

Characterization of 3YSZ/LaPO₄ composites coatings made by an atmospheric plasma spraying method

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3YSZ/LaPO₄ composites applied for thermal barrier coatings (TBC) were deposited by an atmospheric plasma spraying (APS) method. The residual stresses and thermal conductivity of 3YSZ/LaPO₄ composite coating samples were investigated. The thickness of the APS coating layer on the substrate metal was about 115 to 130 μm. Residual stresses of APS coating samples were observed to be both compressive and tensile. Residual stresses of APS coating samples were changed by the amount of LaPO₄. As the amount of LaPO₄ increased, the compressive residual stresses of APS coating samples were increased. The differences of the residual stress of APS coating samples were increased from 49.44 MPa of 3YSZ/10 vol% LaPO₄ to 305.9 MPa of 3YSZ/40 vol% LaPO₄. The thermal conductivity of the 3YSZ/LaPO₄ composite coating layer was calculated by utilizing APS coating layer on the substrate metal. The calculated value of the thermal conductivity of coating layers ranges from 0.11 to 0.19 W/m·K.

Key words : YSZ, LaPO₄, APS method, residual stress, thermal conductivity.

Introduction

Thermal barrier coatings (TBC) have been used to protect metallic substrates of gas turbines at high temperatures. Advanced materials required for industries such as aerospace and power plant etc. were developed, because the traditional turbine materials have reached the limits of their temperature capabilities [1-3]. Moreover, these ceramic coatings of gas turbine used in aerospace and power plants were required to protect the components of gas turbine from corrosion, oxidation and mechanical property degradation as well as thermal resistance [4]. Therefore, ceramic protection coatings in gas turbine are very important.

Recently, the coating materials have been mainly yttria stabilized zirconias (YSZ), because these materials have low thermal conductivity and a coefficient of thermal expansion similar to that of the substrate metal. However, the operation temperature of YSZ is limited below 1200 °C, because of the volume change as a result of the phase transformation from monoclinic to tetragonal at this temperature. To overcome this problem of YSZ, many studies have been made to get novel advanced materials by controlling the microstructure and coating processing. Firstly, novel advanced materials should be based on YSZ co-doped with one or more rare earth oxides [5-8] and the other on the pyrochlore-type zirconates (M₂Zr₂O₇, M = Sm, Nd, Gd)

[9-12]. These materials have excellent thermal properties such as high temperature stability, low thermal conductivity and a high thermal expansion coefficient. Second, the microstructure is a very important factor in a TBC. The thermal properties of TBC materials are affected by pore contents, architecture, and aspects of the topology of the coating such as layering, grain size, etc. Finally, coating processing such as APS and EB-PVD technique influences the coating properties such as durability and thermal insulation in TBC.

In this study, we focused on the fabrication of coating layers, which have a low thermal conductivity and high thermal stability composites rather than monolithic zirconia. To improve the high temperature stability and low thermal conductivity of zirconia, 3YSZ/LaPO₄ nanocomposites were fabricated, rather than rare earth oxide doped zirconia. LaPO₄ has a high temperature stability, a lower thermal conductivity and a higher thermal expansion coefficient than dense zirconia. Moreover, it has good corrosion resistance in an environment containing sulfur and vanadium salts. In previous studies, the mechanical and thermal properties of 3YSZ/LaPO₄ nanocomposites were investigated as a function of the amount of LaPO₄ [13-15].

In this study, these composite materials applied as TBCs were deposited by an atmospheric plasma spraying method. The residual stresses and thermal properties of 3YSZ/LaPO₄ composite coating samples were investigated.

Experimental Procedures

Powder preparation

Starting materials used were 3 mol% yttria stabilized

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zirconia (TZ-3YE, Tosoh Corp., Japan) and LaPO₄ (monazite-type, Shin-Etsu Chem. Co. Ltd., Japan). The amount of LaPO₄ into 3YSZ was varied from 10 to 40 vol % LaPO₄. The powders were mixed in ethanol for 24 h. The slurry was dried using a rotary evaporator, and kept in a dry oven at 55 °C for 12 h. Dried composite powders was ball-milled in a pot for 24 h.

