Heat treatment for TGO growth on NiCrAlY for TBC application

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Abstract

The TGO (thermally grown oxide) is a layer of TBC (Thermal Barrier Coating), which develops and grows at the interface between the bond coat (BC) and ceramic top coat (TC) in high temperature, and is composed mainly of aluminum oxides. The TGO layer improves the effective adhesion between BC/TC and effectively protects against oxidation and hot corrosion. However, this layer is the main failure of TBC and, thus, required further research. This work studied the initial growth of the TGO when exposed to NiCrAlY (BC) at high temperatures. The NiCrAlY samples obtained from its powder by isostatic pressing, sintered by hot uniaxial pressing at 1150 °C for one hour (10 MPa), and the TGO was grown by heat treatment in the air and vacuum at 800, 1100, and 1150 °C for four hours. The results indicated that with increased temperature, surface roughness increases and the oxide layers in the vacuum process are larger than in the air. SEM found that at 1100 °C, samples obtained the most appropriate oxide layer thickness. In vacuum treatments, x-ray diffraction analyses showed the formation of greater quantities of aluminum oxides.

1. Introduction

Thermal barrier coating (TBC) has been widely used on hot section components for aircraft applications in gas turbine engines and blades to improve the thermal efficiency, protecting and prolonging its lifetime [1]. The TBC systems consist of a metal substrate, metallic bond coat (BC), thermally grown oxide (TGO), and ceramic top coat (TC) [2, 3]. The bond coat is composed of MCrAlY, in which M can be Ni, Co, or a combination of them [2].

The most common ceramic composition for TC is 8 YSZ (zirconia stabilized with 7.6 ± 1 mol% yttria), which offers high thermal insulation due to its low thermal conductivity, and it is essentially transparent to oxygen at high temperatures. The BC protects the substrate from the oxygen reaction and oxidation resistant metal coating, which should not only protect against oxidation but also provide sufficient bonding of the TC to the substrate and reduce the thermal expansion mismatch between the ceramic and the substrate.

When the temperature exceeds 700 °C, oxidation of BC is inevitable and forms the TGO. The composition of the TGO is based mainly on a thin layer (<10 μm) and dense Al2O3 (TGO) [4–6].

The basic protection against high temperature oxidation is associated with the evolution of the TGO layer (especially α- Al2O3 scale) at the interface between TC/BC formed during processing layers and in service. The TGO serves as a barrier to delay the diffusion of cations and oxygen through this stable oxide scale and often plays the most important role in adherence to the TBC. [1, 3, 7, 8].

The TGO layer helps to reduce the corrosion of the underlying substrate thus allowing the engine to operate at a higher efficiency. The operational lifetime of the system is delimited by its structural integrity; however, the TGO is also a major generator of faults and causes of system failure. In general, the thickness of the TGO layer is considered to play an important role in determining the remaining lifetime of a TBC system due to series of thermal cycles during service and thermal stresses [1, 2, 9].

The TBCs are subjected to mechanical loads, thermal stresses, sintering, and thermal shock [10]. Due to differences between the physical, thermal, and mechanical properties of the layers, residual stresses developed in...
TBCs may result in coating failures such as coating delamination at the interface of TC/TGO or TGO/BC. Another factor that may compromise the reliability and durability of the TBC is the formation of problematic intermetallic aluminide systems and spinels, such as Ni3Al, Fe3Al, FeAl, or orthorhombic alloys (Ti5AlNb) [11, 12]. Non-protective oxides, such as Cr2O3 and NiO, are formed because the diffusion of Al from BC to the surface is too slow to maintain an exclusive scale in the initial stage of oxidation, though Al is more active to react with oxygen than Cr and Ni [11, 13]. The Y2O3 scale indicates that adhesion of the TGO formed during TBC service at high temperature could enhance the service life of the coating or depletion from the coating [14, 15].

The growth rate and adherence of the protective alumina scale depend on both the coating chemical composition and the surface condition before oxidation exposure [16]. The majority of previous studies found longer TBC lifetimes for specimens with an MCrAlY BC with pre-thermal treatment compared to without pre-treatment [12, 17–19].

The pre-oxidation is a post method to preform an exclusive α-Al2O3 scale before using samples in oxidation and corrosive environment [11].

Most of the previous studies [1, 10, 20, 21] have dealt with the processes which were investigated to form TGO by heat treatment in samples of MCrAlY (BC). This work proposes an implementation strategy to improve the adherence scale of TGO coatings for TBC applications by verifying the necessarily formed phases, layer thickness, and roughness for ceramic adhesion. In addition to those features, the TGO growth process controlled by heat treatment in the air and a vacuum. This process can regulate properties such as growth rate, composition, and adherence of the TGO, which are important factors determining the performance, integrity, and lifetime of TBCs.

