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Thermal Conductivity and Sintering Behavior of Hafnia-based Thermal Barrier Coating Using EB-PVD

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ABSTRACT

In general, 8mass%Y_2O_3-ZrO_2(8YSZ) coating materials are used as the top layer of thermal barrier coatings (TBCs). The development of hafnia-based TBC was started in order to realize the high reliability and durability in comparison with 8YSZ, and the 7.5mass%Y_2O_3-HfO_2 (7.5YSH) was selected for top coating layer. By the investigation of Electron Beam-Physical Vapor Deposition (EB-PVD) process, 7.5YSH top coating with about 200µm thickness was formed. The thermal conductivity of 7.5YSH coating was lower than that of 8YSZ coating at temperature range of 1000°C ~ 1300°C and became lower with rising the test temperature. From the result of sintering behavior obtained by heating test for 7.5YSH coating, it was recognized that the thermal durability for sintering behavior of 7.5YSH coating was improved up to about 100°C in comparison with 8YSZ coating.

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 coating (TBC) on the blades have been carried out continuously.

Generally, TBCs are two layered system which incorporates an about 250µm thickness layer of ceramic top coating applied to the outer surface of the substrate and an about 150µm thickness underlying of metallic bond coating. The metallic bond coating performs two functions: 1) to provide oxidation resistance and 2) to adhere the ceramic to the super alloy substrate physically and chemically. Nowadays, the bond coating materials are MCrAlYs(M:Ni and/or Co) and top coating materials are partially stabilized zirconia (PSZ). The thermal conductivity of PSZ coating is about 2 W/mK and lower than that of supper alloys.

Ceramic top coatings are made by several methods, such as plasma spraying, chemical vapor deposition and physical vapor deposition (PVD). The plasma spraying process is well-known process and used widely for the coating of TBCs. The coating structure made by the plasma spraying is the porous lamination of sprayed powders. The electron beam physical vapor deposition (EB-PVD) process is an advanced method of ceramic deposition (Meier and Gupta 1992). In the EB-PVD process, the electron beam is directed onto the surface of ceramic ingot contained within a crucible. The ceramic ingot is heated, melted, and then vaporized. The substrates are positioned above the molten ingot in the crucible in order to receive the ceramic vapor. The coating structure made by EB-PVD process typically consists of individual free-standing ceramic columns, which are essentially separated from adjacent columns, but are tightly bonded to the bond coating surface. This structure compensates the difference of thermal expansion between ceramic and substrate. In general, 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 (Wortman et al. 1989). 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 been 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 shown in Figure 1. The hafnia has a very similar crystalline structure and phase transformation behavior as zirconia (ZrO_2). The hafnia and hafnia-based ceramics were totally reviewed in comparison with the zirconia (Wang and Stevens 1992) and the phase diagram for hafnia(HfO_2)-yttria(Y_2O_3) system was studied (Stubican 1988). The mechanical properties of hafnia-based ceramics were investigated by many researchers. Namely, Young's modulus of 8mass% yttria partially stabilized hafnia was reported by Scheidecker(1979).

In this work, we newly developed the hafnia-based TBC. The 7.5mass%Y_2O_3-HfO_2 (7.5YSH) was selected for the coating material and the EB-PVD process was adopted, because this process was able to control the nano-level microstructures such as pores and crystalline size. The coating durability was discussed based on experimental observations of the sintering behavior of 7.5YSH coating and the thermal expansion property of 7.5YSH sintered ceramic in comparison with 8mass%Y_2O_3-ZrO_2 (8YSZ).

EXPERIMENTAL PROCEDURES

EB-PVD coating of 7.5 YSH

The IN738LC was chosen for the substrate material for EB-PVD. The TBC system was 2 layers with MCrAlY bond coating and ceramic top coating. At first, the oxidation characteristics of thermal sprayed MCrAlYs were investigated by heating test at 900°C in air and NiCoCrAlY was selected because of the excellent oxidation behavior as a bond coating. The chemical composition of NiCoCrAlY spraying powder is 21.54mass%Co, 16.91mass%Cr, 12.4mass%Al, 0.66mass%Y and balance Ni.

