**Influence of Cr additions on the structure and oxidation resistance of multilayered TiAlCrN films**

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**Abstract**

Ti1−xAlxN coatings with NaCl-type structure have been widely used in advanced machining and other high temperature applications due to their excellent mechanical, thermal and tribological properties. Here, we investigated the influence of Cr additions on the structure, mechanical properties and oxidation resistance, including the oxide scale characterization, of multilayered TiAlN/CrAlN coatings deposited by magnetron sputtering. The properties of Cr rich coatings were compared to a TiAlN film deposited as reference. XRD diffraction analysis revealed that all coatings showed an fcc NaCl-type structure. However, for the TiAlN monolayer Ti and Al are forming a solid solution whilst, for Cr rich coatings, a multilayer structure alternating TiAlN and CrAlN layers, also forming solid solutions, was grown as a result of the geometry of the targets distribution inside the deposition chamber in combination with a slow rotation of the sample holder and a sufficiently high deposition rate. TGA measurements showed that Cr additions increased the oxidation performance of the coatings. For Ti0.47Al0.46N, dual oxide layers occur when tested at 800 ºC, being the porous inner one of TiO2 and the outer a compact and continuous layer of Al-oxide which protects the coating from the oxidation. At 900 ºC the oxidation resistance of this film degraded due to the fast Ti ions diffusion to the surface which impedes the formation of the continuous and protective Al oxide layer. Cr rich coatings showed different oxides scales depending on their chemical composition. For Ti0.30Al0.46Cr0.26N and Ti0.28Al0.34Cr0.42N, a Ti-O rich layer is formed on the top of a protective Al-Cr-O layer when the samples were tested at 900 ºC and 1000 ºC, being the oxide layers thicker for the higher temperature. Concerning the coating with the highest Cr content (Ti0.28Al0.31Cr0.51N), a compact and continuous Cr(Al)2O3 oxide layer was formed at 900 and 1000 ºC with residual TiO2 islands on the top, contributing for a significant enhancement of the oxidation resistance.

**Introduction**

Machining industry is the biggest customer for PVD deposited hard coatings. TiN hard films deposited by sputtering were the first generation of coatings used for cutting tools protection. In spite of the suitable values for their mechanical and friction properties, their low oxidation resistance (onset point of oxidation at ~600 ºC) obliged to find alternative solutions as, for example, their alloying with chemical elements that could in anyway improve their thermal behavior and, consequently, their in-service life [1]. The most known system is TiAlN, which has higher mechanical strength and oxidation resistance than TiN [2]. Ti1−xAlxN coatings with cubic NaCl structure, where Al substitutes the Ti positions in the TiN, is one of the most preferred material for industrial applications due to their properties at high temperature [3]. Al content of the Ti1−xAlxN films plays an important role on the mechanical and thermal properties as well as on their preferred crystal structure. When the coatings are deposited as a single fcc NaCl-type phase, they exhibit excellent mechanical properties and oxidation resistance. However, for Al content exceeding the maximum solubility (xmax ~0.7) a mixed cubic-NaCl and wurtzite structure is formed and degradation of the mechanical and thermal properties is observed. At extremely high Al concentrations, a single wurtzite structure can be formed showing excellent oxidation resistance but unsatisfactory mechanical properties [4]. TiAlN coatings with NaCl type structure exposed to air at temperature below 850 ºC form a bilayer oxide scale structure: a continuous and protective Al2O3 layer on the top and a porous TiO2 layer underneath. However, for higher temperatures a degradation of the oxidation resistance is observed due to the fast Ti ions diffusion to the surface, which inhibits the formation of the protective continuous Al2O3 layer [5]. In order to increase the oxidation resistance of the cubic TiAlN films, different alloying elements have been added to the coating system, such as Cr [6, 7], Si [8, 9], Nb [10], Ta [11, 12], Y [13], Zr [14] or Hf [15]. Most of the results showed that adding these elements in a mole fraction < 0.1 have the most positive effect on the mechanical and thermal stability properties. Regarding the specific case of Cr addition to the NaCl-type films, it has been shown that Cr restrains the spinodal decomposition by slowing the diffusion and formation of c-TiN and c-AlN domains. The spinodal decomposition results in age hardening; the presence of Cr within the AlN phase delays the formation of the detrimental wurtzite phase, leading to a substantial improvement of the thermal stability compared to the quasi-binary (TiAl)N or (CrAl)N alloys [16]. .Moreover, Cr improves the oxidation resistance and the tribological performance of TiAlN coatings. The influence of Cr additions on the properties of TiAlN films have been extensively investigated in monolayered (TiAlCrN) [17] and multilayered (TiAlN/CrN [18, 19] and TiAlN/CrAlN [20]) coatings. In both cases the thermal stability of the coatings and their oxidation performance were investigated; however, the oxide scale growth has not been studied extensively and only at temperatures up to 950 ºC. Yamamoto et al. [17] showed that monolayer TiCrAlN film exhibited a higher onset point of oxidation than TiAlN film, but no references to the oxide scale growth were given. Donohue et al. [21] conducted isothermal oxidation tests at 900 and 950 ºC during 1 h on a Ti0.44Al0.53Cr0.03N film: i) at 900 ºC the authors did not show/reveal the position of the Cr on the oxide scale, ii) at 950 ºC a complex oxide structure was developed and the position of the Cr on the oxide scale was described: TiO2 crystals on the top followed by two consecutive layers, one of an Al-rich oxide and the other of a Ti-rich oxide. Cr accumulation was observed at the lower and at the upper interfaces of the latter Ti-rich oxide sublayer. However, according to their results, the majority of Cr on the oxide scale was coming from the substrate, since a loss of Cr from the steel was detected close to the interface. The same author later on [22] studied the influence of low concentrations of chromium on the oxidation behavior TiAlN films. Glancing X-ray diffraction studies showed that severe oxidation of TiAlCrN initiated above 850 ºC but, again, no information about the oxide scale formation was given. Wadsworth et al. [23] investigated the oxidation resistance of TiAlN/CrN multilayer coatings and found that the resistance to oxidation was dependent on the Cr content. Xu et al. [6] compared the structure, mechanical and thermal properties of Ti0.52Al0.48N and Ti0.44Al0.50Cr0.06N coatings. The experiments revealed the better oxidation performance of Cr-rich coating. Isothermal tests performed at 850 ºC during 10 h showed that a thin oxide scale (~0.55 μm) for TiAlCrN coating was formed exhibiting a bilayer structure: Al- rich oxide at the top-layer and porous Ti-rich oxide as a sublayer. Further studies were focused on the structure and thermal properties of two TiAlN/CrN films with low and high Cr concentrations (Ti0.44Al0.37Cr0.08N and Ti0.28Al0.23Cr0.37N films) and compared to a TiAlN film [7]. Isothermal oxidation tests performed at 850 °C during 10 h demonstrated the better oxidation resistance of Cr-containing coatings. For Ti0.44Al0.37Cr0.08N, a dual layer structure was formed (Ti-rich oxide at the top layer and Al-rich oxide as sublayer), but for Ti0.28Al0.23Cr0.37N film a single monolayer oxide scale was formed. Again, almost no characterization of the oxide scale for Ti0.28Al0.23Cr0.37N film was given.

