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The effect of residual carbon on the phase stability of $LaPO_4$ at high temperatures

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Abstract

Samples containing $LaPO_4$ and polymeric binders were heated or hot-pressed in oxygen-poor environments to temperatures as high as 1585°C. Carbon analysis, powder X-ray diffraction and thermogravimetric analysis revealed that the residual carbon from the binders caused the $LaPO_4$ to decompose into a lanthanum-rich phosphate compound, La_3PO_7, or a lanthanum oxide, La_2O_3, at temperatures above 750°C. These results agree with thermodynamic data, indicating that the driving force responsible for this carbothermic reduction reaction is the free energy of formation of P_2O_5, which is higher than the free energy of formation of CO above 750°C. It was also observed that this phenomenon would be detrimental to composites of $LaPO_4$ and Al_2O_3, because $LaAl_{11}O_{18}$ and $LaAlO_3$ were found to form at the interface, unless the samples were annealed in air after binder burnout.

Keywords: Carbon; Chemical properties; Composites; Hot pressing; $LaPO_4$

1. Introduction

Lanthanum orthophosphate ($LaPO_4$), also known as monazite, has been found to be a debond material for high-temperature oxide/oxide composites.[1,2] Fracture energy measurements have shown that the Al_2O_3/$LaPO_4$ interface is weak enough, when compared to Al_2O_3, to satisfy the He and Hutchison debonding criteria for bimaterial interfaces.[2–4] The carbothermic reduction of monazite was noticed by the current authors and another group[2] while exploring the properties of $LaPO_4/Al_2O_3$ composites. Because these composites have great potential in high-temperature applications[1,2,5–11] and because very little information is available on this phenomenon for phosphates,[12] the carbothermic reduction of monazite and its effect on $LaPO_4/Al_2O_3$ composites was investigated.

Carbothermic reduction is the phenomenon of a material being reduced, i.e. losing oxygen, in the presence of carbon, usually at elevated temperatures and in oxygen-poor environments. In some cases of carbothermic reduction, the carbon replaces the oxygen, ultimately transforming the material into a carbide.[13,14] These cases are represented by the reaction:

$$MO_2 + 3C \rightarrow MC + 2CO. \quad (1)$$

In other cases, the carbon replaces the cation, creating a free metal and releasing carbon monoxide ("direct solid-state reaction").[15,16] These cases are represented by the reaction:

$$MO_x + C \rightarrow M + xCO. \quad (2)$$

Lastly, carbon monoxide can react with the oxide, creating a free metal and releasing carbon dioxide ("indirect reaction via an intermediate gas phase").[16] This case is represented by the reaction:

$$MO_x + xCO \rightarrow xCO_2 + M. \quad (3)$$

With the goal of determining the nature of the carbothermic reduction of monazite, experiments were conducted on samples containing lanthanum phosphate and polymeric binders, which are often used as ceramic processing aids and are a common source of carbon contamination. In order to determine the effects of car-

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bothermic reduction on $LaPO_4/Al_2O_3$ composites, experiments were also conducted by hot-pressing samples containing lanthanum phosphate and alumina that had been fabricated with binders, one of which had also been heat treated in air after binder burnout.

2. Experimental procedures

2.1. Lanthanum phosphate samples with binders

The first monazite powder was stoichiometric $LaPO_4$, furnished by Rockwell International Science Center, Thousand Oaks, CA.[2,5] A dip-coating slurry was made using this monazite powder and polyvinyl alcohol as the primary ingredients. Some of this dip-coating slurry (Sample no. 1) was subjected to a binder burnout cycle, consisting of ramping up slowly and holding the sample at 600°C in nitrogen for 1 h, and part of that sample was subsequently heat treated in air at 750°C for 2 h (Sample no. 2). Thermogravimetric analysis (Cahn, model TG-171) was conducted on some of the burned-out dip-coating slurry (Sample no. 1). The sample was held in a quartz bucket (platinum sample holders would have been susceptible to attack by phosphorus-bearing gas) and heated to 1100°C in nitrogen. Phase analysis was conducted using powder X-ray diffraction. A sample of the slurry before and after heat treatment in air was sent off for carbon analysis (LECO, XRAL, Ann Arbor, MI).

