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Effects of vacuum pre-oxidation process on thermally-grown oxides layer of CoCrAlY high temperature corrosion resistance coating

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Abstract: The influence of the certain specific vacuum pre-oxidation process on the phase transformation of thermally-grown oxides (TGO) was studied. The CoCrAlY high temperature corrosion resistance coatings were produced onto the nickel-based superalloy substrate by high velocity oxygen fuel (HVOF). It suggests that the TGO usually consists of a great number of chromium oxides, cobalt oxides and spinel oxides besides alumina during the initial period of the high temperature oxidation if the specimens are not subjected to the appropriate vacuum pre-oxidation process. Furthermore, the amount of alumina is strongly dependent on the partial pressure of oxygen; while the $CoCr_2O_4$ spinel oxides are usually formed under the conditions of higher partial pressure of oxygen during the initial period of the high temperature of the isothermal oxidation. After the appropriate vacuum pre-oxidation process, the TGO is mainly composed of alumina that contains lower Y element, while alumina that contains higher Y element sporadically distributes, and the spinel oxides cannot be found. After a longer period of the isothermal oxidation, a small amount of porous $CoCr_2O_4$ and the chrome oxide sporadically distribute near the continuous alumina. Additionally, after the appropriate vacuum pre-oxidation process, the TGO growth rate is relatively slow.

Key words: vacuum pre-oxidation process; thermally-grown oxides (TGO); high velocity oxygen fuel (HVOF); spinel oxides

1 Introduction

Thermal barrier coatings (TBCs) have been widely used to protect the hot sections of gas turbine from high temperature oxidation in the areas of aerospace and electric power plant for several decades, thus it can significantly prolong the service lifetime of gas turbine [1–3]. A typical TBCs system usually consists of a bond coat MCrA1Y (M: Co, Ni or Co+Ni) and a ceramic top coat 7–8YSZ (7%–8% yttria stabilized zirconia, mass fraction). The MCrA1Y coatings were commonly used to protect the hot section parts of the gas turbine from the high temperature corrosion as well as applied to making the sensor parts for evaluating the performance of the gas turbine. In general, the TBCs system could be deposited by means of air plasma spraying, low pressure plasma spraying, vacuum plasma spraying, high velocity oxygen fuel, and electron beamphysical vapor deposition [4,5]. The performance of the coatings deposited by means of high velocity oxygen fuel (HVOF) commonly presents high density, high bond strength, and lower content of oxides.

In general, the performance of the NiCoCrAlY coatings with a certain amount of cobalt usually displays excellent plasticity, strong high temperature oxidation, especially much stronger corrosion resistance [6,7] than that of the NiCrAlY coating. In order to improve the mechanical properties and the resistance ability in high temperature oxidation and corrosion environment, the NiCoCrAlY coatings can be selectively modified by adding some trace elements such as Si, Ta, Hf and Mo. In addition, the CoCrAlY coatings that have high content of cobalt, chromium and aluminium can significantly

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improve the sulfur corrosion resistance ability in the gas turbines [8,9], but the high temperature oxidation resistance ability is lower than that of the NiCrAIY coating (650–900 °C). Currently, compared with the NiCoCrAIY, NiCrAIY and NiPtAl coatings, the published papers regarding the high temperature resistant CoCrAIY coatings cannot be easily found.

Previous studies indicate that the service lifetime of the MCrAlY high temperature corrosion resistance coatings is strongly dependent on the elemental inter-diffusion between the bond coat and the substrate as well as on the aluminium impoverishment in the bond coat. Furthermore, in the high temperature environment, the aluminium depletion in the metallic bond coat of TBCs may cause the presence of spinel oxides in TGO, which can lower the adhesive ability at the interface of TGO/topcoat; while the external diffusion of refractory elements in the substrate as a result of the elemental inter-diffusion between the bond coat and the substrate therefore degrades the resistant ability of high temperature oxidation and corrosion. Additionally, the presence of spinel oxides with large grains in the thermally-grown oxides layer often plays a significantly negative role, thus the presence of dense, continuous and pure alumina with slower growth rate and good adhesive ability is very helpful for prolonging the service lifetime of coatings. The factors such as the chemical composition of thermal spray powder, the parameter of thermal spray, the microstructure of thermally-grown oxides, and the certain specific pre-oxidation process should be taken into account carefully.