Coating

Stainless steel (SUS304) was used as a substrate metal. 3YSZ/LaPO₄ composite coatings on the substrate metal were made by an atmospheric plasma spraying (APS) method. Plasma spraying was carried out by an A-2000 atmospheric plasma spraying equipment with F4-MB gun (Sulzer Metco AG, Switzerland). The feedstock was utilized with a Twin-System 10-V feeder (Plasma-Technik Ag, Switzerland). Deposition conditions are shown in Table 1.

Table 1. Deposition conditions for 3YSZ/LaPO₄ composite coatings

Current (A)	H ₂ (slpm)	Ar (slpm)	Voltage (V)	Spray distance (mm)	Spray power (kW)
620	12	42	70	120	43.4

Characterization

The thermal properties of APS coating layers were measured. The microstructure of the coating layers was observed by a color 3D profile microscope (VK-9500, Keyence, Japan) and a scanning electron microscope (SEM, model S-5000, Hitachi Co., Ltd., Japan). Residual stress of APS coating samples was measured by XRD equipment with a position sensitive proportional counter (PSPC) (PSPC-RSF, Rigaku, Japan) using CrK α radiation. The measurement area (i.e., X-ray spot size) was a circle 4 mm in diameter. Residual stress was measured at intervals of 6 mm between the centers of the X-ray spots. The thermal properties of APS coating samples were investigated. The thermal diffusivity was measured using a laser flash thermal constant analyzer (TC-7000, Ulvac-Riko, Japan). The specific heat was measured using a differential scanning calorimeter (DSC404C, NETZSCH, Germany).

Results and Discussion

Fig. 1 shows the XRD patterns of composite powders and APS coating layers with different compositions of 3YSZ/LaPO₄ powder. The XRD patterns of 3YSZ and

