RESIDUAL STRESSES OF EB-PVD THERMAL BARRIER COATINGS EXPOSED TO HIGH TEMPERATURE

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ABSTRACT

The substrate material was nickel-based superalloy (In738LC), and CoNiCrAlY was pressureless plasma-sprayed on the substrate as the bond coating. As the top coating, zirconia with 4 mol% yttria was electron beam-physical vapor deposited (EB-PVD) on the rotating substrate. The rotation speeds in the EB-PVD process were 5, 10 and 20rpm. The specimens were exposed to 1273K in air atmosphere for 200h. The in-plane residual stress was measured by a conventional X-ray method, and the out-of-plane residual strain was measured by the strain scanning method using hard synchrotron X-rays. For the specimens rotated at 5 and 10rpm, in-plane compressive residual stresses were relieved by the high temperature exposure. For the specimen rotated at 20rpm, the in-plane residual stress did not change by the high temperature exposure, because it was very small before the exposure. The in-plane residual stress near the interface was a large compression for all cases examined. For the specimens rotated at 5 and 10rpm, out-of-plane stresses were small near the coating surface but became compression near the interface. Both in-plane and out-of-plane residual stresses of the specimen rotated at 20rpm were very small. From a viewpoint of reduction of the residual stress, the rotation speed of 20rpm was excellent. The EB-PVD TBC was made by columnar structure, which was composed of core and peripheral parts. The peripheral part had feather-like structure. According to the observation with scanning electron microscopy, the feather-like structure cohered and shrunk after the high temperature exposure. The volume reduction of the columnar structure relieved the in-plane residual stresses.

INTRODUCTION

Electron beam-physical vapor deposited (EB-PVD) thermal barrier coating (TBC) is one of the key technologies in gas turbine engines in the future. The EB-PVD TBC made on a rotating substrate has a unique columnar structure with the feather-like peripheral part. The EB-PVD TBC has a large compressive residual stress [1], but it can be reduced by the rotation method [2]. According to our previous studies, the in-plane compressive residual stresses decreased with the increase in the rotation speed, and the out-of-plane residual stress was small [1,2]. Therefore, the EB-PVD with the rotation method is endowed with excellent
resistance against the thermal stress. The thermally grown oxide (TGO) and the morphological change in coatings have been investigated extensively [3-7], but there are still many uncertain points. Especially, the oxidized EB-PVD TBC had a large compressive stress according to the other reports [3,4,7]. However, it is unbelievable that the TBC possesses such a large compressive stress.

In this study, the EB-PVD TBCs were exposed to 1273K for 200h and the residual stress distributions were measured by the combination of laboratory X-rays and synchrotron X-rays. The morphological change of the microstructure due to oxidization was observed by the scanning electron microscope (SEM).

**EXPERIMENTAL METHOD**

**COATINGS AND HIGH TEMPERATURE EXPOSURE**

The substrate material was nickel-base superalloy (IN738LC) with a length of 40mm, a width of 20mm and a thickness of 2.8mm. As the bond coating, CoNiCrAlY was pressureless plasma sprayed on the substrate. The thickness of the bond coating was about 0.18mm. Zirconia with 4mol% yttria was evaporated from an ingot by an electron beam with 45kW, and deposited on the bond coating. The substrate was rotated in the EB-PVD process at the rotation speeds of 5, 10 and 20rpm. All specimens were kept at 1223K in the coating process, and the coating time was 1500s. In this paper, the specimens are named R5, R10 and R20 where number corresponds to the rotation speed. According to microscopic observation of the cross section, the top coating thickness was about 0.12mm. The deflection of the coated specimen due to the residual stress was not considered.

To oxidize the TBC specimen, the several specimens of R5, R10 and R20 were exposed to 1223K in air atmosphere for 200h. The exposed specimens were named R5X, R10X and R20X respectively.

**IN-PLANE STRESS MEASUREMENT**

The in-plane residual stress was measured by the \( \sin^2 \psi \) method. In consideration of the preferred orientation of the top coating, the specimen was rotated during the measurement of the residual stress. The 133+331 diffraction from ZrO\(_2\) by Cr-K\(\alpha\) was used. For the specimens R5X and R10X, the diffraction profile was separated into the 133 and 331 profiles with Gauss functions. The peak angle was determined from the mean value of the 133 and 331 peak angles. For the specimen R20X, the 133 diffraction was predominant, so the peak angle was determined from the 133 diffraction. The \( \psi \) angles used for recording the diffractions were 35°~40° and 50°~55° for R5X and R10X, were 36°~42° and 70~72° for R20X. For the top coating, Young's modulus \( E=123\)GPa and Poisson's ratio \( \nu=0.3 \) were used for the X-ray stress calculation, which were obtained by the nano-indentation method in our previous study [1].

