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Microstructure and Sintering Behavior of Hafnia-based Thermal Barrier Coating by EB-PVD Process

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The development of hafnia-based thermal barrier coating was started and the 7.5mass%Y_2O_3-HfO_2 (7.5YSH) was selected for top coating layer. The 7.5YSH top coating with about 200μm thickness was formed by electron beam-physical vapor deposition. The 7.5YSH coating layer formed at substrate temperature of 956°C was composed of a large solid columns aligned in the <110> and the <211> direction of tetragonal crystallite. From the result of sintering behavior obtained by thermal exposure for 7.5YSH coating, it was recognized that the sintering resistance of 7.5YSH coating was improved by about 100°C over that of 8mass%Y_2O_3-ZrO_2 coating.
Key words: thermal barrier coating, electron beam -physical vapor deposition, hafnia, microstructure, sintering

1. INTRODUCTION

The worldwide energy saving and reduction of global warming effect gas (CO_2) are required very strongly. In order to comply with these requirements, the effort to develop the high efficiency gas turbine has been performed and therefore, the improvements of gas turbine blade material, cooling technology and thermal barrier coatings (TBCs) on the blades have been carried out continuously.

Generally, TBCs are two layered system and the top coating materials of 7~8mass% yttria partially stabilized zirconia (YSZ) are used and show totally excellent properties. However, TBCs have a tendency to spall under thermal cycling, corrosion and erosion from ambient conditions corresponding to the extremely high operating temperature in the hot section of a gas turbine [1]. It is well known that the sintering of YSZ coating occurs above the surface temperature about 1200°C.

In order to improve the thermal durability in comparison with the YSZ coating, we have selected the hafnia (HfO_2) as a coating material, which has high melting point of 2900°C and low thermal conductivity of 1.5 W/mK as shown in Figure 1. The hafnia has a very similar crystalline structure and phase transformation behavior to zirconia (ZrO_2). The hafnia and hafnia-based ceramics were totally reviewed in comparison with the zirconia [2] and the phase diagram for hafnia(HfO_2)-yttria(Y_2O_3) system was studied [3].

In this work, we newly developed the hafnia-based TBC. The electron beam-physical vapor deposition (EB-PVD) process was adopted, because this process was able to control the nano-

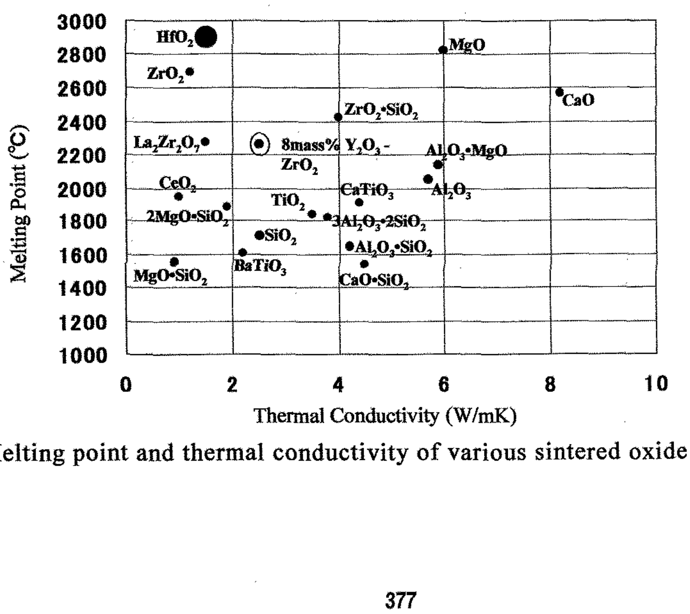

Fig.1 Melting point and thermal conductivity of various sintered oxide ceramics.

level microstructures such as pores and crystalline size. The microstructure and sintering behavior of 7.5YSH coating were discussed in comparison with 8mass%Y_2O_3-ZrO_2 (8YSZ).

