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Short communication

Pressureless sintering of machinable $Al_2O_3/LaPO_4$ composites in N_2 atmosphere

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Abstract

$Al_2O_3/LaPO_4$ composites were fabricated by pressureless sintering in N_2 atmosphere. The effect of sintering temperature and sintering time on densification was examined, as well as the dependence of mechanical properties and microstructure on $LaPO_4$ content. Provided the ratio of La/P was close to 1:1, no reactions were observed after 2 h at 1650 °C in N_2 atmosphere. The 30 wt.% $LaPO_4/Al_2O_3$ composites could be machined using cemented carbide drills as those pressureless sintered in air. $LaAl_{11}O_{18}$ was formed when the composite was sintered at 1700 °C for 1 h in N_2 atmosphere, and the composites were not machinable.

Keywords: $Al_2O_3/LaPO_4$ composite; Pressureless sintering; Machinable

1. Introduction

Ceramic materials like alumina have been widely used as engineering materials. However, their difficulty in machining restricts their use due to high strength and high hardness. In recent years, attempts have been made to develop machinable ceramics [1–4]. According to the research of Morgan et al., two-phase composites consisting of rare-earth phosphates (e.g., $CePO_4$ and $LaPO_4$) and refractory oxides (e.g., Al_2O_3, ZrO_2 and mullite) can be cut and drilled using conventional tungsten carbide metal-working tools instead of expensive diamond tools. $Al_2O_3/LaPO_4$ composites are stable in oxidizing environments [5,6]. When the stoichiometric $LaPO_4$ is used, there are no reactions at temperatures up to 1750 °C in air.

Recently, machinable $Al_2O_3/LaPO_4$ composites have been fabricated by different sintering method (pressureless sintering, hot pressing sintering) [2,7,8]. However, there are no reports on fabrication of $Al_2O_3/LaPO_4$ composites by pressureless sintering in N_2 atmosphere considering higher sintering temperature than that of hot pressing may lead to carbothermic reduction of $LaPO_4$ [9].

In the present work, the pressureless sintering of $Al_2O_3/LaPO_4$ composites in N_2 atmosphere was researched. The compatibility of the system $Al_2O_3/LaPO_4$ composites in N_2 atmosphere up to 1700 °C was examined. The effects of sintering temperature and sintering time on the densification were examined. The relationship of mechanical properties and microstructure with $LaPO_4$ content was also revealed.

2. Experimental procedure

$LaPO_4$ powder was prepared by calcining rhabdophane-type $LaPO_4{\cdot}0.5H_2O$ at 1300 °C for 6 h. The calcined powder was milled with silicon nitride balls in ethanol for 3 days and sieved through 200-mesh screen. X-ray diffraction (XRD) patterns of the calcined powder showed that only $LaPO_4$ phase existed. The La/P atomic ratio of the calcined powder (ICP) was 0.99. Commercial alumina powder was used.

The mixtures of Al_2O_3 and $LaPO_4$ (10, 30, 50 and 80 wt.%) powders were ball-milled and sieved using a 200-mesh screen. Pure Al_2O_3, $LaPO_4$ and the mixtures of Al_2O_3

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and $LaPO_4$ were uniaxially dry-pressed at 50 MPa to bars (4 mm ×5 mm ×40 mm), then cold isostatic pressed at 200 MPa. The samples were placed in an alumina crucible, covered with alumina powders, and the alumina crucible was placed in a graphite die. These details are important to decrease carbothermic reduction of $LaPO_4$. The samples were sintered at 1400–1700 °C for 1–5 h in N_2 atmosphere.

The bulk density and relative density were measured by the Archimedes method. The bending strength was measured by the three-point bending method with specimen dimensions of (3 mm ×4 mm ×36 mm), at a bending span of 30 mm, and cross-head speed of 0.5 mm/min. The machinability was tested using tungsten carbide drills at 450 rpm, with a drop of water placed at the drill tip at the beginning of each run. The crystalline phases of composites were determined by X-ray diffraction (XRD) with Cu Kα, operating at 40 kV and 100 mA. The fracture surface of composites was observed under scanning electron microscopy (SEM).

