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Effect of polymorphism of Al_2O_3 on the synthesis of magnesium aluminate spinel

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Abstract

$MgAl_2O_4$ spinel was prepared by reaction sintering and the effect of polymorphism of Al_2O_3 on the synthesis and densification of the spinel studied. γ-Al_2O_3, ρ-Al_2O_3 and α-Al_2O_3 were mixed with analytical reagent of MgO according to the stoichiometric spinel ratio, respectively, and pressed into billets with diameter of 20 mm and height of 15 mm. The green-body billets then were sintered at temperature from 800 °C to 1600 °C in an air atmosphere. Bulk density, porosity, linear expansion changes, phase composition, microstructure and grain size of final sintered products were analyzed. The results indicated that γ-Al_2O_3 is beneficial for synthesize of spinel because it has a crystal structure similar to that of spinel. Among materials sintered at 1600 °C for 3 h, samples using γ-Al_2O_3 as raw material had the highest density, up to 91% of the theoretical density of $MgAl_2O_4$, and had the largest grain size of spinel.

Keywords: A. Sintering; D. Alumina; Magnesium aluminate spinel; Densification

1. Introduction

Magnesium aluminate spinel (MA), which is the only stable compound in the MgO–Al_2O_3 system, possesses a high melting point (2135 °C), good mechanical strength and an excellent chemical resistance etc. [1–3]. It has become an important material in refractories and ceramics [4]. For example, MgO-MA refractory is used in place of magnesia–chrome refractories in steel and cement applications because chrome can form hexavalent chrome, an environmental hazard [5]. However, the reaction of MgO and Al_2O_3 to form MA is accompanied by a volume expansion of approximately 5%, making it difficult to obtain a dense reaction-sintered body [6]. Hence, very high sintering temperatures are sometimes necessary. Researchers have studied several other processes to form MA such as freeze–drying [7], sol–gel processing of metal alkoxides or inorganic [8], and hydroxides coprecipitation [9]. However, these chemical processes also have some intrinsic disadvantages. For instance, coprecipitation usually uses aluminum and magnesium chloride or nitrate salts, making repeated washing necessary to remove the anions, which will alter the composition of the precipitates. This makes it difficult to control the chemical composition of the designed compound and requires large quantities of water [10].

The formation of MA from its constituent oxides is a counter diffusion process of Al^{3+} and Mg^{2+} ions [11] that depends on large number of parameters. Ritwik Sarkar et al. [12] studied the effect of milling time of raw material on the densification of MA with both the single-stage and double-stage sintering processes. They found that milling accelerated the densification of MA no matter what kind of sintering process was used. A maximum relative density of 99.5% was obtained when the raw material was milled for 6 h and without any presynthesization of MA. Ritwik Sarkar et al. [13] also studied the effect of calcinations temperature of Al_2O_3 on the densification of rich magnesium spinel (MgO 34 wt.%). The results showed that sintered density does not

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change greatly with increasing in calcinations temperature of alumina up to 1200 °C, but 1600 °C calcination resulted in reduced sinterability.

Other researches used various additives to enhance the MA formation and to densify the material at lower temperatures. Ritwik Sarkar et al. [14] studied the effect of various oxides additives on the densification of reaction-sintered and presynthesized stoichiometric MA. They found TiO_2 showed the greatest beneficial effect and that Cr_2O_3 showed some benefit on densification of all the presynthesized and reaction-sintered MA. However, V_2O_5 and B_2O_3 showed detrimental effects on the densification behavior of presynthesized and reaction-sintered MA. Kostic et al. [15] reported that the fluorine ion from AlF_3 or CaF_2 increased the solid-state reaction synthesis of magnesium aluminate spinel by increasing the cation vacancy.

Al_2O_3 has several polymorphic forms, for example, α-Al_2O_3, γ-Al_2O_3, κ-Al_2O_3, and ρ-Al_2O_3. Fig. 1 gives the transformation sequence of different Al_2O_3 to α-Al_2O_3 [16]. Table 1 gives the physical properties of different polymorphs of Al_2O_3 and MA. Usually people use α-Al_2O_3 as a raw material in the formation of MA because α-Al_2O_3 is a common industry product. However, the production temperature of α-Al_2O_3 is high, usually up to 1400 °C in industry, which results in a decrease of Al_2O_3 activity and an increase in energy consumption. At the same time, the process of α-Al_2O_3 transformation to MA is accompanied by a large volume expansion because of its higher density. However, γ-Al_2O_3 has a low density, which makes it have a smaller volume expansion in the formation of MA. Also, the temperature at which boehmite transfers to γ-Al_2O_3 is rather low, resulting in a γ-Al_2O_3 powder with higher activity. Furthermore, γ-Al_2O_3 has the same crystal structure as MA (cubic system). It may be beneficial to use γ-Al_2O_3 instead of α-Al_2O_3 as raw material in the formation of MA. ρ-Al_2O_3 is a noncrystal and is produced from gibbsite quickly heated around 700 °C for a short time and cooled quickly [17]. In very high purity corundum or MA castables, ρ-Al_2O_3 was usually a setting agent because of its hydrating properties [18]. It is interesting to study the effect of ρ-Al_2O_3 on the formation and densification of MA. In this paper, the influences of α-Al_2O_3, γ-Al_2O_3 and ρ-Al_2O_3 as raw materials in the formation and densification of MA will be studied.