The second powder was non-stoichiometric $LaPO_4$ with a La/P ratio of 0.85 (determined by ion-coupled plasma atomic emission spectroscopy). Details of the synthesis and characterization of this powder can be found elsewhere.[17] Powder X-ray diffraction and SEM investigation showed that the powder was actually a mixture of $LaPO_4$ and LaP_3O_9 after synthesis at room temperature and a mixture of $LaPO_4$ and an amorphous glass phase, which contained La and an excess of phosphorus, after high temperature (1500°C) exposure. This powder was mixed with ethylene-ethyl acrylate (Union Carbide, Danbury, CT) and methoxy polyethylene glycol (MPEG 550, Carbowax) in a ratio of 50:49:1 by volume in a plasti-corder (C.W. Brabender, South Hackensack, NJ). This green mixture was formed into a billet, subjected to the burnout cycle in nitrogen, and then hot-pressed at 1585°C for 3 h in graphite dies. The resulting components (Sample nos. 3 and 4), discussed below, were then identified using powder X-ray diffraction and sent off for carbon analysis.

2.2. Lanthanum phosphate/alumina samples with and without binders

In order to investigate the effects of carbothermic reduction on high temperature oxide composites, two $LaPO_4/Al_2O_3$ fibrous monoliths[18–20] were made with alumina/ethylene-ethyl acrylate filaments that had been covered with the monazite dip-coating slurry described above. Both were burned out in nitrogen, but one (Sample no. 5) was heat treated at 1100°C in air for 1 h prior to hot pressing, while the other was not (Sample no. 6). The heat treatment in air was intended to remove, via oxidation reaction with the air, the residual carbon from the sample that was left behind after burnout. Hot-pressing of both fibrous monolith composites was conducted in nitrogen at 1400°C for 1 h. Both of the $LaPO_4/Al_2O_3$ fibrous monoliths contained 15–20% $LaPO_4$ by volume. Phase analysis on all of these samples was conducted using thermal etching and powder X-ray diffraction. Carbon content analysis was also conducted on these samples.

3. Results

3.1. Lanthanum phosphate samples with binders

The results of the thermogravimetric analysis of the burnt-out dip-coating slurry (Sample no. 1) are shown in Fig. 1. The weight loss of the monazite dip coating slurry was 5%. Since the carbon content of this sample was measured to be 2.6%, this indicates that more than carbon left the sample. X-ray diffraction of the powder from the TGA run revealed that the resulting powder was $LaPO_4$ and La_3PO_7, a lanthanum-rich phosphate whose presence indicated a loss of phosphorus, as seen in Fig. 2. In Table 1, it can be seen that heat treating the burned out slurry in air eliminates most of the carbon contamination (Sample no. 2).

When the billet made from the non-stoichiometric lanthanum phosphate powder was removed from the graphite hot press dies, it crumbled into small gray chunks (Sample no. 3) and a gray powder (Sample no. 4). Carbon analysis results, Table 1, of the chunks and powder revealed that the level of carbon was 0.02 and 1.1 wt.%, respectively. The X-ray diffraction pattern of the small gray chunks revealed that they were $LaPO_4$. The X-ray diffraction pattern, in Fig. 3, of the gray powder showed that it was mainly composed of $La(OH)_3$ with small amounts of $LaPO_4$ and boron nitride, which was used to isolate the sample from the graphite die. $La(OH)_3$ is not surprising because La_2O_3 is extremely hygroscopic and some time elapsed (several weeks) between hot pressing and X-ray diffraction.

3.2. Lanthanum phosphate/alumina samples with and without binders

When a piece of the $LaPO_4/Al_2O_3$ fibrous monolith billet that was not heat treated (Sample no. 6) was ground into powder and X-rayed, the pattern showed

$LaAl_{11}O_{18}$ and $LaAlO_3$ peaks in addition to the $LaPO_4$ and Al_2O_3 peaks, as shown in Fig. 5. When thermally etched, this sample showed a reaction zone of $LaAl_{11}O_{18}$ platelets, a compound with the β-alumina crystal structure, between the monazite and alumina, as shown in Fig. 4(a). When a sample from the heat treated

