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Effects of monazite-type LaPO₄ and powder processing on the mechanical and thermal properties of yttria stabilized zirconia composites

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To apply a thermal barrier coating, the coating materials must satisfy the basic requirements. This paper explains composite powder processing and the characterization of sintered materials. The composite powders were prepared by two types of method: conventional ball-milling and chemical precipitation. The morphology of the powder differed with the processing method. In chemically precipitated powder, the surface of zirconia was coated with LaPO₄. The samples were fabricated from these powders, using the PECSed method. The flexural strength of the nanocomposites was decreased with an increase in the amount of LaPO₄ due to its poor mechanical properties. However, the thermal properties, such as thermal conductivity and high temperature stability, were lower and more stable than that of the monolith.

Key words: 3YSZ, LaPO₄, powder processing, mechanical properties, thermal properties.

Introduction

To apply a thermal barrier coating (TBC), the coating materials must satisfy the basic requirements, such as a high melting point, low thermal conductivity, low thermal expansion coefficient difference with the substrate metal, no phase transformation between room temperature and the operating temperature, chemical stability, good adhesion on the metallic substrate, low sinterability to maintain a porous structure, etc [1-3]. A single material is not suitable as a TBC. Therefore, a TBC has to have multifunctional layers using various materials. Among many factors, the selection of coating materials is very important in a TBC.

Recently, yttria stabilized zirconia (YSZ) based materials have mainly been used for a TBC [4-5]. But these materials have a problem, which is the phase transformation at 1200 °C. To improve the thermal properties of YSZ, studies of novel TBC materials have been progressed actively. The advanced TBC materials should have CeO_2/YSZ [6], a mixture of a rare earth oxide [7], $La_2Zr_2O_7$ [8-10], and $La_2Zr_2O_7/YSZ$ multilayer [11], etc. The materials in TBC are affected by the operating conditions such as the environment and temperature, etc. According to extensive research, the rare earth oxides are effective materials to improve the thermal properties. For example, a $La_2Zr_2O_7/8YSZ$ [11-13] coating gives excellent thermal cycling performance, and a $CeO_2/8YSZ$ coating [1] is used for improving thermal shock resistance. Many researchers have been interested in monazite materials. The monazites (LnPO₄, Ln = La, Ce, Th, etc.) have good thermal properties (high temperature stability, lower thermal conductivity and higher thermal expansion coefficient than dense zirconia) and good chemical stability (good corrosion resistance in an environment containing sulfur and vanadium salts). However, these monazites have been limited in application to coatings because of poor bonding properties between monazite and oxides [14].

In this study, a monazite-type LaPO₄ with 3YSZ having high temperature stability and low thermal conductivity was fabricated. These composite powders were prepared by different powder processing methods such as conventional ball-milling and a chemical precipitation method. The suitability of 3YSZ/monazite-type LaPO₄ nanocomposites was investigated in terms of thermal stability, thermal conductivity and microstructure.

Experimental Procedures

Materials

3YSZ (TZ-3YE, Tosoh Corp., Japan), LaPO₄ (monazitetype, Shin-Etsu Chem. Co. Ltd., Japan), La₂O₃ (99.9%, Shin-Etsu Chem. Co. Ltd., Japan), HCl (6 mol/l, Wako Pure Chem. Ind. Ltd., Japan), H₃PO₄ (Wako Pure Chem. Ind. Ltd., Japan), and ammonia water (28%, Ishizu Seiyaku Ltd., Japan) were used as-received.

Preparation of composite powders

The preparation of composite powders was made by two methods, which are conventional ball-milling and chemical precipitation [15-16].

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Conventional ball-milling method

3YSZ and LaPO₄ were ball-milled in ethanol for 24 h. The ball-milled slurries were completely dried using an evaporator and a dry-oven. The dried mixed powders were ball-milled in a pot for 24 h. After ball milling, the slurry was washed several times with de-ionized water and acetone. Then the powder was dried for 24 h in a dry oven and calcined at 700 °C for 2 h in air. The calcined powders were ball-milled in a pot for 24 h.

