Hard amorphous Ti–Al–N coatings deposited by sputtering

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Abstract

Ti–Al–N coatings were deposited by direct current reactive magnetron sputtering using two titanium and two aluminum targets. Two series of films with Al/(Al + Ti) atomic ratios of ≈ 23.5 and ≈ 34.5% were studied. The amount of nitrogen in the films was varied from 0 to 44at.%. The incorporation of N atoms led to a change of the α-Ti lattice preferential orientation from <100> to <001>, a decrease in the degree of crystallinity, and subsequently to the collapse of the crystalline structure. Annealing at 975K promotes the formation of the Ti3Al compound. The hardness increases smoothly with the nitrogen content. The high hardness values (31 and 41GPa) measured for the films with the highest N contents may be explained by the deposition of a nanocomposite phase. For the Ti–Al–N film deposited with Al/(Al + Ti) atomic ratio of 34.5% the α-Ti structure was completely transformed to TiO2 upon oxidation. The high oxidation resistance of the film deposited with 44at.% N at 1075K is characteristic of Ti–Al–N films.

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1. Introduction

In recent years, (Ti,Al)N films have been widely studied mainly because they exhibit high hardness, good wear resistance and high oxidation resistance at elevated temperatures (over 1075K) [1–3]. For this reason (Ti,Al)N has become one of the best solutions as coating material for cutting tools, especially for dry and high speed machining [4,5]. However, (Ti,Al)N coatings are less efficient when used for the protection of moulds, particularly those made of low strength materials which are used in moulding industry for prototyping purposes, mainly due to their high friction coefficient and the consequent sticking effects during in-service applications. Decreasing the Al content of (Ti, Al)N films promotes a drop of the friction coefficient, due to the decreasing amount of hexagonal close packed (h.c.p) AlN in the coatings [6], while a good resistance to oxidation is still retained (up to a temperature of 1075K [7]). On the other hand, the lower N content in Ti–Al–N films should allow achieving much higher thermal expansion coefficients than in traditional stoichiometric nitrides, such as WN, TiN and TiAIN, which can induce a reduction in the thermal stresses of the films. As a result, Ti–Al–N films with low Al and N contents could allow reaching a good compromise between high hardness, low friction coefficient and good corrosion/oxidation resistance. Such coatings could be very interesting for the low strength materials mould industry as they could improve the lifetime of prototyping moulds and, in the best cases, allow their use for small and mid series production.

In previous works both the deposition of Ti–Al films by magnetron sputtering [8] and the use of different target configurations to produce Ti–Al–N films with low nitrogen content [9,10] were studied. Following these works, the main objective of the present report is to investigate the influence of N and Al on the structure, hardness, thermal stability and oxidation resistance of Ti–Al–N coatings deposited by co-sputtering from pure Ti and Al targets.

2. Experimental details

Ti–Al–N films were deposited by direct current magnetron sputtering in a closed field magnetron system (Teer Coatings UDP 650) using two titanium and two aluminium targets (38 ×
17 × 0.6cm, 99.95%). The Ti targets were placed facing at 90° from the Al targets. A total operating current of 10.5A was used in all experiments. The sputtering chamber was evacuated down to an ultimate vacuum pressure of less than 3 × 10⁻⁴Pa before each experimental run. All films were deposited on polished AISI M2 steel (round substrates of 5mm diameter and 1.5mm thickness) and Si substrates placed on a rotating cylinder (5rpm). The substrates were not intentionally heated during deposition. The substrate bias voltage was kept constant at −50V and a 20sccm Ar flow (99.999%) was always used. Two series of experimental runs were carried out using Al target currents of 1.25 and 1.75A. Within each series, four depositions were done with nitrogen flows (99.999%) of 0, 3, 6 and 9sccm, resulting in deposition pressures in the range from 0.16 to 0.20Pa. In all deposition runs a Ti interlayer was grown during 2min before the film deposition (Ti target current = 7.5A and bias voltage = −100V). Annealing of the films was carried out for 1h at 975K in a dynamic hydrogenated argon atmosphere. The quartz tube was previously evacuated down to an ultimate vacuum pressure of less than 3 × 10⁻³Pa.