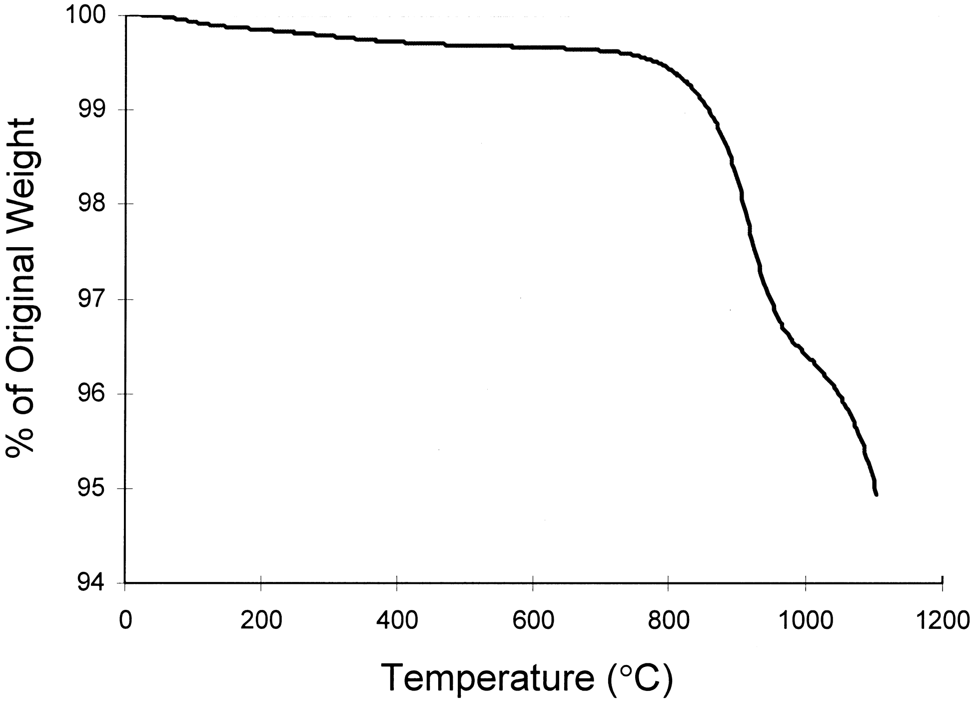

Fig. 1. Thermogravimetric analysis of $LaPO_4$ dip-coating slurry subjected to burnout in nitrogen (sample no. 1). Carbon analysis showed that this sample only contained 2.6 wt.% carbon.

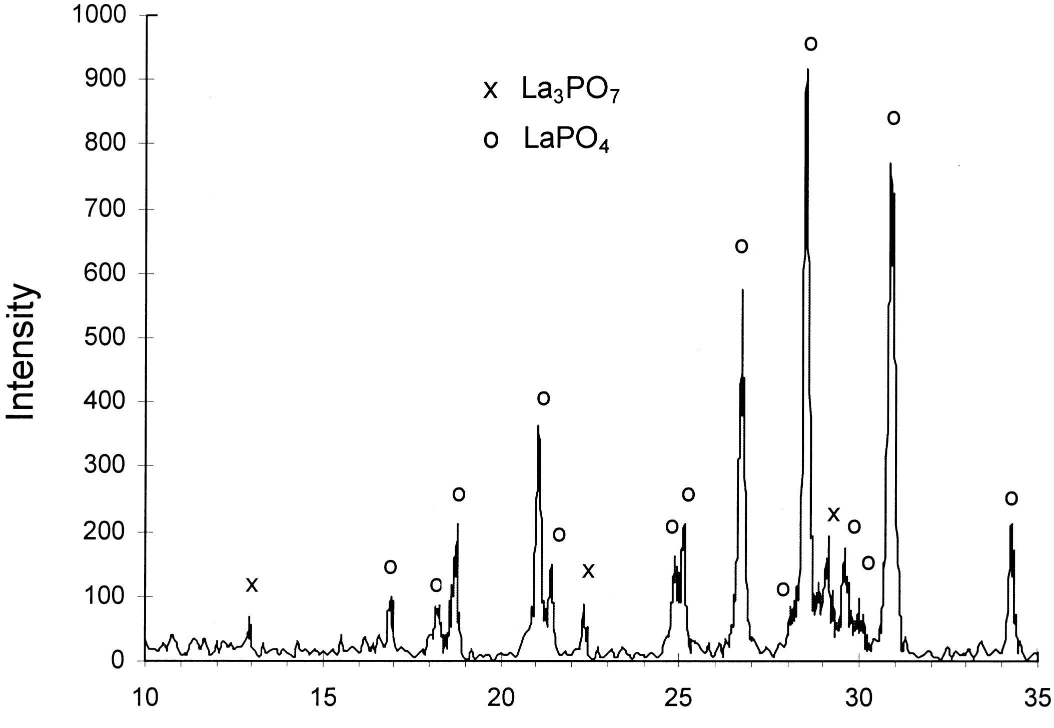

Fig. 2. Powder X-ray diffraction of the monazite dip-coating slurry after the TGA run shown in Fig. 1.