In this paper, TiAlN/CrAlN coatings with different Cr concentration were prepared by DC reactive magnetron sputtering to better understand the effect of Cr on the structure, mechanical properties and oxidation performance at 900 and 1000 ºC. The oxide scale of the coatings was characterized in detail by XRD, SEM-EDS, and elemental line profiles obtained along the cross section. Comparison of the results with those achieved for a reference TiAlN film is presented.

**2. Experimental procedure**

TiAl(Cr)N coatings with increasing Cr content were deposited in an industrial CemeCon 880/9 MLT coating chamber (400 x 400 x 430 mm) by unbalanced close field magnetron sputtering using DC power supplies. Fig. 1 shows the schematic diagram of the interior of the deposition chamber. The chamber has four cathodes: cathodes 1 and 2 are positioned with an angle of 40º and the other two facing these ones with the same geometry (see Fig.1). Two Ti targets, containing 48 Al pellets evenly distributed along the race track, were placed in cathodes 1 and 2 together with Al and Cr targets (cathodes 3 and 4); the targets dimensions were 500x88x10 mm and targets materials purity 99.9%. The substrate holder rotates the samples in front of the targets in the following order: TiAl, TiAl, Cr and Al. The power applied to the TiAl targets was constant, whereas the power to Al and Cr targets progressively decreased and increased, respectively. In this way, coatings with similar Ti (to remove the influence of Ti on the coatings properties), increasing Cr and decreasing Al contents were produced. For comparison purposes, a reference TiAlN film was deposited from four TiAl targets with 48 Al pellets each.

Polished tungsten carbide coupons, 16×10 mm (for cross section morphology analysis, thickness measurements, hardness measurements, and chemical composition evaluation, FeCrAl alloy substrates (20x20x1 mm; 72,8%Fe, 22% Cr, 5% Al, 0,1% Y, 0,1%Zr – Goodfellow, for oxidation tests and XRD diffraction analysis),were used as substrates. The FeCrAl alloy substrates had a small hole drilled in the middle to facilitate the complete covering of the whole surface. Prior to the depositions, all the substrates were ultrasonically cleaned in acetone for 10 min and alcohol for 15 min. The substrates were mounted in a substrate holder which underwent three axes rotation and the target to substrate distance was 60 mm. Prior deposition, the chamber was evacuated down to 1.3 ×10-4 Pa. The substrates were heated to 300 ºC and, then, etched with Ar ion sputtering using 650V and 350 kHZ applied to the RF power supply, connected to the substrate holder, for 60 min. In all the depositions, the total working gas pressure was kept constant at 0.58 Pa, using an argon flow of 240 sccm and increasing N2 flow from 110 to 130 sccm, with increasing power applied to the Cr target. TiAlN film was produced using a N2 flow of 110 sccm. All the depositions were performed using a pulsed negative bias of 40V (250 kHz). The deposition time for TiAlN coating was 135 min and for Cr-doped films 200 min. A summary of the deposition conditions is shown in Table 1.

