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Development and Evaluation of Thermal Barrier Coatings for the 1700℃-class Closed-cycle Gas Turbine Corresponding to CO_2 Collection

Mitsutoshi OKADA[1], Masato NAKAYAMA[1]
Taiji TORIGOE[2], Tsuneji KAMEDA[3], Hideyuki ARIKAWA[4], Tohru HISAMATSU[1]
[1] Yokosuka Research Laboratory
Central Research Institute of Electric Power Industry
2-6-1 Nagasaka, Yokosuka-city, Kanagawa 240-0196, JAPAN
Phone: +81-46-856-2121, FAX: +81-46-856-5571
[2] Mitsubishi Heavy Industries, Ltd.
[3] Toshiba Corporation
[4] Hitachi Ltd.

ABSTRACT

In Japan, in order to develop the power generation system which could collect all the emitted carbon dioxide (CO_2) and achieve higher than 60% of efficiency (HHV) by means of 1700℃-class gas turbine utilizing the combustion of methane (LNG) and oxygen, a national project was carried out from 1999 to 2001. In this project, in order to increase the durability of thermal barrier coating (TBC) used for the blade of the gas turbine, the material and microstructure of top coat were mainly examined, and the basic technology for TBC was developed. As future problems, since the sintering of top coat causes the increase of the temperature at substrate surface and the decrease of the resistance to thermal cycles, it is clarified that the improvement of the resistance of top coat to sintering is important.

INTRODUCTION

In Japan, electric industry occupies about 1/4 of whole amount of carbon dioxide emission, and in term of reduction of CO_2 emission, higher efficiency of thermal power is expected. At present, in combined cycle power generation with gas turbine and steam turbine, 1500°C-class gas turbine has been installed, and higher than 50% of thermal efficiency has been realized in the plant (Tsukuda, 2000). Moreover, "the development of technology for 1700°C-class closed-cycle gas turbine corresponding to CO_2 collection", which aimed at increasing firing temperature and higher efficiency in order to decrease drastically the CO_2 emission, was conducted by New Energy and Industrial Technology Development Organization (NEDO).

The objective of this project was to develop the technology for the power generation system which could collect all the emitted carbon dioxide and achieve higher than 60% of efficiency (HHV) by means of a closed-cycle with 1700°C-class gas turbine utilizing the combustion of methane (LNG) and oxygen. The results of research and development of hydrogen combustion turbine in "World Energy Network (WE-NET) Phase 1 (1993 ~ 1998)" project was also applied to the project above (Hisamatsu, 1999). The first phase of this research project started as 5-year program from 1999, but it was finished in 2001 because of administrative decision. As a part of this program, the development was carried out for the basic technology of high-temperature materials which were necessary to realize turbine blade for the gas turbine.

In this paper, the development of thermal barrier coatings (TBCs) for turbine blade conducted in the program is described.

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1700°C-CLASS CLOSED-CYCLE GAS TURBINE CORRESPONDING TO CO_2 COLLECTION

System

Figure 1 shows the schematic representation of a closed-cycle with 1700°C-class gas turbine system utilizing the combustion of methane (LNG) and oxygen corresponding to CO_2 collection (Koda, 2002). This system is based on the topping regenerative cycle developed for hydrogen–combustion turbine system (Koda, 1999). Since methane is used for fuel, working fluid includes CO_2 as well as steam, and CO_2 is extracted as non-condensed gas from condenser, and collected. In the topping cycle, methane and oxygen are supplied to combustor in gaseous state, and combusted. After combustion gas (1700°C, 4.5MPa) turns high-temperature turbine, it is cooled in regenerative heat changer and returned to combustors through compressor. In the bottoming cycle, after a part of combustion gas extracted from the topping cycle turns low-pressure turbine, it is condensed in condenser and CO_2 is removed and collected. While a part of condensed water is discharged out of the system, the other part is evaporated and heated in regenerative heat changer after it is compressed by pump, and goes to combustor through high-pressure turbine.

Environment for thermal barrier coating

Table 1 indicates the environment of TBC in closed-cycle gas turbine corresponding to CO_2 collection. In this developed gas turbine, the gas temperature and pressure are higher than in conventional gas turbines for power generation. Moreover, the main component of combustion gas is steam, and it is also used as coolant for blades. These factors lead to higher coefficients of heat transfer on the exterior and interior surfaces of blade and to extremely high heat

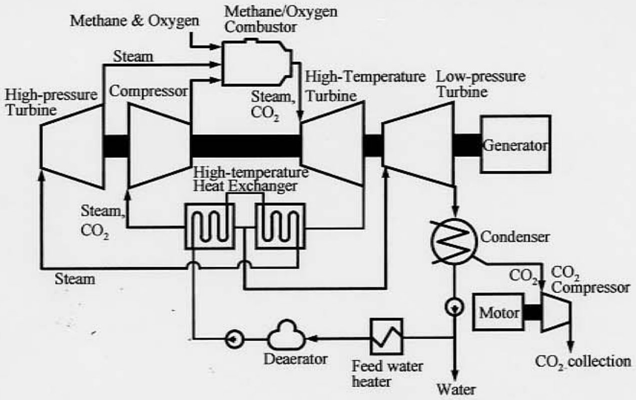


Fig. 1 Schematic representation of the 1700°C-class closed-cycle gas turbine system corresponding to CO_2 collection

Table 1 Environment of Thermal barrier coating

Factors		Condition
Combustion Gas (At the entrance to vanes)	Temperature	1,700 ℃
	Pressure	4.5 MPa
	Gas Composition	H_2O: 87 vol% CO_2: 11.5 vol% O_2: 1.5 vol%
Maximum heat flux		3~4 MW/m^2 (At leading edge or near leading edge in suction side)
Maximum temperature of TBC surface		1,300 ℃ (Development objective)
Maximum temperature difference in TBC		350 ℃ (Development objective)

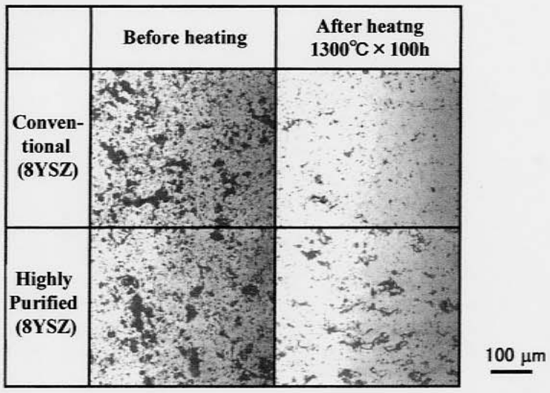


Fig. 2 Microstructural change of higly purified and conventional YSZ after furnace test