The structure of the coatings was studied by X-ray diffraction (XRD) using a Phillips diffractometer operated in Bragg–Brentano configuration with Co(Kα) radiation. The chemical composition of the coatings was determined by Electron Probe Microanalysis (EPMA) using a Cameca SX-50 equipment with an acceleration voltage of 15keV and Ti, Al and BN standards. The hardness tests were performed by depth-sensing indentation technique using a Fisherscope H100 with a Vickers indenter and a maximum indentation load of 20mN. Each hardness value is a result of at least eight indentation tests. Due to geometrical imperfections of the indenter and indentations, the hp values were corrected by the method proposed by Antunes et al. [11]. Thermogravimetric tests were carried out on a high resolution Polymer Science thermobalance (0.1mg) at 1075K. The films were placed in the sample holder and heated up to the oxidation temperature at a fixed heating rate of 30K/min. A constant isothermal time of 60min was used. Industrial air (99.995% purity) flowing through a dehumidification unit was introduced into the furnace with a flow rate of 55sccm during the entire test.

3. Results and discussion

3.1. Influence of nitrogen flow

The coating thickness was determined by the ball crater method and yielded values between 1.5 and 3μm. The oxygen contamination level in the films varied between 3 and 5at.% and the carbon content was always under the EPMA detection limit (≈ 0.5at.%). The deposition rate measured for the series of Ti–Al–N films deposited using 1.75 and 1.25A at the Al target is shown in Fig. 1 as a function of the nitrogen flow. For both series, the deposition rate slightly increases with the introduction of a minor amount of nitrogen in the discharge gas (N flow = 3sccm). Further increase of nitrogen flow leads to a drop of the deposition rate down to 12nm/min at 9sccm. Up to 6sccm of N flow the deposition rate is higher for the films produced with a higher Al target current. As the total current was maintained constant in all depositions, increasing the Al target current leads to an increase of the number of sputtered species at the Al target and to a decrease of the number of sputtered species at the Ti target. As the sputtering yield of Al is higher than the sputtering yield of Ti [12], the net result of increasing the Al target current is an increase of the total number of ejected species and, consequently, an increase of the deposition rate.

The Al/(Al + Ti) atomic ratio for both series of films is shown in Fig. 2a as a function of the nitrogen flow rate. As expected, the films deposited with a higher Al target current have a higher Al/(Al + Ti) atomic ratio. For the films deposited without nitrogen in the discharge gas and with a N flow of 3sccm the Al/(Al + Ti) atomic ratio was ≈ 23.5% and ≈ 34.5% for Al target currents of 1.25 and 1.75A, respectively.

Increasing the N flow leads to a slight decrease of the Al content for both series of films. This decrease in Al content is simultaneous with both the deposition rate drop (see Fig. 1) and a decrease of the Al target potential which suggests that the Al targets are poisoned during deposition. On the contrary the potential at the Ti targets is kept constant, suggesting that no poisoning effect is occurring in spite of this phenomenon readily taking place during TiN deposition. The easier poisoning of the Al target can be attributed to the much lower specific discharge current applied to the Al than to the Ti target in this work [13].

The N/(N + Ti + Al) atomic ratio, as measured by EPMA, is shown in Fig. 2b as a function of the nitrogen flow. In spite of the higher deposition rate measured for the films deposited with higher Al target current, the N/(N + Ti + Al) ratio is similar in both series of films. For both Al target currents, an increase in nitrogen flow during the deposition process leads to gradually higher nitrogen contents in the coatings. This monotonous trend was not observed in other research studies [14]. As explained by these authors, for low nitrogen pressures, the gradual increase was due to the incorporation of nitrogen atoms in the octahedral sites of the α-Ti lattice. Afterwards, they observed a steeper rise in nitrogen content beginning at about a N2/Ar pressure ratio of 10% which was associated to the formation of the ε-Ti2N phase. Finally, another increase of the nitrogen content (≈ 30at.%) was observed at a N2/Ar pressure ratio of 17.5% due to the formation of δ-TiN. In the present study, the nitrogen content in the films...
increases almost linearly with the nitrogen flow (up to ≈ 44\text{at.\%} of N in the films) and no steep increases were observed. This result seems to indicate that no one of the cubic Ti-based phases has been deposited.