Table 1
Carbon analysis results

Sample no.	Sample description	Amount of carbon
1	$LaPO_4$ dip coating slurry (after burnout)	2.6% by wt.
2	$LaPO_4$ dip coating slurry (after burnout and firing)	0.07%
3	$LaPO_4$ billet (after hot-pressing) — chunks	0.02%
4	$LaPO_4$ billet (after hot-pressing) — powder	1.1%
5	$LaPO_4/Al_2O_3$ fibrous monolith — heat treated (after hot-pressing)	0.04%
6	$LaPO_4/Al_2O_3$ fibrous monolith (after hot-pressing)	0.12%

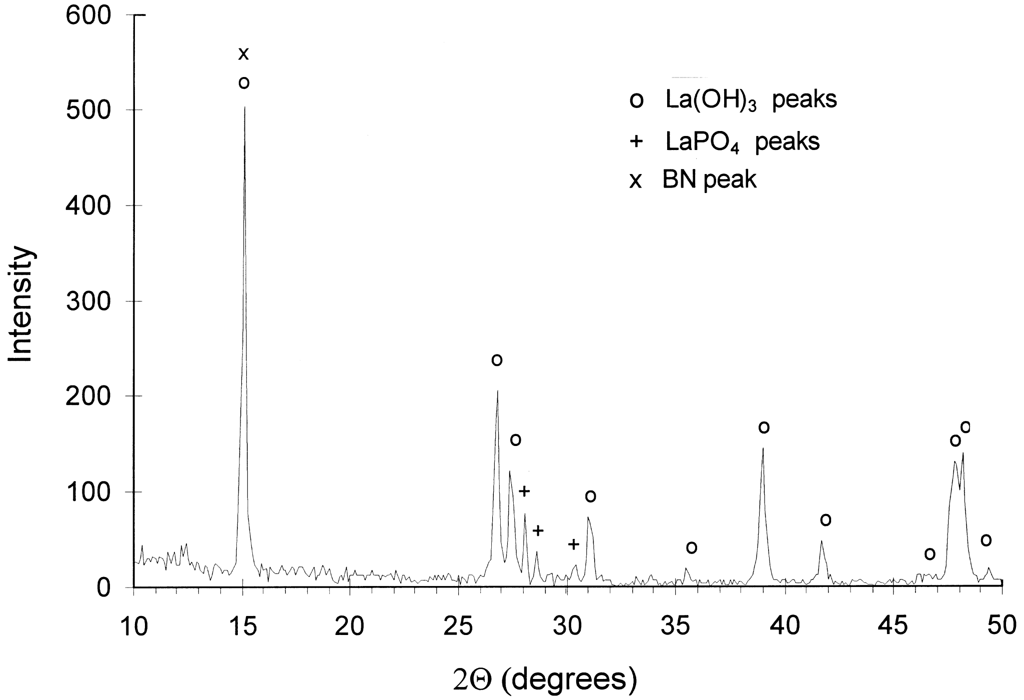

Fig. 3. Power X-ray diffraction pattern of gray powder from the hot-pressed monazite/binder billet (sample no. 4). The sample appears to be mainly $La(OH)_3$, the hydrated version of La_2O_3.

billet (Sample no. 5) was thermally etched, no evidence of a reaction was observed, as shown in Fig. 4(b). Powder X-ray diffraction confirmed that the only phases present in Sample no. 5 were monazite and alumina. The results of the carbon analysis showed that the untreated billet had a carbon content of 0.12%, which was higher than the 0.04% carbon of the treated billet.

4. Discussion

Clearly, the monazite dip-coating slurry (Sample no. 1) and the hot-pressed monazite/binder billet (Samples nos. 3 and 4) had undergone carbothermic reduction resulting in a loss of phosphorus, presumably as a gas phase. Hot-pressing in graphite dies at 1585°C for 3 h produced the most severe conditions resulting in complete reduction to La_2O_3, despite excess phosphorus being present in the starting powder. The thermogravimetric analysis produced less severe conditions and less reduction, resulting in partial reduction to La_3PO_7, because it was configured for a maximum temperature of only 1100°C.