In this work, a certain specific vacuum pre-oxidation process was applied to the CoCrAIY coating and the parameters of this process were optimized. Subsequently, the samples placed into quartz crucible were set in a high temperature furnace. Finally, the phase compositions of the TGO were systematically studied.

2 Experimental

The Inconel 718 superalloy rods were sectioned into

the disc shape samples ($d25.4 \text{ mm} \times 3 \text{ mm}$). At first, the samples were blasted by use of the grit blasting machine (size of sand: white corundum $Al_2O_3/150-180$ µm; blasting pressure: 0.7 MPa; angle: 80°-90°), and subsequently cleaned in the mixture of the ethanol and acetone solution by using ultrasonic cleaning machine, finally dried by the electric heating constant temperature drying box. The chemical composition of CoCrAlY thermal spray powder (PWA 1348-2, Praxair Inc., USA) is listed in Table 1. The self-developed and energy-saving high velocity oxygen fuel system (TJ-9000, Tianjin University, China) produced by the thermal spray laboratory of Tianjin University was used to prepare the CoCrAlY coatings successfully, and the thickness of the prepared coating reached 200 µm roughly. The parameters of the high temperature corrosion resistance coatings deposited by using HVOF are shown in Table 2. Afterwards, the high vacuum sintering and heat treatment furnace (VHS-8812, Shenyang Jiayu Vacuum Technology Inc., China, limitation of vacuum degree: 2.6×10^{-3} Pa) was conducted for 4 h, and the heat rate was set as 8 °C/min from the room temperature. Ultimately, the samples placed in high temperature box furnace were conducted at 1050 °C for 8 h and 100 h, respectively. To identify the phase compositions of the thermally-grown oxides after isothermal oxidation, we used a Rigaku Dmax/2500 diffractometer using Cu K_a radiation (DMAX 2500, Rigaku Inc., Tokyo, Japan) equipped with grazing incident diffraction (GIXRD) (Grazing incidence: 2°, 2θ :10°-90°, scanning step: 0.02°, scanning speed: $3 (^{\circ})/\text{min}$), and the phase compositions were analyzed by the Jade 6.5 phase analysis software. The ultra-high resolution field emission scanning electron microscope (NoVaTM Nano SEM 430, FEI Inc., USA) equipped with X-ray energy dispersive spectrometer (EDS) was employed to characterize the morphologies and the chemical composition of thermally-grown oxides, and the chemical compositions of certain measurement areas was characterized by using the point scanning mode, line scanning mode and map scanning mode of EDS.

 Table 1 Chemical compositions of Inconel 718 superalloy substrate and PWA1348-2 thermal spray powder (mass fraction, %)

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Sample	Ni	Cr	Fe	Мо	Nb	Co	Mn	Si	Cu	Al	Ti	Y
Inconel 718	50-55	17-21	Bal.	2.8-3.3	4.75-5.5	1	0.35	0.35	0.3	0.2-0.8	0.7-1.15	_
PWA1348-2	_	23	_	_	_	Bal.	_	_	_	13	_	0.5

Table 2 Parameters of high velocity oxygen fuel process								
Propane		Oxygen		N ₂		Powder feed	Stand-off	
Pressure/MPa	$Flow/(m^3 \cdot h^{-1})$	Pressure/MPa	$Flow/(m^3 \cdot h^{-1})$	Pressure/MPa	$Flow/(m^3 \cdot h^{-1})$	$rate/(r \cdot min^{-1})$	distance/mm	
0.6	1.0	0.7	12	0.6	0.96	1	260-300	

3 Results and discussion

3.1 Effects of high temperature oxidation on CoCrAIY high temperature corrosion resistant coating

As shown in Fig. 1, the thickness of the CoCrAlY coating sprayed by HVOF process reaches 200 μ m roughly, and the presence of the wavy oxides with lamellar microstructure in the coatings can be obviously found compared with the NiCrAlY coating.