2. Experimental procedures

The starting materials used in this study are γ-Al_2O_3, ρ-Al_2O_3, α-Al_2O_3 and an analytical reagent grade of MgO. The γ-Al_2O_3 was produced from boehmite heated at 700 °C for 4 h, α-Al_2O_3 was produced from gibbsite heated at 1400 °C for 4 h and ρ-Al_2O_3 was obtained from the Zhengzhou Research Institute of Light Metals, China. Composition, particle size and surface area of three kinds of Al_2O_3 and MgO are given in Table 2 and their X-ray patterns shown in Fig. 2. γ-Al_2O_3 and α-Al_2O_3 are the dominant crystal phases, there are no other phases in the XRD pattern, which means at 700 °C and 1400 °C, boehmite and gibbsite have already been converted to γ-Al_2O_3 and α-Al_2O_3, respectively (Fig. 2A and C). In Fig. 2B, phases of AlO(OH), $Al(OH)_3$ are found. They may come from two possible reasons: one is a residue or incomplete decomposition of $Al(OH)_3$ during the production of ρ-Al_2O_3; the other is a hydration of ρ-Al_2O_3 because ρ-Al_2O_3 is easily hydrated in air.

Targeting a stoichiometric MA ratio, γ-Al_2O_3, ρ-Al_2O_3 and α-Al_2O_3 were mixed with analytical reagent MgO, and referred to as samples A, B and C, respectively. The three types of starting powders were ball-milled for 5 h, using highly pure Al_2O_3 balls as a milling medium. The mixtures were pressed at 200 MPa in a stainless steel die

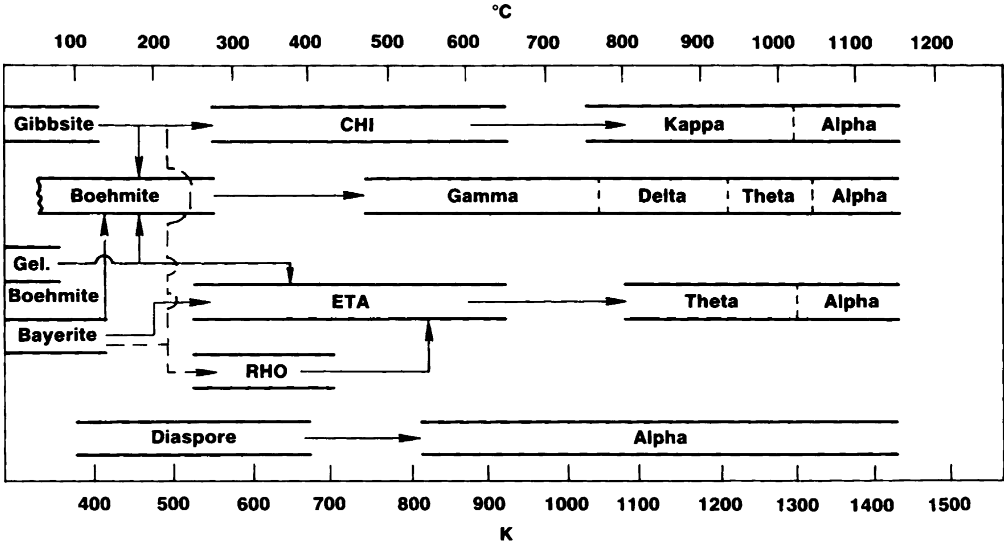

Fig. 1. The transformation sequence of different Al_2O_3 to α-Al_2O_3.

