

## Corrosion Behavior of $\text{AlNbO}_4$ /Mullite Composite as Environmental Barrier Coating in Water Vapor Environment

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**Abstract:**  $\text{AlNbO}_4$ /mullite composite environmental barrier coating (EBC) with 5mol%  $\text{AlNbO}_4$  content was prepared on  $\text{Si}_3\text{N}_4$  substrate by atmospheric plasma spraying (APS). There was evidence that the weight loss rate of  $\text{Si}_3\text{N}_4$  substrate coated by  $\text{AlNbO}_4$ /mullite composite was less than that of  $\text{Si}_3\text{N}_4$  substrate coated by mullite during the first 50h corrosion test. The improved protective capacity of  $\text{AlNbO}_4$ /mullite composite coating was ascribed to the formation of glassy  $\text{AlNbO}_4$  top surface. After 100h corrosion test, the  $\text{AlNbO}_4$ /mullite coating was still stable and no further corroded cavities were observed. However, slight delamination of the coating and a faster weight loss rate was observed after long time corrosion due to the coefficient of thermal expansion (CTE) mismatch between  $\text{AlNbO}_4$ /mullite composite and  $\text{Si}_3\text{N}_4$  substrate.

**Key words:** mullite;  $\text{AlNbO}_4$ ; environmental barrier coating; water vapor corrosion

On the development of ceramics gas turbine systems, Si-base ceramics, especially  $\text{Si}_3\text{N}_4$  and SiC, are potential materials because of their excellent high temperature strength and durability<sup>[1-2]</sup>. However, recent studies of silicon nitride gas turbine components have shown that recession occurs after engine field tests due to the high volatilization of normally protective silica layer<sup>[3]</sup>. Thus environmental barrier coating (EBC) is needed to protect Si-based ceramic components to ensure long-term mechanical reliability and lifetime performance<sup>[4-5]</sup>. Mullite, because of its high temperature mechanical strength, low thermal expansion coefficient and excellent oxidation resistance, was thought to be a promising candidate for EBC<sup>[6-8]</sup>. However, the poor high temperature water vapor resistance limits the use of mullite ceramics in combustion environments, which contain a lot of water vapor<sup>[4-5, 9]</sup>. Recent studies have proved that the decomposition of mullite in water vapor environment was caused by the formation of volatile  $\text{Si}(\text{OH})_4$ <sup>[9]</sup>.

To overcome this problem, EBC systems for non-oxides ceramics have been proposed by several research groups<sup>[1, 4-5]</sup>. Many materials such as YSZ, BSAS,  $\text{Ta}_2\text{O}_5$  and rare earth disilicates are all thought to be potential candidates for EBC.  $\text{Nb}_2\text{O}_5$  has similar CTE and other properties with  $\text{Ta}_2\text{O}_5$ , so  $\text{Nb}_2\text{O}_5$  and/or its relative composites may be also promising materials for EBC sys-

tem.

In this study, mullite and  $\text{AlNbO}_4$ /mullite composite coatings were prepared by APS method on  $\text{Si}_3\text{N}_4$  substrate and tested in water vapor environment. The correlation between the corrosion protection and phase transformation, microstructure evaluation and chemical composition of the coatings were studied by XRD, SEM and EDS analysis.

## 1 Experiment

Two kinds of powders with nominal compositions of  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  and  $(3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2)_{0.95}(\text{AlNbO}_4)_{0.05}$  were synthesized by commercially available  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Nb}_2\text{O}_5$  (99.9% purity, Beijing Modern Eastern Fine Chemical, Co. Ltd, Beijing, China) powders. The oxides were mixed by a conventional ball milling process with  $\text{ZrO}_2$  balls in ethanol for 48h then sintered in Multifunctional Furnace (High-mulit 5000, Naberthern, Germany) for 10h at 1600°C to obtain mullite and  $\text{AlNbO}_4$ /mullite composite powders. After spray drying process, the powders with average diameters of 40 $\mu\text{m}$  were deposited on  $\text{Si}_3\text{N}_4$  substrate by APS method. The average thicknesses of the coatings were about 100 $\mu\text{m}$ . A summary of the APS conditions is given in Table 1.