The NiCoCrAlY bond coating was formed on the substrate by

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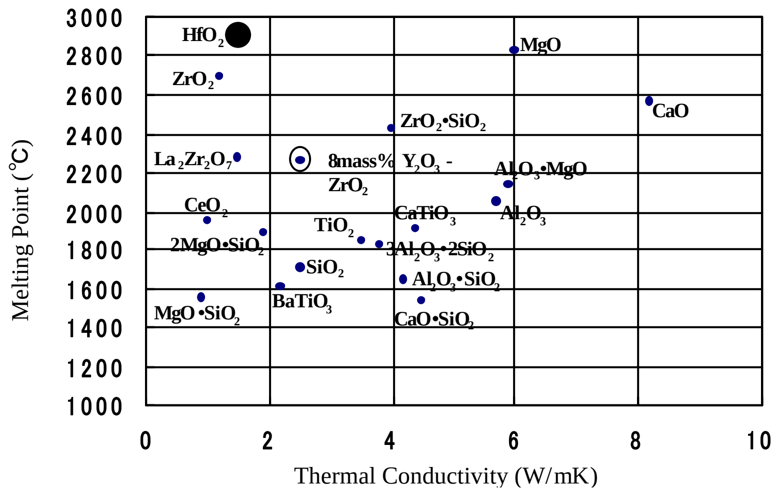

Fig.1 Melting point and thermal conductivity of various sintered oxide ceramics, hafnia(HfO_2) has higher melting point of 2900°C and low thermal conductivity of about 1.5 W/mK in comparison with 8mass% yttria stabilized zirconia

low pressure plasma spraying process. After forming the NiCoCrAlY bond coating, the substrates with NiCoCrAlY bond coating were cut as size of 20×20×5 mm.

The 7.5YSH top coating was formed on the bond-coated substrates by EB-PVD. The coating apparatus is shown in Figure 2. It had inner heaters 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 at 890°C of substrate temperature. In order to maintain the stoichiometric oxygen composition of HfO_2 coating during the EB-PVD process, some oxygen was bled into the chamber during the vaporizing of ingot.

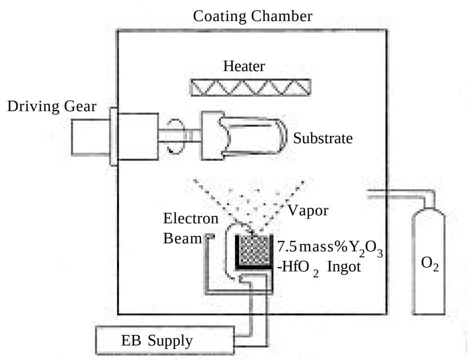

Fig.2 Schematic diagram of the developed EB-PVD apparatus that has inner heaters enable to control substrate temperature.

Thermal conductivity measurement for 7.5YSH and 8YSZ coating

The substrate material was IN738LC with NiCoCrAlY bond coating above mentioned. The sample size was 10mm in diameter and 1mm in length. The 7.5YSH coating was formed on the substrate by EB-PVD, the 8YSZ coating was also formed for comparison. The specific heat of 7.5YSH sintered material and substrate with bond coating was measured at temperature range of 25°C ~ 1300°C. The thermal diffusivity of coating materials and substrate were measured at the temperature range of 25°C ~ 1300°C by a laser flash method. And then, thermal conductivities of the 7.5YSH and 8YSZ coating were determined using two-layer composite analysis.

Sintering behavior for EB-PVD coating of 7.5YSH and 8YSZ

In order to investigate the sintering behavior of 7.5YSH coating, high temperature heating tests and thermal expansion measurement were carried out. The substrate material for heating test 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 comparison. Heating test in the electric furnace was carried out for 100 hours in air at 1300°C and 1400°C, respectively. After heating tests, the microstructure of coating surface was observed using FE-SEM.

For the thermal expansion measurement, sintered 7.5YSH and sintered 8YSZ samples were prepared. The sample size was 5×5 × 20mm. The thermal expansion were measured by using differential expansion method at a heating rate of 5°C/min from 100°C to 1500°C and 60min holding at 1500°C, and then at a cooling rate of 5°C /min from 1500°C to 100°C.

EXPERIMENTAL RESULTS

EB-PVD coating of 7.5YSH

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 7.5YSH ingot for the first time, and the coating fundamental conditions were made clear. The electron beam current was from 400mA to 900mA to be able to melt and vaporize 7.5YSH ceramics. This electron beam current was the same for 8YSZ ceramics ingot. The 7.5YSH top coating with a thickness of about 200µm could be formed during 1.5 to 2 hours. Figure 3 shows the cross sectional microstructure of 7.5YSH. It was observed that the columnar crystal with a diameter of about 3µm grew perpendicular to the substrate.

