

Influence of Sintering Additives on the Porous Structure and Mechanical Properties of Porous Alumina

Ảnh hưởng của phụ gia thiêu kết đến cấu trúc và cơ tính của nhôm oxit xốp

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Received: January 10, 2017; accepted: June 9, 2017

Abstract

The aim of the present work is to investigate and to compare the influence of the two sintering additives Cr_2O_3 and TiO_2 on the porous structure and the mechanical properties of the sintered porous alumina. Alumina based porous ceramics were fabricated by sacrificial template technique via powder metallurgy route from alumina powder using ammonium bicarbonate $(NH_4)HCO_3$ as the pore former. The results showed that the use of sintering additives led to a remarkable enhancement of the bonding between alumina particles hence the strength of the alumina based porous ceramics. Between the two sintering additives, TiO_2 was more effective in aiding sintering (densification) of alumina than Cr_2O_3 . Consequently, the sintered porous alumina using TiO_2 as sintering additive has a smaller pore size, 190–30 μm compared to 220–40 μm of that with Cr_2O_3 , and lower porosity. The porosity of the sintered samples increased with the concentration of the pore-forming agents and reaches the highest value of 79.3 % and 82.6% corresponding to TiO_2 and Cr_2O_3 used. The mechanical strength of the porous alumina varied inversely with porosity.

Keywords: Porous alumina, Titanium dioxide, Chromium oxide, Sintering additive

Tóm tắt

Bài báo trình bày nghiên cứu vai trò và so sánh sự ảnh hưởng của hai loại phụ gia thiêu kết TiO_2 và Cr_2O_3 đến cấu trúc và tính chất cơ học của gốm xốp nhôm oxit sau thiêu kết. Vật liệu gốm xốp nhôm oxit được chế tạo bằng kỹ thuật mẫu chảy thông qua phương pháp luyện kim bột từ bột nhôm oxit ban đầu sử dụng bột muối ammoni cacbonat đóng vai trò chất tạo xốp. Kết quả nhận được chứng minh việc sử dụng phụ gia thiêu kết làm tăng đáng kể liên kết giữa các hạt bột nhôm oxit và qua đó làm tăng mạnh độ bền của mẫu sau thiêu kết. Trong hai phụ gia thiêu kết sử dụng, TiO_2 hiệu quả hơn trong việc tăng khả năng thiêu kết của vật liệu. Do vậy, mẫu nhôm oxit xốp sử dụng TiO_2 làm phụ gia thiêu kết có kích thước lỗ xốp nhỏ hơn (190–30 μm so với 220–40 μm của mẫu sử dụng Cr_2O_3) và có tỷ phần xốp ít hơn. Độ xốp của mẫu sau thiêu kết tỷ lệ thuận với hàm lượng chất tạo xốp và đạt giá trị cao nhất là 79,3 % và 82,6% tương ứng với phụ gia thiêu kết TiO_2 và Cr_2O_3 . Độ bền của mẫu tỷ lệ nghịch với độ xốp đạt giá trị cao hơn đối với các mẫu sử dụng phụ gia thiêu kết TiO_2 .

Từ khóa: nhôm oxit xốp, oxit titan, oxit crom, phụ gia thiêu kết

1. Introduction

Advanced porous ceramics have been utilized in a broad range of applications in environmental, biological, and transportation issues [1]. Ceramic materials possessed many advantages over other materials such as polymers or metals. The properties of hardness, chemical inertness, thermal shock resistance, corrosion and wear resistance, and low density are essential to many applications [2-3].

Porous ceramics could be prepared through many processing techniques divided into three basic routes: replica, sacrificial template, and direct foaming [3]. Among the processing techniques,

sacrificial template method appears to be the most effective method for processing foams intended for thermal insulation applications. For highly porous ceramics, the relatively high mechanical strength could be attainable by this method with a relatively well established microstructure. The sacrificial template processing technique incorporates pore former to act as a place holder within the ceramic powder or slurry. Once the green body is formed, the pore former is removed to leave behind the empty pores [3]. Powder metallurgy is one of the widely used methods within sacrificial template route. The process consists of applying a pressure uniaxially or isostatically to form a green body. Whatever the compaction process, the pore former is uniformly mixed to the starting powder before compaction and is eliminated during sintering step [4].

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Recently, alumina is the most commonly used ceramic material. It possesses high temperature stability and low thermal conductivity that are requirements for thermal insulators. Porous alumina could be processed by a partial sintering method without pore former. However, partial sintered products usually possess random microstructure and low porosity (<30%) [5]. High porosity could be attained using different pore formers such as wax spheres, naphthalene particles, PMMA, NaCl, starch... [6]. The porous fraction must be controlled in relation to mechanical strength, since these properties are generally inversely related.

