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A New Laser CVD Process for Thermal Barrier Coatings

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Yttria stabilized zirconia (YSZ) films were synthesized at a high deposition rate of 180 nm/s (660 μm/h) by laser chemical vapor deposition using $Zr(dpm)_4$ and $Y(dpm)_3$ precursors. Morphology of YSZ films changed from a columnar to a cone structure with increasing deposition rates. YSZ films with the columnar structure showed significant (200) orientation. A strong plasma light emission was appeared during the deposition around the substrate. The charges of electrons and ions were detected in the light-emitting zone. The emitted light had a continuous spectrum similar to the Planck distribution.

Keywords: yttria stabilized zirconia, thermal barrier coatings, laser chemical vapor deposition, high deposition rate, plasma diagnosis

1. INTRODUCTION

The operation temperature of gas turbines is now increasing up to more than 1500 K to improve the efficiency of energy consumption. The conventional Ni-base superalloys as structural materials cannot stand in such severe corrosive environment. Thermal barrier coatings (TBCs) combined with a cooling system would enable superalloys to use for gas turbines. Since TBCs should have high chemical inertness, low thermal conduction and high thermal expansion, yttria stabilized zirconia (YSZ) has been widely chosen for TBCs. As TBCs should be several hundred micrometers in thickness, high-speed deposition processes such as thermal spraying[1)] and electron beam physical vapor deposition (EB-PVD) [2,3)] have been commercially employed.

On the other hand, chemical vapor deposition (CVD) can provide highly pure and dense coatings with controlled microstructures. However, CVD has been regarded as a slow deposition process, being unsuitable for TBCs to fabricate thick coatings more than several hundreds of micrometers. Auxiliary energy sources such as plasma or laser have been induced to CVD to enhance deposition rates and to lower deposition temperatures. In the previous laser CVD, however, no work has been conducted to obtain wide-area and thick YSZ coatings. We found that the laser energy significantly increases the deposition rate of CVD YSZ coatings. This paper describes the effect of laser on microstructure and deposition rate of YSZ coatings in the laser CVD.

2. EXPERIMENTAL

A CVD chamber was made from stainless steel, attaching several quartz viewing ports. $Zr(dpm)_4$ (dpm=dipivaloylmethanate) and $Y(dpm)_3$ were used as source materials, whose 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 total pressure was kept at 0.93 kPa. The CVD conditions are summarized in Table I. Alumina substrates (15 mm × 15 mm × 2 mm) were pre-heated up to 1023 K on a hot stage. Nd:YAG laser (wavelength:1063 nm, maximum power:250 W) was irradiated to substrates with the spot size covering the whole substrate surface. The substrate temperature was measured by a pyrometer (IR-FBIH-SP, Chino) with an optical filter to cut off the incident laser light.

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

Surface and cross-sectional microstructures were observed by scanning electron microscopy (SEM). Crystal structure was determined by X-ray diffraction (XRD). Yttrium content was measured by electron probe X-ray microanalysis.

Plasma-light emission was observed above the substrate during the deposition. A spectrometer (Otsuka denshi, MCPD-7000) was used to analyze the emission spectra in the wavelength range from 400 to 900 nm with the resolution of 0.1nm. A Langmuir probe was prepared by a tungsten wire (0.7mm in diameter, 7mm in length), and set in a light emission zone above the substrate. The probe was settled to avoid the incident laser beam, and a counter was lead to the ground level.

3. RESULTS AND DISCUSSION

Fig. 1 shows the relationship between laser power (P_L) and substrate surface temperature (T_{sub}) at the pre-heating temperature of 1023 K. The T_{sub} linearly increased with increasing laser power at every T_{sub}, and the increase in T_{sub} was more significant with decreasing T_{sub}. The highest increase in T_{sub} was 250 K at P_L = 200 W without pre-heating of the substrate.

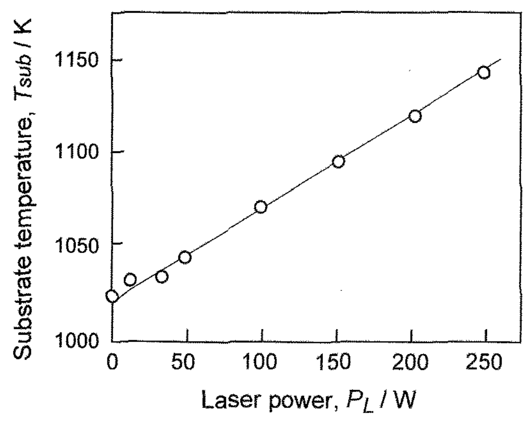

Fig.1 Relationship between laser power and substrate surface temperature (Substrate pre-heating temperature: 1023 K).

