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Synthesis and characterization of $LaPO_4$-coated α-Al_2O_3 powders

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Abstract

$LaPO_4$-coated α-Al_2O_3 powders were successfully synthesized through the heterogeneous precipitation method. The coated powders were characterized by XRD, TEM, EDS, and zeta-potential measurements. According to the XRD results, the coated powders consisted of only α-Al_2O_3 and monoclinic $LaPO_4$. The TEM examinations and EDS analysis showed that under alkaline condition a homogeneous coating with thickness of ~10 nm was obtained on the α-Al_2O_3 powder surface. The zeta-potential measurements showed the coated powders to have a pH value of 7.85 at isoelectric point, similar to that of $LaPO_4$ (pH value of 8.21). This was in good agreement with the TEM and EDS results, indicating a successful coating process in our experiment.

Keywords: A. Powders: chemical preparation; B. Composites; C. Chemical properties; Heterogeneous nucleation processing

1. Introduction

In order to improve the machinability of ceramic materials [1], one method is to introduce another weak interphase or layered structure material into the matrix to facilitate crack deflection during machining [2]. Lanthanum phosphate ($LaPO_4$) is a suitable and effective oxide interphase [3]. Incorporating $LaPO_4$ into Al_2O_3 matrix, the $LaPO_4/Al_2O_3$ interface is weak enough to make the composite easily machined [4,5]. The traditional way to make the $LaPO_4/Al_2O_3$ composite is to mix the two powders directly. In this case a large amount of $LaPO_4$ is needed, leading to serious degradation of the composite strength [6]. In order to avoid such disadvantage, powder coating is introduced as a method to minimize this degradation. This method could make interfacial bond at the $LaPO_4/Al_2O_3$ interface weak [7,8]. The requested $LaPO_4$ amount is therefore decreased to some extent. Among the powder surface coating methods [9–13], the heterogeneous nucleation process has been applied recently [14] due to the uniformity of the coating thickness by controlling the concentration of coating materials between the critical values of homogeneous and heterogeneous nucleation [15]. The preparation of $LaPO_4$-coated α-Al_2O_3 powders through heterogeneous precipitation is not reported at our knowledge up to now in the literature.

The objective of this work was to synthesize $LaPO_4$-coated α-Al_2O_3 powders by incorporating $LaPO_4$ onto the α-Al_2O_3 particle surface by heterogeneous precipitation. The coated powders were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), and zeta-potential measurements.

2. Experimental procedure

In order to prepare a stable particle suspension, the as-received α-Al_2O_3 particles with a mean diameter of 200 nm were firstly dispersed in a bath for 40 min to minimize the particle agglomeration. An appropriate amount of 0.01 M $La(NO_3)_3$ solution was added into the suspension. After this, the same amount of 0.01 M Na_3PO_4 was dropped into the suspension under strong magnetic stirring. During the dropping process, the pH value of the suspension was kept constant by using NaOH and HCl solutions. The resulting suspension was continuously stirred for 2 h and then filtered. The obtained powders were washed with distilled water for three times and dried in an oven at 60 °C for 12 h.

The phase composition of the coated powders was identified through XRD. The powder morphology was observed using

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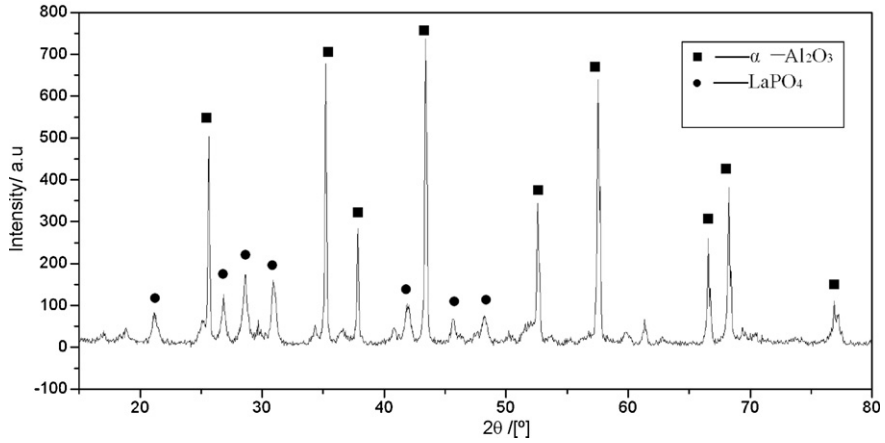

Fig. 1. XRD patterns of the $LaPO_4$-coated α-Al_2O_3 powders.