Table 1
The physical properties of different polymorphs of Al_2O_3 and of MA

Morphology	κ-Al_2O_3	γ-Al_2O_3	χ-Al_2O_3	θ-Al_2O_3	α-Al_2O_3	MA
Crystal system	Hexagonal	Cubic	Hexagonal	Monoclinic	Rhombohedral	Cubic
Density (g/cm^3)	3.72	3.45	3.76	3.69	3.99	3.58

Table 2
Compositions (mass%), particle size (μm) and surface area (m^2/g) of raw materials used to make MA

Type	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	K_2O	Na_2O	IL	MgO	Particle size	Surface area
γ-Al_2O_3	98.00	0.35	0.09	0.02	0.04	0.21	–	–	4.61	55.98
ρ-Al_2O_3	89.68	0.15	0.07	0.02	0.08	0.45	7.79	–	4.05	70.32
α-Al_2O_3	97.86	0.88	0.07	0.02	0.08	0.45	–	–	5.06	43.36
MgO	0.01	0.14	0.08	0.07	0.09	0.08	–	99.30	5.00	46.03

Note: IL is ignition loss. The operation temperature is 1000–1050 °C for 1 h.

to make the billets with a diameter of 20 mm and a height of 15 mm. The billets then were heated at 800 °C, 1000 °C, 1200 °C, 1400 °C and 1600 °C for 3 h in an air atmosphere.

XRD analysis was conducted using Ni-filtered Cu Kα under the following conditions: scanning speed of 2° min^{-1} and temperature of 16 °C. The density and porosity of the sintered specimens was measured by the Archimedes

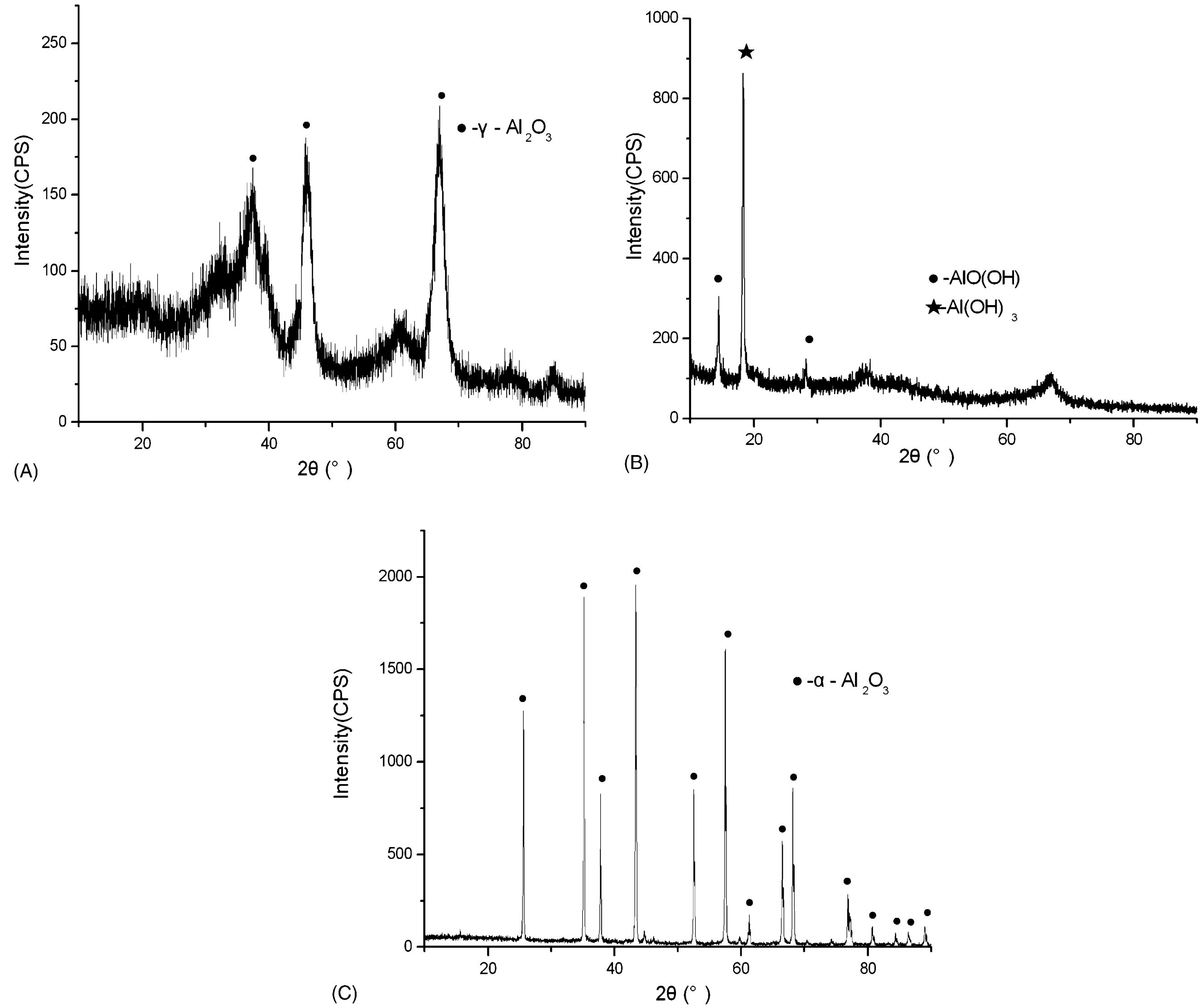

Fig. 2. X-ray patterns of (A) boehmite sintered at 700 °C for 4 h, (B) ρ-Al_2O_3 and (C) Al $(OH)_3$ sintered at 1400 °C for 4 h.