The chemical composition of the coatings was accessed by energy dispersive spectroscopy (EDS). CrAlN and CrAlTiN films deposited in previous works of the research group [24, 25], with the chemical composition measured by EPMA (Electron Probe Microanalysis), were used as references for the EDS analysis. Scanning electron microscopy (SEM) was used to examine the fracture cross section morphology and thickness of the films. Crystallographic structure of the films was evaluated by X-ray diffraction (X’ Pert Pro MPD diffractometer) working in conventional mode. The hardness and Young’s modulus of the coatings were evaluated by nanoindentation technique (diamond Berkovich tip, max load 10 mN, load and unload rate 10 mN/min). The onset point of oxidation was evaluated by thermogravimetric analysis (TGA) using industrial air (99.99% purity). The coatings were heated up to 1200 ºC at a rate of 20 ºC/min and the mass gain was acquired at regular 2 s intervals using a microbalance with an accuracy of 0.01 mg. Another set of specimens was then isothermally exposed at different temperatures (800 and 900 ºC for TiAlN film and 900 and 1000 ºC for Cr rich coatings) for 2 hours. After oxidation tests, X-ray diffraction was performed on the oxidized surface of the specimens. Cross section morphology of the coatings was characterized by scanning electron microscopy (SEM) equipped with EDS. EDS elemental lines along the cross sections of the annealed samples were acquired to characterize the distribution of the main elements in the films and consequently to distinguish the different oxide scales.

**3. Results and discussion**

3.1 Chemical composition

The elemental chemical composition of the coatings measured by EDS is shown in Table 2. As expected, increasing and decreasing the power applied to the Cr and Al targets, respectively, whilst maintaining constant the power applied to the TiAl targets, gives rise to coatings with approximately a constant Ti content, lower Al and higher Cr contents. The reference TiAlN coating shows a stoichiometric composition and higher Ti content than Cr rich coatings. On the other hand, the last ones are N depleted, with nitrogen decreasing from 49.7 down to 47.5 at% with increasing power applied to Cr target. Although the nitrogen flow was adjusted (increased) with the power applied to the Cr target, to ensure the same deposition pressure as for the reference TiAlN coating, the chemical composition suggests that the nitrogen flow was not enough to produce fully stoichiometric films. It is well known that Ti reacts much more readily with nitrogen than aluminum and chromium, due to its higher value of enthalpy energy (80.8 kcal/mol) in comparison to AlN (76.2 kcal/mol) and CrN (29.8 kcal/mol) [26]. Thus, the incorporation of N is less intense with the increase of the content in Cr. The increase of the total power applied to the Al plus Cr targets (3950, 4000 and 4200 W) used on the depositions also strengthens this effect, since more metallic atoms are available for the same content of N2 in the deposition chamber. For easy coating identification, hereinafter, the coatings will be designated as TixAlyN and TixAlyCrzN, where x, y and z denotes the Ti, Al and Cr content in the films.

3.2 Cross section morphology and structure

Typical cross section morphology of the coatings is shown in Fig. 2. All coatings displayed a columnar morphology with columns extending from the substrate to the surface. No significant variations on the columns size are observed when Cr was added. Ti0.47Al0.46N film is 2.2 µm thick. Although the total power applied to the targets to produce Cr rich coatings was lower than for the reference film, the thickness of Cr-containing coatings was much higher, in good agreement with their higher deposition time. The progressive increase of the power applied to the Cr target led to the increase of the coatings thickness (3.6, 4.0 and 4.3 µm for Ti0.30Al0.46Cr0.26N, Ti0.28Al0.34Cr0.42N and Ti0.28Al0.31Cr0.51N films). Taking into account the low enthalpy energy formation of CrN, as compared to AlN and TiN, and the non-stoichiometric composition of Cr rich films in relation to N content (slightly lower than 50 at%), it is likely that the increasing of the thickness of the coatings with Cr content is due to the reduction of the poisoning of Cr target.

