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# High temperature behavior of a diffusion barrier coating evolved from $ZrO_2$ precursor layer

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ABSTRACT

The zirconia ($ZrO_2$) as a precursor layer for the diffusion barrier coating (DBC) was deposited by electron beam physical vapor deposition (EB-PVD) between the René N5 superalloy substrate and NiCrAl coating. The high temperature exposure for the N5/$ZrO_2$/NiCrAl system was carried out at 1000 °C for 5 h, 100 h and 200 h in atmosphere to investigate the structure evolution of the $ZrO_2$ precursor layer and the elements interdiffusion of the system compared with the N5/NiCrAl system. The results showed that a sandwich structural DBC ($\alpha$-$Al_2O_3$/rich-Zr/$\alpha$-$Al_2O_3$) was formed through redox reaction between zirconia and aluminum under high temperature, leading to the transformation of N5/$ZrO_2$/NiCrAl system into the N5/DBC/NiCrAl system. It was found that the sandwiched DBC could effectively suppress the interdiffusion of elements compared to the N5/NiCrAl system.

## 1. Introduction

The single-crystalline Ni-based superalloys as high-temperature structure materials have been widely applied in aerospace industry due to their excellent mechanical performance, especially the creep strength [1–3]. The outstanding performance is attributed to the increase of refractory metal elements, such as tantalum, rhenium, tungsten, and molybdenum [4]. However, the oxidation and corrosion resistance of the superalloys would deteriorate due to the reduction of Al and Cr relative contents.

MCrAlX (M: Ni, Co or Ni + Co, X: Y, Si, Hf) coatings have been used to protect Ni-based superalloys in high-temperature oxidation and corrosion environments. However, some problems would arise due to the elements interdiffusion between the MCrAlX coatings and the Ni-based superalloy substrate during high temperature service. The continuous growth of protective oxide film ($Al_2O_3$) on the MCrAlX coating surface would be hindered by the inward diffusion of Al and Cr from coating to substrate and the outward diffusion of the refractory elements. The Kirkendall voids could be produced through elements diffusion at the interface between the substrate and the coating, which could weaken the bonding force of substrate and MCrAlX coating [5]. The second reaction zone (SRZ) and topological close packed (TCP) phases in the substrate would be formed, resulting in the degradation of the creep strength [6].

In order to prevent the elements interdiffusion, many studies have been reported, such as equilibrium coatings (EQ coatings) and diffusion barrier coatings. The EQ coatings were developed to be in thermodynamic equilibrium with the underlying Ni-based substrate, which could minimize the elements interdiffusion and suppress the formation of SRZ due to the equal chemical potentials of the alloying elements between the coating and substrate [7–9]. Diffusion barrier coatings are mainly divided into two types, metals and ceramics. The metallic diffusion barriers, i.e. Ru [10], Re-Cr-Ni [11], Ni—W [12], have good bonding strength between Ni-base superalloy substrate and MCrAlX coating, but have poor blocking ability of elements interdiffusion. The ceramic diffusion barriers, i.e. AlN [13] and $\alpha$-$Al_2O_3$ [14], have a good ability to prevent interdiffusion but have the weak bonding strength due to their much lower thermal expansion coefficients than that of the substrate and MCrAlX coatings [15]. Therefore, the active diffusion barriers have been proposed by researchers [16–19]. As a source of oxygen, a precursor oxide layer with the lower thermodynamic stability than $\alpha$-$Al_2O_3$, such as $Cr_2O_3$ [16], Cr-O-N [17,18] and yttria partially stabilized zirconia [19], was applied to the interface between the substrate and MCrAlX coating to form a sandwich structural diffusion barrier coating ($\alpha$-$Al_2O_3$/rich-Metal/$\alpha$-$Al_2O_3$) through redox reaction. This sandwich structure can effectively prevent the elements interdiffusion, and also possesses high reaction bonding strength.

In this paper, the pure zirconia ($ZrO_2$) as a precursor layer of the active diffusion barriers was deposited between the N5 superalloy substrate and NiCrAl coating by electron beam physical vapor

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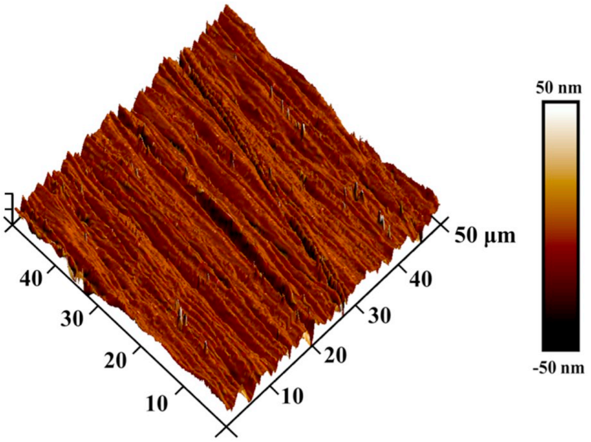

