Microstructural evaluation of YSZ/NiCrAlCo-Y₂O₃ coatings after isothermal oxidation at 1050 °C

A G González-Hernández¹, H Ageorges² and M E López³
¹ Universidad Industrial de Santander, Bucaramanga, Colombia
² Université de Limoges, Limoges, France
³ Universidad de Antioquia, Medellín, Colombia
E-mail: aggonzal@uis.edu.co

Abstract. In this study, the microstructure of the bond coat of the YSZ/NiCrAlCo-Y₂O₃ systems after isothermal oxidation was examined. The ceramic top coating (YSZ) and bond coat (NiCrAlCo-Y₂O₃) were manufactured by atmospheric plasma spraying (APS) process and were sprayed onto Inconel 718 superalloy. The thickness of the NiCrAlCo-Y₂O₃ bond coat was 140 ± 10 µm. Isothermal oxidation tests were performed at 1050 °C during 100 and 200 h in static air. The thermally grown oxide (TGO) layer was formed at the interface between the top coat and the bond coat as a consequence of the isothermal oxidation tests. Cross-section samples after isothermal oxidation were evaluated using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The analysis of EDS was performed to the TGO and the lamellas of bond coat near to the TGO. The results showed that the TGO layer was composed mainly of chromium and oxygen as resulting from its diffusion and oxidation. The analysis of the lamellas near to the TGO showed elements such as Ni, Cr, and Co, which are related to the chemical composition of the bond coat. Additionally, Inconel 718 alloys constituents such as Fe and Nb were found in the same area as the result of the diffusion of these elements through the bond coat.

1. Introduction
Thermal barrier coatings (TBCs) systems fabricated via electron beam physical vapor deposition (EB-PVD) and atmospheric plasma spraying (APS) are widely used in aero-engines for propulsion and power generation, because they can provide thermal and corrosion protection for the metallic hot-section components achieving extender your durability [1–9]. Usually, the typical TBC system consist of a metallic bond coat (BC), acting as a layer resistance to oxidation and corrosion, and a ceramic top coat (TC), which works as a thermal insulation layer to reduce the heat transfer to metallic substrates. For over 30 years, the yttria stabilized zirconia (YSZ) has been the first choice for ceramic top coat (100-500 µm in thickness) thanks to the fact that has low thermal conductivity, relatively high thermal expansion coefficient, good durability and thermal stability at temperatures below 1200 °C, and high chemical stability [10,11]. In regard to bond coats (75-150 µm in thickness), both MCrAlY (M = Fe, Co and/or Ni) and Pt modified aluminide coatings are prevailing as the typical chemical compositions of these layers [1,12]. Moreover, the BC provides adhesion and physical compatibility between the ceramic TC and the Ni-based superalloy substrate.

On the other hand, one of the most important causes of failure in the TBCs usually occurs at the interface between the TC and BC. In this interface, a dense layer of thermally grown...
oxide (TGO) is often formed as a result of oxidation of BC under high temperature conditions [12–15]. Generally, aluminium is selectively oxidized firstly in the BC. $\alpha$-$\text{Al}_2\text{O}_3$, usually with columnar morphology, is the preferred oxide formed at the BC/TC interface due to its chemical stability, better adherence to bond coat and lower standard free energies of formation than other compounds [13,16,17]. As the TGO thickens and the concentration of aluminium decreases, other oxides including NiO, Cr$_2$O$_3$ or NiO and spinel-type Ni(Cr,Al)$_2$O$_4$ are generated by the outward diffusion of Cr and Ni [12,13,16,18]. In other studies, the formation of a triple-layered TGO was also observed, which successively consists of a layer of NiCr$_2$O$_4$-NiO/Cr$_2$O$_3$/Al$_2$O$_3$ or NiO/NiCr$_2$O$_4$/Al$_2$O$_3$ [19,20]. The growth of these mixed oxides or spinels is accompanied with large volume changes and the resulting stresses within the TGO lead to the formation and propagation of microcracks, thereby producing an accelerated coating failure [18]. It appears that the addition of a small amount of Y in the bond coat can reduce the growth rate of TGO due to the precipitation of Y at grain boundaries in the TGO. This segregation of the Y can reduce the mobility of the grain boundaries and inhibit the growth of Al$_2$O$_3$ grains in the TGO [18]. The controversial results in the literature suggest that the effect of Y-addition on the YSZ/NiCrAlY interface oxidation is complex and fundamental understanding of the oxidation process is far from clear [18]. For these reasons, the aim of this paper is to investigate the microstructural evolution of the bond coat (NiCrCoAl-Y$_2$O$_3$) after isothermal oxidation at 1050 °C during 100 and 200 h, using a combination of SEM and energy dispersive X-ray spectroscopy (EDS).

