Influence of Al and Y content on the oxidation resistance of CrAlYN protective coatings for high temperature applications: new insights about the Y role

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Abstract

CrAlYN hard coatings with two different average Al contents: ~16 at.% and ~25 at.%, and Y concentration varying between 1.2 and 5.7 at.% were deposited by direct current reactive magnetron co-sputtering of mixed Cr-Al and Y targets on commercial M2 steel substrates. The samples were heated to 1000 °C in air during 2 h to study their oxidation resistance and thermal stability. The Y content is critical and the coatings present different behaviour depending on the Al content. The best oxidation resistance and thermal stability are obtained for the coating with ~16 at.% Al and 3.4 at.% Y. The initial film microstructure and the cubic phase (fcc-CrAlN) were retained, and a thin (Cr,Al)₂O₃ oxide protective scale was formed. At lower Y content (1.2 at.%) iron from the substrate crosses the coating, while a higher content (4.6 at.%) avoided the iron diffusion at the expense of a thicker oxide scale with new oxide phases. The coatings with higher Al content (~25 at. %) were not thermally stable at 1000°C. A good oxidation resistance was obtained for 2.6 at.% of Y although new phases (hcp-AlN and Cr-Fe) were formed. Higher amount of yttrium (~5.7 at. %) led to the complete oxidation of the coating.

Introduction

Cr_{1-x}Al_xN 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]. In addition, the oxidation and corrosion resistance is improved with respect to CrN [7, 11-14], due to the development of dense and adherent mixed aluminium and chromium oxide scales that eventually suppresses the diffusion of oxygen into the bulk and the outward diffusion of metallic cations [7, 15-17], thereby providing excellent oxidation resistance up to temperatures higher than $900\text{ }^{\circ}\text{C}$ [8, 18]. But, the increasingly demanding operating conditions of industrial processes such as dry or high speed cutting of high-strength materials [1-2] require the use of materials capable of withstanding working temperatures of $1000\text{ }^{\circ}\text{C}$ or higher. This pre-requisite necessitates the design of advanced coatings with superior oxidation resistance and thermal stability. There are two reported approaches to enhance these properties. On the one hand, an architectural arrangement (e.g. superlattice effect) as already proven with CrN-based multilayer systems like CrN/AlN [19-20], CrN/CrAlN [21], TiAlN/CrAlN [22] or TiAlSiN/CrAlN [23]. On the other hand, the incorporation of yttrium as a reactive element (RE) in CrAlN coatings, which reduces the oxide scale growth rate and increase the onset of decomposition to 1100°C [24-30]. However, some discrepancies are found in the literature concerning the effect of the RE [31-34] and the optimum Y content [27, 29, 35], which seems to be dependent on the Al content, the film architecture and microstructure. These aspects as well as the influence of the substrate have been studied and revised in our previous publications with multi-layered CrAlYN coatings [25-26, 36]. In this sense, in this work, we have prepared two series of CrAlYN coatings by co-sputtering with two different Al contents: $\sim 16\text{ at.}\%$ (set I) and $\sim 25\text{ at.}\%$ (set II), and Y concentration varying between 1.2 and $5.7\text{ at.}\%$. We focus special attention to the microstructure evolution during the oxidation processes, the Y location, and the chemical phases formed after the annealing treatment at $1000\text{ }^{\circ}\text{C}$ in ambient air. This study allows shedding new light about the oxidation mechanism and the effect of the RE of Y, on coatings deposited on M2 steel, which is eventually used in the final foreseen application.

Experimental

CrAl(Y)N coatings were prepared on M2 steel and (100) silicon substrates by direct current magnetron sputtering in a commercial equipment (CemeCon® CC800/8) provided with two rectangular targets ($200\text{ mm} \times 88\text{ mm} \times 5\text{ mm}$): one mixed AlCr

(99.95 purity, AlCr20 for set I and AlCr10 for set II), and a second one made of yttrium (99.5% purity). The base pressure of the vacuum chamber was $\sim 1 \times 10^{-4}$ Pa and the working pressure set at 1 Pa, with at Ar/N₂ ratio of 1.5. The sputtering conditions were set to 3000 W for the AlCr mixed targets and 500, 750 and 1000 W for Y target. The sample holder was negatively biased in the range of 5-10 V and the measured temperature span from 200 to 400 °C. Table 1 summarizes synthesis conditions, chemical composition, and mechanical properties of the samples under investigation divided into two categories (Set I and II) depending on the average Al content (16 and 25 at.%) respectively. The average thickness of the coatings is ~ 5 μm .

Chemical composition of the samples was obtained by electron probe microanalysis (EPMA). The equipment was a JEOL JXA-8200 SuperProbe instrument equipped with four wavelengths detectors (WDS) and one energy-dispersive X-ray (X-EDS). Glow discharge optical emission spectroscopy (GD-OES) was used for obtaining the chemical depth profiling employing a Horiba Jobin Yvon RF instrument. This equipment was operated in argon plasma of 650 Pa and forward power of 40 W with a 4 mm diameter copper anode.

The X-ray diffraction (XRD) patterns were obtained in a X'Pert Pro PANALYTICAL diffractometer in the conventional θ -2 θ Bragg-Brentano configuration using Cu K $_{\alpha}$ radiation. The texture of the films was characterized by the texture parameters (T_{hkl}) and the grain sizes were estimated by the well-known Scherrer equation for all peaks. As preferential orientation is often present in thin films, the textural parameters were used as weight factors in order to average the crystal values obtained from different peaks as described in [37].

