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Synthesis of porous Al_2TiO_5 ceramic by reaction sintering method

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In this paper, porous aluminum titanate (Al_2TiO_5) ceramic was fabricated by reaction sintering method using Al_2O_3 and TiO_2 as raw materials and corn starch as pore-forming agent. In order to decrease the decomposition and improve strength of porous Al_2TiO_5 ceramic, 5 wt % of Fe_2O_3 and 4 wt % of SiO_2 were added as modifying agents. The influences of sintering temperature and content of pore-forming agent on phase constitution, apparent porosity, compressive strength and elemental distributions of the sintered products were investigated. The results show that porous Al_2TiO_5 ceramics with apparent porosity about 45–48% can be produced by reaction sintering method at temperature of 1500°C for 2 h. The synthesis yield of pure Al_2TiO_5 can achieve more than 95% using 5 wt % Fe_2O_3 and 4 wt % of SiO_2 as modifying agents when sintering temperature was 1500°C. The distributions of Fe, Ti, Al and O are homogeneous in the grain, however majority of Si distributed in the grain boundaries of Al_2TiO_5 which is proved by the EMPA (elemental mapping image analysis).

Key-words : Reaction sintering, Porous ceramic, Al_2TiO_5

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1. Introduction

Aluminum titanate is one of the most excellent ceramic with low thermal expansion coefficient and high temperature resistance. Its melting point and thermal expansion coefficient is about 1860 ± 10°C and $1.5 \times 10^{-6}\,K^{-1}$, respectively.[1] Additionally because it has excellent thermal shock resistance, low elastic modulus, good corrosion resistance, slagging resistance and alkali resistance properties, it has been widely used in many fields, such as corrosion resistant coating, anti-oxidation coating and thermal barrier coating under high temperature,[2),3)] refractory materials and structural materials in the metallurgical industries and automotive industries.[4)–6)] However, practical applications of this material have been severely restricted because of two major limitations, low sintering strength and decomposition in temperature range 750 to 1300°C.[7),8)] Therefore, many researches have been done to overcome these two major limitations. Some thermal stabilizers, such like SiO_2,[9)] MgO,[10)] Fe_2O_3 and $FeTiO_3 + Fe_2O_3$[10)] had been used to improve the stabilization of Al_2TiO_5. The results show that Si^{4+} can inter into the oxygen octahedra in the structure of Al_2TiO_5 forming interstitial solid solution, which can restrain the decomposition of Al_2TiO_5.[9)] When Fe_2O_3 was added, a transitional phase with the composition of Fe_2TiO_5 is obtained firstly, which can be used as the crystal nucleus for Al_2TiO_5. Then the synthesis temperature of Al_2TiO_5 is decreased effectively.[6),10)]

Based on the excellent physicochemical properties of Al_2TiO_5, porous Al_2TiO_5 ceramic will be a promising candidate for use as high temperature flue gas filtration supporter and substrates in catalytic converters for motor vehicles. In this paper, porous Al_2TiO_5 ceramic was synthesized by reaction sintering method, using Al_2O_3 and TiO_2 as the raw material, SiO_2 and Fe_2O_3 as modifying agents, corn starch as a pore forming agent, respectively. At the same time, the influences of different sintering temperatures and pore forming agent (corn starch) on the properties of porous Al_2TiO_5 ceramic were studied.

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2. Experimental procedures

The starting materials used were as follows: α-Al_2O_3 of analytically pure with the grain diameter of 10–30 μm, TiO_2 of analytically pure with the grain diameter of 2–10 μm. Analytically pure graded SiO_2 and Fe_2O_3 were used as modifying agents, and spherical corn starch with grain diameter of 5–20 μm was used as pore-forming agent.

