Isothermal Oxidation Behavior of Novel Al$_2$O$_3$ / NiCrAlY / Ti$_3$Al System at 850°C

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Abstract: The novel Al$_2$O$_3$ / NiCrAlY /α$_2$-Ti$_3$Al system obtained by APS technique was tested against long (500h) isothermal oxidation at 850°C in air for prospective use in aerospace applications. EDX-SEM, X-ray diffraction (XRD) and Raman investigations were conducted to substantiate structural, textural and mass gain modifications underwent by the Al$_2$O$_3$ / NiCrAlY /α$_2$-Ti$_3$Al system in comparison with bare α$_2$-Ti$_3$Al and NiCrAlY /α$_2$-Ti$_3$Al system. Improved oxidation resistance of the double-coated system is based on moderate oxygen and thermal barrier role played by the mixture of δ- and α-Al$_2$O$_3$ present in the top ceramic coat.

Keywords: isothermal oxidation, titanium aluminate, diffusion barrier

1. Introduction

High-temperature structural materials for aerospace and automotive purposes [1] operate in one of the harshest environments being exposed to severe mechanical loads, high temperature, as well as corrosion and erosion conditions. That enforces continuous development of new generations of TiAl alloys with improved properties (low density, high specific strength and melting temperature, good creep resistance, excellent fireproof performance) in comparison with Ti-alloys which replaced Ni-superalloys [2,3]. Both conventional Ti-alloys and titanium aluminate alloys, especially in alpha form with rich titanium content α$_2$-Ti$_3$Al, show poor oxidation and corrosion resistance at elevated temperatures in air as well as in marine environments at ambient temperature [1-6]. Choice of titanium richer alloys, TiAl (γ phase), Ti$_2$AlNb (o-ortho phase) and α$_2$-Ti$_3$Al alloys, is ruled by their superior mechanical characteristics [7, 8]. At the time when extensively studied Ti-48Al-2Nb-2Cr alloy was used for the first time in 2006 as rotating parts of a Boeing engine [3], application of the α$_2$-Ti$_3$Al alloys with unsatisfactory oxidation resistance at service temperature of 800-1000°C has been limited [3,8]. The latter alloys form a mixed unprotected layer of TiO$_2$ and Al$_2$O$_3$ during exposure at high temperature in air and/ or oxygen in contrast with dense protective alumina scales, formed onto the richer aluminum alloys, which act as an effective diffusion barrier against further oxidation of the titanium aluminate support [1]. Despite the fact that Al$_2$O$_3$ is more stable than TiO$_2$, faster rate of the TiO$_2$ formation was recorded at beginning of the oxidation process of titanium aluminides [9].

Addition of other elements (Nb, Mo, Cr, Y, etc.), surface treatment and /or coating deposition on the surface of a α$_2$-Ti$_3$Al base alloy were developed in order to increase its oxidation resistance and prevent overheating of the base material [3]. Commonly, high-temperature doped-titanium alloys rely, for their resistance against oxidation attack, on formation of oxide scales with highly protective properties, i.e., Al$_2$O$_3$, Cr$_2$O$_3$, or SiO$_2$ [10], and suppression of TiO$_2$ as rutile growth [11]. Based on the thermodynamic stabilities of the these oxides, it can be derived that only alumina is a suitable oxide to

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act as a protective scale in the case of γ-TiAl alloys, because both Cr$_2$O$_3$ and SiO$_2$ are less stable than TiO$_2$ at high operating temperatures.

