High-temperature oxidation of CrAlYN coatings: implications of the presence of Y and type of steel

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ABSTRACT

Nanolayered CrAl(Y)N coatings are deposited on M2 and 316 steel substrates and heated to 1000 °C in air for 2 h to study their oxidation mechanism, the thermal stability and the reactive element (RE) effect of yttrium. CrAlN on M2 develops a Cr₂O₃/Al₂O₃ passivation layer that preserves in high degree the fcc-CrAlN structure however iron ions leave the substrate and travel to the surface along the column boundaries. The CrAlYN (Y content 1.6 at.%) coatings deposited on steels are not stable at 1000 °C, and the initial fcc-CrAlN phase is partially transformed to hcp-Al(O)N and Cr-Fe phases (M2) and Cr₂N and Al₂O₃ (316). The addition of Y changes the predominant scale growth direction. Inward oxygen diffusion becomes dominant but a reduction of the oxide scale thickness as compared to CrAlN is not observed. The advanced microstructural analysis made by transmission electron microscopy combined with electron energy-loss spectroscopy determined that yttrium migrates mainly to the oxide scale (forming mixed oxides with substrate elements - V and Mo, either as dispersed particles or segregated at the grain boundaries) in M2, and to the oxide interface and column boundaries (forming Al-Y oxides and YN, respectively) in 316 steels. The benefits of addition of Y in improving the oxidation resistance are discussed comparatively with literature data. The RE effect of yttrium is thus observed to be dependent on the substrate, film architecture and composition.

1. Introduction

$\text{Cr}_{1-x}\text{Al}_x\text{N}$ films deposited by physical vapor deposition have proven to be excellent candidates for advanced machining and protection for high-temperature applications due to their excellent hardness, wear, corrosion and oxidation resistance properties [1-9]. The incorporation of Al atoms in the face-centered cubic (fcc) lattice of CrN leads to a substantial hardening by the formation of a metastable solid solution, when $x=0.60$ to 0.75 . Beyond this critical threshold, the formation of a hexagonal closed-packed (hcp) AlN structure occurs, leading to a strength diminution [4,10]. Conversely, the increase of the Al content favors the segregation of some Al atoms along the grain boundaries, forming a continuous amorphous AlN network that further strengthens the coating [11].

The oxidation and corrosion resistance is also improved with respect to CrN, as previously reported by many authors [7,12-14]. The improvement is correlated with the development of a mixed Cr/Al-rich oxide layer, which acts as an effective diffusion barrier. The formation of dense and adherent mixed aluminum and chromium oxide scales eventually suppresses the diffusion of oxygen into the bulk and the outward diffusion of metallic cations, thereby providing excellent oxidation resistance up to temperatures higher than $900\text{ }^{\circ}\text{C}$ [15,16].

The increasingly demanding operating conditions of industrial processes require the use of materials capable of withstanding working temperatures in the order of $900\text{--}1000\text{ }^{\circ}\text{C}$ in machining and cutting tools or even higher (case of aeronautic applications). This pre-requisite necessitates the design of advanced coatings with superior oxidation resistance and thermal stability. In principle, there are two possible approaches to reach these objectives. On the one hand, multi-layered coatings CrN/AlN [17], TiAlN/CrAlN [18], TiAlSiN/CrAlN [19] have been demonstrated to provide superior hardness and oxidation resistance compared with single layer CrAlN coatings. On the other hand, the incorporation of yttrium as a reactive element (RE) in CrAlN coatings has also been proved to be effective for this purpose; it reduces the oxide scale growth rate and increases the onset of decomposition to $1100\text{ }^{\circ}\text{C}$ [20-23]. The thermal stability is also observed to increase as the onset for hcp-AlN precipitation, N_2 release and hcp-Cr₂N transformation shifts from ~ 900 to $1100\text{ }^{\circ}\text{C}$ [24]. Moreover, other beneficial effects of RE-addition are the decreased accumulation of voids at the substrate/scale interface [25] or the improvement of the mechanical properties of the scale by the modification of the

oxide scale structure [26]. Many mechanisms have been proposed to explain the oxidation resistance enhancement by RE-incorporation, although in most cases, they were performed on metallic bulk alloys and metallic coatings [27,28]. From a literature survey, it is suggested that the reduction of the oxide scale growth is presumably the most relevant factor due to the modification of the ion transport processes. The segregation of RE ions at oxide grain boundaries would block the outward diffusion of Cr and Al due to their larger size, thus preventing the inward diffusion of oxygen. Since the diffusion rate of anions is slower than that of cations, a reduction in the oxide scale growth rate would be expected.

The benefits with respect to the oxidation resistance of ternary and quaternary metallic nitrides due to the incorporation of yttrium have been successfully attempted for yttrium concentrations below a certain amount (2 mol% YN in TiAlCrN [29], 2-4 mol% YN in CrAlN [20], <1.3 at.% Y in CrAlN [17], 2 at.% in multilayered CrAlYN [30, 31]). Although this critical value varies depending on the aluminum content and the deposition process, there is a general consensus on the detrimental effect of an excess of yttrium. Y-overdoping directly results in severe internal oxidation and accelerated oxide scale growth due to its high oxygen affinity. Another important aspect on the oxidation and thermal resistance properties of CrAlYN coatings is the selection of the substrates for the study. Some of the previously published data highlight the excellent performance of free-standing CrAlYN films [13, 24] deposited on inert substrates as silicon [7,17, 22,] or alumina [20,30], high temperature alloys [31] to exclude substrate interferences or subjected to thermal annealing in vacuum or inert gas atmosphere [10,24,32]. Although this would be valid for the determination of the phase stability and decomposition temperatures, the interdiffusion phenomena of substrate elements and the interaction with film-constituting phases make it necessary to complete the characterization by studying annealing of samples directly deposited on the substrate, which are eventually used in the final foreseen application.