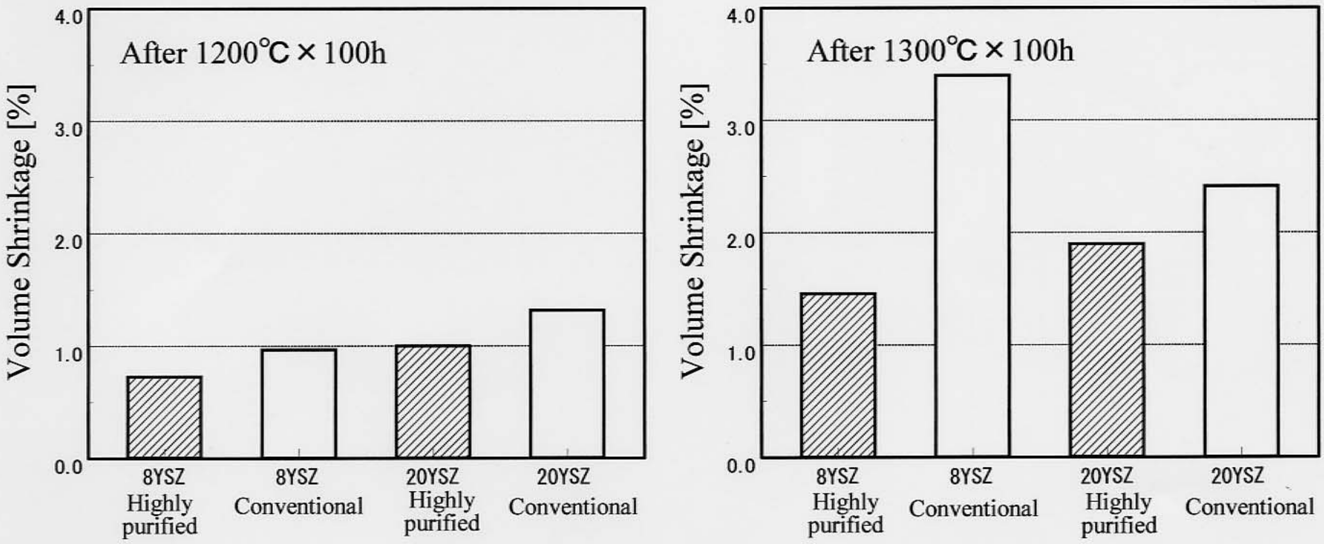


Fig. 3 Volume shrinkage of highly purified YSZ and conventional YSZ after furnace test

flux flowing through blade surface. As a result, the temperature difference between the outside and inside of TBC is increased and the surface temperature of TBC is also raised. In the developed gas turbine, the high performance of TBC is required since the temperature at top coat surface and the temperature difference between its outside and inside would reach higher than 1300°C and 350°C, respectively.

In conventional TBC, 8% yttria stabilized zirconia (YSZ) is applied as top coat by atmospheric plasma spray (APS), it is said that its tolerant temperature is about 1100°C, and that its temperature difference between the outside and inside of top coat is about 200°C. Particularly the top coat applied by APS sinters at the temperature higher than 1000°C (Itoh, 1998), and it is considered that the sintering proceeds rapidly at 1300℃(the development objective). Therefore, following degradation and damage in TBC are estimated after long-term service in the severe environment; ①densification of top coat and decrease of heat resistance coefficient, ② damage and delamination of top coat due to caused stress, ③ microstructural degradation and recession of top coat due to combustion gas flow (particularly due to steam) and ④delamination of top coat due to oxidation of bond coat caused by ① and ③.

In order to improve the durability of TBC, the material and microstructure of top coat were mainly examined, and the basic technology for TBC was developed.

DEVELOPMENT OF THERMAL BARRIER COATING

Examination on higher purification of ZrO_2 top coat

In order to examine the effect of high purification of YSZ on the sintering, the powder of highly purified YSZ was prepared for spraying, and the resistance to sintering was examined by means of the coated specimens applied by APS. As for two kinds of materials such as 8YSZ and 20YSZ, in which 8wt% and 20wt% of yttria stabilizer were added, respectively, conventional powder and highly purified one were prepared, and coated specimens were produced by means of APS. While the contents of impurities (the sum of SiO_2, Al_2O_3, TiO_2, CaO and Fe_2O_3) in conventional coatings were about 0.53% for 8YSZ and about 0.41% for 20YSZ, those in highly purified powder were about 0.023% for 8YSZ and about 0.012% for 20YSZ. In other words, the content of impurities was reduced to less than 1/10 in the highly purified powders.

Figure 2 shows the microstructural change of TBC after furnace test in air (1300°C, 100hours). While micro pores and undeposited gaps like micro cracks, which were typical microstructure in top coat, were observed both in conventional and highly purified coatings before furnace test, they were reduced during the test due to sintering. The decrease of them in highly purified coating was smaller than that in conventional one, and it implies that high purification of top coat improves the resistance to sintering.

Figure 3 shows the volume shrinkage of highly purified and conventional YSZ measured after furnace test at 1200°C and 1300°C for 100hours. The volume shrinkage was caluculated by measuring

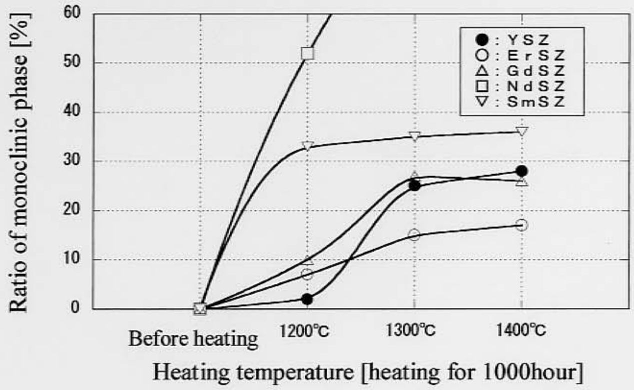


Fig. 4 Ratio of monoclinic phase in top coats after furnace test

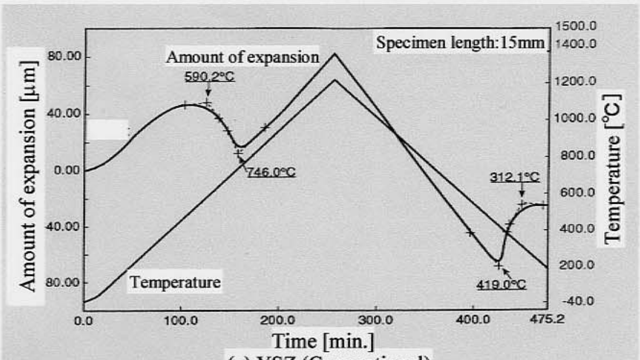
the length, width and thickness of specimen with micrometer. In each test condition, volume shrinkage due to sintering was found, and it was more significant at higher temperature. The volume shrinkage in highly purified coating was smaller than in conventional one, and it is clarified that high purification improves the resistance to sintering. Focused on the volume shrinkage measured after furnace test at 1300°C for 100hours, while 20YSZ was smaller than 8YSZ in conventional coating, and the former was larger than the latter in highly purified coating. In highly purified coating, the improvement of the resistance to sintering was not observed due to the increase of stabilizer addition.