Fig. 1 Cross-sectional features of CoCrAlY coating deposited onto nickel-based substrate

As demonstrated in Fig. 2(a), the phase compositions of the thermally-grown oxides mainly consist of y-Co, Co27Al73, CoAl, CrO and Cr2O3. As shown in Fig. 2(b), after isothermal oxidation at 1050 °C for 40 min, the thermally-grown oxides layer is mainly composed of CoO, Co₂O₃, Co₂CrO₄, CrO and Cr₂O₃. For the samples subjected to the isothermal oxidation for 8 h, the phases such as CoO, CrO, Cr₂O₃, Co₂CrO₄, CoCr₂O₄ and α -Al₂O₃ can be found. The type of thermally-grown oxide decreases considerably after the isothermal oxidation for 50 h and only CoO, Co_2CrO_4 and α -Al₂O₃ can be identified. After the isothermal oxidation for 100 h, the phases in the TGO consist of CoO, CrO and Co₂CrO₄. However, the main phases in the TGO are α -Al₂O₃, Cr₂O₃ and CoCr₂O₄ after the appropriate vacuum pre-oxidation process.

As displayed in Fig. 3 (a), the thermally-grown oxides within the non-vacuum pre-oxidation specimens present two types of layers after the isothermal oxidation for 50 h. In Figs. 3(b) and (c), the granular and bulk oxides sporadically distribute onto the alumina that has small grains. In Fig. 3(d), according to the EDS line scanning analysis, the dark area is pure alumina layer, while the bright area consists of mixed oxides that probably contain chromium oxides, cobaltous oxides and spinel oxides. As presented in Table 3, the metallic



Fig. 2 GIXRD patterns showing phases of high temperature corrosion resistance coatings (a) and thermally-grown oxides scale as function of different time of isothermal oxidation at 1050 °C (b)

cations such as Ni²⁺, Co²⁺, Cr³⁺ and Al³⁺ will follow the principles of the thermodynamics and kinetics (according to the $\Delta_{\rm r}G_{\rm m}-T$ diagram that can evaluate the selective grain nucleation, the growth kinetics and thermodynamics), and the order of chemical reactions is as below: $Al_2O_3 \rightarrow Cr_2O_3 \rightarrow Ni(Co)Cr_2O_4$ (spinel) \rightarrow Ni(Co)O. This implies that the metallic elements may selectively oxidize at the initial stage of the isothermal oxidation for 8 h and the phases in the TGO are mainly composed of Al₂O₃, Cr₂O₃ and CoO whose grain sizes are less than 10 µm. As shown in Fig. 4(a), the thickness of the spinel layer significantly increases after the isothermal oxidation for 100 h. As presented in Fig. 4(d), the oxides whose grain sizes are above 10 µm can be easily found in the TGO besides the small ridged-grains. According to the EDS map (Fig. 4(e)), it can be supposed that the Co₂CrO₄ spinel oxides with large grains densely distribute among the alumina and cobalt oxides. In general, α -Al₂O₃, Cr₂O₃, NiO and (Ni, Co)(Cr, Al)₂O₄ oxides can be usually found in the TGO, and the proportions and morphologies of these oxides may strongly influence the degradation mechanism of TBCs.



Fig. 3 SEM images of specimens (non-vacuum pre-oxidation process) subjected to isothermal oxidation at 1050 °C for 8 h: (a) Cross-section of TGO; (b, c) Surface morphologies of TGO; (d) EDS line scan analysis of elements in TGO

Table 5 Standard Globs free energy at 1575 K						
Oxide	$\Delta_{\rm r} G_{\rm m}^{\Theta} / ({\rm kJ} \cdot {\rm mol}^{-1})$					
Al ₂ O ₃	-1239.1					
CoO	-135.7					
NiO	-122.8					
Cr ₂ O ₃	-769.6					
Y_2O_3	-106.2					

Table 3 Standard Gibbs free energy at 1373 K

Furthermore, the adhesive strength between the α -Al₂O₃ and top coat can be enhanced; while other oxides are often found to be porous, brittle and relatively low oxidation resistance. It is widely accepted that the nickel and cobalt elements in the coatings may be oxidized selectively as a result of the presence of the aluminium depletion area and the higher partial pressure of oxygen. The formerly formed spinel oxides can react with alumina, and finally Co₃O₄ and spinel and NiO mixture (CSN) with relatively large grains were found in the thermally-grown oxide layer. Compared with α -Al₂O₃, the spinel oxides whose grains are much larger usually sporadically distribute in the thermally-grown oxide layer. Generally, the spinel oxides not only present less adhesive ability [10] and discontinuous feature, but also excessively consume a large amount of alloy elements thus accelerating the degradation of the coatings. In fact, the presence of the spinel oxides can be responsible for the crack nucleation and propagation of the interface between the coatings and metallic substrate, while the continuous alumina with strong chemical stability and high fracture resistance usually have positive effects on prolonging the service lifetime of the coatings. There are following essential conditions for the formation of pure α -Al₂O₃: 1) low diffusion and reaction velocity of the oxygen ion and metallic cation; 2) strong chemical and thermodynamic stability of the formed instant oxides [11].