Firstly, raw materials were mixed homogeneously according to the stoichiometry of Al_2TiO_5 with mole ratio between α-Al_2O_3 and TiO_2 of 1:1. In addition 5 wt % of Fe_2O_3 and 4 wt % of SiO_2 were added as modifying agents respectively. The powders were mixed by wet-milling using water or anhydrous ethanol and alumina balls for 2–3 h. The resulting powders after drying were mixed homogeneously with different contents of corn starch by dry mixing method, the contents of corn starch are shown in **Table 1**. Subsequently, the mixed powders were pressed into 20 mm diameter cylinders by uniaxial pressing at 50 MPa using polyvinyl alcohol (PVA) solution as binder. Finally all the green bodies were dried and sintered in air with proper temperature-programmed to the temperature of 1400, 1450 and 1500°C for 2 h by using a chamber electric furnace, respectively. Five such specimens for each composition were tested to obtain an average apparent porosity and compressive strength.

Phase composition was observed using X-ray diffraction (XRD) on a D/MAX-YB model (Japan Rigaku) X-ray diffractometer with Cu Kα radiation and a scanning speed of 0.5°/min. The morphologies of the sintered specimens were observed by scanning electron microscopy (SEM) (KYKY-2800B). The

Table 1. Content of pore-forming agent and experimental scheme

Sample	Mass of the raw materials $Al_2TiO_5 + SiO_2 + Fe_2O_3$ (wt %)	Corn starch (wt %)
1	100.00	0.00
2	90.90	9.10
3	86.96	13.04
4	83.30	16.70
5	80.00	20.00
6	76.90	23.10

elemental mapping images were analyzed by electron probe micro-analysis (EPMA) on a JXA-8230 model electron probe. The apparent porosity was calculated using Archimedes principle. The compressive strength was measured using WDW3100 model dynamic universal testing machine, and the speed of cross-beam is 2 mm/min. The synthesis weight percent of pure aluminum titanate could be calculated by using the formula $\alpha = I^{(110)}_{Tio_2}/(I^{(110)}_{Tio_2} + I^{(023)}_{Al_2Tio_2}) \times 100\%$.[11)]

3. Results and discussion

3.1 Phase constitution

Figure 1 shows the XRD patterns of products sintered at different temperatures from 1400 to 1500°C for 2 h with 20 wt% content of pore-forming agent. The X-ray analysis shows that diffraction peaks are migrated a little compared with pure phase of Al_2TiO_5, and the main phase should be solid solution of $Al_{2(1-x)}Fe_xTiO_5$ according to the JCPDS Card File 41-0258 for Al_2TiO_5, and no SiO_2 and Fe_2O_3 phase were observed. The calculated synthesis weight percent of pure phase Al_2TiO_5 is about 95% at temperature of 1500°C.[11)]

3.2 Microstructure analysis

Figure 2 shows the fracture surface of porous Al_2TiO_5 ceramic with 20 wt% content of pore-forming agent sintered at different temperatures. A lot of unequal connective pores with the sizes of 50–200 µm are clearly observed in the sample [Fig. 2(a)], and the pore size changed a little with increasing of calcined temperature, as shown in Fig. 2(b), which are mostly formed from the burning of agglomerated corn starch. The SEM micrograph in **Fig. 3** displays the fracture surface after the test of compressive strength. From Figs. 3(c) and 3(d), we can see that most of the large pore walls collapsed after the test of compressive strength. However some little pores with the size of 2–6 µm still existed in the framework of pore structure, which indicated that the sample has a double-pore structure. The double-pore structure is distributed in discrete size ranges of 50–200 and 2–6 µm. From