method in kerosene to avoid hydration of unreacted MgO. The surface area was measured using the Brunauer–Emment–Teller (BET) method. The microstructure and grain size of the sintered samples was examined via SEM. Linear changes were obtained by comparing the diameter of the specimens before and after sintering. Moreover, the relative content of MA in the three samples sintered at 1200 °C have been measured using the standard-free qualitative method proposed by Zheng [19]. This is not an accurate method to measure phase content in samples, but it can be used to compare the phase content in samples processed by the same conditions using different Al_2O_3 polymorphisms. The phase content can be calculated from formula as follows:

$$\begin{cases}\sum_{i=1}^{n}\left[\left(1-\frac{I_{iJ}}{I_{iK}}\right)x_{iK}u_{mi}\right]=0\\ \sum_{i=1}^{n}x_{iK}=1\end{cases}$$

where I_{iJ} and I_{iK} are the intensities of i phase of samples J and K, respectively; x_{iK} is content of i phase of sample K. In order to minimize error, polynominal liner regressor was used to arrive at a solution.

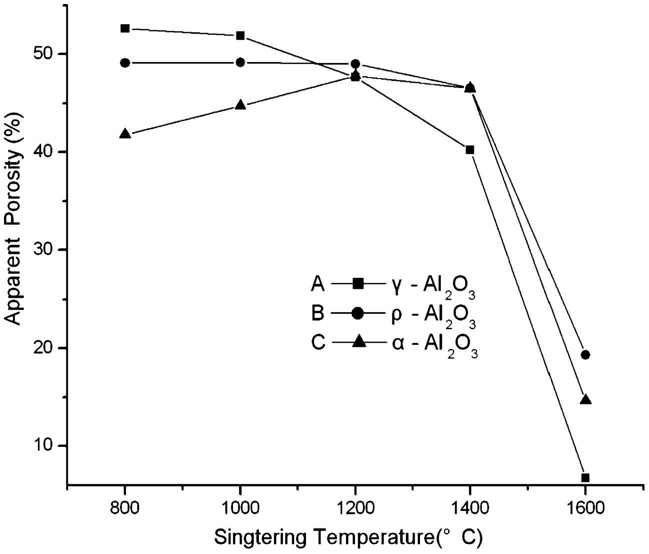

Fig. 4. Apparent porosity of samples as a function of sintering temperature.

3. Results and discussion

3.1. *Influence of polymorphism of Al_2O_3 on densification*

The bulk density, porosity and linear changes occurring in samples containing MgO and different polymorphs of Al_2O_3 as a function of sintering temperature are shown in Figs. 3–5, respectively. It is noticed that the density of samples with γ-Al_2O_3 (A) increased and porosity decreased with increasing temperature, but the porosity is more than that of samples with ρ-Al_2O_3 and α-Al_2O_3 (B and C) when the sintering temperature is lower than 1200 °C. However, when the sintering temperature is higher than 1200 °C, the porosity of sample A is less than that of samples B and C; and the higher the temperature, the more the difference in porosity among samples A–C. After sintering at 1600 °C for 3 h, samples using γ-Al_2O_3 as a raw material had the greatest density (up to 3.25 g/cm^3, 91% of the theoretical density of MA) and the least porosity. It is worth noticing that the linear shrinkage of sample A (γ-Al_2O_3) sintered from 1000 °C to 1600 °C is always larger than that of samples B and C sintered at the same temperature and that no expansion occurred in sample A when heated at any temperature. The linear change of sample A is always larger than samples B and C because the density difference between MA and γ-Al_2O_3 is less than that between MA and α-Al_2O_3 or ρ-Al_2O_3. All the results show

