

Ion Beam Analyses in Titanium Nitride Technology

I. J. R. Baumvol

*Instituto de Física, Universidade Federal do Rio Grande do Sul
91540-000 Porto Alegre, RS Brasil*

Received March 3, 1993

The technology of hard coatings based on stoichiometric titanium nitride thin films has been innovated since the past few years in order to fulfill the demands for better performance and lower processing cost put by the large scale industrial users. The different strategies used to improve the performance consist in (i) modifying the coating composition by introducing other elements than Ti and N in the film (multicomponent coatings), (ii) modifying the coating structure by using multilayered composites, and (iii) altering the coating density and porosity by using plasma and ion beam assisted processes. All these different strategies bring about new materials which have to be characterized as an essential part of the research and development work. In the present article the use of ion beam analyses is described (mainly Rutherford backscattering and nuclear reaction analyses) to characterize the thickness, composition, depth profile, contamination and structure of new thin film protective coating materials based on titanium nitride.

I. Introduction

The improvement of the wear, friction and corrosion performance of steel engineering components by means of protective coatings based on stoichiometric titanium nitride thin films is well established since over fifteen years. It became available for any user of steel-made cutting and drilling tools, moulds, dies and several other metallic items, as commercial services for titanium nitride coating deposition set up all over the world. Many plants making massive quantities of relevant metallic products, like in the automobile, aerospace and plastic injection industries have their own titanium nitride deposition services. Titanium nitride technology is finding also an increasing number of applications in decorative coatings and in the glass industry. Even in Brasil there are already two commercial services of titanium nitride coatings and several other companies having their indoor deposition facilities.

From the very beginning it was clearly established that the so called "titanium nitride technology" could be accomplished through different thin film deposition techniques. We will mention here the ones more often used for industrial purposes: reactive electron beam evaporation, ion plating, arc discharge, reactive sput-

tering and chemical vapour deposition. Some other common characteristics of the titanium nitride thin films used in industry are worth mentioning here: film thicknesses range from 2 to 6 μm in most cases; the most acknowledged stoichiometry is TiN, which has a characteristic gold color; the Knoop hardnesses range from 2200 to 4000, and the Vickers hardnesses range from 1000 to 3000.

The results obtained in the reduction of wear, friction and corrosion have fully justified from the economical side the large scale use of titanium nitride coatings even if the processing cost was and still is rather high. More recently, in the last five years, new trends have appeared in this technology aiming to reduce the processing cost and improving the performance of the coatings. These aims can be achieved by reducing the coating thicknesses (and consequently processing time), by increasing their adherence to the substrates, by producing far more dense and pore-free titanium nitride films, by reducing the interface stresses, and by increasing the hardness and elastic modulus of the coatings. These new trends are based on different strategies concerning the thin film coating deposition methods and the corresponding film composition and structure, which have effectively improved enormously the performance of titanium nitride technology as well as reduced consider-

ably the cost of it. In the last major conference of this area (the Plasma in Surface Engineering Conference, Garmisch, Germany, November 1992) it was made clear by many companies and research laboratories that there are still many directions of development to follow in titanium nitride technology demanding a great deal of research^[1]. The search for new materials was and still is decisive for the development of the technology as well as in making it accessible for industrial use. The titanium nitride film thicknesses, the depth profile of the N/Ti stoichiometric ratio, the film composition and contamination among several other characteristics of the coating can be rather nicely accessed by ion beam analyses (IBA). We have addressed the titanium nitride technology with IBA for the first time in 1988, within the framework of the PUC/RJ-Porto Alegre cooperation: RBS of a-particles and (a,a) nuclear resonant scattering were used to determine the film thickness and the nitrogen depth profiles in titanium nitride films deposited by ion plating and by reactive magnetron sputtering^[2]. After that first exploratory work a continuous and intensive research program was developed by the cooperation between the PUC-Rio and UFRGS- Porto Alegre in this field and many of the results presented here were obtained in this research program.

In this article we present the main results of the characterization of new titanium nitride-based thin film coatings using IBA methods with the facilities available in the Van de Graaff Laboratory at PUC-Rio, the Ion Implantation Laboratory at the Instituto de Física-Porto Alegre, the Laboratory for Material Analyses with Ion Beams (LAMFI) at USP-São Paulo and the Groupe de Physique des Solides at Jussieu-Paris. The performance achievements of these new materials are illustrated with hardness, wear and corrosion tests made at UFRGS-Porto Alegre and at the University of Heidelberg (Germany). In the following session we present the bases of the new trends in titanium nitride technology and their purposes. In Section III we present a summary of the ion beam analyses methods that were used in the present work. Sections IV to VI contain the experimental results and the discussion of them and in Section VII we present the conclusions and some prospects for future investigation.