According to the above results, it is clarified that the high purification of sprayed powder can improve the resistance to sintering of top coat produced by APS. However, even in highly purified 8YSZ, sintering and volume shrinkage proceeded at 1300°C , which was surface temperature of the development objective, and about 1.5% of volume shrinkage was observed only for 100hours. Therefore, taking the longer durability at high temperature into consideration, new top coat materials with excellence in thermal resistance and durability are required.

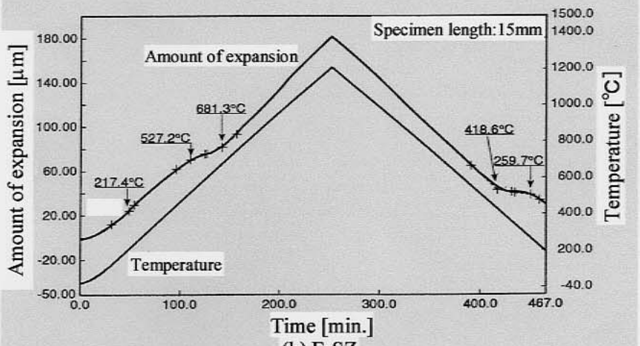
Examination on stabilizer material of ZrO_2 top coat

In order to develop new top coat materials with better stability at high temperature than conventional YSZ, stabilizers of ZrO_2 were examined. As candidates of stabilizers, oxides of rare earth elements, which had been hardly reported, were focused. By means of Nd_2O_3, Sm_2O_3, Gd_2O_3 and Er_2O_3, the sprayed powders of ZrO_2-Nd_2O_3(NdSZ), ZrO_2-Sm_2O_3(SmSZ), ZrO_2-Gd_2O_3(GdSZ), and ZrO_2-Er_2O_3(ErSZ) were prepared. In terms of the stability of crystal structure, the addition of stabilizer was set as about 18wt% (about 6mol%), and it was larger than 8wt% (about 4.5mol%) of conventional 8YSZ. Considering the resistance to sintering and to thermal cycles, high purification of top coat was performed and the amount of impurities such as SiO_2 was less than 0.01wt%.

In order to examine the high-temperature stability of these ZrO_2, high-temperature furnace tests were carried out by means of coated specimens. After the test, microstructure of cross section was observed, and crystal structure was analyzed and the physical properties were measured. Figure 4 indicates the ratio of monoclinic phase in the top coats after furnace test according to X-ray diffraction. While monoclinic phase was not found in any kind of specimen before the test, the crystal structure changed during long-term heating, and monoclinic phase was formed. However, the ratio of monoclinic phase was smaller in ErSZ than in YSZ, and it was excellent in the stability of crystal structure. Figure 5 shows the thermal expansion curve of YSZ and ErSZ specimens after long-term furnace test (1300°C×1000hours). After the heating, crystal structure changed (monoclinic phase was formed), and large winding was found during heating and cooling processes in thermal expansion curve of YSZ.



(a) YSZ (Conventional)



(b) ErSZ

Fig. 5 Thermal expansion curve of top coat after furnace test (1300℃ × 1000h)

Also in the thermal expansion curve of ErSZ, winding was found, but it was small compared with YSZ because the ratio of monoclinic phase was lower than in YSZ. These results clarify that highly purified ErSZ has higher stability of crystal structure at high temperature than conventional YSZ.

In order to examine the influence of stabilizer on the resistance to thermal cycles, TBC specimens were prepared by means of various kinds of ZrO_2, and thermal cycle tests were performed using laser heating. In TBC specimen, after about 100μm thick of bond coat (NiCoCrAlY) was applied on IN738LC substrate by low-pressure plasma spray (LPPS), about 500μm thick of top coat was deposited by APS. In the test apparatus for thermal cycle test using laser heating, the surface of TBC specimen was heated by means of CO_2 gas laser and its back was cooled by compressed air. Thus, during the thermal cycle test, the temperature gradient was given in the direction of TBC thickness. In order to accelerate the TBC fracture, severe test condition was set as 1420°C at TBC surface and 900°C at the boundary between top coat and bond coat. Figure 6 shows the number of cycles to delamination of TBC. In this test condition, the number of cycles to delamination of GdSZ and ErSZ was larger than that of YSZ, and particularly ErSZ was extremely superior. And the thermal cycle test was carried out under the test condition of 1300°C at TBC surface and 950°C at substrate surface, which simulated the temperature condition in the gas turbine corresponding to CO_2 collection. As a result, while top coat was delaminated at about 100 cycles in YSZ, the delamination was not observed in ErSZ even at about 1600cycles, and it is ensured that ErSZ improves the resistance to thermal cycle.

Examination on development of new material for top coat

In terms of thermal conductivity, thermal expansion and stability of crystal structure, $La_2Zr_2O_7$ and CeO_2 were selected as candidates of top coat materials other than ZrO_2, thermal properties and stability at high temperature were examined by means of the specimens coated by APS.

