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Formation and behavior of thermal barrier coatings on nickel-base superalloys①

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Abstract: Plasma-sprayed thermal barrier coatings (TBCs) have been used to extend the life of combustors. Electron beam physical vapor deposited (EB-PVD) ceramic coating has been developed for more demanding rotating as well as stationary turbine components. Here 3 kW RF magnetron sputtering equipment was used to gain zirconia ceramic coatings on hollow turbine blades and vanes, which had been deposited NiCrAlY by cathodic arc deposition. NiCrAlY coating surface was treated by shot peening; the effects of shot peening on the residual stress are presented. The results show that RF sputtered TBCs are columnar ceramics, strongly bonded to metal substrates. NiCrAlY bond coat is made of β, γ′ and Cr phases, ZrO_2 ceramic layer consists of t' and c phases. No degradation occurs to RF ceramic coatings after 100 h high temperature oxidation at 1 150 ℃ and 500 thermal cycles at 1 150 ℃ for 2 min, air-cooling.

Key words: magnetron sputtering; thermal barrier coating; shot peening; high temperature oxidation
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1 INTRODUCTION

Performance improvements in high temperature mechanical systems have resulted in increasingly severe operating environments for high temperature structural materials, particularly in gas turbines. The efficiency of gas turbines for aircraft propulsion has steadily improved in recent years. The need for great performance of advanced turbine engines requires even higher operating temperatures and longer operating lifetimes[1]. Thermal barrier coatings deposited on the hot components are developed for these applications[2-6]. The main difficulty for TBCs is the abrupt change in composition and properties at the interface, which tends to promote ceramic layer spallation. So this type of coating demands special microstructure for the service requirement[7, 8].

There are a lot of methods to produce insulating ceramic coatings[9-12], and the price of the deposition equipment is very different. In this study, the RF sputtering method is adopted because it is a rather simple and economic method. In the early time, TBCs on gas components are generally produced by plasma spraying, which provides better thermally isolating TBCs. But the strain accommodation capability of the ceramic is impaired, and the coatings have less tolerance against mechanical and erosive attack. Electron beam physical vapor deposition is another method to obtain TBCs. EB-PVD yields smooth aerodynamically attractive coatings with outstanding high temperature capabilities, but the equipment is expensive. TBCs by RF sputtering have similar columnar microstructure with EB-PVD TBCs, and the cohesive strength and adhesive strength are much higher than those of other coatings.

2 EXPERIMENTAL

First, NiCrAlY coatings were produced on blades and specimens by cathodic arc deposition. The chemical compositions of NiCrAlY coating and DD3 single crystal superalloy substrate are shown in Table 1. The bond coat was sprayed onto a rotating substrate with arc current of 600-700 A, bombardment voltage of 300 V, and workpiece voltage bias of 20-30 V. Second, they were vacuum heat treated at 950 ℃ for 1-3 h. Then shot peening was used to give a smooth surface, 30-100 μm in thickness of the NiCrAlY bond coats were peened with d150-200 μm stainless steel beads. Third, the ceramic coatings with the target compositions of 8% Y_2O_3 stabilized ZrO_2 were prepared. The average distance between substrate and the target was 100 mm. Zirconia was deposited by RF sputtering at 3-5 μm/h on the rotating substrates. It is important the Ar and oxygen gas flows are fixed, and the working gas pressure remains 0.8-1.2 Pa, sputtering power 1.5-2.5

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Table 1 Chemical compositions of NiCrAlY coating and DD3 alloy(mass fraction, %)

Material	Cr	Co	Al	Mo	W	Y	Ti	Ni
NiCrAlY coating	22 - 23	–	8 - 10	–	–	0.1 - 0.3	–	66.9 - 69.9
DD3 alloy	9.5	5.0	5.9	3.8	5.2	–	2.2	Bal.

kW, cathode voltage 1 800 - 2 200 V and discharge current 1 - 3 A. The thickness of ZrO_2 coating is from 60 μm to 200 μm.

The coated samples were investigated by scanning electron microscopy(SEM). The chemical compositions were determined by X-ray diffraction(XRD) phase analysis and electron probe microanalysis(EPMA). The density of bond coat was analyzed using volumetric weight method.

