EB-PVD process and thermal properties of hafnia-based thermal barrier coating

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Received 8 November 2002; revised 18 December 2002; accepted 20 January 2003

Abstract

Thermal barrier coatings (TBCs) are being developed for the key technology of gas turbine and diesel engine applications. In general, 8 mass% Y₂O₃–ZrO₂ (8YSZ) coating materials are used as the top coating of TBCs. The development of hafnia-based TBC was started in order to realize the high reliability and durability in comparison with 8YSZ, and the 7.5 mass% Y₂O₃–HfO₂ (7.5YSH) was selected for coating material. By the investigation of electron-beam physical vapor deposition (EB-PVD) process using 7.5YSH ceramic ingot, 7.5YSH top coating with about 200 μm thickness could be formed. The microstructure of the 7.5YSH coated at coating temperature of 850°C showed columnars of laminated thin crystals. On the other hand, the structure of the 7.5YSH coated at coating temperature of 950°C showed solid columnars. From the result of sintering behavior obtained by heating test of 7.5YSH coating, it was recognized that the thermal durability of 7.5YSH coating was improved up to about 100°C in comparison with 8YSZ coating. This tendency was confirmed by the experimental result of the thermal expansion characteristics of sintered 7.5YSH and 8YSZ.

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Keywords: Hafnia; Zirconia; Thermal barrier coating; Electron-beam physical vapor deposition; Sintering; Columnar structure

1. Introduction

The world-wide energy saving and reduction of global warming effect gas (CO₂) are required very strongly. In order to comply with the requirements, the effort to develop the high efficiency gas turbine has been made 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, TBC is a two layer’s system which incorporates about 250 μm thickness layer of ceramic top coating applied to the outer surface of the substrate and about 150 μm 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. In general, 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 sputtering, plasma spraying, chemical vapor deposition and electron beam-physical vapor deposition (EB-PVD). The plasma spraying is well-known process and used widely. The coating structure made by plasma spraying is the porous lamination of spraying powders. The EB-PVD process is an advanced method of ceramic deposition [1]. 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 columnars, which are essentially separated from adjacent columnars, but are tightly bonded to the bond coating surface. This structure compensates the difference of thermal expansion between ceramic and substrate. In general, the 7–8 mass% yttria partially stabilized zirconia (YSZ) top coating materials are used and show totally excellent properties. However, TBC has a tendency to spall under thermal cycling, corrosion and erosion from ambient conditions corresponding to the extremely high operating conditions in...
the hot section of a gas turbine [2]. 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 investigated hafnia (HfO2) as a coating material, which has high melting point of 2900 °C and low thermal conductivity of 1.5 W/mK shown in Fig. 1. Hafnia has a very similar crystalline structure and phase transformation behavior as zirconia (ZrO2). Hafnia and hafnia-based ceramics were totally reviewed in comparison with zirconia by Wang [3] and the phase diagram for hafnia (HfO2)–yttria (Y2O3) system was studied by Stubican [4]. The mechanical properties of hafnia-based ceramics were investigated by many researchers. Namely, Young’s modulus of 8 mass% yttria partially stabilized hafnia were reported by Scheide [5].

In this work, we newly developed the hafnia-based TBC. The 7.5 mass% Y2O3–HfO2 (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 8 mass% Y2O3–ZrO2 (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 contains generally apparent porosity of 25–50% and realize the stable vaporization from molten pool of ingot without cracking by the electron beam irradiation. This property is also needed for hafnia ingot. In this work, the 7.5 mass% Y2O3–HfO2 (7.5YSH) was selected for hafnia-based coating material because of the crystal structure stabilization by adding Y2O3. In order to form 7.5YSH ingot applicable for EB-PVD, trial manufactures and investigations of ingot were repeated. The 7.5YSH ingot was sintered 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 for EB-PVD. The TBC system was two 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 composition of NiCoCrAlY spraying powder is 21.54 mass%Co, 16.91 mass%Cr, 12.4 mass%Al, 0.66 mass%Y and balance Ni.

The NiCoCrAlY bond coating was formed on the substrate by low pressure plasma spraying at spraying distance of 400 mm, powder supply of 60 g/min, plasma current of 1500 A, plasma voltage of 40 V, Ar supply of 90 l/min, He supply of 25 l/min and pressure of 4.7 kPa. After forming the NiCoCrAlY bond coating, the substrates were cut as size of 20 x 20 x 5 mm³.

The 7.5YSH top coating was formed on the bond-coated substrates by EB-PVD. The coating apparatus is shown in Fig. 2. It had inner heaters enable to control the coating temperature. The target material of top coating was 7.5YSH ingot of 35 mm in diameter and 30 mm in length. The 7.5YSH ingot was evaporated by an electron beam irradiation in vacuum and the vapor was condensed onto bond-coated substrates. We investigated the top coating conditions of EB-PVD process about electron beam current,
coating temperature, coating time and coating thickness. The coating temperature of 850 and 950 °C were tested in this experiment. In order to maintain the stoichiometric oxygen composition of HfO₂ coating during the EB-PVD process, some oxygen was bled into the chamber.

After forming the 7.5YSZ top coating, the microstructures of 7.5YSH coating surface were observed by FE-SEM.