TEM and EDS. In order to evaluate the surface potential of the powders, the zeta-potential measurements were performed.

3. Results and discussion

As from the XRD patterns of the $LaPO_4$-coated α-Al_2O_3 powders shown in Fig. 1, no other impurities than α-Al_2O_3 and monoclinic $LaPO_4$ were detected, indicating a phase composition of the powders only α-Al_2O_3 and monoclinic $LaPO_4$.

Fig. 2 shows the TEM images of the $LaPO_4$-coated α-Al_2O_3 powders synthesized under different pH values. Under the pH values of 1 and 6, the coated powders have a clear core-shell structure (Fig. 2(a) and (b)). A uniform coating, however, has been objected. The coating thickness varies from 10 to 110 nm. When the pH value was increased to 10, the coating is quite uniform, as shown in Fig. 2(c). The coating thickness is estimated to be 10 nm approximately. This sample was calcined at 1000 °C, the TEM image of the powders after 1000 °C calcination is shown in Fig. 3. The formed nanocoating before calcination decomposed to spherical nanoparticles and agglomerated on the surface of α-Al_2O_3 particles due to the heat treatment. The average diameter of the nanoparticles is around 8 nm.

In order to identify the chemical elements of the coated particles, the EDS analysis was performed on the $LaPO_4$-coated α-Al_2O_3 powders after 1000 °C calcination which was synthesized under pH value of 10. The EDS result of the whole area of Fig. 3 is shown in Fig. 4, the peaks of La, P, Al, and O could be found. It is clearly shown that the coated powders were composed of α-Al_2O_3 and $LaPO_4$.

The detailed coating process, however, is believed to be related to the surface potential of the particles since the thickness and uniformity of the $LaPO_4$ coating could be adjusted via altering the pH value of the suspension. The zeta-potential measurements were therefore performed under different pH values to evaluate the surface potential of the powders (Fig. 5). As seen from Fig. 5, the zeta-potential of α-Al_2O_3 particles shows a switching isoelectric point from positive to negative at pH of 9.31. When the suspension was adjusted to acidic, the following chemical reactions are proposed (Eqs. (1) and (2)) [16]:

$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O \quad (1)$$

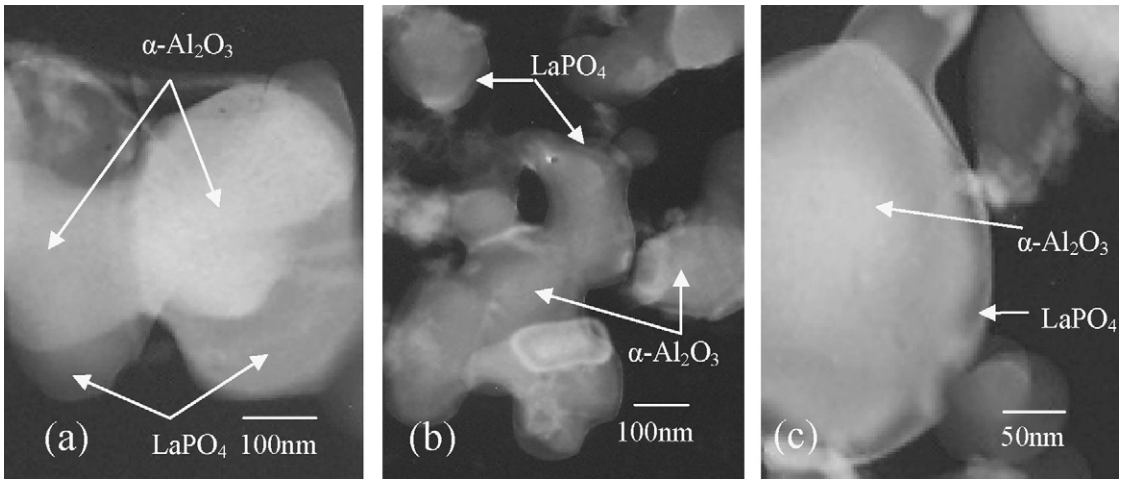

Fig. 2. TEM images of the $LaPO_4$-coated α-Al_2O_3 particles before calcination under pH value of 1 (a), 6 (b), and 10 (c).