### 3.2. Structure analysis

The structural evolution of the as-deposited Ti–Al–N films synthesized with an Al/(Al + Ti) atomic ratio of ≈ 23.5 is shown in Fig. 3 as a function of the nitrogen flow. The film deposited without nitrogen shows the h.c.p. Ti phase diffraction lines with a strong \textit{b} 100\text{N} preferential orientation (pattern a) in Fig. 3A). The position of the Ti (100) peak is close to that reported in the literature [15] and its small full width at half maximum (FWHM) indicates a high degree of crystallinity. The incorporation of 11\text{at.\%} of nitrogen in the films causes both a change in the preferential orientation from \textit{b} 100\text{N} to \textit{b} 001\text{N} and a broadening of the diffraction peaks (pattern b) in Fig. 3A). Increasing the N content (25.2\text{at.\%}) promotes a shift of the \textit{\alpha}-Ti (002) peak position to lower diffraction angles (pattern c) in Fig. 3A). Further increasing the N content (44.1\text{at.\%}) leads to the deposition of films with a XRD amorphous phase (pattern d) in Fig. 3A). In this work, the term “amorphous phase” denotes a material which has no diffraction peaks when characterized using Bragg–Brentano geometry, i.e., which gives no reflection from the planes parallel to the sample surface.

The \textit{\alpha}-Ti lattice is only able to dissolve about 3 to 4\text{at.\%} of nitrogen at 800K according to the binary phase diagram representing thermodynamic equilibrium [16]. As PVD is a thermodynamically non-equilibrium process, this limit may be overcome mainly due to the low mobility of the deposited species. Therefore, a metastable oversaturated solid solution of nitrogen in titanium can be obtained up to nitrogen concentrations well above those predicted by thermodynamics. The accommodation of the nitrogen atoms in interstitial octahedral \textit{\alpha}-Ti sites causes lattice expansion which explains the shift of the diffraction peaks to smaller angles as stated by the Bragg equation. The XRD diffraction peaks become fairly broad, indicating a high internal local stress and/or a small grain size. However, in the case of substoichiometric titanium nitride films, for a certain N concentration the precipitation of the \textit{\epsilon}-Ti\textsubscript{2}N phase can occur due to its more energetically favourable lattice configuration. Kohlscheen et al. [14] have reported \textit{\epsilon}-Ti\textsubscript{2}N formation in the range from 10 to 15\text{at.\%} N while Vaz et al. [17] have found \textit{\epsilon}-Ti\textsubscript{2}N precipitation in the range from 20 to 30\text{at.\%} N in the films. In the present study precipitation of the \textit{\epsilon}-Ti\textsubscript{2}N was never observed. The \textit{\alpha}-Ti lattice is stable up to nitrogen contents above 25.2 and 27.8\text{at.\%} for the films deposited with...
Al target currents of 1.25 and 1.75A, respectively. Furthermore, the δ-TiN phase was never formed up to nitrogen contents of 44.1 and 42.1at.% for the same Al target currents. Instead, over saturation under non-equilibrium conditions leads to vanishing lattice order and to a quasi-amorphous state. This result seems to indicate that the presence of Al in the films prevents the formation of the Ti-based cubic phases and extends the N solubility range in the α-Ti lattice. The Ti3Al compound, which is reported in the Ti–Al phase diagram between 20 and 30at.% Al [16], is never formed. As it is well known, the sputtering process involves the ejection and deposition of highly energetic species. For this reason, the formation of ordered phases such as Ti3Al is not usually observed in the as-deposited films and only occurs after annealing [18].

