Abstract

Distribution and arrangement of nanopores in an YSZ (7 wt% Y₂O₃–ZrO₂)-thermal barrier coating (TBC) deposited by an electron beam-physical vapor deposition (EB-PVD) have been investigated by means of transmission electron microscopy. The YSZ-TBC deposited by the EB-PVD showed a typical columnar structure normal to the bond coat surface on the substrate. It has been generally believed that one column is a single crystal and grows continuously from the substrate. In the present study, however, it was found that each column consisted of a number of subcolumns with different misorientations and contained nanopores at the subcolumn boundaries. In addition to the nanopores at the subcolumn boundaries, nanopores with smaller size were observed within subcolumns, and were arranged periodically perpendicular to the growth direction of the subcolumns. Such arrangement and distribution of nanopores may be due to the misorientation of YSZ plate-like grains in the formation and coalescence processes of the YSZ subcolumns.

Keywords: Thermal barrier coating; Yttria-stabilized zirconia; Electron beam-physical vapor deposition; Nanopore

1. Introduction

Thermal barrier coatings (TBCs) [1–6] to protect substrate materials against thermal corrosion and oxidation have been widely applied to the fields of corrosion-resistant and high-temperature structural materials in gas turbine engine and power generation systems. TBCs lengthen the lifetimes of metal substrates by lowering the temperature of the substrates and reducing the driving forces for the creep failure and thermal fatigue. Therefore, it is of practical importance to develop TBCs with improved thermal insulation by controlling chemical compositions and microstructures in TBCs [7,8].

Among many kinds of ceramics for TBC materials, an yttria (Y₂O₃)-stabilized zirconia (YSZ) [9,10] has been dominantly used because of its low intrinsic thermal conductivity, relatively high thermal expansion coefficient and good corrosion-resistance compared to other ceramics. When metal ions having smaller ionic valences than 4+ are added to ZrO₂, anion vacancies are induced to maintain the charge neutrality of the whole system [11], which play a role for reducing the thermal conductivity effectively by scattering phonons [12]. The efficiency of thermal insulation is also closely related to the porosity of TBC materials. The degree of reduction in the thermal conductivity is governed by the sizes, the morphologies, the volume fraction and the distribution of pores within TBCs [7,8]. A large number of studies, therefore, have been focused on developing TBC materials with low intrinsic thermal conductivities and on deposition processes capable of controlling the microstructures and porosity.

Although it has been recognized that pores are very useful to reduce the thermal conductivities of TBCs, as mentioned above, distribution and structures of pores in TBCs have not been understood in detail. In the present study, therefore, the distribution of pores, especially nanopores, in an YSZ-TBC deposited by an electron beam-vapor deposition (EB-PVD) [2,13–16] has been examined mainly by transmission electron microscopy (TEM).
2. Experimental procedures

A single crystal of Hasteloy superalloy with chemical compositions of 22.0% Cr−9.0% Mo−20.0% Fe−0.15% C−bal.% Ni (wt%) was used as a substrate. A nickel alloy with chemical compositions of 45.2% Ni−23.0% Co−19.0% Cr−12.5% Al−0.3% Y (wt%) was deposited on the substrate by a low-pressure plasma spray to a 110 μm thick as a bond coat (BC), and then 7 wt% Y2O3–ZrO2 (YSZ) was deposited on the BC as a TBC using an EB-PVD. The deposition of YSZ was carried out by Chromalloy Corporation Ltd, USA.

The YSZ-coated specimen was cut from the bulk to a size of 30 × 20 × 10 mm³, mechanically grinded, polished, and its cross-section was observed by an optical microscope. In order to investigate microstructures of YSZ columns on the BC surface, a portion of the TBC layer was intentionally fractured into two pieces at the BC/TBC interface, and was supplied for the microstructural observation by a scanning electron microscope (SEM). Thin foil specimens for TEM were prepared from the cross-section of the YSZ-TBC block and then punched using an ultrasonic cutter. The punched disks were grinded mechanically to 50 μm thick, dimpled to about 20 μm thick, and finally thinned by a standard Ar ion-sputtering method at a voltage of 4 kV and at a low irradiation angle. The thin foils were examined in a JEM 2010HC (high contrast) operated at 200 kV.

