Influence of Al$_2$O$_3$/YSZ micro-laminated coatings on high temperature oxidation and spallation resistance of MCrAlY alloys

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Abstract. Al$_2$O$_3$/YSZ micro-laminated coatings with different layers were prepared on MCrAlY alloys by magnetron sputtering and characterized by high-resolution field emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD). Results indicated that the laminated structures of Al$_2$O$_3$ and YSZ layers were observed with compact microstructure and the thickness at sub-micron level each layer. High-temperature cyclic oxidation test at 1000°C in air was performed to investigate the oxidation and spallation resistance of the coatings on MCrAlY substrates. Result shows that the coatings exhibit more excellent oxidation and spallation resistance with the increase of the layers, which can be attributed to the increase of stress tolerance and fracture toughness in the laminated coatings by the thinner layers and crack deflection toughening.

Keywords: Al$_2$O$_3$; YSZ; micro-laminated coatings; oxidation and spallation resistance; fracture toughness

1. Introduction
Due to the formation of a slowly growing protective alumina scale, MCrAlY-coatings (M=Ni, Co) are commonly used in the hottest sections of gas turbine components [1]. In industrial gas turbines, coatings of MCrAlY type are used as overlay coatings and as bond coats for thermal barrier coatings (TBCs) [2]. Constituents in a TBC system include superalloy substrate, superalloy bond coat (which is generally MCrAlY or Pt-modified nickel aluminate), ceramic coating (which is typically yttria-stabilized zirconia, YSZ), and thermally grown oxide (TGO) formed at the interface between the
bond coat and ceramic coatings during high temperature operation [3]. It is generally accepted that the growth rate, morphology, microstructure and adherence of the aluminum-based TGO scale during high-temperature service is of crucial importance for TBC life [4]. After long term exposure, the alumina scales have been shown to be prone to cracking and spallation due to the thermal expansion mismatch between the oxide and the metallic substrate [5]. So the processes of cracking and spallation are the key factors influencing the service lifetime [6]. In order to circumvent the drawback, it is a practical way to add a transition layer between MCrAlY and the ceramic top coating to form a more effective obstruction of oxygen diffusing and improve the interface situation [7].

The design of laminated composite coatings has been accepted as an effective way to improve the fracture toughness generally. Clegg and his assistants prepared the SiC/C laminated composite ceramic; the fracture toughness reached 15 MPa · m$^{1/2}$ and the fracture energy reached 4625 J/m$^2$, which are far greater than that of conventional materials [8]. It’s reasonable to deduce that the laminated composite coatings can exhibit beneficial effects in the high-temperature application. He Y D and his co-workers developed the Al$_2$O$_3$/YSZ micro-laminated coatings in various preparation methods, which exhibit more excellent oxidation and spallation resistance than the coating with single phase [9,10]. Tomaszewski et al. demonstrate that the crack deflection in alumina layer was found to be the main mechanism responsible for an increase in mechanical properties of the layerd zirconia/alumina composites [11]. So it’s necessary to investigate the influence of laminated coatings on the high-temperature oxidation and spallation resistance in more detail.

As an effective technology to prepare coatings, the magnetron sputtering (MS) succeeds in application of many fields [12-14]. MS has sorts of comparative advantages such as higher deposition rate, more excellent density and bonding property. In this paper, thinner Al$_2$O$_3$/YSZ laminated composite coatings were prepared on MCrAlY substrates by magnetron sputtering. When verifying the number of layers, the influence of Al$_2$O$_3$/YSZ coatings on the high-temperature oxidation and spallation resistance was investigated and the mechanisms of such excellent performance were discussed.

2. Experimental procedure
Laminated composite coatings were sputtered onto the surface of MCrAlY by magnetron sputtering, with the layers of Al$_2$O$_3$ prepared by reactive magnetron sputtering. In the procedure of preparing Al$_2$O$_3$, DC electrical source was adopted with some influencing factors as 120°C of the substrate temperature, 0.5Pa of Ar and O$_2$ as working gas with the proportion of 7:1, 540V of voltage, 160mA of current flow, and 70mm of distance between target and samples. During the preparation of YSZ, RF electrical source was used with 0.5Pa of Ar as working gas, the same substrate temperature and distance between target and samples. The scale of substrate is 10mm × 10mm × 3mm. The ingredient of MCrAlY is Ni-39.5, Co-32, Cr-20, Al-8, Y-0.5. All the surface of samples were ground to #2000 abrasive, followed by ultrasonic cleaning with acetone and ethanol, and then cleaned by ionized water.