A closer look at the coatings reveals that the reference Ti0.47Al0.46N film displays a monolayer structure, whilst a multilayer structure with period of 30 and 39 nm has been formed for Ti0.28Al0.34Cr0.42N and Ti0.28Al0.31Cr0.51N films, respectively. EDS analysis performed at the multilayer structure shows that the bright phase is much richer in Cr than the dark phase suggesting that the first is CrAlN with Cr and Al in solid solution and the latter TiAlN with Ti and Al in solid solution. It should be pointed out that the multilayered structure was achieved due to the geometry of of the targets arrangement on the deposition chamber and the combination of a slow rotation of the sample holder with a sufficiently high deposition rate; it is expected the formation of intermix layers with a gradient interface. SEM picture of the coating with low Cr content does not show a multilayer structure; however, taking into account the targets arrangement inside the deposition chamber, the preview thickness of each individual layer, based on the total power applied to the Al and Cr target as compared to the other Cr rich coatings, there is no reason to be not observed. It is well known from literature, for this kind of multilayers, that a bilayer period over  > 2 nm should give rise to multilayer arrangements [19, 27]. The low contrast in the observation between TiAlN and CrAlN layers, in addition to the large intermixing already mentioned before, makes very difficult distinguishing the multilayer arrangement. More powerful techniques, such as high resolution transmission electron microscopy, would be required to shed some light on this subject.

Fig. 3 presents the XRD patterns of the as-deposited coatings onto FeCrAlY alloy substrates obtained in conventional mode. Excluding the substrate contribution, all the coatings shows diffraction peaks assigned to an fcc NaCl-type structure. Ti0.47Al0.0.46N film shows a [111] preferential orientation. The XRD diffraction peaks of this film are slightly shifted to higher and lower angles when compared to the reference TiN (87-0633) and AlN (25-1495) ICCD cards, respectively, suggesting that a solid solution is being formed. Therefore, it might be assumed that both elements (Ti and Al) occupy randomly the lattice positions in the single fcc Na-Cl type structure. Indeed, as Al has lower atomic radius (0.143 nm) than Ti (0.147 nm), it promotes the lattice constrain with the XRD peaks placed between TiN and AlN standards. This result agrees well with those from literature, where Ti1-xAlxN coatings with a fcc substitutional solid solution structure have been always produced for Al concentrations lower than 35 at.% (i.e. x < 0.7) [4]. However, the diffraction peaks position can also be influenced by the intrinsic and thermal residual stresses.

The addition of Cr leads to a significant broadening of the diffraction peaks, that can be interpreted based on the above suggested microstructure of the Cr-containing coatings, as follows: (i) the presence of a multilayer consisting of two similar structural phases, but with different chemical composition (TiAlN and CrAlN) and, thus, different lattice parameters, which should give rise to XRD diffraction signals placed at different angles; (ii) the existence of large chemical composition gradient interfaces between the two layers should lead, in the XRD pattern, to a sequence of shifts of the diffraction peaks in relation to the positions of the individual layers phases. Both these factors, contribute for an enlargement of the width of the diffraction peaks, determined by the existence of a sequence of lattice parameters, from that of the TiAlN to the CrAlN phases. The deconvolution of the XRD peaks is not easy to be performed due to the contribution of the interface mixing. However, the progressive change of the peaks intensities ratios of the coatings, with the increase of Cr content, gives a good support to our interpretation. In fact, for higher Cr content, a decrease of the (111) and an increase of the (200) diffraction peaks intensities are observed, which is in accordance to the ICDD card (76-2494) of CrN phase that has the highest intensity for the (200) peak; therefore, the Cr rich phase (CrAlN layer) should give rise to higher (200) intensity.”

3.3 Hardness and Young´s Modulus of coatings

The hardness and Young’s modulus evolution of the coatings with Cr additions is presented in Table 3. The higher hardness of reference Ti0.47Al0.46N can be explained by the solid solution hardening effect, as suggested by the XRD diffraction results. Moreover, it is clear from Table 3 that the coatings with added Cr are softer and have lower Young’s modulus than Ti0.47Al0.46N. As it is well known from the literature, the superlattice effect (significant hardness enhancement) produced by multilayered films arrangement is dependent on the thickness of the multilayers. In many materials combinations, the evolution of the hardness as a function of the bilayer modulation period shows a characteristic behavior, with maximum hardness values typically obtained for ʎ between 2 and 10 nm [27]. The high hardness has been reported to be caused by the blocking dislocations motion at the layer interfaces, due to differences on the shear moduli of the individual layers materials and by coherency strain causing periodical strain-stress fields in the case of lattice mismatched multilayered films. Further increase of the period thickness led to a progressive decrease of the coating hardness up to the moment that remains fairly constant, due to the total loss of the superlattice effect. At this point, multilayers start to behave as individual layers and the hardness of the films starts to be represented by the weighted average of the hardness of the individual layers. Thus, the lower hardness and Young’s modulus of Cr-containing coatings than Ti0.47Al0.46N can be interpreted by the high period thickness of the multilayers structure, which avoids the establishment of the superlattice effect, and the presence of CrAlN layer which is softer than TiAlN. Unexpectedly, an increase of the hardness and Young’s modulus was also observed with the increase of Cr content, which is against the previous statement since more CrAlN phase is present. Nevertheless, XRD diffraction showed a progressive increase of the (200) and decrease of the (111) peaks intensitieswith Cr addition, which have been reported to give higher TiN and CrN hardness values [28, 29], thus, justifying the hardness increase.