2. Materials and method

Ni-based superalloy (Inconel 718) bars of 25.4 mm in diameter and 5 mm in thickness were used as substrates. These were grit blasted with alumina particles to create a desired surface with an average roughness (Rₐ) between 4 and 5 µm. Grit blasted is generally used to obtain better mechanical adhesion of the thermal sprayed particles on the substrate surface. Inconel 718 superalloy was supplied by Mega Mex (Houston, USA) and its chemical composition was verified by X-Ray Fluorescence (FRX).

On the other hand, atmospheric plasma spraying (APS) process was used to elaborated the YSZ and NiCrAlCo–Y$_2$O$_3$ coatings using F4-MB torch (Sulzer-Metco, Wolhen, Suiza) with Multicoat system. Metco 461NS powder was used to manufactured the BC on the substrate, whereas the H.C. Starck (Amperit 827.423) YSZ powder was used as raw material to obtain the ceramic TC on the BC. The APS parameters are listed in table 1.

| Parameters                  | NiCrCoAl-Y$_2$O$_3$ | YSZ  |
|-----------------------------|---------------------|------|
| Spray distance (mm)         | 100                 | 100  |
| Current intensity (A)       | 500                 | 650  |
| Nozzle diameter of the F4 torch (mm) | 7               | 7    |
| Flow rate of Ar-H$_2$ flow rate (l/min) | 45-15          | 45-15|
| Powder feed rate (g/min)    | 25-30               | 25-30|
| Injector diameter (mm)      | 1.8                 | 1.8  |
| Carrier gas flow rate (l/min) | 4.8            | 4.8  |
| Preheating temperature (°C) | 300                 | 300  |
| Spray time (min)            | 2                   | 4    |
Morphological characterization of the NiCrCoAl-Y₂O₃ powder and the cross-section of the YSZ/NiCrCoAl-Y₂O₃ coatings was carried out by SEM in the JEOL JSM-6490LV equipment. The cross-section of the coatings was polished according the standard ASTM E1920-03. The chemical composition of the BC and its raw material (Metco 461NS powder) was determined by FRX.

For the isothermal oxidation tests, the samples were pushed into the muffle furnace in static air at 1050 °C for 100 and 200 h and then cooled down inside the furnace. Finally, to evaluate this isothermal oxidation, the cross-section of the samples were analysed by SEM and EDS in the JEOL JSM-6490LV equipment. For the EDS technique, the analysis of elemental composition was performed in the TGO and lamellas of bond coat near to this one.

3. Results

The chemical composition of the Inconel 718 superalloy is shown in table 2. This superalloy contains significant levels of iron to reduce its cost. Niobium is present in moderate amount (≈5 wt%) and generally contribute to solid solution strengthening in the alloy, increasing its mechanical properties through carbides formation and precipitation hardening [21]. Thus 718 alloy has not only excellent mechanical properties, such as tensile strength, creep resistance and low-cycle fatigue strength up to 650 °C but also good formability and weldability.

Table 2. Chemical composition of the Inconel 718 superalloy in wt% by FRX.

| Ni  | Fe  | Cr  | Nb  | Mo  | Al  | Ti  | Cu  | Si  | Others |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|--------|
| 52.37 | 18.74 | 18.31 | 5.21 | 3.06 | 0.90 | 0.86 | 0.09 | 0.046 | 0.414 |

The starting powder to elaborate the bond coat is shown in figure 1. The powder exhibit particles with irregular shapes (see figure 1(a)) and these are related with the fabrication method (mechanically clad). The particle size distribution of the powder is between 15 µm (d₁₀) and 90 µm (d₉₀). According to the EDS spectrum (see figure 1(b)), the surface of particles are mainly composed of aluminium and low amount of Co and Y, while the interior of the particles (see figure 1(c)) are composed of nickel and chromium as shown in figure 1(d).

Figure 1. SEM images of the starting powder: (a) particles, (b) EDS analysis of the point 1, (c) Cross-section of a particle, and (d) EDS analysis of the point 2.

