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Ceramics International 40 (2014) 2853–2856

CERAMICS INTERNATIONAL

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# Effect of $LiAlSiO_4$ particle size on the properties of LAS/SiC porous ceramics with near zero thermal expansion

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Received 31 July 2013; received in revised form 3 October 2013; accepted 7 October 2013
Available online 17 October 2013

## Abstract

Near zero thermal expansion porous ceramics were fabricated by using SiC and $LiAlSiO_4$ as positive and negative thermal expansion materials, respectively, bonded by glassy material. The microstructure, mechanical properties, and thermal expansion behavior of LAS/SiC porous ceramics with different particle sizes of $LiAlSiO_4$ were investigated. The results indicated that the coefficient of thermal expansion of the LAS/SiC porous ceramics decreased from $0.5206 \times 10^{-6}$ to $-1.1053 \times 10^{-6}\ K^{-1}$ with increasing the $LiAlSiO_4$ particle size from ~45 μm to ~125 μm. It was attributed to the reduction in the reaction between $LiAlSiO_4$ and $SiO_2$ as the particle size of $LiAlSiO_4$ increased. Young's modulus increased from 36 MPa to 54 MPa as the sintering temperature increased from 850 °C to 950 °C because of the good bonding between the SiC grains and the glass materials.

*Keywords:* C. Thermal expansion; Porous materials; $LiAlSiO_4$; Silicon carbide; Young's modulus

## 1. Introduction

Porous silicon carbide ceramics have attracted considerable interest because of their many advantageous properties, such as low bulk density, high permeability, high temperature stability, and high corrosion resistance [1]. In addition, low or zero coefficient of thermal expansion (CTE) opens additional applications for porous ceramic materials, such as microelectronics, optics, and high-precision machinery [2,3]. The combination of ceramics with positive thermal expansion and negative thermal expansion materials has been proposed to fabricate near-zero thermal expanding ceramic materials [4–6].

Among the negative CTE materials, β-eucryptite is expected to be the most promising useful material for developing the low CTE ceramic composites. The thermal behavior of β-eucryptite is highly anisotropic. β-Eucryptite was first characterized by Gillery [7], who found values of $\alpha_a = \alpha_b = +8.21 \times 10^{-6}\ K^{-1}$ and $\alpha_c = -17.6 \times 10^{-6}\ K^{-1}$ between room temperature and 800 °C. Dense LAS–SiC nano-composites [8], as well as LAS/Cu [9] and LAS/$Al_2O_3$ [10] composites, with very low CTE have recently been developed. However, thermal mismatch stress could be generated both in the reinforcement particles and in the matrix of the composites because of their different CTEs [11], which would deteriorate the mechanical properties [12] and affect the thermal expansion behavior of the composites [13].

Our group has developed low thermal expansion LAS/SiC porous ceramics using SiC as a positive thermal expansion material and $LiAlSiO_4$ as a negative thermal expansion material bonded by a glassy material [14–16]. However, the chemical reaction between the $LiAlSiO_4$ and $SiO_2$ has introduced $LiAlSi_2O_6$ into the composites because $LiAlSiO_4$ is metastable and easily decomposes or reacts with glassy materials. Subsequently, the CTE of the porous ceramics was inconsistent with the theoretical values [14,15]. There are two possibilities to decrease the reaction between $LiAlSiO_4$ and glassy materials: one is to sinter it at a temperature lower than

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http://dx.doi.org/10.1016/j.ceramint.2013.10.028

its decomposition temperature, and the other way is to increase the particle size of $LiAlSiO_4$. These two methods are combined in this study.

In the present research, near-zero thermal expansion LAS/SiC porous ceramics were fabricated through low-temperature sintering using $LiAlSiO_4$ with different particle sizes as the negative thermal expansion material. The effects of $LiAlSiO_4$ particle size and sintering parameter on the sintering behavior, Young's modulus and the CTE of LAS/SiC porous ceramics were investigated.

## 2. Experimental procedure

### 2.1. Synthesis of $LiAlSiO_4$

$LiAlSiO_4$ was synthesized by a solid-state reaction according to the following reaction: $Li_2CO_3+2SiO_2+Al_2O_3\rightarrow 2LiAlSiO_4+CO_2$. The mixture of $Li_2CO_3$ (Nacalai Tesque), $SiO_2$ (Nacalai Tesque), $Al_2O_3$ (Strem Aldrich) in a stoichiometric ratio were milled for 24 h in a polyethylene pot. The powder mixture was placed in an electrical furnace and sintered at 1000 °C for 4 h to eliminate the $CO_2$, after that, it was ground to homogenization; then, the powder was heated at 1100 °C for 12 h, after that, it was ground to homogenization and finally heated at 1200 °C for 12 h. All the powder was heated in air atmosphere with a heating rate of 300 K/h.