2. EXPERIMENTAL PROCEDURES

2.1 Preparation of 7.5YSH ingot for EB-PVD

In the EB-PVD process, it is required that the ceramic ingot for EB-PVD does not crack by the electron beam irradiation. The YSZ ingot for EB-PVD generally contains apparent porosity of 25~50% and realize the stable vaporization from molten pool of ingot without cracking by the electron beam irradiation. The same property is needed for hafnia ingot for EB-PVD. In this work, the 7.5mass%Y_2O_3-HfO_2 (7.5YSH) was selected for coating material, because of the crystal structure stabilization by adding Y_2O_3. The 7.5YSH ingot was sintered so as to have appropriate porosity after mixing of hafnia and yttria powders and then, thermal shock characteristic of ingot was investigated by the electron beam irradiation.

2.2 EB-PVD coating of 7.5YSH

The SUS304 stainless steel was chosen for the substrate material with size of 20×20×5 mm for EB-PVD. The TBC system was composed of 2 layers with MCrAlYs(M:Ni and/or Co) bond coating and ceramic top coating. The NiCoCrAlY bond coating was formed on the substrate with about 150μm thickness by low pressure plasma spraying process. The chemical compositions of NiCoCrAlY spraying powder are 21.54mass%Co, 16.91mass%Cr, 12.4mass%Al, 0.66mass%Y and balance Ni.

The 7.5YSH top coating was formed on the bond-coated substrates by EB-PVD. The coating apparatus is shown in Figure 2.

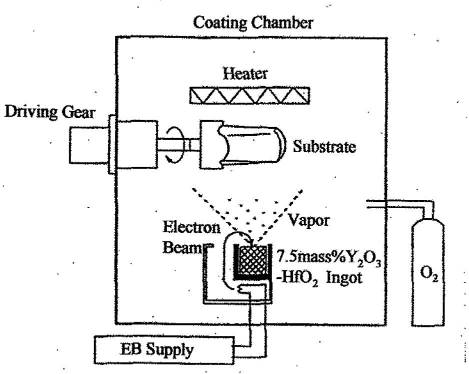

Fig.2 Schematic diagram of the developed EB-PVD apparatus.

It had an inner heater which enable to control the substrate temperature. The target material of top coating was 7.5YSH ingot of 35mm in diameter and 30mm in length. The 7.5YSH ingot was evaporated by an electron beam irradiation in vacuum and the vapor was condensed onto bond-coated substrates.

In order to maintain the stoichiometric oxygen composition of 7.5YSH coating, some oxygen was bled into the chamber during coating process. We investigated the top coating conditions of EB-PVD process about electron beam current, substrate temperature, coating time and coating thickness. The effects of substrate temperature were tested in the range from 700°C to 1000°C monitared by a thermocouple attached with the substrate.

After forming the 7.5YSH top coating, the microstructures of 7.5YSH coating surface were observed by FE-SEM and the orientations of the columnar grains were investigated by X-ray diffraction.

2.3 Thermal exposure EB-PVD coating of 7.5YSH

In order to investigate the sintering behavior of 7.5YSH coating, the thermal exposure was carried out. The substrate material for the thermal exposure was alumina ceramics with size of 20×20×5 mm. The 7.5YSH coating was formed on the alumina substrate by EB-PVD, the 8YSZ coating was also formed for the comparison. The thermal exposure in the electric furnace was carried out for 100 hours in air at 1300°C and 1400°C, respectively. After the thermal exposure, the microstructure of coating surface was observed using FE-SEM.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Firstly, the 7.5YSH ingot applicable for EB-PVD was developed. This ingot had the apparent porosity of about 50% and did not crack by electron beam irradiation. The EB-PVD coating was tried using the 7.5YSH ingot for the first time, and the coating fundamental conditions were clarified. The electron beam current ranging from 400 to 900 mA was able to melt and vaporize the 7.5YSH. This electron beam current was the same as that for ranging for 8YSZ ceramics ingot [4]. The 7.5YSH top coating with about 200 μm in thickness could be formed during 1.5-2 hours. Figure 3 shows the cross sectional microstructure of 7.5YSH coating.

It was observed the columnar grains with a diameter of about 2 μm grown perpendicular to the substrate.

