*Materials Transactions*, Vol. 44, No. 3 (2003) pp. 421 to 424

RAPID PUBLICATION

# Rapid Synthesis of Yttria-Stabilized Zirconia Films by Laser Chemical Vapor Deposition

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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 (laser CVD) using $Zr(dpm)_4$ and $Y(dpm)_3$ precursors. Morphology of YSZ films changed from columnar to cone structure with increasing deposition rate. YSZ films with the columnar structure showed significant (200) orientation.

(Received December 11, 2002; Accepted January 16, 2003)

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

## 1. Introduction

Since the operation temperature of gas turbines has been increasing up to 1300 K, conventional Ni-base superalloys would not stand due to severe oxidation and mechanical degradation. Thermal barrier coatings (TBCs) combined with a cooling system for turbine blades would enable one to use superalloys in such harsh environment. As TBCs should have high chemical inertness, low thermal conductivity and high thermal expansion coefficient close to that of superalloys, yttria stabilized zirconia (YSZ) has been widely used for TBCs. As TBCs are required to be several hundred micrometers in thickness, high-speed deposition processes such as thermal spraying and electron beam physical vapor deposition (EB-PVD) have been employed in practical applications. However, heterogeneous microstructures of thermal spray TBCs have often caused spalling in relatively short period. EB-PVD process is able to fabricate an appropriate columnar microstructure, however the oxidation through the coarse columns could shorten the life time of EB-PVD TBCs.

Chemical vapor deposition (CVD) can produce highly pure and dense coatings with controlled microstructures. However, CVD has been considered to be not suitable for TBCs because the deposition rates of CVD are usually too small, around a few to several tens μm/h. Recently, several groups are trying to improve the deposition rate of CVD YSZ coatings, and relatively high deposition rates around 100 to 120 μm/h have been achieved by thermal CVD[1,2] and plasma-enhanced CVD.[3]

In this study we have newly developed laser CVD to increase the deposition rate of YSZ coatings. So far, several kinds of laser CVD have been reported in literatures,[4] where those methods would be divided into two categories, *i.e.*, pyrolytic and photolytic laser CVD. In the pyrolytic laser CVD, laser light was irradiated to heat specific points in substrates. In the photolytic laser CVD, laser light was irradiated gases near a substrate enhancing chemical reactions yielding low temperature deposition often without substrate heating. Generally, the laser power has been ranged from several mW to several W and the laser beam has been at most several mm in diameter. However, so far no report has been published on thick and wide area coatings by laser CVD. We have succeeded high deposition rates of YSZ coating on large substrates by laser CVD and proposed the possibility of TBCs by laser CVD. This paper describes the effect of laser radiation on microstructure and deposition rates of YSZ films in our new laser CVD process.

## 2. Experimental

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 temperature of $Zr(dpm)_4$ (dpm = dipivaloylmethanate) and $Y(dpm)_3$ ($T_{Zr}$ and $T_Y$) were 523 to 573 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 the nozzle and the substrate was 25 mm. Total gas flow rate was fixed at $4.66 \times 10^{-6}$ m$^3$/s. Total pressure was kept at 0.93 kPa. The CVD conditions are summarized in Table 1. Alumina substrates (15 mm × 15 mm × 2 mm) were pre-heated up to

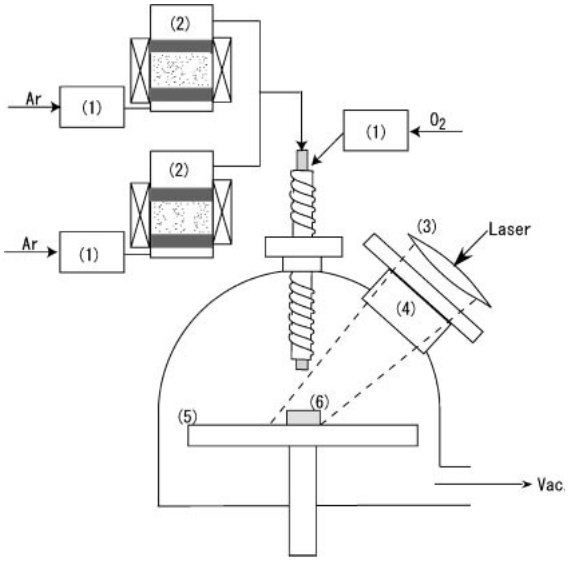


Fig. 1 Schematic diagram of laser CVD apparatus. (1) mass flow controller, (2) precursor evaporator, (3) optical lens, (4) quarts window, (5) substrate folder, (6) substrate.

