Superplasticity and machinability in a four-phase ceramic

Danju Men, Martha L. Mecartney*

University of California, Irvine, Department of Chemical Engineering and Materials Science, Irvine, CA, 92697-2575, USA

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ABSTRACT

Fine grained four-phase ceramic materials were fabricated to have a combination of high temperature superplasticity and room temperature machinability. The composite ceramics were made of 25 vol.% 3Y-TZP/8YSZ, 25 vol.% MgAl2O4, 25 vol.% MgAl2O4, and LaPO4, using LaPO4 powders fabricated in-house. X-ray diffraction and scanning electron microscopy revealed that the grain size for the best mixed samples was in the range of 600 nm, tetragonal ZrO2 transformed into monoclinic, and reactions in the sintered samples produced a new phase, magnetoplumbite (LaMgAl12O19) with lattice-like grains. The formation of magnetoplumbite was facilitated by the presence of yttria and by a liquid phase generated at elevated temperatures. These four-phase ceramics had a maximum hardness of 12 GPa and fracture toughness was no more than 3 MPa.m^0.5. Deformation rates at 1400 °C under 40 MPa stress were in the superplastic range of 10^−3 s^−1 for most compositions. These four-phase ceramics were machinable as demonstrated using conventional tungsten drill bits.

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1. Introduction

Monazite (LaPO4) has received considerable attention as a machinable ceramic, either as a single phase or a two-phase composite containing either Al2O3 or ZrO2 [1–4]. The strength of the interfacial bonding between monazite and alumina or zirconia is low. Cracks propagate preferentially along these interfaces. This deflection and branching effectively blunts the crack [1,5,6]. These aspects, when combined with easy room temperature plastic deformation of the monazite [7], make machining possible using conventional tools [6,8].

Fine-grain size superplasticity typically requires the grain size of ceramics to be less than 1 µm in order for grain-boundary sliding to be the major deformation mode [9]. Grain-size refinement increases the strain rate and decreases the flow stress for superplastic forming of materials [10]. Equivolumetric multiphase ceramic composites with a uniform fine grain size are one way to minimize grain growth and maintain a fine grain size, by separating grains of the same phases [11]. If two compositionally dissimilar grains are in contact with one another, grains cannot grow simply by atoms attaching to a new grain orientation across the grain boundary. Interphase boundary diffusion from a grain with a similar composition that is not a nearest neighbor can be required, and this can require long distance diffusion, slowing grain growth [11–14]. In three dimensions, the use of four phases should theoretically allow for the design of a uniform microstructure where every grain boundary is an interface between dissimilar phases (Fig. 1), and this would be an optimal microstructure for limiting grain growth.

The main material system studied containing 3Y-TZP (3 mol% tetragonal zirconia), Al2O3, MgAl2O4, and LaPO4 was chosen to combine (a) the high fracture toughness of 3Y-TZP, (b) high hardness and strength of Al2O3, (c) compatibility of 3Y-TZP, Al2O3, and MgAl2O4 at high temperature, and (d) machinability of LaPO4 [11]. The goal of this current research is to evaluate four-phase ceramic composites for shape forming via either room temperature machinability or high temperature superplasticity and to determine the grain size, phase stability, hardness, fracture toughness, high temperature deformation rates, and machining rates for these composites.

2. Experimental procedure

Four-phase ceramic composites of 3 mol% yttria tetragonal zirconia polycrystals (3Y-TZP), alumina (Al2O3), Mg-spinel (MgAl2O4) and La-monazite (LaPO4) were prepared by attrition milling the mixture of starting powders in isopropanol alcohol for 8 or 24 h. Equal volumes of the four phases were used. Two types of LaPO4 powders were prepared in the lab using a previously published synthesis method [15]. The first type of LaPO4 had approximately 10% excess phosphorus and the second type had a La:P ratio closer to stoichiometry (noted as LaPO4*). Cubic 8 mol% yttria-stabilized zirconia (8YSZ) was used instead of 3Y-TZP for one set of samples to prevent the tetragonal-to-monoclinic phase transformation observed when 3Y-TZP. The specific surface area of the powders used is given in Table 1, and the four-phase powders...
after 8 h milling, drying and sieving had an average specific surface area of 26 m²/g (measured by BET). After cold isostatic pressing at 380 MPa in silicone molds, the samples were sintered for 3 h at 1400 °C, 1500 °C and 1600 °C, respectively. Bulk density of the sintered bodies was measured using the Archimedes method.