3. Results and discussion

3.1. Chemical compatibility

The compatibility of the $Al_2O_3/LaPO_4$ system was investigated by analyzing the possible existing phases using X-ray diffraction (XRD). Fig. 1 shows the corresponding XRD results. It can be seen that there were only $LaPO_4$ and Al_2O_3 phase when the sample was sintered in N_2 at 1650 °C for 2 h. The result indicates that both phases of the system were compatible at 1650 °C. However, $LaAl_{11}O_{18}$ was found in the outer layer when sintered up to 1700 °C. Morgan et al. reported that there were no reactions in $Al_2O_3/LaPO_4$ system up to 1750 °C in air [5]. It shows $Al_2O_3/LaPO_4$ system is more stable in air atmosphere. The reason is that the carbon of the graphite die diffused through the cruible and led to carbothermic reduction of the $LaPO_4$. This resulted in a loss of phosphorus and $LaAl_{11}O_{18}$ could be formed in the presence of excess La.

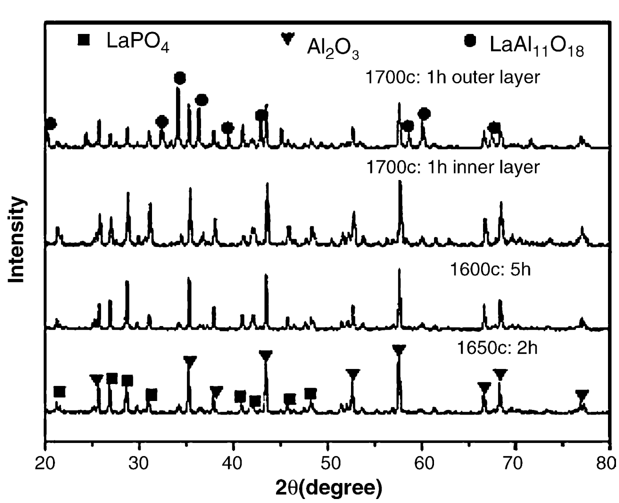

Fig. 1. XRD patterns of the $Al_2O_3/LaPO_4$ composites.

It is well known that the formation of $LaAl_{11}O_{18}$ occurs in two stages [10–12]. The formation of $LaAlO_3$ occurs at lower temperatures (<800 °C) and $LaAlO_3$ is converted to $LaAl_{11}O_{18}$ at higher temperatures (>800 °C). The reaction speed of the conversion of $LaAlO_3$ to $LaAl_{11}O_{18}$ is slow and more than 1800 °C is required for complete conversion for 24 h. In our experiments, $LaAlO_3$ was not detected on the 30 wt.% $LaPO_4/Al_2O_3$ composites sintered at 1700 °C in N_2 atmosphere. The reason is that $LaAlO_3$ formed at 1700 °C (>800 °C) instead of lower temperatures (<800 °C). $LaAlO_3$ phase is less stable than $LaAl_{11}O_{18}$ at 1700 °C. The formation of $LaAlO_3$ and conversion of $LaAlO_3$ to $LaAl_{11}O_{18}$ occurred at the same time.

3.2. Densification

The relationship of bulk density with sintering temperature and sintering time of the 30 wt.% $LaPO_4/Al_2O_3$ composites (the ratio is chosen to ensure machinability) was summarized in Fig. 2. The densities of the composites increase with the increase of sintering temperature and sintering time. The bulk density of 30 wt.% $LaPO_4/Al_2O_3$ composite sintered at 1650 °C for 2 h is close to theoretical density. There are reactions at higher sintering temperature, according to XRD results (Fig. 1). Therefore, the sintering temperature was determined as 1650 °C.

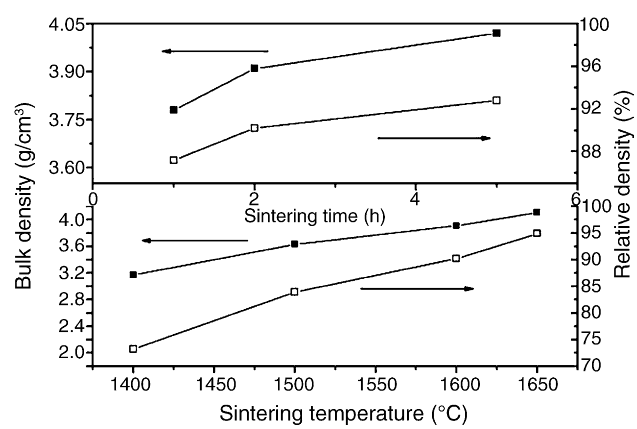

Fig. 2. Effects of sintering time and sintering temperature on the bulk densities and relative densities of the $Al_2O_3/LaPO_4$ composites.

