

Structure, hardness and thermal stability of Ti(Al,N) coatings

J.C. Oliveira ^{a,*}, A. Manaia ^{b,1}, A. Cavaleiro ^a, M.T. Vieira ^a

^a ICEMS, GMES, Dept. Engenharia Mecânica, Univ. Coimbra, Pinhal de Marrocos 3030-201 Coimbra, Portugal

^b IPN, Instituto Pedro Nunes, Rua Pedro Nunes 3030-199 Coimbra, Portugal

Available online 25 September 2006

Abstract

In the past two decades, coatings of the Ti–Al–N ternary system have attracted considerable research and industrial interest. Nevertheless, the Ti–Al–N system still offers new interesting possibilities for coating developments such as the addition of low N contents to Ti–Al films in order to reach a good compromise between high hardness and a low friction coefficient.

Ti–Al–N coatings with low nitrogen content were deposited by closed field unbalanced magnetron sputtering using two facing Ti targets inserted with Al rods. The Al/(Al+Ti) and N/(Al+Ti+N) atomic ratios were varied from 21 to 28 at.% and 0 to 33 at.%, respectively.

Hexagonal close-packed (hcp) α -Ti with a preferential $\langle 001 \rangle$ orientation was the only phase detected by X-ray diffraction in the as-deposited films. A decrease in the α -Ti c lattice parameter was observed as aluminium was added to the films. Nitrogen addition increased the c lattice parameter and led to a progressive loss of crystallinity until quasi-amorphous films were obtained. A hardness of ≈ 13 GPa was obtained for the as-deposited films without nitrogen. A continuous increase in hardness was observed with increasing nitrogen content. The highest hardness values (up to 27 GPa) were obtained for the quasi-amorphous films. Annealing of the films with low aluminium content (Al/Al+Ti ≈ 21 at.%) did not significantly affect their structure as hcp Ti remains the only phase detected. On the contrary, annealing of the films deposited with higher aluminium contents (Al/(Al+Ti) ≈ 24 and ≈ 28 at.%) resulted in the formation of face centered cubic (fcc) Al or Ti₃Al, showing that the thermal stability of the films decreased with aluminium incorporation.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Titanium; Aluminium; Sputtering; Magnetron; X-ray diffraction; Vickers Hardness test

1. Introduction

In the past two decades, coatings of the Ti–Al–N ternary system have attracted considerable research and industrial interest. Nowadays, Ti, Al and their respective nitrides are commonly applied in many industrial applications. In recent years, (Ti,Al)N films have been widely studied mainly because they exhibit good wear resistance and high oxidation resistance at elevated temperatures (over 800 °C) [1–3]. For this reason (Ti, Al)N has become one of the choice coating materials for cutting tools, especially for dry and high speed cutting. Ti–Al films have also drawn substantial attention since coatings of the low density intermetallic phases TiAl and Ti₃Al, which are promising structural materials for high temperature aerospace and engine

applications, have a potential for high temperature applications [4–6]. Nevertheless, the Ti–Al–N system still offers other interesting possibilities for coating developments such as the addition of low N contents to Ti–Al films in order to reach a good compromise between high hardness and a low friction coefficient. Furthermore, low N content Ti–Al–N films should allow achieving much higher thermal expansion coefficients than the traditional stoichiometric nitrides, such as WN, TiN and TiAlN, reducing the thermal stresses in the films. 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 case, allow the use of low strength materials moulds for the production of small and mid series.

In previous works both the deposition of Ti–Al films by magnetron sputtering [7] and the use of different target configurations to produce Ti–Al–N films with low nitrogen content [8] were studied. Following these early works, the main objective of the present report is to investigate the influence of N and Al on the structure, hardness and thermal stability of Ti–Al–N

* Corresponding author. Tel.: +351 239 790745; fax: +351 239 790701.

E-mail address: joao.oliveira@dem.uc.pt (J.C. Oliveira).

¹ Tel./fax: +351 239 700 912.