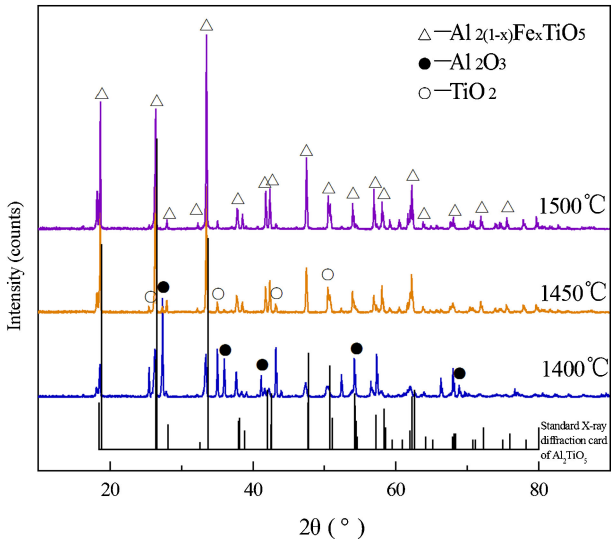

Fig. 1. (Color online) XRD patterns of products sintered at different temperatures. (a) 1400°C, (b) 1450°C, (c) 1500°C.

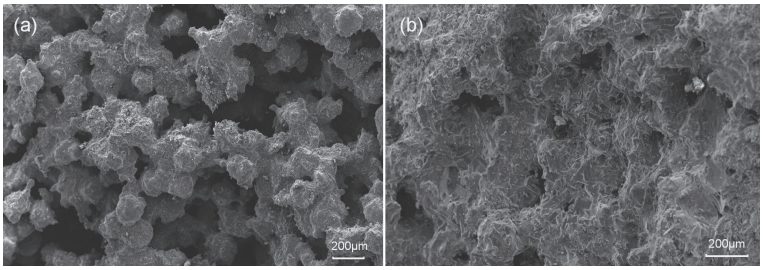

Fig. 2. Morphology of fracture surface of porous Al_2TiO_5 with 20 wt% content of pore-forming agent (a) 1400°C, (b) 1500°C.

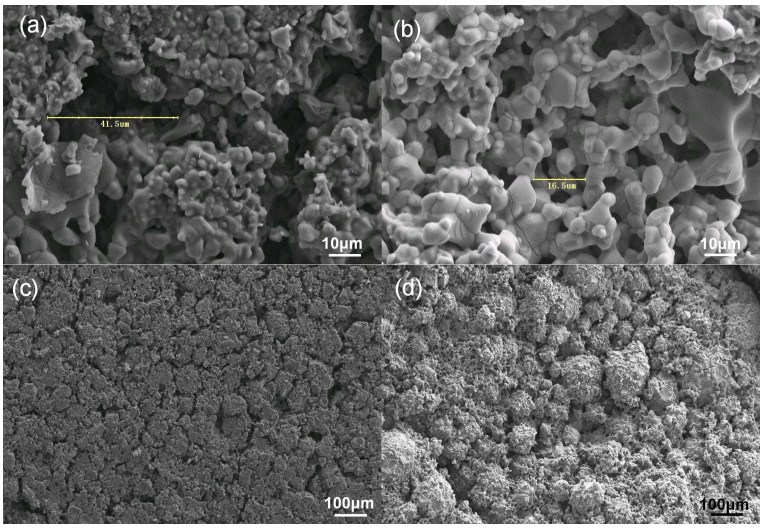

Fig. 3. (Color online) Hole morphology of fracture surface after compressive testing (a) 1400°C (1000×), (b) 1500°C (1000×), (c) 1400°C (100×), (d) 1500°C (100×).

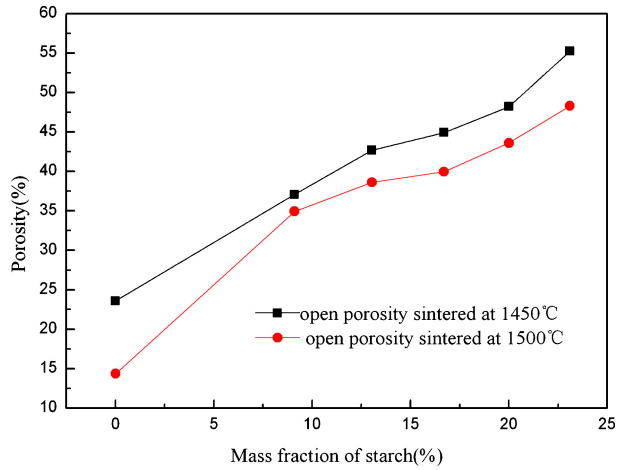

Fig. 4. (Color online) Curve of relationship between apparent porosity and contents of corn starch.