As a result of furnace test in air by means of the coated specimens (1300°C and 1400°C×100, 500hours), the phase transforma-

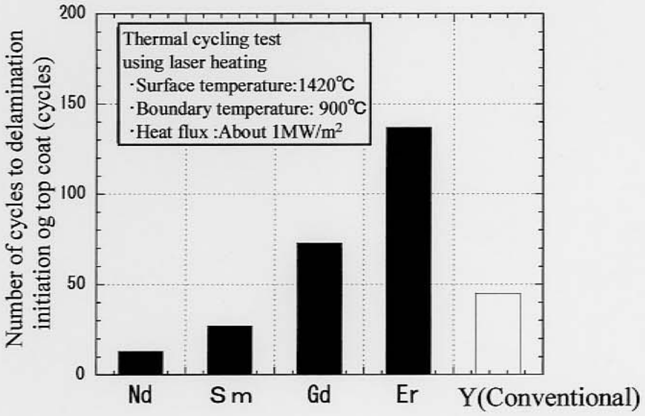


Fig. 6 Relation ship between stabilizing materials and number of cycles to top coat delamination in thermal cycle test

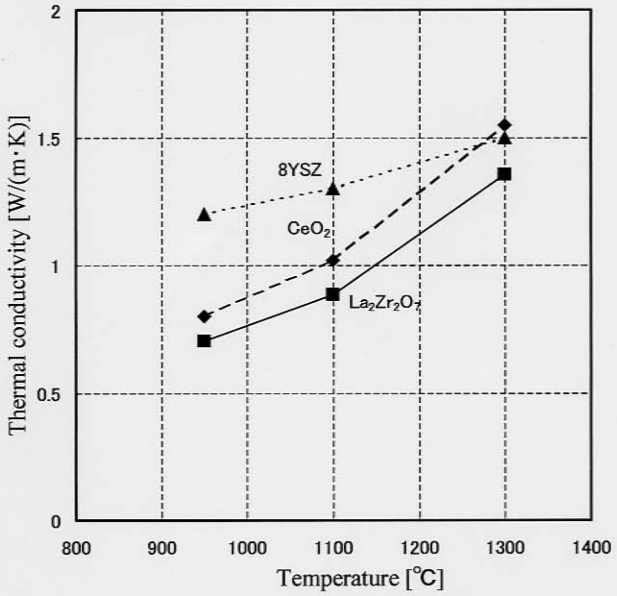


Fig. 7 Relationship between thermal conductivity of top coats and temperature

tion did not occur in $La_2Zr_2O_7$ and CeO_2 specimens, and it is ensured that they are superior in the stability of crystal structure. Figure 7 indicates the relationship between the thermal conductivity and the temperature of $La_2Zr_2O_7$ and CeO_2. The thermal conductivities of both materials were lower than that of 8YSZ at 950°C ~ 1100°C, but they were increased as the increasing temperature, and they showed almost equal values as 8YSZ at 1300°C. As for the coefficient of thermal expansion, $La_2Zr_2O_7$ and CeO_2 showed almost equal values as 8YSZ, but $La_2Zr_2O_7$had larger one than CeO_2 and 8YSZ.

Figure 8 shows the volume shrinkage of top coat after furnace test. The volume shrinkage was caluculated by measuring the length, width and thickness of specimen with micrometer. In all the specimens, the volume shrinkage had the tendency to increase according to the increasing temperature and time. While the volume shrinkage of $La_2Zr_2O_7$ was 1/2 ~ 2/3 of 8YSZ, that of CeO_2 was 2 ~ 3 times larger than 8YSZ. It is clarified that CeO_2 is inferior in the resistance to sintering.

Focused on $La_2Zr_2O_7$, which was superior to 8YSZ and CeO_2 in terms of thermal conductivity, thermal expansion and the resistance to sintering, thermal cycle test was performed by means of the test apparatus using burner heating. In the specimen for burner heating test, about 100 ~ 150μm thick of bond coat (NiCoCrAlY) was applied on Ni-base single-crystal superalloy by LPPS, about 300μm thick of top coat ($La_2Zr_2O_7$) was deposited by APS. The test condition of thermal cycle test was set as 1300°C at surface temperature and heating time and cooling time were 3 minutes, respectively. Table 2 indicates the result of thermal cycle test. While 8YSZ of top coat was not delaminated at 20cycles, $La_2Zr_2O_7$ top coat was delaminated at 7cycles. According to the observation of the cross sections of the specimens after the tests, $La_2Zr_2O_7$ top coat had tendency to be denser than 8YSZ. It implies the possibility that the effect of stress relaxation is low and that the resistance to thermal cycle is decreased in $La_2Zr_2O_7$. Also, it is said that the increase in thermal conductivity and the decrease in Poisson's ratio, Young's modulus, thermal expansion and density improve thermal shock resistance (The Ceramic society of Japan, 1979). Since $La_2Zr_2O_7$ was lower in thermal conductivity and larger in thermal expansion and Young's modulus compared with 8YSZ, it was inferior in terms of thermal shock resistance and thermal cycles.

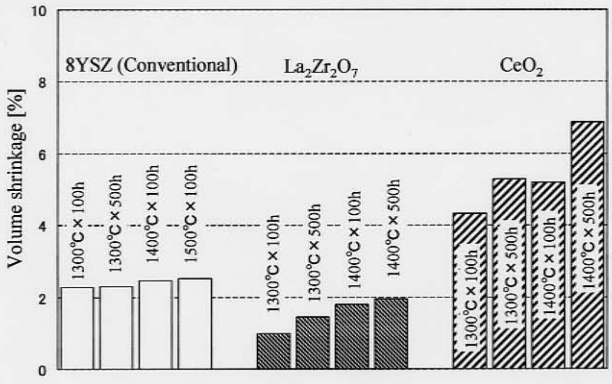


Fig. 8 Volume shrinkage of top coats after furnace test

Table 2 Results of burner rig test

	$La_2Zr_2O_7$	8YSZ (Conventional)
Number of cycles to delamination	7	>20

Examination on microstructure of coating

The TBC applying columnar ceramics as top coat by means of electric beam-physical vapor deposition (Columnar TBC) is superior to conventional sprayed TBC in terms of the resistance to thermal cycle. On the other hand, since it is inferior in environmental barrier, the oxide grows more at the boundary between top coat and bond coat. Focused on Sc_2O_3 stabilized zirconia (ZrO_2-7.5wt%Sc_2O_3: ScSZ) and Ce_2O_3 stabilized zirconia (ZrO_2-18wt%CeO_2 : CeSZ), which are excellent in corrosion resistance, the effect of columnar structure on the resistance to thermal cycles was examined. Moreover, the effect of environmental barrier layer installed between top coat and bond coat (shown in Figure 9) on the restraint of oxidation at the boundary was examined

Figure 10 shows the result of thermal cycle test of columnar TBC by means of Ar+H_2 plasma heating using plasma gun for spraying. In TBC specimen, after about 100~200μm thick of bond coat (NiCoCrAlY) was applied on IN738LC substrate by LPPS, about columnar top coat was deposited by EB-PVD. The test condition was set as about 2MW/m² of heat flux calculated from the temperature difference of thermocouples, and at about 1300°C of estimated surface temperature, and heating time and cooling time are 3minutes, respectively. While the number of cycles to delamination was less than 10cycles in sprayed YSZ, the top coat delamination was not found even at 50cycles in all the columnar TBCs. It is ensured that columnar structure of top coat drastically improves the resistance to thermal cycle.