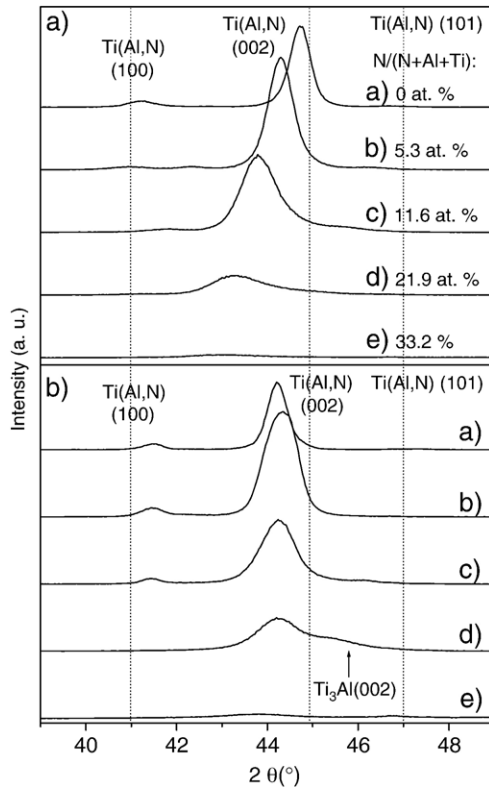


Fig. 1. Structural evolution of the films with an Al/(Ti+Al) atomic ratio of 21% as a function of nitrogen content: a) as-deposited and b) after annealing at 975 K for 1 h.

coatings deposited by sputtering from Ti targets inserted with Al rods.

2. Experimental

The Ti–Al–N films were deposited by dc magnetron sputtering in a closed field magnetron system (Teer Coatings UDP 650) using two titanium targets ($30 \times 17 \times 0.6$ cm, 99.95%) with embedded aluminium rods (8 mm of diameter, 99.95%). The targets were placed facing each other and were operated with a current of 7.5 A in all experiments. The sputtering chamber was evacuated down to an ultimate vacuum pressure of less than 3×10^{-4} Pa before each experimental run. All films were deposited on polished AISI M2 steel substrates (round substrates of 5 mm diameter and 1.5 mm thickness) placed on a rotating cylinder (5 rotations per minute). The substrates were not intentionally heated during deposition. The substrate bias voltage was kept constant at -50 V and a 20 sccm Ar flow (99.999%) was always used, resulting in deposition pressures in the order of 0.16 Pa. Three series of experimental runs were carried out using 22, 26 and 30 aluminium rods incrustated in each target. Within each series five depositions were carried out with nitrogen flows (99.999%) from 0 to 12 sccm. In all deposition runs a Ti interlayer was grown during 2 min before film deposition (Ti target current = 7.5 A and bias voltage = -100 V). For this purpose, a third target of pure Ti was placed 90° relatively to the composite targets. Annealing of the films was

carried out for 1 h at 975 K in a dynamic hydrogenated argon atmosphere. The quartz tube was previously evacuated down to an ultimate vacuum pressure of less than 3×10^{-3} Pa.

The structure of the coatings was studied by X-ray diffraction (XRD) using a Phillips diffractometer operated in Bragg-Brentano configuration with $\text{Co(K}\alpha)$ radiation. The c parameter of the α -Ti lattice was calculated from the angular position of the α -Ti (002) peak and Voigt functions were used for deconvolution of overlapping peaks. The chemical composition of the coatings was determined by Electron Probe Microanalysis (EPMA) using a Cameca SX-50 equipment with an acceleration voltage of 15 keV 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 20 mN. Each hardness value is a result of at least five indentation tests. Due to geometrical imperfections of the indenter and indentations, the h_p values were corrected by the method proposed by Antunes et al. [9].

3. Results

The coating thickness was determined by the ball crater method and yielded values between 2.5 and 3 μm with deposition rates of ≈ 30 nm/min. The Al/(Al+Ti) atomic ratio in the films deposited with 22, 26 and 30 aluminium rods incrustated in each Ti target resulting in values of ≈ 21 , ≈ 24 and $\approx 28\%$, respectively.