The high-temperature behavior of coatings was investigated by cyclic oxidation at 1000°C in air. After sputtered, the test samples were exposed in high-temperature environment induced by tube type resistance furnace 10 hours every time in quartz crucibles. After every break the samples and quartz crucibles were cooled to the room temperature by natural cooling, then the total weight and the weight
of quartz crucible without sample were both measured by electronic balance with an accuracy of $10^{-5}$ g. With a series of mentioned data, the curve of weight gain and spallation per unit area can be drew, where we can get some useful information about high-temperature behavior.

Si substrate was used to observe the cross-section morphology of the composite coatings due to its electronical conductivity and brittle fracture characteristic. The cross-section morphology and surface image of coatings were obtained by high-resolution field emission SEM. Phases of the laminated coatings and oxide scales formed after oxidation were both analyzed by X-ray diffraction ($\text{CuK}_\alpha$, $\lambda=0.15406$ nm, step wise of 0.02°, continuous scanning).

3. Results

3.1 Characterization of $\text{Al}_2\text{O}_3$/YSZ laminated composite coatings with different layers

The FE-SEM images of $\text{Al}_2\text{O}_3$/YSZ laminated composite coatings with different layers prepared by MS were showed in the figure 1. It’s clearly revealed in figure 1(a) that the coatings are very dense and comprised with uniform nano-particles. Figure 1(b) shows the cross-section of the $\text{Al}_2\text{O}_3$ single coating, and figure 1(c)~1(f) shows the cross-sections of the laminated composite coatings with three layers, five layers, seven layers and nine layers. For convenience, they are simplified as 1-layer, 3-layer, 5-layer, 7-layer and 9-layer. The total thickness of each component is mainly constant while the aggregate thickness is about 6 μm. The interfaces between layers are distinct without any cracks or flaws due to the compact bond from the magnetron sputtering.

![Figure 1. FE-SEM images of $\text{Al}_2\text{O}_3$/YSZ laminated composite coatings: (a) surface of the coatings; (b) 1-layer coating; (c) 3-layer coatings; (d) 5-layer coatings; (e) 7-layer coatings; (f) 9-layer coatings.](image)

3.2 High-temperature cyclic oxidation test of the micro-laminated coatings on MCrAlY substrates

Figure 2 shows the experimental results of cycle oxidation test of different samples at 1000°C in air for 400h. It can be illustrated from figure 2(a) that all the samples with different layers have smaller
weight gain than the blank sample (1.34 mg/cm$^2$). And the oxidation resistance of samples with different layers is improved greatly as the layers increase. The 9-layer laminated coatings exhibit the best oxidation resistance with 0.26 mg/cm$^2$ weight gain per unit area. Figure 2(b) reveals that the spallation resistance of samples with different layers exhibits an ascensive trend when increasing the number of the layers. The spallation of the sample with nine layers is as few as 0.09 mg/cm$^2$, which is much smaller than that of the blank sample and the sample with 1-layer coating. With a same total thickness, more layers of Al$_2$O$_3$ and YSZ means more interfaces and each layer becomes thinner. From these oxidation kinetic curves of samples, there is a trend summarized that the more layers of Al$_2$O$_3$ and YSZ at a certain total thickness, the better high temperature oxidation and spallation resistance the specimen has.

![Figure 2](image2.png)

**Figure 2.** Cyclic oxidation kinetic curves of samples with laminated coatings at 1000℃ for 400h (a) weight gain per unit area versus time; (b) spallation per unit area versus time.

3.3 Characterization of samples after high-temperature cyclic oxidation test

![Figure 3](image3.png)