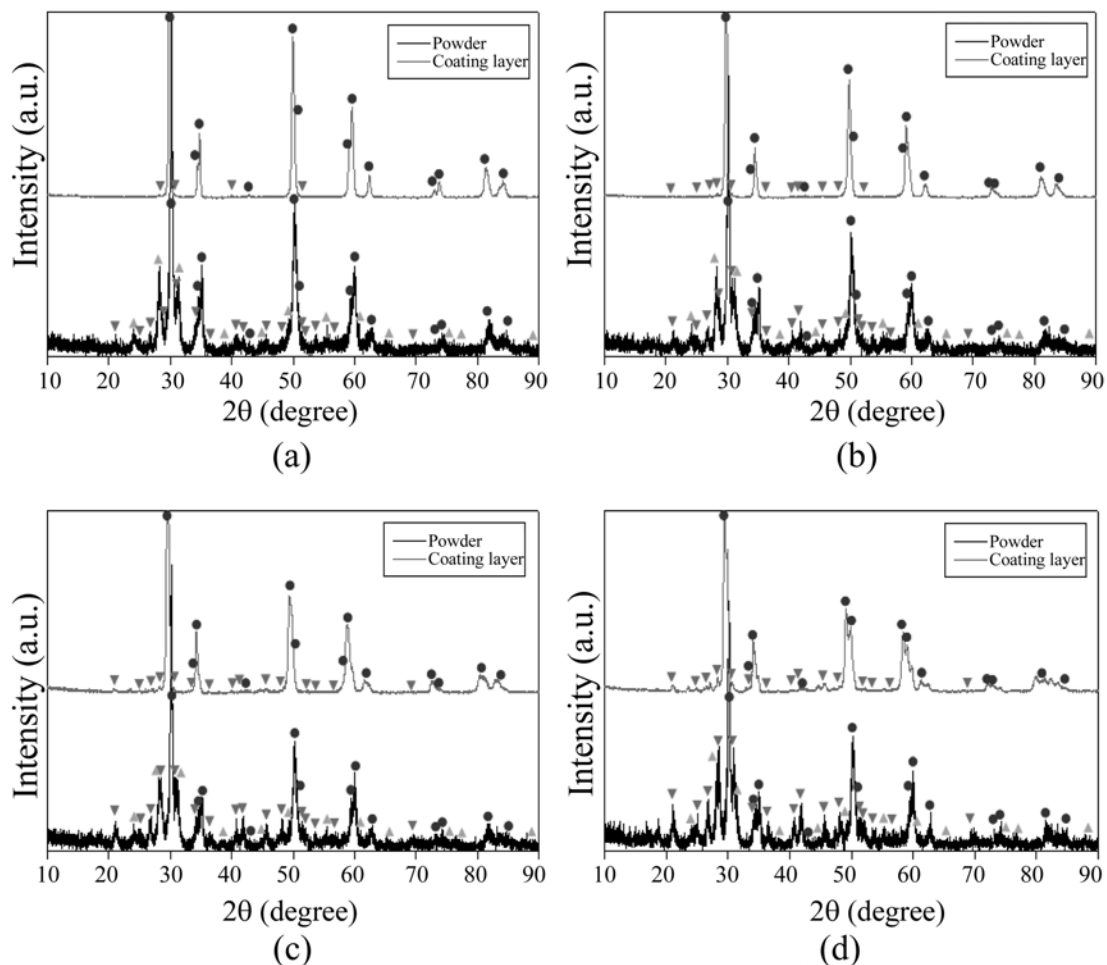


Fig. 1. XRD patterns of powders and coated layers of 3YSZ/LaPO₄ composites with different LaPO₄ contents; (a) 10 vol.%, (b) 20 vol.%, (c) 30 vol.%, and (d) 40 vol.% (● : tetragonal, ▲ : monoclinic, ▼ : monazite).

LaPO₄ powders have mostly a tetragonal phase including a little monoclinic phase and a monazite-type phase, respectively. After APS coating, the 3YSZ/LaPO₄ composite coating layers was transformed from the monoclinic phase of zirconia to the tetragonal phase, as shown in Fig. 1. The peak shift of the XRD patterns was caused by the bending of samples due to the misfit of the thermal expansion coefficient between the substrate metal and ceramic coating layer. The phase of the LaPO₄ was the monazite-type. The peak intensity from LaPO₄ in the APS coating samples was decreased in comparison with that of the composite powders. We consider that the decrease of the peak intensity from the LaPO₄ was affected by the decomposition or vaporization at the high spraying temperature, because the melting point of monazite-type LaPO₄ (2074 °C) was lower than that of ZrO₂ (2710 °C). According to our previous results [15], the weight loss of monolithic LaPO₄ rapidly decreased above 1000 °C. However, the weight loss of 3YSZ and 3YSZ/LaPO₄ composite powders was lower than that of monolithic LaPO₄. The different weight loss between 3YSZ/LaPO₄ composite powders and monolithic LaPO₄ was extremely large above 1000 °C.

The surfaces of APS coating samples were observed by a color 3D profile microscope. The surface morphology of APS coating samples was observed to be rough, as

shown in Fig. 2. The surface roughness (Ra) was about 8.92 to 11.25 μm. Maximum peak to valley roughness height (Ry) of APS coating samples was about 83.60 to 106.57 μm. These rough surfaces were confirmed by SEM microscopy. Fig. 3 shows the cross-sectional microstructures of APS coating layer. The APS deposition conditions were