3 RESULTS AND DISCUSSION

3.1 Effects of shot peening on microstructure and residual stress of NiCrAlY coating

A small quantity of porosity and microgap were observed in the NiCrAlY bond coat deposited by the cathodic arc method. They were found to disappear after shot peening. The microstructures of the coatings are shown in Fig. 1. The surface became smoother. The coarseness test results show that R_z value is changed from 16.4 μm to 3.3 μm. The surface changed denser. The density measurements indicate that the average density before shot peening is 5.420 g/cm^3, and it increases to 7.057 g/cm^3 after shot peening. The improvement of density is sure to increase the cementation obstruction of oxygen element to the coating at high temperature.

Cyclic oxidation curves are shown in Fig. 2. The experiment was carried out using DD3 single crystal superalloy, NiCrAlY coating and peened NiCrAlY coating. The thicknesses of the coatings are respectively 70 μm and 60 μm. The samples were annealed at 1 150 ℃ for 55 min, then followed by air quenching for 5 min.

It has been found that the oxidation resistance of DD3 substrate is very low, four hours later lose mass began. NiCrAlY coating gains mass to the highest nearly 10 h later, and loss of mass appeared 60 h later. Peened NiCrAlY coating has higher endurance, and 40 h later gains mass to the highest, and 85 h later loss of mass appeared. The oxidation resistance of shot peened coatings has been improved 3 times than that of the unpeened coatings. The optimizing of shot peening parameters and heat treatment process can enhance the oxidation property of the coatings.

Residual stress measurement was carried out on

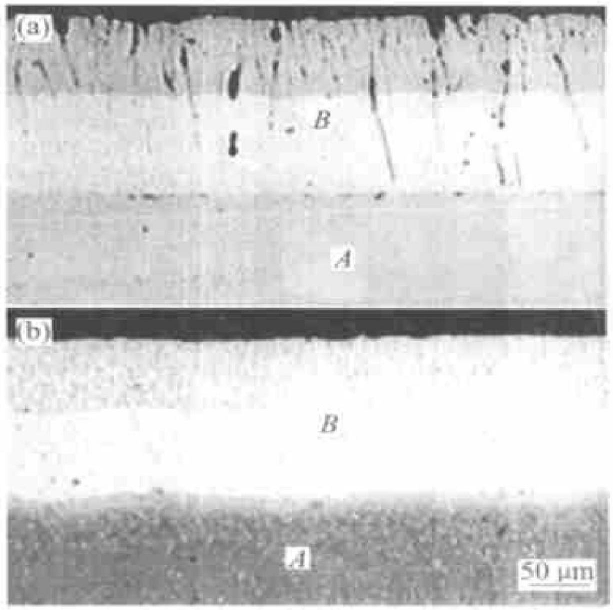

Fig. 1 Microstructure of NiCrAlY coatings
(a) —Before shot peening; (b) —After shot peening
A —Substrate; *B* —NiCrAlY coating

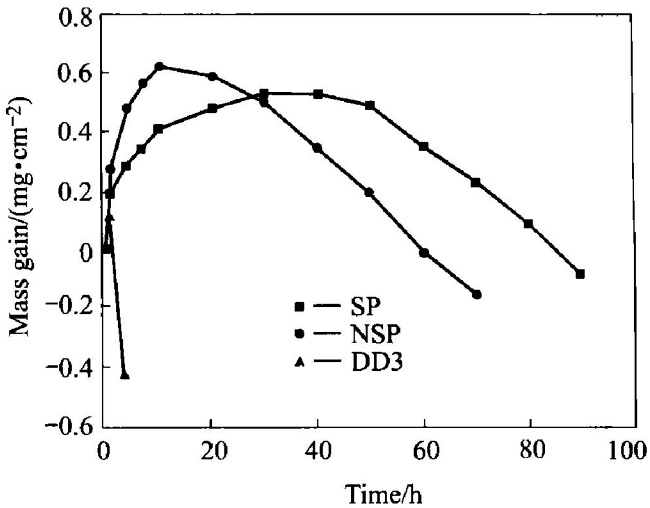

Fig. 2 Cyclic oxidation behaviors of coatings
NSP —No shot peening; SP —Shot peening;
DD3 —DD3 superalloy

X-ray strain diffractometer using CuK$_\alpha$ radiation[13]. The determinations of σ_r have relation to shot diameter and shot peening intensity. Fig. 3 shows the σ_r-δ curves of the unpeened and peened specimens. Investigation on NiCrAlY coatings and peened coatings reveals that the NiCrAlY bond coat shows residual tensile stress, after shot peening, the whole depth profile changes to residual compressive stress. The depth of compressive stress is above 100 μm. In the mean time, the effects of heat treatment temperature on the residual stress have been investigated. When the temperature is above 500 ℃, the compressive stress decreases significantly. When the sample was aged at 1 100 ℃ for 1 h, the residual compressive stress disappeared completely.