Raman spectra (200-2000 cm^{-1}) were measured using a LabRAM Horiba Jobin Yvon spectrometer equipped with a CCD detector and a diode-pumped solid state laser (532 nm) at 5 mW. All of the samples were analyzed during 100 s of exposure time and with an aperture hole of 100 μm .

The morphology and thickness of the as-prepared coatings deposited on silicon substrates were studied using a high resolution scanning electron microscope (SEM HITACHI-S4800 equipped with a field emission gun (FEG) and X-EDS detector (Bruker, XFlash-4010). Cross-section views were obtained by cleaving the coated silicon substrates. For the transmission electron microscopy (TEM) characterization of the as-prepared coatings, cross-sections specimens were prepared from coated silicon pieces following the conventional procedure of mechanical polishing followed by argon

ion milling to electron transparency. Cross-sections lamellas of the heated samples at 1000°C deposited on M2 steel were prepared using a dual focused ion beam (Dual-Beam Helios). To get microstructural and chemical information, a FEI Tecnai FEG scanning transmission electron microscope (STEM), mod. G2F30 with an S-Twin objective lens was used. The STEM microscope operated at 300 kV, with 0.2 nm point resolution, and equipped with a high angle annular dark field (HAADF) detector from Fischione with 0.16 nm resolution and an X-EDS detector SSD model INCA X-Max 80. Electron energy-loss spectroscopy (EELS) was obtained using a Gatan Imaging Filter (GIF) attached to the Tecnai microscope (QUANTUM SE model). EELS spectra were recorded in STEM mode using a probe with a size of less than 1 nm, with a spectrometer collection angle of 9.6 mrad. Under these conditions, the energy resolution of the couple microscope/spectrometer system was ~0.8 eV.

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 avoid the influence of the substrate.

Results and discussion

Characterization of the initial coatings

The microcrystalline composition of the as-deposited CrAlYN coatings deposited on M2 steel is studied by XRD in θ -2 θ geometry (Fig. 1). The diffractograms are congruent with a cubic structure fcc-CrN (JCPDS ref. 76-2494) whose peak positions and intensities are correlated with the Al and Y incorporation into the CrN lattice. With increasing Y content the XRD peaks shift to smaller 2 θ diffraction angles, indicating an increase in the lattice constant and/or in the film residual stress. An increment of the mean lattice constant is expected by substitution of Cr and Al positions in the CrAlN lattice by yttrium atoms with bigger atomic radius. A clear [200] preferred orientation is observed for the coatings Al(16)Y(3.4) and Al(25)Y(2.6) while (220) peaks develops for the rest. Further confirmation is concluded from the analysis of the texture parameters T_{hkl} for all samples. Figure 2a reveals that $T_{200} > 2$ for the samples cited previously and a preferential growth of the (220) peak for the samples with the smallest

and the highest Y content. The texture parameters were used as weight factors for the calculation of the average crystal sizes from Scherrer equation of all observed peaks (Fig. 2b). The biggest size (14 nm) is observed for the coating with the lowest Al and Y content, while a slight decrease (from ~7 nm to 5 nm) is observed in parallel to the Al and Y increase.

Figure 3 displays representative cross-section SEM images of the CrAlYN films of the two sets. The film microstructure is characterized by a dense and columnar morphology, with column width in the order of ~10nm. The films Al(16)Y(3.4) and Al(25)Y(2.6) deposited on silicon were selected from each set to be further studied by X-TEM. HRTEM images (Fig. 4 and Fig. 5 respectively) show the crystalline character of the columns with a measured width between 6 and 12 nm. The measured d-spacing's lattice fringes can be assigned to the {200}, {220} and {111} family planes of the fcc-CrAlN phase. The digital diffraction pattern (DDP) obtained from Fig. 4, shows the polycrystalline character of this coating, in agreement with XRD results. Moreover, it is observed a certain preferential orientation of the crystallites of the (200) and (111) planes along the growing direction. In Fig 5, the quasi-coherent growth of the columns is clearly noticed and confirmed by the different DDP's calculated in the square areas marked along the column. The indexed DDP corresponds to a Cr(Al)N crystal oriented along the [100] zone axis. A slight disorientation of the (200) plane is observed to occur as the columns grow up.

The hardness of samples (see table 1) ranges between 23 to 30 GPa, values that are similar to previously reported [25-26]. The highest values are obtained for Al(16)Y(3.4), Al(25)Y(5.7) coatings, but there is not a clear relationship with the composition, crystal size or texturing, as observed by Martinez et al. [36], who reported nanohardness values of 10-12 GPa for (111) CrN textured films while 18.5 or even 28 GPa for (200) CrN one.

Oxidation resistance and thermal stability

The coatings deposited on M2 steel were annealed at 1000 °C in air during 2 h to study their oxidation resistance and thermal stability. Fig. 6 shows the aspect of all samples after thermal annealing. The samples Al(16)Y(1.2), Al(16)Y(3.4) and Al(25)Y(2.6) present the best appearance, while coatings with the highest Y content from both sets look oxidized and partially peeled off.