In fact, the main reasons for the failure of the high temperature corrosion resistance coatings are as follows: 1) the macro thermal stress caused by the mismatch of thermal expansion coefficient between the coating and metallic substrate; 2) the aluminium depletion and local stress caused by TGO unstably growth [12]. The continuous and pure α -Al₂O₃ with slow growth rate can provide a barrier for high temperature diffusion,



Fig. 4 SEM images of specimen (non-vacuum pre-oxidation process) subjected to isothermal oxidation at 1050 °C for 100 h: (a) Cross-section of TGO; (b–d) Surface morphologies of TGO; (e–h) EDS mappings of specimen in TGO; (i) Secondary electron image

indirectly extending the span life of the coatings. Paradoxically, the degradation of coatings is closely related to the TGO growth and the evolution of the inner thermal stress.

3.2 Effects of vacuum pre-oxidation process on high temperature corrosion resistant coating after isothermal oxidation

It is widely believed that the partial pressure of oxygen has significant effects on the formation of

different oxides in TGO, and the phases in TGO can be indirectly controlled under the controllable partial pressure of oxygen. As illustrated in Fig. 2(b), alumina cannot be found due to the high partial pressure of oxygen after 40 min isothermal oxidation, and a small amount of alumina is formed as the partial pressure of oxygen gradually decreases after the isothermal oxidation for 8 h. After the isothermal oxidation for 50 h, the intensity of alumina peak continues to increase, and the significant reduction of the chromium oxides and

cobalt oxides is probably because of the chemical follows: $(Cr_2O_3)CrO+(Co_2O_3)CoO \rightarrow$ reaction as Co₂CrO₄. For the CoNiCrAlY coatings, the spinel oxides form firstly, and then the Cr₂O₃ and Al₂O₃ oxides generate at the initial stage of the isothermal oxidation at 1000 °C [13]. The reason why the coatings degrade is probably because the thermally-grown oxide layer reaches a critical thickness that is strongly relied on the TGO growth rate and the adhesive ability. For instance, the doping with active elements (0.2%-0.5%) such as Y, Hf and La in MCrAl alloys can considerably increase the adhesion strength between the surface thermally-grown oxides and the coatings, to some extent, and enhance the critical thickness of the thermally-grown oxides layer when the coatings degrade. The specific mechanism for prolonging the service lifetime of coatings is to react with sulfur [14] and reduce the vacancy density of the interface between the thermally-grown oxides and coatings [15]. However, the overabounding yttrium in the alumina oxides of TGO will increase the growth rate of the thermally-grown oxide layer, and the specific mechanism of oxygen delivery short-circuit can result in the earlier failure of the coatings [16]. Moreover, the earlier study had shown that, compared with the single doping, the doping of yttrium and hafnium will not only strengthen the adhesion of thermally growth oxides, but also improve the properties of the thermal shock resistance [17]. As displayed in Fig. 5 and Table 4, the alumina (point A) and the spinel oxides (point B) can be easily found, and the YAG oxides (point C) that can distinguish them by the tiny pore, and the YAG with overabounding yttrium can provide much more channels for diffusion [18] than pure α -Al₂O₃, which can reduce the high-temperature oxidation resistance of the thermally-grown oxide layer. Nevertheless, many studies have indicated that the YAG oxides can improve the mechanical properties of the coatings due to the pinning



Fig. 5 SEM image of specimen (non-vacuum pre-oxidation process) subjected to isothermal oxidation at 1050 °C for 100 h, showing chemical composition and microstructure of peg thermally-grown oxide