The thermogravimetric analysis sample (no. 1) was the only one fired in an environment that did not contain graphite, so the results of this sample will be the basis for our discussion of the mechanism of this reduction reaction. Since a lower lanthanum phosphate, La_3PO_7, rather than lanthanum carbide, was the product left behind from the carbothermal reduction of lanthanum phosphate at high temperatures in nitrogen environments, as in Eq. (2), the equation for the carbothermic reaction is proposed to be the following:

$$3LaPO_4(s) + 5C(s) \rightarrow La_3PO_7(s) + P_2(g) + 5CO(g) \tag{4}$$

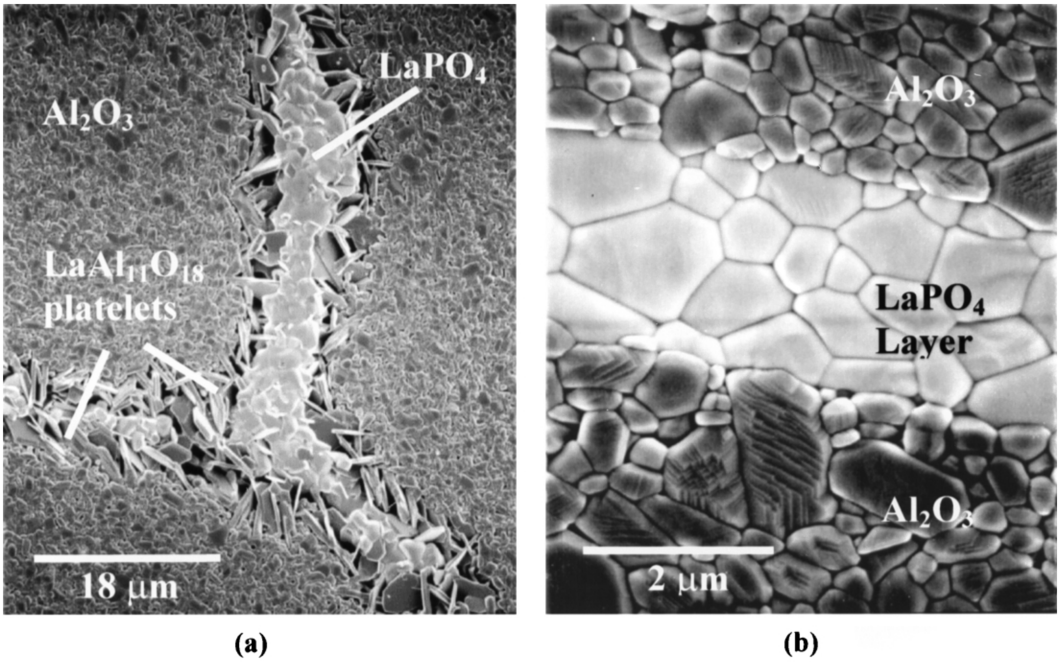

Fig. 4. SEM micrographs of thermally etched surfaces of alumina/monazite fibrous monoliths. (a) Sample that did not undergo annealing prior to hot-pressing. (b) Sample that was annealed in air prior to hot-pressing.