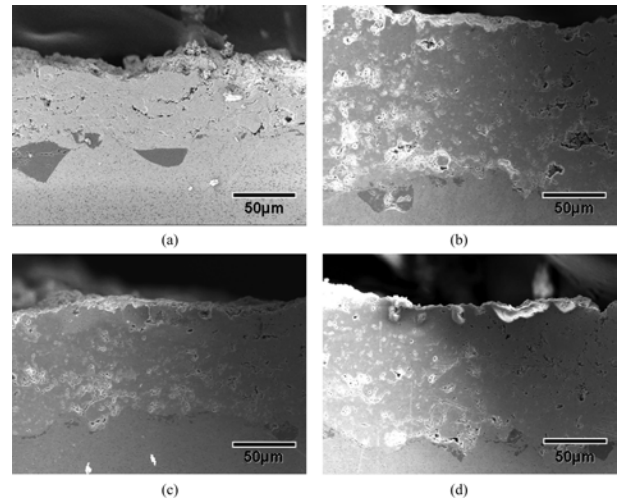


Fig. 3. SEM micrographs of the cross-section of APS 3YSZ/LaPO₄ composite coating samples as a function of the amount of LaPO₄; (a) 10 vol.%, (b) 20 vol.%, (c) 30 vol.%, and (d) 40 vol.%.

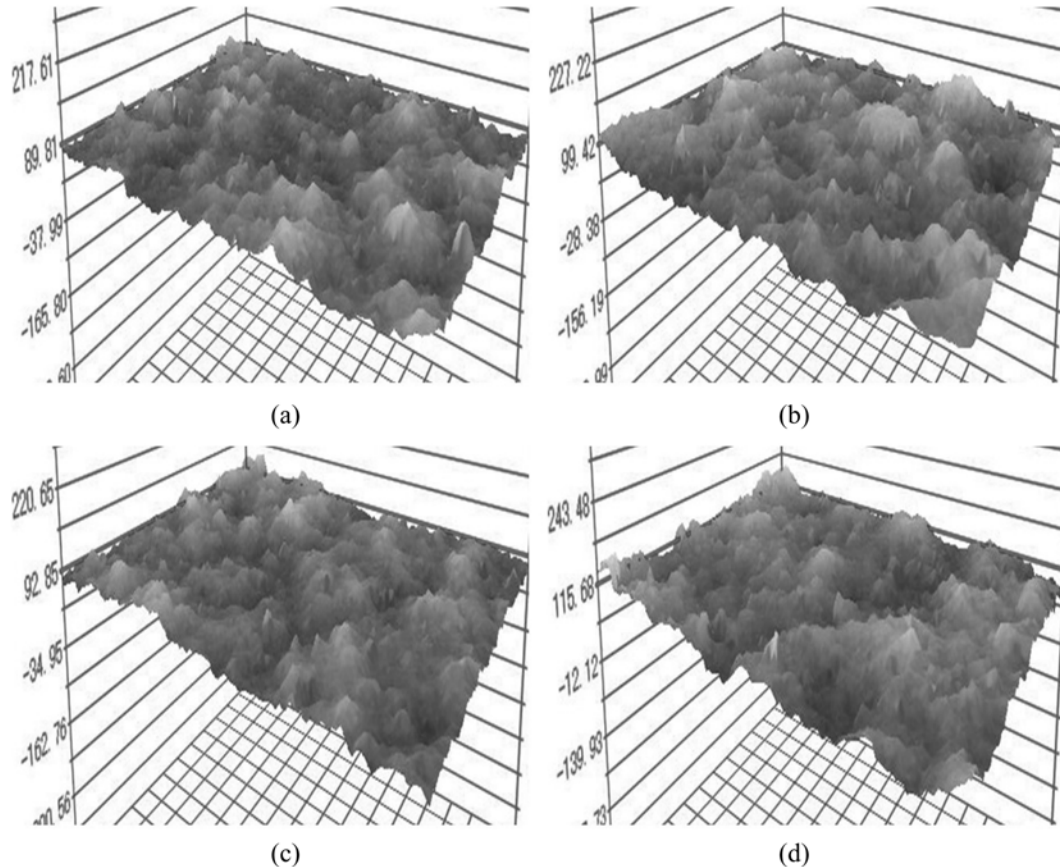


Fig. 2. The morphology of APS 3YSZ/LaPO₄ composite coating surfaces as a function of the amount of LaPO₄; (a) 10 vol.%, (b) 20 vol.%, (c) 30 vol.%, and (d) 40 vol.%.

