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Thermal Conductivity of Yttria-stabilized Zirconia Films Measured by a Laser-heating AC Method

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8 mol%Y_2O_3-stabilized zirconia films were prepared on alumina substrates by laser chemical vapor deposition, and the thermal conductivity was measured by a laser-heating AC method. The thermal conductivity decreased from 1.3 to 0.7 W/mK with increasing deposition rate from 50 to 450 μm/h. Many nano-pores were formed at high deposition rates, and the decrease in the thermal conductivity was caused by the phonon scattering at the nano-pores.
Key words: laser CVD, YSZ, thermal conductivity, nano-coating, laser-heating AC method

1. INTRODUCTION

Since yttria-stabilized zirconia (YSZ) has low thermal conductivity, high thermal expansion coefficient and superior chemical inertness, YSZ coatings have been used as thermal barrier coatings to protect superalloy components in gas turbines. YSZ coatings have been prepared by plasma spraying[1], electron beam physical vapor deposition (EB-PVD)[2,3], thermal CVD[4,5], plasma-enhanced CVD[6] and laser CVD[7]. EB-PVD and CVDs are able to prepare YSZ coatings with an anisotropic columnar structure which is preferable for elongating the life-time of TBCs.

Although TBCs should have low thermal conductivity, there has been no report on precise measurement of thermal conductivity for YSZ coatings attaching with substrates. A laser flash technique is widely used for thermal conductivity measurement for bulk materials, whereas not suitable for thick coatings[8]. A 3-ω method[9] and a photo-acoustic method have been developed for the measurement of thin films, but not applicable for thick coatings. On the other hand, a laser-heating AC method can be appropriate to measure thermal conductivity of thick coatings such as TBCs [11]. We have measured thermal conductivities of YSZ films on alumina substrates prepared by magnetron sputtering, and reported that the laser-heating AC method can accurately measure the thermal conductivity of YSZ films attaching to substrates.[12].

In this study, the thermal conductivity of YSZ coatings prepared by laser CVD were measured by the laser-heated AC method, and the relationship between nano-structure of YSZ films and thermal conductivity was investigated.

2.EXPERIMENTAL

2-1. Preparation and characterization

Figure 1 shows a schematic diagram of laser CVD apparatus used in this study. A vertical cold-wall type CVD chamber was made of stainless steel. The vaporization temperatures of Zr(dpm)$_4$ (dpm=dipivaloylmethanate) and Y(dpm)$_3$ (T_{Zr} and T_Y) were 523 K and 443 K, respectively. The source vapors were carried by Ar gas into the CVD chamber. O_2 gas was separately introduced with a double tube nozzle, and mixed with the precursor vapors above the substrate. The distance between nozzle and substrate was 25 mm. The total gas flow rate was fixed at 4.66×10^{-6} m^3/s, and the total pressure was kept at 0.93 kPa. The CVD conditions are summarized in Table I. Alumina substrates (30 mm×3 mm×0.1 mm) were pre-heated up to 750°C on a hot stage. A silica glass plate was placed on the alumina substrate to cover a half of the substrate for the thermal conductivity measurement. Nd:YAG laser (wavelength:1063 nm, maximum power:250

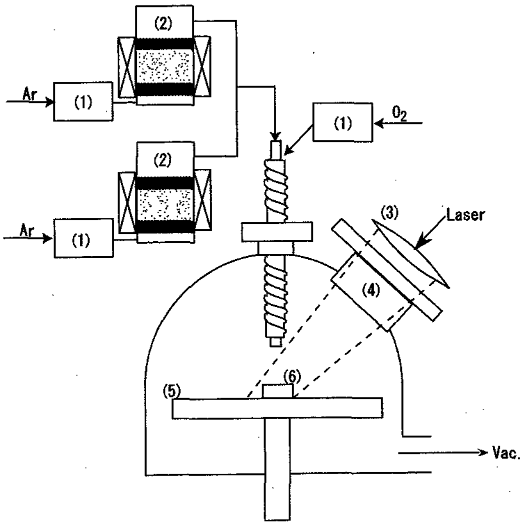

Fig.1 A schematic diagram of laser CVD apparatus.(1):mass flow controller, (2):precursor evaporator, (3):optical lens, (4):quarts window, (5):substrate folder, (6): substrate.