In previous works we have demonstrated the benefits of including Y vs. Zr as REs on the oxidation and thermal resistance as well as the influence of the Y-distribution in CrAlYN multilayered coatings with a low Al content (<10 at.%) [21,33,34]. Nevertheless, little is known about the mechanisms of action of this rare earth element, chemical state and location in metal nitrides. Moreover, the oxidation products and the oxidation resistance depend on the chemical composition, element

distribution and substrate composition; presumably better at higher Al contents. Therefore, this work seeks to explore the oxidation resistance and thermal stability of CrAlYN/CrAlN multilayered coating with higher aluminum contents (~ 25 at.% Al / $\text{Cr}_{0.51}\text{Al}_{0.46}\text{Y}_{0.03}\text{N}$) with an Y concentration of approximately 2 at.% deposited on M2 steel, (used in the final foreseen application) and compared with a non Y-doped CrAlN (~ 25 at.% Al / $\text{Cr}_{0.50}\text{Al}_{0.50}\text{N}$). The behavior of the same $\text{Cr}_{0.51}\text{Al}_{0.46}\text{Y}_{0.03}\text{N}$ coating deposited on 316 steel will also be studied, in order to analyze the influence of the substrate. In particular, by applying advanced microscopic analytical techniques, we will devote special attention in studying how the microstructure evolves during the oxidation processes, the role of Y, its location, and the chemical phases formed after the annealing treatment at 1000 °C in ambient air. This investigation results are interesting for understanding the protective effect of this type of coating under the working conditions of dry high speed machining, with temperatures on this order of magnitude.

2. Experimental

CrAl(Y)N coatings were prepared on polished M2 and 316 steels substrates by dc magnetron sputtering. The chemical composition of both types of steel is presented in Table 1 as given by the suppliers. The film deposition was performed in a commercial equipment (CemeCon® CC800/8) provided with four rectangular targets (200 mm $\times$ 88 mm $\times$ 5 mm): two mixed Al/Cr (80:20) and two alternated aluminum (99.5% purity) for the preparation of the CrAlN reference coating and two mixed Al/Cr (80:20), one aluminum (99.5% purity) and one yttrium (99.5% purity), for the CrAlYN films. The mixed targets are composed of Cr pellets inserted in the sputtering track of an Al block. The base pressure of the vacuum chamber was $\sim 1 \times 10^{-4}$ Pa, and the working pressure was set at 1 Pa, with an Ar/N₂ ratio of 1.5. The reactive gas mixture was selected based on previous optimized conditions for CrN coatings [5]. The sputtering conditions were set at 3000 W for the Al/Cr mixed targets, 1500 W for Al and 1000 W for the Y targets. The sample holder was negatively biased in the range of 110–120 V, and the measured temperature span was from 200 to 400 °C.

The chemical composition of the samples was obtained by electron probe microanalysis (EPMA) and glow discharge optical emission spectroscopy (GD-OES). Quantification was done by calibration using appropriated standard materials with

known compositions. The EPMA equipment was a JEOL JXA-8200 SuperProbe instrument equipped with four wavelength detectors (WDS) and one energy-dispersive X-ray detector (XEDS). Three measurements were carried out at 15 kV ($I = 20$ nA) on different positions separated more than 500 μm with a spot size of 20 μm . GD-OES was used to obtain the chemical depth profile with a Horiba Jobin Yvon RF instrument. This equipment was operated in argon plasma at 650 Pa and a forward power of 40 W with a 4 mm diameter copper anode. Quantified profiles obtained automatically using the standard Jobin Yvon Quantum Intelligent Quantification (IQ) software. Further details about operating conditions can be found elsewhere [15].

The X-ray diffraction (XRD) patterns were obtained in an X'Pert Pro PANALYTICAL diffractometer using $\text{Cu-K}\alpha$ radiation at an incidence angle of 5° .

The mechanical properties were measured with a Fischerscope H100 dynamic microprobe instrument using a conventional Vickers indenter at loads up to 10 mN. The maximum load was selected in such a way that the maximum indentation depth did not exceed 10–15 % of the coating thickness to decrease the influence of the substrate.

For transmission electron microscopy (TEM) characterization, cross-section lamellas were prepared using a dual focused ion beam FIB (Dual-Beam Helios). A FEI Tecnai field emission gun scanning transmission electron microscope (STEM-FEG), G2F30 model with an S-Twin objective lens was used at 300 kV, with a 0.2 nm point resolution, and equipped with a high angle annular dark field (HAADF) detector from Fischione with a 0.16 nm point resolution and an XEDS detector SSD (INCA X-Max 80). Electron energy-loss spectroscopy (EELS) and filtered imaging were obtained using a Gatan Imaging Filter (GIF) attached to the Tecnai microscope (QUANTUM SE model) with a bright field/dark field detector with an energy range of 0-2000 eV and an energy resolution of 0.3 eV. EELS spectra were recorded in STEM mode using a probe with a size of less than 1 nm, with a spectrometer collection angle of 19 mrad. Under these conditions, the energy resolution of the couple microscope/spectrometer system was ~ 0.8 eV. A spectrum-image (S.I.) [35] procedure was used to obtain the EELS spectra in each pixel from a selected area, and furthermore, to extract the elemental and compositional maps. After experimental acquisition, the S.I. data were processed using Gatan Digital Micrograph software for EELS spectra background subtraction, quantification and mapping. A multiple linear least square MLLS routine was used to obtain the chemical phase maps using reference EELS spectra. The Gatan digital

micrograph software was also used to acquire images and perform further image processing.

The oxidation behavior of the films was studied by annealing in open air in a static furnace as high as 1000 °C at a heating rate of 10 °C/min with a holding time of 2 h. This temperature was chosen to replicate operating conditions in dry high speed machining applications.

3. Results and discussion

3.1. Characterization of the as-deposited coatings

Table 2 summarizes the chemical composition obtained by EPMA, hardness and Young's modulus values for the as-prepared CrAlN and CrAlYN coatings. The slight excess in nitrogen in respect to a stoichiometric metal nitride is attributed to the quantification method by EPMA as metal/nitrogen ratio estimated by EELS is approximately 0.5. Therefore, the film stoichiometries shown in the table 2 were normalized to a nitrogen content of 50% ($\text{Cr}_{0.50}\text{Al}_{0.50}\text{N}$ and $\text{Cr}_{0.51}\text{Al}_{0.46}\text{Y}_{0.03}\text{N}$); however, for the sake of clarity, hereafter, the coatings will be labelled simply as CrAlN and CrAlYN. The hardness properties are found to be similar for both coatings (28 and 30 GPa, respectively) with H/E ratios close to 0.05. These mechanical properties are on the same order of previous published results [9,10,36,37].

