

Interfacial Evolution Behavior of $ZrO_2(ZrB_2)$ Active Diffusion Barrier

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Abstract: Two sample groups, N5/(ZrB₂+ZrO₂)/NiCrAl and N5/ZrO₂/NiCrAl, were prepared on Ni-based single crystal alloy (Rene N5) substrate by electron beam physical vapor deposition (EB-PVD). Both sample groups were exposed to isothermal oxidation at 900 °C for 5 h and at 1000 °C, for 250 h, 300 h or 350 h. The microstructural evolution and deterioration failure behavior was investigated by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The results suggest that the introduction of ZrB₂ decelerates the interfacial reaction rate of the active diffusion barrier of Al₂O₃ but does not affect the final formation of the Al₂O₃ diffusion barrier with anti-diffusion properties. Moreover, the introduction of ZrB₂ prolongs the service life of active diffusion barrier structure and changes its failure mode.

Key words: MCrAlY coating; diffusion barrier; interfacial evolution

MCrAlY ($M = Ni, Co, Fe$) coatings, due to their outstanding oxidation resistance and good mechanical properties at high temperatures, have been widely used as a protective coating for Ni-based single crystal alloys and adhesive layers in thermal barrier coatings for the surface of aviation engine blades [1-3]. However, during the long-term service at high temperature, elemental interdiffusion occurs between the alloy substrate and MCrAlY coating [4], resulting in the continuous diffusion of Al in MCrAlY coatings towards the side walls of the substrate, while other alloying elements of the alloy substrates diffuse to the side walls of the coating. The interdiffusion behavior leads to the formation of a secondary reaction zone and the TCP harmful phase [4,5]. As a result, the service life as well as the creep resistance of engine blade is reduced [6]. Furthermore, with the constant increase of the bearing temperature in airplane blades, the insoluble alloying elements (Re, Mo and W) in Ni-based single crystal alloys became more complex, and hence the impact of interdiffusion was enhanced [5,6].

Therefore, researchers have applied a protective barrier

(i.e. diffusion barrier) in order to control the interdiffusion behavior between alloy substrate and MCrAlY coating [7-11]. The diffusion barrier materials normally include metal [7,8] (e.g. Pt, W, Ru) and ceramic [9-11] (e.g. Al₂O₃, TiN, CrN), among which Al₂O₃ exhibits the best barrier effect [9,11]. However, the directly prepared Al₂O₃ diffusion barrier has a weak bonding with the substrate, which easily leads to the occurrence of fracture during the application [12,13]. Wang et al. [9,14] introduced Ytria Stabilization Zirconia (YSZ) active diffusion barrier, namely a precursor layer of ZrO₂ that was first prepared between substrate and coating. Through an interfacial reaction, the compact and stable layer of Al₂O₃ was produced afterwards. The previously prepared diffusion barrier can significantly enhance the bonding between diffusion barrier and substrate or diffusion barrier and coating. However, the characteristic of active diffusion barrier was still a ceramic phase (Al₂O₃), so it had a higher thermal expansion coefficient than that of the nickel-based single crystal substrate and MCrAlY coating [9,14-16]. This means that thermal mismatch will occur when the coating is subjected to cyclic oxidation, leading to formation and growth of cracks,

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and eventually, the overall coating fails.

Therefore, in this research, on the basis of secondary phase strengthening mechanism, ZrB_2 particles were introduced into a ZrO_2 precursor layer to prepare ZrB_2 dispersion strengthening and ZrO_2 active diffusion barrier (BDSZ active diffusion barrier). The formation mechanisms of BDSZ active diffusion barrier and YSZ diffusion barrier and their interfacial evolution behavior during high-temperature service were investigated and compared.

1 Experiment

The substrate material was Ni-based single crystal superalloy, Rene N5 (Cr 7%, Co 8%, Mo 2%, W 5%, Ta 7%, Re 3%, Hf 0.15%, Al 6.2%, Ni 61.65%). The samples' dimensions were $\Phi 15 \text{ mm} \times 2 \text{ mm}$, and the EB-PVD target materials were ZrO_2 (99.9%), ZrO_2 -10% ZrB_2 (99.9%), and 61Ni-2Cr-11Al (99.9%).