Table I Deposition conditions for YSZ films by laser CVD.

Vaporization temperature of precursors	
$Zr(dpm)_4$ (T_{Zr})	523 - 573 K
$Y(dpm)_3$ (T_Y)	433 K
Substrate preheating temperature (T_{sub})	RT-1027 K
Total Pressure (P_{tot})	0.93 kPa
Flow rate of carrier gas	
Ar gas for Zr precursor (FR_{Zr})	5.00×10^{-6} m^3/s
Ar gas for Y precursor (FR_Y)	1.67×10^{-6} m^3/s
Flow rate of oxygen gas (FR_O)	5.00×10^{-6} m^3/s
Total gas flow rate (FR_{tot})	1.17×10^{-5} m^3/s
Laser power (P_L)	0-200 W

W) was irradiated to substrates with a spot size about 20 mm in diameter.

Surface and cross-sectional microstructures were observed by scanning electron microscopy (SEM, HITACHI S-3100H) and transmission electron microscopy (TEM, JOEL JEM-2000EX). Crystal structure and composition were determined by X-ray diffraction (XRD, RIGAKU RAD-C) and electron probe x-ray micro analysis (EPMA, JEOL JXA-8621MX), respectively. The thermal conductivity of YSZ films was measured at room temperature by the laser-heating AC method (ULVAC-Riko LaserPIT).

2-2.Fundamentals of the laser-heating AC method

Assuming the one-dimensional thermal conduction, the change of temperature (T) with time (t) and position (x)will be given by eq.(1).

$$\frac{\partial^2 T}{\partial x^2}-\frac{1}{D}\frac{\partial T}{\partial t}=0 \qquad (1)$$

where D is thermal diffusivity. If a specimen is periodically heated at x=0, and the temperature at x=0 ($T_{x=0}$) may change as eq.(2).

$$T_{x=0}=T_0+A\cdot\cos(\omega t) \qquad (2)$$

where T_0 is the initial temperature, A is a constant, ω is angular frequency. The temperature at x=x ($T_{x=x}$) will given as eq.(3).

$$T_{x=x}=T_0+A\cdot\exp\left(-\sqrt{\frac{\omega}{2D}}x\right)\times\cos\left(\omega t-\sqrt{\frac{\omega}{2D}}x\right) \qquad (3)$$

The maximum temperature change at x ($\Delta T_{max,x=x}$) may be given by eq.(4).

$$\Delta T_{max,x=x}=A\cdot\exp\left(-\sqrt{\frac{\omega}{2D}}\cdot x\right) \qquad (4)$$

Then the relationship between ΔT_{max} and x can be givenby eq.(5).

$$\frac{d(\ln\Delta T_{max})}{dx}=-\sqrt{\frac{\omega}{2D}} \qquad (5)$$

Therefore, the thermal diffusivity D can be calculated from the slope of logarithmic temperature change against position (x).

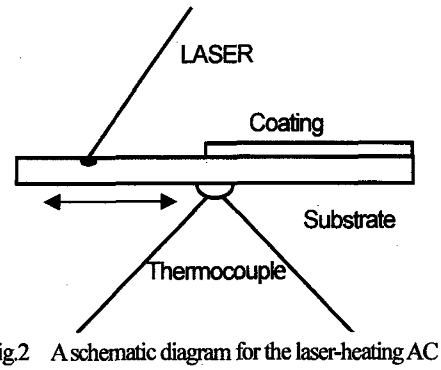

Fig.2 A schematic diagram for the laser-heating AC method.

The whole thermal diffusivity of a film attached with a substrate D_{12} is described as

$$D_{12}=\frac{D_1C_1d_1+D_2C_2d_2}{C_1d_1+C_2d_2} \qquad (6)$$

where D, d and C are thermal diffusivity, thickness and heat capacity, respectively. The subscript number 1 and 2 means film and substrate, respectively.