Chemical precipitation method

LaPO₄ was synthesized from La₂O₃ powder. La₂O₃ powder was completely dissolved in HCl (6 mol/l, Wako Pure Chem. Ind. Ltd., Japan) to form LaCl₂. 3YSZ was added to this solution (LaCl₂) and ball-milled for 12 h. The aqueous solution of H₃PO₄ (Wako Pure Chem. Ind. Ltd., Japan) was added to the 3YSZ slurry (the ratio of La to P was 1 : 1), and more mixed for 6 h. After ball milling for 6 h, ammonia and water (28%, Ishizu Seiyaku Ltd., Japan) was added to precipitate the powder. This slurry was ball-milled for 6 h to precipitate powders more homogenously. After ball milling, the slurry was washed several times with de-ionized water and acetone. The powder was dried for 24 h in dry oven and calcined at 700 °C for 2 h in air. The calcined powders were ball-milled in a pot for 24 h.

Preparation of composites

3YSZ/LaPO₄ nanocomposites were fabricated by a pulse electric current sintering (PECS) method using synthesized composite powders. The sintering conditions were 1300 °C, 30 MPa for 5 minutes in an Ar gas flow environment. The rise in temperature was 100 K ·minute⁻¹.

Measurements

The characterization of composites powders were determined by using X-ray diffraction (RINT2500, Rigaku, Japan) and thermochemical techniques such as thermogravimetric analysis (TGA) and different thermal analysis (DTA) (TG-DTA2000S, MAC Science Co., Ltd., Japan). The thermal conductivity of 3YSZ/LaPO₄ nanocomposites was calculated using the density, thermal diffusivity and specific heat. The density, thermal diffusivity and specific heat of 3YSZ/LaPO₄ nanocomposites were measured using the Archimedes immersion methods in toluene solvent, a laser flash thermal constant analyzer (TC-7000, Ulvac-Riko, Japan) and a differential scanning calorimeter (DSC404C, NETZSCH, Germany), respectively. The microstructure of 3YSZ/LaPO₄ composites were observed using scanning electron microscopy (SEM, model S-5000, Hitachi Co., Ltd., Japan).

Results and Discussions

Processing and characterization of compositing powders

XRD patterns of $3YSZ/LaPO_4$ composite powders are shown in Fig. 1. The patterns from the composite powders were not changed by the powder processing method of conventional ball-milling and chemical precipitation. The XRD patterns of the 3YSZ was mainly the tetragonal phase including a little monoclinic phase, as shown in Fig. 1. On the other hand, the XRD patterns from LaPO₄ were the monazite-type. The intensity from LaPO₄ of the conventional ball-milled composite powders was stronger than that from chemically precipitated composite powders. We consider that the difference of intensity is related to the morphology of the composite powders.

The morphology of the 3YSZ/LaPO₄ composite powders is compared in Fig. 2. There were a distinct difference



Fig. 2. SEM micrographs of 3YSZ/20 vol% LaPO₄ composite powders with different composite processing; (a) conventional ball-milling method, and (b) chemical precipitation method.



Fig. 1. XRD patterns of $3YSZ/LaPO_4$ composite powders with different composite processing; (a) conventional ball-milling method, and (b) chemical precipitation method ($\mathbf{\Theta}$: tetragonal, \mathbf{A} : monoclinic, $\mathbf{\nabla}$: monazite).

between the conventional ball-milled composite powder and the chemical precipitated composite powder. The conventional ball-milled composite powders were just mixed 3YSZ and LaPO₄ particles. However, the chemical precipitated composite powders had LaPO₄ coatings on the 3YSZ surfaces. Therefore, the particle sizes of the chemically precipitated composite powders were larger than that of the conventional ball-milled composite powder, as shown in Fig. 2. Thickness of coated LaPO₄ layer was about 10 nm. We consider that the weak XRD intensity of LaPO₄ in the chemically precipitated composite powder