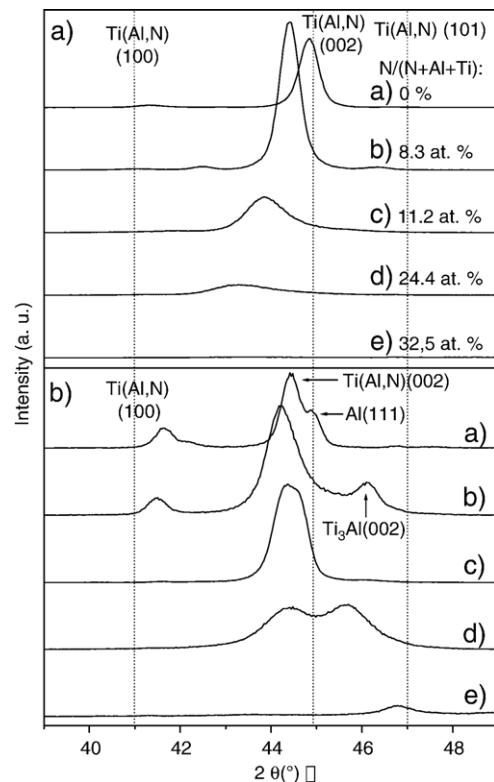


Fig. 2. Structural evolution of the films with an Al/(Ti+Al) atomic ratio of 24% as a function of nitrogen content: a) as-deposited and b) after annealing at 975 K for 1 h.

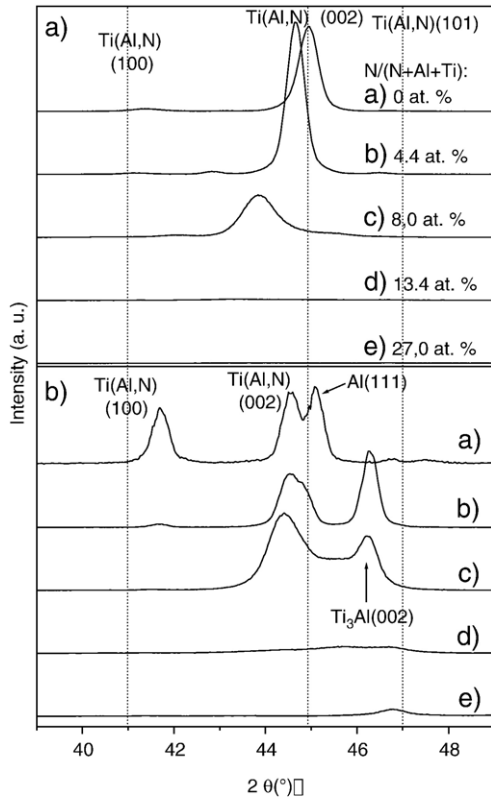


Fig. 3. Structural evolution of the films with an Al/(Ti+Al) atomic ratio of 28% as a function of nitrogen content: a) as-deposited and b) after annealing at 975 K for 1 h.

The structural evolution of the as-deposited Ti–Al–N films synthesized using 22 aluminium rods on each Ti target (i.e., with an N/(Al+Ti) atomic ratio of ≈21%) as a function of N flow is shown in Fig. 1a. The film deposited without nitrogen (spectrum a in Fig. 1a) shows the hcp Ti phase diffraction lines with a strong <001> preferential orientation. The position of the Ti (002) peak is close to that reported in the ICCD diffraction card [10] and the small FWHM of the diffraction peaks indicate high crystallinity. As the nitrogen content in the films is increased, the α-Ti (002) peak position is shifted to lower diffraction angles (spectra b and c in Fig. 1a). This result is due to an increase of the hcp Ti *c* lattice parameter as N atoms are incorporated in inter-

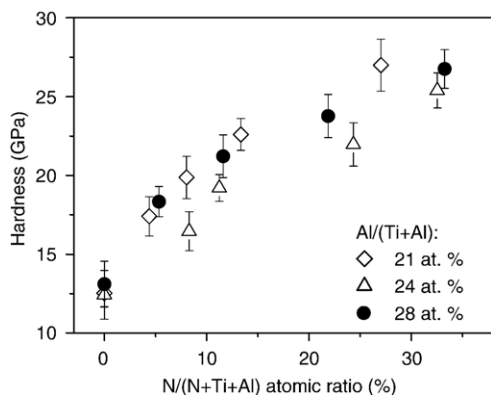


Fig. 4. Hardness as a function of nitrogen content in the films.