Eq.(6) was changed to calculate the thermal conductivity of a film (κ_2) as given by eq.(7).

$$\kappa_2=D_2\cdot C_2=\left\{\left(\frac{d_1}{d_2}+1\right)\left(\frac{D_{12}}{D_1}-1\right)+\frac{C_2}{C_1}\right\}\times D_1 \qquad (7)$$

In this study, YSZ coatings were prepared on a half surface of substrate as shown in Fig.2. The thermal conductivity of YSZ coatings can be calculated by measuring D_1 and D_{12} from eq.(5). The literature values of C_1 and C_2 were used in eq.(7).

3.RESULTS AND DISCUSSION

Figure 3 shows the effects of substrate pre-heating temperature(T_{sub}) and laser power(P_L) on the deposition rate (r) at Zr precursor temperature of T_{Zr}=523 K (Zr precursor flux : 1.2×10^{-6} mol/s). The deposition rate increased with increasing T_{sub} and P_L. The highest deposition rate was 450 μm/h at T_{sub}=550°C and P_L=200 W. When the Zr precursor flux is 2.0×10^{-6} mol/s at T_{Zr}=573 K, the deposition rate reached to 660 μm/h at T_{sub}=750°C and P_L=200 W. The cross-section of YSZ films at the highest deposition rate of 660 μm/h had a cone-structure (Fig.4), which is often observed at a high deposition rate in CVD.

Figure 5 shows cross-sectional SEM images of YSZ films prepared at r=50 μm/h (T_{sub}=550°C, P_L=70 W) and r=450 μm/h (T_{sub}=550°C, P_L=200 W). Both films had the columnar structure, and the columns were more aligned at higher laser power. XRD patterns of these films are shown in Figure 6. Every peaks were indexed with cubic YSZ. The lattice parameters were 0.518 nm at r=50 μm/h, and 0.519 nm at r=450 μm/h. Y_2O_3 contents of these films estimated from lattice parameter[13] were 8.2 and 7.9 mol%, respectively. These Y_2O_3 contents agreed with the results of EPMA (8.2 mol% and 8.0 mol%Y_2O_3, respectively). The YSZ films showed a (200) orientation, which was significant in the film

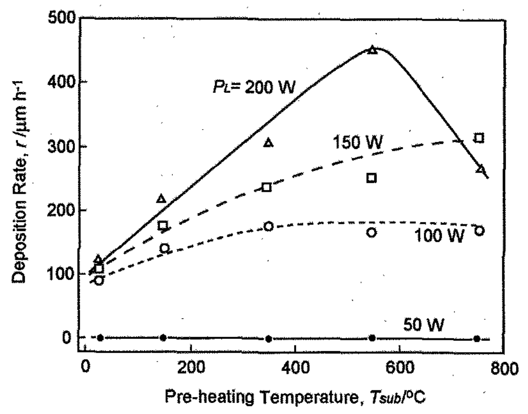

Fig.3 Effects of T_{sub} and P_L on deposition rate.

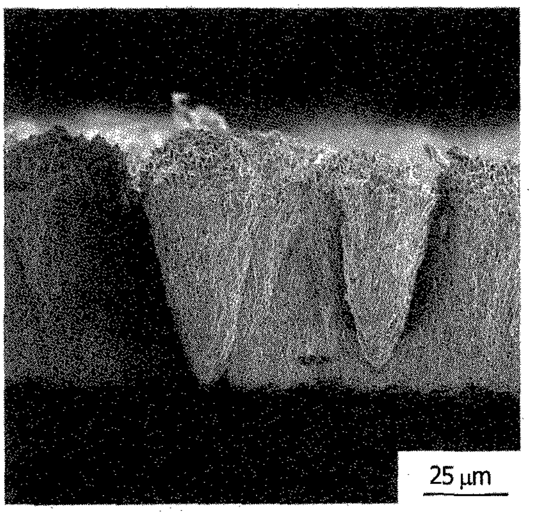

Fig.4 Cross-sectional SEM images of YSZ films prepared at P_L=200 W, T_{sub}= 750°C, T_{Zr}= 300°C (r =660 μm/h).