The initial CrAlN and CrAlYN coatings deposited on M2 steel present a columnar structure and a multi-layered architecture of different chemical composition, as observed in the HAADF-STEM images depicted in figures 1a and 3a, respectively. The HRTEM micrographs (Figs. 1b and 3b) show the monocrystalline nature of the columns and the coherent growth of the different layers, which form the multilayer structure. Figure 2 illustrates the local changes in the chemical composition across this nanolayered structure obtained by EELS from a line scan performed in the CrAlN coating. The quantification of the Al, Cr, N and O contents along the line profile depicted in Fig. 2a reveals that the CrAlN coating is formed by a stack of layers with different Al and Cr contents and an oxygen impurity <7 at. %. This amount of oxygen is overestimated due to the ultra-thin thickness of the film lamella and the air exposure required for the TEM specimen preparation. No oxygen could be measured in the bulk initial films, as determined by EPMA. The N-K edge EELS spectra (Fig. 2c), measured

from Cr-rich (location 1) and Al-rich layers (location 2), exhibit the characteristic signatures of an fcc-CrAlN phase. The small difference in the near-edge structure is due to the distinct aluminum content [33]. The Al-K edges measured in both locations (see inset) displays the same type of structure, which was previously observed in an fcc-CrAlN phase [38]. In the CrAlYN coating, the Al and Y-rich layers are separated by a Cr-rich layer, as observed in the elemental distribution map inserted in Fig. 3a. The different chemical composition of the multilayered system is produced by the sequential exposure of the substrates to different target compositions during rotation in the deposition chamber. An investigation of the influence of the target distribution on the chemical composition of the multilayers and the oxidation resistance after annealing to 1000°C can be found in our earlier works [33,34].

Figure 4 depicts the crystalline structure determined by XRD analysis of the as-deposited CrAlN and CrAlYN coatings at 5° of grazing incidence (Figs. 4a and 4c). The diffractograms are congruent with a cubic structure (fcc-CrN) for both nitride films with Al incorporated in the CrN lattice as a solid solution and (111) reflection at 37.6° as main peak. The aluminum incorporation is still below the limit established for the preferential formation of the hcp-AlN phase. The left-shift of the peaks of both samples with respect to the fcc-CrN phase can be attributed to residual compressive stresses and the increase of the lattice parameter produced by the Y incorporation, as previously observed [34].

3.2. Oxidation performance of CrAlN

The XRD pattern of the CrAlN coating after thermal annealing at 1000 °C in air for 2 hours is depicted in Fig. 4b. The strong peaks are assigned to the fcc-CrN phase, which indicates a good oxidation resistance. The shift to higher angles after the annealing treatment is likely attributed to the release of compressive stresses and to the formation of hcp-AlN. The presence of this latter phase has been clearly determined via TEM observation as demonstrated later. Furthermore, some small peaks corresponding to Cr₂O₃, Fe₃O₄ phases indicated the formation of a thin oxide scale and the outward diffusion of iron from the steel. The asymmetric broadening of the peak at 44.5° due to c-Cr(Al)N towards the side of higher angles can be attributed to the presence of a Fe-Cr phase.

Fig. 5a shows the GD-OES profiles of the annealed CrAlN sample. The oxygen signal is essentially limited to a superficial region of less than 500 nm (zone I), and no noticeable inwards diffusion is observed beyond this, which is indicative of a good oxidation resistance. In this region, the N signal decreases abruptly, while the Cr and Al profiles present sharp peaks that may correspond to two consecutive oxide layers. The higher mobility of chromium ions might explain the formation of a Cr-rich oxide layer on the topmost surface followed by an Al-rich oxide layer, thereby forming a bilayer, as described by other authors [31,40]. It is known that although Al_2O_3 is preferentially formed due to its higher free enthalpy of formation in comparison to Cr_2O_3 , a Cr-rich outer layer is generated, as Cr species possess a higher mobility. The presence of iron and carbon on the top is attributed to the migration of these elements from the substrate through the coating, which is in agreement with the Fe_3O_4 and Fe-Cr phases detected by XRD. Iron diffusion appears to be hindered by the oxide layer, and it exhibits a maximum at the interface. Under the oxide scale (zone II), the Al content remains almost constant (~20 at.%), while Cr and N display average values of approximately 30 and 35 at.%, respectively, with a slight tendency to decrease. This second region extends for approximately 5 μm , corresponding to the composition of the initial film; this confirms the passivation character of the top-oxide layer. In the vicinity of the interface with the substrate (zone III), an enrichment of Cr and C is denoted due to element interdiffusion.

A HAADF-STEM study performed on a cross-section lamella extracted from the oxidized coating revealed the changes of the microstructure along the film thickness (cf. Fig. 6a). In the most superficial region (zone I) a compact oxide scale of approximately 450 nm is observed. The chemical composition obtained by X-EDS (Fig. 6b) in the region near the scale/coating interphase is consistent with the formation of $(\text{Cr,Al})_2\text{O}_3$ or a mixture of Cr_2O_3 and Al_2O_3 phases. XRD showed evidences of crystalline Cr_2O_3 but not of Al_2O_3 . A small peak of iron is also detected in this area. Underneath (zone II), the coating still exhibits the columnar morphology and multilayer nanostructure but some precipitates from 50 to 200 nm are observed inside. The density of these crystals increases towards the substrate. The quantitative elemental maps obtained by X-EDS from a smaller area (orange square) in this zone (Fig. 6c) confirmed the multilayer structure, alternating Cr- and Al-rich layers together with the presence of Fe and O as a consequence of the corrosion processes. The Fe ions are distributed preferentially along