Crystalline phases were identified by X-ray diffraction (XRD) after sintering but prior to polishing to eliminate any possible tetragonal-to-monoclinic zirconia transformation induced by polishing. Scanning electron microscopy (SEM, Zeiss Ultra Plus 55) was conducted for microstructure characterization. Grain size measurements were conducted on the four-phase composites using software Image J (freeware from NIST). In each sample, at least 100 grains were analyzed for each 3Y-TZP/8YSZ, LaPO₄, and Al₂O₃/MgAl₂O₄ phase. Hardness and fracture toughness were measured by indentation techniques. Creep tests were conducted under compression to investigate high-temperature superplasticity. Machinability tests were carried out on a standard drill press operating at 450 rpm, using conventional tungsten carbide drill bits with a 1 mm diameter. The samples were mounted on a scale and tested by manually applying a fixed normal force of 50 N to the drill, while measuring the drilling rate. A new drill bit was used at the beginning of each run for each sample for consistency.

3. Results and discussion

Table 2 shows the density, hardness, and fracture toughness data corresponding to the different compositions and sintering strategies. Microstructural characterization was conducted for samples sintered at 1500 °C only, since increasing the sintering temperature from 1500 °C to 1600 °C did not lead to increased density. This could be due to new, lower density phases that form more easily at higher temperatures (1600 °C). The hardness and fracture toughness values for the individual components and calculated for the composite using the rule of mixtures are shown in Table 3. 3Y-TZP was probably not effective for most compositions for promoting transformation toughening since the toughness was low for most composites.

Prior results have shown that single phase LaPO₄ with excess phosphorus forms a phosphorus-rich liquid intergranular phase during sintering (Fig. 2) [16,17]. P₂O₅ itself melts at 340 °C. This
Magnetoplumbite composites similar (Table 4) phase Al₂O₃ and sintering scattering formation was SEM only monoclinic Al₂O₃–MgAl₂O₄–LaPO₄* detected not magnetoplumbite that Fig. 3. Theoretical density, hardness and fracture toughness for the components and four-phase composite calculated using the rule of mixtures.

<table>
<thead>
<tr>
<th></th>
<th>Density (g/cm³)</th>
<th>Hardness (GPa)</th>
<th>Kᶜ (MPa m¹/²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3Y-TZP</td>
<td>6.05</td>
<td>10</td>
<td>7–12</td>
</tr>
<tr>
<td>8YSZ</td>
<td>5.90</td>
<td>9</td>
<td>2–3</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.97</td>
<td>23</td>
<td>4–6</td>
</tr>
<tr>
<td>MgAl₂O₄</td>
<td>3.58</td>
<td>16</td>
<td>1–2</td>
</tr>
<tr>
<td>LaPO₄</td>
<td>5.13</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>LaMgAl₁₁O₁₉*</td>
<td>4.29</td>
<td>14</td>
<td>5</td>
</tr>
</tbody>
</table>

Four-phase composite including: 3Y-TZP 4.68 14 4 8YSZ 4.65 14 3

* Magnetoplumbite (LaMgAl₁₁O₁₉) phase formed during sintering which will be discussed later.

liquid phase formation is expected to form in four-phase composites also when using non-stoichiometric LaPO₄. Four-phase samples with excess phosphorus had a higher density than those without excess phosphorus (same heat treatment), indicating that the liquid phase acts as a sintering aid to assist in densification.