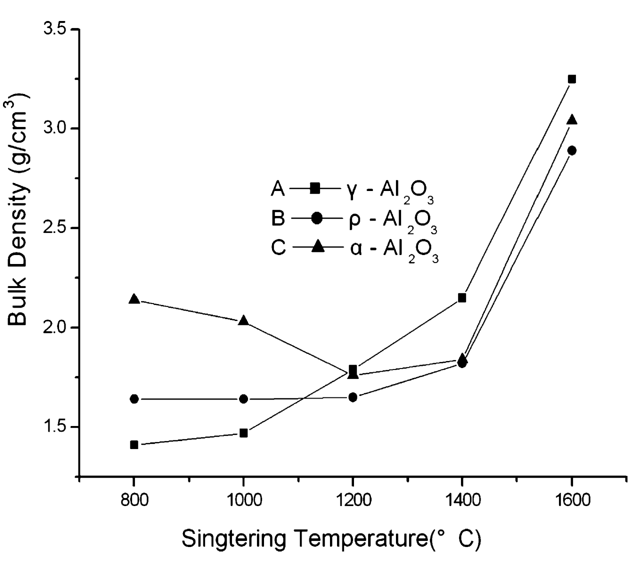

Fig. 3. Bulk density of samples as a function of sintering temperature.

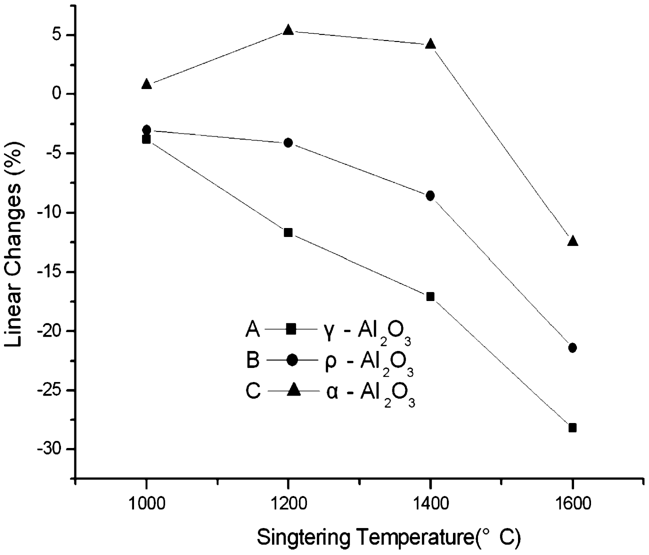

Fig. 5. Linear changes in samples as a function of sintering temperature.