Water vapor corrosion test was carried out in a High Raise Temperature Tube Furnace (SJG-16C, Yuxi, Chi-

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na). The samples were placed on a platinum holder into an aluminum tube and heated up to 1400°C for 100h at the rate of 1°C/min. A wet gas consisted of about 50vol% H<sub>2</sub>O and 50vol% air was introduced into the tube. The weight losses of the corroded samples were recorded every 10h.

The CTE of the AlNbO<sub>4</sub>/mullite composite was measured by Differential Scanning Calorimetry (TG/DSC, STA 409 PC/PG, NETZSCH, Germany). The phase transformation, microstructure evaluation and chemical composition changes before and after the corrosion test was studied by X-ray diffractometer (XRD, D/max-III, Rigaku, Japan) and scanning electron microscope (SEM, LEO1530, LEO, Germany) equipped with the energy dispersive X-ray spectra (EDS).

## 2 Results and discussion

Figure 1 shows the weight losses of Si<sub>3</sub>N<sub>4</sub> substrates coated by mullite and AlNbO<sub>4</sub>/mullite composite, respectively. In the first 50h, the weight loss of Si<sub>3</sub>N<sub>4</sub> coated by AlNbO<sub>4</sub>/mullite composite is 0.18mg/cm<sup>2</sup>, which is much less than that of Si<sub>3</sub>N<sub>4</sub> coated by mullite, 0.30mg/cm<sup>2</sup>. Less weight loss rate indicates that AlNbO<sub>4</sub>/mullite composite coating has improved protective capacity. However, in the second 50h, an accelerated weight loss rate is observed for AlNbO<sub>4</sub>/mullite composite coated Si<sub>3</sub>N<sub>4</sub> substrate, the final weight loss is 0.85mg/cm<sup>2</sup>, which is higher than that of mullite coated

Si<sub>3</sub>N<sub>4</sub> substrate, 0.46mg/cm<sup>2</sup>. The reason for the accelerated weight loss will be discussed hereinafter.

Figure 2(a) and (b) show the surface SEM images of as-prepared APS mullite coating and AlNbO<sub>4</sub>/mullite composite coating. Both of the surfaces are formed of sphere-like particles with average diameters of 40μm.

Figure 2(c) and (d) display the surface SEM images of the coatings after 100h corrosion test. For mullite coating, corroded cavities can be observed anywhere. High resolution SEM image reveals that the particles are corroded, leaving big cavities on the surface, as shown in Fig. 2(e). While for the AlNbO<sub>4</sub>/mullite composite coating, it is very surprised that no corroded cavities appear on the surface. Comparing to Fig. 2(e), the spherical particles are formed of small sheets and covered by a glassy layer, as shown in Fig. 2(f).

The EDS analysis of the sheet particles in Fig. 2(f) is shown in Fig. 3(a). The EDS analysis of the sheets confirms that the most common chemical composition is  $n(\text{Al}):n(\text{Si}) \approx 3:1$ . Therefore, the closest chemical composition is 3Al<sub>2</sub>O<sub>3</sub> · 2SiO<sub>2</sub>. While Fig. 3(b) reveals that the glassy phase contains large amounts of Al and Nb with  $n(\text{Al}):n(\text{Nb}) \approx 1:1$ . Some Si and Na elements can also be detected. Combining the XRD results hereinafter, the glassy phase is mainly AlNbO<sub>4</sub>.

Figure 4 displays the XRD patterns of mullite coating and AlNbO<sub>4</sub>/mullite composite coating before and after corrosion test. It is noticed that the as-prepared mullite coating consists of mullite and Al<sub>2</sub>O<sub>3</sub>. After 100h corrosion, the amount of Al<sub>2</sub>O<sub>3</sub> increases significantly due to the decomposition of mullite and volatilization of Si(OH)<sub>4</sub>. For the AlNbO<sub>4</sub>/mullite composite coating, no Al<sub>2</sub>O<sub>3</sub> can be detected, mullite is the primary phase, coexisting with AlNbO<sub>4</sub> phase. After corrosion test, mullite phase decreases causing by its decomposition, meanwhile AlNbO<sub>4</sub> phase increases clearly.