2. Materials and method

The samples were prepared using a NiCrAlY powder (Praxair Surface Technologies, USA) with 57.35 wt% Ni, 31 wt% Cr, 11 wt% Al, and 0.65 wt% Y. The samples were compacted by uniaxial pressing at 200 MPa with a binder (polyvinylalcohol) and isostatic pressing at 300 MPa. The sintering occurred by hot uniaxial pressing at 10 MPa and 1150 °C for one hour [22].

Then, in this work, the samples were polishing and submitted to heat treatment for TGO formation in the air and a vacuum (10^-5 Pa) in temperatures of 800 °C, 1100 °C, and 1150 °C for four hours.

The sample studied were designated AT800, AT1100, AT1150, VT800, VT1100, and VT1150, with AT referring to heat treatment in air and VT in vacuum; the numbers denote the processing temperature.

The surface roughness characterization was analyzed by Optical Profilometry (Veeco WYKO NT1100). X-ray diffraction (XRD, Philips Panalytical—X’Pert Pro) was performed to analyze the phases formed at each temperature. The morphology of the samples and cross-section of oxide scales were observed by scanning electron microscopy (SEM, Zeiss LEO 435 VPI) equipped with an Energy Dispersive Spectroscopy (EDS) detector to determine the semi-quantitative chemical compositions of surfaces formed by NiCrAlY and TGO.

3. Results and discussion

The characterizations and details of the sintering process formed compact and dense samples of NiCrAlY to promote the growth of TGO on the surface, as shown in previous work done by the authors [22]. The sintering by hot uniaxial pressing at 1500 °C was the best characterization of all conditions studied. This condition results in low apparent porosity 0.35% and good relative density 98.75% by Archimedes’ Principle. The sample was chosen because the initial conditions of NiCrAlY samples (dense, compact, and homogeneous) are essential to study the TGO grown by heat treatment and control the microstructure of the NiCrAlY and its thermal stability.

The surface of NiCrAlY after heat treatment with the EDS analysis, shown in figure 1, is the average of two measurements in two different regions. In general, similar composition of the powder was observed for heat treatment at 800 °C. The Al2O3 formation was favorable at 1100 °C, while yttrium oxide formation was better at 1150 °C.

The top surface samples of AT1100, AT1150, and VT1100 (figures 1(C), (E), and (D), respectively) exhibited higher quantities of the aluminum, indicated by the EDS analysis. This result suggested that the increased temperature caused the formation of higher quantities of Al2O3, alumina phases.

The VT1150 (figure 1(F)), in which EDS detected higher quantities the yttrium and nickel elements, formed more yttrium and nickel oxides phases than Al2O3.

This Al enrichment suggested alumina formation during heat treatments. Alumina is the preferred oxide formation because of its low oxygen diffusivity and superior adherence [23]. The results indicated that the Al2O3 layer formed on the surface of NiCrAlY.
The dispersed Al₂O₃ can hinder the diffusion of Ni, Cr from the inside to the surface and the growth rate, slowing down Cr₂O₃ and NiCr₂O₄ [24].

The Y is used to control interface adhesion retards the growth rate of the α-Al₂O₃ once nucleated. When yttria domains of sufficient size are incorporated into the TGO, it thickens more rapidly in these regions and produces imperfections, the most common being the thickness [2, 3].

The element enrichment detected in the EDS analyses was confirmed in the XRD diffractograms illustrated in figure 2. The highest intensities of the α-Al₂O₃ peaks were in VT1100 and the highest intensity peaks of Y₂O₃ in VT1150.

Diffraction peaks for Ni, Ni₃Al, and NiAl were essential for NiCrAlY material [2]. EDS detected Ni and Al enrichment in some places, generally in dark gray grains, visible in figure 1, presumably corresponding to phases formed by Ni₃Al and NiAl.

The samples before the heat treatment [22], identify NiAl and Ni₃Al phases for NiCrAlY buck. Subsequently, in this work after the heat treatments O, Al and Y phases were identified on the surface (figure 2). Increased heat treatment temperature reduced the grain boundary for all conditions (figure 1), and, as observed, the NiAl and Cr phase decreased while Al₂O₃ and Y₂O₃ increased.

The time that the oxides grew clearly changed the roughness and undulations at the surface. The layer increased with the exposure time and temperature. The surface profile (figure 1) was analyzed by Profilometry. In the analyze in figure 3 (VT1100), the surface morphology is quite homogeneous and dense by visual aspect (interferential color).