the column boundaries, serving as tunnels to the surface, while oxygen is more homogeneously dispersed. The oxygen content is below 7 at. % (comparable to the initial measured values), which again indicates a good oxidation resistance. A large crystal emerging from the columns (marked as *) is found to be composed of Al and N. The signatures of the fine structure of the N-K and Al-K edge EELS spectra measured on them (Fig. 6d) are characteristic of the hcp-AlN phase [38], while the spectra obtained from the multilayers present the typical signature of the original fcc-CrAlN structure (Fig. 2c). The presence of the hcp-AlN precipitates is in agreement with the partial decomposition of the ternary nitride ($\text{fcc-CrAlN} \rightarrow \text{fcc-Cr} + \text{hcp-AlN} + \text{N}_2$) that occurs at 900 °C [20]. The Cr out-diffusion from the fcc-CrAlN phase, the higher mobility of Cr than Al, and the stronger Al-N vs. Cr-N bonding favor the precipitation of the hcp-AlN phase [13]. The release of metallic chromium and the outward diffusion of elements from the substrate, particularly Fe, accounts for the corrosion products formed. Iron atoms combine with chromium to form a Fe-Cr alloy and with oxygen to form Fe_3O_4 on the top surface.

In the innermost region near the substrate, a polycrystalline structure is developed (not shown here, cf. Figs. 1 and 2 of supporting information, SI). The quantitative chemical analysis and phase identification performed with EELS helped to identify the presence of hcp-AlN, fcc-CrAlN, Cr_7C_3 and Fe-Cr phases. The formation of Cr_7C_3 was also reported in similar CrAlN coating (Al<10 at.%) deposited on M2 [34].

3.3. Oxidation performance of CrAlYN on M2 steel

The XRD pattern of the oxidized CrAlYN coating deposited on M2 substrate is depicted in Fig. 4d. The absence of peaks belonging to the chromium nitride phase indicates the transformation of the initial crystalline nitride phase. Most of the peaks relative to the oxide scale lie between diffraction peaks of $\alpha\text{-Cr}_2\text{O}_3$ (PDF #1-84-315 and 38-1479) and $\alpha\text{-Al}_2\text{O}_3$ (PDF #1-71-1684). This result suggests the formation of a $\alpha\text{-(Cr,Al)}_2\text{O}_3$ mixed oxide scale. Both Cr_2O_3 and Al_2O_3 crystallize in the same rhomboedric structure and have similar lattice parameter values. Less intense peaks corresponding to a second rhomboedric Al_2O_3 phase (PDF #1-77-2135) with different lattice parameters are also observed. The peak at 32° could be assigned to an yttrium-

molybdenum mixed oxide ($\text{Y}_2\text{Mo}_3\text{O}_{12}$), which is attributed to the diffusion of the latter element from the substrate. The strong peak at 44.5° corresponds to the intermetallic Fe-Cr phase. Some unidentified peaks can be attributed to an oxidized hcp-AlN phase based on information obtained later by TEM analysis.

Fig. 5b show the GD-OES profiles of this coating after oxidation at 1000°C in ambient air. The oxygen signal is extended along the entire film thickness and its content decrease from ca. 50 at.% (topmost surface) to 40 at.% in a first step (zone Ia) for a thickness of about $\sim 1\ \mu\text{m}$. In the next portion, the O content remains approximately constant at 37 at.% up to a thickness of $\sim 2.5\ \mu\text{m}$ (zone Ib), where a sharp and continuous decrease starts (zone II). In the vicinity of the substrate interface, a high degree of intermixing of elements from the steel and coating is clearly denoted (zone III), including oxygen diffusion into the substrate. Yttrium and molybdenum signals are clearly observed in the topmost layer where oxygen reached its highest content. This is consistent with the formation of mixed Y-Mo oxides, as previously demonstrated by XRD. The other metallic elements (Cr, Al, Fe) and N display variable signals across the different regions. It is worth mentioning that the Cr and Al profiles do not present peaks in zone Ia as commented in the case of CrAlN. Al, Cr and O profiles present a plateau in the following region (oxide scale -zone Ib) while N, although present, is in a much lower concentration. The depletion in the N content in this region is indicative of its partial removal by the oxidation of the fcc-CrAlN phase. In zone II, nitrogen, aluminum and iron showed their maximum values, which is in agreement with the lower film decomposition and oxidation. An accumulation of Cr and C is observed beyond the substrate interface, similarly to the CrAlN film. Nevertheless, carbon did not move beyond this region, thus preventing their outward diffusion and Cr_3C_7 formation, as demonstrated in [34] by the incorporation of yttrium as the reactive element in the film composition. On the contrary, yttrium content (1.6 at.%) appears to be insufficient to inhibit the release of iron from the substrate.

In the HAADF-STEM image or Z-contrast of the oxidized CrAlYN sample shown in Fig. 7 two different regions, zone I and II, can be distinguished. A deeper region (zone III) also exists, although it is not displayed in this image. The microstructural study has been focused on both zones that will be analyzed separately in Figs. 8 and 9 respectively. The oxide scale, shown in the HAADF-STEM image depicted in Fig. 8a, exhibits regions of bright contrast in a predominantly dark matrix

composed of $(\text{Cr,Al})_2\text{O}_3$, as stated by X-EDS and EELS analysis (see Fig. 8b). An iron content of 0.8 at.% was determined, much lower than in CrAlN coating. Inside this scale, the presence of crystals (200–300 nm) of mixed Y-Mo and Y-V oxides can be concluded from the X-EDS analysis (cf. Fig. 8c, points 1 and 2, respectively). The presence of these phases is in agreement with previous GDOES and XRD results. Yttrium is also found in the grain boundaries of the $(\text{Cr,Al})_2\text{O}_3$ phase as denoted by the bright contrast observed in the HAADF image and X-EDS analysis (point 3 in Fig. 8c). The darkest contrast can be attributed to the existence of pores or small precipitates of Al(O)N. The analysis made in one of this black spots (point 4) revealed the presence of N (nitrogen was also detected by GDOES) and a higher Al/Cr ratio compared to the previous points, which confirms the existence of Al(O)N grains. Figure 9a shows a z-contrast image of the layer below the oxide scale. This region still exhibits the multilayer nanostructure, but it is covered by a huge amount of small crystals. By combining X-EDS (Fig. 9b) and EELS analysis (Fig. 9c), hcp-Al(O)N (point 1) and Fe-Cr (point 2) phases have been identified in different positions. Peaks of Y, Mo and V are also detected in the X-EDS spectra of this region, although their intensities are much lower than those in the oxide scale.