stitial positions within the crystalline lattice, forming a super-saturated metastable solid solution. When more N atoms are incorporated in the films (spectra d and e in Fig. 1a) the α-Ti (002) diffraction peak broadens until a quasi-amorphous structure is obtained at the highest N content. The incorporation of N atoms in the α-Ti lattice leads to 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 α-Ti phase with a preferential <001> orientation is still detected in all the films after annealing at 975 K for 1 h (see Fig. 1b). The only new diffraction feature is observed at the onset of the Ti (002) peak broadening (spectrum e in Fig. 1b): a new peak appears as a shoulder of the Ti (002) peak in the high angle side which corresponds to the (002) diffraction line of the Ti₃Al phase [11]. After annealing, the angular position of the Ti (002) peak of the film deposited without nitrogen (spectrum a in Fig. 1b) is shifted towards lower values while it is shifted in the opposite way for the films deposited with the three highest nitrogen contents (spectra c, d and e in Fig. 1b). The net result is that after annealing the position of the α-Ti (002) diffraction peak reaches a similar angular position for all the films independent of their nitrogen content.

Increasing the number of Al rods incrustated in each Ti target to 26 (i.e., increasing the Al/(Al+Ti) atomic ratio in the films to ≈24%) did not significantly affect the structure of the as-deposited films (see Fig. 2a). In all the diffraction spectra, the α-Ti phase with a preferential <001> orientation remains the only phase detected. As was observed for the lower aluminium content films, the angular position of the Ti (002) diffraction peak is shifted towards lower values and a progressive loss of crystallinity is observed as more nitrogen is added, until amorphous films are formed with the highest N content (spectrum e in Fig. 2a).

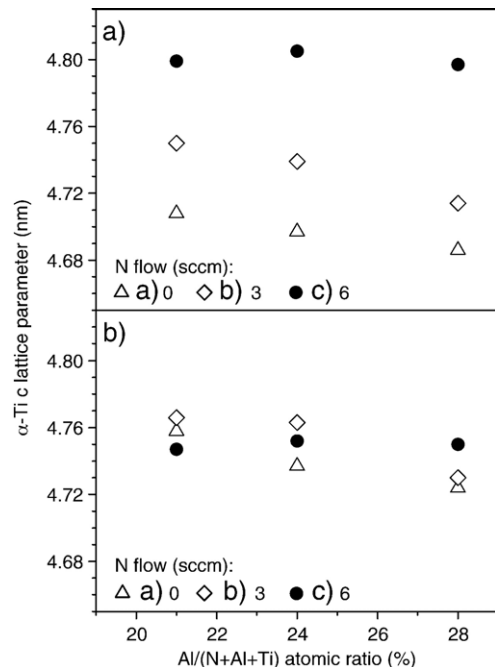


Fig. 5. Evolution of the α-Ti *c* lattice parameter with aluminium content in the films: a) as-deposited and b) after annealing at 975 K for 1 h.

After annealing of the film deposited without nitrogen a new peak appears on the high angle side of the α -Ti (002) peak which was indexed as the fcc Al (111) [12] diffraction line (spectrum a in Fig. 2b). The Ti_3Al phase is still detected at the onset of the amorphization process (spectrum d in Fig. 2b) but the (002) Ti_3Al peak has now a similar intensity as the (002) α -Ti peak. Once again the (002) α -Ti peak is shifted during the annealing process in such a way that it reaches a similar angular position for all the films independent of their nitrogen content.

In spite of an increase of the number of Al rods incrustated in each Ti target to 30 (i.e., increasing the $\text{Al}/(\text{Al}+\text{Ti})$ atomic ratio in the films to $\approx 28\%$), the diffraction features of the as-deposited films are still very similar to the results obtained with the lower aluminium content films (see Fig. 3a). In all the diffraction spectra the α -Ti structure with a preferential $\langle 001 \rangle$ orientation remains the only phase detected and the angular position of the Ti (002) diffraction peak is shifted towards lower values as the N content in the films increases. However, the progressive loss of crystallinity with increasing nitrogen content is enhanced by the presence of more aluminium atoms in the α -Ti lattice, and a quasi-amorphous structure is already detected at an $\text{N}/(\text{N}+\text{Ti}+\text{Al})$ atomic ratio of 13.4%.