The XRD diffractograms measured after the thermal annealing in air are shown in Fig. 7. For samples from set I (Al~16 at.%) with 1.2 and 3.4 at.% Y, the strongest peaks are assigned to the fcc-Cr(Al)N phase indicating a good oxidation resistance and thermal stability at this temperature. The presence of less intense peaks laying between the diffraction peaks of β -Cr₂O₃ and β -Al₂O₃ points to the formation of a β -(Cr,Al)₂O₃ mixed oxide scale. Some small peaks attributed to Al₂O₃ and Fe₂O₃ phases are also observed for the lowest Y content [Al(16)Y(1.2)]. The presence of iron oxides is signal of the iron diffusion from the substrate. For the sample of set I with the highest Y content (4.6 at.%) a higher degree of oxidation is concluded from the appreciable increase in the peaks corresponding to oxide phases. A similar behaviour has been described previously for an excess of yttrium [30]. The XRD pattern of the sample of the set II with the lowest Y content [Al(25)Y(2.6)] presents a strong peak at 44.5°, laying between fcc-CrN and Cr-Fe phases, together with peaks attributable to a hcp-AlN phase. These corrosion products demonstrate the decomposition of the fcc-CrAlYN in fcc-Cr and hcp-AlN concomitantly with the iron diffusion from the substrate. Similarly to the first set, no evidences of crystalline forms of yttrium-derived phases are observed at this point. However, for the highest Y contents from both sets (4.6 and 5.7 at.%, respectively) yttrium-containing phases (Y₂O₃ and Al₅O₁₂Y₃ and AlYO₃) could be identified. Other dominant peaks for the annealed Al(25)Y(5.7) sample correspond to the β -(Cr,Al)₂O₃ mixed oxide. The presence of hcp-Cr₂N phase cannot be discarded. As a general conclusion increasing the Y content above 5 at.% for the set II, containing the highest Al content in the film composition, has determined the overall oxidation of the coating. These results are in agreement with the previous published works when increasing the RE content [27, 29]. An excess of the RE has a detrimental effect by increasing the oxidation rate. This negative effect produced by this “overdoping” is probably due to an increase of oxygen diffusion through the vacancies in the formed RE oxides [38]. The XRD results demonstrated that coatings with Al content ~ 16 at.% (set I) were stable after annealing at 1000°C in air while those with Al content ~ 25 at.% (set II) were partially decomposed [Al(25)Y(2.6)] or even completely oxidized [Al(25)Y(5.7)].

Fig. 8 depicts the depth profiling chemical spectra obtained by GD-OES for the coatings of set I after annealing at 1000°C for 2h. Likewise, Figs. 9a and 9b plot the GD-OES results for the coating Al(25)Y(2.6), from [set II], obtained after heating at

1000 °C for 2 h and 900 °C for 9h, respectively. For all samples, except Al(16)Y(4.6), the oxygen signal is essentially limited to a superficial region in the range of 0.5 to 1 µm, and no noticeable inwards diffusion is observed beyond, indicating a good oxidation resistance. Under the oxide scale Al, Cr and N contents remain almost constant however for Al(16)Y(4.6) sample the oxygen penetrates deeply in the coating and the N amount decreases abruptly. At this content, the inward oxygen penetration becomes the dominant mechanism leading to substantial CrAlN decomposition and oxidation processes. Additionally, for the samples containing the lowest yttrium contents, the Cr and Al profiles present sharp peaks at the oxide-film interface pointing out to Cr and Al out-diffusion processes. The Cr peak is found more external than Al as a consequence of the higher mobility of Cr ions during diffusion processes [39]. Nevertheless, at higher Y contents, the mobility of Cr ions is reduced in respect of Al according to the RE effect [26,30], favouring an enrichment of the oxide scale in Al. Regarding yttrium, their profiles appear fairly constant until the scale interface where decreases followed by a maximum inside the oxide scale. Comparatively, the samples with the lowest Y content, Al(16)Y(1.2) and Al(25)Y(2.6) (cf. Figs. 8a and 9a) exhibit iron profiles that indicate an outward iron diffusion from the substrate. Iron profiles are just blocked at the interface with the oxide scale and diminish towards the surface. However, the relevance of the iron out-diffusion decreases with the Y content, as previously reported in multilayered CrAlYN coating [26]. The best result is obtained for the intermediate value of 3.4 at.% of Y (cf. Fig. 8b) as an additional increment enhances the oxygen inward penetration favouring a faster oxidation and thicker scale (Fig. 8c). These results are in agreement with the XRD results, where iron oxides phases were only observed for Al(16)Y(1.2). The influence of the temperature in the ion diffusion processes is clearly demonstrated in Fig. 9 for the Al(25)Y(2.6) [set II] sample. The GD-OES of this sample heated at 900 °C for 9h revealed that it is still stable at this temperature. No cation diffusion is yet observed, neither from the coating nor the steel.

Fig. 10 shows the Raman spectra for the coatings of set I and II after oxidation at 1000 °C ordered by increasing Al and Y contents. At a first sight it is obvious that the samples exhibiting less transformation are Al(16)Y(3.4) and Al(25)Y(2.6), which correspond to the samples less oxidized as stated by XRD and GD-OES. The remaining samples display different peaks that can be assigned to different chromium, aluminium and yttrium oxides. Thus, the characteristic peaks of Cr₂O₃ phase at approximately 350 and 565-585 cm⁻¹ are often present [9,40,41]. The broad band centred around 700-730

cm^{-1} can be attributed to mixed chromium-aluminium oxides ($\text{Al}_x\text{Cr}_{2-x}\text{O}_3$) whose maximum shifts toward higher values as Al content increases [9]. A small shoulder at 669 cm^{-1} in the sample Al(16)Y(1.2) can be also assigned to CrO_2 phase [42]. These Raman features correlates with an enrichment in Al_2O_3 with respect to chromium oxides (CrO_2 and Cr_2O_3) in the scale. The peaks appearing at wavenumber values higher than 800 cm^{-1} should be related to new oxide phases that might include yttrium in their composition as they are detected in the samples exhibiting the highest Y content from set I and II.