**Fig. 1.** AFM images of N5 superalloy substrates after polishing processing.

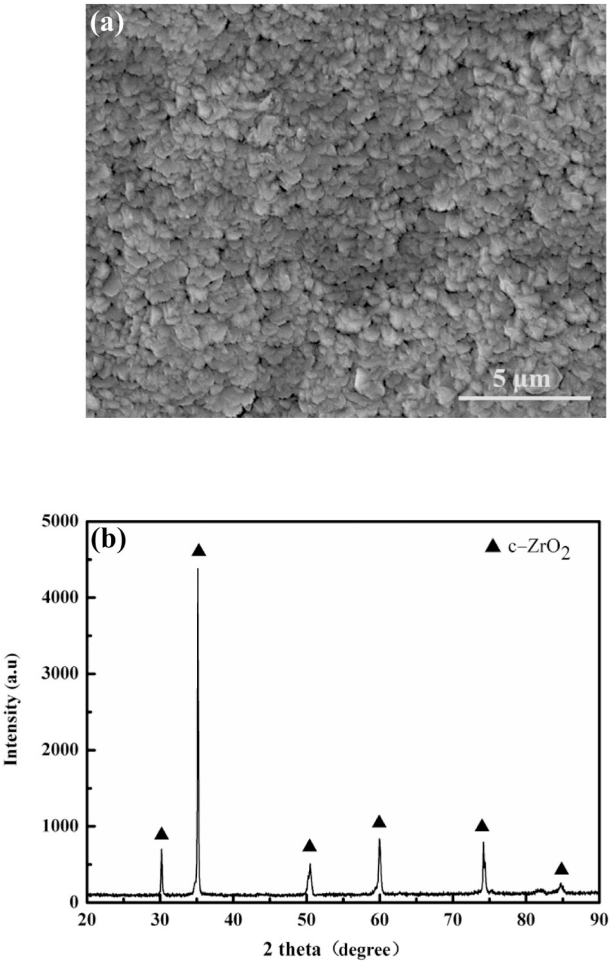

**Fig. 2.** Surface (a) and XRD pattern (b) of the as-deposited $ZrO_2$ coating.

deposition (EB-PVD). The structure evolution of the $ZrO_2$ precursor layer was investigated at 1000 °C with different exposure time. The interdiffusion and oxidation behaviors of the N5/DBC/NiCrAl system were analyzed compared to the system without DBC.

## 2. Experimental procedures

The single-crystalline Ni-based superalloy René N5 (nominal chemical compositions: 7 wt% Cr, 7.5 wt% Co, 5.0 wt% W, 6.2 wt% Al, 6.5 wt% Ta, 1.5 wt% Mo, 3.0 wt% Re, 0.15 wt% Hf, Ni: Bal.) was used as the substrate in this study. The N5 superalloy was cut into cylinder-shape with 10 mm diameter and 3 mm thickness. The surface of the specimens was cleaned by ultrasonic within ethanol and acetone after polishing.

The N5/$ZrO_2$/NiCrAl system was manufactured by electron beam physical vapor deposition (EB-PVD). The thin $ZrO_2$ precursor layer (purity: 99.9%) was deposited on the substrate at 800 °C, and then the Ni-20Cr-10Al coating was deposited on the $ZrO_2$ layer. The electron beam current for evaporating the $ZrO_2$ and NiCrAl targets was set at ~1.2A and ~1A, respectively. During the deposition, the vacuum of the evaporation chamber was kept at $\sim 10^{-3}$ Pa. The deposited thickness of the $ZrO_2$ precursor layer was 2 µm and that of the deposited NiCrAl coating was 15 µm. The N5/$ZrO_2$ system was produced to explore whether the $ZrO_2$ was dissolved during the deposition. The N5/NiCrAl system was also prepared for comparison.

After deposition, the high temperature exposure for N5/$ZrO_2$/NiCrAl system was carried out at the temperature of 1000 °C for 5 h, 100 h, and 200 h in air to observe the structure evolution of the $ZrO_2$ precursor layer. The interdiffusion and oxidation behaviors of the system were investigated by comparing with the N5/NiCrAl system at 1000 °C for 200 h.

The roughness of the substrate was characterized by Atomic Force Microscope (AFM, DIMENSION ICON, Bruker, USA). The surface and cross-section morphologies of the coatings were observed by scanning electron microscopy (SEM, JSM-6460, JEOL Ltd., Japan) equipped with the energy-dispersive spectrometer (EDS, X-Sight, Oxford instruments Co, Oxford, UK). The chemical bonding states of elements were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB250Xi, USA). The X-ray diffraction (XRD, D/MAX-2500, Rigaku, Japan) tests were performed to identify the phase constitution.

## 3. Results and discussion

### 3.1. Microstructural characterization of the as-deposited samples

Before depositing the $ZrO_2$ precursor layer, the surface roughness of the substrate was characterized by AFM. As shown in Fig. 1, the scanning area was 50 µm × 50 µm in every different regions of the substrate surface to calculate the mean value of Ra, and finally the obtained Ra was 13.1 nm.

Fig. 2 shows the surface morphology of the precursor layer in as-deposited N5/$ZrO_2$ system and corresponding XRD pattern. As shown in Fig. 2a, the rough surface is composed of fine grains. The XRD pattern (Fig. 2b) display that the component of the precursor layer was c-$ZrO_2$, which indicated that $ZrO_2$ was not decomposed during deposition.

Fig. 3 represents the surface image and XRD pattern of the NiCrAl coating. As shown in Fig. 3a, the surface of the NiCrAl coating presents a relative smooth surface. The XRD pattern (Fig. 3b) indicates that γ′-$Ni_3Al$, β-NiAl, and α-Cr were precipitated in as-deposited NiCrAl coating. According to the ICDD database, β-NiAl and α-Cr are bcc lattice structures with close lattice parameters ($a = 0.2880$ nm in β-NiAl and $a = 0.2879$ nm in α-Cr). Therefore, it is difficult to distinguish the two phases in XRD pattern. It was reported that, at ambient