The elastic strain to failure of the coatings is shown in table 3 through the ratio H/E [30]. Ti0.47Al0.46N film shows the worst resistance to the plastic deformation. Increasing the Cr content leads to a progressive increase of the H/E ratio revealing the beneficial influence o Cr additions on the toughness of the coatings which can be related with the multilayer arrangement which allows deflection of cracking and improving toughness fracture resistance [25].

3.4. Continuous and isothermal oxidation in air

Fig. 4 shows the oxidation weight gain curves of the coatings acquired at continuous increase of temperature (RT to 1200 ºC at 20 ºC/min). The onset point of oxidation of Ti0.47Al0.46N film is 850 ºC. This temperature agrees well with that of the works of Xu, et al. [6] and Koller et al. [11]. The mass gain of Ti0.47Al0.46N film increases rapidly in the temperature range of 1000 – 1100 ºC suggesting a fully oxidized coating. Alloying TiAlN coating with Cr leads to a higher onset point of oxidation (increment about 200 ºC) and a clear progressive decrease of the oxidation weight gain as a function of Cr content. Donohue et al. [22] reported an onset point of oxidation of 920 ºC for a Ti0.44Al0.53Cr0.03N film with low Cr content. Yamamoto et al. [17] have also shown that alloying TiAlN films with Cr deposited with a monolayered structure led to a higher onset point of oxidation by ~200 °C.

The results of the thermogravimetric analysis performed on the films at different isothermal temperatures for 2 h are shown in Fig. 5. The reference Ti0.47Al0.46N film was exposed to temperatures 800 and 900 ºC, whilst Cr containing coatings were tested at 900 and 1000 ºC. Oxidation weight gain of Ti0.47Al0.46N film tested at 800 ºC and Cr rich coatings tested at 900 ºC obeys a parabolic evolution as a function of time suggesting the formation of a protective oxide layer. Increasing the test temperature to 900 ºC suddenly decreases the oxidation resistance of Ti0.47Al0.46N film, which follows an exponential evolution. This behavior is well documented in the literature being attributed to the fast growth of an outer TiO2 oxide layer [7]. Chen et al. [4] showed an improvement on the onset point of oxidation of TiAlN films and, consequently, an increase of the oxidation resistance of the films with increasing Al content. All Cr doped coatings annealed at 900 ºC displayed comparable oxidation weight gain, which was at least 6 times lower when compared to Ti0.47Al0.0.46N film. This reveals the clear beneficial influence of Cr addition on the oxidation resistance of TiAlN films. Increasing the isothermal test temperature to 1000 ºC results in the increase of the oxidation weight gain of Cr rich coatings, in accordance with the enhanced diffusion controlling the oxidation process. All the curves still display a parabolic evolution as a function of time, as a consequence of the presence of a protective oxide layer.

In order to understand the oxidation behavior, XRD, SEM and EDS analyses were performed after oxidation tests with the main emphasis focused on the formation and composition of the surface oxide layers. Fig. 6 shows the XRD diffraction patterns of the annealed coatings. The Ti0.47Al0.46N film oxidized at 800 ºC exhibits a small shift of the fcc diffraction peaks toward higher angles and a slight decrease of their intensity with a simultaneously broadening as compared with as-deposited film (spectrum ii) in Fig. 6 a)), suggesting that only minor structural changes at this temperature have occurred. The shift of the fcc diffraction peaks to higher 2 Ɵ angles during annealing might be attributed to the release of residual stresses. Additionally, a small left shoulder of (111) peak appeared. The cross section morphology of the oxidized film (see Figure 7 a)) shows the presence of a thin two-layer oxide structure (total thickness ~130 nm), with a porous inner layer and an outer compact and continuous layer. EDS analysis revealed that the porous layer was Ti-rich whereas the more dense top layer was Al rich. This agrees well with the results from previous works, where the layered oxide scale of Ti1-xAlxN coatings was attributed to the simultaneous outward diffusion of Al through the oxide/air interface, to form Al2O3, and inward diffusion of O toward the oxide/nitride interface, to grow a porous TiO2 layer [4, 5, 31]. Although the analysis indicated the presence of a double thin oxide layer, XRD diffraction peaks related to the oxide phases are missing. As it is well known (e.g. Yang et al. [5]), close to this temperature, Ti1-xAlxN films also undergoes spinodal decomposition. Thus, the broadening of the fcc peak, as well as the appearance of the left shoulder peak, can be either attributed to the Ti1-xAlxN spinodal decomposition, or to the first weak traces of oxidation of the film. In fact both c–TiN, w–AlN (ICDD card 03-1144) and TiO2 (ICDD card 76-0649) phases can fit the shoulder in the diffraction peak (see insert in Fig. 6 a)).