3.3. Oxidation performance of CrAlYN on 316 steel

The phases formed after the oxidation of the CrAlYN coating deposited on 316 stainless steel are significantly different (Fig. 4e). The strongest peaks in the XRD diffractogram are assigned to the hcp- Cr_2N phase, which arises from the first step of the decomposition of the fcc-CrAlN phase [13,20]. Several broad and very little intense peaks are likely attributed to a thin poorly crystalline oxide scale. These peaks could be assigned to phases as CrO, $\text{CrMn}_{1.5}\text{O}_4$, indicative of a lower degree of oxidation of chromium atoms. Some small peaks can be assigned Mn_3O_4 . The presence of Mn-phases indicates the outward diffusion of elements from the substrate.

The GDOES profiles (Fig. 5c) across the coating show that lower amount of oxygen penetrates into the coating in comparison with M2 steel. The surface is rich in chromium and oxygen and iron migration is almost non-existent. Cr profile displays a peak in this zone indicative of the formation of Cr-rich oxide phase (zone I). Just below, the Y profile displays a maximum at the scale interface. In the intermediate region (zone II), there is a continuous oxygen gradient from 20 to 5 at.% in parallel with an

increment of the N signal associated to the fcc-CrAlN decomposition and hcp-Cr₂N formation observed by XRD. In the innermost part of this region, the oxygen decreases below 5 at.%, and the nitrogen reaches its maximum concentration. The substrate/film interface (zone III) appears clearly defined without the Cr and C intermixing observed in M2 steel.

To supplement the XRD and GDOES study, the oxidized coating was analyzed by means of TEM on a cross-section lamella. Two different regions (I and II) can be observed in the general Z-contrast image of Figure 10a corresponding to the oxide scale and inner region respectively. The oxide scale presents a variable thickness from 300 nm to 600 nm, and it is formed by huge grains (~300 nm) combined with black holes (~150 nm, the darkest contrast). The X-EDS and EELS spectra, (figure 3 of SI) obtained in different grains of zone I are congruent with the formation of Cr_xO_y, (Cr,Mn)_xO_y, and Al₂O₃ phases. The presence of Mn released from the 316 steel in the oxide scale was also indicated by XRD (cf. Fig. 4). X-EDS elemental (Fig. 10b) and phase maps (Fig. 10c) obtained across the interface between zone I and II (red square) show a transition from a mixture of chromium and aluminum oxides to chromium nitride grains surrounded by alumina. The chemical map of a selected area marked in white underneath (shown as inset) revealed the existence of aligned grains consisting of yttrium, which traces regular pathways between the columns. The microstructure of the zone II is characterized by the presence of rounded bright grains embedded in a dark matrix. Using the EELS spectra measured in different grains contained in the rectangle marked in green in Fig. 10a, a chemical phase mapping is performed. Fig. 11 illustrates the distribution of hcp-Cr₂N (green) and Al₂O₃ (red) phases in this region. The N-K and Cr-L_{2,3} edges of EELS spectra measured at point 1 show the characteristic signatures of the hcp-Cr₂N phase [42]. The O-K and Al-K edge EELS spectra measured at point 2 correspond to the Al₂O₃. The blue color indicates the location of the small Y-containing precipitates. The O-K edge EELS spectra measured on them (point 3) do not correspond to Y₂O₃ or mixed Al-Y oxide phases [43]. This fact and the presence of nitrogen suggest that Y in these precipitates must be in the form of nitride as Y(Cr)N. The detection of oxygen is due to the existence of an Al₂O₃ matrix; therefore, the blue color shows the distribution of a yttrium nitride phase embedded in the Al₂O₃ matrix.

In a HRTEM image of a deeper inner region (cf. Fig. 12), the presence of crystalline grains embedded in an amorphous matrix is observed. The crystal marked in

white corresponds to fcc-CrAlN, in agreement with the associated digital diffraction pattern obtained from this area (shown as inset). The d-spacings (2.0 and 2.3 Å) and the geometric disposition of the spots correspond to the [110] zone axis of this phase. This result denotes the presence of some remaining fcc-CrAlN crystals. Moreover, larger interplanar distances of 2.5 and 2.8 Å have been measured in the column boundaries and in small rounded crystals (~10 nm), which can be assigned to a fcc-YN phase. The amorphous matrix corresponds to the Al₂O₃ detected by EELS.

4. Discussion of the oxidation mechanism

The experimental results shown in this paper prove the direct influence of the incorporation of yttrium and the type (composition) of the substrate on the oxidation mechanism and obtained corrosion products of CrAlN multilayered protective coatings after thermal annealing at 1000°C in atmospheric air. Moreover, it has been possible to determine the chemical state and location of the different elements after oxidation supporting the dynamic-segregation theory to explain the reactive element effect [28].

For CrAlN on the M2 substrate, the coating maintains the fcc-CrAlN phase in a layered structure with some hcp-AlN precipitates. A dense and compact oxide bilayer (crystalline Cr₂O₃ and amorphous Al₂O₃) of approximately 450 nm is formed at the surface, which prevents further diffusion of oxygen into the coating [18]. The external layer richer in Cr is favored by its higher ion mobility as observed by other authors [20]. However, iron diffuses out from the substrate through the column boundaries, forming a Fe₂O₃ on the surface.