The chemical composition of the starting powder used as raw material and the bond coat elaborated by APS, is shown in table 3. Comparing the chemical composition of the BC and the starting powder presented in table 3, it can see that the amount of aluminium and the
cobalt (Co present in others) decreases due possibly to the evaporation or sublimation of these elements during the APS process, especially that they are present on the surface of the particles of the starting powder according to the SEM image and EDS spectrum showed in figure 1(a) and (b), respectively. Additionally, the aluminium protects the particles of the oxidation during its application by the APS process and also has a great effect on the oxidation resistance of the BC.

### Table 3. Chemical composition of the Metco 461NS powder and the BC by FRX (wt%).

|          | Ni   | Cr   | Al   | Si  | Y    | Co   | Others |
|----------|------|------|------|-----|------|------|--------|
| Starting powder | 40.91 | 12.49 | 38.52 | 0.82 | 0.73 | 5.79 | 0.74   |
| Bond coat   | 67.53 | 17.78 | 10.77 | 1.02 | 0.94 | -    | 1.96   |

On the other hand, the TBC system after 100 h of isothermal oxidation is shown in figure 2(a). The YSZ ceramic top coat exhibits a thickness of 760 ± 30 µm, whereas the thickness of the BC presents 140 ± 10µm. The morphology of the BC after isothermal oxidation is shown in figure 2(b). The formation of the TGO in the TC-BC interface is observed in this figure, as well as the formation of oxides in the boundaries of the lamellas (black zones). Also, the BC-substrate interface is not appreciable due to the high degree of melting in this interface thanks to the great similarity in the chemical composition of both materials.

Figure 2(c) shows the TGO, which is mainly composed of chromium and oxygen according the EDS spectrum carried out in the zone 1 (see figure 2(d)). In the same EDS spectrum, small amounts of elements such as nickel, cobalt, titanium, and aluminium are also presented in the TGO. According to the EDS 2 shown in figure 2(e), the main elements of the BC such as nickel
and chromium were presented in a high concentration. A representative amount of niobium and iron were revealed near the TGO, as shown in figure 2(e). These elements have their origin from the substrate of Inconel 718 and were able to diffuse through the BC. This behavior can be prejudicial to the substrate because it can decrease its mechanical properties.

The elemental chemical composition of the TGO after 100 and 200 h at 1050 °C carried out by EDS, is shown in table 4. The concentration of the oxygen present in the TGO exhibited an increase of ≈20 to 32 wt% during the two evaluated times. Consequence of this behavior, the concentration of all elements of the TGO (Ni, Cr, Al, Co) decreases except the titanium that diffuse from the substrate. According to the results described above, the principal compound formed in the TGO is composed of a chromium oxide and taking into account other researches [1], the most predominant and stable oxide in this TGO is the Cr$_2$O$_3$. This oxide is possibly formed by reaction between the α-Cr and solid-soluted Cr in the γ-Ni of the bond coat with the oxygen [22].

The difference of the elemental chemical composition of the bond coat near to the TGO after 100 and 200 h of isothermical oxidation is shown in table 5. It is noticeable that the elements that diffuse from the substrate increase their concentration, for instance the iron passes from 3.3 to 6 wt%, while the niobium rises from 1.5 to 3.1 wt%. Consequently, the other elements of the bond coat decrease their concentration slightly due to the effect the Fe and Nb. It is important highlight that the oxygen presented a low concentration in the BC (<2%) comparing with the high concentration displayed in the TGO (>20%) during the 100 and 200 h of the test.

| Time (h) | Cr   | O    | Ni  | Al  | Ti  | Co  |
|----------|------|------|-----|-----|-----|-----|
| 100      | 70.4 | 20.9 | 3.1 | 2.2 | 0.3 | 3.1 |
| 200      | 63.5 | 32.0 | 2.1 | 1.2 | 1.2 | —   |

| Time (h) | Ni  | Cr   | Co  | O   | Fe  | Nb  |
|----------|-----|------|-----|-----|-----|-----|
| 100      | 71.2| 19.9 | 2.5 | 1.7 | 3.3 | 1.5 |
| 200      | 70.8| 17.8 | 2.3 | —   | 6.0 | 3.1 |

The morphology of the BC and TGO after 200 h of the isothermal oxidation is shown in figure 3. Figure 3(a) shows that the dark zones of the boundaries of the lamellas of the BC is more affected by the oxidation than that presented at 100 h to exposure.

Figure 3(b) presents the interface TC-TGO-BC after 200 h of isothermal exposure at 1050 °C.