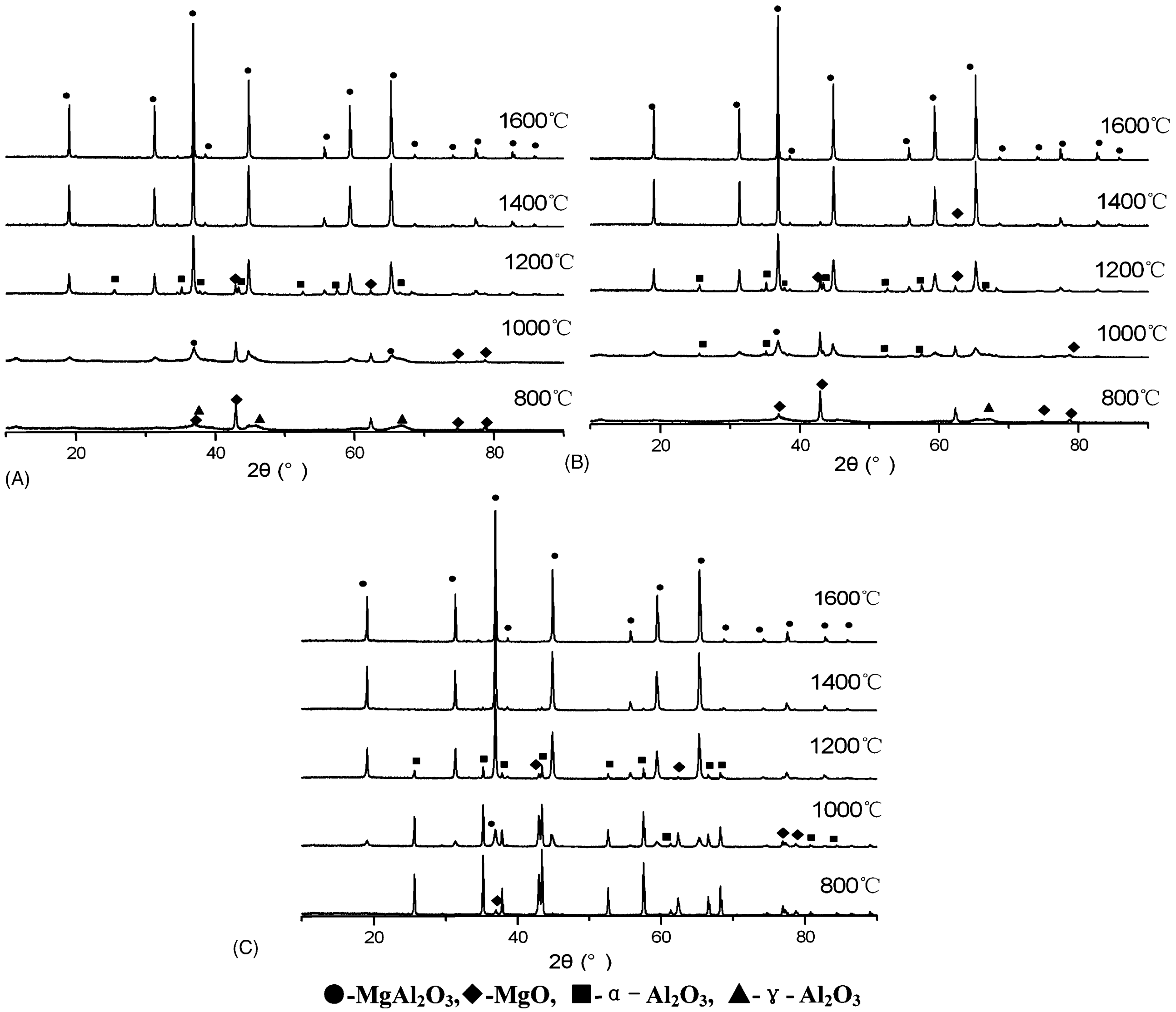

Fig. 6. XRD patterns for specimens sintered at different temperatures: (A) γ-Al_2O_3, (B) ρ-Al_2O_3 and (C) α-Al_2O_3.

that using γ-Al_2O_3 to synthesize MA is beneficial for densification. This is because during the formation of MA, using different Al_2O_3 sources brings about different volume changes. When calculated by density differences, while forming 1 mol of MA, an expansion of 2.93 cm^3 occurs when α-Al_2O_3 is used, but a volume shrinkage of 1.08 cm^3 occurs when γ-Al_2O_3 is used.

3.2. *Influence of polymorphism of Al_2O_3 on phase component*

From Fig. 6, there is no visible evidence to confirm the superiority of γ-Al_2O_3 for the formation of MA in samples heated at 800 °C. This is probably because γ-Al_2O_3 has a similar crystal structure to MA, so it is difficult to tell MA from γ-Al_2O_3 in X-ray diffraction patterns. After processing at 1000 °C, MA peaks appear in all samples, the peaks of α-Al_2O_3 are found only in the sample with ρ-Al_2O_3, and no α-Al_2O_3 peaks are found in the sample starting with γ-Al_2O_3.

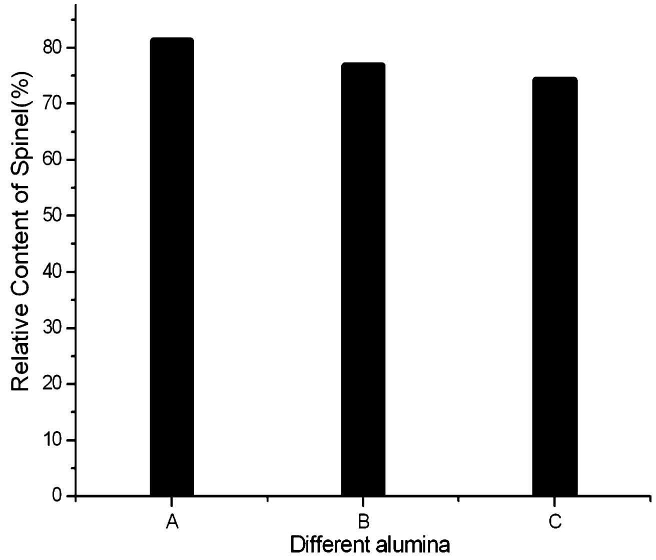

Fig. 7. Relative content of MA in samples sintered at 1200 °C.