XRD patterns show that the yttria stabilized tetragonal zirconia phase had partially transformed into the monoclinic phase during sintering for all 3Y-TZP containing samples (XRD data for the TZP–Al₂O₃–MgAl₂O₄–LaPO₄* sample is presented in Fig. 3 as an example). This confirms why the toughness was so low, as there was not tetragonal to monoclinic phase transformation as cracks propagated since the material was already transformed to monoclinic on the surface. A new phase of magnetoplumbite LaMgAl₁₁O₁₉ was detected in the XRD pattern in Fig. 3, and was formed by the reaction of Al₂O₃ with dissolved LaPO₄ and MgAl₂O₄. Magnetoplumbite can be considered to consist of spinel blocks separated by mirror planes that contain La (Fig. 4 [18]). The formation of magnetoplumbite in all samples was confirmed by SEM coupled with energy-dispersive X-ray spectroscopy (EDS) but only for TZP–Al₂O₃–MgAl₂O₄–LaPO₄* (Fig. 3) was the concentration of magnetoplumbite LaMgAl₁₁O₁₉ high enough to be easily detected by XRD. Magnetoplumbite has much lower X-ray scattering intensity than zirconia. XRD results are also strongly affected by any preferred crystalline orientation, and as will be shown later, magnetoplumbite forms highly anisotropic lath-like grains. The density and mechanical properties of magnetoplumbite (Table 2) contribute to the mechanical properties of the samples that contain magnetoplumbite grains (Table 3).

The overall microstructures of all four-phase samples are similar (Fig. 5) but there are differences in the grain sizes (Table 4). Grain size measurements are shown in Table 4. The grain sizes of Al₂O₃ and MgAl₂O₄ phases were analyzed together, since it is difficult to distinguish these two phases by the composition-contrast shown in SEM images due to similar densities of the two phases (Fig. 5(a)). It was also difficult to define the grain boundaries of the LaPO₄ grains in some samples when severe microcracking occurred and split whole grains into smaller pieces (Fig. 5(b)). The samples milled 24 h had a better dispersion of the four phases and a 60% smaller average grain size due to fewer similar phase boundaries that would allow easy grain growth.

The volume expansion from the tetragonal-to-monoclinic phase transformation in 3Y-TZP grains resulted in raised TZP grains with a twinned surface texture. This volume expansion also generated microcracks in adjacent LaPO₄ grains, observed in all samples except 8YSZ–Al₂O₃–MgAl₂O₄–LaPO₄ (Fig. 5). This transformation is most likely promoted by the liquid phase due to

![Fig. 3. X-ray diffraction pattern of sample TZP–Al₂O₃–MgAl₂O₄–LaPO₄* (attrition milled for 8 h and sintered at 1500°C for 3 h) shows that Y-TZP has partially transformed into the monoclinic phase during sintering, possibly promoted by liquid phase leaching out yttrium from the ZrO₂ grains. A new phase, magnetoplumbite LaMgAl₁₁O₁₉, formed from Al₂O₃, and partial dissolution of LaPO₄ and MgAl₂O₄. In other samples, X-ray diffraction from magnetoplumbite was not detected, even though magnetoplumbite could be observed by SEM.](image)

![Fig. 4. Unit cell of LnMgAl₁₁O₁₉ magnetoplumbite, consisting of a packing of spinel blocks separated by mirror planes containing the Ln³⁺ ions. This figure was reproduced from Ref. [18] with permission from Elsevier.](image)
excess P leaching out yttrium from the YSZ grains. This would leave the ZrO2 grains low in yttrium and not stable in the tetragonal phase at room temperature. Min et al. [4] observed this same phenomenon in two-phase LaPO4–ZrO2 composites, which most likely also had a liquid phase formed from excess P. Even the composition with the nominally stoichiometric LaPO4 has transformed zirconia grains. In that case, a liquid phase could form due to the magnetoplumbite leaving behind excess P as it consumes monazite, spinel and alumina. Thermal expansion mismatch and residual stresses may also play a secondary role in promoting this transformation at the surface.