During oxidation at 800 ºC of the Ti0.47Al0.46N film, Al first reacts with oxygen due to their selective oxidation (see Ellingham diagram [32]). At the same time, Ti diffuses to the interface unoxidized coating / oxide surface layer, where, due to the inward diffusion of O, porous TiO2 is grown. The formation of porous Ti-O is reported to be caused by the generation of compressive residual stresses, which can cause crack formation and thereby fast oxidation with its growth [7]. Then, Al diffuses through the Ti-O porous layer to the coatings surface to form Al-O. Once the thickness and compactness of the Al-O layer at surface is sufficient, it acts as a very effective diffusion barrier, limiting the ions diffusion and protecting the coating from further oxidation. The establishment of a continuous, compact and protective Al-O layer on the surface explains the parabolic weight gain evolution of the coating with time, displayed in Fig 5 a).

At 900 ºC, all the XRD diffraction peaks related to the cubic fcc phase disappeared (see spectrum iii) in Figure 6 a)) and, instead, reflections of TiO2 and corundum-type Al2O3 (ICDD card 02-1373) are detected. This corroborates the cross section EDS profiles and the morphology presented in Fig. 7 b), which showed the complete oxidation of the coating. A dual oxide layers structure, composed by an outer layer of large crystals, corresponding to TiO2, and an inner layer formed by two phases, islands of TiO2 embedded in a matrix of porous Al2O3 phase, was formed. According to Xu et al. [7], the fast Ti ions diffusion through the oxide scale to the surface, to form TiO2, inhibits the formation of a protective and compact Al–O layer, thus degrading the oxidation resistance of the coatings.

In relation to Cr-doped coatings, XRD patterns of the coatings annealed at 900 ºC displayed only small changes, in good agreement to their small weight gain values and the very thin formed oxide scale. Similarly to the reference Ti0.47Al0.46N film, a shift of the fcc diffraction peaks to higher 2Ɵ angles their broadening and a small shoulder on the (111) peak appeared on the XRD diffraction patterns of Ti0.30Al0.46Cr0.26N and Ti0.28Al0.34Cr0.42N films. Elemental line profiles of the Ti0.30Al0.46Cr0.26N and Ti0.28Al0.34Cr0.42N films revealed that a Ti-O rich zone was formed on the top, followed by an Al-Cr-O rich zone which signal increased as the probe moved to the interior of the coating (see Fig. 8 a) for Ti0.30Al0.46Cr0.26N film). The Ti-O rich zone was thicker for the film with lower Cr content, showing the beneficial influence of chromium alloying on the decrease of the Ti diffusion to the surface. None of the previous oxides phases were detected by XRD; however, TiO2 phase can fit in the left shoulder of (111) peaks. Nevertheless, taking into account the spinodal decomposition, which often occurs for this coating system for annealing temperatures above 800 ºC [6], the broadening of the fcc diffraction peak and the appearance of the shoulder peak can be interpreted based on either that phase transformation or on the weak signal from the oxidation of the film. The continuous Al-Cr-O rich phase, formed at the interface film/oxide, grows amorphous, as no crystalline peaks were detected by XRD. However, such phase should protect the coating from oxidation as revealed by the very low mass gain registered by TGA. Chang and Hsiao [33], who tested isothermally a Cr0.40Ti0.22Al0.36Si0.02N film, with low Si additions, at 900 ºC during 2h, observed a similar oxide scale. The broadening and the shift to higher angles of the fcc diffraction peaks, as well as the appearance of a left shoulder to the (111) peak, was also observed for the coating with the highest Cr content (Ti0.28Al0.31Cr0.51N). Again, it can be correlated to the spinodal decomposition and/or the oxidation of the film. However, crystalline peaks reflections from Cr2O3 (ICDD 38-1479) were also indexed. EDS analyses, carried out at the oxidized surface, showed discontinuous and evenly distributed islands rich in Ti-O phase on the top of a Cr-O rich layer. The cross section morphology and the elemental line profiles analyses confirmed the formation of a continuous and compact oxide layer of Cr-O (Fig. 8 b)), in good agreement to the signal of Cr2O3 phase detected by XRD. Although the position of the XRD peaks of Cr2O3 phase is very close to the ICDD reference position and the EDS analysis distribution in the top layers clearly shows that Cr intensity is increasing towards the surface inversely to the Al signal, we cannot disregard the Al presence in solid solution in the Cr-O phase.

