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Microstructure of YSZ Films Prepared by MOCVD

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Metal-organic chemical vapor deposition (MOCVD) was applied to prepare yttria stabilized zirconia (YSZ) films using $Zr(dpm)_4$ and $Y(dpm)_3$ precursors. YSZ films with a well-developed columnar structure and a significant (200) orientation were obtained at T_{dep} = 923 to 1073 K. The deposition rate showed the highest value of 108 μm h^{-1} at T_{dep} = 1073K and total pressure P_{tot} = 0.8 kPa. Many nano-sized pores were observed along the columnar grain boundary.

Key words: yttria stabilized zirconia; metal-organic chemical vapor deposition; microstructure; deposition rate, nano pore

1. INTRODUCTION

Yttria stabilized zirconia (YSZ) has been employed as thermal barrier coatings (TBCs) on nickel-based superalloys because of its chemical inertness, low thermal conductivity and high thermal expansion coefficient compatible with metals [1]. The YSZ films intended for TBCs have been mainly fabricated by atmospheric plasma spray (APS) [2] or electron-beam physical vapor deposition (EB-PVD) [3, 4], which can provide thick coatings of several 100 μm in thickness. On the other hand, chemical vapor deposition (CVD) is capable to prepare high quality YSZ films with excellent conformal coverage [5~8]; however, deposition rates of conventional CVD were usually too slow to obtain thick coatings.

Metal-organic complex precursors, such as $Zr(acac)_4$ (acac = acetylacetonate) [9], $Zr(O\text{-}t\text{-}C_4H_9)_4$ [10], $Zr(dpm)_4$ (dpm = dipivaloylmethanate) [11] and $Zr(thd)_4$ (thd = 2,2,6,6,-tetramethyl-3,5,-heptanedionate) [12~14] can yield high deposition rates at relatively low temperatures due to their high vapor pressures and reactivities. In these precursors, $Zr(dpm)_4$ can be expected to obtain YSZ films at high deposition rates due to its high vapor pressures (1.3 kPa at 553 K) and thermal stability at high temperatures [15].

We have selected $Zr(dpm)_4$ and $Y(dpm)_3$ precursors and constructed a cold-wall type CVD apparatus to achieve high deposition rates of YSZ films [16]. In the present study, the effects of CVD conditions (i. e., oxygen gas ratio, molar ratio of precursor and deposition temperatures) on microstructure and deposition rate of YSZ films were reported.

2. EXPERIMENTAL

A vertical cold-wall type CVD apparatus was constructed to prepare YSZ films [16]. Source precursors of $Zr(dpm)_4$ and $Y(dpm)_3$ were vaporized at 483 to 593 and 393 to 473 K, respectively. The source vapors were carried with Ar gas into the CVD reactor. The Y_2O_3 contents in the YSZ films were controlled by changing the evaporation temperature of $Y(dpm)_3$ precursor. O_2 gas was separately introduced by using a double tube nozzle, and mixed with precursor vapors in a mixing chamber placed above a substrate holder. The molar ratios (x_i) of Ar, O_2 and precursor vapors was defined as eq. (1),

$$x_i = M_i / (M_{Zr} + M_Y + M_{O2} + M_{Ar}) \quad (1)$$

where the amount of precursors (M_{Zr}, M_Y) were calculated from the mass loss of precursors after experiments. The values of x_{Zr}, x_Y and x_{O2} were changed from 0.0005 to 0.02, 0 to 0.002 and 0.05 to 0.5, respectively. The total gas flow rate was fixed at 3.33×10^{-6} m^3 s^{-1}. The total pressure in the CVD reactor was fixed at 0.8 kPa. Details of deposition conditions are summarized in Table 1. Hastelloy-XR alloy (49Ni-22Cr-18Fe-9Mo-0.9Mn-0.3Si, mass%) disks (10 in diameter 1 mm

Table I Deposition conditions of YSZ film by MOCVD.

