Transactions of the Materials Research Society of Japan 29 [2] 397-400 (2004)

Microstructure modification of YSZ layers prepared by EB-PVD

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Microstructures and texture of yttria-stabilized zirconia (YSZ) layers prepared by electron beam physical vapor deposition (EB-PVD) were investigated, focusing on the effect of deposition conditions. All the YSZ layers showed a columnar and feather-like structure and significant difference was found in their microstructures. Morphology, porosity, and texture of the layers changed drastically by substrate motion during deposition. The stationary deposited layer showed a relatively dense columnar structure with less intercolumnar gaps and indistinct feather-like structures, and no texture. Rotational motion was very effective in developing feather-like structures within each column leading to increased porosity. In addition, rotational motion caused strong (100) texture. These results are attributed to the flux shadowing effect caused by substrate motion. The influence of electron beam power and substrate temperature was also investigated.

Key words: EB-PVD, zirconia, columnar structure, feather-like structure, thermal barrier coating

1.INTRODUCTION

The majority of today's thermal barrier coatings (TBCs) are based on partially yttria-stabilized zirconia (YSZ) because of its low thermal conductivity, high melting point, relatively high thermal expansion coefficient, and good erosion resistance. The electron beam physical vapor deposition (EB-PVD) process is currently applied to TBCs for aircraft engines[1]. The most characteristic feature of EB-PVD films is the columnar structure of crystallites with gaps between columns (intercolumnar porosity) and finer pores and gaps in each column (intracolumnar porosity), a so-called 'feather-like' structure[2]. Due to such a unique structure, EB-PVD TBCs have advantages in resistance to thermal shock and thermal cycling for their applications. On the other hand, EB-PVD TBCs have higher thermal conductivity, namely lower thermal barrier efficiency, than that of plasma sprayed TBCs. Such characteristics are strongly related to microstructure influenced by the preparation method.

In the EB-PVD process, a high power electron beam melts and evaporates a source material and the evaporated materials are deposited on a substrate. The greatest advantage of the EB-PVD process is the ability to precisely control microstructures on the nanometer scale compatible with high deposition rate, because EB-PVD involves deposition from a dense vapor stream consisting of atoms, molecules, and nano-clusters. Precise control of microstructures, such as nano-scale pores and gaps in the columns, can improve dramatically the properties of EB-PVD TBCs. Some approaches to improve the properties of TBCs by tailoring the microstructure of coatings have been recently pursued[3,4].

In this study, we investigated the effects of deposition conditions on the microstructure and texture of YSZ layers prepared by EB-PVD, in order to understand fundamental parameters controlling coating microstructures on the nanometer level by EB-PVD.

2.EXPERIMENTAL

The EB-PVD equipment used in this study utilizes a 150kW EB gun and consists of separate chambers for loading, preheating, coating, with facilities for transferring between each chamber, and manipulation and rotation of a substrate on a horizontal axis in the coating chamber. An ingot was melted and vaporized by an electron beam and the vapor was deposited onto a substrate positioned just above the ingot. The ingot of 63mm diameter was fed into the crucible at a constant rate to ensure continuous and stable deposition. Ceramic ingots of 4mol% Y_2O_3-ZrO_2 were used. Inconel 738LC plates of 55mm x 20mm x 2.5mm polished by #1200 abrasive were used as substrates. In order to produce stoichiometric zirconia, a controlled amount of oxygen was bled into the coating chamber. The total pressure of the coating chamber was adjusted to 1Pa. The distance between substrates and the evaporation pool was 300mm. Deposition time was fixed at 20min in all experiments. The substrates were preheated by radiation heating using carbon heaters. Substrate temperature was measured by thermocouples inserted in the substrate holder.

The microstructure of PVD layers is strongly influenced by various deposition conditions: substrate temperature, rotation speed, the vapor incidence angle (VIA), deposition rate, chamber pressure, and so on. One of the main mechanisms of microstructure formation is based on the shadowing effect, because EB-PVD is a line-of-sight deposition process. The shadowing phenomenon is highly influenced by VIA and relates closely to substrate motion. In order to investigate the effect of substrate motion, substrates were moved in various manners: stationary (placing the substrate perpendicular to the vapor flow), 360° rotation, and 180° rotation (rotating the substrate back and forth through 180° centering around the vapor flow direction). The rotation speed was varied from 1 to 20rpm for both rotation modes. The EB power was varied from 35 to 60kW. For an examination of the effect of substrate motion, the EB power was fixed at 45kW. In order to maintain the same substrate temperature throughout the deposition, the preheating temperature was set to a stable temperature determined mainly by radiation from the evaporation pool that is strongly dependent on the EB power: 850°C for 35kW, 950°C for 45kW, and 1060°C for 60kW. Table I summarizes the experimental conditions in this study.

