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Development of EBC for Silicon Nitride

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Abstract: Various coating methods of EBC layer for silicon nitride were discussed. High density EBC layer was successfully coated by different techniques such as sputtering, sol-gel and reaction sintering methods. Water vapor corrosion and recession mechanisms of $Lu_2Si_2O_7$ which is a potential material for EBC were discussed. The problems in the development of EBC revealed by corrosion tests were summarized. The most important problem addressed here was the corrosion of silica at grain boundary. Due to corrosion of silica at the boundary, formation of porous surface is inevitable, then the silicon nitride substrate gets easily oxidized and/or corroded by water vapor. To resolve this issue, we propose a new EBC material without boundary silica and the corrosion mechanism of this improved EBC material is discussed.

Introduction

Silicon nitride ceramics (Si_3N_4) are excellent candidates for gas turbine materials because of their high thermal and mechanical properties at elevated temperatures [1,2]. Recently, silicon nitride ceramics for high temperature application having a strength over 1 GPa has been produced, and the improvement of high temperature strength is achieved by adding heavy rare earth oxides as sintering agents such as Yb_2O_3, Lu_2O_3, etc.[2]. During sintering, the rare earth oxide reacts with silica and silicon nitride in nitrogen atmosphere to form rare earth-silicon oxynitride, i.e., J-phase ($Ln_4Si_2O_7N_2$, Ln=rare earth element), at the grain boundaries. These improved silicon nitride ceramics are suitable high temperature structural materials. However, problem arises by this J-phase when used at high temperatures in air or in the actual gas combustion environments. This J-phase decomposes to rare earth di-silicate during said above conditions with large volume shrinkage of approximately 70% [1]. This large volume change induces many micro-cracks at the surface of the silicon nitride [3], which leads to deterioration in the reliability of the mechanical properties. In addition, silicon nitride ceramics are also easily oxidized and corroded at high temperatures in water vapor environments such as gas combustion fields [4,5]. Hence, environmental barrier coating (EBC) layers are necessary for the application of silicon nitride as gas turbine engine components.

The hydro corrosion [6] and recession [7] mechanisms of silicon nitride ceramics in high velocity combustion gas flow are well known. The sample surface after recession test in high velocity combustion gas flow is covered with thin silica film [7]. It has been suggested that the recession of silicon nitride ceramics by water vapor and/or combustion gas is caused by the combination of oxidation/corrosion of silicon nitride ceramics substrate and corrosion of silica that formed on silicon nitride ceramics, where silica component is volatile. It is believed that the silica phase that is formed by the oxidation of silicon nitride ceramics is easily corroded by water vapor to form resultant $Si(OH)_4$ at high temperatures. There are many data available on the solubility of silica into water in the textbook [9].

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However, the water vapor corrosion and/or recession mechanisms for other materials are not reported in detail. Yoshimura *et* al. reported that pure zirconia is resistant to hydro corrosion at high temperature [10]. Recently, we reported that in the event of occurrence of no defects, titania well is resistant water vapor corrosion at high temperatures [11]. However, materials such as zirconia and titania have thermal expansion coefficients much higher than that of silicon nitride ceramics and hence, it is difficult to coat these materials directly on silicon nitride.

Therefore, the thermal expansion coefficient (TEC) of EBC material, which is coated on silicon nitride substrate, should be closer to that of silicon nitride ceramics. Because the silica is formed by the oxidation of silicon nitride, it is advantageous that EBC material contains silica as one of its components. Mullite ($Al_6Si_2O_{13}$), zircon ($ZrSiO_4$), BSAS and rare earth di-silicate ($Ln_2Si_2O_7$, Ln = rare earth element) are among the silicates that possess low TEC. Among these, mullite and BSAS EBC have been already documented in detail for silicon based materials [12,13].

In this paper, we report the formation of high density EBC layer such as rare earth di-silicate, mullite, etc. by various coating techniques such as sputtering, sol-gel and reaction sintering techniques. Water vapor corrosion and/or recession mechanisms for $Lu_2Si_2O_7$ phase are discussed. The problems encountered while developing the EBC are summarized. The corrosion mechanism of proposed EBC material without boundary silica is discussed.

