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Zirconia based ceramic coating on a metal with plasma electrolytic oxidation

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Abstract. We challenge to fabricate a thermal barrier coating (TBC) made of ZrO_2 based ceramics on a Ni based single crystal superalloy with plasma electrolytic oxidation (PEO) by incorporating metal species from electrolyte into the coating. The PEO process is carried out on the superalloy **galvanized with aluminium** for 15min in $\text{Na}_4\text{O}_7\text{P}_4$ solution for an oxygen barrier coating (OBC) and is followed by PEO in $\text{K}_2[\text{Zr}(\text{CO}_3)_2(\text{OH})_2]$ solution for TBC. We obtained the following results; (1) Monoclinic-, tetragonal-, cubic- ZrO_2 crystals were detected in TBC. (2) High porosity with large pores was observed near the interface between OBC and TBC. The fine grain structure with a grain size of about 300nm was typically observed. (3) The adhesion strength between PEO coatings and substrate was evaluated to be 26.8 ± 6.6 MPa. At the adhesion strength test, PEO coatings fractured around the interface between OBC and TBC. The effect of coating structure on adhesion strength is explained through the change in spark discharge during PEO process.

1. Introduction

The improvement of the thermal efficiency of jet engines is required for the reduction of fuel consumption and CO_2 emission. In order to improve the efficiency, the turbine inlet temperature increases year by year. Nowadays the temperature is set to be higher than the melting point of the Ni based single crystal superalloy (SA) which is applied to turbine blades. Consequently the metal blades are conventionally coated with ZrO_2 as a thermal barrier. The thermal barrier coating (TBC) is usually processed with electron-beam physical-vapor-deposition¹ or air-plasma-spray² technique, which are very expensive. In this study, we focus on plasma electrolytic oxidation (PEO) technique for ceramic coating because the PEO is low cost processing and can be applied for machinery parts with large size and complex shape³. The ceramics coatings with PEO are usually generated through the oxidation of a metal, which means it seems to be rather difficult to realize ZrO_2 coating on SA with PEO. However, we challenge to fabricate ZrO_2 based ceramic coating on SA with PEO by incorporating metal species from electrolyte into the coating. And also we examine the microstructure of the coating and the adhesion strength between the coating and SA substrate.

2. Experimental procedure

The chemical composition of SA is expressed as 5.6Al-9Co-6.5Cr-0.6Mo-6.5Ta-1Ti-6W-3Re-bal.Ni (wt%), which is called CMSX-4 conventionally. SA galvanized with aluminium was set on anode to be coated with oxide ceramics on the one hand and isotropic graphite was on cathode on the other hand in PEO system. PEO treatment was carried out on a circular surface with a diameter of 6mm under a constant voltage in the range of 100~250V with a pulse of 10% duty ratio at 1kHz. In this study, we carried out two-step PEO processes. At the first step, the SA galvanized was oxidized with spark discharge on anode for 15min in $\text{Na}_4\text{O}_7\text{P}_4$ solution (0.25mol/L) in order to make an oxygen barrier coating (OBC), which was made of Al_2O_3 based ceramics. At the second step, PEO treatment was carried out for SA with OBC in $\text{K}_2[\text{Zr}(\text{CO}_3)_2(\text{OH})_2]$ solution (2.54mol/L) to make TBC. Crystalline phases in the coating were examined with XRD. The microstructure of the coating was observed with FE-SEM. During SEM observation, the mapping of the chemical composition in coating was carried out with EDX. The adhesion strength between the coating and SA substrate was measured with a testing machine by using an apparatus designed to apply a tensile load to the interface between the coating and substrate perpendicularly.