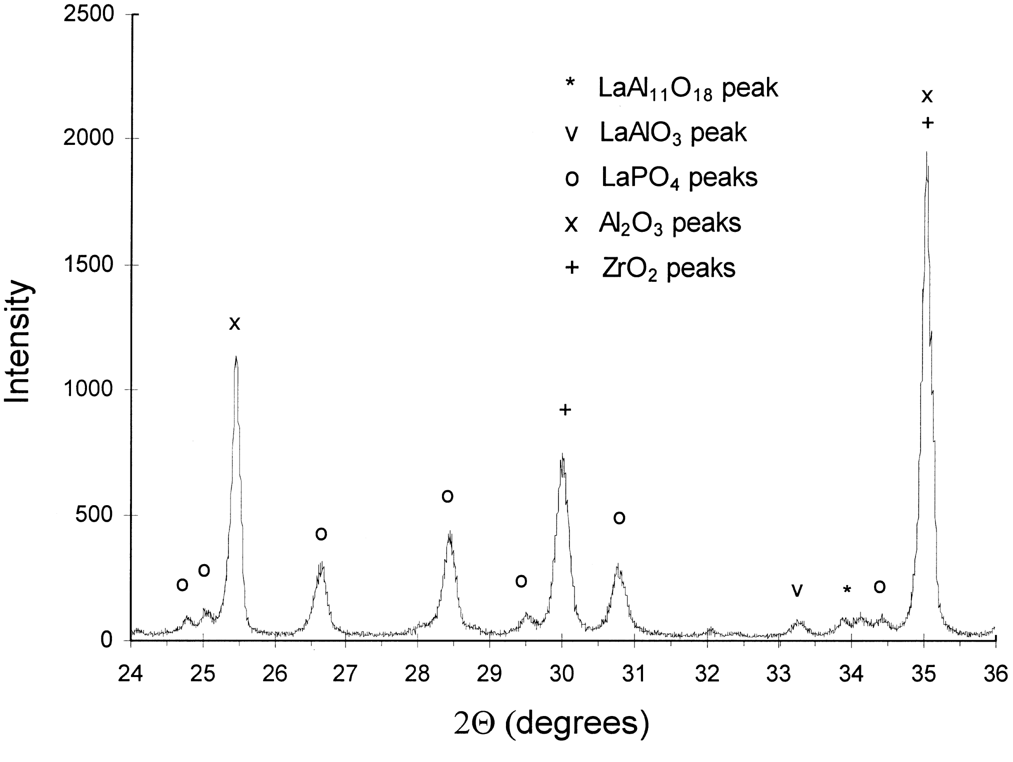

Fig. 5. Powder X-ray diffraction pattern of the hot-pressed alumina/monazite fibrous monolith that was not heat treated prior to hot-pressing (sample no. 6).

As shown in Fig. 6, the Richardson-Ellingham chart for the formation of oxides[21] shows that above 750°C, the free energy of formation of CO from C and O_2 is lower than the free energy of formation of P_2O_5 from P_2 and O_2. This indicates that at high temperatures, CO is more stable than P_2O_5. It can be seen from Fig. 1 that the carbothermic reduction of monazite begins to occur around 750°C, the temperature predicted by the Elling-

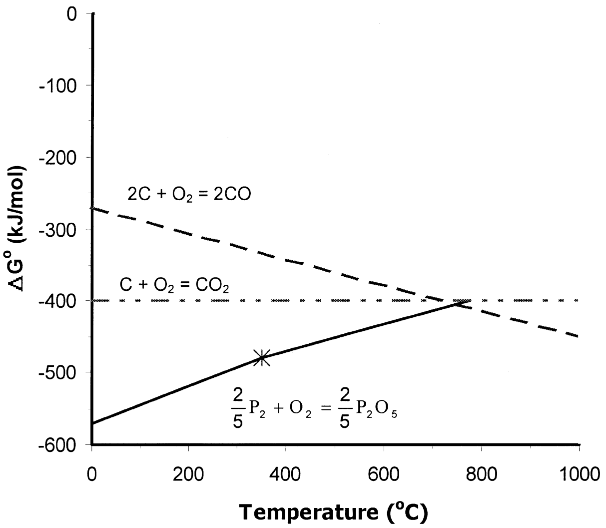

Fig. 6. Richardson–Ellingham plot for the formation of P_2O_5, CO, and CO_2. After R.T. DeHoff.[21]

ham diagram. In our experiments, the oxygen needed to form CO was taken from the phosphate in the sample because oxygen was not available in the atmosphere. While $LaPO_4$ is not on the Ellingham chart, it appears that the carbothermic reduction behavior of this material is caused by the low free energy of formation of carbon monoxide with respect to phosphorus oxide at high temperatures.

Although it cannot be supported by thermodynamic arguments, the reaction for complete reduction of $LaPO_4$ to La_2O_3, either directly or indirectly as a series of reactions forming sequentially lower phosphates, as seen in hot-pressed monazite-only sample (nos. 3 and 4), is given by the equation:

$$2LaPO_4(s) + 5C(s) \rightarrow La_2O_3(s) + P_2(g) + 5CO(g) \quad (5)$$

The power of even small amounts of residual carbon to reduce copious amounts of $LaPO_4$ to La_2O_3 can be seen in the equation:

$$\%LaPO_4 \text{ reduced by vol.} = 779(X)(100 - X) \quad (6)$$

where X is the percentage of carbon contamination by weight. If we assume for example 2.6 wt.% carbon contamination after burnout, as in Sample no. 1, we should expect to see 20.8% of the volume of $LaPO_4$ in the sample to be reduced to La_2O_3. The derivation of Eq. (6) can be found in the Appendix.