Experimental procedures

1. Preparation of monolithic silicates bulk

High purity Al_2O_3 (99.99% purity with 0.001% sodium, High Purity Chemicals Co. Ltd.,) and SiO_2 (99.9% purity, High Purity Chemicals Co. Ltd., 0.8μm particle size) powders were used as the starting materials for the preparation of mullite bulk. And high purity Lu_2O_3 (99.99% purity, Shin-Etsu Chemical Co. Ltd., 4μm particle size) and SiO_2 powders were used as the starting materials for the preparation of $Lu_2Si_2O_7$ bulk. A stoichiometric molar ratio of these powders, Al_2O_3:SiO_2=3:2 for mullite and Lu_2O_3 : SiO_2=1:2, was mixed in an agate mortar. The mixed powders were hot pressed at 1600°C for 3 hours in Ar atmosphere under an applied load of 20MPa. The sintered plates were cut into small specimens of size 40x4x3 mm for static state corrosion test. The Phase identification was performed by X-ray diffraction method. For the preparation of mullite/$Lu_2Si_2O_7$ eutectic, Lu_2O_3, SiO_2 and Al_2O_3 were used as starting materials. These powders were mixed in an agate mortar according to molar ratio Al_2O_3:SiO_2:Lu_2O_3 = 27.3:54.6:18.1 according to Murakami *et al*. [14]. The mixed powder was packed in a platinum crucible and heated at 1550°C for 12 hours in air. The furnace was slowly cooled down to 1000°C at a cooling rate 0.8°C/min. and then cooled down to room temperature.

2. Static state corrosion test

A high temperature static state water vapor corrosion test was performed using a Corrosion Testing Machine (Japan Ultra-high Temperature Materials Research Center). The sample was placed in a high purity Al_2O_3 jig for mullite bulk and $Lu_2Si_2O_7$ jig for $Lu_2Si_2O_7$ bulk and then corrosion test was carried out under the following conditions; Temperature: 1300-1500°C, Time: 100 hours, Gas flow: 30wt% water (air:H_2O=70:30 (wt%)), gas flow rate: 175ml/min that is corresponding to the gas velocity of 4.6×10^{-4} m/s. To exclude the water vapor corrosion occurring at low temperatures, the corrosive gas was introduced when the temperature reached 1300 °C and the gas flow was stopped after the 100 hours testing period. Phase identification was carried out by X-ray diffraction and surface was examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) for the specimens before and after the corrosion tests. The phase compositions were determined by energy dispersive X-ray (EDX) analysis.

3. Coating of EBC layer on silicon nitride

3-1 Sputtering method

$Lu_2Si_2O_7/Lu_2SiO_5$ layer was coated on silicon nitride by sputtering method [15]. For the sputtering processes, a mixed silica and lutetium oxide bulk was used as the target substrate. 25 pieces of 11mm diameter lutetium oxide pellets were placed on the surface of a piece of bulk silica of 3 inches (75mm) diameter. The operating power was 200W and the coating time was 3 hours for each face of the test piece.

3-2 Sol-gel method

$Lu_2Si_2O_7$ layer was also coated by sol-gel method [16]. $Lu(NO_3)_3 \cdot nH_2O$ (99.5% purity, Wako Pure Chemical Industries), TEOS (ethyl silicate, $Si(OH)_4$) (95% purity, Wako Pure Chemical Industries) and 96% 2n-propanol were used as the starting materials. Firstly, $Lu(NO_3)_3 \cdot nH_2O$ was dissolved in 2n-propanol at 40°C and subsequently TEOS was slowly added to the solution. The precursor sol was applied on silicon nitride substrate and then, dried in air at room temperature and then at 100°C for 24 hours. The coated sample was sintered at 1550°C for 4 hours in air.