A deposited coating, called thermal barrier coating (TBC), usually consists in several layers with different functionality, namely a top ceramic (TC) layer, a metallic bond coat (BC) and a thermally grown oxide (TGO) layer at the BC/TC interface formed during high temperature operation in air. Selection of the TBC’s materials is ruled by the following parameters: low thermal conductivity, chemical inertness, high melting points and wear resistance, matching of the CTE with the substrate [1, 12]. The most known BC of MCrAlY (where M stands for Ni and Co) ensures oxidation protection and adhesion of TBC to the support [1] while the ceramic outer layer or the thermal barrier prevents overheating of the support due to its very low thermal transfer coefficients. In fact, TC reduces temperature of the TBC surface by 100-300°C range [13]. Moreover, the ceramic layers deposited by air plasma spraying (APS) as well as by high-velocity oxygen fuel spraying (HVOF) are porous and do not block the diffusion of oxygen to the support [14], a real diffusion barrier against oxygen is represented by the TGO layer grown between the bond coating and thermal barrier [15,16]. Given the fact that thermodynamically studies pointed out that α-Al$_2$O$_3$ is the most stable alumina polymorph [17] and a TGO of α-Al$_2$O$_3$ is difficult to obtain on titanium aluminides operating below 1100°C in air [18], recently some researchers have been investigated possibility to deposit a sandwich layer of Al$_2$O$_3$ as a diffusion barrier included in a TBC system [8,19]. Also, top ceramic coats of Al$_2$O$_3$ and Al$_2$TiO$_5$/Al$_2$O$_3$ were applied to diminish oxygen diffusion inwards the γ-TiAl alloys [20].

Since α$_2$-Ti$_3$Al alloy does not develop a continuous layer of protective α-Al$_2$O$_3$ during oxidation, the purpose of our work was to deposit a Al$_2$O$_3$ layer by APS onto a NiCrAlY / Ti$_3$Al system and to study its behavior both as a diffusion barrier against oxygen and thermal barrier, during long isothermal oxidation at 850°C for 500 h. Results of this study will complete our previous reported data [21] on the same system exposed to cyclic oxidized conditions.

2. Materials and methods

The cast α$_2$-titanium aluminide with a chemical composition of Ti-19Al-10Nb-3V (at. %) and shaped into 20x20x2 mm specimens served as support material. Surface of the specimens were polished with emery paper, micro powder alumina and further ultrasonically cleaned in distilled water. Two types of coatings were successively deposited on the specimen surfaces by APS technique, a metallic coat of NiCrAlY (Amdry 9621) with a bonding role (BC) and a top ceramic coat consisting in α-Al$_2$O$_3$ (Metco 105NS), respectively. The main characteristics of the powders (Sulzer Metco) used to obtain these two coatings were presented in Table 1.

| Powder                  | Ni (wt %) | Cr (wt %) | Al (wt %) | Y (wt %) | Grain size (µm) |
|-------------------------|-----------|-----------|-----------|----------|-----------------|
| NiCrAlY (Amdry 9621)    | base      | 22        | 10        | 1        | -90 ± 45        |
| α-Al$_2$O$_3$ (Metco 105NS) | -         | -         | 98.0      | -        | -45 ± 15        |

Both coatings were deposited by an Ar–H$_2$ plasma jet generated by means of a METCO 7 M gun operating at plasma arc power of 34 - 35 kW. The specific deposition parameters for the APS coating are illustrated in Table 2.
Table 2. Selected parameters for APS sprayed coatings

| Parameters     | Amdry 9621 | Metco 105NS |
|---------------|------------|-------------|
| Voltage (V)   | 68         | 70          |
| Current (A)   | 500        | 500         |
| Ar (L/min.)   | 45         | 40          |
| H₂ (L/min.)   | 12         | 13          |
| Powders feed rate (g/min.) | 38 | 40 |
| Spraying distance (mm) | 120 | 120 |
| Nozzle diameter (mm) | 2 | 1.8 |

Thermal oxidation tests of all specimens were conducted in a Vulcan 3-130 Ney furnace at 850°C for 500 h, in air. The mass gain of each isothermal oxidized specimen was measured by using an analytical balance (accuracy ±0.1mg). Three identical specimens of each system were analyzed in order to confirm reproducibility.

The coatings characterization was carried out by microscopic and spectroscopic methods, as follows: Scanning Electron Microscopy (SEM), Raman Spectroscopy and X-ray diffraction.