The coating Al(16)Y(4.6) displays a band at 823 cm^{-1} overlapping the $\text{Al}_x\text{Cr}_{2-x}\text{O}_3$ region and a narrower peak at 946 cm^{-1} . The first has also been observed in polycrystalline Cr_2O_3 sample while the second correlates with Cr(VI)-O terminating structures giving rise to strong lines in the $800\text{-}1000\text{ cm}^{-1}$ region [40]. The formation of Y-Al mixed oxide perovskite (YAP) is also plausible in this region as YAlO_3 exhibits active Raman modes at wavenumbers above 900 cm^{-1} [43]. This feature is congruent with XRD analysis revealing peaks of AlO and AlYO_3 for this sample. The coating Al(25)Y(5.7) shows intense peaks at 262, 376, 838 and 893 cm^{-1} . Yttrium sesquioxide (Y_2O_3) presents a very intense line at 376 cm^{-1} due to A_g mode [44] and Y-Al garnet (YAG) single crystal reveals also strong bands at 257 and $\approx 370\text{ cm}^{-1}$ [45] that could correspond satisfactorily to those observed in this case. This assignment is consistent with the XRD analysis for this sample where YCrO_3 , Y_2O_3 and $\text{Al}_5\text{O}_{12}\text{Y}_3$ could be identified. The Cr-O-Cr bending frequencies are situated around 880 cm^{-1} in the Cr(VI) oxide species as suggested earlier. In addition, the Cr_2O_5 and Cr_8O_{21} phases display strong Raman modes at 880 and 889 cm^{-1} , respectively, that can account for the strong peak at 893 cm^{-1} [40]. A summary of the oxide products determined by Raman analysis of the annealed samples is displayed in Table 2.

A deeper characterization of the samples displaying the best oxidation behaviour was done using STEM, X-EDS and EELS techniques with high lateral resolution in order to determine the location of yttrium and the phases formed. This would provide additional information about the oxidation mechanism and the RE effect of yttrium. Fig. 11a shows a general TEM image of Al(16)Y(3.4) heated sample, where two regions are well distinguished: a surface layer of 250-350 nm and a thick layer beneath of $\sim 4\text{ }\mu\text{m}$ that maintains the columnar nanostructure. Some bright grains observed in the top oxide layer and the scale/film interface correspond to holes formed during oxidation. A HAADF/STEM image of the topmost surface is presented in Fig. 11b, where features

with different contrast appear embedded in a matrix (dark areas correspond to phases with lower Z or thickness). The quantitative analysis of the X-EDS measured in the matrix (spectrum from point 1) is consistent with the formation of $(\text{Cr,Al})_2\text{O}_3$ phase with Cr/Al ratio ≈ 1 . The X-EDS measured in the brightest grains (point 2) and in the oxide grain boundaries (marked as *) show the presence of Mo, W, and Y. These results indicate that the substrate elements diffuse along coating and reach the surface. Besides, Y diffuses to the scale, segregating to the oxide grains boundaries and forming metal oxides grains. The darkest areas that appear in the scale correspond to holes and voids, also previously commented in the TEM image (Fig. 11a), which are produced by arranging of vacancies, defect annihilations, grain growth and element diffusion during thermal annealing, [46]. Aluminium and yttrium enrichment is detected at the scale/coating interface (see the X-EDS elemental map obtained from the marked area shown in Fig. 11c). On one hand, yttrium appears segregated forming grains at the interface what helps to improve the scale adhesion (by preventing fast growth of voids) and block iron out diffusion as highlighted in the literature and previous works [26,34]. On the other hand, aluminium seems to form a very thin aluminium oxide layer, which makes more difficult the oxygen diffusion towards the film, preventing the progress of the oxidation [13]. These experimental observations of yttrium segregation support the dynamic-segregation theory to explain the RE effect previously reported in metal and alloys [34]. The segregation of yttrium ions at the scale grain boundaries inhibits the further outward diffusion of chromium and aluminium due to its larger size, and the inward diffusion of oxygen. Macroscopically, since the diffusion rate of anions is slower than that of cations, a reduction in the oxide scale growth rate is achieved.

Fig. 12 exhibits a HAADF- STEM image and X-EDS elemental maps taken from the inside of this coating. The quantitative analysis obtained from point 1 is congruent with the initial composition (Al ~ 16 at.%) and the N, Cr and Al elements appear homogeneously distributed inside the coating. Iron and yttrium appear dispersed mainly along the column boundaries. Upon heating the iron atoms diffuse upwards from the substrate along the column boundaries and yttrium released from the CrAlYN columns contributes to interrupt this motion, by filling these pathways.

A general TEM image of the Al(25)Y(2.6) coating after heating at 1000°C is presented in Fig. 13a. The thickness of the oxide scale is found to be approximately 200 nm (see detailed HAADF/STEM picture in Fig. 13b) and its quantitative elemental composition is in agreement with the formation of $(\text{Al}_{1.2}\text{Cr}_{0.8})\text{O}_3$ phase (X-EDS