Table 1
Densities of the $Al_2O_3/LaPO_4$ composites by pressureless sintering at 1650 °C

Content of $LaPO_4$ (wt.%)	Bulk density (g/cm^3)	Relative density (%)	Machinability
0	3.89	97.5	No
10	3.96	96.8	No
30	4.11	94.9	Yes
50	4.18	91.7	Yes
80	4.47	91.2	Yes
100	4.96	96.8	Yes

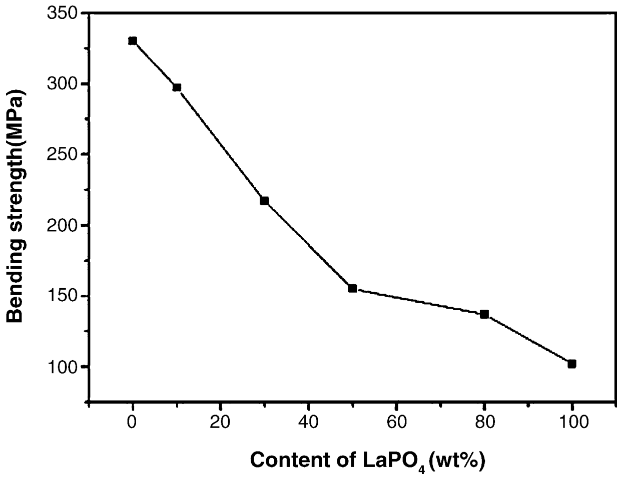

Fig. 3. Effect of $LaPO_4$ content on the bending strength Fig. 5. Hole drilled in $Al_2O_3/LaPO_4$ composite of $Al_2O_3/LaPO_4$ composites using tungsten carbide drills Second electron image Backscattered electron image (a) 10 wt.% $LaPO_4$ Second electron image Backscattered electron image (b) 50 wt.% $LaPO_4$.

Table 1 shows the densities of the xLaPO$_4$/(1 − x)Al$_2$O$_3$ (x = 0, 10, 30, 50, 80 and 100%) composites sintered at 1650 °C for 2 h. The densities of the composites increased with the increase of $LaPO_4$ content due to the higher density of $LaPO_4$, while the relative densities of composites

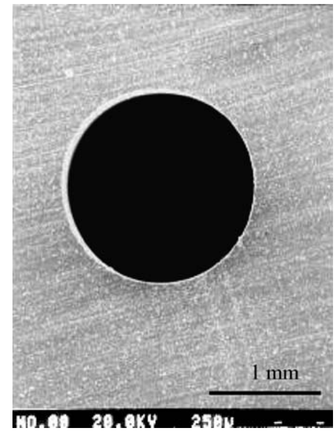

Fig. 5. Hole drilled in $Al_2O_3/LaPO_4$.

decreased. The introduction of $LaPO_4$ particles in the matrix retarded the sintering.

3.3. Mechanical properties

Variations in bending strength with $LaPO_4$ content for $Al_2O_3/LaPO_4$ composites are shown in Fig. 3. As compared with those of Al_2O_3 ceramics (330 MPa), the bending strength of composites remarkably reduced due to lower