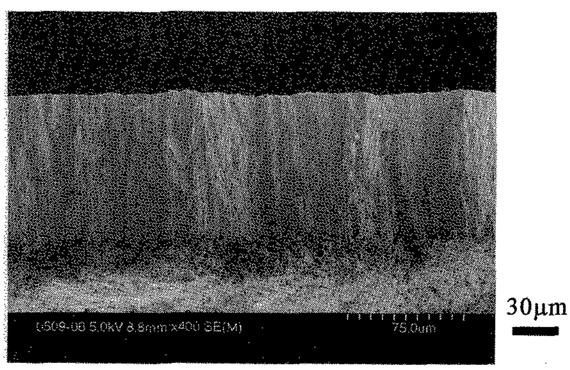

Fig.3 Cross sectional microstructure of 7.5YSH coating formed by EB-PVD.

The morphology of the columnar grains strongly depends on the substrate temperature during a coating

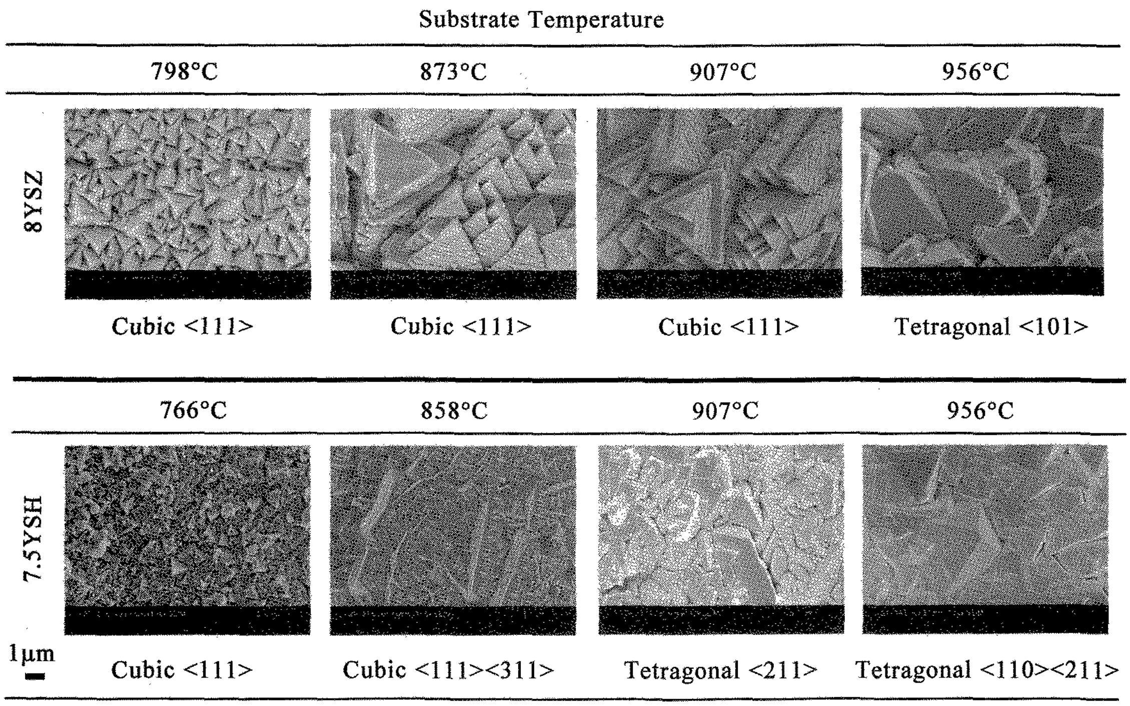

Fig. 4 Effect of substrate temperature on the surface morphology and crystal orientation in 8YSZ and 7.5YSH coatings.

process. The scanning electron micrographs of surface morphology for 8YSZ coatings and 7.5YSH coatings formed at several temperatures are shown in Figure 4. The orientations of each coatings from the results of X-ray diffraction are also shown in Figure 4. As the substrate temperature becomes higher, the columnar grain size increases in the both coatings, in addition, the phase of the coatings changes from cubic to tetragonal. The 8YSZ columnar grains formed at lower temperature (798°C, 873°C, 907°C) are aligned in the <111> direction of cubic and those at 956°C are aligned in the <101> direction of tetragonal. In the 7.5YSH coating, the columnar grains formed at lower temperature (766°C, 858°C) are aligned in the <111> and the <311> directions of cubic and those at higher temperature (907°C, 956°C) are aligned in the <211> and the <110> directions of tetragonal. It is considered that crystalline growth