Magnetoplumbite forms as long lath-like grains, with the long axis the [0 0 1] direction [18]. Fig. 6 shows low magnification images to illustrate the distribution of magnetoplumbite. The formation of the new phase, LaMgAl11O19, at 1400 °C is not unexpected based on the La2O3–Al2O3–MgO phase diagram [19]. The following reaction would both produce magnetoplumbite and P2O5 which is a liquid phase above 340 °C:

$$9\text{Al}_2\text{O}_3 + 2\text{MgAl}_2\text{O}_4 + 2\text{LaPO}_4 \rightarrow 2\text{LaMgAl}_{11}\text{O}_{19} + \text{P}_2\text{O}_5$$

The existence of liquid phase in the samples during sintering, consisting of phosphorus from LaPO4 phase and perhaps yttria

Table 4
Grain size in nm for four-phase composites sintered at 1500 °C for 3 h (units in μm).

<table>
<thead>
<tr>
<th>Composition</th>
<th>3Y-TZP/8YSZ</th>
<th>Al2O3/MgAl2O4</th>
<th>LaPO4</th>
<th>Average grain size</th>
</tr>
</thead>
<tbody>
<tr>
<td>3Y-TZP</td>
<td>Grain size</td>
<td>Standard</td>
<td>Grain size</td>
<td>Standard deviation</td>
</tr>
<tr>
<td>Al2O3</td>
<td>0.8</td>
<td>±0.2</td>
<td>1.1</td>
<td>±1.4</td>
</tr>
<tr>
<td>MgAl2O4</td>
<td>1.3</td>
<td>±1.3</td>
<td>1.0</td>
<td>±1.2</td>
</tr>
<tr>
<td>LaPO4</td>
<td>(8 h milling)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3Y-TZP</td>
<td>Grain size</td>
<td>Standard</td>
<td>Grain size</td>
<td>Standard deviation</td>
</tr>
<tr>
<td>Al2O3</td>
<td>0.8</td>
<td>±0.8</td>
<td>1.1</td>
<td>±1.3</td>
</tr>
<tr>
<td>MgAl2O4</td>
<td>1.2</td>
<td>±1.2</td>
<td>1.0</td>
<td>±1.1</td>
</tr>
<tr>
<td>LaPO4</td>
<td>(8 h milling)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3Y-TZP</td>
<td>Grain size</td>
<td>Standard</td>
<td>Grain size</td>
<td>Standard deviation</td>
</tr>
<tr>
<td>Al2O3</td>
<td>0.4</td>
<td>±0.3</td>
<td>0.6</td>
<td>±0.5</td>
</tr>
<tr>
<td>MgAl2O4</td>
<td>0.7</td>
<td>±0.7</td>
<td>0.6</td>
<td>±0.6</td>
</tr>
<tr>
<td>LaPO4</td>
<td>(24 h milling)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8YSZ</td>
<td>Grain size</td>
<td>Standard</td>
<td>Grain size</td>
<td>Standard deviation</td>
</tr>
<tr>
<td>Al2O3</td>
<td>0.5</td>
<td>±0.5</td>
<td>0.5</td>
<td>±0.5</td>
</tr>
<tr>
<td>MgAl2O4</td>
<td>0.7</td>
<td>±0.6</td>
<td>0.6</td>
<td>±0.5</td>
</tr>
<tr>
<td>LaPO4</td>
<td>(24 h milling)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
leached from the YSZ phase, would act as a fast diffusion route to assist LaMgAl$_{11}$O$_{19}$ grain growth. However, there are fewer LaMgAl$_{11}$O$_{19}$ grains observed in TZP–Al$_2$O$_3$–MgAl$_2$O$_4$–LaPO$_4$ (8 h milling, with excess P) compared with TZP–Al$_2$O$_3$–MgAl$_2$O$_4$–LaPO$_4^*$ (8 h milling, stoichiometric La/P) (Fig. 6(a and b)). As discussed previously, dissolution of LaPO$_4$ and incorporation of La into growing magnetoplumbite grains would provide excess phosphorus which would form a low melting point liquid phase even without the presence of excess phosphorus initially.