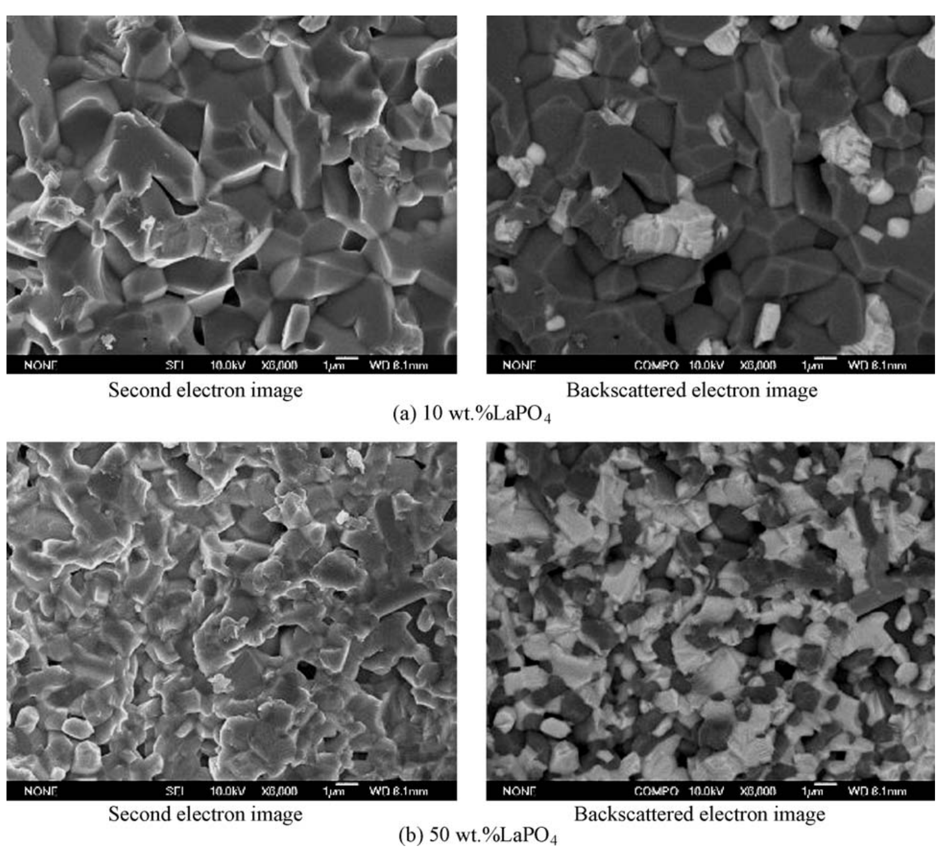

Fig. 4. SEM of $Al_2O_3/LaPO_4$ fracture surfaces at 1650 °C.

bending strength of $LaPO_4$ ceramics (102 MPa) and lower densification. With increase of $LaPO_4$ content, the bending strength of composites decreased.

3.4. Microstructure

Fig. 4 shows the SEM micrographics of the fracture surface of 10 and 50 wt.% $LaPO_4/Al_2O_3$ composites. $LaPO_4$ grains distributed at the Al_2O_3 grain boundaries and impeded the grain growth of Al_2O_3. The fracture mode of Al_2O_3 grain in composites was mainly intergranular due to the weak bonding of Al_2O_3 and $LaPO_4$ phases.

3.5. Machinability

The monolithic Al_2O_3 ceramics were not machinable, while the pure $LaPO_4$ ceramics were easily machinable using tungsten carbide drills. The $x LaPO_4/(1-x)Al_2O_3$ ($x > 30\%$) composites could be machinable. Fig. 5 shows a hole drilled by a tungsten carbide drill on the 30 wt.% $LaPO_4/Al_2O_3$ composites. The hole was cleanly drilled, with no evidence of cracking or chipping. The reason that composites were machinable is that layered $LaPO_4$ phase and the weak interfaces between the two phases are helpful to the machinability, which was discussed by Davis et al. [2]. The 30 wt.% $LaPO_4/Al_2O_3$ composites sintered at 1700 °C were not machinable. The formation of $LaAl_{11}O_{18}$ is detrimental to weak interface of $LaPO_4$ and Al_2O_3 phases.

4. Conclusion

Machinable $Al_2O_3/LaPO_4$ composites ceramics could be fabricated by pressureless sintering in N_2 atmosphere in a carbon furnace. $LaPO_4$ is compatible with Al_2O_3 in a carbon furnace at 1650 °C. $LaAl_{11}O_{18}$ formed due to the carbon reduction reaction at 1700 °C. The sinterability and bending strength of $Al_2O_3/LaPO_4$ composites decreased with the increase $LaPO_4$ content. The 30 wt.% $LaPO_4/Al_2O_3$ composites sintered at 1650 °C could be machined using cemented carbide drill. The formation of $LaAl_{11}O_{18}$ is detrimental to machinability.

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