II. New Trends in Titanium Nitride Technology

The modifications introduced in the titanium nitride - based coatings in respect to lower processing cost and performance improvement can be classified in three major groups: i) multicomponent thin films, which means to improve the mechanical characteristics of the coating by introducing other elements than Ti and N (like C, Cr, Al and others) in the film, producing compound (or multicomponent) coatings like the now widely used Ti(C,N) and (Ti,Al)N; ii) multilayered thin film structures (like Ti/TiN and TiN/AlN multilayers), which can eliminate interface stresses and reduce appreciably the film porosity; and iii) plasma or ion beam assistance to the deposition process, which can lead to better adherence of the coating to the steel substrate, relaxation of the film-substrate interface stresses, increasing of the film density and decreasing of its porosity.

We have studied the structure and composition of new titanium nitride-based coatings belonging to the three above mentioned groups. In group i) we have analysed the composition of titanium-aluminium nitride films deposited by reactive co-sputtering deposition; in group ii) we have determined the composition and wavelength of many different multilayered structures deposited by different methods; and in group iii) we analysed the modifications in structure and composition of titanium nitride films prepared by ion beam assisted deposition (IBAD).

III. Ion Beam Analyses Methods

The methods used to analyse the titanium nitride-based films of the present work were:

i) Rutherford backscattering spectroscopy (RBS) of a-particles with energies between 0.76 and 2.5 MeV, which allow the determination of the thickness of the films, the wavelengths of multilayers, and the composition and depth profiles by means of simulations and fitting of the experimental spectra using the RUMP program^[3];

ii) $^{14}\text{N}(d,p)$ and $^{14}\text{N}(d,\alpha)$ nuclear reactions (NRA) induced by a deuteron beam at energies around 0.61

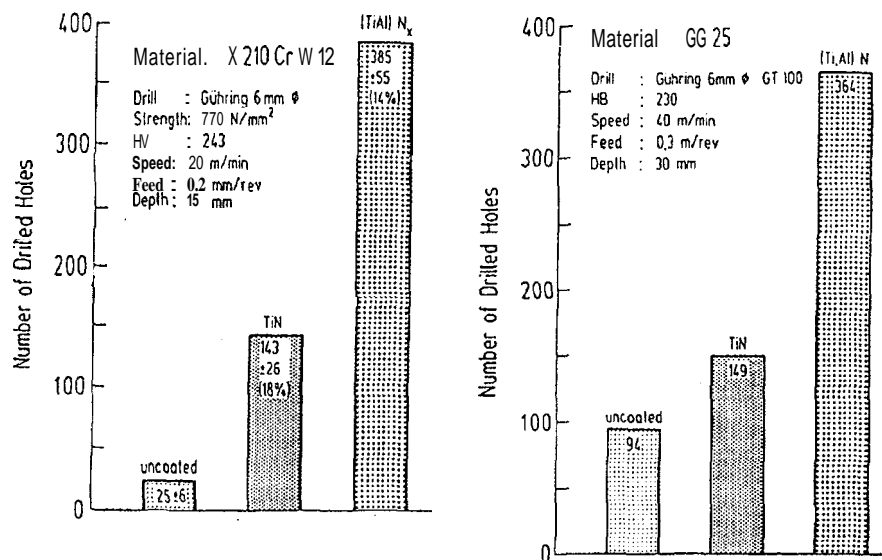


Figure 1: Tool manufacturer drill tests in Cr-W steel (left) and in grey cast iron (right) made with HSS cutting steel uncoated, coated with TiN and coated with (Ti,Al)N. The drilling parameters and the number of drilled holes in each case are indicated in the figure (from Reference 6).

and 1.6 MeV, respectively, which allow the determination of the total concentration of nitrogen in the films by comparison with adequate standards^[4];

iii) $^{14}\text{N}(p,\gamma)$ and $^{27}\text{Al}(p,\gamma)$ nuclear resonances, induced by protons of energies between 276 and 330 KeV, which allow the determination of the concentration versus depth profiles of nitrogen and aluminum in the films^[5].