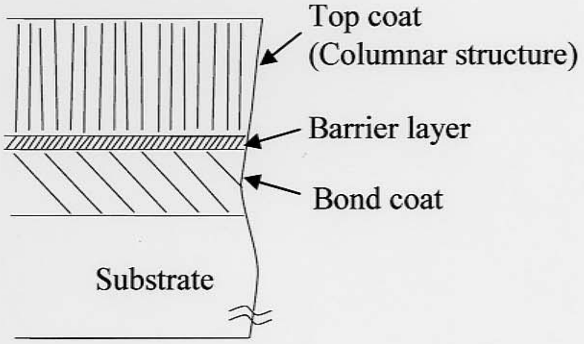


Fig. 9 Schematic representation of columnar-structure TBC

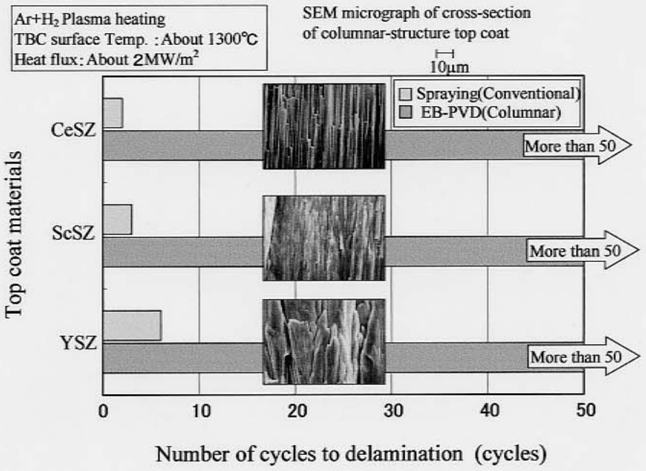


Fig. 10 Results of thermal cycling test of columnar-structure TBC

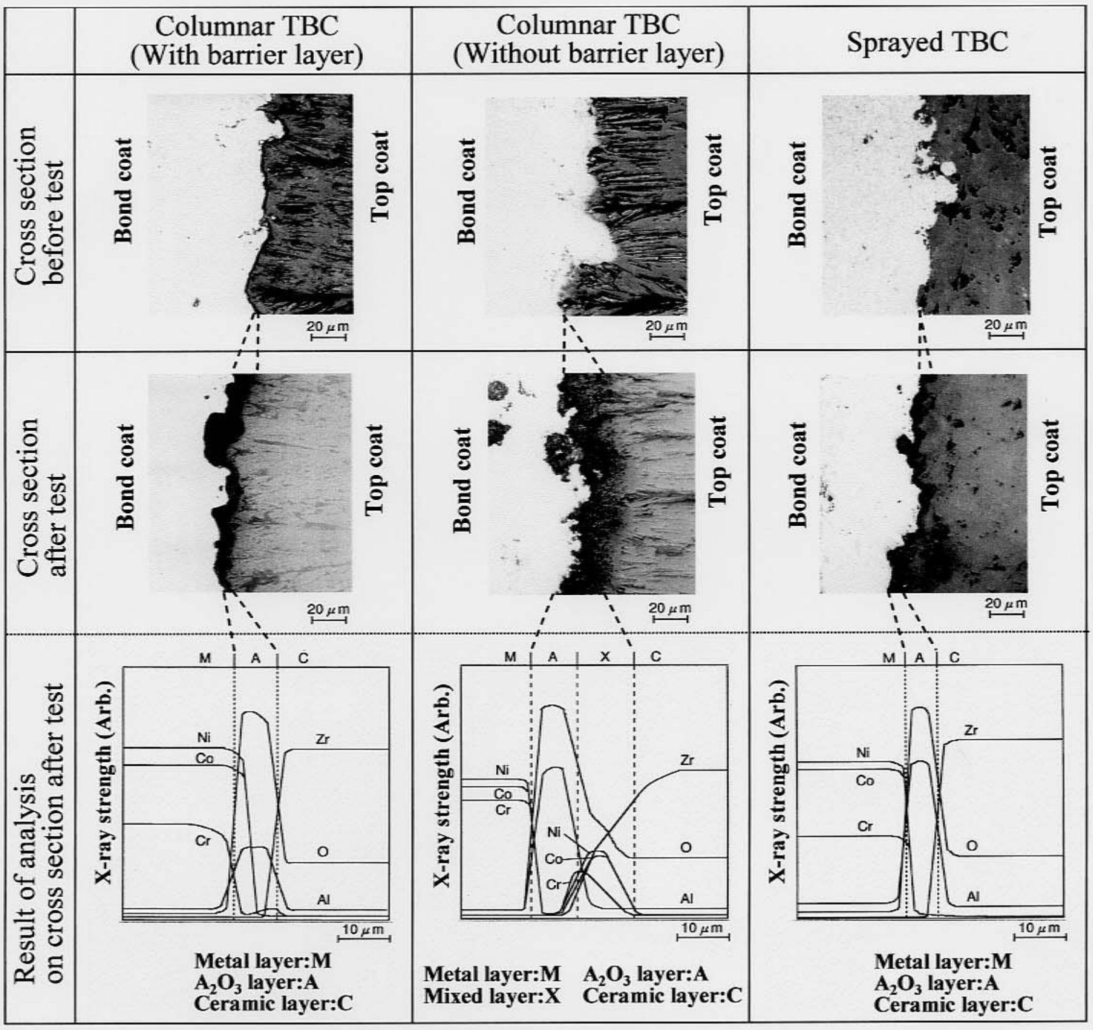


Fig. 11 Cross section of specimen and result of analysis after oxidation test in air (1000℃ × 1000h)

As for the environmental barrier layer, Al_2O_3 was selected in terms of barrier to oxygen, chemical stability and adherence. In the preparation of the columnar TBC specimens with environmental barrier layer after NiCoCrAlY bond coat (about 100μm thick) was applied on IN738LC substrate by LPPS, about 2μm thick of Al_2O_3 layer was deposited by means of EB-PVD. Moreover, as for top coat, about 100μm thick of columnar YSZ was coated by means of EV-PVD. In order to evaluate the effect of the environmental barrier layer, high-temperature oxidation test was carried out in air at 1000°C for 1000hours. For comparison, the oxidation test was performed by means of columnar TBC without environmental barrier layer and sprayed TBC.