Figure 5 shows the cross-section SEM images of mullite coating and AlNbO<sub>4</sub>/mullite composite coating after 0, 50 and 100h corrosion test. It is noticed that no obvious cavities are observed in both as-prepared coatings, as shown in Fig. 5(a) and (b). After 50h corrosion test, some cavities with size of about 20μm are observed for mullite coating. Meanwhile, the corroded cavities formed in AlNbO<sub>4</sub>/mullite composite coating are much less. This also indicates that AlNbO<sub>4</sub>/mullite composite coating has improved protective capacity. With increasing of corrosion time to 100h, the corroded cavities in mullite coating becomes more and larger, as shown in Fig. 5(e). On the contrary, for AlNbO<sub>4</sub>/mullite composite coating,

Table 1 Spray parameters for EBC coatings

Current /A	Voltage/V	Spray distance/mm	Plasma gas, Ar/(L · min <sup>-1</sup> )	Powder feeding/(g · min <sup>-1</sup> )
550	65	100	3	40

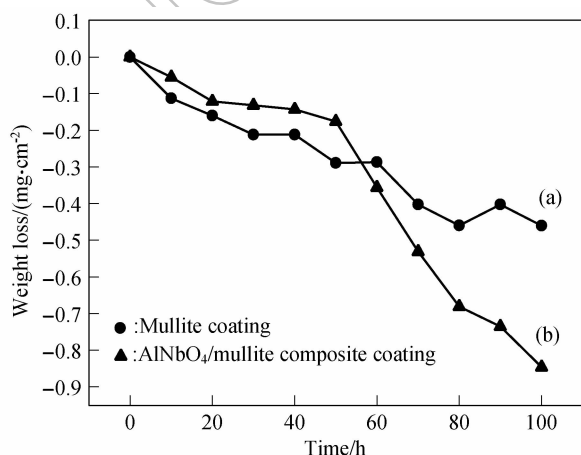


Fig. 1 Weight loss of Si<sub>3</sub>N<sub>4</sub> substrate coated by (a) mullite and (b) AlNbO<sub>4</sub>/mullite composite

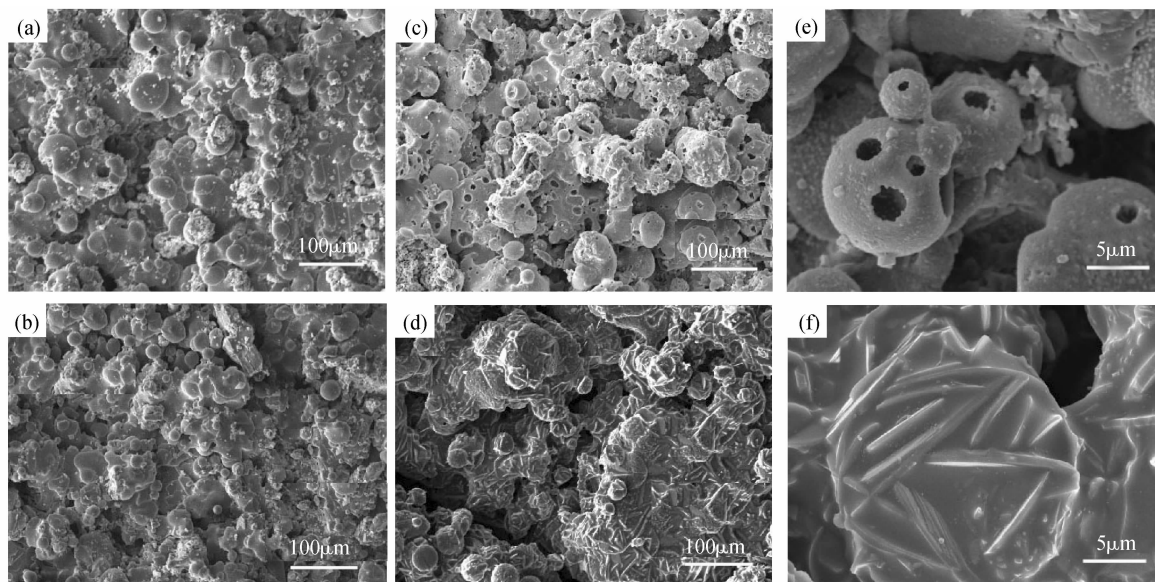


Fig. 2 The surface SEM images of (a) as-prepared mullite coating, (b) as-prepared  $\text{AlNbO}_4$ /mullite coating, (c) and (e) corroded mullite coating, (d) and (f) corroded  $\text{AlNbO}_4$ /mullite coating