IV. (Ti,Al)N Thin Films

The use of the ternary system Ti-Al-N as a base for a new hard coating material is one of the most successful new trends in titanium nitride technology. Many recent reports from industry as well as research laboratories have shown the improvements made on cutting and drilling lifetime versus speed performance, wear and friction reduction and corrosion resistance when these materials are used in the coating of tools. In Figure 1 we give some results from industrial uses of Ti-Al-N coatings which illustrate the kind of improvement they give with respect to TiN coatings^[6]. All these improvements were seen to depend rather strongly on the composition and structure of the titanium-aluminium nitride coatings^[7].

We have analysed titanium-aluminium nitride thin films deposited by reactive magnetron co-sputtering de-

position, using pure Ti and pure Al targets and a rotating substrate holder. The films for ion beam analyses were deposited onto silicon wafers and polyimide films 25 μm thick. The films deposited onto silicon were analysed by the resonant nuclear reactions $^{14}\text{N}(p,\gamma)^{15}\text{O}$ and $^{27}\text{Al}(p,\gamma)^{28}\text{Si}$ and by RBS with 2 MeV α -particles, while the films deposited onto polyimide were analysed by RBS with 0.76 MeV α -particles. In Fig. 2 we show the γ -ray spectra from the (p,γ) reactions in ^{14}N and ^{27}Al which were used to determine the concentrations of N and Al in the titanium-aluminium nitride films by comparison with silicon nitride and pure aluminium standards, respectively. In Fig. 3 we show the RBS spectra at 0.76 MeV incident α -particle energy for samples deposited at various Al cathode rf powers while maintaining the Ti cathode dc power and the Ar and N_2 partial pressures constant. A similar study made with much thicker films deposited on silicon substrates was made with RBS at 2 MeV, and typical results are shown in Fig. 4. The combination of the nuclear reaction measurements of the N and Al concentrations and the Ti concentration as measured by RBS allowed the determination of the $\text{N}/(\text{Al} + \text{Ti})$ and Al/Ti stoichiometric ratios as a function of the Al cathode power for different Ti-cathode powers and different nitrogen partial pressures in the deposition chamber. The results of the present analyses are summarized in Fig. 5.

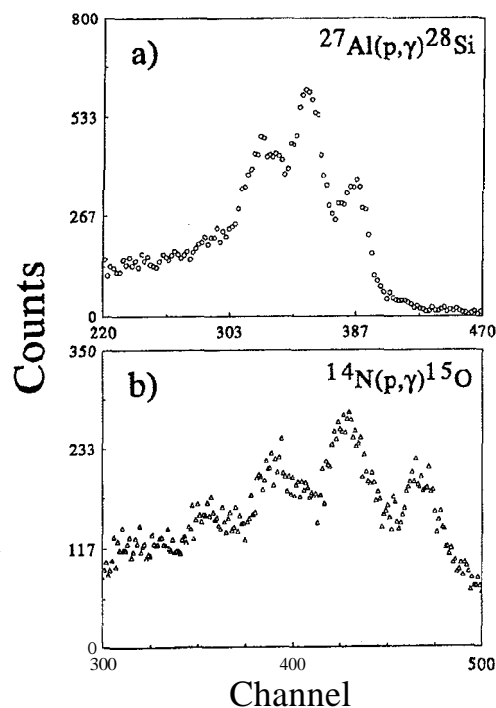


Figure 2: Energy windows in the γ -ray spectra resulting from the nuclear resonances (a) $^{27}\text{Al}(p,\gamma)$ (resonance energy $E_R=326$ KeV, resonance width $\Gamma_R = 1$ KeV, γ -ray energies $E_\gamma=7.6, 7.2$ and 6.2 MeV) and the (b) $^{14}\text{N}(p,\gamma)$ $E_R=278$ KeV, $\Gamma_R=1.6$ KeV, $E_\gamma=6.82$ and 6.14 MeV) used to determine the concentrations of aluminum and nitrogen at various depths in the (Ti,Al)N films.