Evaporation temperature of precursors	
$Zr(dpm)_4$, T_{Zr} / K	483~593
$Y(dpm)_3$, T_Y / K	393~473
Deposition temperature, T_{dep} / K	873~1173
Total pressure, P_{tot} / kPa	0.8
Deposition time, t_{dep} / ks	0.9
Molar ratio of precursors	
$Zr(dpm)_4$, x_{Zr}	0.0005~0.02
$Y(dpm)_3$, x_Y	0~0.002
Molar ratio of oxygen, x_{O2}	0.05~0.5
Total gas flow rate, FR_{tot} / 10^{-6} m^3s^{-1}	3.33

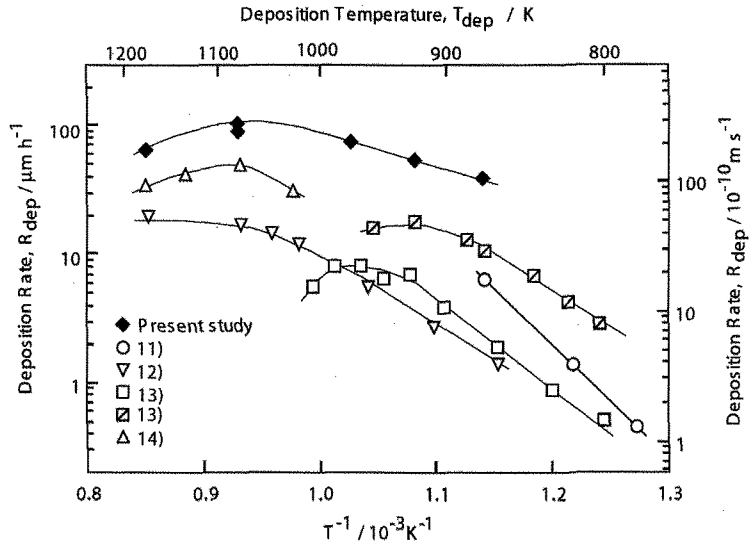

Fig. 1 Relationship between deposition rate of YSZ film and T_{dep}.

in thickness), and fused quartz glass plates (10 by 15 by 1 mm) were used as substrates. The crystal structure was studied by X-ray diffraction (XRD). The microstructure and thickness of films were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The Y_2O_3 content was determined by electron probe microanalysis (EPMA).

3. RESULTS AND DISCUSSION

Figure 1 summarized the deposition rates as a function of T_{dep} reported in literatures and the present study at P_{tot} = 0.8 kPa and x_{Zr} = 0.018. In the present study, a high deposition rate of 3.0×10^{-8} m s^{-1} (108 μm h^{-1}) was obtained at 1073 K. This value may be comparable to those of APS and EB-PVD (2.7 to 6.8×10^{-8} m s^{-1}) [17]. The deposition rates showed a slight maximum around 1073 K. The similar trend was reported by Pulver [13] and Wahl [14]. It is known that the decrease of deposition rates may be caused by homogeneous powder formation in gas phase at a high temperature region. Akiyama et al. reported that the activate energy (E_a) of 180 kJ mol^{-1} suggests a reaction controlled process [11]. Bourhila et al. and Pulver et al. obtained the activation energy of 105 to 135 kJ mol^{-1}. They explained that chemical reactions associated with $Zr(thd)_4$ could be a dominant process [12, 13]. In the present study, the activation energy at 900 to 1100 K was about 60 kJ mol^{-1}, suggesting that the rate-controlling process could be diffusion in a gas phase.

Figure 2 presents the effect of Zr precursor molar ratio (x_{Zr})

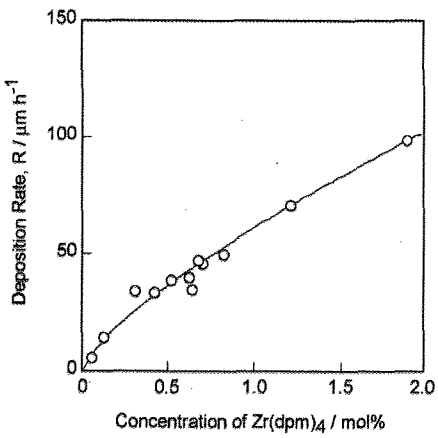

Fig. 2 Relationship between deposition rate of YSZ film and concentration of $Zr(dpm)_4$.