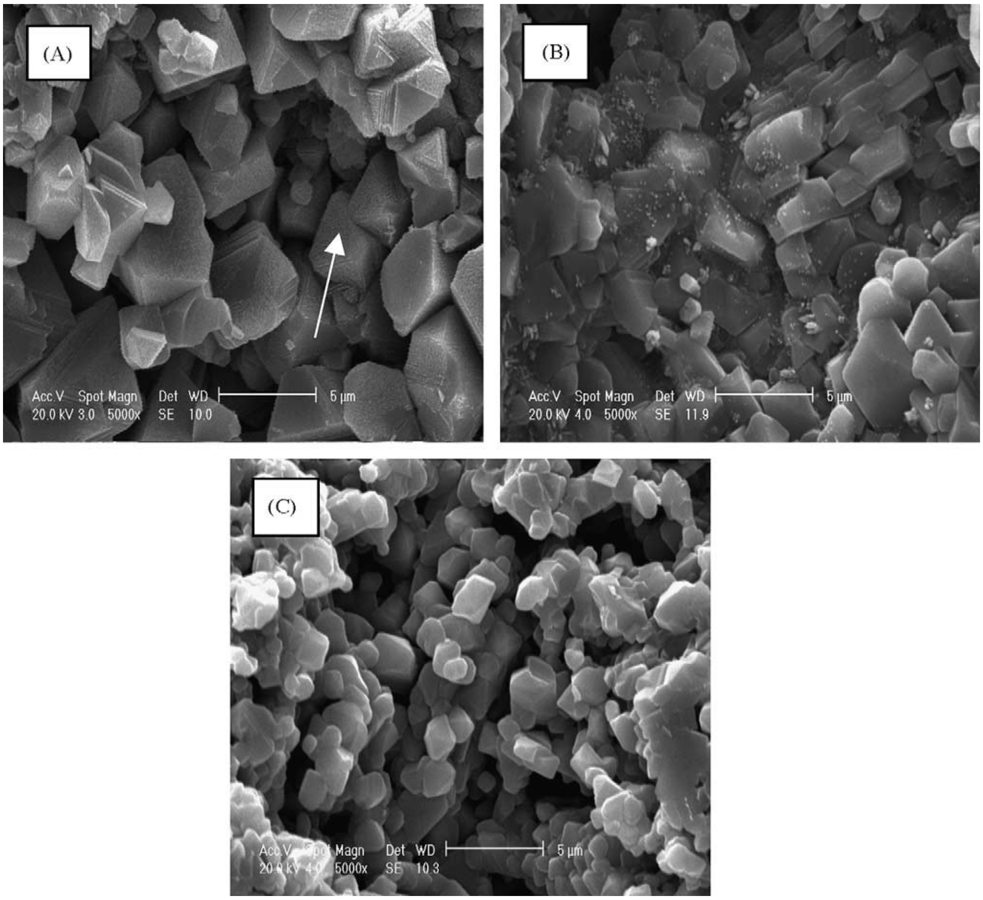

Fig. 8. SEM photographs of the samples sintered at 1600 °C for 3 h: (A) γ-Al_2O_3, (B)ρ-Al_2O_3 and (C) α -Al_2O_3.

Comparing X-ray diffraction patterns of the samples heated at 1200 °C, it is found that peak intensity of α-Al_2O_3 in the sample with γ-Al_2O_3 is the least. That means that most γ-Al_2O_3 has converted to MA, and that only a small amount of γ-Al_2O_3 has converted to α-Al_2O_3.

Fig. 7 gives the relative content of MA in the samples heated at 1200 °C containing different Al_2O_3 paramorphs. It is found that MA content in samples with γ-Al_2O_3 is more than that formed with α-Al_2O_3 and ρ-Al_2O_3 as a starting material. As the crystal structure of γ-Al_2O_3 is similar to crystal structure of MA, γ-Al_2O_3 is easy to convert to MA.

3.3. Influence of polymorphism of Al_2O_3 on microstructure

Scanning electron photomicrographs of the three samples sintered at 1600 °C for 3 h are shown in Fig. 8. It is noted in Fig. 8 that at the same sintering temperature, different samples have different grain size. The grain size of sample A varies from 3 µm to 5 µm. The grain size of sample B is between those of samples A and C. Sample C has the smallest grains, with a size less than 2 µm. All grain sizes were measured by the perlineal intercept method [20]. The sample with γ-Al_2O_3 has the largest MA grain size because the MA seeds in sample A form earlier than seeds in samples B and C and can grow to be larger than samples B and C. At the same time, the grain shape of MA in the samples made with different Al_2O_3 polymorphs is different. Sample A shows a column structure similar to boehmite crystal, and has clearly defined grain boundaries, and many full-grown (1 1 1) surfaces (arrowhead in Fig. 7A). Sample C has tabular shapes similar to gibbsite crystal. These differences come from the particle shape of hydroxides of aluminium that are used as raw materials used to produce the different aluminas (the starting particle shape of gibbsite is tabular and boehmite is columnar [16]). The alumina obtained by the decomposition of hydroxides keeps the contour of its particle shape, a pseudomorph, until MA is formed. This is the reason why the three samples made using different paramorphs of Al_2O_3 have different shapes of MA grains, and hints why the mechanism of MA formation may be that of Mg^{2+} diffusion into alumina.