Figure 11 indicates the morphologies of the cross sections of TBC specimens after the tests and the results of analysis. While about 10μm thick of oxide layer was formed at the boundary between top coat and bond coat in the sprayed TBC specimen,

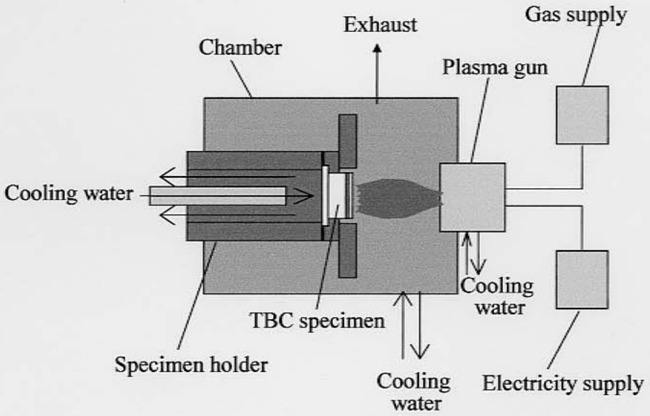


Fig. 12 Schematic representation of high heat flux test apparatus

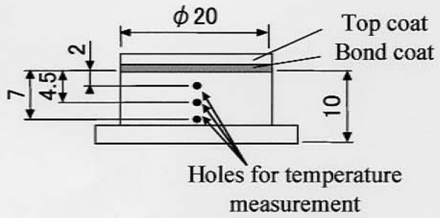


Fig. 13 Schematic representation of TBC specimen

10~20μm thick of oxide layer was formed in the columnar TBC with the environmental barrier layer, and this oxide layer was identified as Al_2O_3. Also, 20~40μm thick of oxide layer was formed at the boundary in the columnar TBC without environmental barrier. As a result of the analysis, it is clarified that this oxide layer consists of dual structure; one was Al_2O_3 in the bond coat side, and the other was the oxide of Cr, Ni and Co in the top coat side. It implies that most of aluminum in the bond coat was consumed due to oxidation and that main components of bond coat, Cr, Ni and Co, were oxidized. According to the above results, the installation of the environmental barrier layer to columnar TBC has the effect to restrain the oxidation at the boundary, but it is not sufficient. It is necessary to investigate better method to restrain the oxidation at the boundary.

EVALUATION OF DEGRADATION AND DAMAGE

Test method and TBC specimen

High heat flux heating test was carried out by means of TBC specimens according to the results above, and their resistance to thermal cycles and the influence of steam on the degradation and damage of TBC were examined.

Figure 12 indicates the schematic representation of heating test apparatus for developed TBCs. In this test apparatus, TBC specimen is heated by means of plasma flow and is cooled by water. Thus, it is possible to realize the high heat flux heating simulating the temperature difference between the surface and the back of top coat in the developed gas turbine. Although Ar gas is necessary to protect electrodes in plasma gun, arbitrary gas can be used for plasma gas except and plasma gas composition can be controlled.

Figure 13 shows the schematic representation of TBC specimen. The size of the specimen substrate was 20mm of diameter and 10mm thick. The substrate was Ni-base single-crystal superalloy TMS-75, which was candidate material for the developed turbine blade. K-type thermocouples with 0.5mm of diameter were installed into the holes on the side of the specimen, and the temperature at the substrate surface and the heat flux were calculated.

Table 3 illustrates 4 kinds of TBC specimens used for the test; YSZ, ErSZ, $La_2Zr_2O_7$, and ScSZ. ScSZ was columnar TBC applied by EB-PVD, and others were applied by APS. As for ErSZ, in order to improve the resistance to thermal cycle, the porosity was set higher (15~20%) compared with conventional top coat. The heat resistance of 3kinds of top coat except for highly purified YSZ was set as 1.1m²K/W. The number of specimen for each top coat is one, but the qualitative characteristic can be understood.

Table 3 Basic characteristics of developed TBC specimen

		Highly purified YSZ	ErSZ	$La_2Zr_2O_7$	ScSZ
Top coat	Material (Process)	ZrO_2-8%Y_2O_3 (APS)	ZrO_2-18%Er_2O_3 (APS)	$La_2Zr_2O_7$ (APS)	ZrO_2-7.5%Sc_2O_3 (EB-PVD)
	Thickness (mm)	0.25	0.16	0.135	0.25
	Heat resistance (m^2K/W)	1.6×10^{-4}	1.1×10^{-4}	1.1×10^{-4}	1.1×10^{-4}
Bond coat	Matrial	NiCoCrAlY	NiCoCrAlY	NiCoCrAlY	NiCoCrAlY
	Thickness (mm)	0.15	0.10	0.10	0.15

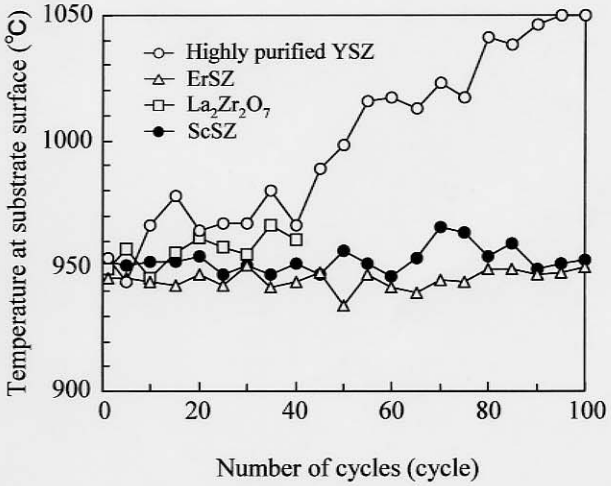


Fig. 14 Change of temperature at substrate surface of TBC specimen in thermal cycle test

The condition for thermal cycle test was set initially as about 950°C of substrate surface and about 3MW/m² of heat flux (the temperature at TBC surface was estimated as about 1300°C at this condition), and heating time and cooling time were 3minutes and 2minutes, respectively. By comparing between plasma gas with only air and with air and steam (about 30vol%), the influence of the steam on the degradation and damage of TBC was examined. As for highly purified YSZ, steam was not added to plasma gas. And, since its heat resistance was larger than other TBCs, the heat flux was set as about 2.3MW/m² and the temperatures at substrate surface and TBC surface were set initially as equal to ohter TBCs.