Table 4	Phase and	alysis of th	nermally-gro	wn oxides	scale at	Iter
isotherm	al oxidatio	on at 1050	°C for differ	ent time		
Point	$w(\Omega)/\%$	w(Al)/%	w(Cr)/%	w(Co)/%	$w(\mathbf{Y})/\mathbf{G}$	%

Point	w(O)/%	w(Al)/%	w(Cr)/%	w(Co)/%	w(Y)/%
A	12.66	66.30	7.70	13.34	_
В	18.04	4.04	29.50	48.42	-
С	18.49	49.77	14.37	12.31	5.06
D	17.34	62.14	7.21	10.94	2.37
Ε	20.21	71.68	3.08	3.59	1.45
F	20.26	33.73	14.06	29.02	2.93
G	30.13	40.21	13.61	14.21	1.84
H	25.95	44.69	12.86	10.65	5.85
Ι	30.75	57.90	5.35	3.53	2.46
J	22.75	34.58	21.98	17.76	2.94
Κ	23.87	73.89	0.69	1.06	0.49

effect (point *C*). Consequently, the mechanism of pinning effect often occurs when yttrium can be found in the alumina oxides, which has dual functions.

As shown in Figs. 6(a) and (c) and Table 4, after a certain specific vacuum pre-oxidation process, the main phases in the TGO can be found to be alumina with high yttrium (points D and F) and alumina with low yttrium (points E and G) that sporadically distributes. The grain sizes of these oxides range from 0.4 to 1 µm, and the spinel oxides cannot be easily found (Fig. 6(c)). This suggests that the control of the pressure of oxygen by appropriate vacuum pre-oxidation process can effectively reduce the initial formation of the spinel oxides. In general, the yttrium atom whose diameter is large can dissolve into the grain lattices of alumina partly, which have effects on the θ -Al₂O₃ $\rightarrow \alpha$ -Al₂O₃ phase transformation and the growth rate of TGO. HAN et al [19,20] believes that the thermal stability of alumina is strongly affected by the physical properties and diffusion behaviours of other cations except for Al³⁺ during the thermal diffusion. The process of phase transformation can be significantly influenced by different cations, indirectly changing the growth rate of the metastable θ -Al₂O₃ (or γ -Al₂O₃) and the stable α -Al₂O₃ when the aluminium atom is adequate. The doping cations with large diameters such as hafnium and yttrium can inhibit the formation of α -Al₂O₃ because these doping cations mostly solute into the grain lattice of the metastable Al₂O₃, while the doping cations with small diameter tend to solute into the stable Al₂O₃ with dense microstructure thus accelerating the growth rate of α -Al₂O₃.

It is very critical to point out that the mechanism of aluminium diffusion is modified due to the inadequate aluminium during the high temperature oxidation. In order to prolong the service lifetime of coatings, the CSN oxides should be reduced to a certain degree and



Fig. 6 SEM images of specimen after vacuum pre-oxidation process: (a) Cross-section of TGO; (b, c) Surface morphologies of TGO

indirectly decrease the thickness of TGO and the TGO growth rate. The spinel oxides cannot be easily formed in a low oxygen pressure environment. Meanwhile, the formation of α -Al₂O₃ may reduce the oxygen pressure further, which can prevent the formation of the adverse oxides. The reduction of both the TGO growth rate and the content of spinel oxides can decrease the residual stress in the TGO, thus the oxidation resistance and the thermal cycling of the coatings can be extended.

As shown in Fig. 7(a) and Fig. 8, the TGO layer mainly contains alumina after isothermal oxidation at 1050 °C for 8 h. In Table 4, the bright area (point *H*) that consists of yttrium in the alumina shows a similar chemical composition compared with the specimens within the vacuum pre-oxidation process. In Figs. 7(b) and (c), the spinel oxides cannot be easily found in the TGO, and the grain size of the alumina is much more uniform (0.5 μ m). As shown Fig. 9(a) and Fig. 10, the TGO layer is mainly composed of alumina after



Fig. 7 SEM images of specimens (vacuum pre-oxidation process) subjected to isothermal oxidation at 1050 °C for 8 h: (a) Cross-section of TGO; (b, c) Surface morphologies of TGO