The coating preparation process was as follows: firstly, the Rene N5 nickel-based single crystal high-temperature alloy was ground and polished. Secondly ZrO_2 -10% ZrB_2 precursor layer (denoted as BDSZ) and ZrO_2 precursor layer were deposited on the surface of substrates separately using EB-PVD equipment. Finally, NiCrAl coatings were simultaneously deposited in the two experiments, so that two sample groups, N5/ ZrO_2 /NiCrAl and N5/BDSZ/NiCrAl, were prepared. These two sample groups experienced isothermal oxidation at 900 °C for 5 h and at 1000°C for 250, 300 h or 350 h in a muffle furnace.

The microstructures of the coated samples were observed by a JSM-6700F field-emission scanning electron microscope (FESEM) with secondary electron images. And the INCAx-sight 7574 energy dispersive spectroscopy (EDS)

was used to analyze the chemical composition and elemental distribution within the micro-regions of the samples.

2 Results and Discussion

2.1 Microstructure of the as-received coating

Fig.1 presents the as-prepared interfacial microstructure of the two sample groups and the corresponding EDS line scanning results. As can be observed from Fig.1, the interfaces of N5 substrate/BDSZ precursor layer and BDSZ precursor layer/NiCrAl adhesive layer are clear, smooth and well bonded. The thicknesses of BDSZ precursor layer and NiCrAl adhesive layer are approximately 2 μm and 15 μm , respectively. No diffusion region is observed on the two interfaces of the BDSZ precursor layer. The combination of microstructure and EDS scanning results presented in Fig. 1c indicates that the element substrates in adhesive layer and substrate has some migration, while a clear diffusion barrier structure has not yet formed at the interface. However, regarding to the ZrO_2 activate diffusion barrier system (Fig.1b), the thicknesses of ZrO_2 precursor layer and NiCrAl adhesive layer are approximately 2 and 15 μm , respectively, which is consistent with those in the N5/BDSZ/NiCrAl system, indicating that introducing ZrB_2 into ZrO_2 precursor layer does not affect the deposition rate of the coating. Also, a dark contrasted laminar diffusion region is observed at the interface of ZrO_2 /NiCrAl adhesive layer. Combining with the of EDS scan results presented in Fig. 1d, the region could be determined as an Al_2O_3 layer, which indicates that, during the preparation process, the Al in NiCrAl diffuses into the ZrO_2 layer, reacts and forms Al_2O_3 diffusion barrier at the ZrO_2 /NiCrAl interface. However, no Al_2O_3 diffusion barrier is formed at the ZrO_2 /substrate interface, which

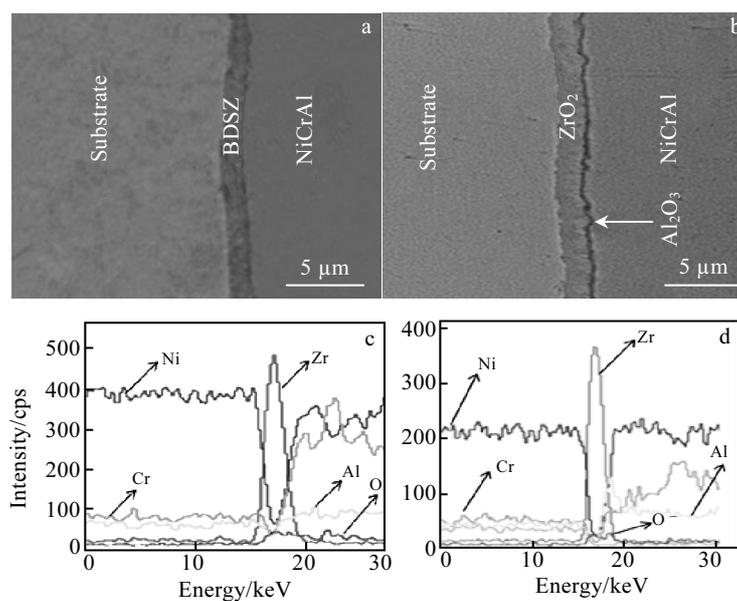


Fig.1 Cross-sectional SEM images (a, b) and EDS elemental line scanning (c, d) of N5/BDSZ/NiCrA (a, c) and N5/ ZrO_2 /NiCrAl (b, d) as-received coating

could be attributed to the slower diffusion rate caused by lower Al content in the substrate.