Results and discussion

Figure 14 shows the change of temperature at substrate surface during thermal cycle test without steam. Since it is considered that the coefficient of thermal conductivity of columnar ScSZ in the direction of top coat thickness did not change due to sintering, the temperature at substrate surface was hardly changed as the number of cycles increased. On the other hand, as for porous TBCs applied by APS, the temperature of substrate surface in highly purified YSZ and $La_2Zr_2O_7$ increased according to the number of cycles. Particularly in highly purified YSZ, the temperature at the substrate surface increased 100°C during 100cycles. As for ErSZ, the increase in the temperature at substrate surface was small in the extent of this experiment, and it is clarified that it is significantly superior in the resistance to sintering.

Figure 15 shows the results of thermal cycle test for the developed TBCs. When steam was not added to plasma gas, top coat was not delaminated even at 200cycles in highly purified YSZ and at 100cycle in ErSZ. Figure 16 and 17 show the morphologies of cross section of highly purified YSZ specimen and of ErSZ specimen in the thermal cycle test without steam addition, respectively. While longitudinal cracks on the surface and delaminating cracks at the vicinity of the boundary between top coat and bond coat were propagated at 50cycles in highly purified YSZ, those cracks were hardly propagated even at 100cycles in ErSZ. However, when steam was added to plasma gas, the sintering of ErSZ proceeded, longitudinal and delaminating cracks were propagated at earlier number of cycles, and the top coat was delaminated. Figure 18 shows the morphologies of cross section of $La_2Zr_2O_7$ specimen before and after the thermal cycle test without steam addition. In $La_2Zr_2O_7$ specimen, regardless of steam addition, longitudinal cracks on surface and delaminating cracks at the vicinity of the boundary were initiated at early number of cycles, and these cracks grew and led to top coat delamination. Since delaminating cracks propagated along undeposited gaps between sprayed layers in $La_2Zr_2O_7$, it is considered that the delamination was caused due to the low adherence between sprayed layers. Figure 19 shows the morphologies of cross section of ScSZ specimen before and after the thermal cycle test. In ScSZ specimen, regardless of steam addition, delamination cracks were not observed even at 100cycles. When steam was not added, columnar crystals had a tendency to coalesce each other due to sintering. On the other hand, when steam was added, columnar crystals had a tendency to separate each other. Also, in case of steam addition, the oxidation was promoted at the boundary between top coat and bond coat in all the kinds of TBC specimens.

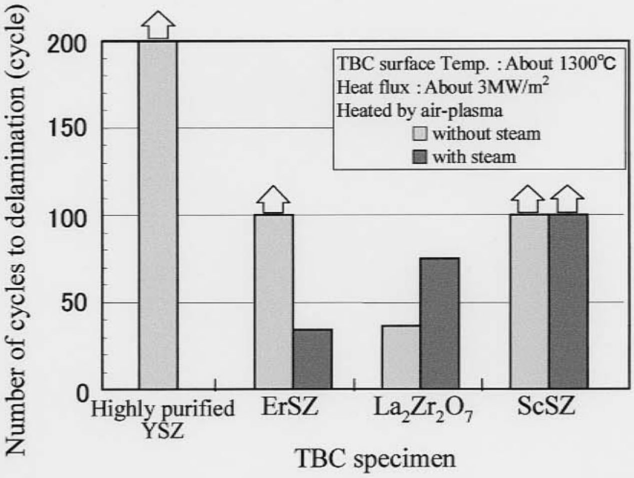


Fig. 15 Results of thermal cycle test for developed TBC

According to the above results, since the sintering of top coat caused the increase of the temperature at substrate surface and the decrease of the resistance to thermal cycle, it is important to improve the resistance of top coat to sintering. Also, it is implied that the addition of steam to plasma gas is possible to influence the top coat sintering and the oxidation at the boundary between top coat and bond coat. However, during the thermal cycle test, since steam is added into ultra high-temperature plasma, it is possible that radical is initiated in the plasma. Thus, it is necessary to examine the influence of steam on degradation and damage of TBC in more detail.

Since this program was finished in 2001, the outlook of TBC develoment could not be achieved. However, the possibility of new coating material was shown, and the basic data for TBC development in future were acquierd. It is considered that only the improvement of the conventional technology cannot solve the problems in TBC for ultra high-temperature gas turbine and that the development of innovative technology is necessary.The authors hope that the results in this program contribute to the gas turbine technology in future.

CONCLUSION

As for the development of TBC in the project of closed-cycle gas turbine corresponding to CO_2 collection, the results are described in this paper. In order to improve the durability of TBC, material and microstructure of top coat were examined, and the results are as follows.

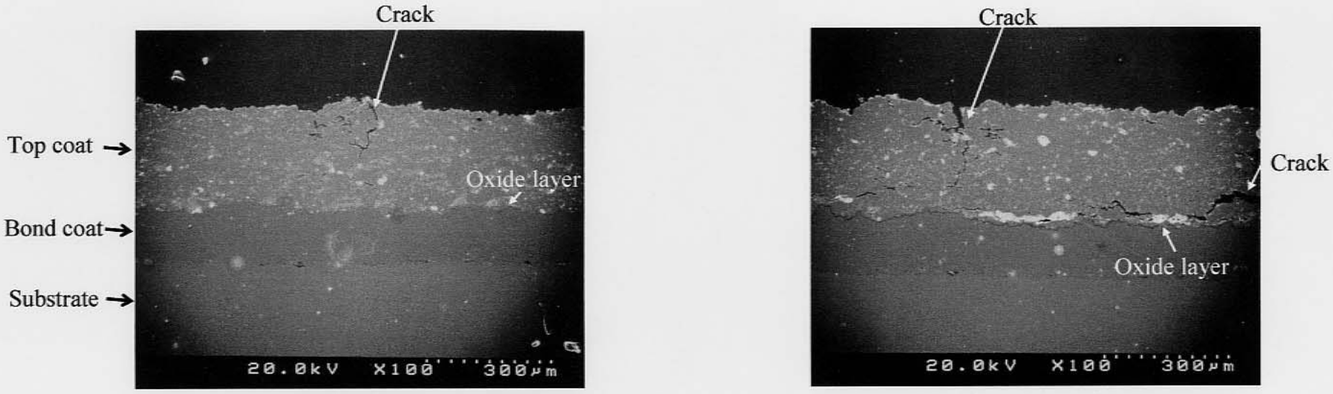
(1) High purification of sprayed powder of YSZ can improve the resistance of top coat applied by APS to sintering.