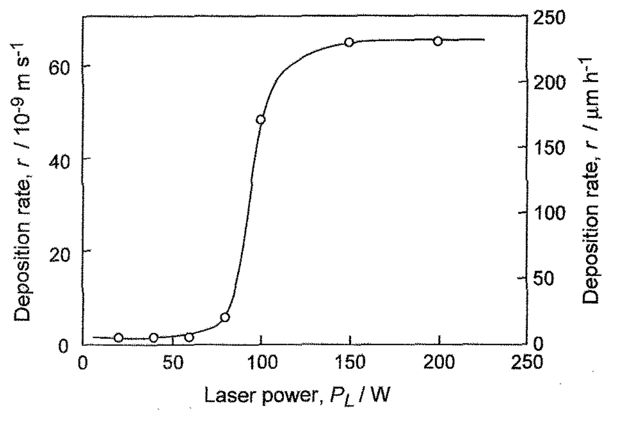

Fig.3 Effect of laser power on the deposition rate of YSZ films.

Fig. 2 shows the cross-sectional SEM images of YSZ films at the laser power (P_L) of 100 and 150 W at T_{Zr}=523 K (Zr flux rate: 1.2×10^{-6} mol/s). The well-developed columnar microstructure was observed. The film thickness was almost uniform over the whole substrate surface. No cracks and pores were observed at the interface between substrate and film.

Fig. 3 shows the relationship between laser power and the deposition rate at T_{Zr}=523 K. The deposition rates were 0.28 to 0.56 nm/s (1.0 to 2.0 μm/h) in the laser power range below P_L=70 W. In conventional thermal CVD, the deposition rates of YSZ films were reported to be 2.8 to 28 nm/s (10 to 100 μm/h) at 1050 K. In the present study, the distance between nozzle and substrate was too long (25 mm) to obtain usual deposition rates, because the laser light should be introduced to the substrate. The deposition rates significantly increased above P_L=70 W, and reached to a constant value of 64 nm/h (230 μm/h) at P_L=150 to 200 W. The highest deposition rate in the present study was 180 nm/s (660 μm/h) at P_L=200 W and T_{Zr}=573 K. This value is the highest among the reported deposition rates of YSZ films by CVD, being almost comparable to those of thermal spray and