2.2 Formation of active diffusion barrier

Fig.2 shows the cross-sectional morphologies of the two sample groups and their corresponding EDS line scanning results, after the 900 °C/5h isothermal oxidation. As can be observed in Fig.2a, after 900 °C/5 h heat treatment, the N5/BDSZ/NiCrAl has a good bonding between the coating and the substrate and a smooth and compact interface between the coatings. Furthermore, dark contrasted strip areas appear at the interfaces of the N5substrate/BDSZ and the BDSZ/NiCrAl. The combination of the morphology and EDS scanning analysis (Fig.2c) indicates that, the dark contrasted strip areas are primarily composed of Al and O, and Ni, Cr form certain enrichment compounds in the vicinity of these areas. The results indicate that, during the isothermal oxidation heat treatment, the Al element in the substrate and the adhesive layer presents significant diffusion behavior and reacts with BDSZ layer to form Al_2O_3 diffusion barrier at the two interfaces. The formed Al_2O_3 diffusion barrier blocks the diffusion behavior of Ni, Cr and other elements, resulting in a certain enrichment of Ni and Cr elements around the Al_2O_3 diffusion barrier. In addition, it is also found that, lamellar morphology occurs inside the BDSZ layer, i.e. the side adjacent to the NiCrAl coating is dark gray contrasted while the side near substrate is light gray contrasted (Fig.2a). EDS line scanning analysis (see Table 1, Spectra 4 and 5) reveals that, the contents of Ni, Cr, Al in Spectra (5) are significantly higher than the corresponding content values in Spectra (4), which indicates that the formation rate of Al_2O_3 diffusion barrier at the side of BDSZ/NiCrAl is relatively low, so that a

certain amount of Ni and Cr could diffuse into the BDSZ layer before the compact barrier layer is formed.

This is probably due to the introduction of ZrB_2 which reduces the absolute content of ZrO_2 ; therefore, during the interfacial reaction process, the number of collisions between Al and ZrO_2 atoms at the BDSZ/NiCrAl interface is fewer than that at the ZrO_2 /NiCrAl interface, namely the frequency factor of BDSZ/NiCrAl interface is lower than that of ZrO_2 /NiCrAl. Also, introducing ZrB_2 may also affect the orientation of ZrO_2 in collision^[17]. The overall impact of these factors finally results in the lower reaction rate at the diffusion barrier interface of the BDSZ system, and thus more Ni and Cr diffuse into the BDSZ layer. For the N5-based/ ZrO_2 /NiCrAl system (see Fig. 2b), after high-temperature heat treatment, the coating still possesses a good bonding with the substrate and the interface is still smooth, compact and defect-free; dark contrasted strip areas are formed at both sides of ZrO_2 layer. Combined with EDS analysis, it is found that Al_2O_3 diffusion barrier is formed at these locations, and the Al_2O_3 diffusion barrier formed adjacent to the NiCrAl coating is thicker, due to the higher Al content in NiCrAl coating than that in the substrate, which is consistent with the results of the as-prepared samples (Fig. 1b).

2.3 Evolution behavior of interfacial structure under high temperature service

Fig.3 shows the SEM analysis results of cross-sectional micro-morphologies of the two coating systems after 1000 °C/250 h isothermal oxidation. As presented in Fig.3a, each coating of the N5/BDSZ/NiCrAl system remains intact with no cracks; the bonding between coatings is good and more uniform. The thickness of Al_2O_3 diffusion barrier on