In summary, for the isothermal tests performed at 900 0C, alloying TiAlN coating with Cr delays the fast diffusion of Ti to the surface due to the formation of an inner protective amorphous layer of Al-Cr-O or, for the coating with the highest Cr content, a crystalline Cr(Al)2O3 layer. Such layers inhibit either the Ti ions diffusion to the surface or the inwards O diffusion to the TiAlCrN film and, thus, improve the oxidation resistance. It is evident thata small Cr addition is enough efficient to improve the oxidation resistance. Higher Cr contents, although reducing slightly the thickness of the oxide scale and promoting the formation of a Cr(Al)2O3 inner protective layer, do not further improve the oxidation resistance, as demonstrated in Fig. 5.

Cr-rich coatings annealed at 1000 ºC exhibited structural changes in relation to lower temperatures. According to XRD patterns, the main oxide phases detected on oxidised Ti0.30Al0.46Cr0.26N and Ti0.28Al0.34Cr0.42N films were: TiO2 and a phase with XRD peaks positioned in-between the standard positions of Cr2O3 and corundum-type Al2O3 oxides, which can be identified as a (Cr,Al)2O3 compound. On the other hand, Cr2O3 and TiO2 (sole peak at 27.4 º) phases were indexed in the case of the highest Cr content film (Ti0.28Al0.31Cr0.51N). Again, in spite of the close position of the peaks to the ICDD Cr2O3 standard, the presence of Al in this phase cannot be ignored. All the fcc diffraction peaks of TiAlCrN films are shifted to angles closer to the reference TiN card as compared to the corresponding diffraction patterns of the coatings annealed at 900 ºC, in accordance to the occurrence of the spinodal decomposition. The cross section morphology of the coatings shown in Fig. 9 clearly demonstrates that increasing Cr addition progressively decreased the oxide scale thickness of the films in good agreement with the isothermal oxidation curves in Fig. 5. Cross section EDS profiles of Ti0.30Al0.46Cr0.26N film (Fig. 9 a) show a Ti-O rich layer on the top surface. Below this region, a mixture of Al-Cr-O was formed. These results are in line with the two different regions observed by SEM: a continuous and rough layer on the top, corresponding to TiO2, and a porous layer of Al, Cr and O underneath; they also agree with the XRD results. Ti0.28Al0.34Cr0.42N film shows a similar oxide scale structure; however, both the thicknesses of the overall oxide scale and the individual oxide layers are smaller. EDS chemical profile again shows a Ti-O layer on the top surface and an Al-Cr-O layer underneath. However, the latter is much less porous. Concerning the coating with the highest Cr content, a compact and continuous monolayer, of about 170 nm thick, was formed (see Fig 9 c)) which, according to the EDS elemental profiles and XRD results, could be described as Cr(Al)2O3. EDS analysis performed at the oxidized surface allowed to detect islands of Ti-O phase, evenly distributed on the surface (not shown), in good agreement with the TiO2 detection by XRD diffraction. The presence of this continuous and compact oxide layer rich in Cr, suggests a more performing diffusion barrier than Al2O3 and (Cr,Al)2O3 phases found in TiAlN and TiAlCrN (low and intermediary Cr content) films, respectively.

The experimental evidence shows that the mechanisms of oxidation are complex and dependent both on temperature and Cr content. It is clear that Cr addition increases the oxidation resistance of the coatings. At 900 ºC, the oxide scale of TiAlCrN coatings is different from that of conventional TiAlN and depends on the Cr content of the film. Chromium promoted the formation of a protective amorphous Al-Cr-O layer below a thin Ti-O layer for Ti0.30Al0.46Cr0.26N and Ti0.28Al0.34Cr0.42N coatings which hindered either the fast Ti ions diffusion to the surface or the inward diffusion of O. For the coating with the highest Cr content a different oxide scale was grown. A protective Cr(Al)2O3 layer was established on the surface of the film, with TiO2 islands dispersed on the top. At the initial stage of the oxidation for Ti0.30Al0.46Cr0.26N and Ti0.28Al0.34Cr0.42N films, Al-O forms first as suggested by the highest affinity to oxygen when compared to Ti and Cr. However, titanium diffuses quickly to the surface to form Ti-O layer with the oxidation of both Al and Cr underneath. For Ti0.28Al0.31Cr0.51N film, due to the high amount of Cr, a Cr(Al)2O3 layer is preferentially formed. After some time, the thickness of the inner Al-Cr-O or Cr(Al)-O layer is sufficient to delay significantly further oxidation.

Annealing at 1000 ºC results on the growth of similar oxide scales as for 900 ºC but with higher thicknesses. Additionally, oxides which were amorphous at 900 ºC became crystalline. Coatings with low and intermediary Cr contents showed a bilayer structure: a TiO2 layer on the surface and, below, a (Cr,Al)2O3 compact and continuous layer. Similarly to the Cr-rich coatings tested at 900 ºC, at the beginning of the oxidation, fast Ti ions diffusion causes the initial formation of a Ti-O layer and, subsequently, the formation of the Cr-Al-O sublayer. However, due to the enhanced diffusion, the thickness of the oxide scales is higher. In the Ti0.28Al0.34Cr0.42N, the oxide scale growth progresses more slowly than for Ti0.30Al0.46Cr0.26N film, due to its higher amount of Cr. Therefore, an Al-Cr-O sublayer much richer in Cr is formed, more resistant to Ti ions diffusion. The oxidation kinetics is reduced and, consequently, the oxidation resistance of the film is improved. Finally, for Ti0.28Al0.31Cr0.51N film, due to the very high Cr content, a thin Cr2O3 oxide layer, which can contain Al, forms on the surface of the film quickly, with residual TiO2 islands on the top (almost not detectable by XRD and SEM cross section). Such a layer reduces even more efficiently the inward and outward diffusion of ions and, consequently, improves the oxidation performance.