the same for all compositions. The thickness of the APS coating layer on the substrate metal was about 115 to 130 μm . However, the thickness of the 3YSZ/10 vol% LaPO₄ composite coating sample was about 80 μm . The cross-sectional microstructure of APS coating layers was observed to be a lamellar structure, with voids and remaining unmelted particles, as shown in Fig. 3. The density of APS coating layer was low due to the existence of the voids and remaining unmelted particles. APS coating layers having these microstructures influences the thermal conductivity and residual stress. The residual stress of APS coating samples was measured as a function of the amount of LaPO₄.

Fig. 4 shows the residual stresses of APS coating samples. The residual stresses were obtained from full width at half maximum of peaks of the XRD. The average residual stresses were observed to be tensile residual stresses in the 3YSZ/10 vol% LaPO₄ composite coating sample and compressive residual stresses of the other composition samples. Actually, Fig. 4 shows the relationship between residual stresses of APS coating samples and the amount of LaPO₄. The compressive residual stresses of APS coating samples were increased by increasing the LaPO₄ content. For that

reason, the difference of residual stresses between the maximum (+, tensile stress) and minimum (-, compressive stress) were increased with increasing LaPO₄ content, as shown in Fig. 4. The difference of residual stresses of APS coating samples was increased from 49.44 MPa (Min. = -14.16 MPa, Max. = 35.28 MPa) of 3YSZ/10 vol% LaPO₄ to 305.9 MPa (Min. = -185.01 MPa, Max. = 120.85 MPa) of 3YSZ/40 vol% LaPO₄. We consider that the increments of residual stresses of 3YSZ/LaPO₄ composite coatings were related to the amount of LaPO₄ and non uniform coating thickness. With a high fraction of LaPO₄ content in APS coating samples the surfaces were more even. The difference in residual stresses at an X-ray spot was related to the thickness of the APS coating layer and the movement of the nozzle. Non uniform residual stresses of APS coated samples during deposition by plasma spraying were influenced by the non uniform coating thickness and the deformation of the substrate metal due to thermal stresses. Therefore, there was an analogy between the residual stresses of APS coating samples and the deformation of the substrate metal.