3.2 Microstructure and chemistry of TBCs

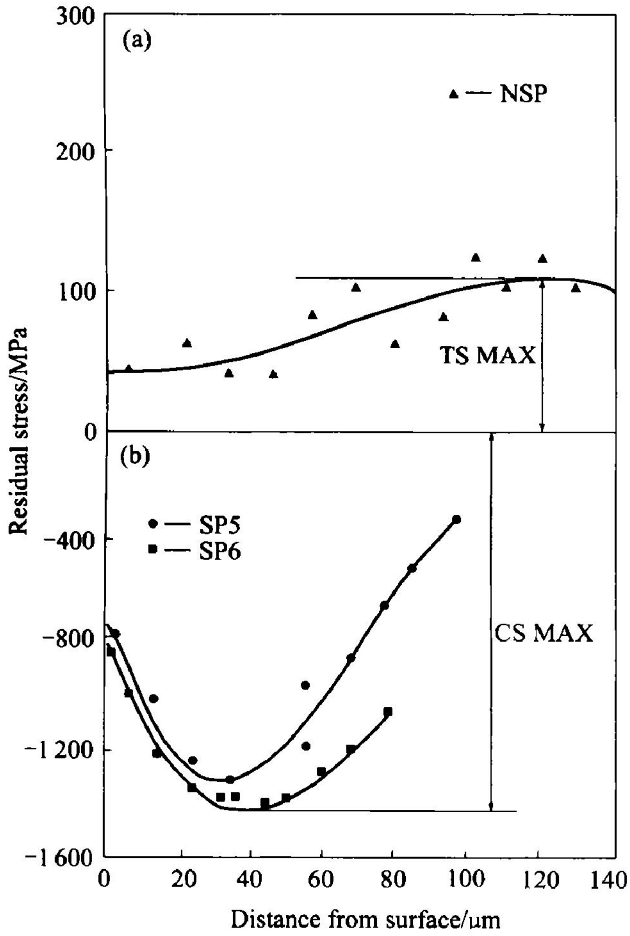

Fig. 3 Depth profile of σ_r- δ curves for NiCrAlY and shot peening coatings

NSP —No shot peening; SP5 —Shot peening sample 5; SP6 —Shot peening sample 6

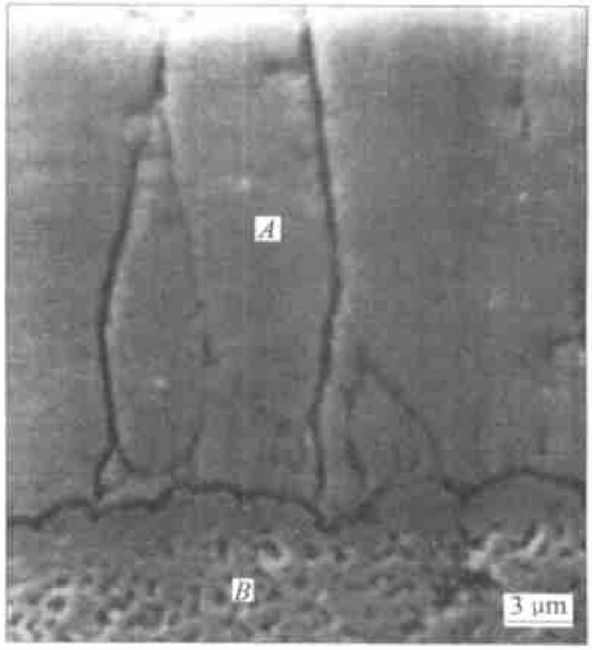

Fig. 4 Micrograph of thermal barrier coating obtained by RF sputter

A —ZrO_2 coating; *B* —NiCrAlY bond coat

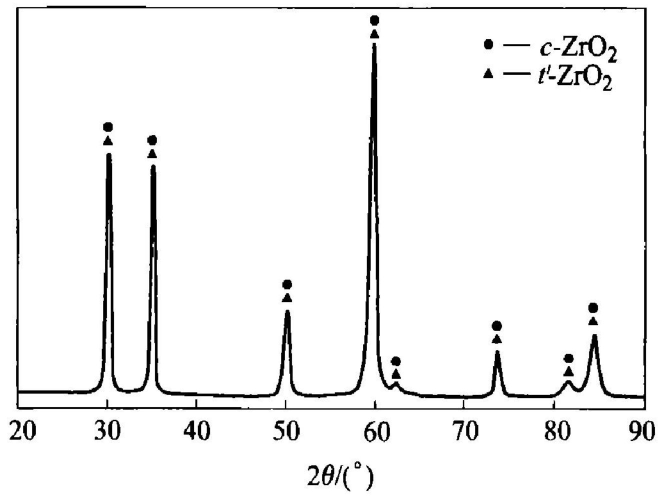

Fig. 5 X-ray patterns of ZrO_2 ceramic layer

The surfaces of thermal barrier coatings are quite smooth with gray color, and they change white through aging. Fig. 4 shows the cross-section of a typical coating. The ZrO_2 layer is dense and columnar growth ceramic. The columnar structure is perpendicular and tightly bonded to the surface of the NiCrAlY bond coat. After 1 h ageing, a continuous alumina layer was present between the NiCrAlY layer and the ceramic coating. Observation reveals that the structures are hillocks in shape, and they are homogeneous equiaxial grains with reliable adherence to each other. No cracks and porosity were found on the specimen.

X-ray diffraction result of NiCrAlY bond coat is γ' and Cr phases, and β(NiAl) phase is found near the interface of ceramic and metallic coating. The as-deposited ZrO_2 ceramic layer mainly consists of t'-ZrO_2 and c-ZrO_2. The X-ray patterns are shown in Fig. 5. The distinction between c and metastable non-transformable t' phases by peak separation within the {400} peak area necessitates careful analytical work on adequate high resolution XRD equipment. Depending on the yttria content, either the cubic phase or the tetragonal t' phase is stabilized. This result is different from the report, which confirms the occurrence of single phase t' in EB-PVD TBCs, the formation of t' phase via a rapid quenching process during PVD is assumed to occur. In this paper, there is an obvious change of phases content after annealing treatment with different experimental conditions, cubic ZrO_2 increases, and t'-ZrO_2 decreases with prolonging treatment temperature and time.

3.3 High temperature oxidation and thermal shock resistance

The following three kinds of samples were subjected to oxidation test: ZrO_2/NiCrAlY coatings whose thicknesses of metallic coatings were separately 30 μm, 60 μm and 60 μm. The thicknesses of the thermal barrier coatings were 90 μm, 120 μm and