From SEM images, the volume fractions of LaMgAl$_{11}$O$_{19}$ formed were approximately 4% for TZP–Al$_2$O$_3$–MgAl$_2$O$_4$–LaPO$_4$ (8 h milling), 13% for TZP–Al$_2$O$_3$–MgAl$_2$O$_4$–LaPO$_4^*$ (8 h milling), and 10% for 8YSZ–Al$_2$O$_3$–MgAl$_2$O$_4$–LaPO$_4$. No evidence of LaMgAl$_{11}$O$_{19}$ formation can be found for the 24 h milled TZP–Al$_2$O$_3$–MgAl$_2$O$_4$–LaPO$_4$ sample (Fig. 6(c)), due to the fact that after the longer time of milling, a finer grain size and more uniform mixing occurred. In contrast, LaMgAl$_{11}$O$_{19}$ grains appear in 8YSZ–Al$_2$O$_3$–MgAl$_2$O$_4$–LaPO$_4$, which also had 24 h attrition milling but had a higher yttria

![Fig. 6. Scanning electron microscopy of (a) TZP–Al$_2$O$_3$–MgAl$_2$O$_4$–LaPO$_4$ (8 h milling), (b) TZP–Al$_2$O$_3$–MgAl$_2$O$_4$–LaPO$_4^*$, (c) TZP–Al$_2$O$_3$–MgAl$_2$O$_4$–LaPO$_4$ (24 h milling), and (d) 8YSZ–Al$_2$O$_3$–MgAl$_2$O$_4$–LaPO$_4$, all sintered at 1500 °C for 3 h.](image)

![Fig. 7. Scanning electron microscopy of (a) TZP–Al$_2$O$_3$–MgAl$_2$O$_4$–LaPO$_4$ (8 h milling), (b and c) TZP–Al$_2$O$_3$–MgAl$_2$O$_4$–LaPO$_4^*$, and (d) 8YSZ–Al$_2$O$_3$–MgAl$_2$O$_4$–LaPO$_4$, all sintered at 1500 °C for 3 h. The magnetoplumbite grains grow rapidly and encapsulate smaller grains of the other phases.](image)
content. This supports the hypothesis that yttria helps form a eutectic phase and plays a key role in LaMgAl11O19 formation during sintering.

Fig. 7 shows that the LaMgAl11O19 grains grow rapidly and incorporate smaller grains of other phases, especially zirconia and some monazite. This rapid growth is representative of growth in the presence of a liquid phase. Fig. 7(a) seems to indicate that at times there is a common nucleation site for monazite with growth out from a central point, most likely where the composition first became liquid. Alumina grains are not found near magnetoplumbite grains, and there is often less spinel nearby, as these phases are consumed by the growing magnetoplumbite (Fig. 7).

Fig. 8 shows compression test data on the four-phase composites at 1400 °C. These four-phase materials display strain rates comparable with superplastic TZP at the same temperature and stress [20]. At higher stress/faster strain rates, all samples tend to have similar deformation behaviors. Generally, the rate of increase of strain rates tends to decelerate with increasing stresses, suggesting a possible change of deformation mechanism and a reduction of strain rate due to grain growth.

TZP–Al2O3–MgAl2O4–LaPO4 (24 h milling) has no LaMgAl11O19 grains formed that could be detected and this material initially creeps fastest with its fine-grained microstructure as expected. However, after loads of 30 MPa, its strain rate became slower relative to 8YSZ–Al2O3–MgAl2O4–LaPO4 and TZP–Al2O3–MgAl2O4–LaPO4 (8 h milling). Any liquid phase formed from yttria and phosphorus at elevated temperature that provides a rapid transport path for the growth of LaMgAl11O19 also can assist deformation. There is a relatively smaller amount of liquid phase present in TZP–Al2O3–MgAl2O4–LaPO4 (24 h milling) to assist deformation, as discussed in the microstructure characterization section. Once deformation started at 1400 °C, given enough time for liquid phase formation in situ and grain structure rearrangement, 8YSZ–Al2O3–MgAl2O4–LaPO4 with the highest yttria concentration increased its strain rate disproportionally after 30 MPa, due to easier formation of liquid phases from the higher yttria concentration. There is a trade-off of liquid phase formation, which makes deformation easy, and the formation of long lath-like magnetoplumbite, which would inhibit creep.