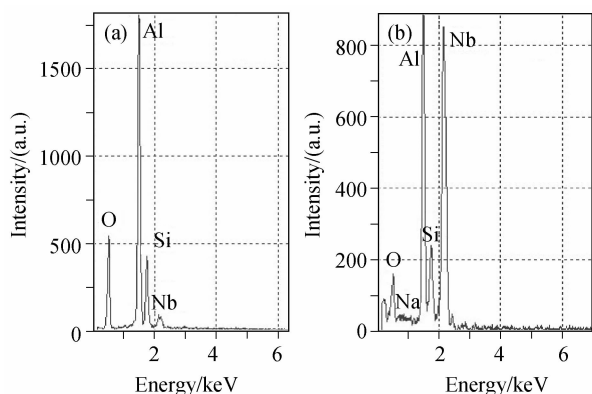


Fig. 3 EDS analyses of (a) sheet particles and (b) glassy phase

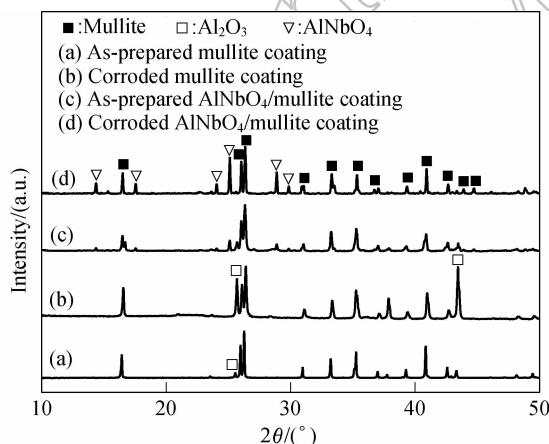


Fig. 4 XRD patterns of mullite coating and  $\text{AlNbO}_4$ /mullite composite coating before and after 100h corrosion test

no significant increase of corroded cavities is observed due to its improved stability in water vapor environment. However, the  $\text{AlNbO}_4$ /mullite coating has delaminated partially from the  $\text{Si}_3\text{N}_4$  substrate, which is thought to be

the reason for the accelerated weight loss from 50h to 100h.

The improved stability of  $\text{AlNbO}_4$ /mullite composite coating in water vapor environment is ascribed to the appearance of glassy  $\text{AlNbO}_4$  layer. Lee *et al* reported that mullite and its  $\text{SiO}_2$ -rich boundary phase were easily corroded in water vapor environment by forming volatile  $\text{Si}(\text{OH})_4$ <sup>[1]</sup>. In the present work, it is noticed that the  $\text{AlNbO}_4$ /mullite composite coating was covered by a layer of glassy  $\text{AlNbO}_4$  phase and could not contacted directly with the corrosive water vapor. Therefore the decomposition of mullite was restrained. Although the Al element could also volatilize from  $\text{AlNbO}_4$  phase by forming  $\text{Al}(\text{OH})_3$ , as suggested by Fritsch *et al*, the volatilization rate was much less than that of  $\text{Si}(\text{OH})_4$ <sup>[9]</sup>. The accelerated weight loss from 50h to 100h was due to the slight delamination of  $\text{AlNbO}_4$ /mullite composite coating. The CTE of  $\text{AlNbO}_4$ /mullite composite is tested to be  $7.5 \times 10^{-6}/\text{K}$ , which is larger than that of mullite ( $5.5 \times 10^{-6}/\text{K}$ ) and  $\text{Si}_3\text{N}_4$  ( $4 \times 10^{-6}/\text{K}$ )<sup>[1]</sup>. The CTE mismatch is thought to be the main reason for the delamination of the coating. The design of an adherence layer such as  $\text{SiO}_2$  may solve this problem, which will be our next work.