3. Results and discussion

Optical micrographs showing typical microstructures of the TBC system with YSZ-TBC deposited by the EB-PVD are shown in Fig. 1. The TBC system consisted of three layers [17], i.e. a metallic BC with about 110 μm thickness on the Hasteloy superalloy substrate, an YSZ-TBC with about 700 μm thickness on the BC and a thermally grown oxide (TGO) layer between the BC and the YSZ-TBC as indicated by the arrow in Fig. 1(a). The TGO layer [18, 23], however, is a kind of reaction products formed by the oxidation of BC during the deposition process of TBC and grown on service at high temperatures, and is known to be generally α-Al2O3 with corundum structure. The black contrasts in Fig. 1(b) indicate pores between the columns. In the present study, however, such pores will be no longer mentioned. As can be seen in the top view micrograph of YSZ-TBC shown in Fig. 1(b), the grain sizes of YSZ columns distributed ranging from 3 to 25 μm in diameter.

Fig. 2 shows SEM micrographs observed in the specimen that was intentionally fractured at the BC/TBC interface. The TBC showed a typical columnar structure normal to the BC surface on the substrate (Fig. 2(a)). In Fig. 2(b), which is an enlarged micrograph for the square region enclosed by dotted lines in Fig. 2(a), YSZ columns grew up to about 25 μm height with forming a group as enclosed by dotted circle in Fig. 2(b) and many indistinct lines were observed within columns as indicated by the arrows in Fig. 2(b). As can be seen in the high-magnification micrograph of a column shown in Fig. 2(c), which corresponds to the square region enclosed by dotted lines within the column in Fig. 2(b), the columns consisted of many fragments and the fragments were stacked to the growth direction of columns.

Fig. 3 shows cross-sectional TEM micrographs of a column as shown in Fig. 2(b) and (d). Here, (a)–(c) are a bright field image and dark field images using a reflection from the selected area diffraction patterns inserted within Fig. 3(b) and (c). The diffraction vectors used for Fig. 3(b) and (c) are g = 020 and 220, respectively. As can be seen in Fig. 3(a), one column consisted of several fine subcolumns as marked with SCI through SC4. These subcolumns had different orientations with one another and thus were clearly separated by their boundaries, which correspond to indistinct lines in Fig. 2(b). For example, as can be seen from the selected area diffraction patterns shown in Fig. 3(b) and (c), the incident beam directions are [001] and [114], respectively, and thus the misorientation between SC2 and SC3 can be estimated to be about 20°. From this result, it can be understood that many indistinct lines within the columns shown in Fig. 2(b) correspond to the subcolumn boundaries. Therefore, it can be concluded that one column is formed by the coalescence of several fine subcolumns with various growth orientations. In Fig. 3, it is worthy of notice that pores were formed along the subcolumn boundaries, implying that the subcolumn boundaries can act as effective sites for the formation of nanopores.

Within subcolumns, many rows of nanopores were also observed as shown in Fig. 4. Each subcolumn was distinguishable by the relatively large pores aligned along subcolumn boundaries. The subcolumns contain parallel rows of nanopores inside, which were aligned periodically with a constant spacing of 200−250 nm, normal to the growth direction of subcolumns. Hereafter, the region separated by two rows of nanopores within a subcolumn will be designated as a plate, which probably corresponds to

Fig. 1. Optical micrographs showing typical microstructures of the YSZ-TBC deposited by the EB-PVD. (a) Cross-sectional view, and (b) top view of the TBC.
Fig. 2. Scanning electron micrographs taken in the YSZ-TBC specimen that was intentionally fractured at the BC/TBC interface. (a) Low-magnified micrograph, (b) enlarged micrograph for the region enclosed by a square in (a), (c) interior structure of a column, and (d) schematic illustration for the left side of (b).

Fig. 3. Transmission electron micrographs of an YSZ column. (a) Bright field image, and (b) and (c) dark field images using a reflection from the selected area diffraction patterns inserted within (b) and (c), respectively. One column consists of several fine subcolumns with different orientations with one another and contains nanopores at subcolumn boundaries. The symbol of SC indicates subcolumn.

Fig. 4. (a) Transmission electron micrograph showing configuration of nanopores in a YSZ column, and (b) schematic illustration of nanopore distribution observed in (a).
the fragment shown in Fig. 2(c). In Fig. 4, it should be noted that the directions of all rows of nanopores within a subcolumn are almost identical, but those in other subcolumns are slightly tilted with respect to each other. This is due to misorientations between subcolumns as mentioned in Fig. 3. The misorientation angle between the subcolumns in Fig. 4 seems to be smaller than the angle of 20° as shown in Fig. 3. It is noted here that the misorientation angles between subcolumns depend on the respective subcolumn boundaries.

An enlarged micrograph showing the subcolumn interior structure is shown in Fig. 5. As can be seen in Fig. 5(a), one plate was divided into several fine plates. The fine plate is designated as a subplate hereafter. At the corners where four subplates are encountered, fine nanopores as small as 40 nm in size were observed. It can be seen from the diffraction pattern shown in Fig. 5(b) that each subplate is rotated slightly by about 7° for the adjacent ones, along the normal axis to the growth direction of the subcolumn. It is thought, therefore, that the fine nanopores were formed at the junctions of the subplates due to their slight misorientations.

