rupture (CMOR) values were measured according to the GB/T 3001-2007 standard by the three-point bending test method using a 100-mm span. The cold crushing strength (CCS) values were measured in accordance with the GB/T 5072-2008 standard. The hot MOR values were measured according to the GB/T 3002-2004 standard using the three-point bending test, which was performed at 1400 °C. The compressive creep rate was measured in accordance with the GB/T 5073-2005 standard, which was performed at 1500 °C for a load of 0.2 MPa. X-ray diffraction (XRD) analysis was performed using a Bruker AXS D8 Advance system (CuKα1, λ = 1.5406 Å), and scanning electron microscopy (SEM) imaging was performed using a JEOL JSM-6610 SEM system.

Results and discussion

Physical properties

The physical properties including the bulk density, apparent porosity, cold modulus of rupture, cold crushing strength, and hot modulus of rupture of the fired specimens are shown in Table 1. There was no obvious difference between the bulk densities of the samples. The apparent porosity decreased from 16.7 to 13.3%, and the CMOR, CCS, and hot modulus of rupture (HMOR) increased from 23.3 MPa, 89 MPa and 5.0 MPa to 25.3 MPa, 112 MPa, and 10.9 MPa, respectively. The values can

Table 2 Equation of the fitted curves

Specimen no.	Equation	Adj. R squared
A	$y = 0.386\exp(-x/17.832) - 0.397$	1
AY1	$y = 0.056\exp(-x/3.624) + 0.224\exp(-x/26.328) - 0.28$	0.999
AY2	$y = 0.072\exp(-x/6.136) - 0.072$	0.995
AY3	$y = 0.22\exp(-x/16.994) + 0.053\exp(-x/2.345) - 0.273$	0.999

The fitted equation creep curves: $y = A\exp(-x/a) + B\exp(-x/b) + c$, where y is the creep strain, x is the time, and A , B , a , b , and c are creep parameters

Fig. 2 Results of X-ray patterns of specimens added with 0 and 2 wt% Y_2O_3

be divided into two levels of Y_2O_3 change. From 0 to 2 wt%, the apparent porosity decreased, and the bulk density, CMOR, and CCS increased due to an increase in the formation amount of YAG by the reaction of Y_2O_3 with a solid solution of Al_2O_3 in

spinel. This accelerated the mass transfer and densification processes. From 2 to 3 wt%, however, these values changed into the opposite. This was because the reaction $\text{Y}_2\text{O}_3 + \text{Al}_2\text{O}_3 \rightarrow \text{Y}_3\text{Al}_5\text{O}_{12}$ was associated with a volume shrinkage of about 0.3%, and additional new micropores were produced when more YAG was present. This affected the spinel sintering.

High-temperature creep resistance

The fitted and predicted creep strain/time curves are shown in Fig. 1, and the curves were fitted according to Eq. (1), which was called the θ -Concept Project by Evans R W and Wilshire B [19]. The fitted data are shown in Table 2. The creep strains of the specimens were all quite small, and the creep rates decreased upon the addition of Y_2O_3 . As shown in Fig. 1, the sample without Y_2O_3 addition has a rising shrinkage as the time prolongs, while the samples added with Y_2O_3 have a smaller shrinkage. Their creep strains for 50 h of testing were -0.38% , -0.25% , -0.08% , and -0.26% , respectively. It also can be seen from the predicted creep strain/time curves that the specimens added with Y_2O_3 reached stable creep stage earlier than the specimen without Y_2O_3 .

Fig. 3 Microstructure of the samples with different amounts of Y_2O_3 after sintering: **a** 0 wt%, **b** 1 wt%, **c** 3 wt%, and **d** Y element distribution of the sample with 3 wt% Y_2O_3

$$\varepsilon_t = \theta_1[1 - \exp(-\theta_2 t)] + \theta_3[\exp(\theta_4 t) - 1] \quad (1)$$

where ε_t is creep strain, t is the time, and θ_1 , θ_2 , θ_3 , and θ_4 are creep parameters.

Generally, the earlier the turning point of deceleration creep appears, the shorter the time of deceleration creep is, the smaller the deformation of the material is, and the longer the service life of the material is [20]. As shown in Fig. 1, the samples added with 2 wt% and 3 wt% Y_2O_3 reached the stable creep stage at 10 h and 40 h, respectively, whereas, the samples added with 0 wt% and 1 wt% Y_2O_3 did not get the stable stage even in the duration time of 50 h. The decrease of the compressive creep rate is due to the in situ formation of the second low-creep phase YAG.