spectrum is shown in Fig 13c). The scale/coating interface has a higher content of aluminium, as denoted by the dark contrast in the image (cf. point 2 in Fig. 13b) and confirmed by the X-EDS spectra (Fig. 13d). This is consistent with the Al peak determined by GD-OES at approximately 250 nm and the formation of an aluminium rich oxide layer in the interface, as observed in Al(16)Y(3.4) coating. Molecular nitrogen has also been detected in the marked area (see the EELS spectrum of Fig. 13e) [46]. The formation of nitrogen bubbles results from the release of nitrogen atoms from the fcc-CrAlN transformation during annealing, which nucleate when they are eventually blocked at the scale interface. Underneath the scale, the HAADF-STEM or Z-contrast analysis puts in evidence the presence of phases with different composition. The X-EDS elemental maps shown in Fig. 14a obtained from the marked area corroborate the presence of Cr, Fe, Mo, W and Y in the bright areas, and N with Al in the dark ones. The analysis of the HRTEM image depicted in Fig. 14b demonstrates the formation of hcp-AlN crystalline phase, as confirmed by indexing the DDP obtained from the square area. The amorphous regions correspond to a mixture of Cr, Fe, Y, W and Mo elements originated by the film and substrate during thermal treatment. The presence of fcc-CrAlN phase was detected by EELS in several points of the film as depicted in Fig 14c. The recorded N-K and Al-K edges present the characteristic signatures of the cubic CrAlN phase [47]. These results show that this coating has suffered a chemical transformation during the heating treatment. At temperatures superior to 900°C, fcc-CrAlN phase experiments the partial transformation to fcc-Cr and hcp-AlN. The strong affinity of Cr to Fe and the rest of metals favoured the formation of intermetallic alloy including the rest of elements (Y, Mo and W).

Summary and conclusions

The experimental results shown in this paper proved the importance of the Al and Y (presence and content) on the oxidation mechanism and thermal stability of CrAlYN protective coatings heated at 1000 °C in air deposited on M2 steels. The CrAlYN sample from set I with Al (~16 at.%) and Y (~ 3 at.%) demonstrated the best performance. Lower Y contents led to outwards diffusion of Fe to the surface while higher amount produced almost complete oxidation of the film. The set II prepared with higher Al content (~ 25 at.%) resulted to be more unstable showing higher degree of

fcc-CrAlN decomposition and oxidation. The sample incorporating Y ~3 at.% exhibited a good oxidation resistance but the initial fcc-CrAlN phase was partially decomposed to fcc-Cr and hcp-AlN. Higher Y enrichment (~ 5 at.%) induced a total oxidation.

The use of advanced TEM techniques, has allowed to shed light about the Y role and oxidation mechanism:

- FILM: Y diffused to the column boundaries, hindering the iron migration from the substrate. A critical Y amount (depending on Al content) is needed to avoid that iron reaches the surface.
- FILM/SCALE interface: Segregation of small Y-rich grains has been observed in the interface. These precipitates contribute together with the presence of a thin Al-rich mixed oxide to block the out-diffusion of iron and the oxygen inward penetration, decreasing the degradation of the film.
- SCALE: When the interface is saturated, yttrium atoms also diffuse to the oxide scale and segregate at the grain boundaries as expected by the RE effect. This segregation inhibits the cations transport, mainly Cr, favoring the Al-enrichment of the oxide scale that passivates the surface. Under an adequate yttrium concentration the oxidation kinetics is retarded but over a critical RE content the oxygen diffusion is accelerated. This negative “overdoping” effect is probably due to a faster oxygen transport through the mixed yttrium oxides (Y_2O_3 and $Al_5O_{12}Y_3$ and $AlYO_3$) formed in the scale.

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References

1. M.W. Kim, K.H. Kim, M.C. Kang, S.H. Cho, K.T. Ryu, Mechanical properties and cutting performance of Cr-Al-N hybrid coated micro-tool for micro high-speed machining of flexible fine die, *Curr. Appl. Phys.* 12 (2012) S14-S18.
2. L. Wang, X. Nie, J. Houseden, E. Spain, J.C. Jiang, E.I. Meletis, A. Leyland, & A. Matthews, Material transfer phenomena and failure mechanisms of a nanostructured Cr-Al-N coating in laboratory wear test and an industrial punch tool application, *Surf. Coat. Technol.* 203(2008) 816-821.
3. J. Endrino, G. S. Fox-Rabinovich, A. Reiter, S. V. Veldhuis, R. E. Galindo, J. M. Albella, J. F. Marco, Oxidation tuning in AlCrN coatings, *Surf. Coat. Technol.* 201 (2007) 4505-4511.
4. A.E. Reiter, V.H. Derflinger, B. Hanselmann, T. Bachmann, B. Sartory, Investigation of the properties of $\text{Al}_{1-x}\text{Cr}_x\text{N}$ coatings prepared by cathodic arc evaporation, *Surf. Coat. Technol.* 7 (2005) 2114-2122.
5. M. Brizuela, A. Garcia-Luis, I. Bracerias, J. I. Onate, J. C. Sanchez-Lopez, D. Martinez-Martinez, C. Lopez-Cartes, A. Fernandez, Magnetron sputtering of Cr(Al)N coatings: Mechanical and tribological study, *Surf. Coat. Technol.* 200 (2005) 192-197.
6. J. Lin, B. Mishra, J. J. Moore, W. D. Sproul, Microstructure, mechanical and tribological properties of $\text{Cr}_{1-x}\text{Al}_x\text{N}$ films deposited by pulsed-closed field unbalanced magnetron sputtering (P-CFUBMS), *Surf. Coat. Technol.* 201 (2006) 4329-4334.
7. O. Banakh, P. E. Schmid, R. Sanjines, E. Levy, High-temperature oxidation resistance of $\text{Cr}_{1-x}\text{Al}_x\text{N}$ thin films deposited by reactive magnetron sputtering, *Surf. Coat. Technol.* 163 (2003) 57-61.
8. M. Kawate, A. K. Hashimoto, T. Suzuki, Oxidation resistance of $\text{Cr}_{1-x}\text{Al}_x\text{N}$ and $\text{Ti}_{1-x}\text{Al}_x\text{N}$ films, *Surf. Coat. Technol.* 165 (2003) 163-167.
9. J.C. Sanchez-Lopez, A. Contreras, S. Dominguez-Meister, A. Garcia-Luis, M. Brizuela, Tribological behaviour at high temperature of hard CrAlN coatings doped with Y or Zr, *Thin Solid Films* 550 (2014) 413-420.
10. H. Hasegawa, K. Ohashi, S. Tsukamoto, T. Sato, T. Suzuki, Characterization of quaternary (Cr,Al)N-based films synthesized by the cathodic arc method, *Surf. Coat. Technol.* 202 (2007) 786-789.
11. J.C. Sánchez-López, D. Martínez-Martínez, C. López-Cartes, A. Fernández, M. Brizuela, A. García-Luis, J.I. Oñate, Mechanical behavior and oxidation resistance of Cr(Al)N coatings, *J. Vac. Sci. Technol. A* 23 (2005) 681-686.
12. J. Lin, B. Mishra, J.J. Moore, W.D. Sproul, A study of the oxidation behavior of CrN and CrAlN thin films in air using DSC and TGA analyses, *Surf. Coat. Technol.* 202 (2008) 3272-3283.
13. H.C. Barshilia, N. Selvakumar, B. Deepthi, K.S. Rajam, A comparative study of reactive direct current magnetron sputtered CrAlN and CrN coatings, *Surf. Coat. Technol.* 201 (2006) 2193-2201.
14. S. Mato, G. Alcalá, M. Brizuela, R. Escobar Galindo, F.J. Pérez, J.C. Sánchez-López, Long - term high temperature oxidation of CrAl(Y)N coatings in steam atmosphere, *Corr. Sci.* 80 (2014) 453-460.
15. J. L. Endrino, G.S. Fox-Rabinovich, C. Gey, Hard AlTiN, AlCrN PVD coatings for machining of austenitic stainless steel, *Surf. Coat. Technol.* 200 (2006) 6840-6845
16. R. Escobar Galindo, J. L. Endrino, R. Martinez, J. M. Albella, Improving the oxidation resistance of AlCrN coatings by tailoring chromium out-diffusion, *Spectrochimica Acta Part B* 65 (2010) 950-958.
17. R. Prescott, M. J. Graham, The formation of aluminum-oxide scales on high-temperature alloys, *Oxid. Met.* 38 (1992) 233-254.
18. H. Willmann, P. H. Mayrhofer, P.O.A. Persson, A.E. Reiter, L. Hultman, C. Mitterer, Thermal stability of Al-Cr-N hard coatings, *Scripta Mater.* 54 (2006) 1847-1851.