Table 1 Deposition conditions for YSZ films by laser CVD.

| | |
|---|---|
| Vaporization temperature of precuesors | |
| $Zr(dpm)_4$ ($T_{Zr}$) | 523–573 K |
| $Y(dpm)_3$ ($T_Y$) | 433 K |
| Substrate preheating temperature ($T$) | 1025 K |
| Total Pressure ($P_{tot}$) | 0.93 kPa |
| Flow rate of carrier gas | |
| Ar gas for Zr precuesor ($FR_{Zr}$) | $8.33 \times 10^{-7}$ m$^3$/s |
| Ar gas for Y precuesor ($FR_Y$) | $5.00 \times 10^{-7}$ m$^3$/s |
| Flow rate of oxygen gas ($FR_O$) | $3.33 \times 10^{-6}$ m$^3$/s |
| Total gas flow rate ($FR_{tot}$) | $4.66 \times 10^{-6}$ m$^3$/s |
| Laser power ($P_L$) | 0–250 W |

1023 K on a hot stage. Nd:YAG laser (wavelength: 1063 nm, maximum power: 250 W) was irradiated on substrates with the spot size covering the whole substrate surface (about 20 mm in diameter). The substrate temperatures under laser irradiation were measured by a pyrometer (IR-FBIH-SP, Chino) with an InGaAs photo detector ($\lambda = 1550$ nm), and an optical filter was used to cut off the incident laser light.

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 micro analysis.

## 3. Results and Discussion

Figure 2 shows the relationship between laser power ($P_L$) and substrate surface temperature ($T_{sub}$). The $T_{sub}$ increased linearly with increasing laser power. The pyrometer indicated the $T_{sub}$ of 1140 K at the highest laser power of 250 W.

Figure 3 shows the cross-sectional SEM images of YSZ films at the laser power ($P_L$) of 100 and 150 W and at $T_{Zr} = 523$ K (Zr flux rate: $1.2 \times 10^{-6}$ mol/s). The columnar microstructure was observed in both conditions. The columns obtained at $P_L = 150$ W oriented more perpendicularly to the substrate surface. The edges of each column were round in shape at $P_L = 100$ W, whereas sharp facets at $P_L = 150$ W. The film thickness was almost uniform over the whole substrate surface. No cracks and pores were observed at the interface between substrate and film.

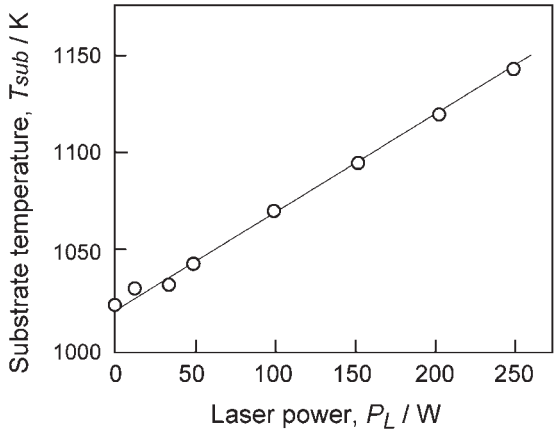


Fig. 2 Relationship between laser power and substrate surface temperature (Substrate pre-heating temperature: 1023 K).

Figure 4 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 60 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. Some un-appropriate geometric configuration of CVD chamber (too far between nozzle and substrate, and too fast gas flow around the substrate) could be caused the smaller deposition rate at $P_L < 60$ W in this study. In contrast, 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.