The thermal conductivity of APS coating samples was

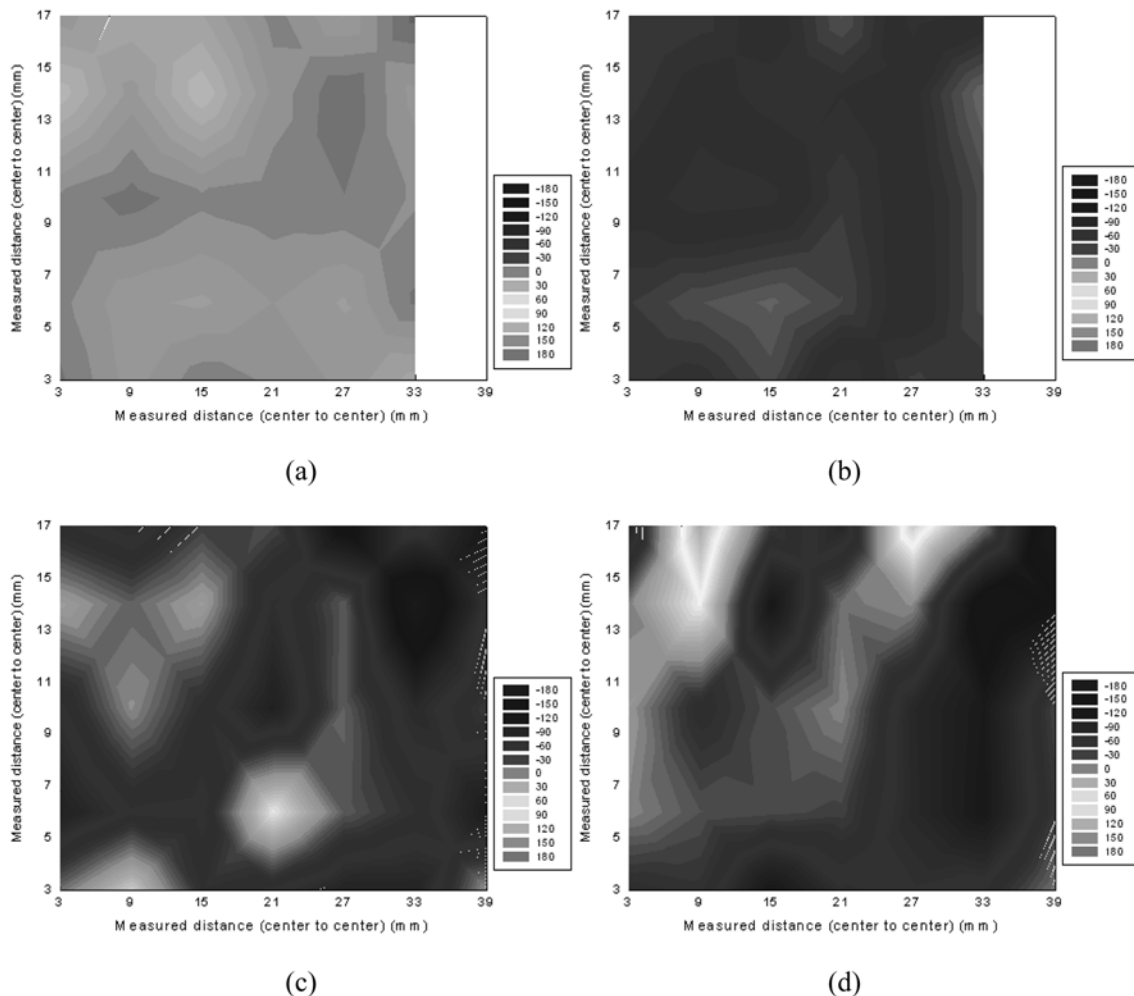


Fig. 4. Residual stresses of APS 3YSZ/LaPO₄ composite coating samples as a function of the amount of LaPO₄; (a) 10 vol.%, (b) 20 vol.%, (c) 30 vol.%, and (d) 40 vol.%.

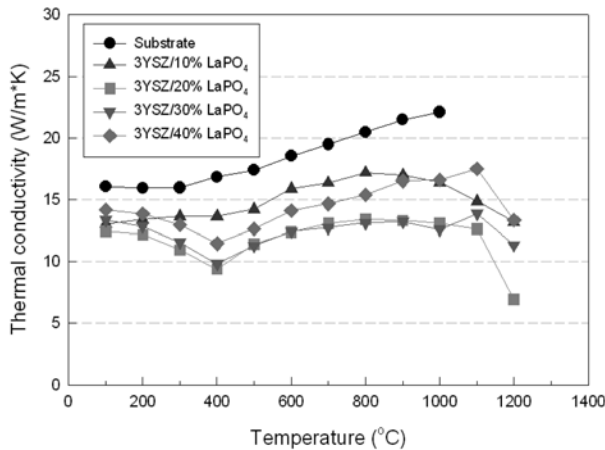


Fig. 5. Thermal conductivity of APS 3YSZ/LaPO₄ composite coating samples as a function of the amount of LaPO₄.