For CrAlYN on the M2 substrate, a thick oxide scale (~2.5 µm) is formed consisting of mainly (Cr,Al)₂O₃ and (Y,Mo,V)_xO_y nanocrystals embedded. Yttrium is also segregated at the oxide grain boundaries, contributing to scale densification. Iron released from the M2 substrate is present along the entire film thickness but a sharp diminution is observed at the oxide/nitride interface, indicating an inhibition of its migration towards the surface. The inner region has a complex nanostructure where small crystals of Fe-Cr are embedded in the remaining multilayer nanostructure consisting of hcp-Al(O)N phase. These corrosion products point out the decomposition of the fcc-CrAlYN leads to fcc-Cr and hcp-Al(O)N, the formation of a mixed oxide

scale, where different metallic-oxides phases coexist, and the diffusion of metallic ions (Fe and Mo) from the substrate.

These results show that the incorporation of 1.6 at.% of Y to this multilayered $\text{Cr}_{1-x}\text{Al}_x\text{N}$ ($x \approx 0.50$) coating on M2 steel did not report benefits to the reduction of the oxide scale. The formation of mixed yttrium oxides in the top layer scale facilitated instead the inwards diffusion of oxygen [41], which became the dominant mechanism, oxidizing the Cr and Al from the CrAlYN coating. Nevertheless, the nanolayered nitride structure is still preserved below this oxide layer consisting of hcp-Al(O)N and Fe-Cr phases.

For CrAlYN on 316 steel, a thinner and complex oxide scale of 300-600 nm is formed, mainly based on Cr, Al and Mn oxides. In the remaining coating, hcp-Cr₂N is the dominant phase as a result of the partial decomposition of fcc-CrAlN phase. The released Al atoms are oxidized forming an amorphous Al_2O_3 with fcc-Y(Cr)N crystalline grains embedded. Yttrium is mainly localized at the column boundaries and the scale/coating interface.

Different mechanisms of action were observed depending on the substrate composition affecting ion transport processes and scale adherence. The incorporation of Y to CrAlN retards the cation diffusion, mainly chromium in M2, favoring the inward penetration of oxygen, reaching the film/substrate interface unlike Y-free CrAlN where a passivation oxide layer is formed. In the case of the CrAlYN coating deposited on M2, the Y ions diffuse to the surface where appears forming $(\text{Y,M})_x\text{O}_y$ crystals and segregated at the $(\text{Cr,Al})_2\text{O}_3$ grain oxide boundaries. This produces an increase of the scale density, hindering further cations diffusion processes. The higher penetration of oxygen can be explained by an easier diffusion through these already formed oxides [41] and the concomitant phase decomposition of the CrAlN coating accelerated by the diffusion of iron from the substrate. For the CrAlYN coating deposited on 316, yttrium segregates instead to the column boundaries as Y(Cr)N, which causes a reduction of intercolumn porosity and rapid short-circuit diffusion through these boundaries. The formation of some Al-Y oxides at the scale interface may favor the oxygen inwards diffusion [22]. The interdiffusion of Cr and C in the substrate interface, forming a Cr-C rich region, is characteristic of M2 steel as a consequence of different chemical composition. It is worth mentioning that oxidation of bare substrates (M2 and 316) led

to the formation of poor adherent iron oxides scale (mainly Fe_2O_3 and $\text{Fe}_3\text{O}_4/\text{Cr}_2\text{FeO}_4$, respectively).

The present multilayered CrAlYN/CrAlN coatings deposited on steels are not stable at 1000°C , and the initial fcc-CrAlYN phase are partially transformed to hcp-Al(O)N and Cr-Fe phases (M2) and Cr_2N and Al_2O_3 (316). The lowest oxide thickness is obtained for the CrAlN coating where the cubic initial phase (fcc-CrAlN) is predominant after annealing in air at 1000°C . This result differs from that obtained for low-Al content coatings (<8 at. %) [34], where a positive effect of yttrium (2-4 at.%) was demonstrated via blocking the out-diffusion of elements from the substrate. For similar aluminum contents than those prepared in this paper, Qi et al. [22] found the best oxidation performance at the lowest Y content (0.3 and 0.7 at.%) with clear detrimental effect at values ≥ 1.3 at.%. Additionally, Rovere et al. [20] proved that the yttrium content must be <4 mol% YN (i.e., 2% Y expressed in atomic fraction) for optimum oxidation resistance with (Al/Cr ≈ 1.2). More recently, Liu et al. found an optimum value of 0.5 at. % at 800°C and increased to 2 at.% for multilayered coatings with lower Al content (Al/Cr ≈ 0.7) heated at 1100°C [31]. These pieces of evidence seem to indicate that the optimum concentration of RE is highly dependent on the Al/Cr ratio and structural characteristics of the films. Another possible factor is varied film architecture (single [20,22,24] or multilayered systems [31]). In the case of multilayer coatings, the presence of large number of interfaces is also expected to affect the oxidation mechanism due to the microstructural changes induced upon annealing. Furthermore, most of the optimum values given in the literature were given after studies carried out in inert substrates (Si [7,17,22], Al_2O_3 [20, 30] or high-temperature alloys (Inconel 718 [31], γ -TiAl [44], hard metals, etc.) or free-standing films [20] where ion interdiffusion from substrate elements are limited or absent. In summary, it is clear that the appropriate selection of the yttrium concentration as a dopant is crucial for developing the RE effect and reducing the oxide scale growth. This value is dependent on the aluminum content, film microstructure, and the substrate characteristics, and it cannot be given a priori as a general rule.

5. Conclusions

In this work, we have studied the oxidation resistance of $\text{Cr}_{0.50}\text{Al}_{0.50}\text{N}$ (deposited on M2) and $\text{Cr}_{0.51}\text{Al}_{0.46}\text{Y}_{0.03}\text{N}$ coatings (deposited on M2 and 316 steels) after annealing in air at 1000 °C for 2 h. The experimental results proved that the CrAlN coating presents the best performance as the cubic initial phase (fcc-CrAlN) is predominant after heating. The formation of a dense $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ layer in the interface scale/coating results effective to avoid fast oxidation of the CrAlN coating. However, iron and other metallic elements released from the steel substrates reached the surface through the column boundaries. The understanding of the potential RE effect of yttrium in these multilayered metallic nitrides has been significantly increased by advanced TEM techniques. The corrosion products, the yttrium location and its oxidation state have been fully determined supporting the decrease of outward cation mobility but favoring the inward diffusion of oxygen. Yttrium segregates at the oxide scale and grain boundaries (M2) and, column interfaces and oxide/coating interface (316). A reduction of the oxide growth rate was not evidenced (differing to the behavior observed in alloys and previous works) although helped to prevent the outward diffusion of iron from the steel substrate and curtailed the transient oxidation of the base metal. A decrease of the thermal stability of the multilayered $\text{Cr}_{1-x}\text{Al}_x\text{N}$ coating ($x \approx 0.50$) deposited onto steel substrates is observed when annealed in air at 1000°C. An adequate balance of Al and Y contents must be thus determined for each particular CrAlN coating depending on the type of substrate and film microstructure as interdiffusion phenomena play an important role in the oxidation behavior.