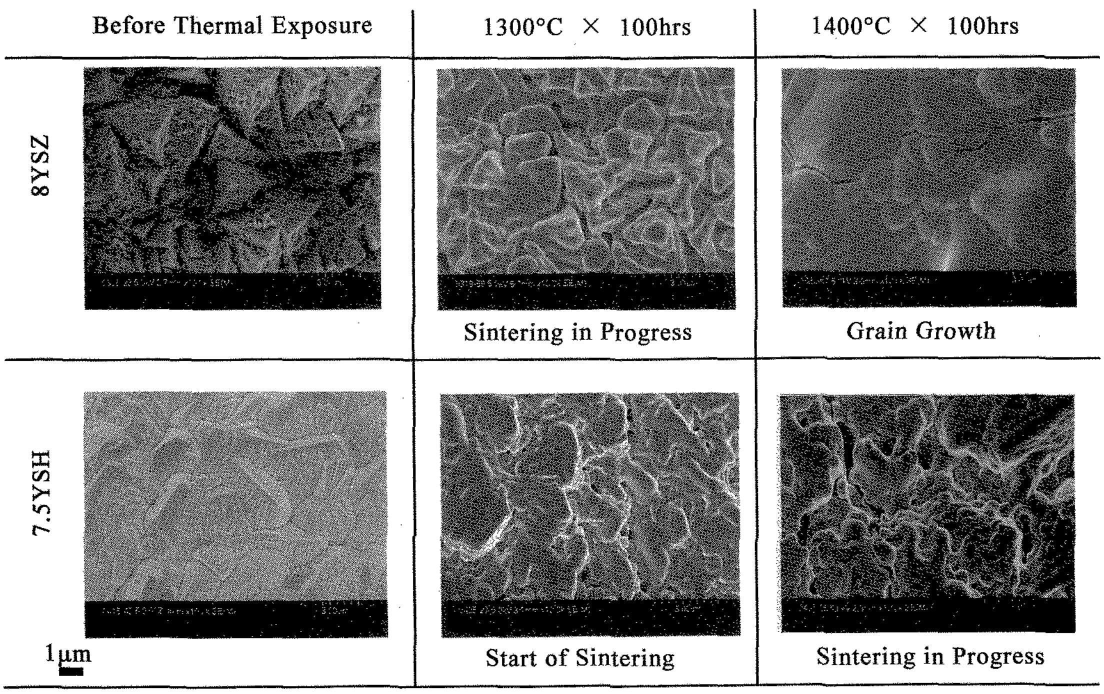

Fig.5 The surface morphology of 8YSZ and 7.5YSH coatings before and after thermal exposure