### 2.2. Preparation and characterization of LAS/SiC porous ceramics

According to modified Kelly's formula [17] includes porosity to predict thermal expansion of composites: $\alpha_c=(\alpha_1 v_1+\alpha_1 v_1+\alpha_1 v_1)(1-P)$, where $P$ is the total porosity of the composites. The calculated CTE values $\alpha=0$ and total porosity$=30\%$ were used under the condition where no decomposition of $LiAlSiO_4$ occurred during sintering. The CTE values of SiC, glassy materials and $LiAlSiO_4$ were 4.0, 4.6 and $-6.2\times10^{-6}\,K^{-1}$, respectively. The synthesized $LiAlSiO_4$ were sieved to 45, 90, and 125 μm, respectively. Commercial SiC powder with a particle mesh size of #120 (Showa Denko K.K, Japan), glassy material (median particle size 10 μm; Nano TEM Co. Ltd., Niigata, Japan), and $LiAlSiO_4$ with different particle sizes were mixed in volume fractions 34.31%, 25% and 40.69% respectively. The chemical composition of the glass materials was as follows: 61 mass% $SiO_2$, 24% $Al_2O_3$, 5% CaO, 2% $Na_2O$, 2% $K_2O$ and 6% other materials. The powder mixture was uniaxially pressed to a parallelepiped shape under 30 MPa for 1 min, and then isostatically cold pressed under 300 MPa for 1 min. The green bodies were sintered using the conventional sintering method at 850 °C for 2 h, 850 °C for 3 h, 900 °C for 1 h, and 950 °C for 1 h at a heating rate of 300 K/h.

Porosity and density were measured by the Archimedes method. The sintered samples were cut into bars with size of 5 mm × 5 mm × 50 mm for thermal expansion measurement in a dilatometer (ULVAC DLY 9200$^{TM}$) from $-19$ °C to 190 °C under a helium atmosphere with a heating and cooling rate of 12 K/min. Young′s modulus of all samples with a size of 1.2 mm × 5 mm × 50 mm were measured at room temperature by the resonant frequency technique (JE-RT, Nihon Techo-Plus Co. Ltd., Japan). The phase composition of the powder and the sintered samples was evaluated by X-ray diffraction (XRD, SHIMADZU XRD-6000$^{TM}$, Kyoto, Japan). The microstructure of the sintered samples was characterized by using scanning electron microscopy (SEM, VE-7800$^{TM}$, KEYENCE, Co. Ltd., Osaka, Japan).

## 3. Results and discussion

The diffraction pattern of the synthesized $LiAlSiO_4$ was in agreement with the X-ray diffraction (XRD) pattern reported for $LiAlSiO_4$, β-eucryptite (JCPDF77-0184). The powders had high purity and were well-crystallized, and the synthesized $LiAlSiO_4$ could be sieved to 45, 90, and 125 μm.

Fig. 1(a) shows the XRD patterns of LAS/SiC porous ceramics after sintering at 850 °C for 2 h, using $LiAlSiO_4$ with different particle sizes as negative thermal expansion material. Besides the SiC and $LiAlSiO_4$ phases, the spodumene ($LiAlSi_2O_6$) and $LiAlO_2$ phases have been detected. The results indicated that a part of $LiAlSiO_4$ was decomposed to $LiAlSi_2O_6$ and $LiAlO_2$ during sintering at 950 °C for 1 h according to the following reaction: $2LiAlSiO_4\rightarrow LiAlSi_2O_6+LiAlO_2$. On the

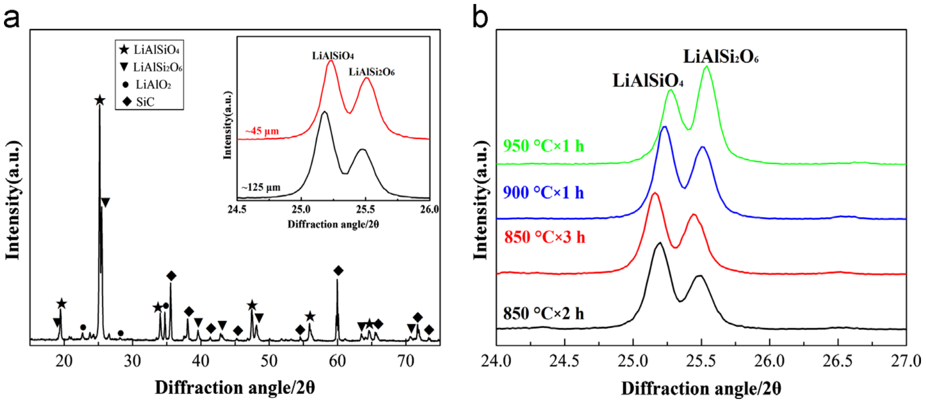

Fig. 1. XRD patterns of the LAS/SiC porous ceramics: (a) samples sintered at 850 °C using $LiAlSiO_4$ materials with different particle sizes and (b) samples sintered at different conditions.