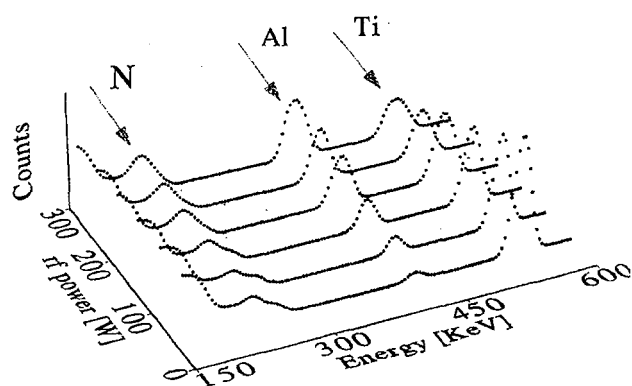


Figure 3: Rutherford backscattering spectra of 0.76 MeV incident α -particles (normal incidence, 165° detection) from thin titanium-aluminum nitride films (thicknesses around 40 nm) deposited by reactive cos-sputtering deposition onto polyimide substrates. The different spectra correspond to different rf power in the Al sputtering target keeping the dc power in the Ti target constant at 220 W. The nitrogen partial pressure during reactive sputtering deposition was 0.02 Pa and the argon partial pressure was 0.3 Pa.

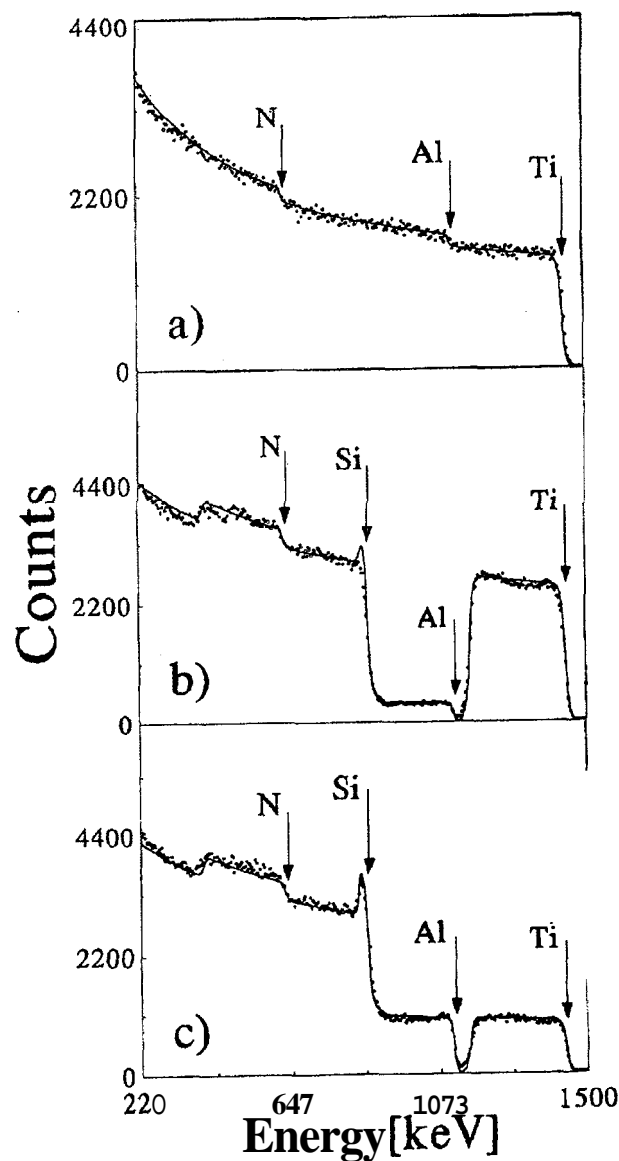


Figure 4: Rutherford backscattering spectra of 2.0 MeV incident α -particles (normal incidence, 165° detection) from thick titanium-aluminum nitride films deposited by reactive co-sputtering deposition onto silicon substrates. The spectra were simulated with the RUMP program (solid lines) using the following parameters: (a) thickness 3000 nm, stoichiometry $\text{TiAl}_{0.3}\text{N}_{1.2}$; (b) thickness 625 nm, stoichiometry $\text{TiAl}_{0.4}\text{N}_{1.3}$; (c) thickness 677 nm, stoichiometry TiAl_3N_3 . The arrows indicate the energy edges of Ti, Al and N at the outermost surface and the energy edge of Si at the nitride-silicon interface. The stoichiometries used in the simulations are consistent with the ones determined by complementary RBS and NRA analyses as explained in the text.