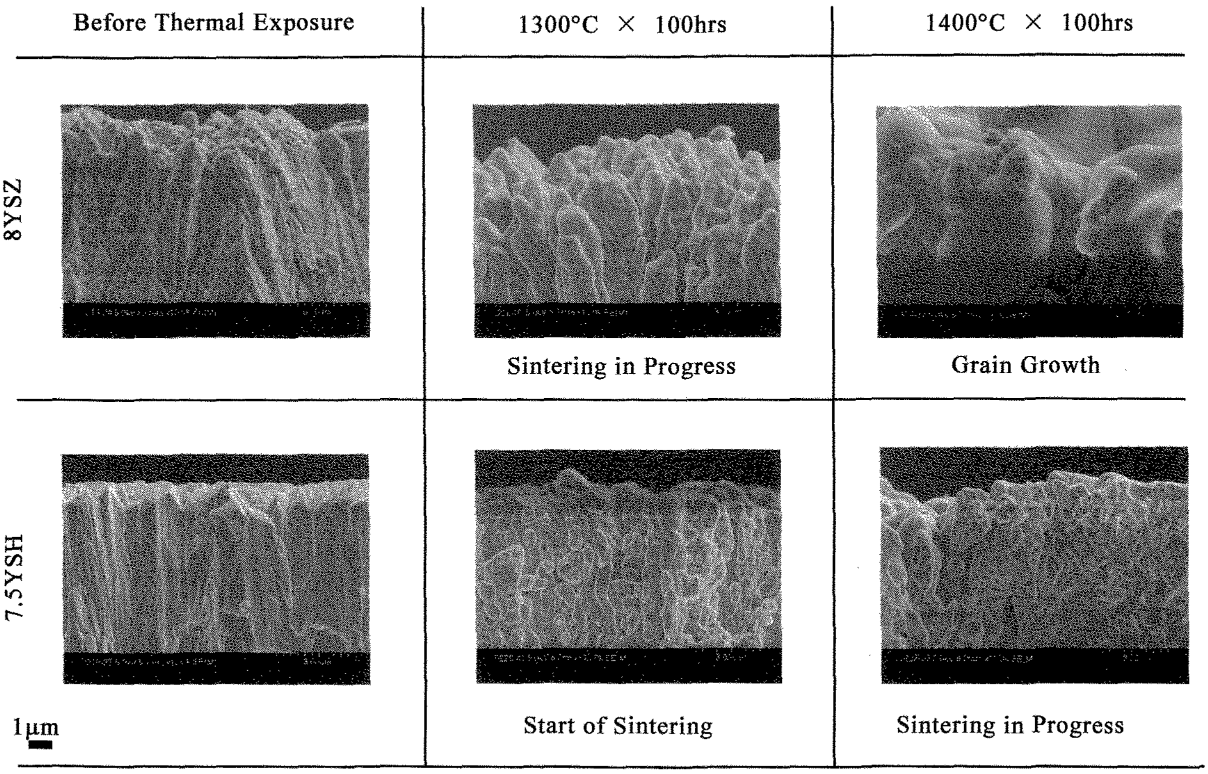

Fig.6 The cross sectional microstructure of 8YSZ and 7.5YSH coatings before and after thermal exposure.

energy is correlated with substrate temperature during coating process.

Figure 5 shows the surface morphology of 7.5YSH and 8YSZ coatings before and after heating tests. Before the heating test, the facet edges of columns showed sharp morphology for both samples. The columnar grains of 8YSZ coating became round and joined between neighbors after 1300°C heating test, that is, the sintering of 8YSZ coating was in progress at 1300°C. After the heating test at 1400°C, the grain growth of 8YSZ coating occurred. On the other hand, the edge of columns of 7.5YSH coating became slightly round, that is, the sintering of 7.5YSH coating started at 1300°C. After the heating test at 1400°C, the columnar grains of 7.5YSH coating joined between neighbors and the sintering of 7.5YSH coating was in progress.

Figure 6 shows the cross sectional microstructure of 7.5YSH and 8YSZ coatings before and after the heating tests. Although the temperature of sintering behavior differs between 7.5YSH and 8YSZ, the mechanism of sintering process was considered as EB-PVD coating. That is, it was considered the following steps.
(1) The columnar structure consists of many piled nano-size crystals. (2) At the beginning of sintering, the piled crystals start to combine each other and the columnar grains start to become round. (3) At the step of sintering in progress, the piled crystals and columns join each other. (4) Finally, the grain growth of coating occurs.

From these results of short time thermal exposure, it is considered that the sintering resistance of 7.5YSH coating is improved by about 100°C over that of 8YSZ coating.

This improvement increases the applying temperature of TBC and it is anticipated that turbine inlet gas temperature raises furthermore.

4. CONCLUSIONS

We newly developed the hafnia-based TBC. 7.5mass%Y_2O_3-HfO_2(7.5YSH) was selected for top coating layer, and the 7.5YSH ingot applicable for EB-PVD was developed. According to the investigation of the EB-PVD process, the 7.5YSH coating with about 200μm in thickness could be obtained for 1.5 to 2 hours.

The 7.5YSH coating layer formed at the substrate temperature of 956°C was composed of large solid columns aligned in the <110> and the <211> direction of tetragonal crystallite.

From the result of sintering behavior at 1300°C and 1400°C, it was considered that the sintering resistance of the 7.5YSH coating was improved by about 100°C over that of 8YSZ coating.

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