### 3 Conclusion

$\text{AlNbO}_4$ /mullite composite EBC was prepared on  $\text{Si}_3\text{N}_4$  substrate by APS method. During water vapor corrosion test, the surface of the coating was covered by a layer of glassy  $\text{AlNbO}_4$ , which performed improved

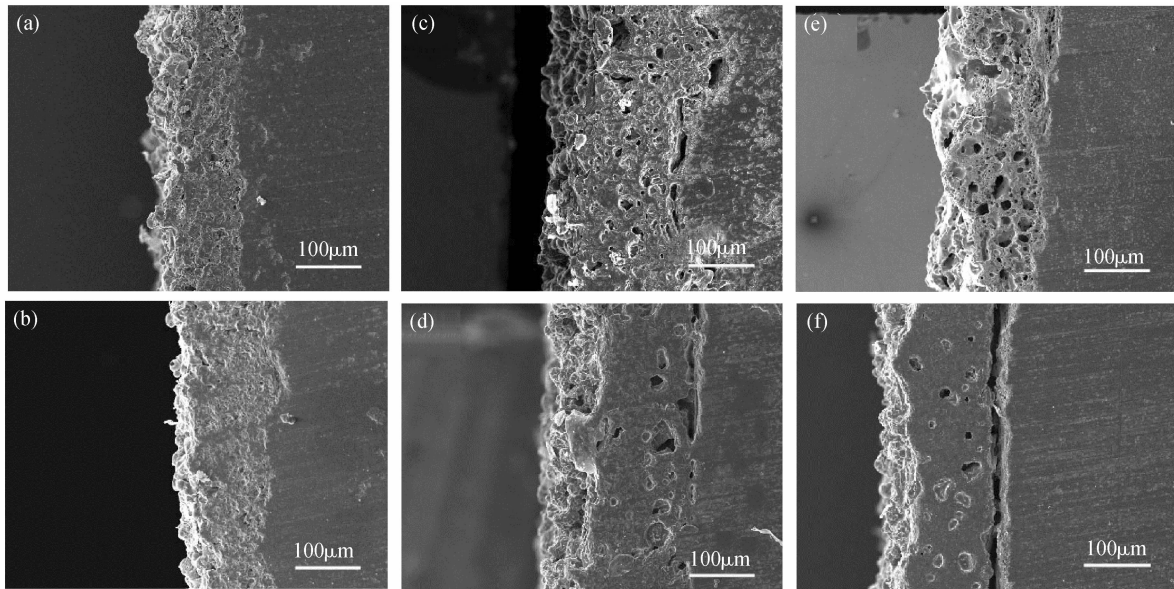


Fig. 5 Cross-section SEM images of mullite coating and  $\text{AlNbO}_4$ /mullite composite coating after (a), (b) 0h, (c), (d) 50h and (e), (f) 100h corrosion tests

protective capability. Unfortunately, slight delamination of the coating caused by CTE mismatch between  $\text{Si}_3\text{N}_4$  and  $\text{AlNbO}_4$ /mullite composite blocked its application. Reducing the CTE mismatch influence by designing a  $\text{SiO}_2$  adherence layer will be the further work.

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## 铌酸铝/莫来石复合陶瓷环境阻障涂层高温水蒸气腐蚀行为研究

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**摘要:** 利用大气等离子喷涂的方法在氮化硅基底上制备了铌酸铝/莫来石复合陶瓷环境阻障涂层. 铌酸铝的含量为 5mol%. 涂层置于 1400℃ 下含有 50vol%  $\text{H}_2\text{O}$  和 50vol% Air 的气氛中进行侵蚀实验. 总压力  $1 \times 10^5 \text{ Pa}$ , 实验时间 100h. 研究表明: 铌酸铝可以在涂层表面形成玻璃相保护层, 提高了涂层在高温水蒸气环境中的耐蚀性. 然而与氮化硅基底之间的热膨胀系数差异会造成涂层在实验过程中发生轻微剥离的现象, 导致试件的失重增加.

**关键词:** 莫来石; 铌酸铝; 环境阻障涂层; 水蒸气侵蚀

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