In the untreated $LaPO_4/Al_2O_3$ fibrous monolith (Sample no. 6), the formation of the $LaAl_{11}O_{18}$ and $LaAlO_3$ compounds suggests the presence of free La_2O_3, presumably from the $LaPO_4$ via carbothermic reduction and subsequent evaporation of phosphorus bearing gas. These results are consistent with previous studies,[5,10,22] one of which showed that when La_2O_3 and Al_2O_3 react in the solid-state, the first product is $LaAlO_3$ which subsequently reacts with Al_2O_3 to form $LaAl_{11}O_{18}$. The $LaAl_{11}O_{18}$ and $LaAlO_3$ compounds were found at the interface, so they could be detrimental to the interfacial crack deflection behavior needed in high temperature composites by strengthening the interface so that the system no longer meets the He and Hutchinson criteria for debonding.[4,5] Therefore, it would be prudent to preserve the $LaPO_4/Al_2O_3$ interface by eliminating residual carbon with a heat treatment in air.

While thermodynamic arguments cannot be applied to the samples that were hot-pressed in graphite dies, for the graphite dies to contaminate the samples with carbon, the carbon would have to diffuse through the sample — a process governed by kinetics. Previous work[23] has shown that the carbon contamination (120 ppm by weight) found in alumina processed without binders and hot-pressed in graphite dies for 30 min at 1600°C was primarily a result of carbon contamination in the alumina starting powder. This indicates a rather slow diffusion rate of carbon through alumina at high temperatures. There is no data on the diffusion of carbon through monazite, however, the alumina/monazite composite samples (nos. 5 and 6) were 80% alumina by volume. Also, the sample that was heat treated to remove the residual carbon (no. 5) did not show any signs of carbothermic reduction, indicating that the thermodynamic arguments above could be a reasonable explanation of the reaction mechanism in the hot-pressed alumina/monazite composites.

5. Conclusions

Although this was a cursory study of the carbothermic reduction phenomenon in phosphates, the results do verify the potential problem of carbothermic reduction of monazite. It was found that $LaPO_4$ decomposed into phosphorus bearing gas and La_3PO_7 in the presence of carbon at temperatures above 750°C in oxygen-poor atmospheres. This behavior appears to be the result of the higher free energy of P_2O_5 with respect to carbon monoxide at temperatures above 750°C. Furthermore, it was found that, theoretically, even small amounts of carbon could cause significant amounts of $LaPO_4$ to decompose. Thus, it follows that it is likely that other phosphates, such as $CePO_4$, YPO_4, and $AlPO_4$, would also undergo carbothermic reduction at high temperatures in oxygen-poor environments.

These results also indicate that when $Al_2O_3/LaPO_4$ samples are fabricated using binders, a heat treat in air to remove residual carbon is necessary and that the $LaPO_4$ in the samples must not come into contact with the graphite dies during hot pressing. Although carbon re-contaminates the specimen during hot pressing in graphite dies, it does not appear to be in sufficient amounts to cause a reaction. The amount of carbon contamination that monazite can tolerate appears to be at least 0.04 wt.%, which was the amount that was found in the alumina/monozite fibrous monolith that was heat treated prior to hot-pressing and did not show any signs of carbothermic reduction after hot-pressing.

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Appendix A

$X = \%$ carbon in sample by wt.

$Y =$ weight of sample (assuming the sample contains only $LaPO_4$ and carbon).

Amount of $LaPO_4$ in sample by weight $= (1-(X/100))Y$.

Amount of carbon in sample by weight $= XY/100$.

No. of mol of carbon in sample $= (XY/100)/12.011$ (12.011 g/mol is the atomic weight of carbon).

No. of mol of $LaPO_4$ reduced by carbon $= (2/5)(XY/100)/12.011$ [from Eq. (5), 5 mol of carbon reduces 2 mol of $LaPO_4$ to La_2O_3].

Amount of $LaPO_4$ reduced by weight $= 233.88(2/5)(XY/100)/12.011 = 0.0779XY$ (233.88 g/mol is the molecular weight of $LaPO_4$).

Percentage of $LaPO_4$ reduced by weight $= 100(0.0779XY)/[(1\text{-}(X/100))Y] = 779(X)/(100-X)$

Percentage of $LaPO_4$ reduced by volume $= 779\ (X)/(100-X)$ (percentage is the same because weight of sample dropped out of equation).

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