Fig. 8 EDS analyses of TGO subjected to isothermal oxidation at 1050 °C for 8 h



Fig. 9 SEM images of specimen (vacuum pre-oxidation process) subjected to isothermal oxidation at 1050 °C for 100 h: (a) Crosssection of TGO; (b, c) Surface morphologies of TGO

isothermal oxidation at 1050 °C for 100 h and the average grain size of alumina reaches 1 μ m (Fig. 9(c)). As displayed in Figs. 9(a) and (b), a small amount of porous CoCr₂O₄ oxides (point *J*) sporadically distribute

in the adjacent of the continuous alumina (point K). In general, the pure, continuous and dense TGO with low growth rates can prevent the coating and the metallic substrate from the high temperature oxidation and



Fig. 10 EDS analyses of TGO subjected to isothermal oxidation at 1050 °C for 100 h

corrosion, and stabilize the whole coating system, but TGO will generate a large growth stress after long time high temperature oxidation. After the vacuum pre-oxidation process, a dense and continuous alumina layer with low growth rate forms, which can suppress the presence of the spinel oxides.

4 Conclusions

1) At the initial stage of the isothermal oxidation for 8 h, the thermally-grown oxide of the CoCrAlY high temperature corrosion resistance coating without the vacuum pre-oxidation process is composed of a large amount of chromium oxides, cobalt oxides and spinel oxides in addition to alumina. The amount of alumina in the thermally-grown oxides is strongly dependent on the partial pressure of oxygen; while the CoCr₂O₄ spinel oxides can be formed under two conditions: high partial pressure of oxygen at the initial stage of isothermal oxidation and chemical reaction at the subsequent stage of isothermal oxidation: $(Cr_2O_3)CrO + (Co_2O_3)CoO \rightarrow$ Co_2CrO_4 .

2) After the appropriate vacuum pre-oxidation process, alumina with low content of yttrium in the thermally-grown oxides layer distributes sporadically near that with high content of yttrium, and the grain sizes of the special alumina range from 0.4 to 1 μ m. The spinel oxides cannot be found in TGO. After isothermal oxidation at 1050 °C for 100 h, the average grain size of the alumina reaches 1 μ m, a small amount of porous CoCr₂O₄ and Cr₂O₃ sporadically distribute in the adjacent of the continuous alumina.

3) After the appropriate vacuum pre-oxidation

process, the TGO growth rate is relatively slow.

References

- EVANS A G, CLARKE D R, LEVI C G. The influence of oxides on the performance of advanced gas turbines [J]. J Eur Ceram Soc, 2008, 28: 1405–1419.
- [2] ERIKSSON R, BRODIN H, JOHANSSON S, OSTERGREN L, LI X H. Influence of isothermal and cyclic heat treatments on the adhesion of plasma sprayed thermal barrier coatings [J]. Surf Coat Technol, 2011, 205: 5422–5429.
- [3] BUSSO E P, EVANS H E, QIAN Z Q, TAYLOR M P. Effects of breakaway oxidation on local stresses in thermal barrier coatings [J]. Acta Mater, 2010, 58: 1242–1251.
- [4] BISON P, CERNUSCHI F, CAPELLI S. A thermographic technique for simultaneous estimation of in-plane and in-depth thermal diffusivities of TBCs [J]. Surf Coat Technol, 2011, 205: 3128–3133.
- [5] TANG F, AJDELSZTAJN L, KIM G E, PROVENZANO V, SCHOENUNG J M. Effects of surface oxidation during HVOF processing on the primary stage oxidation of a CoNiCrAIY coating [J]. Surf Coat Technol, 2004, 185: 228–233.
- [6] SERAFFON M, SIMMS N J, SUMNER J, NICHOLLS J R. The development of new bond coat compositions for thermal barrier coating systems operating under industrial gas turbine conditions [J]. Surf Coat Technol, 2011, 206: 1529–1537.
- [7] MA K K, SCHOENUNG J M. Thermodynamic investigation into the equilibrium phases in the NiCoCrAIY system at elevated temperatures [J]. Surf Coat Technol, 2010, 205: 2273–2280.
- [8] TAWANCY H M, SRIDHAR N, ABBAS N M, RICKERBY D S. Comparative performance of selected bond coats in advanced thermal barrier coating systems [J]. J Mater Sci, 2000, 35: 3615–3629.
- [9] LIANG T Q, GUO H B, PENG H, GONG S K. Microstructural evolution of CoCrAIY bond coat on Ni-based superalloy DZ125 at 1050 °C [J]. Surf Coat Technol, 2001, 205: 4374–4379.
- [10] CHEN W R, WU X, MARPLE B R, NAGY D R, PATNAIK P C. TGO growth behaviour in TBCs with APS and HVOF bond coats [J]. Surf Coat Technol, 2008, 202: 2677–2683.