3. Results and Discussion

3.1. Microstructure and chemical composition distribution of coatings

Figure 1 shows the SEM image of the cross section of the interface between coatings and SA substrate (a), and chemical composition distribution at the interface (b) analyzed with EDX. We successfully obtained TBC with a thickness of about 50 micron through PEO treatment only for 15min. We can see Al-rich SA phase beneath the coatings which is, of course, owing to galvanizing SA with aluminium. Considering the application of this material at elevated temperatures, we should change the Al-rich SA into an intermetallic compound such as Ni_3Al through the diffusion of Al into SA with heat treatment. According to Fig.1, OBC including Al_2O_3 based oxide with a thickness of a few microns was observed between the Al-rich SA phase and TBC. We think OBC should be thickened to be over $10\mu\text{m}$ in order to prevent SA from being oxidized sufficiently. The ratio of Zr to O is about 0.5 in TBC shown in Fig.1 (b) indicates that TBC mainly consists of ZrO_2 . As a result of XRD, monoclinic-, tetragonal-, and cubic- ZrO_2 crystals were assigned in TBC. This suggests that TBC was processed at a relatively high temperature during PEO. Very fine grains with a diameter of about 200-300nm were typically observed in TBC as shown in Fig.2. Since the size of the fine grains is enough small to inhibit phase transformation of ZrO_2 during cooling in solution, tetragonal- and cubic- ZrO_2 crystals, which are usually unstable at an ambient temperature, can be observed. Figure 3 shows SEM image of TBC observed perpendicularly to the interface. The number and volume of pores increase with approaching to the interface according to Fig.3. The characteristic distribution of pores in TBC is developed by spark discharge during PEO process. At the beginning of PEO process, oxide layer on SA is so thin that spark discharge with high energy occurs frequently under constant voltage condition because of the

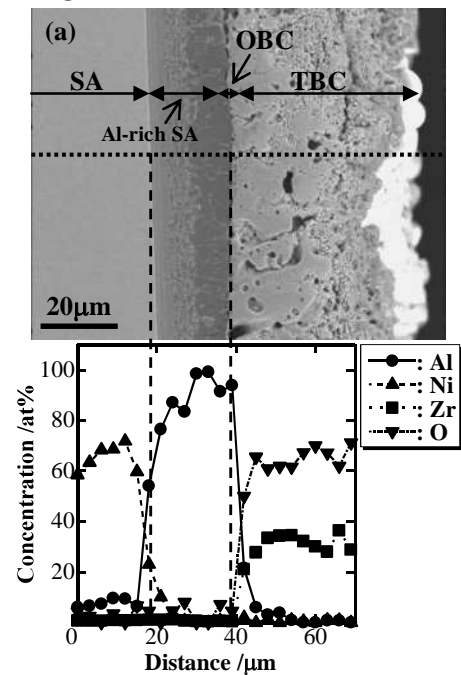


Fig.1 SEM image of the cross section of the interface between coatings and SA substrate (a), and chemical composition distribution at the interface (b) analyzed with EDX

low dielectric breakdown voltage of the thin layer. The spark discharge seems to make a lot of large pores in TBC near the interface. The frequency of spark discharge decreases with an increase in the thickness of TBC with progressing PEO process on the contrary. Then the number and volume of pores are small at the surface of TBC. The gradient distribution of pores may have an advantage for TBC because high porosity near the interface brings low thermal conductivity and rather dense structure around the surface blocks the penetration of oxygen inside the material. In addition to the pore distribution, the fine grain structure shown in Fig.2 also has an advantage for a thermal barrier to realize the low thermal conductivity of TBC because of the enhancement of phonon scattering.