The α-Ti phase with a preferential <100> orientation is still detected after annealing the film deposited without nitrogen at 875K for 1h (pattern a) in Fig. 3B). However, the (002) peak has a lower FWHM and its position is shifted towards higher diffraction angles (by ≈ 0.65°). In the thermodynamic Ti–Al phase diagram, the ordered compound Ti3Al is the equilibrium phase at 25at.% of Al [16]. The shift of the α-Ti (002) peak may be due to a pre-ordering process at the atomic level within the α-Ti lattice during the annealing process. This hypothesis would also explain the narrowing of the diffraction peaks observed upon annealing. The same shift of the α-Ti diffraction peaks towards higher diffraction angles with annealing is also observed for the films deposited with an intermediate amount of nitrogen (patterns b) and c) in Fig. 3B). The peak positions are closer to the value reported in the literature for the α-Ti (002) diffraction peak which indicates that stress release has occurred during the annealing process. The quasi-amorphous structure detected in the as-deposited films with the higher nitrogen content remains unaltered after annealing independently of its aluminium content (pattern d) in Fig. 3B). In spite of the stress relaxation processes and re-arrangements at the atomic level induced by annealing, all the Ti–Al films deposited in this work retain their as-deposited structure after annealing at 875K for 1h.

The α-Ti phase with a preferential <100> orientation is still detected after annealing the film deposited with less Al (Al/(Ti + Al) atomic ratio of 23.5%) and without nitrogen at 975K for 1h (pattern a) in Fig. 3C). Both the angular position and the FWHM of the α-Ti (002) peak are quite the same as after annealing at 875K showing that increasing the annealing temperature to 975K has no effect in the film structure. Annealing of the films deposited with intermediate nitrogen contents leads to the formation of diffraction peaks in the high angle side of the α-Ti (002) which were indexed to the (002) diffraction line of the Ti3Al phase (patterns b) and c) in Fig. 3C). Annealing of the films deposited with the highest nitrogen contents at 975K has no obvious effect on the XRD diffraction pattern as the same quasi-amorphous structure is still observed by XRD (pattern d) in Fig. 3C).

The X-ray diffraction spectra of the as-deposited films with an Al/(Al + Ti) atomic ratio of ≈ 34.5% (see Figs. 3 and 4) are similar to the results obtained for the films deposited with less aluminium. Once again, the incorporation of N atoms leads to a change of the α-Ti lattice preferential orientation from <100> to <001>, a decrease in the degree of crystallinity and subsequently to the collapse of the crystalline structure. The main effect resulting from increasing the Al content in the films is a shift of the α-Ti diffraction peaks towards higher diffractions angles which indicates a decrease of the lattice parameters. A similar shift of the α-Ti diffraction peaks is also observed by comparing the XRD results obtained after annealing at 875K for both series of films. This result was also obtained for Ti(Al,N) films deposited by sputtering from composite targets [10] and is a consequence of the substitution of Ti atoms by the smaller size Al atoms within the α-Ti lattice [19].

Increasing the annealing temperature from 875 to 975K has significantly different results depending on the Al content of the films. While for the film deposited with less Al and without N the α-Ti structure remains unchanged, for the similar film deposited with a higher Al content (pattern a) in Fig. 4C) the position of the diffraction peak is significantly shifted to higher 2θ angles. In fact, for the later film the position of the diffraction
peak after annealing at 975K is very close to the position of the Ti₃Al (002) diffraction line reported in the literature [20] allowing to conclude that annealing promotes ordering of the hexagonal matrix to form the Ti₃Al compound.

Increasing the annealing temperature of the films with higher Al content and with intermediate N contents from 875 to 975K results in the formation of the Ti₃Al phase with a (002) orientation as was already observed for the similar films with less Al. However, the degree of phase transformation depends on the aluminium content of the films. For the films deposited with less aluminium (Al/(Ti + Al) atomic ratio 23.5%) only part of the films is transform to Ti₃Al as shown by the week intensity of the diffraction peaks associated with this phase (patterns b) and c) in Fig. 3C) and the presence of the α-Ti peaks after annealing. For the films with more aluminium (Al/(Ti + Al) atomic ratio 34.5%) the phase transformation is complete as the annealing. For the films deposited with less aluminium (Al/(Ti + Al) atomic ratio 23.5%) only part of the films is transform to Ti₃Al as shown by the week intensity of the diffraction peaks associated with this phase (patterns b) and c) in Fig. 3C) and the presence of the α-Ti peaks after annealing. For the films with more aluminium (Al/(Ti + Al) atomic ratio 34.5%) the phase transformation is complete as the annealing.