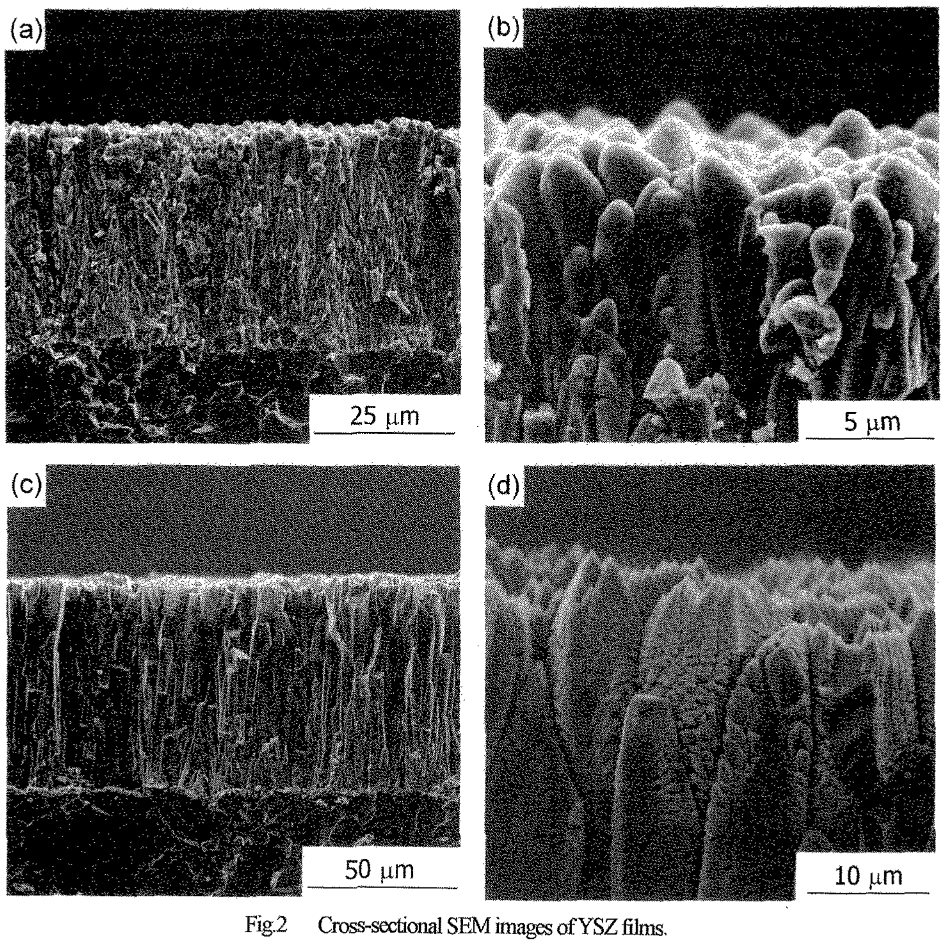

Fig.2 Cross-sectional SEM images of YSZ films.
(a)(b) P_L=100 W, (c)(d) P_L=150 W. (b) and (d) are higher magnifications of (a) and (c), respectively.

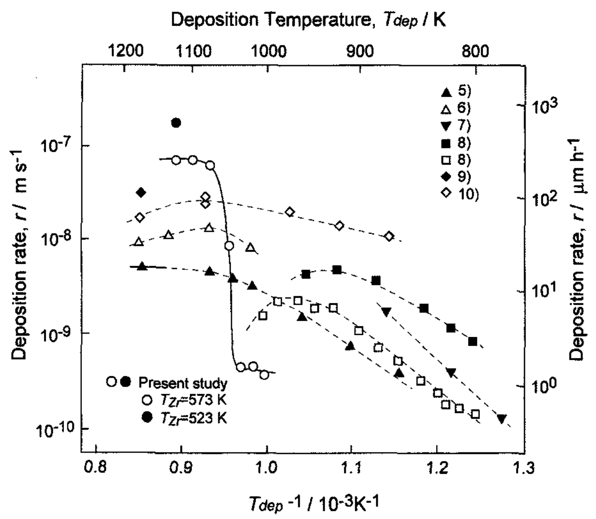

Fig.4 Effect of deposition temperature on the deposition rate of CVD YSZ films.

EB-PVD.

The YSZ films were cubic structure with a (200) preferred orientation. The EPMA showed the Y_2O_3 content of about 8 mol%, where the cubic structure can be stable according to a phase diagram[4]. At T_{Zr}=523 K, the (200) orientation became more significant with increasing laser power corresponding to the well-developed columnar structure. The YSZ films having the highest deposition rate (660 μm/h) showed a cone structure with a weak (200) orientation.

The deposition rates of CVD-YSZ films reported in literatures[5-10] are summarized in Fig.4. There is a general trend that the deposition rates increase with increasing temperature up to about 900 K, and almost constant or slightly decreased with increasing temperature above 900 K[11]. The rate-controlling step of the film formation would closely related with the trend of deposition rate. In a low temperature region, chemical reactions might be rate-controlling with a significant temperature dependence of deposition rates. In an intermediate temperature region, diffusion process in a gas phase could be dominant where the activation energy could be small. In a high temperature region, premature reactions would occur resulting the decrease in deposition rates. In the present study, the deposition rates increased drastically at 1050 K. This trend is significantly different from that of conventional thermal CVD, suggesting a particular effect of laser irradiation.

A strong light emission was observed above the laser power of P_L=70 W, which was well correlated with the drastic increase in deposition rates. The emission zone was a hemisphere and the diameter was about 5cm. The Langmuir probe was set into the light emission zone to detect discharge current. Almost no current was detected below P_L=70 W, while significant discharge current was observed above P_L=70 W and was saturated above P_L=200 W as shown in Fig.5. This trend was well coincident with the deposition rate shown in Fig.3.

Fig. 6 shows the relationship between current density and bias voltage applied to the Langmuir probe. In a positive bias region, the current density significantly increased with increasing bias voltage. In a negative bias region, current density was smaller than that in the positive bias close to linear. The plasma commonly consists of electrons and changed ionic species. Since electrons have much larger mobility than ionic species, current density should increase more significantly with increasing bias voltage in a positive bias region.