Phase composition and microstructure analysis

Figure 2 shows the XRD patterns of the samples added with 0 and 2 wt% Y_2O_3 (the diffraction peaks of the samples added with different amounts of Y_2O_3 are almost the same). Spinel is the main phase in the sample without Y_2O_3 ; spinel and YAG

are the main phases in the sample added with 2 wt% Y_2O_3 , which indicates that YAG can be formed via the reaction of Y_2O_3 with a solid solution of Al_2O_3 in spinel.

Figure 3 shows the microstructure of the samples with different amounts of Y_2O_3 after sintering and Y element distribution of the sample with 3 wt% Y_2O_3 . There were many pores in the specimen without Y_2O_3 as shown in Fig. 3a. Instead, a lot of high-temperature continuums (the light-gray and white fields) form uniformly around the spinel grain boundary in the specimen with Y_2O_3 , as shown in Fig. 3b, c. This forms an interlocking structure with the spinel grain, which can stabilize the grain boundary of spinel. In addition, the content of pores obviously declines. In Fig. 3b, the EDAX results indicate that the constituent elements in the light-gray fields were mostly Al, O, and a small amount of Mg, Y, and Ca (Ca came from fused spinel raw materials). These light-gray fields are the precipitation of $\alpha\text{-Al}_2\text{O}_3$ from spinel, as well as a little amount of Mg–Al–Y solid solution [17]. Figure 3 d shows that Y element distributes on the boundary of the spinel grains according to Fig. 3c. Combining the XRD and EDS results, it can be concluded that the white fields are YAG.

Fig. 4 Schematic illustration for the matrix structure evolution and interface reaction mechanism of spinel refractories with the Y_2O_3 addition

This indicates that the addition of Y_2O_3 results in the expulsion of pores and the formation of YAG had a pinning effect on spinel grain boundary, which improves the mechanical properties and high-temperature creep resistance of spinel refractories.

The microstructure evolution and interface reaction mechanism

According to the XRD and FESEM results, the matrix structure evolution and interface reaction mechanism of spinel refractories upon Y_2O_3 addition can be proposed, as shown in Fig. 4. The solid reaction and sintering are all controlled by ion diffusion at a high temperature. The counter-diffusion of Al^{3+} and Y^{3+} cations occurs at the interface of the spinel and Y_2O_3 . The added Y^{3+} is preferentially dissolved into the spinel lattice by substituting Al^{3+} to form a small amount of the Mg–Al–Y solid solution. When the added Y_2O_3 content exceeds the limit of solubility, the Y_2O_3 can react with spinel to extract Al^{3+} from the spinel structure and form YAG [21–23]. During the cooling process, the second low-creep phase YAG precipitates on the spinel grain boundary, forming an interlocking structure that can stabilize the grain boundary of spinel and prevent grain-boundary sliding. This approach improves the high-temperature creep resistance of spinel refractories.

Conclusions

A low-creep spinel refractory can be prepared by doping Y_2O_3 micropowders, the physical properties, high-temperature creep resistance, and microstructure evolution and interface reaction mechanism of the refractories were investigated. The conclusions can be drawn as follows:

1. The mechanical properties, especially the hot modulus of rupture of the spinel refractories were significantly improved by the added 2 wt% Y_2O_3 .
2. A second low-creep phase YAG could be in situ formed with the addition of Y_2O_3 into a fused spinel. This resulted in a great decrease of the compressive creep strain from 0.36 to 0.08%.
3. The matrix structure evolution and interface reaction mechanism of spinel refractories upon Y_2O_3 addition were proposed. The $MgY_xAl_{2-x}O_4$ solid solution and YAG would be formed in turn with the increasing addition of Y_2O_3 .

Funding information This work was finally supported by the National Natural Science Foundation of China (No.51672195) and the Key Program of Natural Science Foundation of Hubei Province, China (No.2017CFA004).