Table 1 presents the surface roughness—Ra (arithmetic average for absolute values) by the Profilometer technique using the average of five measurements in different regions of the sample. The result of the sample without heat treatment is 41.15 ± 9.03 nm standard deviation. All the samples were polished before the heat treatment.

Figure 1. Surface microstructure of the NiCrAlY substrate after thermal treatment by scanning electron microscopy and EDS map percent result. (A) AT800, (B) AT1100, (C) AT1150, (D) VT800, (E) VT1100, (F) VT1150. SEM detector: BSE.
The TGO growth rate was considerably modified by surface roughness and strongly related to the substrate temperature, diffusion process, and reaction [21, 25, 26]. The TGO growth occurred by an oxygen diffusion–reaction [21, 27, 28]. Increased heat treatment temperature increased the roughness. The surface roughness obtained in the vacuum heat treatment was greater than roughness obtained in the air for the same temperature due to higher growth of the oxide surface, which had irregular surface predominantly in the amount of oxides rich in Al and Y, and the formation primarily occurred of the rough coating surface, the EDS analysis was shown in figure 1.

The initial oxide scale growth was concentrated in the valleys where the TGO layer was thinner than in the peak regions [25]. The monitoring of this layer must be done because large thicknesses or discontinuities produce instability to the TBC system as in VT1150. Taylor et al [27] demonstrated that the MCrAlY bond coat with asperities of high aspect ratios can result in premature chemical failure during isothermal exposures.

SEM cross-section of the TGO layer after heat treatment, illustrated in figure 4, measured the thickness of the layer and is compared in table 2. The samples had valleys and peak regions in the BC/TGO interface, in which VT800 and AT1150 showed spallation in the interface and the other samples exhibited the adhesion.
The total average thickness is listed in Table 2. The TGO layers were evenly distributed on the NiCrAlY surface with the increased temperature. The behavior of TGO growth normally follows the parabolic relationship as time increases \[27\]. A comparison of the results found that TGO layer formation is linked to the availability of reactive oxygen in the atmosphere and excess aluminum from BC to form the oxide. The heat treatment in the air had more oxygen in the atmosphere than in a vacuum. The oxidation in a vacuum used residual oxygen through the interconnected porosity of the BC. The continuous growth of the alumina layer comes from the Al in the underlying BC layer as a result of the selective oxidation \[26\]. Therefore, the heat treatment in a vacuum obtained a average TGO thickness substantially smaller than in air.

**Figure 4.** Cross-section micrograph showing TGO layers formed on NiCrAlY by scanning electron microscopy and EDS analyses. (A) AT800, (B) AT1100, (C) AT1150, (D) VT800, (E) VT1100, (F) VT1150 SEM detector: BSE.

**Table 2.** Average thickness of the TGO layer after thermal treatment in air and a vacuum.

|        | Thickness ± δ (μm) |
|--------|-------------------|
| AT800  | 13.27 ± 0.33      |
| AT1100 | 6.62 ± 0.24       |
| AT1150 | 48.76 ± 0.72      |
| VT800  | 6.53 ± 0.45       |
| VT1100 | 13.65 ± 0.94      |
| VT1150 | 10.61 ± 0.65      |
In figures 4(C)–(F) (AT1100, VT1100, AT1150, and VT1150, respectively), cross-section micrographs of samples after heat treatment showed the formation of a dual layer of TGO, which consisted in an outer layer and an inner layer. The average of the TGO inner layer of the samples at 1150 °C was 4.75 μm in the air and 4.45 μm in a vacuum. At 1100 °C in a vacuum, the average inner layer was 4.02 μm.

Similar to observations reported in the literature [11, 26], the formation of the TGO layer was different for the process in air than vacuum and confirmed by the inner thickness with higher peaks of α-Al2O3 and outer layer of Cr and Ni mixed oxides or exhibiting a minor amount of stringer-like Y/Al-oxide precipitates in the TGO.

As showed in this work, the increased temperature suggests oxidation stage evolution for dual layer. At 800 °C, only one layer was formed, but at 1100 °C and 1150 °C, two layers were identified with a different chemical composition, with the Al2O3 in the inner and the mixed oxides in the outer.

The VT1100 and AT1150 contained the highest percentage of Al and O, decreasing from the inner to the outer layer. The outer had higher Cr percentage in air heat treatment and higher Y percentage in vacuum heat treatment. In VT1150, the Al percentage was more regular than other samples and its inner layer had the highest Y percentage.