Thermal conductivity of 7.5YSH and 8YSZ coating

Figure 4 shows the thermal conductivity of 7.5YSH coating at temperature range of 25°C ~ 1300°C in comparison with the 8YSZ coated by EB-PVD and plasma spraying. The thermal conductivity of 8YSZ became low at temperature range of 25°C ~ 700°C, and then became high at temperature range of 700°C ~ 1300°C. At the temperature of 1300°C, the thermal conductivity of 8YSZ coated by EB-PVD is very higher than that of plasma sprayed 8YSZ. On the other hand, the thermal conductivity of 7.5YSH was lower than

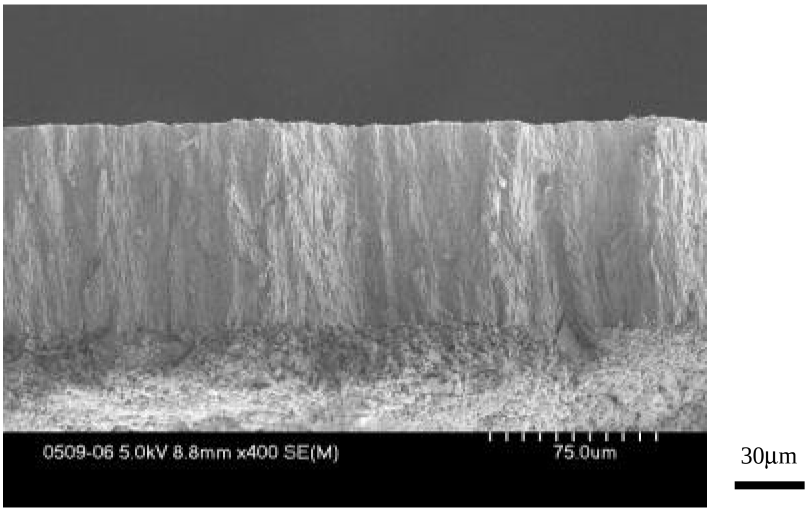

Fig.3 Cross sectional microstructure of 7.5YSH coating by EB-PVD consists of many columns with a diameter of about 3µm perpendicular to the substrate.