4. Conclusions

The polymorph of Al_2O_3 influences the synthesis and sintering of MA. Of the three polymorphs studied, γ-Al_2O_3 was the best for the sintering and synthesis of MA because the starting crystal structure is similar to that of spinel and because shrinkage occurs during the reaction and formation of MA. The grain size of spinel in samples made from γ-Al_2O_3 was larger than those made of α-Al_2O_3 and ρ-Al_2O_3 because in the samples made from γ-Al_2O_3, MA seeds form at a low temperature and can grow in early sintering. The shape of MA grains in the samples made using different paramorphs is different because they keep the pseudomorph of alumina.

References

[1] J.E. Sheehan, J. Sigalovsty, J.S. Haggerty, J.R. Porter, Mechanical properties of $MgAl_2O_4$ single crystal fibers, Ceram. Eng. Sci. Proc. 14 (7/8) (1993) 660–670.

[2] H.S. Tripathi, B. Mukherjee, S. Das, M.K. Haldar, S.K. Das, A. Ghosh, Synthesis and densification of magnesium aluminate spinel: effect of MgO reactivity, Ceram. Int. 29 (2003) 915–918.

[3] G. Baudin, R. Martinez, P. Pena, High-temperature mechanical behavior of stoichiometric magnesium spinel, J. Am. Ceram. Soc. 78 (7) (1995) 1857–1862.

[4] W. Bakkar, J.G. Lindsay, Reactive magnesia spinel, preparation and properties, Am. Ceram. Soc. Bull. 46 (11) (1967) 1094–1097.

[5] D.J. Bary, Toxicity in chromium compounds formed in refractories, Am. Ceram. Soc. Bull. 64 (7) (1985) 1012–1016.

[6] E. Ryshkewitch, Oxide Ceramics, Academic Press, New York, 1960, pp. 257–274.

[7] C.T. Wang, L. Lin, S. Yang, Preparation of $MgAl_2O_4$ spinel powders via freeze-drying of alkoxide precursors, J. Am. Ceram. Soc. 75 (8) (1992) 2240–2243.

[8] O. Varnier, N. Hovnanian, A. Larbot, P. Bergez, L. Cot, J. Charpin, Sol–gel synthesis of magnesium aluminum spinel from a heterometallic alkoxide, Mater. Res. Bull. 29 (1994) 479–488.

[9] G. Gusmano, P. Nunziante, E. Traversa, G. Chiozzini, The mechanism of $MgAl_2O_4$ spinel fomation from the thermal decomposition of coprecipitated hydroxides, J. Eur. Ceram. Soc. 7 (1991) 31–39.

[10] L.B. Kong, J. Ma, H. Huang, $MgAl_2O_4$ spinel phase derived from oxide mixture activated by a high-energy ball milling process, Mater. Lett. 56 (2002) 238–243.

[11] R.E. Carter, Mechanism of solid state reaction between MgO–Al_2O_3 and MgO–Fe_2O_3, J. Am. Ceram. Soc. 44 (3) (1961) 116–120.

[12] R. Sarkar, S.K. Das, G. Banerjee, Effect of attritor milling on the densification of magnesium aluminate spinel, Ceram. Int. 25 (1999) 485–489.

[13] R. Sarkar, A. Ghosh, S.K. Das, Reaction sintered magnesia rich magnesium aluminate spinel: effect of alumina reactivity, Ceram. Int. 29 (2003) 407–411.

[14] R. Sarkar, S.K. Das, G. Banerjee, Effect of additives on the densification of reaction sintered and presynthesised spinel, Ceram. Int. 29 (2003) 55–59.

[15] E. Kostic, S. Boskovic, S. Kis, Influence of fluorine ion on the spinel synthesis, J. Mater. Sci. Lett. 1 (12) (1982) 507–510.

[16] K. Wefers, C. Misra, Oxides and hydroxides of aluminum, Alcoa Technical Paper No.19, Revised, Aleo Laboratories, 1987.

[17] Y.J. Liu, J.J. Sun, W. Cao, Kinetic study of hydration of ρ-Al_2O_3, J. Chin. Ceram. Soc. 26 (6) (1998) 782–786.

[18] Y. Hongo, ρ-Al_2O_3 bonded castable refractories, Taikabutsu 4 (1988) 226–229.

[19] Y.C. Zheng, D.C. Xie, C.K. Zun, Phase X-ray Diffraction Analysis, Metallurgical Industry Publishing House, 1986, p. 156.

[20] J.C. Wrust, J.A. Nelson, Lineal intercept technique for measuring grain size in two phase polycrystalline ceramics, J. Am. Ceram. Soc. 55 (2) (1972) 109.