other hand, a part of $LiAlSiO_4$ reacted with $SiO_2$ (oxide on the surface of SiC powder or in glass powder) to form $LiAlSi_2O_6$ according to the following reaction: $LiAlSiO_4 + SiO_2 \rightarrow LiAlSi_2O_6$ [16]. With the increase of the particle size of β-eucryptite in the starting powder from ~45 μm to ~125 μm, the peak intensity ratio of $LiAlSiO_4/LiAlSi_2O_6$ in the composites increased, which would contribute to the low coefficient of thermal expansion. It was indicated that the reaction of $LiAlSiO_4$ could be restrained by increasing the particle size of $LiAlSiO_4$ due to its small surface area.

Fig. 1(b) shows the XRD patterns of the LAS/SiC porous ceramics sintered at different temperatures using β-eucryptite with a particle size of ~125 μm. The peak of all the samples shows that the $LiAlSi_2O_6$ phase attributed to the chemical reaction during sintering. The peak intensity ratio of $LiAlSiO_4/LiAlSi_2O_6$ slightly decreased with increasing the holding time from 2 h to 3 h at 850 °C. In addition, the peak ratio of $LiAlSiO_4/LiAlSi_2O_6$ also slightly decreased with increasing the sintering temperature from 850 °C to 900 °C. However, when the sintering temperature increased to 950 °C, the peak intensity of $LiAlSi_2O_6$ was evidently higher than that of $LiAlSiO_4$, which indicated the reaction or decomposition of a large amount of $LiAlSiO_4$.

Fig. 2 shows the SEM micrographs of the LAS/SiC porous ceramics after being sintered under different conditions. As shown in it, the silicon carbide grains are embedded and distributed homogeneously in the glasses, and no β-eucryptite grains are observed, indicating that the β-eucryptite grains are covered by the glass materials. Small pores are distributed homogeneously in the glassy materials, and some large pores can be observed. The sample sintered at 850 °C exhibited poor bonding between the SiC particles and glassy bonding agent due to the high viscosity of glass materials at low sintering temperature, as shown in Fig. 2(a). However, the glassy bonding materials for samples sintered at 950 °C were melted and had good wet-ability with the SiC grains. The SiC particles were well bonded by the glassy materials due to the low viscosity of glass materials at high temperature, as shown in Fig. 2(b), which would contribute to the high mechanical properties of the porous ceramics.

Fig. 3 illustrates the dependence of the coefficients of thermal expansions (CTEs) and the peak ratios of $LiAlSiO_4/LiAlSi_2O_6$ on the particle size of the $LiAlSiO_4$ materials. With increasing the particle size of $LiAlSiO_4$ materials from 45 to 125 μm, the CTE of LAS/SiC porous ceramics decreased from $0.5206 \times 10^{-6}$ to $-1.1053 \times 10^{-6}$ $K^{-1}$. The XRD peak ratio of $LiAlSiO_4/LiAlSi_2O_6$ also showed similar tendency. The sample with larger $LiAlSiO_4$ particles has negative CTE values because the amount of preserved $LiAlSiO_4$ in the composites was higher, which was in agreement with the XRD analyses. It suggested that the CTE of porous LAS/SiC ceramics could be adjusted to some extent by changing the particle size of $LiAlSiO_4$ in the starting powder.

Fig. 4 shows the dependence of Young's modulus and porosity on the particle size of the $LiAlSiO_4$ materials. The total porosity of all the samples was ~29%. With increasing the sintering temperature from 850 °C to 950 °C, the closed porosity increased from 6% to 10%. It was due to the low viscosity of the glass materials during the sintering process. For the general case of the percolation model [18], $E = E_0(1-P)^n$, where $P$ is the total porosity, and $E_0$ is Young's modulus of the solid phase, i.e. the densely sintered matrix phase. Although the total porosity of all the samples was similar, Young's modulus decreased as the $LiAlSiO_4$ particle size increased because of the poor bonding between the SiC grains and the glass bonding agent. For the sample with 45 μm $LiAlSiO_4$, Young's modulus increased from 36 to 54 MPa with increasing the sintering temperature from 850 °C to 950 °C. For the porous ceramics, Young's modulus was related to the bonding strength between the reinforcement and the matrix, as well as the neck growth between grains [19]. The glass bonding agent with low viscosity at high temperature would completely cover the SiC and $LiAlSiO_4$ grains, consequently resulting in good bonding and neck growth between the SiC grains and the glass materials, as shown in Fig. 2(b). This result contributed to the resulting high Young's modulus. Meanwhile, the samples sintered at 950 °C have high closed porosity, which also contributed to the high Young's modulus according to Gibson's model [20].