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

1. Li, N., Gu, H.-Z., Zhao, H.-Z.: Refractories. Metallurgical Industry Press, Beijing
2. Ghosh, C., Ghosh, A., Haldar, M.K.: Studies on densification, mechanical, micro-structural and structure-properties relationship of magnesium aluminate spinel refractory aggregates prepared from Indian magnesite. *Mater. Charact.* **99**, 84–91 (2015)
3. Mohammadi, F., Otraj, S., Nilforushan, M.R.: Effect of $MgCl_2$ addition on the sintering behavior of $MgAl_2O_4$ spinel and formation of nano-particles. *Sci. Sinter.* **46**(2), 157–168 (2014)
4. Zhang, W., Shi, G.: Solid solution and precipitation of corundum in alumina-rich spinel. *Naihuo Cailiao* (In Chinese). **46**(6), 414–416 (2012)
5. Li, M.-Q.: Spinel material for crown in oxy-fuel glass furnace. National workshop on glass furnace technology (in Chinese). 63–68 (2011)
6. Naghizadeh, R., Rezaie, H.R., Golestani-Fard, F.: Effect of TiO_2 on phase evolution and microstructure of $MgAl_2O_4$ spinel in different atmospheres. *Ceram. Int.* **37**(1), 349–354 (2011)
7. Kim, T., Kim, D., Kang, S.: Effect of additives on the sintering of $MgAl_2O_4$. *J. Alloys Compd.* **587**(7), 594–599 (2014)
8. Tokariev, O., Schnetter, L., Beck, L.T., Malzbender, J.: Grain size effect on the mechanical properties of transparent spinel ceramics. *J. Eur. Ceram. Soc.* **33**(4), 749–757 (2013)
9. Ceylantekin, R., Aksel, C.: Improvements on the mechanical properties and thermal shock behaviours of MgO-spinel composite refractories by ZrO_2 incorporation. *Ceram. Int.* **38**(2), 995–1002 (2012)
10. Aksel, C., Aksoy, T.: Improvements on the thermal shock behaviour of MgO-spinel composite refractories by incorporation of zircon-3mol% Y_2O_3 . *Ceram. Int.* **38**(5), 3673–3681 (2012)
11. Ji, H.-P., Fang, M.-H., Huang, Z.-H., Chen, K., Xu, Y.-G., Liu, Y.-G., et al.: Effect of La_2O_3 additives on the strength and microstructure of mullite ceramics obtained from coal gangue and γ - Al_2O_3 . *Ceram. Int.* **39**(6), 6841–6846 (2013)
12. Tkachenko, S., Arhipov, P., Gerasymov, I., Kurtsev, D., Vasyukov, S., Nesterkina, V., et al.: Control of optical properties of YAG crystals by thermal annealing. *J. Cryst. Growth.* **483**, 195–199 (2018)
13. Corman, G.S.: Creep of yttrium aluminium garnet single crystals. *J. Mater. Sci. Lett.* **12**(6), 379–382 (1993)
14. Blumenthal, W.R., Phillips, D.S.: High-temperature deformation of single-crystal yttrium-aluminum garnet (YAG). *J. Am. Ceram. Soc.* **79**(4), 1047–1052 (2010)
15. Irankhah, R., Rahimpour, M.R., Zakeri, M., et al.: In situ synthesis-sintering of YAG/MAS composites by reactive spark plasma sintering. *J. Aust. Ceram. Soc.* **16**, 1–5 (2017)
16. Parthasarathy, T.A., Mah, T.I., Keller, K.: Creep mechanism of polycrystalline yttrium aluminum garnet. *J. Am. Ceram. Soc.* **75**(7), 1756–1759 (2010)

17. Liu, J.B., Wang, Z.F., Wang, X.T., Liu, H., Ma, Y.: The effects of in situ formation of $Y_3Al_5O_{12}$ on property improvement of magnesium aluminate spinel refractories. *Ceram. Int.* **44**(7), 7416–7420 (2018)
18. Chandra, K.S., Monalisa, M., Ulahannan, G., et al.: Preparation of YAG nanopowder by different routes and evaluation of their characteristics including transparency after sintering. *J. Aust. Ceram. Soc.* **53**(2), 1–10 (2017)
19. Evans, R.W., Wilshire, B.: *Creep of metals and alloys*[M]. Institute of Metals, London (1985)
20. Han, B., Zhang, H.-J., Zhong, X.-C.: High temperature bending creep properties of bauxite based β -sialon bonded corundum/SiC composites. *J. Chin. Ceram. Soc.* **35**(2), 216–219 (2007)
21. Pošrac, M., Devečerski, A., Volkov-Husović, T., Matović, B., Minić, D.M.: The effect of Y_2O_3 addition on thermal shock behavior of magnesium aluminate spinel. *Sci. Sinter.* **41**(1), 75–81 (2009)
22. Lach, R., Wojteczko, K., Dudek, A., et al.: Fracture behaviour of alumina-YAG particulate composites. *J. Eur. Ceram. Soc.* **34**(14), 3373–3378 (2014)
23. Zhang, B.-W., Ma, B.-Y., Zhu, Q., et al.: In-situ formation and densification of $MgAl_2O_4$ - $Y_3Al_5O_{12}$ and $MgAl_2O_4$ - $MgNb_2O_6$ ceramics via a single-stage SRS process. *Sci. Sinter.* **49**(3), 285–297 (2017)

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.