Fig. 3 shows the TG-DTA results of the composite powders. The TG-DTA results of 3YSZ and $LaPO_4$ were used for the commercial powders. The results from 3YSZwere an exothermic reaction between 220 and 400 °C. This temperature range was observed to give a weight loss. LaPO₄ was observed to give two types of endothermic reaction. The endothermic reaction between 30 and 80 °C was caused by the dehydration of the absorbed water on the surfaces. Another endothermic reaction between 1200 and 1300 °C was related to the decomposition of LaPO₄. The weight loss from LaPO₄ was observed in two steps due to the two types of reaction. The TG-DTA results of the composite powders show a distinct difference between the conventional ball-milled composite powder and the chemically precipitated composite powder. Conventional ball-milled and chemically precipitated composite powders were dominated by exothermic and endothermic reactions, respectively. The endothermic reaction between 200 and 240 °C of the chemically precipitated composite powders was a transition from rhabdophane (LaPO₄·0.5H₂O) to monazite-type (LaPO₄). These endothermic reactions were attended with a weight loss. When the exothermic or endothermic reaction was finished, the weight loss of 3YSZ/LaPO₄ composite powder was constant. The weight loss of 3YSZ/LaPO₄ composite powder at high temperature was lower than that of LaPO₄.

Characterization of PECSed composites

Samples were fabricated by the PECSed method using the two types of composite powder. The XRD patterns of PECSed samples are shown in Fig. 4. The XRD results for composites were observed to the difference trends of the zirconia phase with the composite powder processing methods. As the amount of LaPO₄ increased, the monoclinic phase of zirconia in both composites was increased. The phase transformation of zirconia as a function of the



Fig. 3. TG-DTA of $3YSZ/LaPO_4$ composite powders with different composite processing; (a, c) conventional ball-milling method, and (b, d) chemical precipitation method.



Fig. 4. XRD patterns of $3YSZ/LaPO_4$ nanocomposites fabricated at $1300 \,^{\circ}C$, 30 MPa for 5 minutes in an Ar gas atmosphere with different composite processing; (a) conventional ball-milling method, and (b) chemical precipitation method (\bullet : tetragonal, \blacktriangle : monoclinic, \checkmark : monazite).



Fig. 5. Mechanical properties of 3YSZ/LaPO₄ nanocomposites as a function of the amount of LaPO₄; (a) density, and (b) flexural strength.

amount of LaPO₄ was distinctly different between the conventional ball-milled composite and chemically precipitated composite. In the case of the conventional ball-milled composites, the zirconia phase in the composites including 40 vol% LaPO₄ was completely transformed from the tetragonal to the monoclinic phase. On the other hand, complete phase transformation of zirconia in the case of chemically precipitated composites was observed when 20 to 30 vol% LaPO₄ was added to zirconia. The zirconia phase in 3YSZ/40 vol% LaPO₄ composites was completely tetragonal.

The mechanical properties of $3YSZ/LaPO_4$ nanocomposites as a function of the amount of $LaPO_4$ were compared. As shown in Fig. 5(a), the density of $3YSZ/LaPO_4$ nanocomposites with both powder preparation methods were 97% or more of theoretical density. The flexural strength

of 3YSZ/LaPO₄ nanocomposites were decreased with an increase in the amount of LaPO₄. In general, the flexural strength is related to the grain size according to the Hall-Petch relation. However, the flexural strength of these nanocomposites were little effected by the grain size. The degradation of flexural strength was caused by the dispersed monazite-type LaPO₄. Monazite-type LaPO₄ materials have poor mechanical properties and weak bonding between oxides. As shown in Fig. 5(b), a difference in flexural strength of 3YSZ/LaPO₄ nanocomposites was observed with the composite powder processing methods. The flexural strength of chemical precipitated composites was higher than that of conventional ball-milled composites. We consider that the difference in flexural strength is related to the microstructure. The microstructure of chemically precipitated composites was more homogeneous than that of conventional



Fig. 6. SEM micrographs of the fracture surfaces of $3YSZ/LaPO_4$ nanocomposites as a function of the amount of $LaPO_4$ and different powder processing; (a) $10 \text{ vol}\% \text{ LaPO}_4$, (b) $20 \text{ vol}\% \text{ LaPO}_4$ of conventional ball-milled composites, and (c) $10 \text{ vol}\% \text{ LaPO}_4$, (d) $20 \text{ vol}\% \text{ LaPO}_4$ of chemically precipitated composites

ball-milled composites, as shown in Fig. 6. The reason of heterogeneous microstructure such as partially large grain was caused by the origin of fracture. Fig. 6 shows the fracture behaviors of 3YSZ/LaPO₄ nanocomposites. The fracture behavior of both nanocomposites was dominated by intergranular-type fracture, as shown in Fig. 6. Intergranular-type fracture was caused by the formation of weak bonding between 3YSZ and LaPO₄ [4] due to the interfacial properties of LaPO₄ [14]. Finally, we consider that the degradation of flexural strength of nanocomposites as a function of the amount of LaPO₄ was caused by increasing the weak interface area.