For morphological characterization a microscope FEI Inspect F50 high-resolution field emission equipped with energy dispersive spectroscopy (EDS) was used, while compositional and structural analysis were carried out by means of a micro-Raman spectrometer (LabRam HR800 from Jobin-Yvon–Horiba) equipped with a 514 nm laser and a Rigaku Ultima IV diffractometer with CuKα radiation, operating at 40kV and 30mA and equipped with a thin film attachment for grazing incidence X-ray measurements at an incidence angle ω=0.5°.

3. Results and discussions

3.1 α₂-Ti₃Al base alloy

The bare base alloy of α₂-Ti₃Al was strongly oxidized after 500 h exposure at 850°C. Thus, its surface is covered by a mixture of aluminum and titanium oxides with different morphologies as noticeable in Figure 1 and Table 3.

According to the transversal section in Figure 1a, thickness of the oxide formed coating is considerable reaching about 50-60µm. The layered structure of the grown oxide layer is in agreement with the one reported by Leyens [1] consisting in two main morphologies, here labeled 1 and 2, for small grain of rich aluminum oxides and blocks of columnar titanium rich oxides, respectively. However, due to discontinuous alumina layer and unprotective titanium dioxide formed on bare α₂-Ti₃Al alloy is prone to spallation [1].

This fact is also evidenced by EDX and Raman analysis of the specimen surface (Table 2 and Figure 2). As expected for high temperature exposure, the rutile polymorph [22] of TiO₂ is noticeable.
in Figure 2. Lack of alumina evidence in the Raman spectra [23] collected from spalled and adherent scale is due to the fact that TiO$_2$ is a strong Raman scatterer [24] that masks other spectral contributions regardless its concentration. Shifted and broader bands for the spalled scale might be caused by the smaller crystal size and/or less crystalline grown TiO$_2$.

**Table 3.** Chemical compositions (analyzed by EDXS) of the zones in $\alpha_2$-Ti$_3$Al after 500 h of thermal oxidation at 850 °C (wt. %)

| Analyzed zone | O K | Al K | Nb L | Ti K | V K |
|---------------|-----|------|------|------|-----|
| 1-fig.1a      | 4   | 19   | 10   | 64   | 3   |
| 2-fig.1a      | 7   | 16   | 20   | 41   | 6   |
| 3-fig.1a      | 26  | 2    | 13   | 51   | 8   |
| 4-fig.1a      | 26  | 2    | 9    | 55   | 8   |
| 5-fig.1a      | 35  | 39   | 2    | 21   | 3   |
| 6-fig.1a      | 47  | 28   | 2    | 20   | 3   |
| Global surface| 38  | 18   | 5    | 34   | 5   |
| 1-fig.1b      | 43  | 22   | 5    | 26   | 4   |
| 2-fig.1b      | 38  | 5    | 0    | 50   | 7   |

To improve long term oxidation resistance of the rich titanium alloys as $\alpha_2$-Ti$_3$Al, deposition of protective layers is required.

3.2 $\alpha_2$-Ti$_3$Al coated with NiCrAlY

One of the protocols to improve oxidation resistance of the $\alpha_2$-Ti$_3$Al alloy above 800 °C is to apply a protective layer of NiCrAlY as bond coat (BC) and subsequently to anchor a thermal ceramic (TC) coat [1].

The cross-section analysis of NiCrAlY / Ti$_3$Al specimen obtained in this work by APS is illustrated in Figure 3a. Adhesion between BC and substrate is relatively good since no discontinuities were found at the NiCrAlY-Ti$_3$Al interface. Moreover, several oxide stringers (dark grey streaks) in the inset A of the figure 3a suggest that weak particle oxidation occurred during deposition process. A plausible explanation for these defects in the APS coatings consists in shrinkage of the molten droplets as soon as they splat and rapidly solidify onto substrate [16]. Given the fact that porosity can affect negatively the oxidation resistance of the bond coats [25, 26], an estimated average porosity of 7.5%, obtained by SEM image analysis, for the NiCrAlY coat in this work points out its relatively dense state. Typically, porosity of the bond coat alloys deposited by plasma spraying methods can exceed 10%.