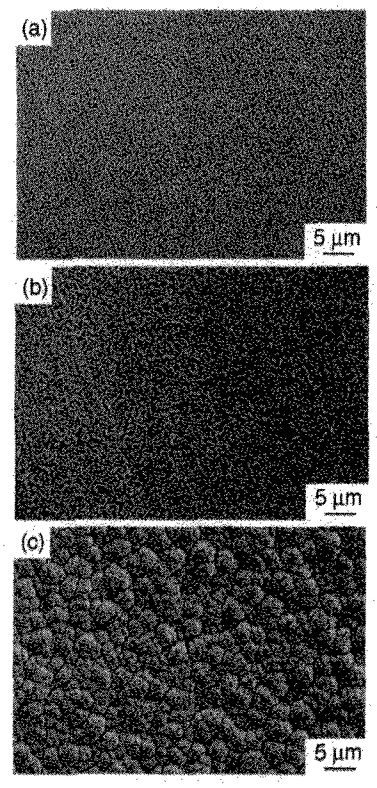

Fig. 3 Surface SEM images of YSZ films deposited on Hastelloy-XR at T_{dep} of (a) 973, (b) 1073 and (c) 1173 K.

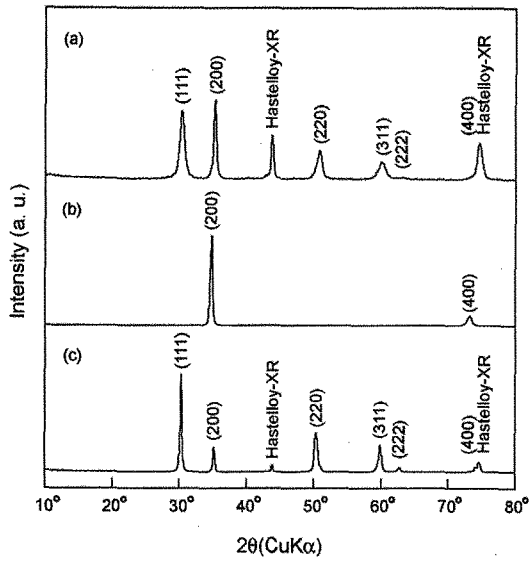

Fig. 4 XRD pattern of YSZ films deposited on Hastelloy-XR alloy at T_{dep} of (a) 973, (b) 1073 and (c)1173 K.

on the deposition rate at T_{dep} = 1073K. The deposition rates increased with increasing x_{Zr} and showed a saturation behavior. Similar relationship was reported in MOCVD of ZrO_2 [13], BN[18] and SiO_2[19].

Figure 3 shows the surface microstructures of YSZ films deposited on Hastelloy-XR alloy at T_{dep} = 973 to 1073 K. The grain size increased from 500 nm to 3 μm with increasing T_{dep}. Figure 4 represents the X-ray diffraction pattern of YSZ films deposited at T_{dep} = 973 to 1073 K. At T_{dep} = 973 K, the film showed a slight (200) orientation and a significant (200) orientation at T_{dep} = 1073 K, while it showed no orientation at T_{dep} = 1173 K.

Figure 5 presents the effect of oxygen gas ratio (x_{O2}) on the morphology of YSZ films prepared on quartz substrates at T_{dep} = 1023 K and P_{tot} = 0.8 kPa. At x_{O2} = 0.05, YSZ films (6.5 mol% Y_2O_3) had a dense and glass-like cross-section, and black in color. Since the P_{O2} in the deposition condition was not low enough to reduce ZrO_2, the black color must have not been resulted from the reduction. Black deposits due to the contamination of free-carbon were often obtained in MOCVD because of insufficient oxygen supply to oxidize organic ligands. In the present study, the black YSZ films could contain a small amount of free-carbon. The black color of the YSZ films changed to white after a heat treatment in air at 1273 K for 36 ks. At x_{O2} = 0.10 to 0.25 (Fig. 5 (b), (c)), YSZ films had a slightly irregular columnar structure. At x_{O2} = 0.25 to 0.40, the YSZ films were white in color. The YSZ film prepared at x_{O2} = 0.40 had a well-developed regular columnar structure (Fig. 5 (d)).

Figure 6 demonstrates the cross-sectional TEM images of an YSZ film with Y_2O_3 content of 4 mol% prepared at T_{dep} = 1073 K, P_{tot} = 0.8 kPa and x_{O2} = 0.40. The YSZ film was composed of many columnar crystals and each columnar was polycrystal as shown at Fig. 6(b). The grain size of ploycrystal was 100 to 400 nm. Many pores were observed parallel to the growth direction. The pores about 100 to 200 nm in diameter were observed along the columnar grain boundary. The thermal conductivity of YSZ film with nano-sized pores was approximately 0.9 W m^{-1} K^{-1} at room temperature. The value was close to that of APS -YSZ films