As shown in Fig. 7, the thermal conductivity of 3YSZ/

LaPO₄ nanocomposites was compared. The thermal conductivity of both nanocomposites was related to the amount of LaPO₄ and temperature. The thermal conductivity of nanocomposites was decreased with an increase in the amount of LaPO₄. Generally, the thermal conductivity of polycrystalline materials is related to the phonon scattering generated by the grain boundaries. As the amount of LaPO₄ increased, the grain size of the nanocomposites was decreased, and consequently area of grain boundaries was increased. Therefore, the decreasing thermal conductivity of nanocomposites was caused by increasing phonon scattering generated by grain boundaries due to increments in areas of the grain boundary. The thermal conductivity of nanocomposites was lower than that of the monolith. The difference in thermal conductivity between the monolith and nanocomposites was increased with an increase in the temperature. The difference in thermal conductivity at high temperature was higher than that at low temperature. The variation of thermal conductivity of chemically precipitated composites was more stable than that of conventional ball-milled composites. We consider that the variation of thermal conductivity with both nanocomposites is related to the existence of a small amount of metastable phase. In the case of conventional ball-milled nanocomposites, 3YSZ containing 30 vol% LaPO₄ was observed to have a small amount of the metastable phase, as shown in Fig. 7(a). However, chemically precipitated nanocomposites were not observed to have any metastable phase.

To investigate high temperature stability, two kinds of nanocomposite were heat treated at 1500 °C for 100 h in an atmosphere environment. The high temperature stability of conventional ball-milled composites and chemically precipitated composites is compared in Fig. 8. After heat treatment, the samples were observed to crack and show surface bloating. The monolith of 3YSZ and LaPO₄ were



Fig. 7. Thermal conductivity of 3YSZ/LaPO₄ nanocomposites with different powder processing; (a) conventional ball-milled composites, and (b) chemically precipitated composites.



Fig. 8. Optical micrographs of 3YSZ/LaPO₄ nanocomposites with different powder processing (a) as-sintered, and (b) heat treated (Up: chemically precipitated nanocomposites, down: conventional ball-milled nanocomposites).

observed to surface bloat and crack. Monolithic 3YSZ and LaPO₄ gave lamellar cracks parallel to the surface and surface microcracks, respectively. On the other hand, the nanocomposites showed mainly marco cracks and micro cracks. Conventional ball-milled nanocomposites showed macro cracks and micro cracks only above 15 vol% LaPO₄. However, chemically precipitated nanocomposites did not show cracks and surface bloating. We consider that the high temperature stability of chemically precipitated nanocomposites macro-posites was improved as compared with conventional ball-milled nanocomposites.

Conclusions

To apply a TBC, the coating materials must satisfy the basic requirements such as low thermal conductivity and high temperature stability. Composite powders for TBCs were prepared by two types of preparation method; a conventional ball-milling method and a chemical precipitation method. The properties of composite powders differed with the different preparation methods. The morphology of conventional ball-milled powder and chemically precipitated powder was a mixture of 3YSZ and LaPO₄, and LaPO₄ coated on the surface of 3YSZ, respectively. The mechanical and thermal properties showed distinct differences between conventional ball-milled powder and chemically precipitated powder. The mechanical properties of nanocomposites were decreased with an increases in the amount of LaPO₄ due to poor mechanical properties of LaPO₄. The low thermal conductivity of nanocomposites was caused by increased phonon scattering generated by grain boundaries. At high temperature, the nanocomposites maintained a low thermal conductivity and high temperature stability as compared with the monolith. Chemical precipitated nanocomposites obtained excellent mechanical and thermal properties as compared with conventional ball-milled nanocomposites.

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