SEM images of YSZ film prepared at $P_L = 200$ W at $T_{Zr} = 573$ K (Zr flux rate: $2.0 \times 10^{-6}$ mol/s) is shown in Fig. 5. The cross-sectional image shows a cone structure which has often reported in CVD films prepared at high deposition rates.[5,6] The deposition rate of the YSZ film of Fig. 5 was 180 nm/s (660 μm/h), This value is the highest among the reported deposition rates of YSZ films by CVD, and is competitive to those of thermal spray and EB-PVD.

Figure 6 depicts XRD patterns of the YSZ films shown in Figs. 3 and 5. The YSZ films were cubic with (200) preferred orientation. The EPMA showed the $Y_2O_3$ content of about 8 mol%, where the cubic structure should be stable according to a phase diagram.[7] The $Y_2O_3$ content in YSZ films prepared by thermal CVD was almost in agreement with that prepared by laser CVD at the same precursor composition. At $T_{Zr} = 523$ K the (200) orientation became more significant with increasing laser power corresponding to the well-developed columnar structure shown in Fig. 3. The YSZ films having the cone structure showed a slight (200) orientation.

The deposition rates of CVD-YSZ films reported in literatures[2,3,8–11] are summarized Fig. 7. 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.[12] The rate-controlling step of the film formation would associate 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 gas phase could be dominant where the activation energy should be small. In a high temperature region, premature reactions would occur resulting the decrease of deposition rates. In this 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. The study on the correlation between deposition rate and laser irradiation is now under way.