In the present study, it has been confirmed that one column was composed of several fine subcolumns with different misorientations and contained nanopores along subcolumn boundaries. Within subcolumns, fine nanopores were arranged periodically perpendicular to the growth direction of the subcolumns. Although the structures of YSZ columns are much complicated, the ordering of nanopores in the YSZ columns should be closely related to the deposition mechanism by EB-PVD. The mechanism for the stacking of fine subplates with a particular direction and the resultant well-arranged nanopores in the subcolumns will be clarified on the basis of microstructural characterization, in close connection with the deposition processes.

4. Conclusions

The TBC system with an YSZ-TBC deposited by the EB-PVD consisted of a metallic BC on the Hasteloy superalloy substrate, the YSZ-TBC on the BC and the TGO layer between the BC and the YSZ-TBC. The YSZ-TBC showed a typical columnar structure normal to the BC surface. One column consisted of several fine subcolumns with different orientations with one another and nanopores were observed along subcolumn boundaries. Each subcolumn was also composed of many YSZ plate-like grains. The plates were stacked periodically along the growth direction of subcolumn with a constant spacing and were slightly rotated with one another. Very small nanopores with about 50 nm in diameter were also observed between the plates. These nanopores at the boundaries of subcolumns and plates are expected to be formed due to the misorientations between subcolumns or between subplates.

Acknowledgements

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

References

[1] P.K. Wright, A.G. Evans, Current opinion in solid state and materials, Science 4 (1999) 255.
[2] C. Leyens, U. Schulz, K. Fritscher, M. Bartsch, M. Peters, W.A. Kaysser, Z. Metallkd 92 (2001) 7.
[3] A.G. Evans, D.R. Mumm, J.W. Hutchinson, G.H. Meier, F.S. Pettit, Prog. Mater. Sci. 46 (2001) 505.
[4] J.T. DeMasi-Marcin, D.K. Gupta, Surf. Coat. Technol. 68/69 (1994) 1.
[5] S.M. Meier, D.K. Gupta, Trans. ASME 116 (1993) 250.
[6] P.K. Wright, Mater. Sci. Engng A245 (1998) 191; R.A. Miller, J. Am. Ceram. Soc. 67 (1984) 517.
[7] C.A. Johnson, J.A. Ruud, R. Bruce, D. Wortman, Surf. Coat. Technol. 108/109 (1998) 80.
[8] S. Gu, T.J. Lu, D.D. Hass, H.N.G. Wadley, Acta Mater. 49 (2001) 2539.
[9] R. Chaim, M. Rühle, A.H. Heuer, J. Am. Ceram. Soc. 68 (1985) 427.
[10] T. Sakuma, Y. Yoshizawa, H. Sato, J. Mater. Sci. 20 (1985) 1085.
[11] S. Fabris, A.T. Paxton, M.W. Finnis, Acta Mater. 50 (2002) 5171.
[12] P.G. Klemens, M. Gell, Mater. Sci. Engng A245 (1998) 143.
[13] R.A. Miller, J. Am. Ceram. Soc. 67 (1984) 517.
[14] A. Bennett, Mater. Sci. Technol. 2 (1986) 257.
[15] T.A. Cruse, S.E. Stewart, M. Ortiz, J. Engng Gas Turbine Power 110 (1988) 610.
[16] J.T. DeMasi-Marcin, K.D. Sheffler, S. Bose, J. Engng Gas Turbine Power 112 (1990) 522.
[17] Y.-C. Jung, T. Sasaki, K. Matsunaga, Y. Ikuhara, T. Yamamoto, T. Tomimatsu, Y. Kagawa, JIM Annual Meeting, November 2002, p. 529.
[18] M.J. Stiger, N.M. Yanar, M.G. Topping, F.S. Pettit, G.H. Meier, Z. Metallkd 90 (1999) 1069.
[19] C. Leyens, U. Schulz, B.A. Pint, I.G. Wright, Surf. Coat. Technol. 120/121 (1999) 68.
[20] X.-Y. Gong, D.R. Clarke, Oxidation of Metals 50 (1998) 355.
[21] M. Gell, K. Vaidyanathan, B. Barber, J. Cheng, E. Jordan, E. Met. Mater. Trans. 30A (1999) 427.
[22] M.Y. He, A.G. Evans, J.W. Hutchinson, Acta Mater. 48 (2000) 2593.
[23] A.G. Evans, M.Y. He, J.W. Hutchinson, Acta Mater. 47 (1999) 1513.