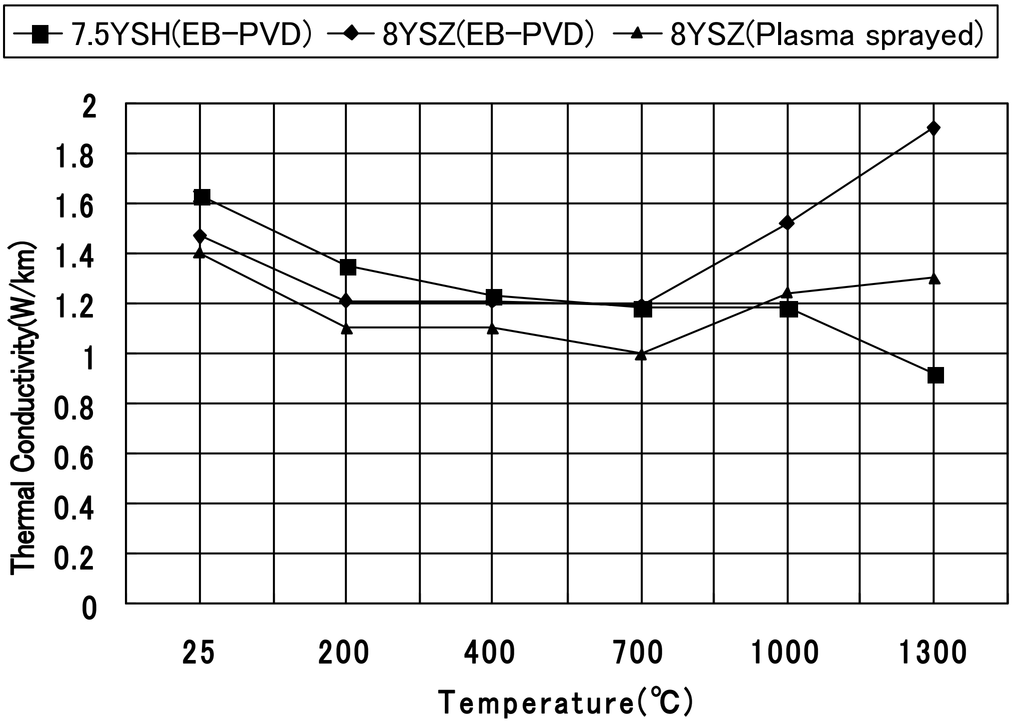

Fig4 Thermal conductivity of 7.5YSH coating is lower than that of 8YSZ coating at the temperature above 1000°C.

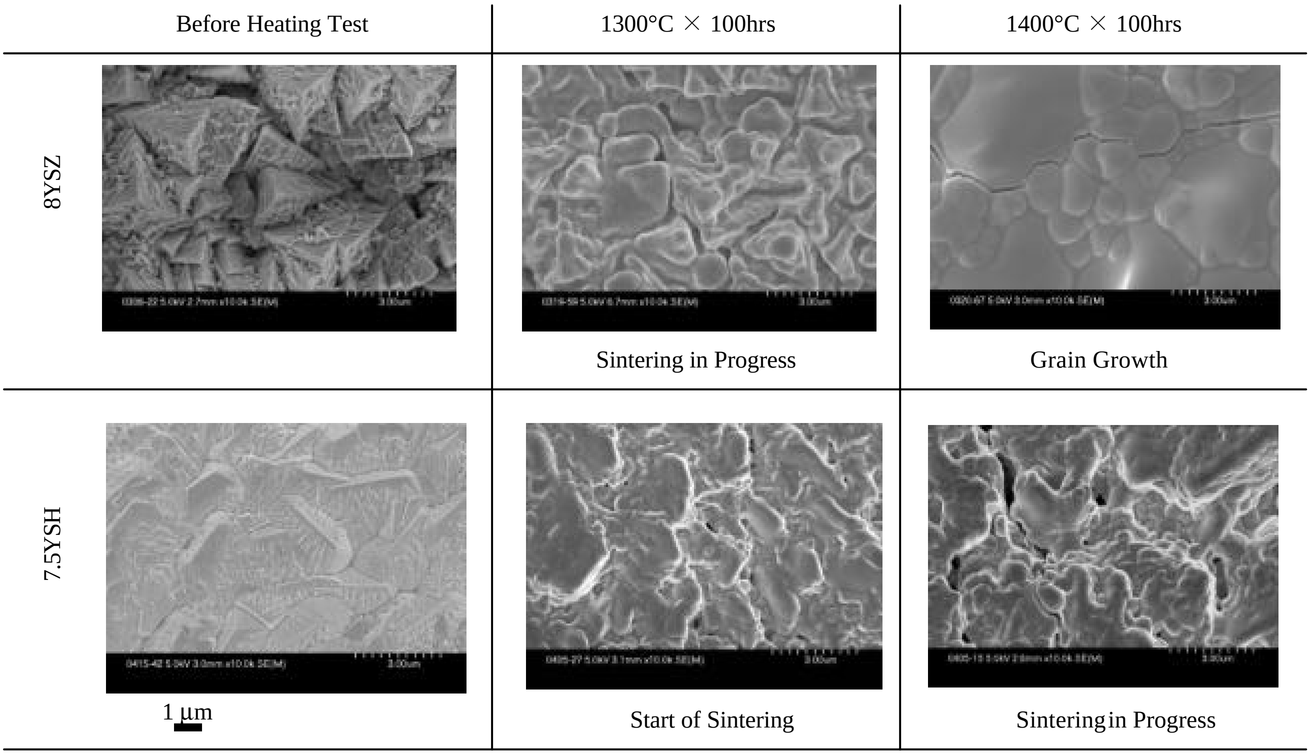

Fig.5 The surface observation of 8YSZ and 7.5YSH coating before and after heating tests. The thermal durability for sintering behavior of 7.5YSH coating is improved up to about 100°C in comparison with 8YSZ coating.

that of 8YSZ at temperature range of 1000°C ~ 1300°C and became lower with rising the test temperature.