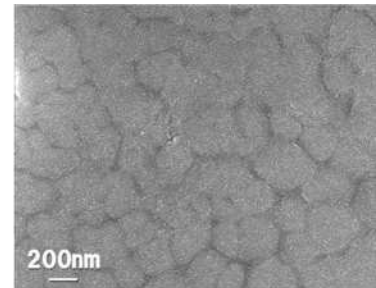


Fig.2 Fine structure in TBC observed with SEM at high magnification

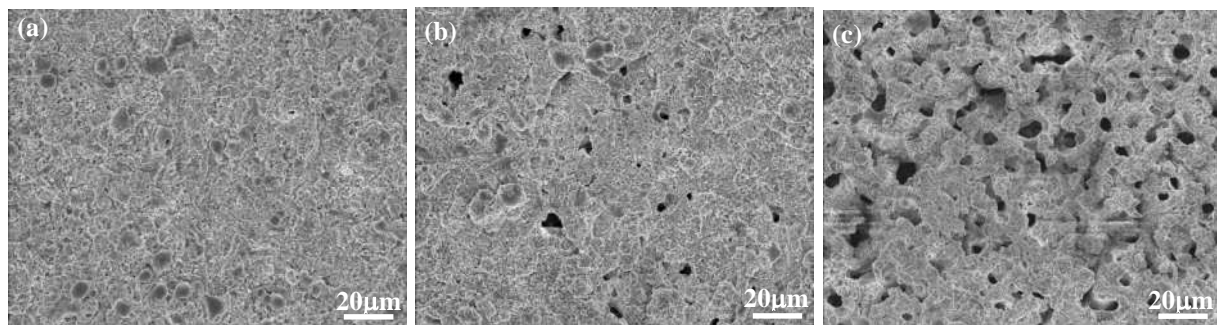


Fig.3 SEM image of TBC observed perpendicularly to the interface between coatings and SA substrate. Surface as received (a), polished at about 30μm from the interface (b) and polished at about 10μm from the interface (c).

3.2. Adhesion strength between coatings and substrate

Adhesion strength between coatings (OBC and TBC) and substrate was evaluated to be 26.8 ± 6.6 MPa. In the case of TBC made with air-plasma-spray, which is actually and commercially utilized as turbine blades, adhesion strength is reported to be 28.4 ± 5.5 MPa⁴. This means that TBC fabricated with PEO has enough high adhesion strength to be utilized for turbine blade. Figure 4 shows the SEM image of fractured surface obtained by the adhesion strength test. We can see dark region as well as bright region on the surface. Chemical composition analyzed with EDX as shown in Table 1 indicates that the dark region (Point A in Fig.4) is made of Al₂O₃ based ceramics on the one hand and the bright region (Point B in Fig.4) mainly contains ZrO₂ based ceramics on the

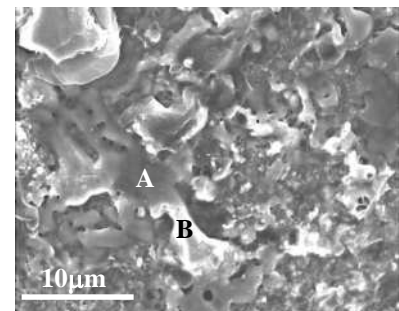


Fig.4 SEM image of fractured surface obtained by an adhesion strength test

other hand. This means that fracture at the adhesion strength test happened at the interface between OBC and TBC. As mentioned above, there are a lot of large pores around the interface, which is attributed to frequent spark discharge with high energy at the beginning of PEO process. Therefore this material fractured at the weak interface between OBC and TBC at the adhesion strength test. The number and volume of pores in TBC, which spark discharge makes, can be controlled by PEO condition such as voltage applied, the frequency and duty ratio of pulse voltage, the concentration

Table 1. Chemical composition observed in Fig.4 analyzed with EDX

Point	Al /at%	Zr /at%	O /at%
A (dark region)	42.20	7.69	50.11
B (bright region)	1.36	25.54	73.10

of an electrolyte, and so on. We believe that the adhesion strength can be improved through the optimization of the PEO condition.

4. Conclusions

We challenged to fabricate TBC made of ZrO_2 based ceramics on SA with PEO by incorporating metal species from electrolyte into the coating. We obtained the following results;

(1) Monoclinic-, tetragonal-, cubic- ZrO_2 crystals were detected in TBC. This means that TBC was processed at a relatively high temperature during PEO. Tetragonal- and cubic- ZrO_2 crystals, which are usually unstable at an ambient temperature, **can be observed because** very fine grains with a diameter of about 200-300nm typically observed in TBC inhibit phase transformation of ZrO_2 during cooling in solution.

(2) High porosity with large pores was observed near the interface between OBC and TBC. This is **attributed to frequent spark discharge with high energy at the beginning of PEO process.**

(3) The adhesion strength between PEO coatings and substrate was evaluated to be $26.8 \pm 6.6 \text{ MPa}$, which is **enough high adhesion strength to be utilized for turbine blade.** At the adhesion strength test, PEO coatings fractured around the interface between OBC and TBC, where a lot of large pores exist.

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