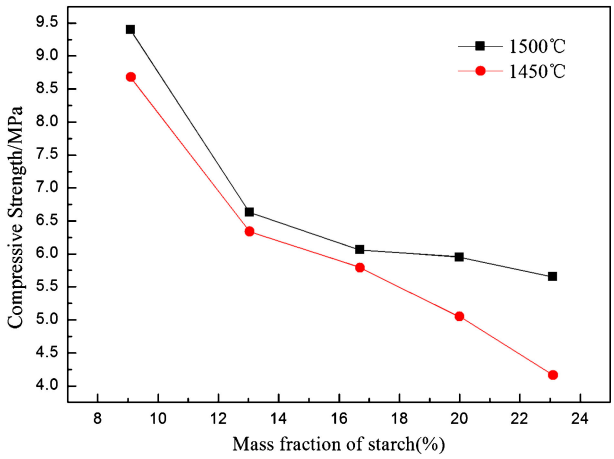

Fig. 5. (Color online) Curve of relationship between compressive strength and contents of corn starch.

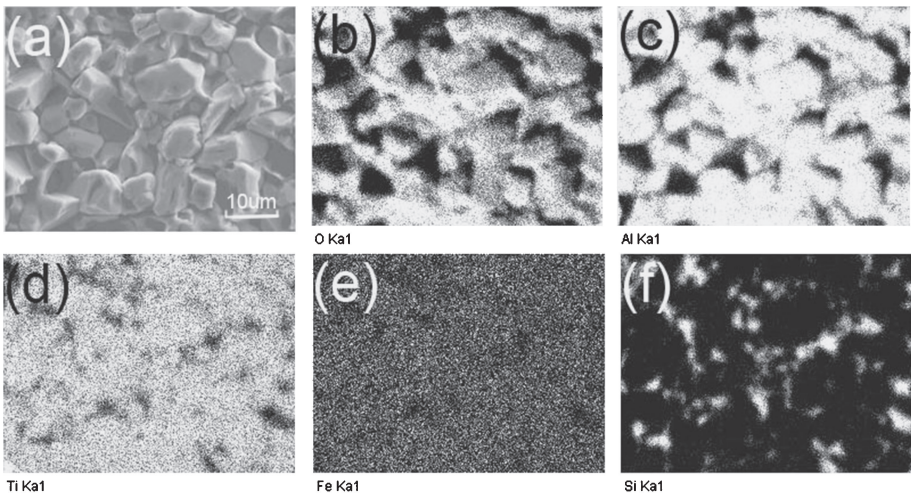

Fig. 6. Secondary electron morphology by EPMA and elemental distributions analysis of Al_2TiO_5 sintered at 1450°C. (a) secondary electron morphology, (b) O Kα1, (c) Al Kα1, (d) Ti Kα1, (e) Fe Kα1, (f) Si Kα1.

Fig. 3(b) we can see that the pores with the size of 2–6 μm were formed by grains packing.

3.3 Apparent porosity and compressive strength

Figure 4 shows the curves of relationship between apparent porosity and contents of corn starch under different temperatures. The apparent porosity increases linearly with the content of corn starch approximately. The apparent porosity can be 55.23% high when the content of pore-forming agent is 23.1 wt %. However, the surface of the sample is badly cracked, which is caused by the volatilization of large number of corn starch. In order to avoid the breakage caused by volatilization of pore-agent, the content of corn starch should be less than 20 wt %. **Figure 5** shows the curves of relationship between compressive strength and contents of corn starch under different temperatures. The compressive strength increases with the increasing of sintering temperature, but decreasing obviously with the increasing of content of corn starch. It is because of the high apparent porosity which affects the compressive strength of the sample. Therefore porous Al_2TiO_5 with compressive strength of 7 MPa and apparent porosity of 45–48% could be obtained using 20 wt % corn starch as pore-forming agent.