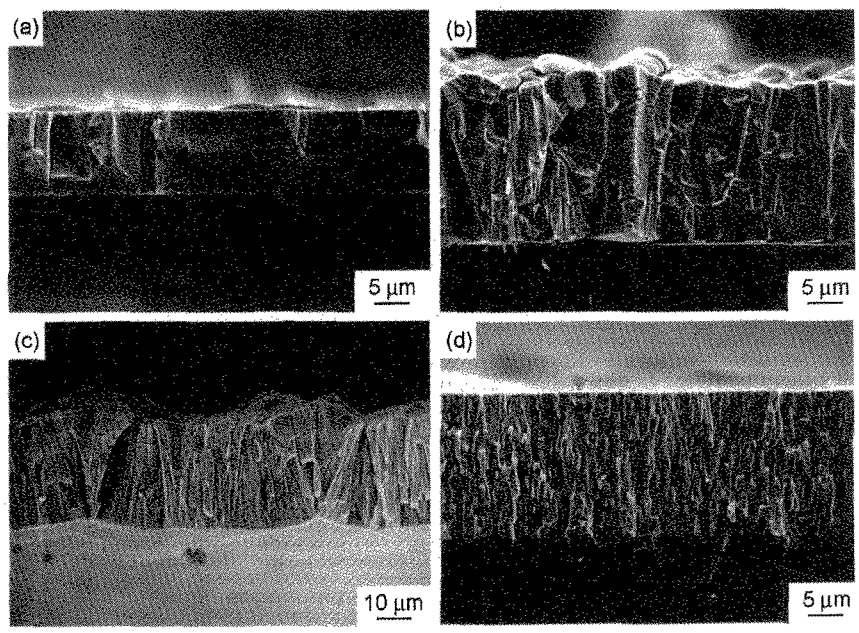

Fig. 5 Cross-sectional microstructures of YSZ films deposited on quartz substrate at T_{dep} = 1073 K, P_{tot} = 0.8 kPa and x_{O2} = (a) 0.05, (b) 0.10, (c) 0.25 and (d) 0.40.

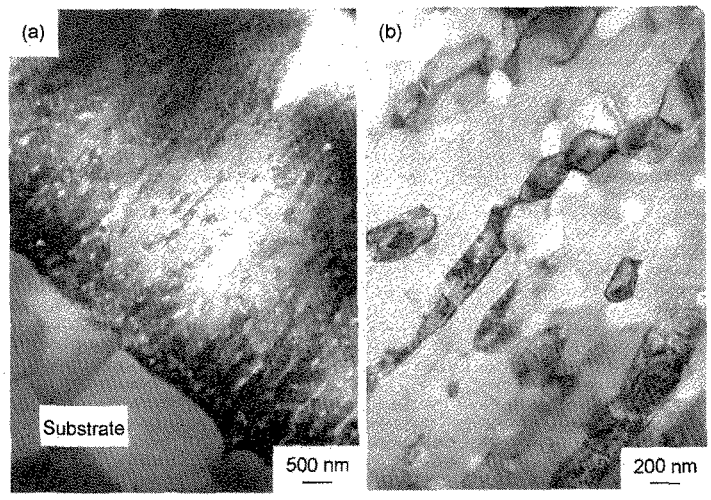

Fig. 6 TEM images of YSZ film prepared at R_{dep} = 52 μm h^{-1}, T_{dep} = 1073 K, P_{tot} = 0.8 kPa and x_{Zr} = 0.01.

(0.8 to 1.1 W m^{-1} K^{-1}) [20] and almost half of EB-PVD YSZ films (1.5 to 1.8 W m^{-1} K^{-1}) [20]. The phonon scattering by the nano-pores could be a main reason to reduce the thermal conductivity.

4. CONCLUSIONS

YSZ films were prepared using $Zr(dpm)_4$ and $Y(dpm)_3$ precursors by MOCVD. The YSZ films had a well-developed columnar structure with a significant (200) orientation at T_{dep} = 923 to 1073 K. The highest deposition rate (108 μm h^{-1}) was obtained at the conditions of T_{dep} = 1073K, P_{tot} = 0.8 kPa, x_{Zr} = 0.018 and x_{O2} = 0.40. Many nano-sized pores along the columnar grain boundary were observed in the YSZ films, yielding a significantly small thermal conductivity of 0.9 W m^{-1} K^{-1} at room temperature.

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