Annealing of the film deposited with 30 Al rods and without nitrogen leads to the formation of the fcc Al phase while the α -Ti (002) peak is shifted to lower angular position and the α -Ti (100) peak intensity increases. For the films deposited with lower nitrogen content (spectra b and c in Fig. 3b), annealing promotes the formation of the Ti_3Al phase instead of cubic aluminium. Once again, the position of the α -Ti (002) peak after annealing is similar in all the films independent of their nitrogen content.

The hardness of the as-deposited films increases smoothly as the nitrogen content is increased (Fig. 4). A similar behaviour was reported by Vaz et al. for TiN_x films also deposited by sputtering [13] in spite of a gradual phase change from α -Ti to ε - Ti_2N . A slow increase in the hardness of TiAlN_x films up to ≈ 25 at.% of nitrogen was also reported by Malz et al. [14] for thin films also deposited by magnetron sputtering. The main cause for this hardness increase is the grain size reduction (Hall–Petch relationship), and consequent dislocation motion reduction, which occurs in order to accommodate the N atoms in the α -Ti lattice.

4. Discussion

α -Ti with a preferential $\langle 001 \rangle$ orientation is the only phase detected by X-ray diffraction in all the as-deposited films. For the films deposited without nitrogen, the incorporation of aluminium atoms within the α -Ti lattice leads to a shift of the α -Ti (002) peak to higher 2θ values, i.e., a decrease of the c lattice parameter (see a in Fig. 5a). This result is a consequence of substitution of Ti atoms by smaller size Al atoms within the α -Ti lattice. When low nitrogen contents ($\text{N}/(\text{N}+\text{Ti}+\text{Al})$ up to 8 at.%) are added to the films, the c parameter still decreases with increasing aluminium content (see b in Fig. 5a). However, as more nitrogen atoms are incorporated in interstitial positions

within the α -Ti lattice, the c parameter becomes independent of the aluminium content (see c in Fig. 5a). At low nitrogen content, the c lattice parameter of the α -Ti phase depends on both the amount of aluminium and nitrogen which have opposite effects: the c parameter increases with increasing N content and decreases with increasing Al content. When higher amounts of nitrogen are incorporated in the film, the α -Ti lattice is highly expanded to accommodate the N atoms and the substitution of Ti atoms by smaller Al atoms has less effect on the c lattice parameter.

Whatever the Al content of the as-deposited films is, the incorporation of increasing amounts of nitrogen in the α -Ti structure leads to a progressive loss of crystallinity until quasi-amorphous films are obtained. However, the loss of crystallinity is enhanced by the presence of higher amounts of Al within the α -Ti lattice. As was pointed out above, when higher amounts of aluminium are incorporated into the films without nitrogen or with low amounts of this element, a decrease of the c lattice parameter is observed. The smaller unit cell of the α -Ti phase deposited at high aluminium content is then only able to accommodate smaller amounts of nitrogen before collapsing and the loss of crystallinity starts at lower nitrogen contents in the films.

As can be concluded from comparing Fig. 5a and b, annealing of the films deposited without nitrogen induces an increase of the c lattice parameter, independent of their aluminium content. The c lattice parameter also increases with annealing for the films deposited with the lowest nitrogen contents (i.e., with a N flow of 3 sccm). However, in the later case the c lattice parameter increase is much lower. On the contrary, the c lattice parameter of the films deposited with a N flow of 6 sccm decreases with annealing. As a result, the α -Ti c lattice parameter of the films deposited with the same aluminium amount tends to assume similar values after annealing, in spite of their large difference in nitrogen content, showing that α -Ti lattice is then able to accommodate a much higher number of nitrogen atoms without increasing the c parameter. This result may be due to a pre-ordering process at the atomic level within the α -Ti lattice during the annealing process. In fact, in the thermodynamic Ti–Al phase diagram Ti_3Al , an ordered intermetallic compound, is the equilibrium phase at 25 at.% of Al, which lies within the range of aluminium contents studied in this work (21 to 28 at.% of Al). Moreover, the fcc Al phase which is formed during annealing of the films deposited with higher aluminium contents and without nitrogen may be interpreted as the segregation of excess aluminium as a result of this pre-ordering process. For the films deposited with nitrogen, the segregation of aluminium leads to the formation of the Ti_3Al phase instead of fcc Al. As a result, the thermal stability of the films was degraded by aluminium incorporation.