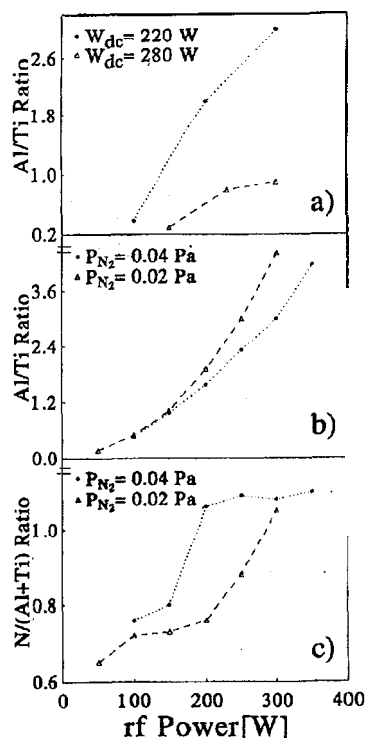


Figure 5: Dependence of the Al/Ti ratio of the films on the aluminum target rf power for samples deposited by reactive co-sputtering (a) under different titanium target dc powers (220 and 280 W) and constant partial pressures ($P_{Ar}=0.03$ Pa and $P_{N_2}=0.02$ Pa); (b) under different nitrogen partial pressures (0.02 and 0.04 Pa) and constant P_{Ar} (0.3 Pa) and dc power in the Ti sputtering target (220 W) (c) Dependence of the $N/(Al+Ti)$ ratio on the aluminum target rf power for the same samples as in (b).

Based on these results it was possible to investigate the correlations between the co-sputtering deposition parameters and the tribological and corrosional performance of steels coated with titanium-aluminium nitrides^[8]. Complementary analyses with X-ray diffraction allowed the determination of the phases of the Ti-Al-N system that were formed and the respective textures^[9].

V. TiN/Ti and TiN/AlN Multilayers

The use of multilayered thin film composite coatings is also a very successful innovation in titanium nitride technology. They can overcome several of the difficulties in producing an adherent, stress free and fully dense coating at a reduced cost. The idea of using TiN/Ti multilayers derives from the already well established

procedure of introducing a Ti intermediate layer between the steel substrate and the TiN coating in order to improve the adhesion, as well as wear and corrosion protection. It is expected that a TiN/Ti multilayered coating will have considerably lower porosity since open structures reaching from the surface to the substrate in the TiN layers might be interrupted by the Ti intermediate films in the multilayer. Furthermore, corrosion or oxidation processes will oxidize Ti to titanium oxide, which has a higher volume than Ti, adding one more contribution to the partial closing of the micropores. By using multilayered coatings it is also possible to relieve interface stresses if couples that develop tensile and compressive stresses are involved, as in the case of TiN and Ti couples. In this case, the relative thicknesses of the two different individual layers play a decisive role in the minimization of interface stresses^[10].

We have used the RBS of 2 MeV α -particles to determine the composition and the wavelength of the multilayers in TiN/Ti and TiN/AlN structures deposited by reactive magnetron sputtering and IBAD. The stoichiometry of the titanium nitride and aluminium nitride individual layers were determined in independent experiments of NRA by calibrating against silicon nitride and titanium nitride standards. In Fig. 6 we show typical spectra that result from the (d,p) nuclear reaction induced by 0.61 MeV deuterons and from the (d, α) nuclear reaction induced by 1.6 MeV deuterons in ^{14}N nuclei in a TiN thin film. In Fig. 7 we show the RBS analysis of a 85/20 nm TiN/Ti multilayer. The simulation was performed with the RUMP program using the 1/1 Ti/N ratio determined by independent RBS and NRA in TiN single layers. The study of the composition and structure of similar multilayered structures and the tests of the aqueous corrosion behaviour of carbon steels coated with them has allowed the determination of the optimum TiN to Ti thickness ratio for corrosion protection. In Fig. 8 the critical current density for iron dissolution (which is proportional to the amount of corrosion) is plotted as function of the Ti/TiN thickness ratio as obtained from RBS analyses^[11]. In a similar study of the corrosion behaviour of TiN/AlN multilayers as a function of thickness ratio we have also analysed

the multilayers by NRA and RBS. A typical RBS spectrum for a 64/36 nm TiN/AlN multilayer is shown in Fig. 9, where the Ti/N and Al/N ratios determined by RBS and NRA in TiN and AlN single layers were used for the simulations with the RUMP program.