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- [11] MATSUMOTO M. The development of plasma-sprayed thermal barrier coatings with low thermal conductivity and high oxidation resistance [J]. J Ceram Soc Japan, 2007, 115: 118–123.
- [12] SELCUK A, ATKINSON A. The evolution of residual stress in the thermally-grown oxide on Pt diffusion bond coats in TBCs [J]. Acta Mater, 2003, 51: 535–549.
- [13] SEO D, OGAWA K, TANNO M, SHOJI T, MURATA S. Influence of heat exposure time on isothermal oxidation degradation of plasma sprayed CoNiCrAIY coatings [J]. Surf Coat Technol, 2007, 201: 7952–7960.
- [14] XIAO C B, HAN Y F. Interfacial behaviour of sulphur and yttrium in modified Ni₃Al-based alloy IC6 during high temperature oxidation [J]. J Rare Earths, 2000, 18: 124–127.
- [15] PINT B A. On the formation of interfacial and internal voids in α -Al₂O₃ scales [J]. Oxid Met, 1997, 48: 303–328.
- [16] PINT B A. Optimization of reactive-element additions to improve oxidation performance of alumina-forming alloys [J]. J Am Ceram

Soc, 2003, 86: 686-695.

- [17] GIL A, NAUMENKO D, VASSEN R, TOSCANO J, SUBANOVIC M, SINGHEISER L, QUADAKKERS W J. Y-rich oxide distribution in plasma sprayed MCrAlY-coatings studies by SEM with a cathodoluminescence detector and Raman spectroscopy [J]. Surf Coat Technol, 2009, 204: 531–538.
- [18] MUMM D R, EVANS A G. On the role of imperfections in the failure of a thermal barrier coating made by electron beam deposition [J]. Acta Mater, 2000, 48: 1815–1827.
- [19] HAN Y J, YE F X, DING K Y, WANG Z P, LU G X. Effects of supersonic fine particles bombarding on thermal barrier coatings after isothermal oxidation [J]. Transactions of Non-ferrous Metals Society of China, 2012, 22(7): 1629–1637.
- [20] HAN Y J, YE F X, LU G X, LIU C, HAO L J. Residual stress evolution of thermally-grown oxide in thermal barrier coatings deposited onto nickel-base superalloy and iron-base alloy with thermal exposure ageing [J]. J Alloys Compd, 2014, 584: 19–27.

预先真空氧化处理对 CoCrAlY 耐高温腐蚀涂层表面 热生长氧化层的影响

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摘 要:研究预先真空氧化处理工艺对耐高温涂层的热生长氧化物(TGO)相变的影响,用超音速火焰喷涂技术在 镍基合金基底上喷涂 CoCrAlY 耐高温腐蚀涂层,然后对其进行特定的预先真空氧化处理。研究表明:未预先真 空氧化处理试样在高温氧化初始阶段,TGO 中除了含有 Al₂O₃,还含有大量的 Cr₂O₃、CoO 和尖晶石类氧化物, 而且 Al₂O₃ 的形成量主要取决于氧分压。CoCr₂O₄ 尖晶石的形成阶段主要在高温氧化的初始高氧分压阶段和随高 温氧化进行的化学反应阶段。经过适当的预先真空氧化处理后,TGO 的主要成分为低 Y 含量的 Al₂O₃,零星分 布着高 Y 含量的 Al₂O₃,未观察到明显的大晶粒尖晶石结构氧化物;随着高温氧化时间的延长,少量多孔状的 CoCr₂O₄ 尖晶石和 Cr₂O₃ 零星分布于连续的 Al₂O₃ 周围。另外,TGO 的生长率比未预先真空氧化处理的低。 关键词:预先真空氧化处理;热生长氧化物(TGO);超音速火焰喷涂(HVOD);尖晶石类氧化物

(Edited by Xiang-qun LI)