The microstructure of coatings was investigated by scanning electron microscopy (SEM). Phase composition and texture were analyzed by X-ray diffraction (XRD). Porosity was calculated from weight gain of the specimens and the coating thickness.

Table I Experimental conditions

	Stationary	360° rotation			180° rotation		
		1 rpm	5 rpm	20 rpm	1 rpm	5 rpm	20 rpm
35kW			O				
45kW	O	O	O	O	O	O	O
60kW			O				

3.RESULTS AND DISCUSSION

3.1 Microstructure, porosity and texture

Figure 1 shows cross-sectional images of YSZ layers deposited under various conditions. All the layers exhibited columnar structures, but significant differences exist between the stationary deposited layer and layers deposited with substrate motion. The stationary deposited layer was relatively dense with less porosity, and the feather-like structure was obscure (Fig. 1(a)). The rotationally deposited layers exhibited wider inter-columnar gaps and more apparent feather-like structures (Figs. 1(b) – 1(d)) . At low rotational speed, typically at 1rpm, layered structures of bent columns are clearly seen, similar to those reported in the literature[1,5]. C-shaped structures (Fig. 1(b)) and s-shaped structures (Fig. 1(d)) are formed on 360° rotated substrates and on 180° rotated ones, respectively. Such layered structures were more pronounced close to the substrate and the periodicity of the bent layers corresponded to the rotational speed. These structures can be explained by the continuous change of the VIA during rotation and periodical facing and interrupting of the vapor flux to the substrate. In the case of low rotation speed, the amount of vapor particles adhered on the growing surface at each VIA is relatively large, and the continuous change of VIA led to formation of apparent bent columns. The actual growth direction of columns closely follows the change of VIA, because EB-PVD is a line-of-sight deposition process. For 360° rotation, rotational direction is the same during deposition and c-shaped columns were formed. For 180° rotation, s-shaped bent columns were formed because the rotational direction alternates. Increasing rotational speed reduces the amount of vapor particles arriving at the growing column top at each VIA and the interval of each bent column becomes shorter, resulting in a straight morphology (Fig. 1(c)).

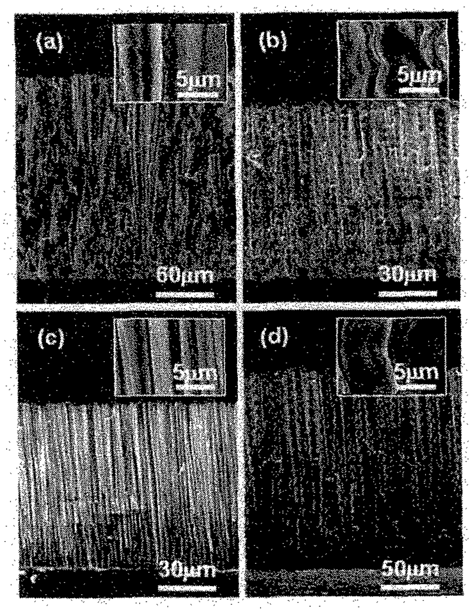

Fig.1 Cross-sectional SEM images of YSZ layers deposited at 45kW: (a) stationary deposition, (b) 360° rotation at 1rpm, (c) 360° rotation at 20rpm, (d) 180° rotation at 1rpm. Inset shows a detailed image at the center of the layer.

Deposition rate and porosity as a function of the EB power are shown in Fig.2(a). As the EB power increases, the deposition rate increased linearly from 100μm/h at 35kW to 430μm/h at 60kW. Increasing the EB power raised the evaporation rate due to increasing energy input to the ingot. In this EB power range, raising the EB power is expected to increase the evaporation rate linearly, which results in a linear increase in the deposition rate. Porosity showed a maximum around 45kW. High EB power promotes the evaporation of the source material and the density of vapor species is increased as a result. Therefore, the probability of cluster formation increases in the vapor stream. The clusters impinge on the growing surface to form mounds. Continuous impingement of clusters makes it difficult for the mounded clusters to relax their structure fully and the gaps between mounds remains as nano-pores, and thus, intracolumnar porosity increases. At the same time, however, increasing the EB power also increases the substrate temperature because radiation from the evaporation pool becomes strong. High substrate temperature promotes surface diffusion of impinged particles and makes the scolumn wider, and the sum of surface area of columns decreases. Nano-pores and nano-gaps related to the feather-like structure usually exist near the surfaces of columns, so they probably decrease with increasing substrate temperature. In addition, high substrate temperature may promote sintering within columns, resulting in decrease in intracolumnar nano-pores. Porosity is likely to be determined by a balance between the phenomena described above and shows a maximum at moderate EB power.