(2) Highly purified ErSZ is superior to conventional YSZ in the resistance to sintering. And the stability of crystal structure is also superior at high temperature and the resistance to thermal cycles is drastically improved.

(3) $La_2Zr_2O_7$ is superior in the resistance to sintering and in the stability of crystal structure. However, since its Young's modulus is high, the resistance to thermal cycles is inferior.

(4) Columnar structure of top coat can improve the resistance to thermal cycles. The installation of Al_2O_3 environmental barrier layer to the boundary between top coat and bond coat can restrain the oxidation at the boundary, but its resistance to oxidation is inferior to that of sprayed TBC.

(5) Since the sintering of top coat causes the increase of the temperature at substrate surface and the decrease of the resistance to thermal cycles, it is important to improve the resistance of top coat to sintering. Also, the addition of steam to plasma gas is possible to influence the top coat sintering and the oxidation at the boundary between top coat and bond coat.



(a) N=50cycles (b) N=200cycles

Fig. 16 Morphologies of cross section of highly purified 8YSZ specimen

ACKNOWLEGDEMENT

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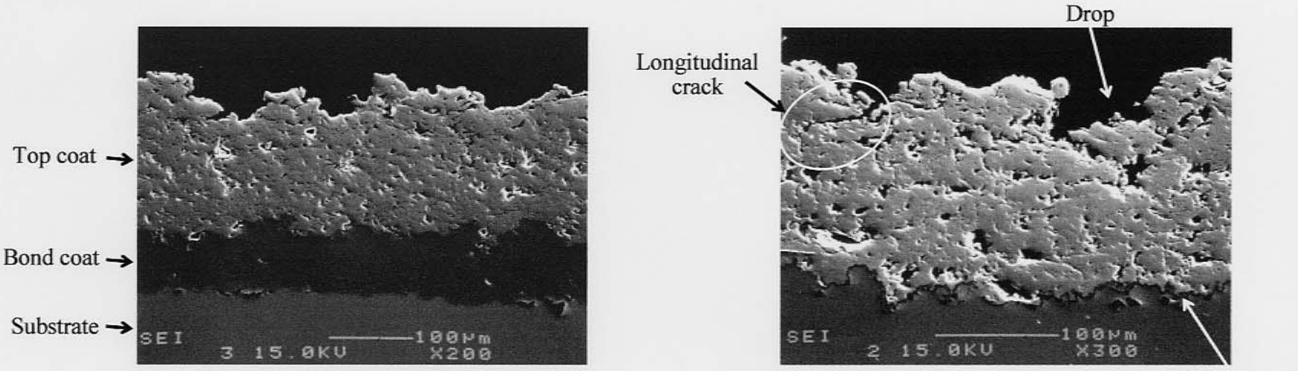
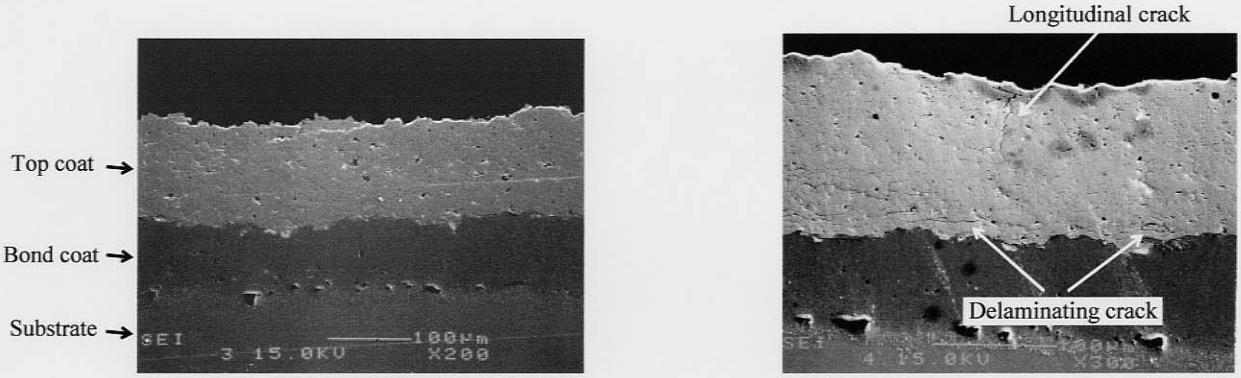


(a) Before test

(b) Without steam
(After 100cycles)

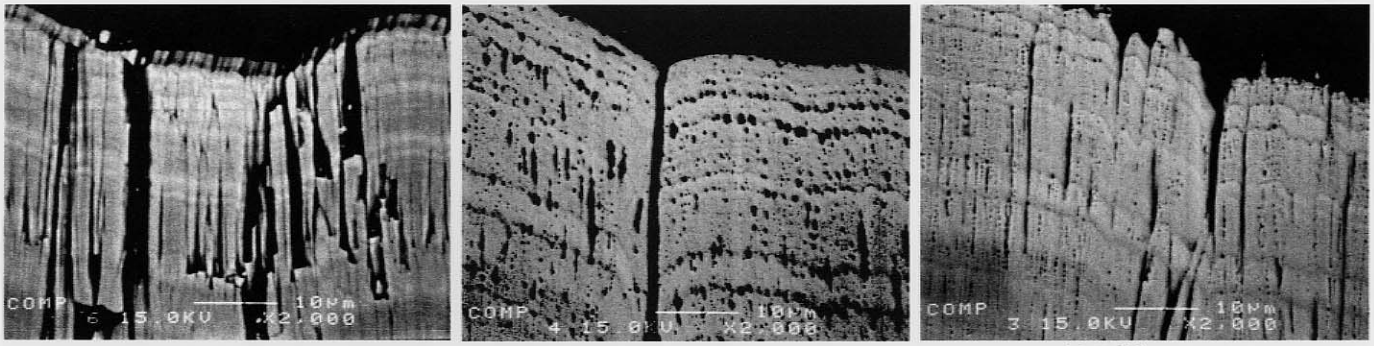
Fig. 17 Morphologies of cross section of ErSZ specimen



(a) Before test

(b) Without steam
(After 36cycles)

Fig. 18 Morphologies of cross section of $La_2Zr_2O_7$ specimen



(a) Before test

(b) Without steam
(After 100cycles)

(c) With steam
(After 100cycles)

Fig. 19 Morphologies of cross section of ScSZ specimen