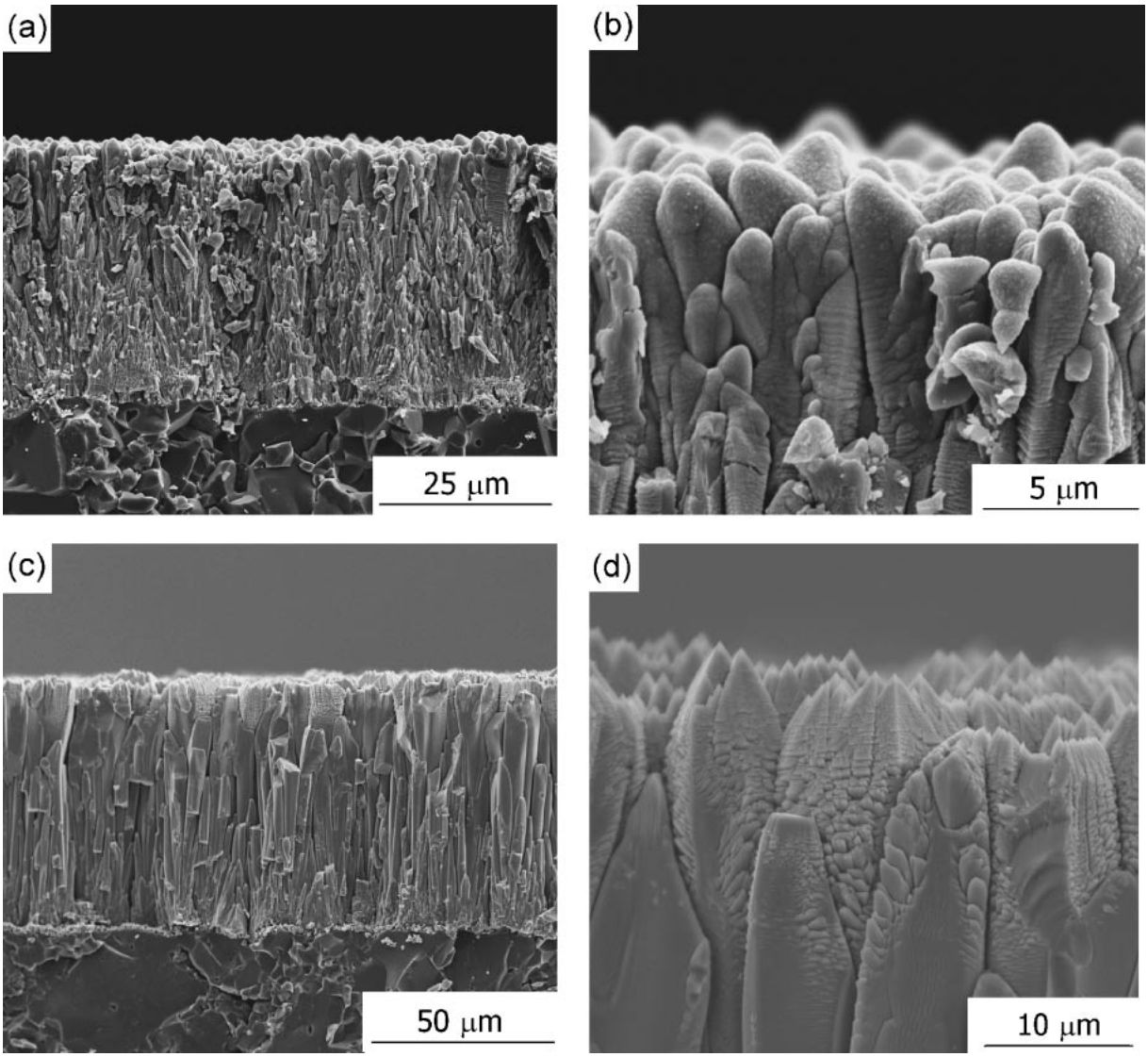


Fig. 3 Cross-sectional SEM images of YSZ films. ((a)(b) $P_L = 100$ W, (c)(d) $P_L = 150$ W. (b) and (d) are higher magnifications of (a) and (c), respectively.)

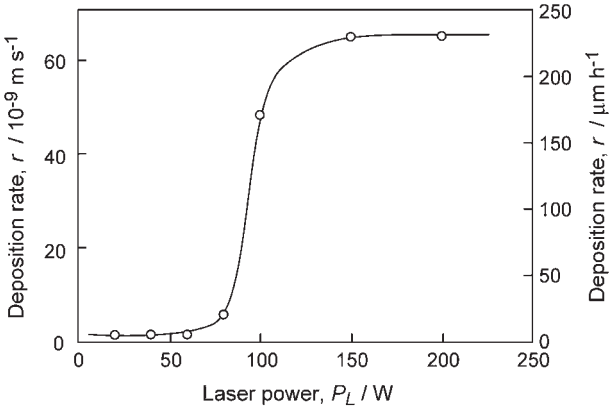


Fig. 4 Effect of laser power on deposition rates of YSZ films. $(Zr(dpm)_4$ vaporization temperature: 1023 K)

## 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 at a deposition rate of 230 μm/h. The highest deposition rate of 660 μm/h was obtained with a cone structure.

## Acknowledgements

This work was performed as a part of Nanostructure Coating Project carried out by New Energy and Industrial Technology Development Organization (NEDO), Japan.