![Figure 2. Raman spectra of the oxide scale formed by $\alpha_2$-Ti$_3$Al specimen](image-url)
Figure 3. SEM images of surface and cross-section of NiCrAlY / Ti$_3$Al specimens after thermal oxidation at 850 °C for 500 h

Although absent in as-obtained NiCrAlY-Ti$_3$Al system, by 500-hour isothermal exposure at 850 °C a significant interdiffusion affected zone of about 20 µm into substrate is formed (see whitish zone 2 in Figure 3a).

The EDXS data and elemental map in figure 4-d show nickel as the main diffusing element from coating to substrate; its concentration reaches about 47% (point 2 in fig. 3a), while Ti diffuses from substrate to coating (Ti map in Figure 4f). A small concentration of chromium (2%) in the interdiffusion substrate zone, suggests its limited involvement.

Table 4. Chemical compositions (analyzed by EDX) of the zones in NiCrAlY / Ti$_3$Al after exposure at 850 °C for 500 h (wt. %)

| Analyzed zone | O K | Al K | Y L | Cr K | Ni K | Ti K | Nb L | V K |
|---------------|-----|------|-----|------|------|------|------|-----|
| 1 - fig.3a    | -   | 19   | -   | -    | 68   | 10   | 3    |     |
| 2 - fig.3a    | -   | 13   | -   | 2    | 48   | 29   | 6    | 2   |
| 3 - fig.3a    | 4   | 7    | 2   | 27   | 56   | 2    | 2    | -   |
| 4 - fig.3a    | 2   | 9    | 3   | 16   | 70   | -    | -    | -   |
| 5 - fig.3a    | 2   | 9    | 3   | 18   | 68   | -    | -    | -   |
| 6 - fig.3a    | 23  | 27   | 2   | 12   | 36   | -    | -    | -   |
| Global surface| 19  | 20   | 2   | 19   | 40   | -    | -    | -   |
| 1 - fig.3b    | 30  | 38   | 2   | 12   | 18   | -    | -    | -   |
| 2 - fig.3b    | 17  | 8    | -   | 12   | 63   | -    | -    | -   |

According to elemental distribution maps presented in Figure 4 it can be assumed that the inferior side of the thin layer formed between substrate and coating is bordered by small aluminum and chromium rich phase due to an inward diffusion of Ni as discussed above. Hence, by longtime oxidation (500 h at 850°C) of the NiCrAlY/ Ti$_3$Al specimens, a grey layer with a thickness of about 5µm at the coating/substrate interface was depicted in Figure 3a between zones 2 and 3. This layer is mainly composed of Cr$_2$O$_3$ and a small quantity of Al$_2$O$_3$ according to EDXS analysis (Table 4) and elemental distribution maps (zone 2 in Figures 4-a, b, c, e). Cr$_2$O$_3$ formation can be ascribed to selective internal oxidation. High affinity of oxygen for chromium and aluminum is the reason for obtaining beneficial Al and Cr oxides with higher stability.

Furthermore, a very thin discontinuous outer layer (Figure 3a - point 6 and Figures 4-b, c, d, e) was grown on NiCrAlY coating by long isothermal oxidation. According to Figures 3b, 4-b, c and 4-d, e the outer oxide scale consists in alumina disrupted by nickel and chromium oxides.
Figure 4. Elemental distribution maps of cross-section of NiCrAlY / Ti₃Al specimen after exposure 500 h at 850 °C

Raman spectrum 500h in Figure 5a point out an intricate composition (Figure 5 and Table 4) of the TGO layer, namely: NiO (bands located at 560, 740 and 1075 cm⁻¹ [27]), low amounts of Y₂O₃ (band at 192 cm⁻¹ [28]) and Cr₂O₃ (305, 350, 533, 623 cm⁻¹ bands [29]) scale and traces of α-Al₂O₃ (418 and 993 cm⁻¹ bands [23]). As expected, no Y and Al oxides were depicted with Raman analysis on the NiCrAlY/Ti₃Al specimen prior oxidation test, namely the NiCrAlY / Ti₃Al_0h spectrum in Figure 5a. XRD analysis of isothermal oxidized NiCrAlY / Ti₃Al specimen oxidized revealed the presence of Cr₂O₃, Al₂O₃, NiO as well as Ni, AlNi₃ (Figure 5b). No diffraction lines corresponding to Y₂O₃ (as was confirmed by Raman spectroscopy) were observed probably due to their lower amount under XRD limit detection (< 5%). Large amount of NiO, traces of α-Al₂O₃ and no TiO₂ were formed during long isothermal oxidation tests at 850° C carried out in this work (Raman spectrum_500h in Figure 5a) in comparison with the NiCrAlY / Ti₃Al specimens cyclic oxidized (10 times x 10 h) at 850° C where transient aluminas were depicted [21].