For both series of Ti–Al–N films deposited in this work the incorporation of high nitrogen amounts (42.1 and 44.1at.% N) results in the formation of an XRD amorphous phase which remains after annealing either at 875 or 975K, irrespectively of the Al content of the films. Deposition of an XRD amorphous Ti–Al–N film was also reported by Musil et al. [21] for sputter-deposited films with an N content similar to the one measured in the amorphous films obtained in this work (≈ 40at.%). It is worth to note that this amorphous phase is obtained when the N content in the films is two high to be accommodated within the α-Ti lattice but two low to allow to formation of the cubic structure, i.e., understoichiometric relative to the Ti–Al–N compound.

3.3. Hardness

The hardness of the as-deposited films is shown in Fig. 5 as a function of the nitrogen content in the films. For both series of coatings, the hardness of the pure titanium films is already relatively high due to the stress and dislocations introduced by bombarding particles during the deposition. The hardness increases smoothly as the nitrogen content is increased up to ≈ 25at.%. The main cause for this hardness increase could be either grain size reduction or increasing stresses which may occur in order to accommodate the N atoms in the α-Ti lattice and consequent reduction in the dislocation movement [22,23].

Increasing the nitrogen content in the films above 40at.% leads to a steep increase of the hardness. The high hardness values (31 and 41GPa) could be explained by the deposition of some sort of nanocomposite structure where nanocrystals of δ-(Ti,Al)N phase are immersed in a non crystallized matrix, probably rich in Al–N phase which, by suppressing the grain boundary sliding, can induce an enhancement of the hardness [24]. The low dimension of the nanocrystals and their dispersion in the amorphous matrix are in the basis of the no detection of any crystalline feature by XRD. The enhancement of the hardness by the formation of nanocomposite phases were already reported for Ti–Al–N films [21]. However, nanocomposite structures in the Ti–Al–N ternary system usually originate XRD patterns with diffraction more or less crystalline type peaks corresponding to the nanocrystalline phase of the composite structure [24]. In our case the high hardness films are characterized by a XRD amorphous structure, i.e., without any crystalline type peaks. On the other hand, the amorphous Ti–Al–N film with 40at.% of N sputter-deposited by Musil et al. [21] only shows a hardness of ≈ 18GPa which is less than half of the hardness measured for the amorphous films deposited in this work. This result could be related to the lesser amount of Al in the amorphous films deposited in this work (Al/(Ti + Al) atomic ratio of 23.5% and 34.5%) as compared to the film deposited these authors (Al/(Ti + Al) ≈ 54.5%). In fact, high hardnes values where also measured by Shieh et al. [25] for Ti–Al–N films with a Al/(Ti + Al) atomic ratio of 25%, i.e., close to the ones used in this work, although the N amount in the film was sufficient to form a δ-TiN based structure. A TEM study of the amorphous Ti–Al–N films deposited in this work is currently under completion in order to clarify this issue and to obtain some insights about the nature of the amorphous film deposited in this work.

3.4. Oxidation

The XRD patterns of three of the films deposited with an Al (Al + Ti) atomic ratio of 34% after isothermal oxidation at
1075K are shown in Fig. 6 as a function of their N content. The film deposited without nitrogen was completely oxidized during the oxidation test as TiO2 [26] is the only phase detected by XRD (pattern a) in Fig. 6. TiO2 is also present in the XRD pattern of the film deposited with an intermediate N content along with the α-Ti phase (pattern b) in Fig. 6 which indicates that this film was only partially oxidized. Additionally, the formation of TiSi2 [27] phase indicates that reaction between the film and the Si substrate occurred during the oxidation test. Finally, the film deposited with the highest N remains amorphous even after oxidizing at 1075K as TiSi2 is the only phase detected by XRD diffraction (pattern c) in Fig. 6.