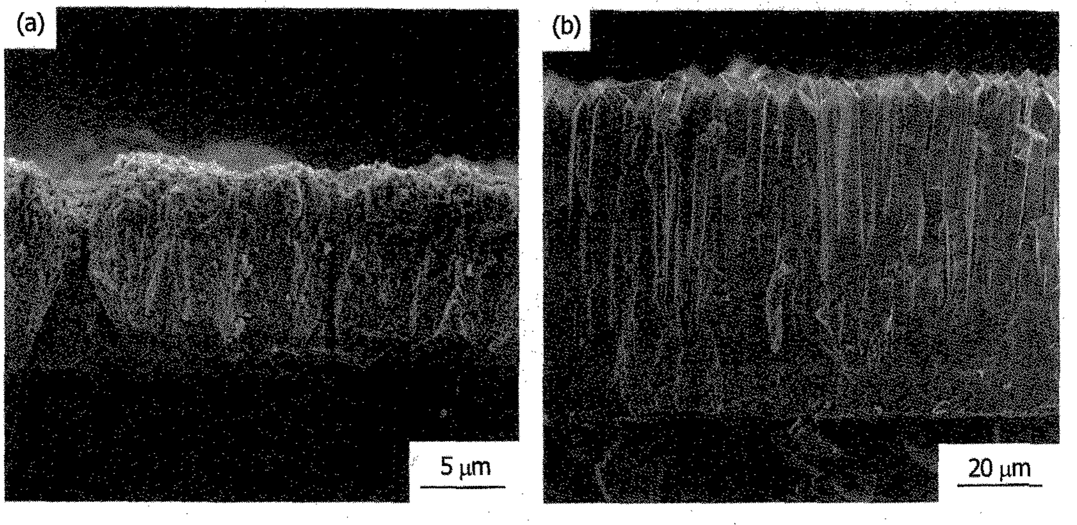

Fig.5 Cross-sectional SEM images of YSZ films prepared at (a) P_L=70 W, T_{sub}= 550°C (r =50 μm/h) and (b) P_L=200 W, T_{sub}= 550°C (r =450 μm/h).

prepared at r=450 μm/h.

Figure 7 shows cross-sectional TEM images of YSZ films prepared at r=50 and 450 μm/h. At r=50 μm/h, each column was almost single crystal and pores of several nm were observed at the column boundary. At r=450 μm/h, each column was poly-crystal and many pores were observed at the column boundary and insides of the columns.

The thermal conductivity of the YSZ film prepared at r=50 μm/h was 1.3 W/mK, which is almost a half of that of bulk cubic YSZ. The thermal conductivity of the YSZ film prepared at r=450 μm/h was 0.7 W/mK. Figure 8 shows that the thermal conductivity of YSZ films decreased with increasing deposition rate. At high deposition rates, the grain boundary and nano-pores are formed in YSZ films, and the presence of the nano-pores would reduce the thermal conductivity by phonon scattering[14].

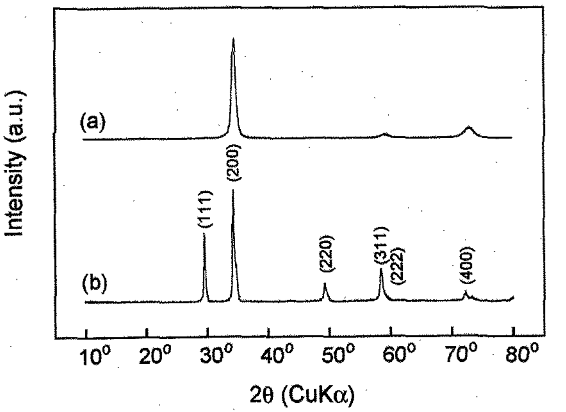

Fig.6 XRD patterns of YSZ films prepared at (a) r = 450 μm/h and (b) r = 50 μm/h.