**Figure 3.** FE-SEM surface images of different samples after cyclic oxidation: (a) blank; (b) 1-layer coating; (c) 3-layer coatings; (d) 5-layer coatings; (e) 7-layer coatings; (f) 9-layer coatings.
Figure 3 illustrates the surface morphologies of the samples after high-temperature cyclic oxidation test. The blank sample exhibits a rough surface with mainly needle-like morphologies of $\theta$-$\text{Al}_2\text{O}_3$ as shown in figure 3(a). It can be found obviously that the scale of all the microcracks existed in different coatings is rather slight. The top layer in figure 3(b) has been fragmented, which means large area of spalling. Compared to others, figure 3(f) shows a more smooth and intact surface morphology with cracks at the smallest size. After high-temperature cyclic oxidation test for 400h, the composite coatings with nine layers maintained the laminated structure comparatively completely, where the smallest residual stress can be inferred. Put in another way, the 9-layer coatings show excellent spallation resistance in the high-temperature environment. Figure 4 shows the cross-section images of sample with 9-layer coatings after cyclic oxidation and that of the blank sample as a comparison. The 9-layer laminated coatings were reserved integrally with some cracks throughout one layer and thin TGO after cyclic oxidation. Besides, the blank sample was oxidation severely with thicker TGO contained many cracks and voids. In figure 5, the XRD results show that, after cyclic oxidation, t-$\text{ZrO}_2$ and $\alpha$-$\text{Al}_2\text{O}_3$ are identified as stable phases at the room temperature which could ensure the excellent oxidation and spallation resistance of the laminated coatings.

![Cross-section images of samples after cyclic oxidation](image1.png)

**Figure 4.** Cross-section images of samples after cyclic oxidation: (a) blank; (b) 9-layer coatings.

![XRD spectra of different samples](image2.png)

**Figure 5.** XRD spectra of different samples after cyclic oxidation at 1000°C for 400h: (a) blank; (b) 1-layer coating; (c) 3-layer coatings; (d) 5-layer coatings; (e) 7-layer coatings; (f) 9-layer coatings.
4. Discussion

It has been acknowledged that the excellent oxidation and spallation resistance of the laminated composite coatings are attributed to fundamental conditions: (1) thermodynamically stable constituent phases [15-17]; (2) entirely sealed structure of the component with low oxygen diffusion coefficient (here is Al\textsubscript{2}O\textsubscript{3} [18]) on the substrate; (3) special mechanical properties which benefit from the as-designed laminated structures. The excellent oxidation and spallation resistance of the Al\textsubscript{2}O\textsubscript{3}/YSZ laminated composite coatings acquired by increasing the number of layers can be analyzed as follows.

(1) The increase of the stress tolerance in the laminated structures

The basic formula about fracture toughness of materials is shown as follows [19]:

\[ K_{IC} = \sigma_c \sqrt{aY} \]  

Where \( K_{IC} \) is the critical stress intensity factor (fracture toughness), \( \sigma_c \) is the critical stress for crack propagation, \( a \) is the half length of crack and \( Y \) is a geometrical factor related to the shape and loading modes. \( K_{IC} \) and \( Y \) are constant in certain conditions. When the total thickness is constant, the thickness of each layer will decrease with the increase of the number of layers. The propagation processes of the cracks in vertical direction could be limited in a shorter length, no more than the thickness of one layer. Thus, it can be inferred from the above formulas that the coatings could stand the higher critical stress, which means the mechanical properties of the laminated coatings could be improved significantly. The shorter micro-cracks guarantee the maximum sealed function as shown in the figure 3(f), which avoids further oxidation of the substrate. So the oxidation resistance can be improved relatively by increasing the number of layers.

(2) The increase of the fracture toughness in the laminated structures

The toughening effect of the laminated structures can be attributed to the energy release mechanisms in various forms, such as crack deflection or crack bifurcation, while there is no macroscopic damage occurred in the coatings. As the cracks in vertical direction can be limited in a shorter length, the cracks deflection will occur more easily, benefited from the more interfaces, which means the cracks propagation path would be extended as shown in figure 6 [20]. And then more strain energy would be released, which could improve the fracture toughness of laminated composite coatings. Thus, with the

\[ \text{Figure 6. Toughening mechanism of crack deflection in laminated composite coatings} \]
increase of layers, the more excellent mechanical properties can bring in the better spallation and oxidation resistance of micro-laminated coatings.

5. Conclusions
In this paper, the oxidation and spallation resistance of Al₂O₃/YSZ micro-laminated coatings with different layers were investigated. The conclusions can be drawn as follows:
(1) The oxidation and spallation resistance of Al₂O₃/YSZ micro-laminated coatings prepared by magnetron sputtering on MCrAlY substrates could be improved significantly by increasing the number of layers while keeping the total thickness constant.
(2) The beneficial effects could be attributed to the increase of stress tolerance and fracture toughness in the laminated coatings by the thinner layers and crack deflection toughening.

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