## 4. Conclusion

Porous LAS/SiC ceramics with very low positive and negative thermal expansion were fabricated by using SiC and $LiAlSiO_4$ with different particle sizes as positive and negative thermal expansion materials, respectively, bonded by glass materials. The CTE of the LAS/SiC porous ceramics decreased from $0.5206 \times 10^{-6}$ to $-1.1053 \times 10^{-6}$ $K^{-1}$with increasing

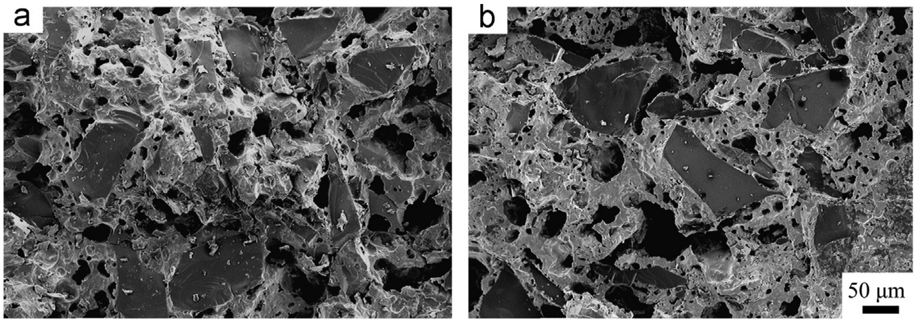

Fig. 2. SEM micrographs of the LAS/SiC porous ceramics sintered at different conditions: (a) 850 °C × 2 h and (b) 950 °C × 1 h.

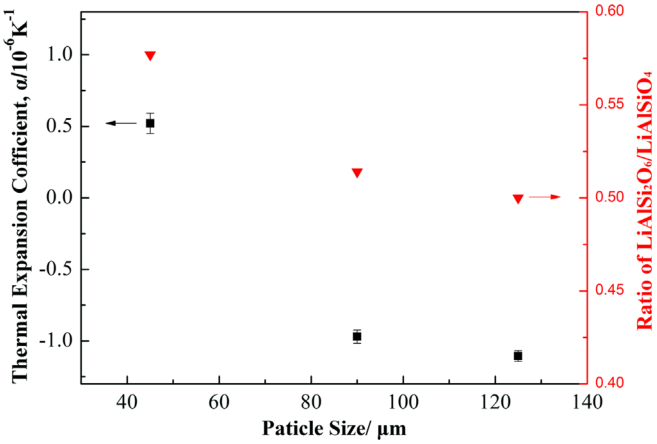

Fig. 3. The dependence of CTEs and the peak ratios of $LiAlSiO_4/LiAlSi_2O_6$ on the particle size of $LiAlSiO_4$ materials.

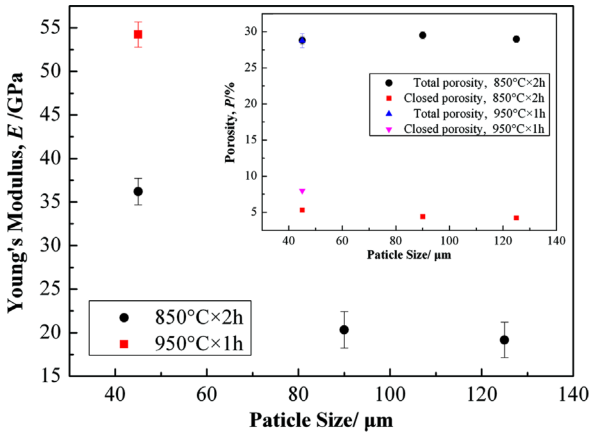

Fig. 4. The dependences of Young's modulus and porosity on the particle size of the $LiAlSiO_4$ materials.

the particle size of $LiAlSiO_4$ from ~45 μm to ~125 μm because the amount of the preserved $LiAlSiO_4$ in the composites increased. It was due to the fact that the reaction between $LiAlSiO_4$ and $SiO_2$ was restrained as the $LiAlSiO_4$ particle size increased. Young's modulus decreased as the $LiAlSiO_4$ particle size increased due to the poor bonding between the SiC grains and the glass bonding agent. A relatively high Young's modulus of ~54 MPa could be achieved by increasing the sintering temperature to 950 °C.

## Acknowledgment

This work was supported by the National Natural Science Foundation of China (Grant No. 51302208, 51272205, 51072157, and A3 Foresight Program-51161140399), by China Postdoctoral Science Foundation (Grant no. 2012M521763), by the Fundamental Research Funds for the Central Universities (xjj201310), by Doctoral Fund of Ministry of Education of China (Grant no. 20100201110036).

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