Sintering behavior of 7.5YSH and 8YSZ coating

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

DISCUSSION

The thermal conductivity of 7.5YSH coating was lower than that of 8YSZ coating at temperature range of 1000°C ~ 1300°C and became lower with rising test temperature. This property was greatly desirable for TBCs. The thermal conductivity of 8YSZ coating became higher above temperature of 700°C in comparison with 7.5YSH coating. The reason was considered as sintering of

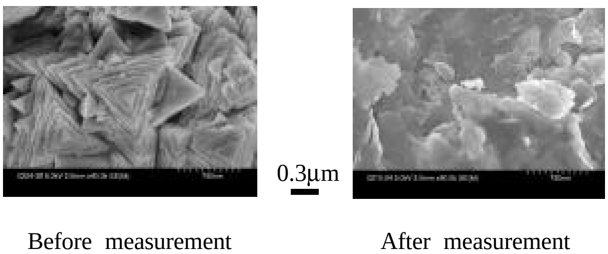

Fig.6 Surface microstructure change of 8YSZ coating before and after measurement up to 1300°C.

8YSZ coating from the observation of surface microstructure of the sample after the measurement at the test temperature up to 1300°C as shown in Figure 6.

Figure 7 shows cross sectional microstructure observation of 7.5YSH and 8YSZ coatings before and after heating test. 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 condensed nano-size particles. (2) At the beginning of sintering, the condensed particles start to combine each other and the columnar structure starts to become round. (3) At the step of sintering in progress, the condensed particles and columns join each other. (4) Finally, grain growth of coating occurred.

The tendency of sintering behavior was corresponded with the result of the thermal expansion measurement. Figure 8 shows the thermal expansion property of sintered 7.5YSH as a function of temperature in comparison with sintered 8YSZ and plasma sprayed 8YSZ. The thermal expansion of sintered 7.5YSH increased linearly up to 1400°C and sintering shrinkage was started at 1500°C. On the other hand, the thermal expansion of sintered 8YSZ increases up to 1300°C and sintering shrinkage was started at 1400°C. At 1500°C, the thermal expansion of sintered 8YSZ was decreased largely. For the plasma sprayed 8YSZ, the sintering shrinkage was started at 1200°C.

From these results of short time heating tests and thermal expansion measurement, it is considered that the thermal durability for sintering behavior of 7.5YSH coating is improved up to about 100°C in comparison with that of 8YSZ coating.

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

Figure 9 shows the thermal expansion coefficient of sintered 7.5YSH as a function of temperature in comparison with that of the sintered 8YSZ. The thermal expansion coefficient of sintered 7.5YSH was 6.7 ~ 9.2×10^{-6}/°C and that of 8YSZ was 7.7 ~ 9.6×10^{-6}/°C at the temperature range from 100°C to 1400°C.