measured using a laser flash thermal constant analyzer and DSC. As shown in Fig. 5, the thermal conductivity of the substrate metal was increased with increasing temperature. However, the thermal conductivity of APS coated samples was decreased up to 400 °C, and was increased above 400 °C. The variation of thermal conductivity of APS coating samples was caused by heat transfer mechanisms such as conduction, and radiation. The heat transfer mechanisms of the substrate metal and composite coating layers were due to the mobility of free electrons and phonon scattering generated by voids and the remaining unmelted particles. Because the thermal conductivity due to free electrons is faster than that due to phonon scattering, therefore, thermal conductivity of the substrate metal was higher than that of the coating layers. The thermal conductivity of APS coated samples decreased up to 400 °C, and then increased again above 400 °C. We consider that the decreasing thermal conductivity of the APS coated samples was related to increasing phonon scattering generated by voids, the remaining unmelted particles, interfaces, etc, but the increasing thermal conductivity above 400 °C was caused by radiation or increasing carrier mobility of the substrate metal. Therefore, the trend of the thermal conductivity of an APS coating above 400 °C was similar to that of metallic substrate. Consequently, the thermal conductivity of APS coated samples of about 120 μm coating thickness was reduced to about 11.6-18.7% at 100 °C, and reduced about 24.8-43.0% at 1000 °C as compared with that of the substrate metal. The thermal conductivity of 3YSZ/LaPO₄ composite coating layers was calculated by utilizing the APS coating layer on the substrate metal. Fig. 6 shows the calculated values of thermal conductivity of the coating layers. The calculated value of thermal conductivity of coating layers ranges from 0.11 to 0.19 W/m·K. In previous research [15], the thermal conductivity of sintered composites was 1.5-3.0 W/m·K. The thermal conductivity of coating layers was lower than that of the sintered composites. The low thermal conductivity was caused by the low density and microstructure of the coating layers. We know that the

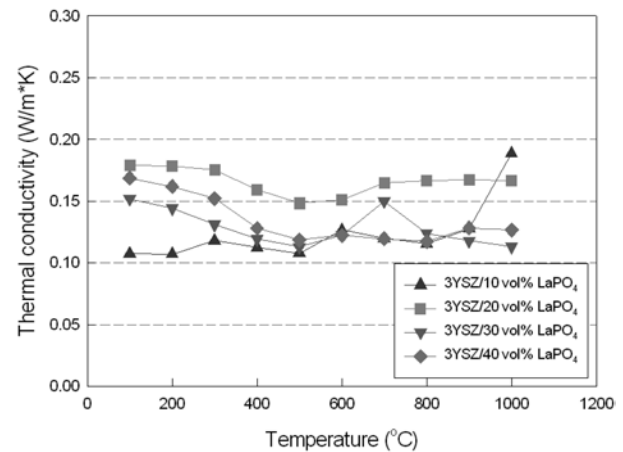


Fig. 6. The calculated thermal conductivity of APS 3YSZ/LaPO₄ composite coating layers as a function of the amount of LaPO₄.

thermal conductivity of air is very low ($\lambda_{\text{air}} \approx 0.023$ W/m·K). Also, the pores in coating layers are very important for thermal barrier coating.

Conclusions

3YSZ/LaPO₄ composite applied TBC were deposited by the APS method. The thickness of APS coating layer on the substrate metal was about 115 to 130 μm. The residual stress and thermal conductivity of APS coated samples were affected by the amount of LaPO₄. The residual stresses of APS coating samples were observed to be both compressive and tensile. The differences of residual stress of APS coated samples were increased with increasing LaPO₄ content. The values were increased from 49.44 MPa of 3YSZ/10 vol% LaPO₄ to 305.9 MPa of 3YSZ/40 vol% LaPO₄. The residual stresses of APS coating samples were caused by the amount of LaPO₄ and coating thickness. The thermal conductivity of APS coated samples with 120 μm of coating thickness was reduced to about 11.6-18.7% at 100 °C, and to about 24.8-43.0% at 1000 °C as compared with that of the substrate metal. The calculated values of thermal conductivity of the coating layers were lower than that of sintered composites. The calculated values of the coating layers range from 0.11 to 0.19 W/m·K. It was found that thermal conductivity of the coating layers was lower than that of sintered materials, because of increasing phonon scattering due to voids and the remaining unmelted particles, etc.

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