3-3 Reaction sintering method

Oxidation bonded by reaction sintering method was employed to coat $Lu_2Si_2O_7$, mullite and zircon layer on silicon nitride ceramics [17]. In this technique, firstly, amorphous silica layer was formed on silicon nitride by the oxidation of silicon nitride substrate at 1100°C for 48 hours. The oxidized specimens were embedded in respective ceramic powder bed with their oxidized face in contact with powder. Sintering was performed at 1500°C with gas pressure up to 6 atm Ar for 2 hours.

Results and discussion

1. Coating of EBC layer on silicon nitride

1-1. Sputtering method

In the event of having open pores or cracks in EBC layer, the silicon nitride ceramic oxidizes and forms a silica phase. Because of this, the composition of the lutetia-silica EBC layer in our present study was aimed at being silica poor, namely, mono-silicate (Lu_2SiO_5). It was expected to become lutetium di-silicate ($Lu_2Si_2O_7$) due to self-healing mechanism as following reaction.

$$Lu_2SiO_5\,(s) + SiO_2\,(s) = Lu_2Si_2O_7\,(s) \qquad (1)$$

By sputtering technique, a high dense layer was successfully coated on silicon nitride [15]. The thickness of this layer was about 4μm. The coating rate could be estimated to be about 1mm/hr. In this method, gasified Lu, Si and O atoms are piled on the substrate at room temperature. Fig.1 shows the surface of the EBC layer. The microstructure looks as if high dense film with no cracks or open pores is obtained for the EBC layer. However, the X-ray diffraction analysis revealed that the as-coated layer consisted of amorphous phase. Therefore, a heat treatment to crystallize the film was necessary. The heat treatment was performed at 1550°C for 10 hours in air. The X-ray diffraction pattern for the heat- treated sample suggested that the coated layer was crystallized to di-silicate/mono-silicate system.

1-2. Sol-gel method

The composition of the EBC layer was silica poor as same as was the case in the sputtering method. An endothermic peak that denotes the crystallization of silicate phase was observed at 1053°C in DTA analysis [16]. X-ray diffraction pattern of the heat treated sample surface suggested that the EBC layer consisted both di-silicate and mono-silicate phases. Fig.2 shows SEM image of the sample surface. High dense di-silicate/mono-silicate mixed layer was successfully prepared by

this method. The grain size of each crystal was less than 1μm (though it is not clearly seen in Fig). Though, high dense EBC layer can be obtained by this method, a lot of parameters have to be optimized. Furthermore, the coating layer is very thin (< 5 μm).

1-3. Reaction sintering method

Mullite, zircon and $Lu_2Si_2O_7$ layer was successfully coated by this method [17]. Because the thickness of the amorphous silica layer that formed by pre-heat treatment at 1100°C was only about 2μm, the thickness of the formed silicate layer was the same or slightly thicker (~ 5 μm) compared with the amorphous silica layer. Figures 3 (a) and (b) show the cross section and surface of $Lu_2i_2O_7$ layer, respectively. Though there is not much difference in the thermal expansion coefficient of $Lu_2Si_2O_7$ and silicon nitride ceramics [18], some cracks were induced on the EBC layer as indicated by arrow in Fig.3 (b). It is revealed that a high density of EBC layer could be formed by this method. X-ray diffraction pattern of the sample surface suggested that the coated layer consisted only of $Lu_2Si_2O_7$ phase. In this method, the oxide bed reacts with silica layer completely, thus the formed silicate layer is a single phase. The subsequent silicate layer formed covers the whole specimen including edges and corners. This is an important merit of this method.

2. Corrosion test

2-1. Sputter coated $Lu_2Si_2O_7$ Layer on Silicon Nitride Ceramics

A static state corrosion test was performed on the silicon nitride with sputter coated $Lu_2Si_2O_7$ layer at 1300°C [15,19]. The weight loss rate of the $Lu_2Si_2O_7$ coated sample was of the order of 10^{-6} $g/cm^2 \cdot hr$ that was the same as that of $Lu_2Si_2O_7$ monolithic bulk [15]. The weight of silicon nitride without EBC layer was increased due to oxidation of the substrate. Only $Lu_2Si_2O_7$ phase was confirmed in the X-ray diffraction pattern after the corrosion test. Fig.4 shows the surface of post corrosion test sample. Each grain was clearly seen, namely, the boundary phase was completely removed. It is understood from previous report that for the preparation of single-phase $Lu_2Si_2O_7$ bulk, about 13mol% excess silica is needed for the stoichiometric composition due to formation of boundary silica [20]. Therefore, a large amount of boundary silica is expected to exist in polycrystalline Lu-silicate phase. It is believed that silica phase was corroded by water vapor at high temperatures according to the equation (2).