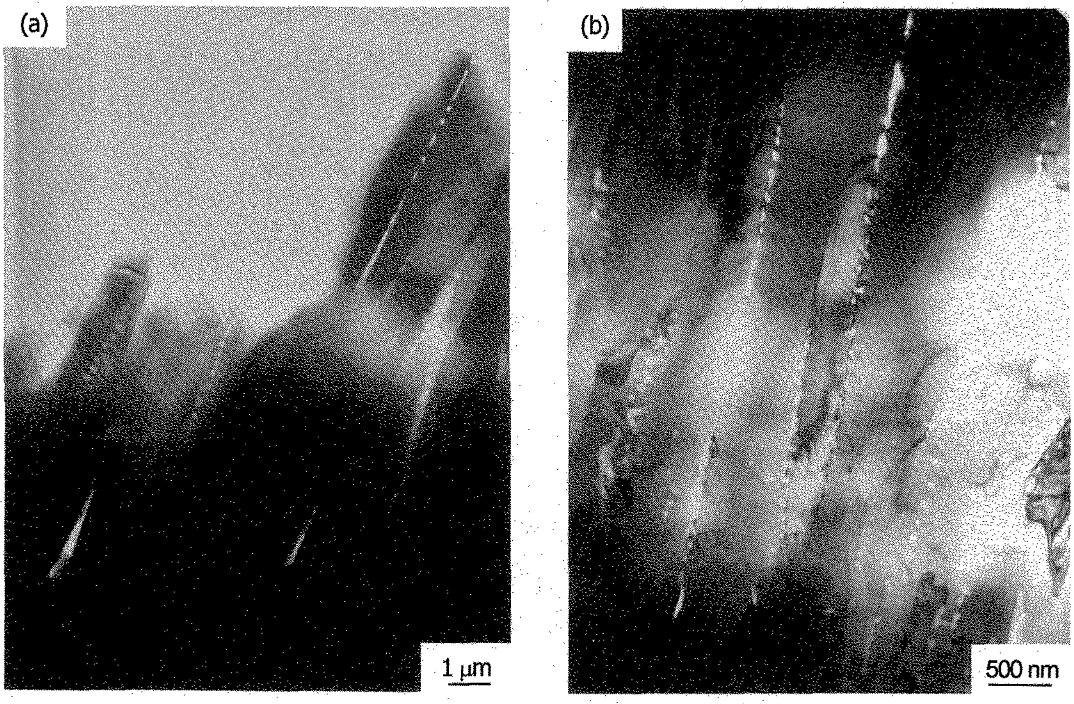

Fig.7 Cross-sectional TEM images of YSZ films prepared at (a) r=50 μm/h and (b) r=450 μm/h.

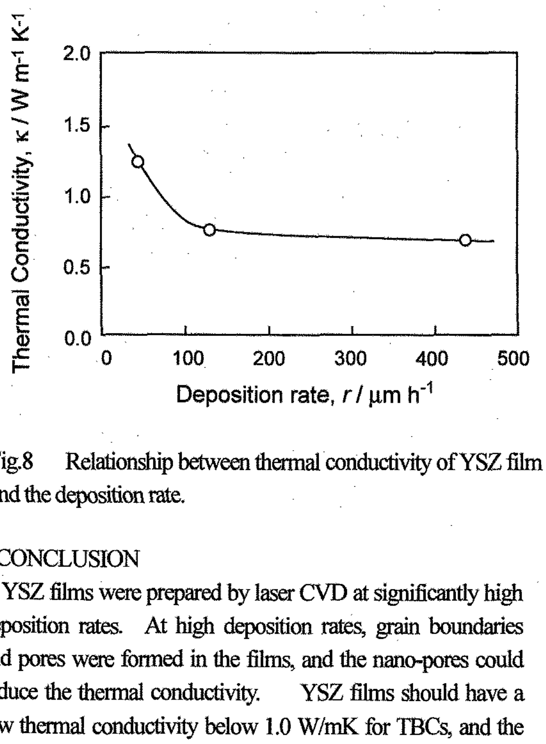

Fig.8 Relationship between thermal conductivity of YSZ film and the deposition rate.

4.CONCLUSION

YSZ films were prepared by laser CVD at significantly high deposition rates. At high deposition rates, grain boundaries and pores were formed in the films, and the nano-pores could reduce the thermal conductivity. YSZ films should have a low thermal conductivity below 1.0 W/mK for TBCs, and the YSZ film prepared by laser CVD had a significantly low thermal conductivity of 0.7 W/mK.

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