The isothermal oxidation curves of the films deposited with an Al/(Al + Ti) atomic ratio of 34.5% obtained at 1075K are shown in Fig. 7. The higher weight gain was measured for the film deposited without nitrogen (0.07mg/cm²). The weight gain curve shows a parabolic trend all along the isothermal plateau indicating that the rate of oxidation is controlled by solid state diffusion of the reactants through the oxide layer growing on the film surface. Krishna et al. [28] found that the oxidation of magnetron sputtered Ti films at temperatures higher than 975K, even for a few minutes, resulted in the complete transformation of the titanium film to titanium oxide. In spite of its aluminium content, the Ti–Al–N film deposited with Al/(Al + Ti) atomic ratio of 31.4% also has the α-Ti structure in the as-deposited state and complete transformation to TiO2 upon annealing occurred as confirmed by the XRD results.

The incorporation of 25.2 at.% of nitrogen in the film leads to a decrease of the final weight gain mass to 0.07mg/cm². The weight gain curve starts with a parabolic trend and switches, after ≈ 20min, to a linear mass gain with a rather low slope, suggesting a change in the mechanism ruling the oxidation process. The initial parabolic behavior of the weight gain curve is very similar to the one observed for the sample deposited without nitrogen which indicates that, with N incorporation, neither the nitrogen content nor the change in the crystallographic orientation of the film have a significant influence on the oxidation process. The change in the weight curve trend after 20min, which is responsible for lowering the final weight gain as compared with the sample deposited without nitrogen, is most likely due to the phase transformation from α-Ti to Ti3Al detected by X-ray diffraction. The phase transformation can induce the formation of a more stable and protective external oxide which is responsible for the decreasing oxidation rate of the global coated sample. As a result the α-Ti is still present at the end of the oxidation process along with TiO2.

Finally, the film deposited with 44at.% N has a very low mass gain up to the end of the isothermal plateau in agreement with the XRD results which did not reveal any evidence of oxidation. Such a behavior suggests that a very protective oxide layer was formed in the early stages of oxidation impeding further metal combination and reducing the weight gain. As referred to above, the presence of an Al–N rich intergranular layer can be in the origin of this protective layer. A similar mechanism was described in the literature for nanocomposite Ti–Si–N system for which the very high oxidation resistance is attributed to the formation of a protective Si–O layer around the TiN nanocrystals [29]. This high oxidation resistance even at 1075K was also found for Ti–Al–N films [7] but having higher Al relative contents.

4. Conclusions

α-Ti with a preferred (100) orientation was the only phase detected by X-ray diffraction in the as-deposited films. The incorporation of N atoms leads to a change of the α-Ti lattice preferential orientation from <100> to <001>, a decrease of the grain size, i.e., a decrease in the degree of crystallinity, and subsequently to the collapse of the crystalline structure. The accommodation of the nitrogen atoms at interstitial octahedral α-Ti sites causes lattice expansion which explains the shift of the diffraction peaks to smaller angles. In our samples precipitation of either ε-Ti2N or δ-TiN based phases was never observed. Instead, over saturation under non-equilibrium conditions leaded to vanishing lattice order and to an amorphous state. This result seems to indicate that the presence of Al in the films prevents the formation of the Ti-based cubic phases and extends the N solubility range in the α-Ti lattice.

In spite of the stress relaxation processes and re-arrangements at the atomic level, all the Ti–Al films deposited in this work retain their as-deposited structure after annealing at 875K for 1h. Increasing the annealing temperature to 975K promotes the formation of the Ti3Al compound. For the films deposited with less aluminium (Al/(Ti + Al) atomic ratio 23.5%) only part of the films transforms to Ti3Al while complete transformation was observed for the films with more aluminium (Al/(Ti + Al) atomic ratio 34.5%).

The hardness increases smoothly with the nitrogen content in the films mainly due to the grain size reduction. The high hardness values (31 and 41GPa) measured for the films with the highest N contents are compatible with the deposition of a some kind of nanocomposite structure, although these films have an XRD amorphous structure.

The Ti–Al–N film deposited with Al/(Al + Ti) atomic ratio of 34.5% and without nitrogen has a parabolic weight gain curve all along the isothermal plateau indicating that the rate of
oxidation is controlled by solid state diffusion of the reactants through a growing surface oxide layer. The high oxidation resistance of the film deposited with 44at.% N at 1075K is characteristic of nanocomposite Ti–Al–N films.

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