Figure 2(b) shows the effect of the substrate motion on the deposition rate and the porosity. Under stationary deposition conditions, the deposition rate was 600μm/h. 360° rotation and 180° rotation decreased the deposition rates to approximately 240μm/h and 420μm/h, respectively. Under stationary deposition conditions, the substrate was always exposed to the vapor flux with normal incidence. 360° rotational motion causes interruption and oblique incidence of vapor flux and reduces the deposition rate. During 180° rotation, the substrates are always exposed to the vapor stream, differing from 360° rotation. Therefore, reduction in deposition rate in 180° rotation is lower than that in 360° rotation. The porosity of the stationary deposited layer was only 7%, while 360° rotation and 180° rotation caused rapid increase of porosity, up to over 20%. This is related to change of microstructure, especially development of the feather-like structure by introducing rotational motion. Intracolumnar nano-pores are likely to increase with increasing rotational speed, because faster rotation is expected to increase scattering of vapor species and collisions of evaporated species in the vapor flow, resulting in formation of nano-clusters.

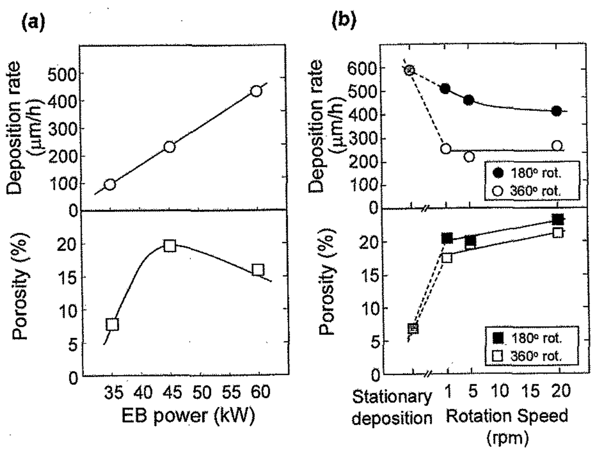

Fig.2 (a) Deposition rate and porosity of YSZ layers as a function of EB power, (b) influence of substrate motion on deposition rate and porosity

Figure 3 shows XRD patterns of the YSZ layers. Peak splits, typically between 73° to 75°, are clearly evident and are attributed to the presence of the metastable tetragonal t' phase reported in EB-PVD YSZ coatings[6,7]. In this EB power range, the EB power did not affect the texture of the YSZ layers and the layers showed (100) texture. The texture of the YSZ layers was very different between the stationary deposited layer and the rotationally deposited ones. The XRD pattern of the stationary deposited layer was similar to that of the powder reference, which means no texture. In contrast, strong (100) texture appears in rotationally deposited coatings, similar to and consistent with observations made on EB-PVD YSZ coatings[8,9]. This is because the shadowing effect is much more pronounced for the rotating substrate. Under the deposition conditions in this study, (100) is thought to be the fastest growth orientation, therefore (100) oriented grains ultimately shadow and extinguish the growth of crystallites with other growth directions growing more slowly. As a result, rotationally deposited coatings exhibit strong (100) preferential growth orientation. At high deposition rate, even slight differences in growth rates can promote this selection of preferential oriented column.

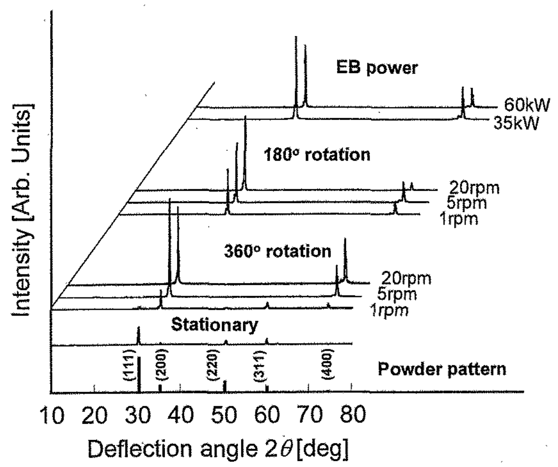

Fig.3 XRD patterns of YSZ layers deposited at various conditions.

3.2. Feather-like structure formation

Structures of YSZ layers deposited without and with rotation are quite different from each other. The stationary deposited layer shows a relatively dense, tapered columnar structure. The rotationally deposited layer exhibits much less tapered columns with wider inter- columnar gaps and the feather-like structure is much more pronounced. Polished cross-sectional SEM images (Figs. 4(a) and 4(b)) and a TEM image (Fig. 4(c)) of the feather-like structure give more detailed information.