The typical sintering temperature of pure alumina is approximately 1700°C in normal laboratory practice [7]. Experimentation have indicated that the sintering temperature of alumina can be lowered when small particles were used. On the other hand, the addition of certain sintering additives such as CuO₂, TiO₂, MgO và Cr₂O₃ could promote the sintering of alumina at temperatures below 1700°C [7,8]. These oxides could react with Al₂O₃ to form either solid solutions with defect lattices or intermediate phases that assist diffusional processes. Moreover, sintering additives not only enhance the sinterability of alumina but also significantly increase the mechanical properties of the sintered products.

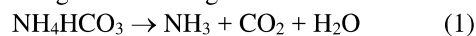
In our previous works, the results showed that the sinterability and the strength of the sintered alumina were considerably improved using Cr₂O₃ and TiO₂ as sintering additives with the suitable concentration of 0.5 and 1.0 wt.%, respectively. In the present work, highly porous alumina was prepared via powder metallurgy method using ammonium bicarbonate (NH₄HCO₃) as the pore former and Cr₂O₃ or TiO₂ as sintering additive. The aim of our research work is to investigate and to compare the role of the two sintering additives on the porous structure and the mechanical properties of the sintered porous alumina.

2. Experimental procedure

The Al₂O₃ starting powder (Xilong Ltd., China) was of 99.5% purity with an average particle size of 8 μm. The sintering additives were chromium oxide Cr₂O₃ powder (99.9%) and titanium oxide TiO₂ powder (99%) with an average particle size of 4 μm, purchased from Xilong Ltd., China. Powder mixtures of 99.5 wt.% Al₂O₃ + 0.5 wt.% Cr₂O₃ and 99.0 wt.% Al₂O₃ + 1.0 wt.% TiO₂ were ball-milled for 24 h using highly pure Al₂O₃ balls prepared in a highly pure ethanol solution and, then dried in an oven at 110°C for 3h. The obtained powder mixtures were then mixed with the pore former using a dried ball-mixing for 3h. Ammonia bicarbonate (NH₄HCO₃)

powder was used as pore formers. In order to investigate the influence of the pore former concentration on the porosity and properties of the sample, the fraction of the pore former was varied from 30 to 80 vol.%. The green pellets were formed by uniaxial pressing in a 20 mm diameter cylindrical steel die with a pressure of 300 MPa.

The green pellets were annealed at 200°C for 2h to totally eliminate the pore former and at 500°C for 1h to remove the PVA binder. At 200°C, ammonium bicarbonate (NH₄HCO₃) was thermally decomposed according the following reactions:



Finally, the pellets were sintered in an electrical resistance heating furnace (HT1600, Linn, Germany) at 1550°C for 4 hours in argon atmosphere.

The densities of green pellets were determined from the weight and volume. Average of the 3 density measurements were taken into consideration. The apparent porosity, bulk density of sintered pellets was measured according to Archimede's principle. First the dry weight of pellets was measured. Then they were soaked in distilled water kept inside a beaker and were evacuated in a vacuum evacuator till all the air bubbles vanished. After removing from vacuum evacuator, the suspended weight and soaked weight of the samples were determined. Porosity in % of the sintered pellets were calculated according to the following formula:

$$\text{Porosity} = (\text{soaked weight} - \text{dry weight}) * 100 / (\text{soaked weight} - \text{suspended weight}).$$

The morphology and EDX analysis were carried out on fracture surface using a scanning electron microscopy (JOEL). The compressive and the bending strengths were tested on MTS 300 according to JIS-R 1608-2003 và JIS-R 1664-2004 standards, respectively.

3. Results and Discussion

The SEM of the Al₂O₃ samples sintered at 1550°C for 4h without and with different sintering additives of 0.5% Cr₂O₃ or 1.0% TiO₂ were shown in Figure 1. When sintering additive was not used (Figure 1a), a very poor bonding was observed at the Al₂O₃ grain boundary. On the other hand, the particle bonding was significantly enhanced with the addition of 0.5% Cr₂O₃ (Figure 1b) or 1.0% TiO₂ (Figure 1c) as sintering additives, especially, in the case of TiO₂. The microstructure of the sintered samples showed a good adhesion at the grain boundary. The obtained results indicated the effectiveness of Cr₂O₃ and TiO₂ in sintering of Al₂O₃. The improvement of the sinterability could be explained by the presence of the intermediate phases on the Al₂O₃ particle surface