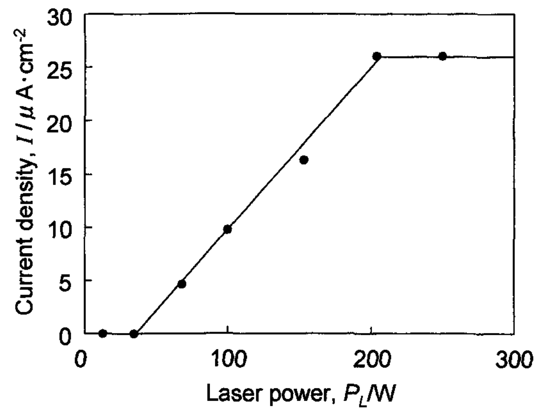

Fig.5 Effect of laser power on the current density at a center of light emission

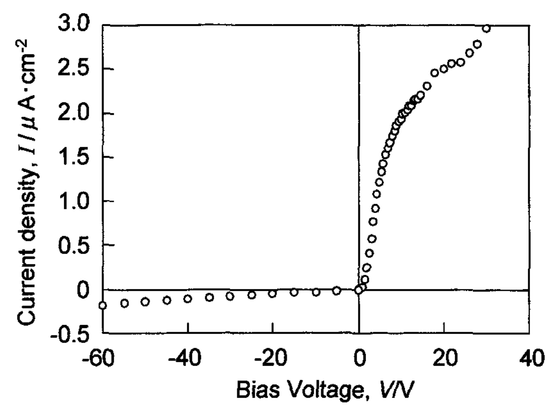

Fig.6 Relationship between bias voltage and current density at the light emitting zone and the laser power of 200W.

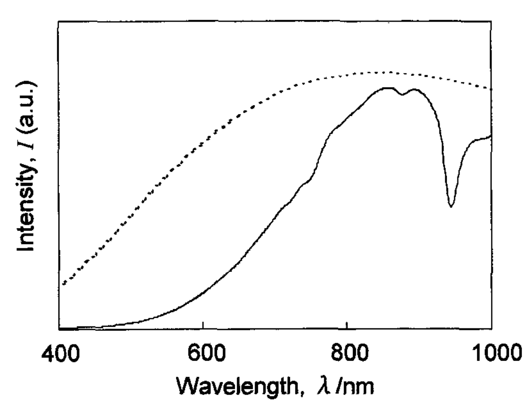

Fig.7 Relationship between emission light intensity and wavelength (laser power: 200W, broken line: Planck distribution).

Therefore, it can be understood that the dissociated electrons and ions are responsible to the plasma light emission.

The spectrum from the light emission zone at the laser power of P_L=200 W is shown in Fig.7. The emission spectrum was continuous having the maximum intensity at 850nm. No characteristic peak except at 950 nm was identified. The adsorption at 980 nm could be caused of the dpm precursors deposited on the viewing port. The emission spectrum was similar to the Planck distribution for black-body radiation[12]. However, the spectrum was slightly narrower than that of the Planck distribution. The temperature of the light emission zone could be estimated as 4200K from Eq.(1).

$$E = \frac{8\pi ch}{\lambda^5} \cdot \frac{1}{e^{\frac{ch}{k\lambda\vartheta}} - 1} \quad (1)$$

where E is spectral energy density of radiation, c is the light velocity, h is the Planck constant, λ is the wavelength at the maximum emission, k is the Boltzmann constant, and ϑ is a temperature. Some polymerized molecules or clusters as intermediate reaction products might be heated, enhanced and excited in the gas phase by laser irradiation. Such exited species might emit light having a continuous spectrum close to the black-body radiation, and become significantly reactive to enhance the deposition rates

4. CONCLUSION

A new laser CVD process was applied to prepare YSZ films. The deposition rate significantly increased at laser power above 70 W. YSZ films with highly (200) oriented columnar structure were obtained. The highest deposition rate was 660 μm/h having a cone structure A plasma was formed around the substrate by the interaction between laser and precursor vapors. The plasma light emission showed a continuous spectrum similar to the Planck distribution. This new laser CVD process would be applicable for preparing thick coatings of TBCs.

Acknowledgement

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