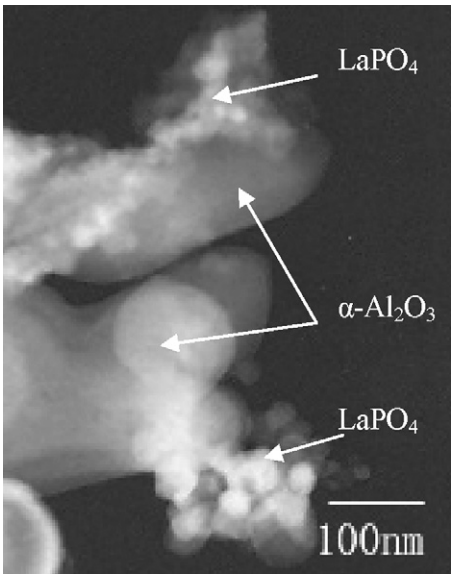

Fig. 3. TEM image of the $LaPO_4$-coated α-Al_2O_3 particles after 1000 °C calcinations.

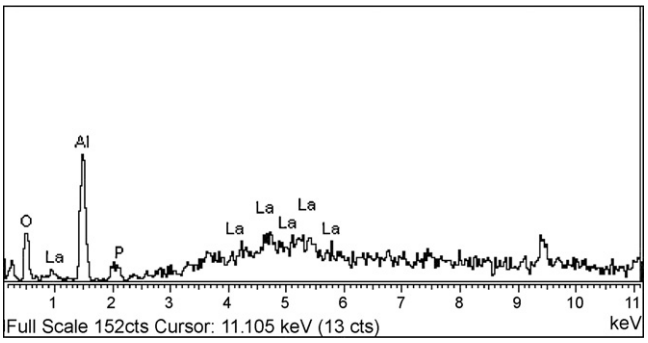

Fig. 4. EDS analysis of the $LaPO_4$-coated α-Al_2O_3 particles after 1000 °C calcinations.

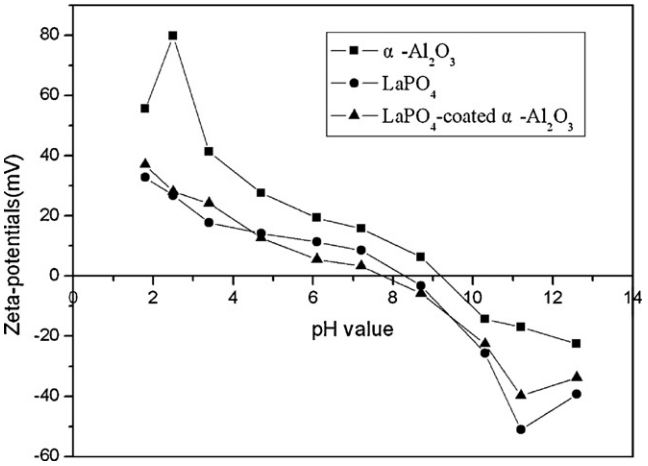

Fig. 5. Zeta-potentials of the α-Al_2O_3 powders, the $LaPO_4$ powders, and the $LaPO_4$-coated α-Al_2O_3 powders under different pH values.