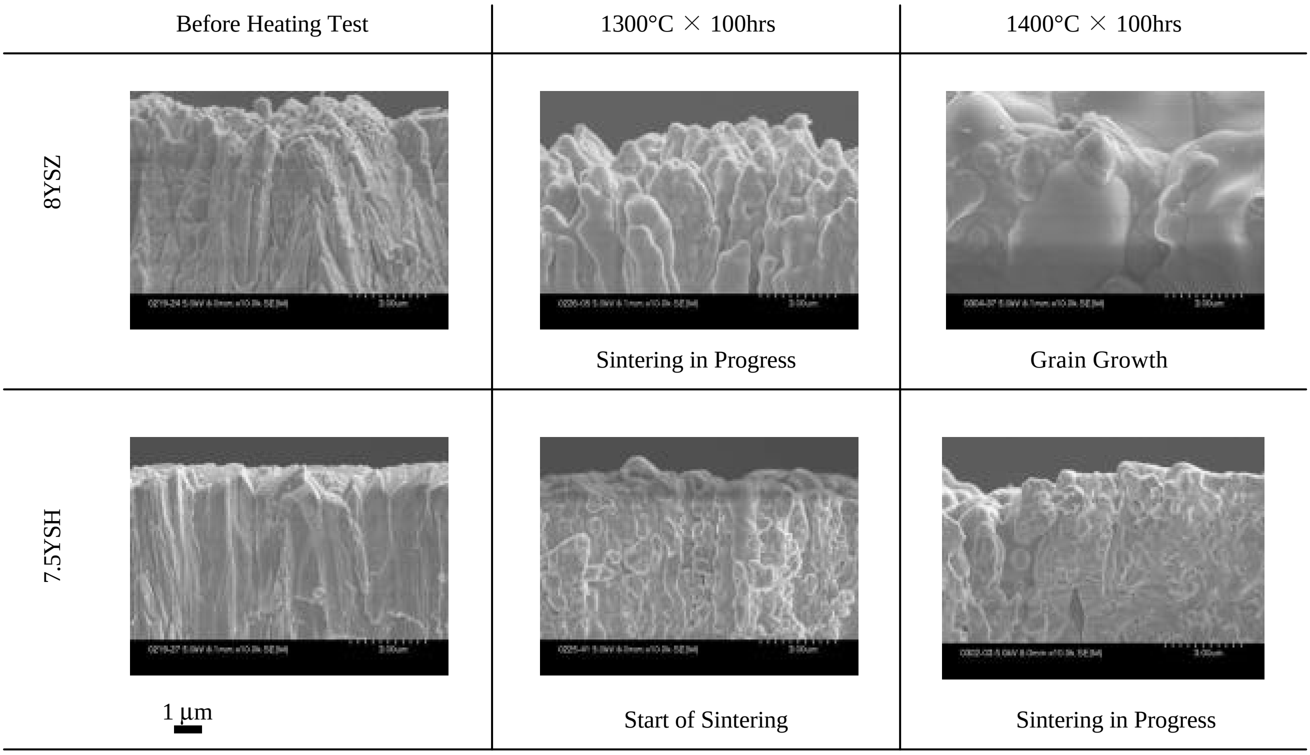

Fig.7 The cross sectional observation of 8YSZ and 7.5YSH coating before and after heating tests.

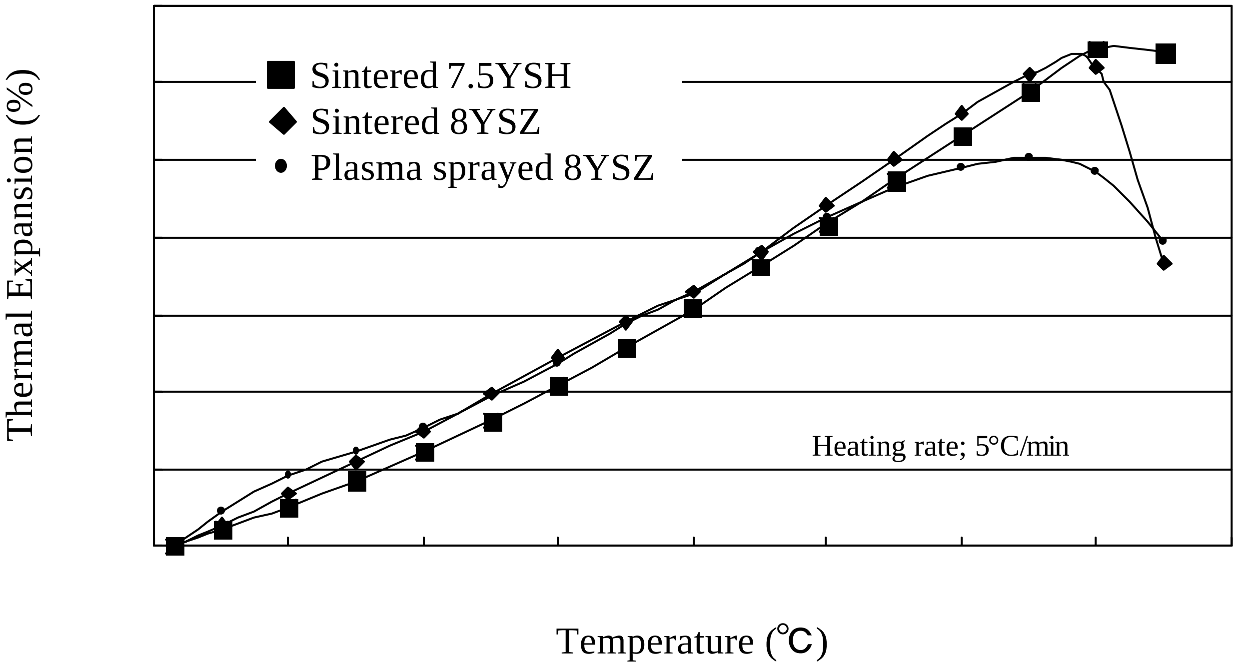

Fig.8 The thermal expansion of sintered 7.5YSH increases linearly up to 1400°C and sintering shrinkage starts at 1500°C, the sintering shrinkage of sintered 8YSZ starts at 1400°C and that of plasma sprayed 8YSZ starts at 1200°C.