when sintering additives were used. These intermediate phases were formed from the solid state reactions between Al_2O_3 and Cr_2O_3 or TiO_2 during sintering process. According to the binary phase diagram of $\text{Al}_2\text{O}_3/\text{Cr}_2\text{O}_3$, the oxides possess the same crystal structure having a hexagonal structure and therefore, could be reacted to form solid solution ($\text{Al}_{2-x}\text{Cr}_x\text{O}_3$) in the whole range composition [9]. In the case of $\text{Al}_2\text{O}_3\text{-TiO}_2$ system, it is reported [10] that the solid solubility of TiO_2 in Al_2O_3 is too small. The solid solution of TiO_2 in Al_2O_3 was found at $>1150^\circ\text{C}$, and the solubility was 0.27% at 1700°C . Beyond the solubility limit, excess TiO_2 coexisted with Al_2O_3 as rutile below 1350°C and as Al_2TiO_5 above 1450°C . The existences of the intermediate phases could not be validated using XRD method due to their low fraction. However, elemental analysis by energy dispersive X-ray (EDX) revealed the existence of Cr or Ti on the surface particle. Besides, the formation of the intermediate phases was also recognized through the colors of the sintered samples (Figure 2). The white color of without-sintering-additive sample turns to pink and grey color corresponding to the addition of Cr_2O_3 and TiO_2 , respectively. The change of the sample color was totally in agreement with the references [11-13].

The porosity and the mechanical properties of the sintered samples without and with sintering additives were showed in Table 1. The addition of sintering additives led to a good bonding between the particles and consequently, enhanced the densification of the samples after sintering. It could be attributed to the lower porosity and much higher compressive and bending strengths of the samples with sintering additives compared to that of sample containing Al_2O_3 alone. The results also prove that TiO_2 is more effective than Cr_2O_3 in aiding sintering of Al_2O_3 . The strength of the sample with TiO_2 was superior than that with Cr_2O_3 .

Table 1. Porosity, bending and compressive strengths of sintered Al_2O_3 without and with sintering additives of 0.5% Cr_2O_3 or 1.0% TiO_2

Sample	Porosity (%)	Bending strength (MPa)	Compressive strength (MPa)
Al_2O_3	39 ± 3	45.2	66.2
$\text{Al}_2\text{O}_3 + 0.5\% \text{Cr}_2\text{O}_3$	38 ± 4	82.0	99.6
$\text{Al}_2\text{O}_3 + 1.0\% \text{TiO}_2$	30 ± 3	128.3	368.5