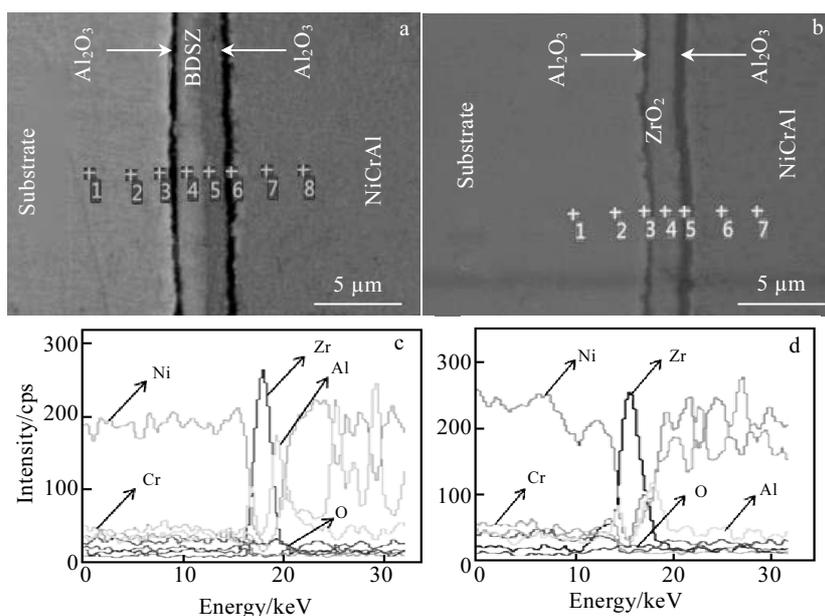


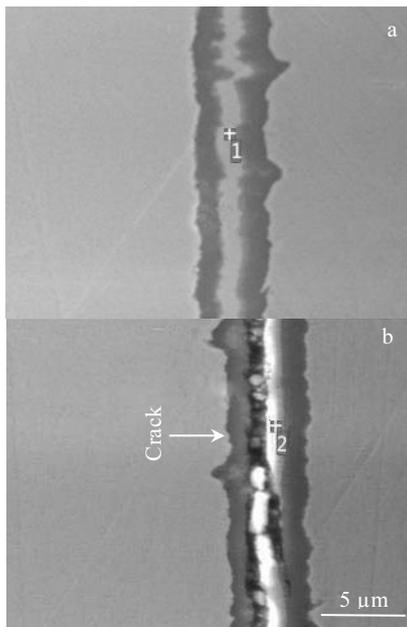
Fig.2 Cross-sectional SEM images (a, b) and EDS elemental line scanning (c, d) of N5/BDSZ/NiCrAl coating (a, c) and N5/ ZrO_2 /NiCrAl coating (b, d) after 900 °C /5 h

Table 1 Chemical composition of points 1~8 marked in Fig.2a obtained by EDS (at%)

Point	O	Al	Cr	Co	Ni	Zr
1		4.99	7.32	8.38	64.68	
2		4.90	6.01	7.21	68.20	
3	24.18	7.87	4.50		21.37	42.08
4	22.16	1.12	2.86		6.99	66.87
5	17.68	10.69	12.44		36.81	22.38
6	9.50	18.47	28.52		40.15	3.36
7		9.33	16.48		74.19	
8		7.17	28.34		64.49	

the two sides of BDSZ is increased, while the thickness of Zr-rich interlayer is decreased to a certain extent, which indicates that during the cyclic oxidation process, the Al on each side has a diffusion reaction with the BDSZ layer, although the extent of the diffusion reaction in this process is not high. However, for the N5/ZrO₂/NiCrAl system (see Fig.3b), after 250 h isothermal oxidation, although the interfaces of both substrate/Al₂O₃ diffusion barrier and the Al₂O₃ diffusion barrier/NiCrAl have good bonding with no defects or cracks, significant fracture damage occurs inside the Al₂O₃/Zr-rich layer/Al₂O₃ "sandwich" structure.

Further investigation with EDS point scanning analysis of the Zr-rich layer (the interlayer in the active diffusion barrier structure) of the two coating systems (see Table 2) shows that, the Ni, Cr, Al atom contents in the Zr-rich layer of the N5/ZrO₂/NiCrAl system are higher than those in the Zr-rich layer of the N5/BDSZ/NiCrAl system, indicating that more substances with Ni, Cr, Al phases are formed around the Zr-rich layer of the N5/ZrO₂/NiCrAl system.

**Fig.3** SEM images of N5/BDSZ/NiCrAl (a) and N5/ZrO₂/NiCrAl (b) sample after 1000 °C /250 h oxidation**Table 2** Chemical composition of points 1 and 2 marked in Fig.3 obtained by EDS (at%)

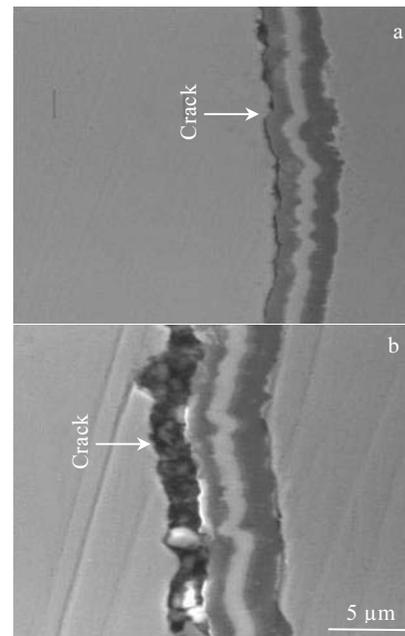
Point	O	Al	Cr	Ni	Zr
1	25.62	5.63	1.92	4.88	61.95
2	33.35	13.78	1.28	6.88	44.71