The inner TGO layer, with larger regions of alumina than chromia and yttria, was distributed constantly along the top surface of the main TGO. The stable Al2O3 on the TGO layer had a low growth rate and a low tendency for crack propagation, which consequently led to an improved TBC durability [28].

In the initial stage of oxidation, the element most likely to react first with oxygen is Al. Whenever Al2O3 is stable, the oxygen activity at the interface is too low to form decreases, and other elements begin to form their respective oxides. Over time, the kinetic processes also play a significant role in phase evolution, and the Al2O3 converts to problematic intermetallic aluminide systems or spinels. When this happens, the durability of the TBC may be compromised [11, 23].

As discussed above, the TGO growth occurred by an oxygen diffusion—reaction [21, 27, 28]. Then, in the air heat treatment, the layer grows by the oxygen and aluminum scalars congregate by diffusional transport, producing the alumina layer. This layer was a protective film against the action of oxygen, which did not allow the growth of the oxide layer, significantly inhibiting the growth of the TGO layer. Between 1100 °C and 1150 °C, the oxide layer grew exponentially. The high temperature, the elements are more reactive and the oxygen which more available in the atmosphere, provide the formation and growth of oxides.

On the other hand, the residual oxygen in the vacuum chamber started the growth of the oxides at 800 °C and 1100 °C, especially Al, Cr and Y oxides, which improved the oxidation resistance of the NiCrAlY bond coats. The alumina was formed immediately below transition metal oxides (the inner TGO—figure 4) and grown with the heat treatment temperature increased, but the layer stopped growing, once the availability of residual oxygen became rare.

As in the EDS result of the sample surface, the cross-section shows that at 800 °C the elements are similar to the initial composition of the powder. For samples at 1150 °C, a higher percentage of yttrium is dropped, and samples at 1100 °C have more detected aluminum, which suggests greater detection of alumina.

4. Conclusion

After the heat treatment in air and vacuum for four hours, the most common oxide of the TGO layer, α-Al2O3, was identified in all samples, and the VT1100 obtained greater intensities of α-Al2O3 peaks.

Roughness in an important parameter for adherence of the ceramic layer in thermal barrier coating, and on average, the samples oxidized in vacuum were rougher than in air at all temperatures studied. The TGO thickness formed in heat treatment in the air had thicker layers than vacuum as analyzed by SEM, due to the higher growth of the oxide surface, which had irregular surfaces predominantly with an amount of oxides.

The formation of the TGO layer for all samples was continuous. This layer had an outer layer and an inner layer for AT1100, AT1150, VT1100, and VT1150. The AT800 VT800 samples had the same chemical composition as the initial powder. The inner layer of VT1150 identified Y enrichment. The VT1100 had two layers of TGO, in which the inner layer was rich in alumina favoring oxidation protection.

According to the results obtained, the condition with the most indicated characteristics to improve the performance of the TBC is VT1100. This heat treatment is predicted to be validated in a future paper that will investigate and discuss the behavior of TGO after deposition of the TC coating for high temperature evaluation used for thermal barrier coating.

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**References**

[1] Zhu W, Cai M, Yang L, Guo J, Wu W, Zhou Y C and Lu C 2015 The effect of morphology of thermally grown oxide on the stress field in a turbine blade with thermal barrier coatings Surf. Coatings Technol. 276 180–7

[2] Grant P 2001 Thermal barrier coatings ed B Cantor, P Grand and H Assender Aerosp. Mater. (Bristol: Taylor & Francis chapter 22 Series in materials science and engineering)

[3] Evans A, Clarke D R and Levi C G 2008 The influence of oxides on the performance of advanced gas turbines J. Eur. Ceram. Soc. 28 1405–19

[4] Leyer R, Schulz U, Pint B A and Wright I G 1999 Influence of EB-PVD TBC Microstructure on advanced Thermal Barrier coating system performance under cyclic oxidation conditions Web 1-17 https://www.osti.gov/servlets/purl/9211

[5] Levi C G 2004 Emerging materials and processes for thermal barrier systems Curr. Opin. Solid State Mater. Sci. 8 77–91

[6] Pint B A, Wright I G, Lee W Y, Zhang Y, Pru K and Alexander K B 2008 Substrate and Bond Coat Compositions: Factors Affecting Alumina Scale Adhesion 245 201–11

[7] Sun F, Tong J, Feng Q and Zhang J 2015 Microstructural evolution and deformation features in gas turbine blades operated in-service J. Alloys Compd. 618 728–33

[8] Schulz U, Leyer C, Fritscher K, Peters M and Saruhan-brings B 2003 Some Recent Trends in Research and Technology of Advanced Thermal Barrier Coatings: Aktuelle Forschungs- und Entwicklungstrends bei Wärmedämmsschichten für die Gasturbine 7 73–80