The distribution of the in-plane residual stress in the top coatings was measured by repeating the X-ray stress measurements after successive removal of the surface layer. The removal
was conducted by polishing with diamond slurry.

OUT-OF-PLANE STRAIN MEASUREMENT

The out-of-plane residual strain was measured by the strain scanning method using hard synchrotron X-rays. The experiment was conducted at the beam line BL02B1 in SPring-8. The wavelength used was 69.54keV. The size of the divergent slit was 0.2mm in height and 5.0mm in width. The X-ray optics of the receiving slits was the double slits, and its size was 0.2mm in height and 5.0mm in width. For the specimens R5X, R10X and R20X, the 422 diffraction from ZrO₂ was used for the strain scanning method, because its diffraction intensity was strong. In the strain scanning method, the specimen was rotated on the spinning stage the same as the in-plane stress measurement.

The difference in the center between the actual and nominal gauge volumes causes the surface aberration effect, and the analytical method to correct it was proposed by the authors [8]. However, the analytical correction method was not used, because the EB-PVD coating had preferred orientation. In this study, it was assumed that the residual stress in the coatings did not remain at high temperature. Heating the specimen at 1273K, the angular shift due to the surface aberration effect was measured by the strain scanning method. The measured diffraction angle, $\theta$, was corrected from the angular shift of the heated specimen.

RESULT AND DISCUSSION

OBSERVATION OF EB-PVD COATINGS EXPOSED AT HIGH TEMPERATURE

Both non-oxidized and oxidized specimens were observed with the scanning electron microscopy. The SEM photographs of the cross section of R10 and R10X are shown in Figs. 1 (a) and (b). TGO is not observed near the interface of the non-oxidized specimens as shown in Fig. 1 (a). On the other hand, the TGO is observed as the gray layer with a thickness of about 3$\mu$m in the oxidized specimens as seen in Fig. 1 (b). According to our

![Fig. 1. Cross section of EB-PVD coating with a rotation of 10rpm.](image)
observation, there was no difference in the thickness of the TGO by the rotation speed of the substrate.

Figure 2 (a) shows the feather-like structure without oxidization. The peripheral part of the columnar structure is covered with the fine feather-like structure. For the oxidized specimen, the feather-like structure shrinks due to sintering at high temperature as shown in Fig. 2 (b). The feather-like structures rounded and stuck together as indicated with the arrows in Fig. 2 (b). A similar feature of the oxidized structure has been reported [7,9].

Figure 3 shows the micrograph of the fracture surface of the columnar structures taken from the broken specimen. As shown in Fig. 3 (a), the non-oxidized columnar structure consists of core part and peripheral parts. The peripheral part is composed of the feather-like structure, and has a large area in the cross section. On the other hand, for the oxidized columnar structure, the core part is occupying a larger area as shown in Fig. 3 (b). The oxidized
peripheral part shrunk due to sintering, and the feather-like structure disappeared. As shown in the figure, the cross section of the oxidized core part is flat, and nano-pores are observed in the core part [10,11]. The shrinkage of the feather-like structure by oxidization causes a relief of the residual stress as described below. However, the residual stress near the interface is not relieved, because the feather-like structure did not grow sufficiently near the interface.

**DISTRIBUTION OF IN-PLANE RESIDUAL STRESS**

Figure 4 shows the distribution of the in-plane residual stress for the oxidized specimens. In the figure, the error bar indicates the 68.3% confidence limit, and the line in the figure indicates the in-plane residual stress for the non-oxidized specimen [2].

As shown in Fig. 4 (a), the compressive residual stress of the specimen, R5X, is smaller than that of non-oxidized specimen, R5. The reduction of the compressive residual stress is caused by the sintering effect of the peripheral part of columnar structure. The compressive residual stress increases near the interface between the bond and the top coatings. When \( \phi \) was defined as the angle between the rotation axis of the substrate and the direction of the stress measurement, the strong diffractions were measured in the directions of \( \phi = 25^\circ \) and \( 115^\circ \), whose directions were mutually orthogonal. Since the residual stress in the direction of \( \phi = 25^\circ \) was almost equal to that of \( 115^\circ \) the in-plane residual stress was equi-biaxial. The distribution of residual stress for the specimen R10X as shown in Fig. 4 (b) is similar to that of R5X. On the other hand, the residual stress for the specimen R20X is very small as shown in Fig. 4 (c).