Acknowledgments

European Regional Development Funds program (EU-FEDER) and Spanish Ministry of Economy, Industry and Competitiveness (projects n° MAT2015-65539-P and MAT2015-69035-REDC), and CSIC (201560E013) are acknowledged for financial support. The authors are grateful to R. Escobar and J.A. Sánchez for performing GD-OES measurements. The lamellae preparation was conducted in the ‘Laboratorio de Microscopias Avanzadas’ at ‘Instituto de Nanociencia de Aragón-Universidad de Zaragoza’. Authors acknowledge the LMA-INA for offering access to their instruments and expertise.

Table 1. Chemical composition of the steel substrates (M2 and 316) (in wt.%).

	C	Mn	Si	Cr	Mo	Ni	V	W
M2	0.85	0.30	0.30	4.15	5.00		1.95	6.42
316	0.08	2.00	0.75	16.00-18.00	2.00-3.00	10.00-14.00		

Table 2. Chemical composition, thickness and mechanical properties of the coatings

	Chemical composition					Thickness	H	E
	Cr at. %	Al at. %	N at. %	Y at. %	Film stoichiometry	μm	GPa	GPa
CrAlN	23.9	24.3	51.8	0.0	Cr _{0.50} Al _{0.50} N	6.6	28±7	604±34
CrAlYN	24.1	22.0	53.9	1.6	Cr _{0.51} Al _{0.46} Y _{0.03} N	4.0 (M2) 3.2 (316)	30±8	556±42

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FIGURE CAPTIONS

Fig. 1. (a) HAADF-STEM and (b) HRTEM images of the as-deposited CrAlN coating on M2 steel.

Fig. 2. (a) HAADF-STEM image of the as-deposited CrAlN coating on M2 and (b) relative composition, obtained by EELS, along the line profile marked in a). (c) EELS spectra (N-K and Al-K edges) measured from point 1 and point 2.

Fig. 3. (a) HAADF-STEM and (b) HRTEM images of the as-deposited CrAlYN coating on M2 steel. Inset in (a) X-EDS elemental maps distribution: green (Y), red (Cr) and blue (Al).

Fig. 4. XRD diffractograms of the CrAlN and CrAlYN coating deposited on M2 and 316 steels before and after oxidation in air at 1000 °C measured in grazing incidence at 5°. JCPDS cards numbers: CrN (PDF #76-2494), Fe₃O₄ (PDF #19-629), Cr₂O₃-a (PDF #1-84-315), Cr₂O₃-b (PDF #38-1479), Fe-Cr (PDF #34-396), hcp-AlN (PDF #1-79-2497), Al₂O₃-a (PDF #1-71-1684), Al₂O₃-b (PDF #1-77-2135), YMo₃O₁₂ (PDF #28-1451), Fe₂O₃ (PDF #1-84-307), Cr₂N (PDF #35-803), CrO (PDF #08-254), CrMn_{1.5}O₄ (PDF #44-909), MnO₂ (PDF #30-820), Mn₃O₄ (PDF #4-732), Fe-Cr (34-396), Fe-inox (1-75-2127).

Fig. 5. GD-OES spectra of the heated coating (a) CrAlN and (b) CrAlYN on M2 steel and (c) CrAlYN on 316 steel.

Fig. 6. (a) HAADF-STEM image of a surface region (zone I and II) of a heated CrAlN coating on M2. (b) HAADF-STEM image of an area from zone II and X-EDS elemental maps of the marked area (scale bars indicate concentration in at.%). (c) EELS spectra (N and Al K-edges) from grain marked in (b).

Fig. 7. HAADF-STEM general image of CrAlYN coating on M2.

Fig. 8. (a) HAADF-STEM image of the oxide scale of the heated CrAlYN coating on M2 steel, (b) EELS spectra from the dark matrix, and (c) X-EDS spectra from marked points.

Fig. 9. (a) HAADF-STEM image of the inner part of the CrAlYN coating on M2 steel, (b) X-EDS spectra from marked points (1 and 2) and (c) EELS spectra from the marked points (1 and 2).

Fig. 10. (a) HAADF-STEM image of the heated CrAlYN coating on 316 steel. (b) X-EDS elemental maps (scale bars indicate the concentration in at.%), and (c) phase map of the red marked area, where the color green is Cr_xO_y , yellow is Al_2O_3 , dark blue is Cr_2N and dark pink is Fe. X-EDS chemical map of white rectangle; Cr (red), Al (green), and Y (yellow) is shown as inset.

Fig. 11. EELS chemical phases map of an inner region (green square marked in fig. 10) of the heated CrAlYN coating on 316 steel and EELS spectra from the marked points. Color legends: hcp- Cr_2N (green), Al_2O_3 (red), Y-containing (blue) phases.

Fig. 12. (a) HRTEM image of the heated CrAlYN coating on 316 steel. Interplanar distances typical of fcc-CrAlN and fcc-YN are marked. (b) Digital diffraction pattern along the [100] direction of a fcc-CrAlN crystal found in the marked white square.

Fig. 1

Fig. 1 (a) HAADF-STEM b) HRTEM images of the as-deposited CrAlN coating on M2 steel.