19. S.K. Tien, C.H. Lin, Y.Z. Tsai, J.G. Duh, Oxidation behaviour, microstructure evolution and thermal stability in nanostructured CrN/AlN multilayer hard coating, *J. Alloy. Comp.* 489 (2010) 237-241.
20. G. Cabrera, J.C. Caicedo, C. Amaya, L. Yate, J.C. Muñoz Saldaña, P. Prieto, Enhancement of mechanical and tribological properties in AISI D3 steel substrates by using non-isosstructural CrN/AlN multilayer coating, *Mater. Chem. Phys.* 125 (2001) 576–586.
21. H.C. Barshilia, B. Deepthi, M. Selvakumar, A. Jain, K.S. Rajam, Nanolayered multilayer coatings of CrN/CrAlN prepared by reactive DC magnetron sputtering, *Appl. Surf. Sci.* 253 (2007) 5076–5083.
22. H.C. Barshilia, B. Deepthi, K.S. Rajam, K.P. Bhatti, S. Chaudhary, Growth and characterization of superlattices prepared by reactive direct current magnetron sputtering, *J Vac. Sci. Technol. A* 27 (2009) 29–33.
23. N. Fukumoto, H. Ezura, T. Suzuki, Synthesis and oxidation resistance of TiAlSiN and multilayer TiAlSiN/CrAlN coating, *Surf. Coat. Technol.* 204 (2006) 902–906.
24. F. Rovere, P. H. Mayrhofer, A. Reinholdt, J. Mayer, J. M. Schneider, The effect of yttrium incorporation on the oxidation resistance of Cr-Al-N coatings, *Surf. Coat. Technol.* 202 (2008) 5870-5875.
25. T. C. Rojas, S. El Mrabet, S. Dominguez-Meister, M. Brizuela, A. Garcia-Luis, J. C. Sanchez-Lopez, Chemical and microstructural characterization of (Y or Zr)-doped CrAlN coatings, *Surf. Coat. Technol.* 211 (2012) 104-110.
26. Dominguez-Meister, S. El Mrabet, R. Escobar-Galindo, A. Mariscal, M.C. Jimenez de Haro, A. Justo, M. Brizuela, T. C. Rojas, J. C. Sanchez-Lopez, Role of Y in the oxidation resistance of CrAlYN coatings, *Appl. Surf. Sci.* 353 (2015) 504-511.
27. Z. B. Qi, Z. T. Wu, Z. C. Wang, Improved hardness and oxidation resistance for CrAlN hard coatings with Y addition by magnetron co-sputtering, *Surf. Coat. Technol.* 259 (2014) 146-151.
28. K. D. Bouzakis, N. Michailidis, S. Gerardis, G. Katirtzoglou, E. Lili, M. Pappa, M. Brizuela, A. Garcia-Luis, R. Cremer, Correlation of the impact resistance of variously doped CrAlN PVD coatings with their cutting performance in milling aerospace alloys, *Surf. Coat. Technol.* 203 (2008) 781-785.
29. F. Rovere, P. H. Mayrhofer, Thermal stability and thermo-mechanical properties of magnetron sputtered Cr-Al-Y-N coatings, *J. Vac. Sci. Technol. A* 26 (2008) 29-35.
30. Shiyo Liu, Yi Yang, Fer Lan Ng, Rong Ji, X.T.Zeng. Oxidation behavior of CrAlYN coating at elevated temperatures. *Surf. Coat. Technol.* 320 (2017) 357-361
31. D. P. Whittle, J. Stringer, Improvements in high-temperature oxidation resistance by additions of reactive elements or oxide dispersions, *Philos. Trans. R. Soc. London Ser. A-Math. Phys. Eng. Sci.* 295 (1980) 309-329.
32. Y. Saito, T. Maruyama, T. Amano, Adherence of oxide scale formed on Ni-20Cr-1Si alloys with small additions of rare-earth elements, *Mater. Sci. Eng.* 87 (1987) 275-280.
33. H. Guo, D. Li, L. Zheng, S. Gong, H. Xu, Effect of co-doping of two reactive elements on alumina scale growth of β -NiAl at 1200 °C, *Corr. Sci.* 88 (2014) 197-208.
34. B.A. Pint, Experimental observations in support of the dynamic-segregation theory to explain the reactive-element effect, *Oxid. Met.* 45 (1996) 1-36.
35. L.A. Donohue, I.J. Smith, W.D. Munz, I. Petrov, J.E. Greene, Microstructure and oxidation resistance of $Ti_{1-x-y-z}Al_xCr_yY_zN$ grown by combined steered-arc/unbalanced-magnetron-sputter deposition, *Surf. Coat. Technol.* 94-95 (1997) 226-231.
36. E. Martinez, R.Sanjines, O.Banakh, F.Levy: Electrical, optical and mechanical properties of sputtered CrN_x and $Cr_{1-x}Si_xN_{1.02}$ thin films. *Thin Solid Films* 447 –448 (2004) 332–336.
37. C. Mansilla, Structure, microstructure and optical properties of cerium oxide thin films prepared by electron beam evaporation assisted with ion beams. *Solid State Sci.* 11 (2009) 1456-1464.
38. S. Chevalier: What did we learn on the reactive element effect in chromia scale since Pleil's patent? *Mater. Corros.* 65 (2014) 109-115