Figure 3(b) presents the interface TC-TGO-BC after 200 h to exposure and it is clearly that this TGO is thicker than that presented at 100 h of exposure (see figure 2(c)). Thus, the average thickness of the TGO at 200 h to exposure was about 5 to 8 µm, while the thickness of this one after 100 h was less than 2 µm. It is important to highlight that there is a critical TGO thickness over which the thermal lifetime decreases more significantly with the development in this thickness [23].
4. Conclusion

The microstructural evolution of the YSZ/NiCrAlCo-Y2O3 interface after 100 and 200 h to exposure at 1050 °C was analyzed by SEM and EDS, leading to the following conclusions:

(i) The starting powder used as raw material to elaborated the BC during the APS process, suffer a high reduction of the concentration of aluminium. According to the EDS carried out above, this decrease is possibly caused by the sublimation of Al present in the surface of the particles.

(ii) TGO layer formed in the TC/BC interface is predominately composed of a chromium oxide in form the Cr2O3 after the two times evaluated.

(iii) The chemical composition of the bond coat near of the TGO is characterised by the presence of iron and niobium that are originated by their diffusion from the substrate through the BC. These elements rise their concentration when the time evaluated increase from 100 to 200 h. This behavior can decrease the mechanical properties of the Inconel 718 superalloy due to that niobium is the responsible to form carbides and generate precipitation hardening in the superalloy.

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References

[1] Liu Y, Zheng S, Zhu Y, Wei H and Ma X 2016 Journal of the European Ceramic Society 36 1765–1774
[2] González A, Ageorges H, Rojas O, López E, Hurtado F M and Vargas F 2015 Boletín de la Sociedad Española de Cerámica y Vidrio 54 124–132
[3] Hajizadeh-Oghaz M, Razavi R S, Ghasemi A and Valefi Z 2016 Ceramics International 42 5433–5446
[4] González-Hernández A G, Ageorges H and López-Gómez M E 2017 Journal of Physics: Conference Series 786 012018
[5] Lazovan A A, Betsofen S Y, Ashmarin A A, Ryabenko B V and Ivanova S V 2016 Journal of Physics: Conference Series 729 012017
[6] Baig M N and Khalid F A 2014 IOP Conference Series: Materials Science and Engineering 60 012053
[7] González A, Hurtado F, Ageorges H, López E and Vargas F 2017 Revista Latinoamericana de Metalurgia y Materiales 37 2–10
[8] Abhinav, Krishnamurthy N and Jain R 2017 Ceramics International 43 15708–15713
[9] Hurtado F M, González-Hernández A, López M E and Ageorges H 2016 Materia (Rio de Janeiro) 21 49–60 ISSN 1517-7076
[10] Leib E W, Vainio U, Pasquarelli R M, Kus J, Czaschke C, Walter N, Janssen R, Müller M, Schreyer A, Weller H and Vossmeyer T 2015 Journal of Colloid and Interface Science 448 582–592
[11] Song X, Liu Z, Kong M, Lin C, Huang L, Zheng X and Zeng Y 2017 Ceramics International 43 14321–14325
[12] Torkashvand K and Poursaeidi E 2018 Surface and Coatings Technology 349 177–185
[13] Liu X, Wang T, Li C, Zheng Z and Li Q 2016 Progress in Natural Science: Materials International 26 103–111
[14] Ali I, Sokolowski P, Grund T, Pawłowski L and Lampke T 2018 IOP Conference Series: Materials Science and Engineering 373 012010
[15] Keyvani A and Bahamirian M 2016 Materials Research Express 3 105047
[16] Poza P, Gómez-García J and Múñez C 2012 Acta Materialia 60 7197–7206
[17] Evans A, Mumm D, Hutchinson J, Meier G and Pettit F 2001 Progress in Materials Science 46 505–553
[18] Hu Y, Cai C, Wang Y, Yu H, Zhou Y and Zhou G 2018 Corrosion Science
[19] Nijdam T, Jeurgens L and Sloop W 2005 Acta Materialia 53 1643–1653
[20] Nijdam T J, van der Pers N M and Sloop W G Materials and Corrosion 57 269–275
[21] Smith G D and Patel S J 2005 Superalloys 718, 625, 706 and Various Derivatives 135–154
[22] Liu Y, Hu X, Zheng S, Zhu Y, Wei H and Ma X 2015 Materials and Design 80 63–69
[23] Dong H, Yang G J, Li C X, Luo X T and Li C J 2014 Journal of the American Ceramic Society 97 1226–1232