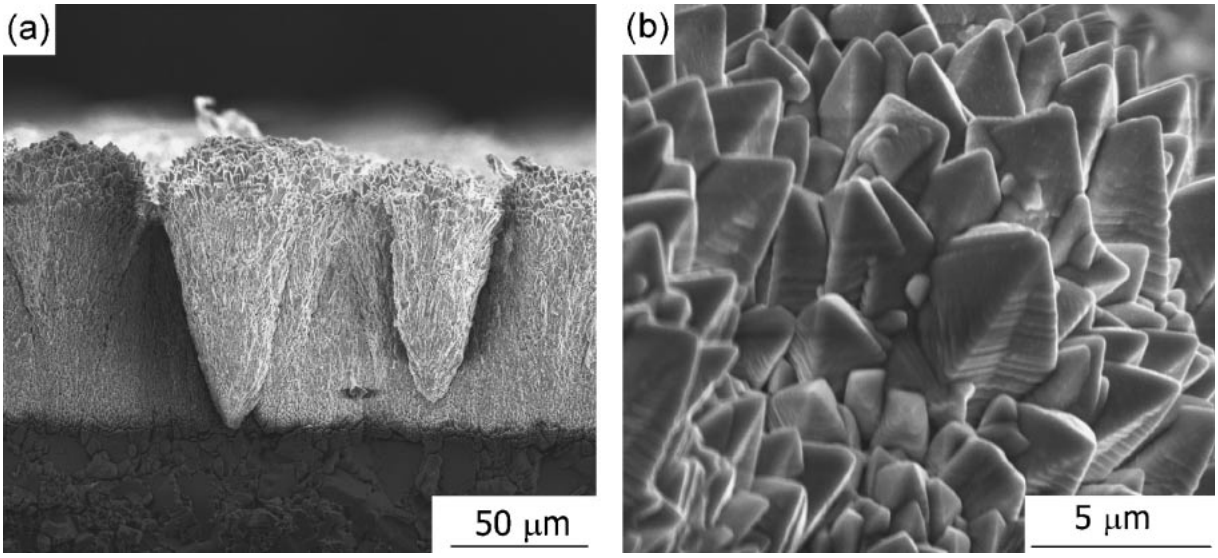


Fig. 5 SEM images of YSZ films. (laser power: 200 W, $Zr(dpm)_4$ vaporization temperature: 573 K) (a) cross-section (b) surface.

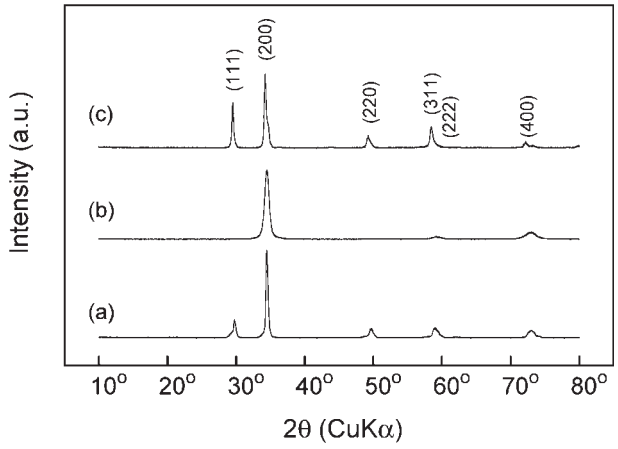


Fig. 6 X-ray diffraction patterns of YSZ films. (a) $P_L = 100$ W, $T_{Zr} = 523$ K, (b) $P_L = 150$ W, $T_{Zr} = 523$ K, (c) $P_L = 200$ W, $T_{Zr} = 573$ K.

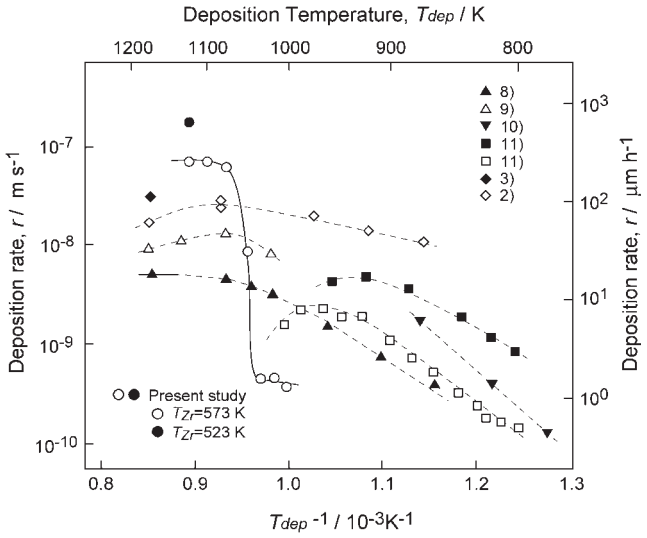


Fig. 7 Effect of deposition temperature on deposition rates of YSZ films.

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