3.4 Elemental distribution analysis

Figure 6 shows the secondary electron morphology and EPMA elemental mapping images of the specimen of Al_2TiO_5 sintered at temperature of 1450°C for 2 h. The sintered specimen is composed of irregular particle shape grains, as shown in its secondary electron morphology. Five elements of Al, Ti, Si, Fe and O are observed in the grain by the X-ray photoelectron spectroscopy analysis (XPS), and elemental mapping images shows that distributions of Fe, Ti, Al, O are homogeneous in the grain, however the distribution of Si is mainly enriched in the boundary corner of the grains. Combined with the phase diagram of $FeO–SiO_2$, conclusions can be drawn that during the calcining process, corn starch are decomposed firstly, and with temperature increasing the carbon are burned, which can produce large amounts of heat and a reducing atmosphere, and then Fe_2O_3 will be reduced to FeO partially, which contributed to the formation of low melting point liquid phase of fayalite ($2FeO·SiO_2$), melting point of which is only 1220°C, so that it has good fluidity and could pervade between particles easily promoting diffusion of solid-state reaction sintering. Therefore, the majority of Si distributed in grain boundaries of Al_2TiO_5 after the sintering process.

4. Conclusions

Porous Al_2TiO_5 ceramic with apparent porosity of 45–48% was obtained by reaction sintering method at temperature of 1500°C for 2 h, using Al_2O_3 and TiO_2 as raw materials, Fe_2O_3 and SiO_2 as modifying agents, 20 wt % content of corn starch as pore-forming agent, respectively. The X-ray analysis shows that the main phase should be solid solution of $Al_{2(1-x)}Fe_xTiO_5$ when 5 wt % Fe_2O_3 and 4 wt % of SiO_2 were used as modifying agents, and no SiO_2 and Fe_2O_3 phase were observed. The calculated synthesis yield of pure phase Al_2TiO_5 could reach 95% at temperature of 1500°C for 2 h. The result of elemental mapping image analysis shows that Fe is distributed homogeneous in grains, however Si is mainly enriched in the boundary corner of grains. The sintered product has a double-pore structure, which is distributed in discrete size ranges of 50–200 and 2–6 μm.

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References

1) Y. X. Huang, A. M. Senos and J. L. Baptista, *J. Mater. Res.*, 15, 357–363 (2000).
2) B. Normand, V. Fervel, C. Coddet and V. Nikitine, *Surf. Coat. Tech.*, 123, 278–287 (2000).
3) W. H. Jiang, G. Feng, J. M. Liu, X. Y. Tan and Y. Yu, *J. Chin. Ceram. Soc.*, 38, 783–787 (2010).
4) A. R. Studart, U. T. Gonzenbach, E. Tervoort and L. J. Gauckler, *J. Am. Ceram. Soc.*, 90, 16–22 (2007).
5) K. Ishizaki, S. Komarneni, M. Nanko, Porous Materials: Process Technology and Applications, Kluwer, Norwell (1998).
6) H. R. Rezaie, R. Naghizadeh, N. Farrokhnia, S. Arabi and M. Sobhani, *Ceram. Int.*, 35, 679–684 (2009).
7) R. D. Skala, D. Li and I. M. Low, *J. Eur. Ceram. Soc.*, 29, 67–75 (2009).
8) S. Bueno, R. Moreno and C. Baudin, *J. Eur. Ceram. Soc.*, 24, 2785–2791 (2004).
9) Y. Shen and Y. Z. Ruan, *Bull. Chin. Ceram. Soc.*, 27, 1221–1229 (2008).
10) T. Korim, *Ceram. Int.*, 35, 1671–1675 (2009).
11) A. R. Studart, U. T. Gonzenbach, E. Tervoort and L. J. Gauckler, *J. Am. Ceram. Soc.*, 90, 16–22 (2007).