[9] Leyer C 2004 Advanced materials and coatings for future gas turbine applications 24th Int. Congr. Aeronaut. Sci. 1 1–5 http://www.icas.org/ICAS_ARCHIVE/ICAS04/PAPERS/04SPDF

[10] Nijdam T J and Slaaf W G 2008 Modelling of composition and phase changes in multiphase alloys due to growth of an oxide layer Acta Mater. 56 972–83

[11] Zhu C, Li P and Wu X Y 2015 A study of the diffusion and pre-oxidation treatment on the formation of Al2O3 ceramic scale on NiCrAlY bond-coat during initial oxidation process Ceram. Int. 42 7708–16

[12] Daroopenvar M, Azizi M and Hajj M 2013 Improvement of thermally grown oxide layer in thermal barrier coating systems with nano alumina as third layer Trans. Nonferrous Met. Soc. China 23 1322–33

[13] Niranjatumpong P, Sukonkhet C and Ninon K 2015 Loss of Y from NiCrAlY powder during air plasma spraying Surf. Coatings Technol. 280 277–81

[14] Gil A, Naumenko D, Vassen R, Toscano J, Subanovic M, Singhieker L and Quadakkers W J 2009 Y-rich oxide distribution in plasma sprayed MCrAlY-coatings studied by SEM with a cathodoluminescence detector and Raman spectroscopy Surf. Coat. Technol. 204 531–8

[15] Toscano J, Va R, Gil A, Subanovic M and Naumenko D 2006 Parameters Affecting TGO Growth and Adherence on M CrAlY-Bond Coats for TBC’s 201 3906–10

[16] Gil A, Shemet V, Vassen R, Subanovic M, Toscano J, Naumenko D, Singhieker L and Quadakkers W 2006 Effect of surface condition on the oxidation behaviour of MCrAlY coatings Surf. Coatings Technol. 201 3824–8

[17] Lau H, Leyer C, Schulz U and Friedrich C 2003 Influence of bondcoat pre-treatment and surface topology on the lifetime of EB-PVD TBCs Surf. Coatings Technol. 165 217–23

[18] Chen W R, Wu X, Marple B R, Lima R S and Patnaik P C 2008 Pre-oxidation and and TGO growth behaviour of an air-plasma- sprayed thermal barrier coating Surf. Coatings Technol. 202 3787–96

[19] Zhu C, Wang Y G, An L N, Javed A, Xiao P and Liang G Y 2015 Microstructure and oxidation behavior of conventional and pseudo graded NiCrAlY/YSZ thermal barrier coatings produced by supersonic air plasma spraying process Surf. Coatings Technol. 272 121–8

[20] Keller I, Naumenko D, Quadakkers W J, Vassen R and Singhieker L 2013 Influence of vacuum heat treatment parameters on the surface composition of MCrAlY coatings Surf. Coatings Technol. 215 24–9

[21] Meng G H, Zhang B Y, Liu H, Yang G J, Xu T, Li C X J and Li C X J 2018 Highly oxidation resistant and cost effective MCrAlY bond paints prepared by controlled atmosphere heat treatment Surf. Coatings Technol. 347 51–65

[22] Takahashi R J, Assisi J M K, Neto F P, Mello A M and Reis D A P 2017 Sintering study of NiCrAlY Mater. Sci. Forum 899 478–82

[23] Evans A G, Mummm D R and Hutchinson I W 2001 Mechanisms Controlling the Durability of Thermal Barrier Coatings 46 505–53

[24] Wu Y N, Qin M, Feng Z C, Liang Y, Sun C and Wang F H 2003 Improved oxidation resistance of NiCrAlY coatings Mater. Lett. 57 4204–6

[25] Shen Q, Yang L, Zhou Y C, Wei Y G and Wang N G 2017 Models for predicting TGO growth to rough interface in TBCs Surf. Coatings Technol. 325 219–28

[26] Taylor M P, Pragnell W M and Evans H E 2008 The influence of bond coat surface roughness on chemical failure and delamination in TBC systems Mater. Corros. 59 508–13

[27] Puetz X, Huang R S, Lima Q and Yang L Z 2010 Characterization of transient oxide formation on CoNiCrAlY after heat treatment in vacuum and air Surf. Coatings Technol. 205 647–57

[28] Liu Y Z, Zheng S J, Zhu Y L, Wei H and Ma X L 2010 Microstructural evolution at interfaces of thermal barrier coatings during isothermal oxidation J. Eur. Ceram. Soc. 36 1765–74