$$SiO_2\,(s) + 2H_2O\,(g) = Si(OH)_4\,(g) \qquad (2)$$

It is believed that the boundary silica in the $Lu_2Si_2O_7$ EBC layer was removed by water vapor according to the equation (2). However, by the corrosion of boundary silica, porous structure was formed as shown in Fig.4. Such porous structure makes corrosive gas to pass through EBC layer. In some places, it is confirmed that silica phase oozed out through the EBC layer as indicated by the arrow in Fig.4.

2-2. $Lu_2Si_2O_7$ bulk

$Lu_2Si_2O_7$ bulk was corrosion tested under the same condition as mentioned above. In the preparation of this bulk, the ratio of lutetia to silica was 1:2. According to the discussions in the previous section, the bulk consisted of di-silicate, monosilicate and as well as grain boundary silica phase (equation 3).

$$Lu_2O_3(s) + 2SiO_2\,(s) = (1\text{-}x)Lu_2Si_2O_7\,(s) + xLu_2SiO_5\,(s) + SiO_2\,(\textit{boundary}) \qquad (3)$$

The weight was decreased in the corrosion test. A detailed discussion was reported elsewhere [19,21]. Fig.5 shows the surface after the corrosion test. It is observed from Fig.5 that the microstructure is not homogeneous. If we look closely at the microstructure, the grains on the right side of this image have been covered with melted component. The composition of this area is analyzed to be close to that of Lu_2SiO_5 with a small amount of silica rich $Lu_2Si_{1+x}O_{5+2x}$.

On the other hand, we observe that the grains on the left side have clear grain boundaries and the grain boundary phase has been completely removed. The composition of this area is analyzed to be $Lu_2Si_2O_7$ with slightly silica poor $Lu_2Si_{2-x}O_{7-2x}$. It is believed that this morphology and phase structure is essentially the same as that of Fig.4. Because the composition of the melted surface is closer to that of Lu_2SiO_5, it could be assumed that Lu_2SiO_5 may have once melted during the corrosion test. However, since the melting point of Lu_2SiO_5 phase is high enough [22] that it is difficult to believe that Lu_2SiO_5 phase was melted. In the SiO_2-H_2O phase diagram [23], the melting point of SiO_2 decreases with H_2O content down to 1100°C. From this, it might be speculated that water vapor attacks boundary silica and then, liquid phase is formed according to equation (4).

$$SiO_2(boundary) + nH_2O\ (g) = SiO_2 \cdot nH_2O\ (l) \qquad (4)$$

As the composition of the left side of Fig.5 is slightly silica poor from $Lu_2Si_2O_7$ composition, it can be assumed that decomposition of $Lu_2Si_2O_7$ phase occurrs at near the grain surface according to equation (5).

$$Lu_2Si_2O_7\ (s) + 2H_2O\ (g) = Lu_2SiO_5\ (s) + Si(OH)_4\ (g) \qquad (5)$$

The results of the recession test in high velocity combustion gas flow [24] also supported above reactions. However, the resultant porous $Lu_2Si_2O_7$ phase from equation (4)-(5) was well sustained under the high velocity combustion gas flow [24]. So it is considered that equation (5) is the rate-limiting step.

2-3. Mullite/$Lu_2Si_2O_7$ eutectic bulk

Polycrystalline $Lu_2Si_2O_7$ bulk and EBC layer possess boundary silica. The most important problem in the water vapor corrosion of these materials is the presence of boundary silica phase. Commonly, polycrystalline silicate compounds contain boundary silica phase. Hence this is a common problem among silicate compounds. There are two ways to solve this problem, (1) multi layered concept, where the topcoat should be without silica component and (2) silicate system with no boundary silica.