**Conclusions**

The current work reports on the influence of Cr additions on the structure, mechanical properties and oxidation behavior of TiAlCrN films deposited as a multilayer, and the comparison to a TiAlN film deposited as reference. The thickness of Cr rich coatings increases and N content decreases with the increase of the power applied to the Cr target, owing to a lower poisoning degree of the Cr target. The hardness of Ti0.47Al0.46N film is higher than that of Cr rich coatings, due to the substitutional solid solution hardening effect. On the other hand, for multilayered Cr rich coatings, the hardness increases with Cr content due to the increase of the CrN phase in the CrAlN layer which progressive increase the (200) and decrease of the (111) diffraction peaks intensities. The Cr addition gave rise to higher values of the onset point of oxidation in relation to the reference TiAlN film, by more than 200 ºC, showing an improvement of the oxidation resistance. Ti0.47Al0.46N film annealed at 800 ºC follows a parabolic oxidation weight gain, controlled by the growth of a protective Al2O3 layer over a porous TiO2 layer. At 900 ºC, the film totally oxidizes as a consequence of the fast Ti ions diffusion to the surface, which hinders the formation of the protective Al-O layer. Cr additions improves the oxidation performance of the films. At 900 ºC, the oxidation weight gain was independent of the Cr content on the films; for Ti0.30Al0.46Cr0.26N and Ti0.28Al0.34Cr0.42N, an amorphous inner Al-Cr-O rich layer is formed below a Ti-O layer, being responsible for the oxidation improvement. For Ti0.28Al0.31Cr0.51N, the oxidation kinetics of the film is controlled by the formation of a crystalline and compact layer of Cr(Al)2O3. At 1000 ºC, Cr rich coatings still display a parabolic oxidation with increasing Cr addition and the oxide scale thickness of the films progressively decreased. Ti0.28Al0.31Cr0.51N film gives the best protection to ions diffusion due to the formation of a continuous and compact Cr(Al)2O3 layer, with some TiO2 islands on the top. For the other two films with lower Cr content the oxidation rate is controlled by a protective (Cr,Al)2O3 layer growing below the top TiO2 layer. The higher the Cr content on these films the richer in Cr the (Cr,Al)2O3 phase is.

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**Figure captions**

Figure 1 - Schematic illustration of the deposition chamber used for the films deposition.

Figure 2 - Cross section morphology of the films. a) Ti0.47Al0.46N, b) Ti0.30Al0.46Cr0.26N, c) Ti0.28Al0.34Cr0.42N and d) Ti0.28Al0.31Cr0.51N.

Figure 3 – XRD diffraction patterns of as the deposited films.

Figure 4 - Thermal gravimetric oxidation rate of coatings deposited on Al2O3 substrates: experiments performed at a linear-temperature ramp (RT to 1200 ºC at 20 ºC/min).

Figure 5 – Isothermal oxidation weight gain of coatings tested at dissimilar temperatures during 2 h. Reference Ti0.47Al0.46N film tested at 800 and 900 0C. Cr rich coatings tested at 900 and 1000 0C.

Figure 6 – XRD diffraction patterns of dissimilar coatings in as deposited condition and after annealing in air at different temperatures. a) Ti0.47Al0.46N, b) Ti0.30Al0.46Cr0.26N, c) Ti0.28Al0.34Cr0.42N and d) Ti0.28Al0.31Cr0.51N. XRD diffraction patterns of as deposited films was labeled in each figure as spectrum i), whilst, spectrum of annealed coatings were labeled as spectrums ii) and iii).

Figure 7 – Fracture cross section morphology and EDX line scan of annealed Ti0.47Al0.46N film: a) at 800 ºC 2h, b) at 900 ºC 2h.

Figure 8 – Fracture cross section morphology and EDX line scan of: a) Ti0.30Al0.46Cr0.26N and b) Ti0.28Al0.31Cr0.51N films, after oxidation at 900 ºC 2h.

Figure 9 - Fracture cross section morphology and EDX line scan of: a) Ti0.30Al0.46Cr0.26N, b) Ti0.28Al0.34Cr0.42N and c) Ti0.28Al0.31Cr0.51N films, after oxidation at 1000 ºC 2h.