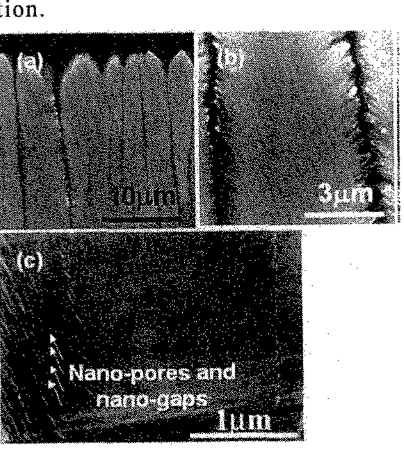

Fig.4 Micrographs of YSZ layers in detail; (a) polished cross-sectional SEM image, (b) higher magnification image of (a), (c) TEM image near microcolumns.

The columnar grains are separated by gaps on the submicrometer scale and each grain consists of a dense core with a few nano-pores, micro-columns on the column surface aligned nearly parallel to each other, and elongated nano-pores and nano-gaps between micro-columns.

Figure 5 shows a schematic illustration of the microstructure of a YSZ layer produced by EB-PVD. This characteristic is strongly influenced by the shadowing process, described as follows: Vapor flux is blocked by previously grown grains, and the region counter to the vapor flux is 'shadowed' so that the vapor cannot reach the shadowed regions directly. If the mobility of the vapor particles on the surface is limited, there is no growth in the shadowed regions. As a result, the grains tend to grow toward the direction of vapor incidence and exhibit a columnar structure. Rotational motion makes the columns perpendicular to the substrate surface as a whole, because VIA ranging from –90° to +90° changes continuously.

Shadowing occurs not only between the main columns but also between finer microstructures within the main columns. We classify the shadowing phenomena into two types: Type I shadowing is intercolumnar shadowing on the micrometer scale, which mainly governs columnar growth. Type II shadowing is intracolumnar shadowing on the nanometer scale. During deposition, a number of islands separated by nano-scale gaps grow on the terminal surface of the main columns. Nano-scale gaps between such islands cause type II shadowing that is closely related to formation of intracolumnar nano-pores. Combination of these shadowing phenomena strongly affects formation of the feather-like structure. A recent investigation reported that a columnar YSZ layer with feather-like structure was also formed on a stationary substrate inclined to the vapor stream without rotation[10]. This result confirmed that the shadowing effect is strongly related to oblique vapor incidence.

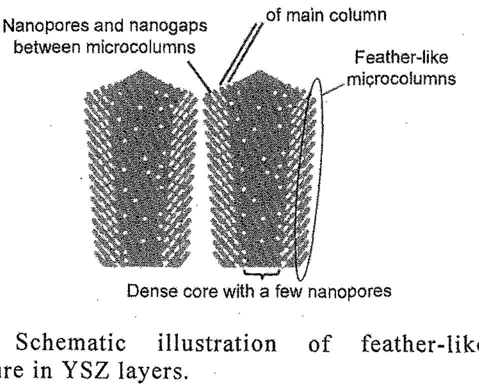

Fig.5 Schematic illustration of feather-like structure in YSZ layers.

As mentioned above, microstructure and texture of the EB-PVD films are strongly influenced by the flux shadowing that depends on VIA. VIA is closely related to substrate alignment to the vapor stream and can be controlled by substrate motion. Therefore, the substrate motion is one of the most important deposition conditions for controlling microstructures, because EB-PVD is a line-of-sight deposition process.

4.CONCLUSION

Microstructure of YSZ layers prepared by EB-PVD was investigated, focusing on the effect of deposition conditions. All the YSZ layers showed a columnar and feather-like structure, and the microstructure and texture strongly depended on deposition conditions. The EB power mainly affected thickness (deposition rate). Coating showed a (100) texture and porosity ranged from 8 to 20%. The stationary deposited layer had a relatively dense columnar structure and indistinct feather-like structure with no texture. Rotationally deposited layers had a columnar structure with wider intercolumnar gaps and well-developed feather- like structure with strong (100) texturing and porosity up to 20%. These results are attributed to the flux shadowing effect caused by combination of substrate motion and high deposition rate.

ACKNOWLEDGEMENT

This work was entrusted by NEDO as "the Nanotechnology Materials Program - the Nanostructure Coating Project'' promoted by METI, Japan.

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(Received October 10, 2003; Accepted March 31, 2004)