5. Conclusions

α -Ti with a preferred $\langle 001 \rangle$ orientation is the only phase detected by X-ray diffraction in all as-deposited films. At low nitrogen content, the c lattice parameter of the α -Ti phase depends on both the amount of aluminium and nitrogen which have opposite effects. The c parameter increases with increasing

N content, i.e., as more nitrogen atoms are incorporated in interstitial positions. On the contrary, the c parameter decreases with increasing Al content as Ti atoms are substituted by smaller Al atoms. When higher nitrogen amounts are incorporated in the films, the α -Ti lattice is highly expanded and the substitution of Ti by Al atoms has less effect on the c lattice parameter.

Independent of the Al content in the as-deposited films, the incorporation of increasing amounts of nitrogen in the α -Ti structure leads to a decrease in crystallinity, until quasi-amorphous films are obtained. The smaller unit cell of the α -Ti phase deposited at high aluminium content is then only able to accommodate smaller amounts of nitrogen before collapsing and the loss of crystallinity starts at lower nitrogen contents in the films.

The α -Ti c lattice parameter of the films deposited with the same aluminium content tends to assume similar values after annealing, in spite of their large difference in nitrogen content. This result may be due to a pre-ordering process at the atomic level within the α -Ti lattice during the annealing process. The thermal stability of the films was degraded by aluminium incorporation as fcc Al or Ti_3Al are formed after annealing.

Acknowledgement

This work was undertaken under project CRAFT-1999-72178 AL-MOULD. The authors would like to acknowledge the financial support given by the European Commission.

References

- [1] F. Mei, N. Shao, L. Wei, G. Li, Mater. Lett. 59 (2005) 2210.
- [2] S. Paldey, S.C. Deevi, Mater. Sci. Eng., A Struct. Mater.: Prop. Microstruct. Process. 342 (2003) 58.
- [3] L. Hultman, Vacuum 57 (2000) 1.
- [4] Y.-W. Kim, J. Met. 46 (1994) 30.
- [5] F.H. Froes, C. Suryanarayana, D. Eliezer, J. Mater. Sci. 27 (1992) 5113.
- [6] A.S. Ramos, M.T. Vieira, Mater. Sci. Forum 426–4 (2003) 1843.
- [7] J.C. Oliveira, A. Manaia, J.P. Dias, A. Cavaleiro, D. Teer, S. Taylor, Surf. Coat. Technol. 200 (2005) 395.
- [8] J.C. Oliveira, A. Manaia, J.P. Dias, A. Cavaleiro, D. Teer, S. Taylor, Surf. Coat. Technol. 200 (2006) 6583.
- [9] J.M. Antunes, A. Cavaleiro, L.F. Menezes, M.I. Simões, J.V. Fernandes, Surf. Coat. Technol. 149 (2002) 27.
- [10] JCPDS-International Centre for Diffraction Data, ICDD card n° 44–1294.
- [11] JCPDS-International Centre for Diffraction Data, ICDD card n° 14–0451.
- [12] JCPDS-International Centre for Diffraction Data, ICDD card n° 85–1327.
- [13] F. Vaz, J. Ferreira, E. Ribeiro, L. Rebouta, S. Lanceros-Méndez, J.A. Mendes, E. Alves, Ph. Goudeau, J.P. Riviére, F. Ribeiro, I. Moutinho, K. Pischow, J. De Rijk, Surf. Coat. Technol. 191 (2005) 317.
- [14] R. Malz, E. Brinksmeier, W. Preuß, J. Kohlscheen, H.R. Stock, P. Mayr, Precis. Eng. 24 (2000) 146.