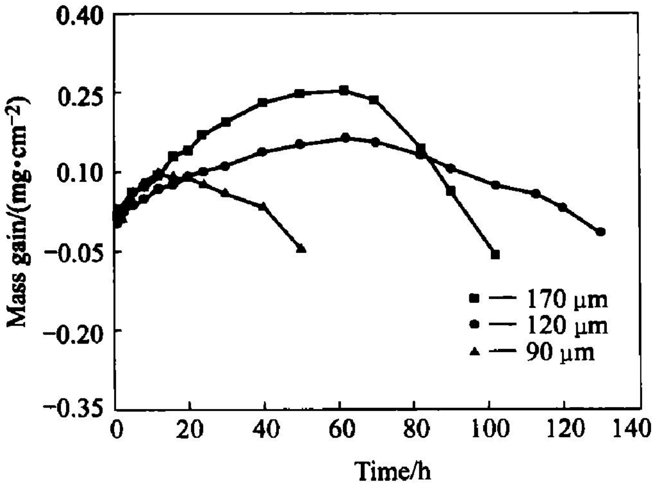

Fig. 6 Oxidation behavior of sputtered TBCs at 1 150 ℃

170 μm. Oxidation behavior is shown in Fig. 6. At 1 150 ℃, the mass gain curve shows before 70 h, outer coating of 170 μm TBCs has higher endurance than that of the others. EPMA results reveal that the Al_2O_3 scales are formed near the interface between ZrO_2 ceramic layer and NiCrAlY bond coat after high temperature oxidation experiment. Prolonged exposure to a high temperature-oxidizing environment may lead to coating failure, crack formation between the ceramic and metal bond coat occurred as the cycle's number approaches to that of loss of mass beginning. Among them most part of 90 μm coating tends to delaminate and spall. Comparatively, additional internal oxide layer of NiO and Cr_2O_3 has been observed beneath the Al_2O_3 layer in 120 μm thick sample, a small amount of breakage appears on the surface.

Experimental and theoretical thermal characterization of TBCs has shown that they can provide significant thermal benefits to blades in operation, but only if the coating integrity is maintained. ZrO_2 ceramic layer is applied on the top of the NiCrAlY coating; the ceramic layer provides thermal insulation, and the NiCrAlY bond coat protects the substrate against oxidation. Zirconia is extensively used as a TBCs since it has low thermal conductivity and a relatively high coefficient of thermal expansion. It is known that the zirconia layer is ventilated to oxygen, the thickness of NiCrAlY bond coat is crucial to the oxidation resistance ability of TBCs. The failure of RF sputtering ceramic happens by cracking associated with the thermally grown oxide layer that forms at the interface between the zirconia ceramic and the underlying metallic bond coat. While this layer is predominantly aluminum oxide, it also may incorporate oxides of other bond coat or substrate metals such as nickel, cobalt and chromium. The mechanical damage factor in the TBCs is the thermoelastic stress within the actual oxide layer, where spallation fracture occurs.

The blade and specimens with ZrO_2/NiCrAlY coatings were annealed at 1 150 ℃ for 2 min, then followed by air quenching for 2 min. No spalling or cracking of TBCs was observed on the surface of the blade after 500 cycles. Fig. 7 shows the surface micrograph of the blade after 500 cycles. The thickness of ZrO_2 ceramic coating is 200 μm. The surface is assumed to be advantageous with respect to cyclic oxidation resistance. The thermal shock resistance test on the turbine blade has shown significant increases in component durability. It is reasonable to expect the adhesion strength of the RF sputtering coating to be higher than that of EB-PVD coating.

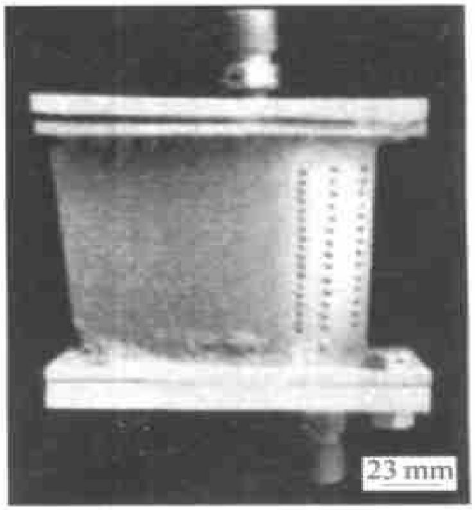

Fig. 7 Micrograph of blade after 500 cycles at 1 150 ℃

4 CONCLUSIONS

1) The present investigations have shown that the microstructure of RF sputtered TBCs is columnar ceramic, strongly bonded to metal substrates. The chemical composition of the coatings includes cubic and t' zirconia, and NiCrAlY bond coat made up of γ', β and Cr phases. Shot peening had been adopted to arc deposited NiCrAlY coating before ceramic layer was produced. All coatings measurement show compressive stresses translating from tensile stresses. A subsequent heat treatment caused clear changes in residual stresses. Measured stress values of annealed samples at 1 100 ℃ became very small. The oxidation resistance of the peened NiCrAlY coating was clearly improved compared with the unpeened coating.

2) Oxidation test investigations at elevated temperature confirmed the blades and specimens with TBCs have superior oxidation performance and good coating adhesion. Excellent thermal shock resistance of these coatings have been demonstrated at 1 150 ℃, 500 cycles. Further enhancement of the resis-

tance to environmental attack must focus on shot peening parameters and heat treatment process.

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