Figure 5. (a) Raman spectra of the NiCrAlY / Ti₃Al specimen initial state (0h) and oxidized at 850 °C for 500 h, and (b), XRD pattern of the NiCrAlY / Ti₃Al specimen oxidized at 850°C for 500 h

Conversely, TGO of the long isothermal treated specimens here are also similar with the preoxidized treated NiCrAlY / Ti₃Al specimens at 1100°C for 2h presented in our prior paper [21]. The latter specimens exposed to cyclic oxidation (10 times x 10 h) at 850°C had a TGO consisting in a
mixture of NiCr$_2$O$_4$ spinels and higher content of corundum (α-Al$_2$O$_3$). Hence, preoxidation treatment at high temperatures (>1000° C) enables formation of richer-α-Al$_2$O$_3$ TGO.

However, discontinuous α-Al$_2$O$_3$ and detrimental NiO present in the scale requires an additional diffusion barrier layer on the NiCrAlY / Ti$_3$Al specimen surface.

### 3.3 α2-Ti$_3$Al coated with Al$_2$O$_3$ / NiCrAlY

α-Al$_2$O$_3$ was selected to cover the NiCrAlY / Ti$_3$Al system in order to protect against interdiffusion processes as well as inward oxygen diffusion. The new Al$_2$O$_3$ / NiCrAlY / Ti$_3$Al system was tested with respect of both diffusion and thermal barrier roles. Although alumina coat deposited by APS technique consists in metastable and amorphous aluminas [18], few strategies (various oxide additions [18], laser surface treatment and annealing above 1000 °C [30]) were used to convert metastable aluminas into α-Al$_2$O$_3$. Since annealing treatment of the APS deposited alumina coat causes formation of micro-cracks and volume reduction of the coat, no pre-oxidation treatment was applied to the Al$_2$O$_3$ / NiCrAlY / Ti$_3$Al system.

![Figure 6. SEM images of surface and cross-section of Al$_2$O$_3$ / NiCrAlY / Ti$_3$Al specimens after 500 hours of thermal oxidation at 850 °C](image)

According to the SEM image in Figure 6a, diffusion processes between the α2-Ti$_3$Al support and the NiCrAlY coating were diminished (Figure 6). This fact is supported by the elemental analysis in Table 5 and Ni map in Figure 7c.

| Analyzed zone | O K | Al K | Y L | Cr K | Ni K | Ti K | Nb L | V K |
|---------------|-----|------|-----|------|------|------|------|-----|
| 1-fig.7b      | -   | 19   | -   | -    | -    | 68   | 10   | 3   |
| 2-fig.7b      | -   | 14   | -   | -    | 27   | 49   | 7    | 3   |
| 3-fig.7b      | 2   | 8    | 1   | 17   | 71   | 1    | -    | -   |
| 4-fig.7b      | 2   | 10   | -   | 20   | 68   | -    | -    | -   |
| 5-fig.7b      | 34  | 66   | -   | -    | -    | -    | -    | -   |
| 6-fig.7b      | 34  | 66   | -   | -    | -    | -    | -    | -   |
| Global-surface| 34  | 66   | -   | -    | -    | -    | -    | -   |

The nickel diffusion is two times smaller than the one recorded for the specimens coated with only NiCrAlY. It can be concluded that the top Al$_2$O$_3$ layer hindered the interdiffusion processes at the NiCrAlY-Ti$_3$Al interface.
EDX analysis (zones 3 and 4 in Figure 6a and Table 5) and elemental distribution maps in Figures 7 b-c-f point out traces of several oxides (especially Al and Cr), very likely formed either during deposition process or long isothermal oxidation at 850 °C. A plausible explanation consists in presence of less dense top coat of Al₂O₃ (Figure 6b) which allows oxygen diffusion towards the bond coat and hence internal oxidation (Figures 7 b-c-e-f).