Comparing the residual stress of the oxidized specimens with the non-oxidized specimen, the residual stress was relieved due to exposure to high temperature. However, the residual stress in the vicinity of the interface remains as shown in Fig. 4. The feather-like structure, which is the peripheral part of the columnar structure, does not grow sufficiently near the interface. As a result, the volume reduction by sintering does not occur near the interface, and the compressive residual stress near the interface is not relieved. Near the interface, the influence of the mismatch of the coefficient of thermal expansion between the top and the
bond coating is predominant for the development of the residual stress.

**DISTRIBUTION OF OUT-OF-PLANE RESIDUAL STRESS**

Figure 5 shows the diffraction profiles with synchrotron X-rays before and after the high temperature exposure. The zirconia 333 and 600 diffractions had the strong intensity before the high temperature exposure. After the exposure, the zirconia 422 diffraction appeared instead of the 333 and 600 diffractions. The feather-like structure was made by growth of $\{110\}$ plane and its growing direction was 36° against the coating plane [2]. The zirconia 333 diffraction was obtained from the feather-like structure of the columnar structure. Due to the exposure, the feather-like structure shrunk and hung down. As a result, the zirconia 422 diffraction appeared.

The distribution of the out-of-plane strain was measured using the strain scanning method, where the out-of-plane strain was measured from each specimen without the surface removal. The strain-free interplanar spacing, $d_0$, is needed to calculate the out-of-plane strain. When an equi-biaxial stress and the plane stress states are assumed on the top coating surface, the $d_0$-value can be determined by

$$
    d_0 = \frac{E}{E + (1-\nu)\sigma_1(0)} \frac{\lambda}{2\sin\theta_{z=0}}
$$

where $\sigma_1(0)$ is the in-plane stress at the surface, $\lambda$ is the wavelength and $\theta_{z=0}$ is the corrected diffraction angle at the surface. The out-of-plane strain, $\varepsilon_3(z)$, was calculated by $d(z)/d_0 - 1$ at each depth, $z$. The out-of-plane stress, $\sigma_3(z)$, was obtained from $\varepsilon_3(z)$ and $\sigma_1(z)$ using the following equation:

$$
    \sigma_3(z) = E\varepsilon_3(z) + 2\sigma_1(z)
$$

![Fig. 5. Difference in diffraction profile of EB-PVD coating before and after exposure.](image-url)
The distribution of the out-of-plane residual stress of the oxidized specimen was shown in Fig. 6. In addition, the residual stress of the non-oxidized specimen is also shown in the figure [2]. The out-of-plane residual stresses for all oxidized specimens were small as shown in Figs. 6 (a)–(c). Especially, the specimen R20X has the smallest residual stress. The out-of-plane residual stress hardly changed before and after high temperature exposure.

Rotating the substrate during deposition is very effective to mitigate the compressive in-plane residual stress in the EB-PVD TBC. The residual stress of EB-BVD TBC by the rotation method is relieved by the high temperature exposure. This is caused by the shrinkage of the feather-like structure. However, the in-plane compressive residual stress in the vicinity of the interface was not relieved because of the non-existence of the feather-like structure. The coefficient of thermal expansion is $\epsilon_{1.86} \times 10^{-5}/K$ for the bond coating [12] and $5.19 \times 10^{-6}/K$ for the EB-PVD TBC [13]. There is a large compressive residual stress according to the calculation, but the measured residual stress is very small due to the columnar microstructure with feather-like structure. The out-of-plane compressive stress near the interface between the top and bond coating exists as shown in Fig. 6. If the strain state near the interface is similar to a plane strain, an out-of-plane compressive stress may generate due to the in-plane residual stress.

**CONCLUSIONS**

The distributions of the residual stresses in the EB-PVD TBCs oxidized at 1273K for 200h were measured by a combination of laboratory X-rays and hard synchrotron X-rays. The changes of the residual stresses distribution by the high temperature exposure were discussed on the bases of the columnar structure of TBCs. The obtained results are as follows:

1. The in-plane residual stress in the columnar structure was relieved by the high temperature exposure. The out-of-plane residual stress did not change so much, because it was small before the exposure.
2. The shrinkage of the feather-like structure due to exposure to high temperature causes
the relief of the in-plane residual stress in the EB-PVD TBCs. However, the residual stress near the interface was not relieved, because the feather-like structure does not develop near the interface.

(3) The feather-like structure shrinks and also sintering proceeds in the core part of the columnar structure by exposure at high temperature. As a result, orientation distribution of TBCs changes.

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