In the Y_2O_3-SiO_2-Al_2O_3 ternary phase diagram, mullite/$Yb_2Si_2O_7$ eutectic exists [14]. Similarly, it has been confirmed by present authors that mullite/$Lu_2Si_2O_7$ eutectic is also possible at the same composition as in the Yb system, with the eutectic temperature at 1500°C [19]. High resolution TEM image suggested that no boundary phase existed [25]. As a consequence, the weight remained unchanged during the corrosion test at 1300°C [25]. This result indicates that the weight loss rate for this eutectic at 1300°C should be less than 10^{-7} g/cm^2·hr. In some places on the surface of test sample, polycrystallization of $Lu_2Si_2O_7$ phase according to equation (5) has been observed.

Summary

By means of different coating techniques such as sputtering, sol-gel and reaction sintering methods, high density silicate EBC layer was successfully coated on silicon nitride ceramics. However, as these silicate layers were polycrystalline in nature, they had silica component as their grain boundary phase. The boundary silica phase was easily corroded by water vapor at high temperatures and porous structure was formed even if the as-prepared EBC layer was of high density. The rate of decomposition of $Lu_2Si_2O_7$ phase is small. Silicate phase without boundary silica, namely mullite/$Lu_2Si_2O_7$ eutectic, is a potential EBC material for silicon nitride ceramics.

References

[1] S. M. Wiederhon and M. K. Ferber, *Current Opinion in Solid State and Materials Science*, **5** (2001) 311-316.
[2] H.J. Choi, J. G. Lee and Y. W. Kim, *J. Mater. Sci.*, **32** (1997) 1937-1942.
[3] H. T. Lin and M. K. Ferber, *J. Euro. Ceram. Soc.*, **22** (2002) 2789-2797.

[4] E. J. Opila, *J. Am. Ceram. Soc.*, **86** (2003) 1238-48.
[5] D. S. Fox, E. J. Opila, Q. N. Nguyen, D. L. Humphrey and S. M. Lewton, *J. Am. Ceram. Soc.*, **86** (2003) 1256-61.
[6] S. Somiya, *Materials Chem. Phys.*, **67** (2001) 157-164.
[7] I. Yuri and T. Hisamatsu, Proc. 2003 ASME TURBO EXPO, Power for Land, Sea and Air, GT2003-38886.
[8] P. K. Iler, "The Chemistry of Silica", A Wiley-Interscience Publication, New York (1979).
[9] J. Felsch, *Structure and Bonding Berlin*, **13,** 99-197 (1973).
[10] M. Yoshimura, F. H. Stott and G. Editors, MRS bulletin, **Oct. 1994**, 20-21.
[11] S. Ueno, D. Doni Jayaseelan, N. Kondo, T. Ohji and S. Kanzaki, *Mater.Trans.JIM*, in press.
[12] K. N. Lee, D. S. Fox, J. I. Eldridge, D. Zhu, R. C. Robinson, N. P. Bansal and R. A. Miller, *J. Am. Ceram. Soc.*, **86** (2003) 1299-306.
[13] N. S. Jacobson, E. J. Opila and K. N. Lee, *Current Opinion in Solid State and Materials Science*, **5** (2001) 301-309.
[14] Y. Murakami and H. Yamamoto, *J.Ceram.Soc.Jpn*, **101** (1993) 1101-1106.
[15] S. Ueno, D.D. Jayaseelan, N. Kondo, T. Ohji and S. Kanzaki, *J. Ceramic Processing Research*, **4**(3) (2003) 1-8.
[16] D. Doni Jayaseelan, S. Ueno and T. Ohji, *Materials Chemistry and Physics*, in press.
[17] D. Doni Jayaseelan, S. Ueno, N. Kondo, T. Ohji and S. Kanzaki, *J. Am. Ceram. Soc.*, in press.
[18] T. Fukudome, S. Tsuruzono, W. Karasawa and Y. Ichikawa, Proc. 2002 ASME TURBO EXPO, Power for Land, Sea and Air, GT2002-30627.
[19] unpublished data
[20] F. Monteverde and G. Celotti, *J. Euro. Ceram. Soc.*, **19** (1999) 2021-202.
[21] S. Ueno, N. Kondo, D. Doni Jayaseelan, T. Ohji and S. Kanzaki, Proc. 2003 ASME TURBO EXPO, Power for Land, Sea and Air, GT2003-38878.
[22] J. Felsch, *Structure and Bonding Berlin*, **13** (1973) 99-197.
[23] G. C. Kennedy, G. J. Wasserburg, H. C. Heard and R. C. Newton, *Am. J. Sci.*, **260** (1962) 501-521.
[24] unpublished data
[25] S. Ueno, D. Doni Jayaseelan, N. Kondo, T. Ohji and S. Kanzaki, Proc. 28th International Cocoa Beach Conference and Exposition on Advanced Ceramics & Composites, in press.