### 2.3. Sintering behavior for EB-PVD coating of 7.5YSH

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 mm³. 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 h in air at 1300 and 1400 °C, respectively. After heating tests, coating surface microstructure was observed using FE-SEM.

For the thermal expansion measurement, sintered 7.5YSH and sintered 8YSZ samples were prepared. The sample size was $5 \times 5 \times 20$ mm$^3$. The thermal expansion were measured by using differential expansion method at a heating rate of 5 °C/min from 100 to 1500 °C and 60 min holding at 1500 °C, and then at a cooling rate of 5 °C/min from 1500 to 100 °C.

3. Experimental results

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 cleared. The electron beam current ingot was from 400 to 900 mA 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 200 μm could be formed during 1.5–2 h. Fig. 3 shows the vertical sectional microstructure of 7.5YSH. It was observed that the columnar with a diameter of about 4 μm grown perpendicular to the substrate.

The coating temperature was the most important parameter for the coating microstructure. The EB-PVD coating had the columnar microstructure, however, the morphology change largely by the difference of coating temperature. Figs. 4 and 5 show surface observation results of 7.5YSH coating formed at coating temperature of 850 and 950 °C. It was clearly recognized that the morphologies of the columnar were different.

The structure of the sample coated at 850 °C was columnar of laminated thin triangle crystals. On the other hand, the structure of the sample coated at 950 °C was solid columnar structure.

In order to compare with 8YSZ, the surface microstructures of 8YSZ samples coated at 640 and 850 °C are shown in Fig. 6. This figure is quoted from the previous work [6]. The microstructure of 8YSZ coated at 640 °C was also columnar of laminated thin triangle crystals and that coated at 850 °C was large columnar structure with a diameter of about 3 μm. The crystal orientation of the 8YSZ layer at 640 °C was $<111>$ and that of the 8YSZ layer at 850 °C was $<200>$ and $<002>$. The crystal orientation difference by the coating temperature was thought to be related to the difference of crystalline growth energy.

As the 7.5YSH microstructure showed the similar tendency compared with 8YSZ, the mechanism of crystal growth was considered as same as 8YSZ. However, the coating temperature with large columnar for the 7.5YSH was about 100 °C higher than that of 8YSZ.
4. Discussion of sintering behavior

Fig. 7 shows surface observation of 8YSZ and 7.5YSH coatings before and after heating tests. Before heating test, the columnar edge showed sharp morphology for both samples. The columnars of 8YSZ coating became round and joined between neighboring columnars after 1300 °C heating test, that is, the sintering of 8YSZ coating was progressed at 1300 °C. After heating test at 1400 °C, recrystallization of 8YSZ coating was occurred. On the other hand, the columnar edge of 7.5YSH coating became slightly round, that is, the sintering of 7.5YSH coating was started at 1300 °C. After heating test at 1400 °C, the columnars of 7.5YSH coating joined between neighboring columnars and the sintering of 7.5YSH coating was progressed.

This tendency was corresponded with the result of the thermal expansion measurement. Fig. 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 thermal durability of 7.5YSH coating is improved up to about 100 °C in comparison with 8YSZ coating.

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

Fig. 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⁻¹ and that of 8YSZ was 7.7–9.6 × 10⁻⁶ °C⁻¹ at the temperature range from 100 to 1400 °C. Ohnysty and Rose showed that the average linear thermal expansion coefficient of 10 mass% Y₂O₃–HfO₂ ceramics was 6.33 × 10⁻⁶ °C⁻¹ and that of 15 mass% Y₂O₃–HfO₂ ceramics was 6.27 × 10⁻⁶ °C⁻¹ at temperature range of 25–2500 °C [7].

Wang reviewed about thermal expansion coefficient of HfO₂ and ZrO₂, and explained that the average thermal expansion coefficient of HfO₂ ceramics was slightly lower than that of ZrO₂ [3]. In this experiment, the thermal expansion coefficient of sintered 7.5YSH is also slightly lower than that of sintered 8YSZ between 100 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.

5. Conclusions

We newly developed the hafnia-based TBC. 7.5 mass% Y₂O₃–HfO₂ (7.5YSH) was selected for coating material, and the 7.5YSH ingot applicable for EB-PVD was developed. This ingot had the low density about 50% and was not cracked by electron beam irradiation. According to the investigation of the EB-PVD process using developed 7.5YSH ingot, it was cleared that the appropriate electron beam current was from 400 to 900 mA for melting and vaporizing the ingot. The 7.5YSH coating with about 200 μm thickness could be obtained for 1.5–2 h. The microstructure of the 7.5YSH coated at coating temperature of 850 °C was columns of laminated thin triangle crystals. The microstructure of the 7.5YSH coated at coating temperature of 950 °C was solid columns. These similar coating microstructures observed for 8YSZ, but the coating temperature for forming the microstructure of solid columns of 7.5YSH was about 100 °C higher than that of 8YSZ. From the result of sintering behavior obtained by heating tests at 1300 and 1400 °C, it was considered that the thermal durability for the 7.5YSH coating was improved up to about 100 °C in comparison with the 8YSZ coating.

Acknowledgements

This work was performed as a part of the Nanostructure Coating Project carried out by the New Energy and Industrial Technology Development Organization.

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