$$AlCl_3 \rightarrow Al^{3+} + 3Cl^- \quad (2)$$

The α-Al_2O_3 particles firstly absorb Al^{3+} to form a positive zeta-potential, as illustrated in Fig. 6(a). In such a case, the NO_3^- ions are absorbed on the particles surface while the La^{3+} ions are far away from the α-Al_2O_3 particles. When the Na_3PO_4 solution is added into the suspension, the reaction between PO_4^{3-} and La^{3+} to form $LaPO_4$ occurs not on the particle surface but far away from the α-Al_2O_3 particles. The resulting $LaPO_4$ coating was therefore not uniform. In the case of the suspension being adjusted to alkaline, the relevant reactions are (Eqs. (3) and (4)) [16]:

$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O \quad (3)$$

$$NaAlO_2 \rightarrow Na^+ + AlO_2^- \quad (4)$$

The α-Al_2O_3 particles firstly absorb AlO_2^-, leading to a negative zeta-potential (Fig. 6(b)). The La^{3+} ions are therefore absorbed onto the α-Al_2O_3 particle surface. When the Na_3PO_4 solution is added into the suspension, it causes a reaction to form $LaPO_4$ on the particle surface. As a consequence, the α-Al_2O_3 surface is coated with a uniform $LaPO_4$ layer.

Fig. 5 also shows the zeta-potentials of the powders of $LaPO_4$ and $LaPO_4$-coated α-Al_2O_3 under different pH values. As seen from Fig. 5, the zeta-potential of the coated powders is

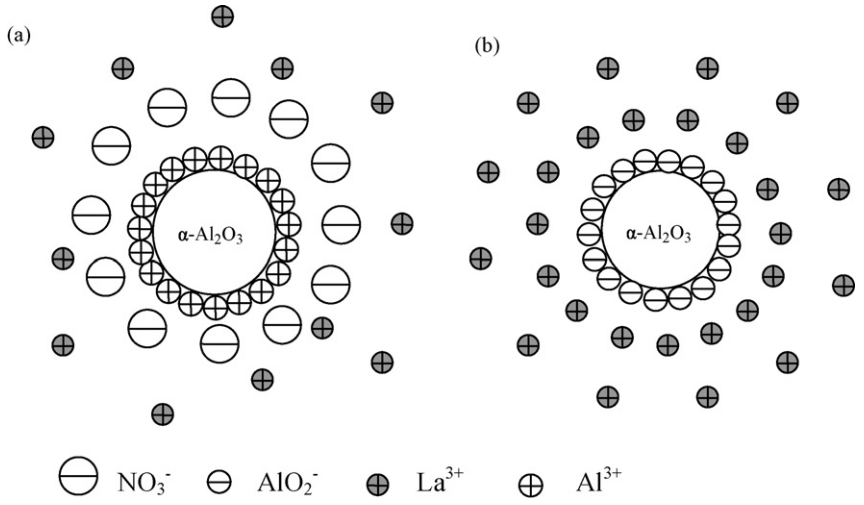

Fig. 6. Schematic illustrations of ions adsorption on the α-Al_2O_3 particle surface: (a) under acidic condition and (b) under alkaline condition.

similar to that of $LaPO_4$ and different from that of α-Al_2O_3. A noticeable pH value shift at isoelectric point for the α-Al_2O_3 powders is observed (9.31–7.85) due to the coating process. This result indicates that the α-Al_2O_3 particles were coated with $LaPO_4$ and possessed a surface potential characteristic similar to that of $LaPO_4$ powders.

In traditional way to make the $LaPO_4/Al_2O_3$ composite, about 30 wt.% of $LaPO_4$ was requested to make the composite machinable [6]. After calculating, the requested $LaPO_4$ amount is decreased to 13.5–19.0 wt.% by the coating method.

4. Conclusion

The synthesis of $LaPO_4$-coated α-Al_2O_3 particles was successfully performed by the heterogeneous precipitation method. According to XRD results the phase composition of the powders was only α-Al_2O_3 and monoclinic $LaPO_4$. TEM and EDS observations showed that under alkaline condition the coatings obtained were uniform with an average thickness of 10 nm. The zeta-potential of the $LaPO_4$-coated α-Al_2O_3 powders was similar to that of $LaPO_4$, which confirmed that $LaPO_4$ formed a surface layer on the α-Al_2O_3 particles and altered the surface chemistry of the α-Al_2O_3.

Acknowledgements

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