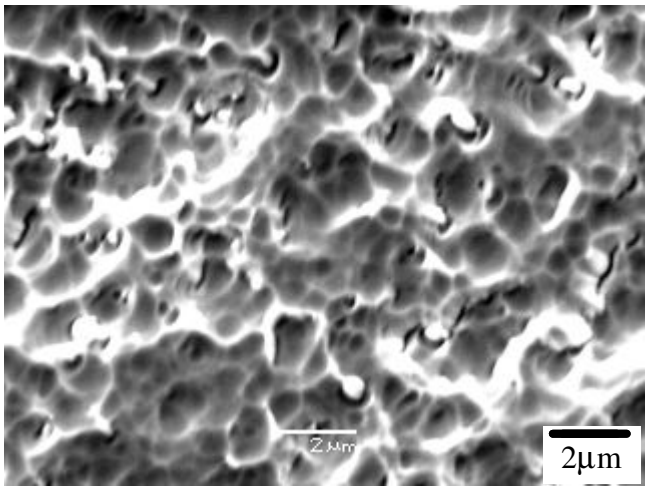

Fig.1 Surface of sputter coated Lu-Si-O EBC layer.

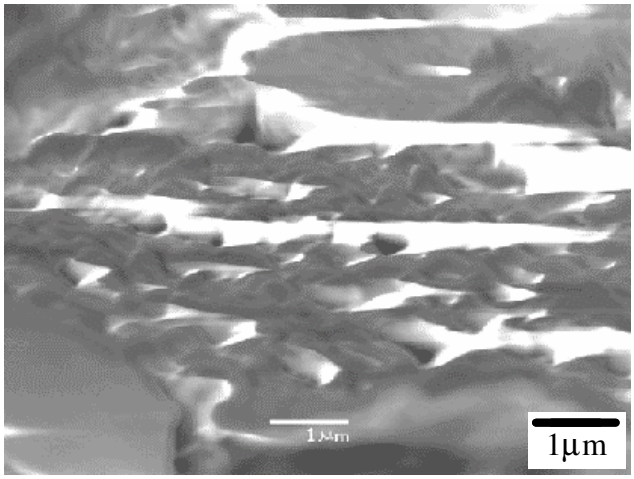

Fig.2 Surface of sol-ge coated Lu-Si-O EBC layer.