Fig. 2

Fig. 2. (a) HAADF-STEM image of the as-deposited CrAlN coating on M2 and (b) relative composition, obtained by X-EDS, along the line profile marked in a). (c) EELS spectra (N-K and Al-K edges) measured from point 1 and point 2.

Fig 3

Fig. 3. (a) HAADF-STEM and b) HRTEM, images of the as-deposited CrAlYN coating on M2 steel. Inset in a) X-EDS elemental maps distribution

Fig. 4. XRD diffractograms of the CrAlN and CrAlYN coating deposited on M2 and 316 steels before and after oxidation in air at 1000 °C measured in grazing incidence at 5°.

JCPDS cards numbers: CrN (PDF #76-2494); Fe_3O_4 (PDF #19-629); $\text{Cr}_2\text{O}_3\text{-a}$ (PDF #1-84-315); $\text{Cr}_2\text{O}_3\text{-b}$ (PDF #38-1479); Cr_7C_3 (PDF #36-1482); Fe-Cr (PDF #34-396); AlN (PDF #1-79-2497); $\text{Al}_2\text{O}_3\text{-a}$ (PDF #1-71-1684); $\text{Al}_2\text{O}_3\text{-b}$ (PDF #1-77-2135); $\text{YMo}_3\text{O}_{12}$ (PDF #28-1451); Fe_2O_3 (PDF #1-84-307); Cr_2N (PDF #35-803).

Fig. 5

Fig. 5. GD-OES spectra of the heated coating (a) CrAlN and (b) CrAlYN on M2 steel and (c) CrAlYN on 316 steel

Fig. 6

Fig. 6. HAADF-STEM image of a surface region (zone I and II) of a heated CrAlN coating on M2 and X-EDS elemental maps (scale bars indicate concentration in at.%)

Fig. 7

Fig. 7 EELS spectra (N and Al- Kedges) from grain marked in figure 6.

Fig. 8

Fig. 7. HAADF-STEM general image of CrAlYN coating on M2

Fig. 9

Fig. 8. (a) HAADF-STEM image of the oxide scale of the heated CrAlYN coating on M2 steel, (b) EELS spectra from the dark matrix, and (c) X-EDS spectra from marked points.

EDX de la matriz $(\text{Cr,Al})_2\text{O}_3$

O: 59.6 atm%

Al: 19.4 atm%

Cr: 20.2 atm%

Fe: 0.8 atm%

Fig.10

Fig. 9. (a) HAADF-STEM image of the inner part of the CrAlYN coating on M2 steel, (b) X-EDS spectra from marked points and (c) EELS spectra from the marked points.

Fig 11

Fig. 10. HAADF-STEM image of the heated CrAlYN coating on 316 steel. X-EDS chemical map (scale bars indicate the concentration in at.%), and phase map of the red marked area, where the color green is Cr_xO_y , yellow is Al_2O_3 , dark blue is Cr_2N and dark pink is Fe. Insert X-EDS Cr, Al, and Y elemental maps of white rectangle.

Fig.12
Mapa de fases

Fig. 11. EELS chemical phases map of an inner region of the heated CrAlYN coating on 316 steel and EELS spectra from the marked points.

Fig. 13

Fig. 12. HRTEM image of the heated CrAlYN coating on 316 steel.

Oxidation performance of CrAlN

Figure 1 shows the polycrystalline structure that has been developed in the region nearest the substrate (zone III), in the CrAlN coating after the heating treatment. The quantitative elemental maps obtained in an area of this zone (Fig. 1b) show the presence of Fe, C, in addition to Al, Cr and N. The iron atoms are located in the same grains as chromium, while carbon is more homogeneously distributed. Al and N are present simultaneously in the rest of the grains.

Fig. 1. (a) HAADF-STEM image of an inner region (zone III) of the heated CrAlN coating on M2 and (b) HAADF-STEM image of a smaller area and X-EDS elemental maps (scale bars indicate concentration in at.%).

From the quantitative chemical analysis, the comparison of the fine structure of the EELS spectra (ELNES) with reference compounds and the XRD results (presented in the manuscript), it is possible to identify the chemical phases of the different grains. Fig. 2a displays a HAADF-STEM image of a small area inside zone III, and a chemical map (Cr, Al and Fe) of the marked area is depicted as the inset. Fig. 2b summarizes the EELS spectra measured in different grains (marked as 1, 2 and 3). Thus, point 1 exhibits a typical spectrum of hcp-AlN [1], while point 2 displays a mixture of metallic iron and fcc-CrAlN. In position 3, carbon and iron, in addition to N, Cr and Al (not shown) from the initial film, have been detected. These elements are present in the form of Cr_7C_3 and intermetallic Fe-Cr phases. The formation of an intermetallic Fe-Cr phase is based on the change of the L_2/L_3 ratio of the Cr- $L_{2,3}$ and Fe- $L_{2,3}$ EELS spectra [2]. The N-K signal is due to the presence of hcp-AlN in this point (Al was found in this location, although it is not shown in the Fig 2).

Fig. 2. HAADF-STEM image of an inner region inside zone III of the heated CrAlN coating on M2 and EELS spectra from the marked points.

Oxidation performance of CrAlYN (316)

Figure 3 illustrates the complex structure of the oxide scale of the CrAlYN coating deposited on 316 steel and heated at 1000°C. The X-EDS and EELS (O K-edge) spectra measured at different locations are congruent with the formation of Cr_xO_y (points 1 and 5), $\text{Cr}_x\text{O}_y\text{-Al}_2\text{O}_3$ (point 2), Al_2O_3 (point 3) and $(\text{Cr,Mn})_x\text{O}_y$ (point 4) phases. The shape of the O-K edge changes from that typical of Cr_xO_y (point 1) to that

of Al_2O_3 (point 3) [3]. In this zone, the Y has been only detected in point 3 with the Al_2O_3 .

Fig. 3 (a) HAADF-STEM or Z-contrast image of the surface of the CrAlYN coating deposited on 316 steel and heated at 1000°C, (b) O K-edge EELS spectra from marked points (Reference spectra of Cr_2O_3 and Al_2O_3 are included for comparison) and (c) X-EDS spectra from marked points.

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