39. Al-Hamil, TEM study of the effect of the Y on the scale microstructure of Cr₂O₃ and Al₂O₃-forming alloys. *Oxid. Mat.* 58 (2002) 23-40
40. O. Monnereau, L. Tortet, C.E.A. Grigorescu, D. Savastru, C.R. Iordanescu, F. Guinneton, R. Notonier, A. Tonetto, T. Zhang, I.N. Mihailescu, D. Stanoi, H.J. Trodahl, Chromium oxides mixtures in PLD films investigated by Raman spectroscopy, *J. Optoelectron. Adv. Mater.* 12 (2010) 1752-1758.
41. H.C. Barshilia, K.S. Rajam, Raman spectroscopy studies on the thermal stability of TiN, CrN, TiAlN coatings and nanolayered TiN/CrN, TiAlN/CrN multilayer coatings, *J. Mater. Res.* 19 (2004) 3196.
42. A. Ozturk, K.V. Ezirmik, K. Kazmanli, M. Urge, O.L. Eryilmaz, A. Erdemir, Comparative tribological behaviors of TiN-, CrN- and MoN-Cu nanocomposite coatings, *Tribol. Int.* 41 (2008) 49.
43. A. Gil, D. Naumenko, R. Vassen, J. Toscano, M. Subanovic, L. Singheiser, W.J. Quadackers, Y-rich oxide distribution in plasma sprayed MCrAlY-coatings studied by SEM with a cathodoluminescence detector and Raman spectroscopy, *Surf. Coat. Technol.* 204 (2009) 531-538.S.
44. Y Repelin, C. Proust, E. Husson, J.M. Beny, Vibrational spectroscopy of the C-form of yttrium sesquioxide, *J. Solid State Chem.* 118 (1995) 163-169.R. Franz, J. Schnöller, H. Hutter, C. Mitterer, Oxidation and diffusion study on AlCrVN hard coatings using oxygen isotopes ¹⁶O and ¹⁸O, *Thin Solid Films* 519 (2011) 3974-3981.
45. A.G.A. Kumar, J. Lu, A.A. Kaminskii, K. Ueda, H. Yagi, T. Yanagitani, N. V. Unnikrishnan, Spectroscopic and stimulated emission characteristics of Nd³⁺ transparent YAG ceramics, *IEEE J. Quantum Elec.* 40 (2004) 747-758.
46. T. C. Rojas, S. Dominguez-Meister, M. Brizuela, A. Garcia-Luis, A. Fernandez, J. C. Sanchez-Lopez, A nanoscale characterization with electron microscopy of multilayered CrAlYN coatings: a singular functional nanostructure, *Microsc. Microanal.* 20 (2014) 14-24.
47. T Mizoguchi, I.Tanaka, M. Kunisu, M. Yoshiya, H. Adachi, W.Y. Ching, Theoretical prediction of ELNES/XANES and chemical bonding of AlN polytypes, *Micron* 34 (2003) 249-254.

FIGURE CAPTIONS

Fig. 1. XRD diffractograms of the as prepared CrAlYN coatings deposited on M2 steel in θ - 2θ geometry. JCPDS card number: CrN (PDF #76-2494).

Fig. 2. (a) Textural parameters (T_{hkl}) and (b) average crystal size calculated for all the coatings.