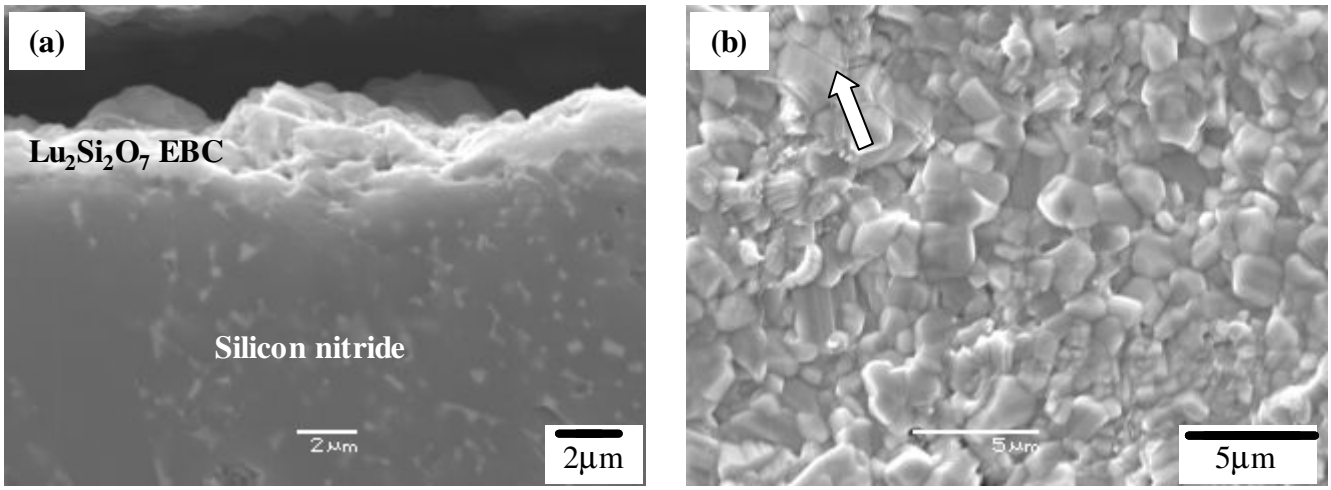

Fig.3 Surface of $Lu_2Si_2O_7$ EBC layer coated by reaction sintering method. (a) cross section view and (b) surface.

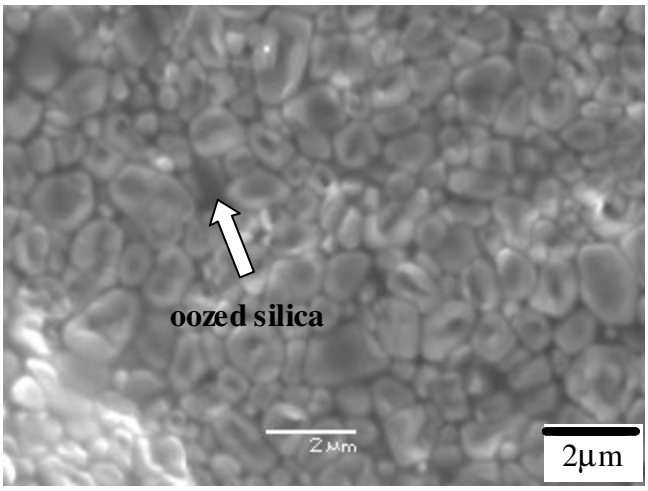

Fig.4 Surface image of sputter coated EBC layer after corrosion test.

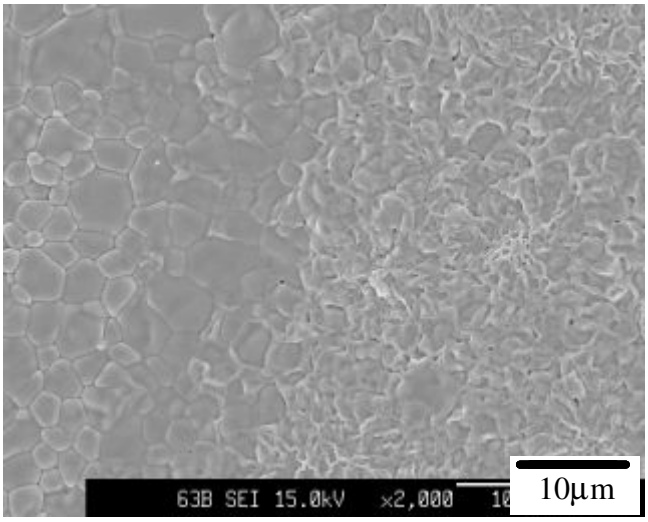

Fig.5 Surface image of $Lu_2Si_2O_7$ bulk after corrosion test.