**Figure 7.** Elemental distribution map of cross-section of Al₂O₃ / NiCrAlY / Ti₃Al specimen after 500 h of thermal oxidation at 850 °C

Presence of transient and/or amorphous aluminas along with traces of dense and protective α-Al₂O₃ are noticeable in Raman spectrum (Figure 8a) of the alumina top coat before exposure to isothermal oxidation. Intriguingly the amount of α-Al₂O₃ polymorph seems to increase as the depth increases (see depth profile Raman spectra in the inset of Figure 8a). Although isothermal oxidation test was conducted bellow 1000 °C, crystallization of δ - θ and α polymorphs of Al₂O₃ are inferred from the Raman spectrum after [31] and XRD patterns in Figure 8.

**Figure 8.** (a) Raman spectra (* stands for α-Al₂O₃ and inset represents the depth profile spectra before oxidation) and (b), XRD pattern of the Al₂O₃ / NiCrAlY / Ti₃Al specimen oxidized at 850 °C for 500 h

By heating above 800°C, gradual crystallization of α-Al₂O₃ is accompanied by densification and lowering of the alumina coat porosity and hence diminishing of the oxygen diffusion through the coating.
Figure 9 shows the mass gain for uncoated and coated specimens during isothermal oxidation at 850°C. Specimens coated with NiCrAlY and Al₂O₃/ NiCrAlY did not fail by spallation during the maximum exposure time, whereas the specimen uncoated exhibits the worst oxidation resistance. The mass gain rate of all specimens was rather steep at the beginning of isothermal oxidation test. Conversely, similar mass gain was recorded for the same specimen pre-annealed at 1100 °C and exposed to cyclic oxidation [21]. After 100 h of oxidation, the specimen coated with diffusion barrier (α-Al₂O₃) exhibits better oxidation resistance than the uncoated and NiCrAlY-coated specimens.

![Figure 9](image.png)

**Figure 9.** Plot of mass gain vs. time during the isothermal oxidation at 850°C of Ti₃Al, NiCrAlY / Ti₃Al and Al₂O₃ / NiCrAlY / Ti₃Al

Decreasing mass gain rate of the alumina-covered specimens illustrated in Figure 9 could be explained by formation of denser and richer α-Al₂O₃ coat when exposed to high temperature for long time. Hence, we can assume that in time the outer alumina coating acts as an oxygen diffusion barrier and protects inner layers against oxidation. This assumption is supported by oxygen concentration measurements performed inside of the bond coating, at 20 μm under alumina coating after different oxidation times, e.g. 300 h- 11 wt %, (results not shown here); 500 hours-2 wt % (Table 5 zones 3 and 4).

Furthermore, a mass gain of about 0.8- 0.95 mg cm⁻² for the Al₂O₃ / NiCrAlY / Ti₃Al specimens during 500 h of isothermal oxidation at 850°C is consistent with data reported for other thermal barrier coatings (0.8-1.4 mg cm⁻² for YSZ / NiCrAl / TiAl) [32] and our previous results for Al₂O₃ / NiCrAlY / Ti₃Al during cyclic oxidation at 850 °C (0.97 mg cm⁻²) [21].

### 4. Conclusions

A new Al₂O₃ / NiCrAlY / Ti₃Al system obtained by APS technique was tested for isothermal oxidation resistance at 850°C for 500 h.

It can be concluded that the top coat of Al₂O₃ has substantially declined oxidation rate for isothermal oxidation of Al₂O₃ / NiCrAlY / Ti₃Al due to its dual role of oxygen and thermal barrier. However, without annealing treatment of α-Al₂O₃ formation, the Al₂O₃ / NiCrAlY / Ti₃Al system should be used in milder operating conditions, e.g. where cyclic oxidation resistance is not required.

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