Fig. 3. SEM cross section views of coatings: Al(16)Y(1.2), Al(16)Y(3.4), Al(25)Y(2.6), and Al(25)Y(5.7).

Fig. 4. (a) HRTEM image of sample Al(16)Y(3.4) (set I). Insets: DDP obtained from all image (b) and from the marked area (top corner). The planes (111), (020) and (002) are indicated in the same figure.

Fig. 5. HRTEM image of sample Al(25)Y(2.6) (set II) and DDP's obtained from the marked areas (1,2,3 and 4). The columnar growth direction is indicated by an arrow.

Fig. 6. A picture of the aspects of coated M2 steels after oxidation in air at 1000°C.

Fig. 7. XRD diffractograms of the CrAlYN coatings after oxidation in air at 1000 °C measured in θ - 2θ geometry. JCPDS cards numbers: Y_2O_3 (PDF #1-79-1256); $Al_5O_{12}Y_3$ (PDF #1-75-1853); Cr_2N (PDF #35-803); $FeCr_2O_4$ (PDF #34-140); $(Cr,Fe)_{23}C_6$ (PDF #1-78-1501); hcp-AlN (PDF #1-79-2497); AlO (PDF #1-75-278); $AlYO_3$ (PDF #33-41); CrN (PDF #76-2494); Fe_2O_3 (PDF #1-84-307); Cr_2O_3 (PDF #38-1479); Fe-Cr (PDF #34-396); Al_2O_3 (PDF #1-71-1684); Al_2O_3 -b (PDF #1-77-2135).

Fig 8. GD-OES spectra of the coatings from set I heated at 1000 °C in air.

Fig 9. GD-OES spectra of the heated coating Al(25)Y(2.6) (set II) at 1000 °C and 900 °C.

Fig 10. Raman spectra of annealed CrAlYN coatings at 1000 °C in air.

Fig. 11. (a) General TEM image of heated Al(16)Y(3.4) sample. (b) HAADF-STEM image of the scale and X-EDS spectra measured in point 1 and 2. (c) High magnified HAADF-STEM image of the scale/coating interface and X-EDS elemental maps obtained from the marked area.

Fig. 12. HAADF-STEM image of an inner region of the heated Al(16)Y(3.4) sample. X-EDS spectrum measured inside a column (point 1) and chemical elemental maps obtained from the marked area.

Fig.13. (a) TEM image of sample Al(25)Y(2.6) heated at 1000°C. (b) High magnification HAADF-STEM image from the scale. (c and d) X-EDS spectra measured in point 1 and 2 respectively and (e) EELS spectra obtained from point 2.

Fig. 14. (a) HAADF-STEM image of an inner region of the Al(25)Y(2.6) sample and X-EDS elemental maps obtained from the marked area. (b) HRTEM image and indexed DDP obtained from the marked square. (c) EELS spectra, N-K, Cr-L_{2,3} and Al-K edges, measured inside the coating.

Oxide scale

Coating

Substrate

Highlights

- Y atoms diffuse and segregate at the scale grain boundaries and interface (RE effect).
- Y diffused to the column boundaries hindering the Fe migration from the substrate.
- CrAl (16%)Y(3%)N presents good oxidation resistance and stability at 1000°C/2h
- Al (25 %) shows higher degree of fcc-CrAlN decomposition and oxidation (Y>3 at.%)
- Excess of Y favors oxygen inward penetration through Y_2O_3 and $Al_5O_{12}Y_3$ and $AlYO_3$

Table 1

Table 1. Synthesis conditions of the two set of CrAlYN coatings prepared by magnetron sputtering: target materials and power applied, elemental chemical composition obtained by EPMA, and mechanical properties.

Sample		Targets	P (W)	Chemical composition (at.%)				H (GPa)	E (GPa)
				N	Al	Cr	Y		
Set I	Al(16)Y(1.2)	AlCr20 Y	3000 500	54.7	17	27.1	1.2	23.9 ±4.2	436± 8
	Al(16)Y(3.4)	AlCr20 Y	3000 750	55.5	15.3	25.8	3.4	29.9±5.5	558 ±13
	Al(16)Y(4.6)	AlCr20 Y	3000 1000	53.9	15.5	25.9	4.6	28.4±5.2	546± 21
Set II	Al(25)Y(2.6)	AlCr10 Y	3000 750	54.4	24.9	18.1	2.6	27.3±4.6	522 ± 21
	Al(25)Y(5.7)	AlCr10 Y	3000 1000	54.1	24	16.2	5.7	30.4 ± 6.2	573 ±19

Table 2

Table 2. Summary of the Raman analysis of the AlCrYN coatings after oxidation in air at 1000°C.

Compound	Raman bands (cm ⁻¹)		Reference	Coating
Cr ₂ O ₃	≈350	565-585	9,40,41	Al(16)Y(1.2) Al(16)Y(3.4) Al(16)Y(4.6) Al(25)Y(5.7)
Al _x Cr _{2-x} O ₃	Broad band (700-730)		9	Al(16)Y(1.2) Al(16)Y(4.6) Al(25)Y(5.7)
CrO ₂		669	42	Al(16)Y(1.2)
Cr(VI)-O	880	946	40	Al(16)Y(4.6) Al(25)Y(5.7)
Cr ₂ O ₅		880	40	Al(25)Y(5.7)
Cr ₈ O ₂₁		889	40	Al(25)Y(5.7)
YAlO ₃ (YAP)		>900	43	Al(25)Y(5.7)
Y ₃ Al ₅ O ₁₂ (YAG)	257	370	45	Al(25)Y(5.7)
Y ₂ O ₃		376	44	Al(25)Y(5.7)

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