The formed substances primarily consist of Al₂O₃, oxygen-deficient zirconia and mixed phases of Ni and Cr. With the increase of high-temperature oxidation time, the presence of Ni and Cr mixed phase will lead to the volume expansion of the interfacial of Al₂O₃/Zr-rich layer, the increase in stress and eventually the formation of cracks. Therefore, in terms of the N5/ZrO₂/NiCrAl system, once cracks appear, they will expand rapidly and result in interfacial fracture, since the formed "sandwich" active diffusion barrier is primarily composed of ceramic phases. In terms of the N5/BDSZ/NiCrAl system, although mixed phase is also formed in the Al₂O₃/Zr-rich layer/Al₂O₃ "sandwich" structure, the presence of ZrB₂ will play the role of dispersion strengthening, which can increase the toughness of such a "sandwich" structure, and prevent the generation and expansion of cracks, thereby increasing the high-temperature service life of the active diffusion barrier structure.

2.4 Failure of BDSZ diffusion barrier

In order to further investigate the failure behavior of BDSZ diffusion barrier, the cyclic oxidation at 1000 °C was carried out on the BDSZ system sample and the results are presented in Fig.4.

After 300 h oxidation at 1000 °C (Fig.4a), cracks emerge in the N5/BDSZ/NiCrAl sample, within a location at the

**Fig.4** Cross-sectional SEM images of N5/BDSZ/NiCrAl sample after 1000 °C /300 h (a) and 1000 °C /350 h (b)

interface between the active diffusion barrier and the substrate, while no cracks are observed at the interface near the NiCrAl. Also, no cracks are found inside the "sandwich" structure "Al₂O₃/Zr-rich layer/Al₂O₃".

However, as the oxidation time reaches 350 h (Fig.4b), the active diffusion barrier/substrate interface has thoroughly fractured with obvious cracks at the interface of active diffusion barrier/NiCrAl, indicating the thorough coating failure. In addition, no cracks are observed inside the Al₂O₃/Zr-rich layer/Al₂O₃ "sandwich" active diffusion barrier. Therefore, it can be inferred that the introduction of ZrB₂ can definitely enhance the self-toughness of active diffusion barrier structure; however during the long-term high-temperature oxidation process, the coarsening phenomena caused by creep behavior of the substrate and the adhesive layer, and the thermal mismatch between the metal and ceramic phases finally lead to the deterioration failure of the BDSZ diffusion barrier.

3 Conclusions

1) The introduction of ZrB₂ decelerates the interfacial reaction of active diffusion barrier structure but it does not affect the final formation of the Al₂O₃ diffusion barrier layer with anti-diffusion properties.

2) The introduction of ZrB₂ can enhance the toughness of the active diffusion barrier and improve the anti-oxidation performance of the coating system at high temperature, which prolongs the high-temperature service life of the coating structure.

3) During the high-temperature serving process, the creep behavior and interfacial coarsening of the BDSZ active diffusion barrier cause the deterioration and failure of sample system.

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ZrO₂(ZrB₂)活性扩散障界面演变行为的研究

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摘要: 采用电子束物理气相沉积(Electron Beam Physical Vapor Deposition, EB-PVD)技术在镍基单晶合金 Rene N5 基体上制备出 N5/(ZrB₂+ZrO₂)/NiCrAl 和 N5/ZrO₂/NiCrAl 两组试样。然后, 同时对其进行 900 °C/5 h 恒温氧化和 1000 °C/250 h、1000 °C/300 h 及 1000 °C/350 h 循环氧化, 并采用 SEM、EDS 分析方法研究了界面演变行为及退化失效行为, 结果表明, ZrB₂ 的加入对活性扩散障界面反应的生成速率有一定的延缓, 但不影响具有阻扩散功能的 Al₂O₃ 扩散障层的最终形成; 并且, ZrB₂ 的加入提高了活性扩散障结构的服役寿命, 改变了活性扩散障结构的失效方式。

关键词: MCrAlY 涂层; 扩散障; 界面演变