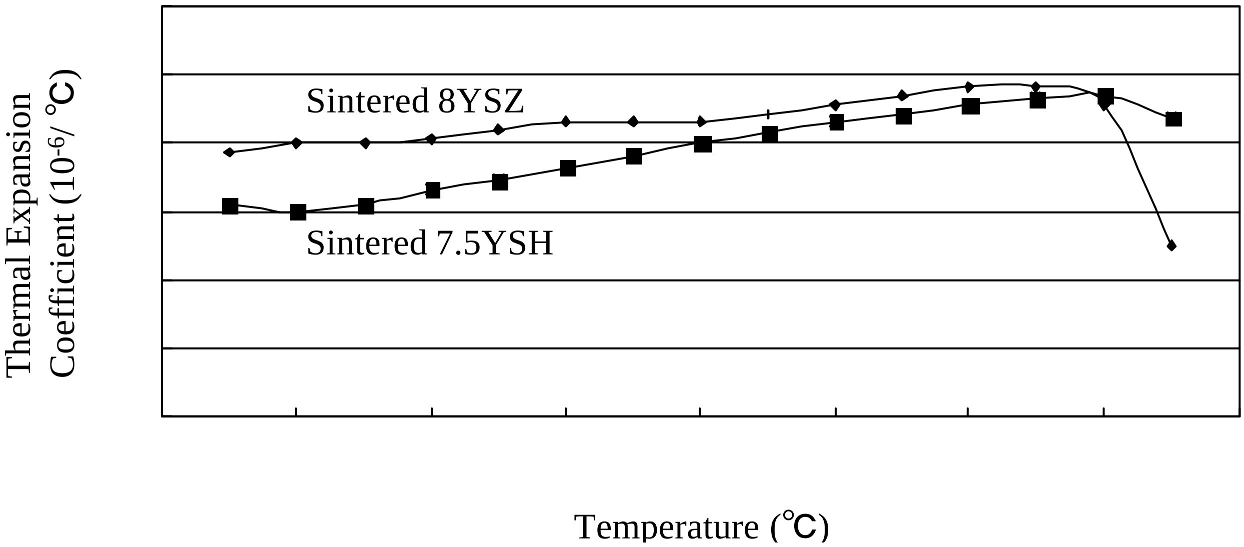

Fig.9 The thermal expansion coefficient of sintered 7.5YSH is slightly lower than that of sintered 8YSZ between 100°C and 1400°C .

Ohnysty and Rose (1964) showed that the average linear thermal expansion coefficient of 10mass%Y_2O_3-HfO_2 ceramics was 6.33× 10^{-6}/°C and that of 15mass%Y_2O_3-HfO_2 ceramics was 6.27× 10^{-6}/°C at temperature range of 25°C ~ 2500°C .

Wang and Stevens (1992) reviewed about the thermal expansion coefficient of HfO_2 and ZrO_2, and explained that the average thermal expansion coefficient of HfO_2 ceramics was slightly lower than that of ZrO_2. In this experiment, the thermal expansion coefficient of sintered 7.5YSH is also slightly lower than that of sintered 8YSZ between 100°C and 1400°C. This property was undesirable from the thermal expansion coefficient difference between the metal substrate and top coat. However, it was considered that the thermal stress was relaxed by segmented columnar structure.

CONCLUSIONS

We newly developed the hafnia-based TBC. The 7.5YSH (7.5mass%Y_2O_3-HfO_2) 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 thickness could be obtained for 1.5 to 2 hours.

Thermal conductivity of 7.5YSH coating was lower than that of 8YSZ(8mass%Y_2O_3-ZrO_2) coating at temperature range of 1000°C ~ 1300°C and became lower with rising the test temperature.

From the result of sintering behavior obtained by heating tests at 1300°C and 1400°C, it was considered that the thermal durability for sintering behavior of 7.5YSH coating was improved up to about 100°C in comparison with that of 8YSZ coating.

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