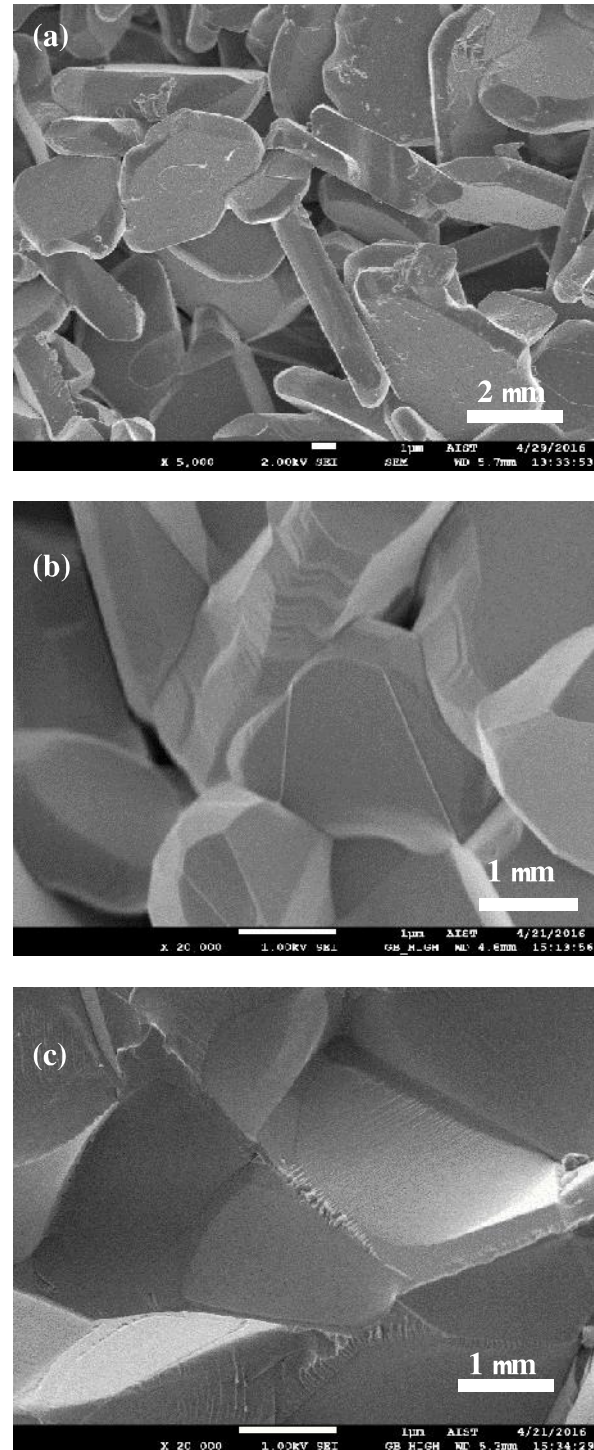


Fig. 1. SEM images of the Al_2O_3 based ceramics sintered at 1550°C for 4h (a) without and with sintering additives of (b) 0.5% Cr_2O_3 (c) 1% TiO_2

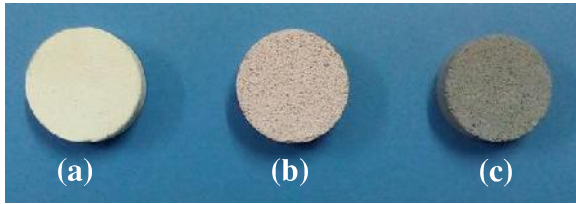


Fig. 2. Images of the Al_2O_3 based ceramics (a) without and with sintering additives of (b) Cr_2O_3 and (c) TiO_2

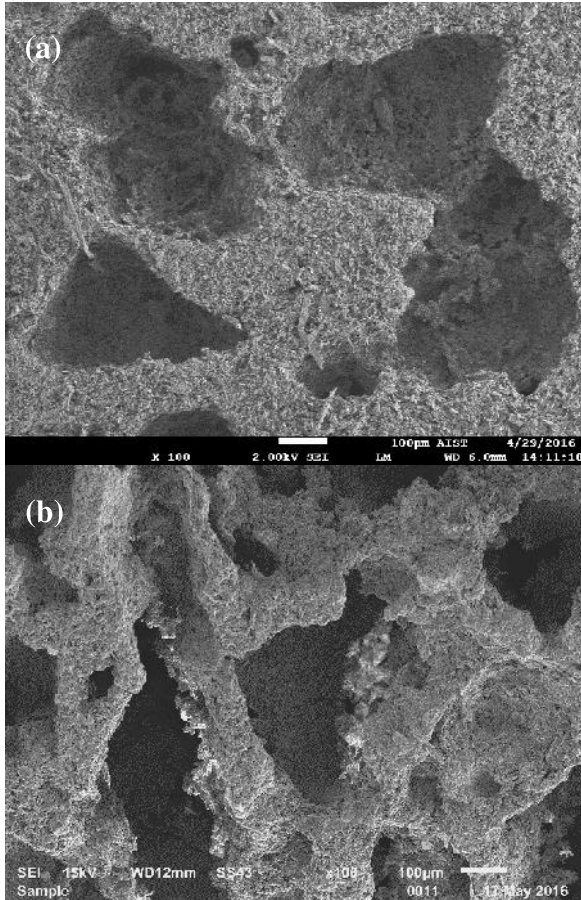


Fig. 3. SEM images of the porous alumina sintered at 1550°C for 4h using sintering additives of (a) Cr_2O_3 (b) TiO_2 with 80 vol% of the pore former ammonium bicarbonate $(\text{NH}_4)\text{HCO}_3$ 80%

SEM images of porous samples fabricated using 80 vol.% of $(\text{NH}_4)\text{HCO}_3$ as the pore former with different sintering additives were shown in Figure 3. Whatever the sintering additive has been used, the samples have irregular pore. However, the average pore size was change with different sintering additives. The pore sizes and pore size distribution of each sample were determined from the corresponding SEM images using ImageJ software. When TiO_2 was used, samples have the average pore size of $190 \pm 30 \mu\text{m}$ which is smaller than that with Cr_2O_3 showing $220 \pm 40 \mu\text{m}$. As can be seen, the pore shape and size

is different from the particle size and shape of the starting pore former. NH_4HCO_3 particles are spherical with the average size of $120 \mu\text{m}$. This phenomena could be performed due to several reasons. They include the agglomeration of the pore former particles during powder mixing, the pressure increasing during pore former removal or the densification of the sample volume during sintering process.