The TZP–Al2O3–MgAl2O4–LaPO4* sample without any liquid phase present initially has the lowest strain rate up to 50 MPa stress. In the course of deformation, the dissolution of LaPO4 and incorporation of La into growing LaMgAl11O19 grains would provide excess phosphorus which forms a low melting point liquid phase, as discussed before. At the end of the compression test, when the stress was returned to 20 MPa again, this slow rate of deformation could provide enough time for the newly generated liquid phase to redistribute among grains to better assist grain boundary sliding. That may be the reason there is an increase of strain rate in the final 20 MPa-stress stage of deformation, compared with the strain rate in the initial 20 MPa-stress stage, when one might expect the opposite if grain growth is present.

Microstructural investigations were conducted by SEM on the four-phase composites after high temperature compression deformation. One example is given in Fig. 9 for the TZP–Al2O3–MgAl2O4–LaPO4 sample. There is not any significant difference of either the grain sizes or the concentration of the LaMgAl11O19 grains before and after deformation. However, excessive cavitation can be observed at the ends of the LaMgAl11O19 grains in the sample after deformation, indicating an inability of those grains to...
accommodate grain boundary sliding due to their long high aspect ratio geometry. This shows that the formation of such grains is detrimental for the superplasticity of the system.

Composites TZP-\(\text{Al}_2\text{O}_3\)–MgAl\(_2\text{O}_4\)–LaPO\(_4\) and TZP-\(\text{Al}_2\text{O}_3\)–MgAl\(_2\text{O}_4\)–LaPO\(_4^*\) were successfully machined by tungsten carbide drills with drilling rates of \(5.2 \times 10^{-3}\) mm/s and \(3.4 \times 10^{-2}\) mm/s respectively (Fig. 10). The drilled surfaces remain clear (Fig. 11) and fracture occurs intergranularly (Fig. 12). The weak bonding between the monazite phase and the other phases contributes to the ease of machining. The applied pressure was the same for drilling both samples, so the increased drilling rate for the sample without excess phosphorus might be due to the difference in sample density, with the higher density samples machining at a slower rate.

4. Conclusions

1. Four-phase composites of \(\text{Al}_2\text{O}_3\), TZP/YSZ, MgAl\(_2\text{O}_4\) and LaPO\(_4\) were found to form the magnetoplumbite phase LaMgAl\(_{11}\text{O}_{19}\) after sintering. The formation of magnetoplumbite can be minimized by better mixing (milling for longer times) of the starting powders for composites including 3Y-TZP, but still forms if the yttria concentration is high, such as when 8YSZ is used instead of 3Y-TZP. Increasing the milling time from 8 h to 24 h was found to effectively reduce the final grain size from over 1 \(\mu\)m to around 600 nm.

2. When LaPO\(_4\) dissolves and La is incorporated into the magnetoplumbite LaMgAl\(_{11}\text{O}_{19}\), excess phosphorus and oxygen remaining can form a low melting point liquid phase combined with other cations at the sintering temperatures, even for samples with a stoichiometric ratio of La:P in the initial LaPO\(_4\) that were not expected to form a liquid phase.

3. Samples using TZP powder as the ZrO\(_2\) phase in the starting materials had the tetragonal ZrO\(_2\) transform into the monoclinic phase, and microcracking was observed in neighboring LaPO\(_4\) grains due to yttria depletion.

4. TZP–\(\text{Al}_2\text{O}_3\)–MgAl\(_2\text{O}_4\)–LaPO\(_4\) (with and without excess phosphorus) four-phase composites are machinable at room temperature. At high temperatures, these four-phase composites have deformation rates in the superplastic range of \(10^{-4}\) s\(^{-1}\) to \(10^{-3}\) s\(^{-1}\) at 1400 °C under stresses from 20 to 50 MPa.

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