In order to investigate the influence of the pore former concentration on the porosity and the strength of the porous sample, the volume fraction of the pore former was varied from 30 to 80 %. Figure 4 exhibits the porosity of the sintered samples with different sintering additives, Cr_2O_3 and TiO_2 , as a function of the pore former concentration. As can be seen, the porosity of the sample increases with the pore former concentration. When the pore former concentration was increased from 0 to 80 vol.%, the porosity of the sintered sample using Cr_2O_3 as sintering additive increased from 38.0 to 82.6% which is higher than that using TiO_2 going from 28.9 to 79.3%. When the pore former excess 80 vol.%, the samples were collapsed after pore former elimination process whatever sintering additive was used.

Figure 5 shows the compressive strength of the sintered samples as a function of pore former concentration. As expected, higher porosity of the sintered sample leads to a lower compressive strength. As TiO_2 using as sintering additive, when the porosity increases from 29.8 to 78.3% corresponding to the pore former concentration going from 0 to 80%, the compressive strength drastically decreases from 368.5 to 1.4 MPa. On the other hand, the compressive strength of the sintered porous alumina using Cr_2O_3 as sintering additive also decreased from 99.6 to 0.9 MPa when the porosity increased from 38.0 to 82.6%.

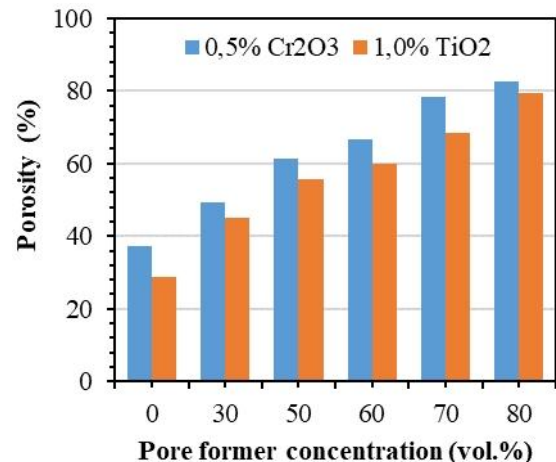


Fig. 4. Influence of the pore former concentration on the porosity of the porous alumina sintered at 1550°C for 4h using different sintering additives

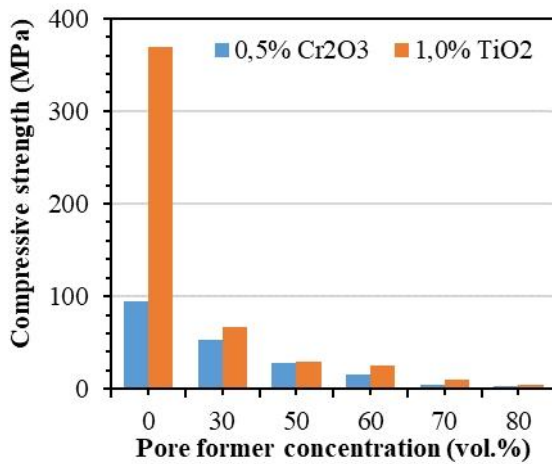


Fig. 5. Influence of the pore former concentration on the compressive strength of the porous alumina sintered at 1550°C for 4h using different sintering additives

The refractoriness of the porous alumina samples without and with different sintering additives were determined by Pyrometrics Cone Equivalent (PCE) test. PCE is measured by making a cone of the refractory and firing it until it bends and comparing it with the standard cone. The result showed that at the maximum temperature 1770°C of the equipment, no cones were bended, which indicated that the heat resistance of the samples are higher than 1770°C.

4. Conclusions

Sintering additives Cr₂O₃ and TiO₂ significantly enhanced the sinterability of alumina at 1550°C and improved the mechanical properties of the products, especially, in the case of TiO₂. Porous alumina prepared by powder metallurgy using NH₄HCO₃ as pore former and TiO₂ as sintering additive has lower porosity, smaller pore size and higher strength than that using Cr₂O₃. The porosity of the sintered porous alumina increased with the concentration of the pore former. However, the strength of the sample changed inversely with the porosity. The heat resistance of the sintered porous alumina are higher than 1770°C whatever sintering additives were used.

Acknowledement

The authors sincerely thank to Dr. DO Minh Duc for the generous help in testing mechanical strength. This research is funded by Hanoi University of Science and Technology (HUST) under project number T2016-PC-151.

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