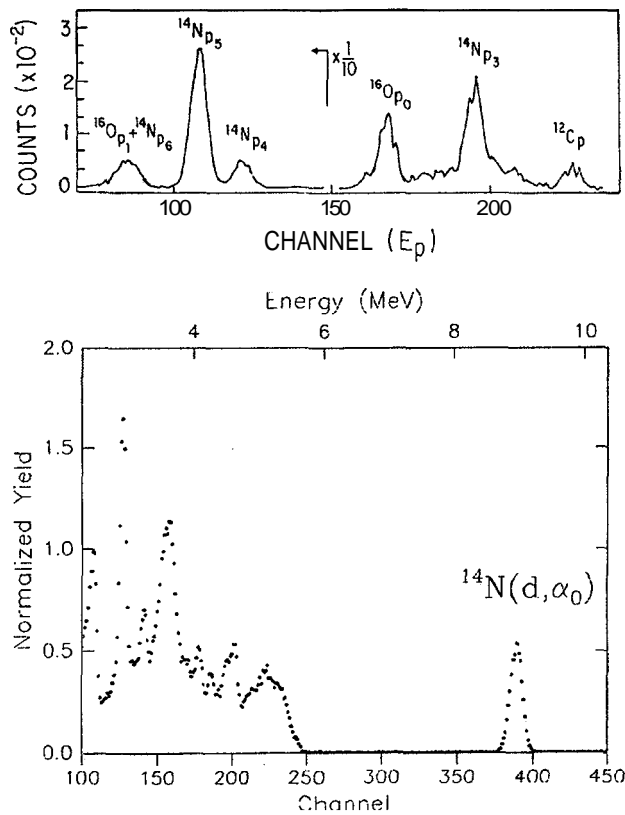


Figure 6: (Top)- Proton spectra from (d,p) nuclear reactions in ¹⁴N, ¹⁶O and ¹²C resulting of the incidence of 0.61 MeV deuterons in a TiN film deposited by reactive sputtering onto a silicon substrate; (Bottom)- the α₀ peak (at an energy of 9 MeV) that results from the ¹⁴N(d,α) nuclear reaction produced by 1.6 MeV deuterons in a TiN film deposited by reactive sputtering onto a silicon substrate. The several peaks on the low energy side of the spectrum are other α-particle and proton groups resulting from nuclear reactions in ¹⁴N and ²⁸Si.

(TiN/Ti)/SiO₂
(80/25) nm

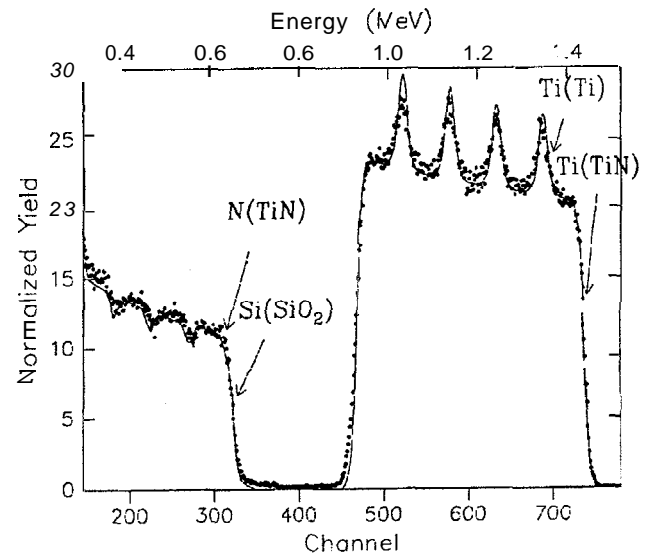


Figure 7 Rutherford backscattering of 2.0 MeV α-particles (normal incidence, 165° detection) from a 80/25 nm TiN/Ti multilayer deposited by reactive sputtering on an oxidized silicon substrate. The solid line corresponds to the simulation made with the RUMP program using the above TiN and Ti thicknesses and a 1/1 N/Ti stoichiometric ratio as determined by combined Rutherford backscattering and ¹⁴N(d,α) nuclear reaction in independent experiments with a TiN single layered film deposited in the same conditions as the individual TiN layers of the multilayered sample. The arrows indicate the energy edges for Ti in the outermost TiN and Ti layers, for N in the outermost TiN layer and for Si at the SiO₂ substrate-nitride interface.

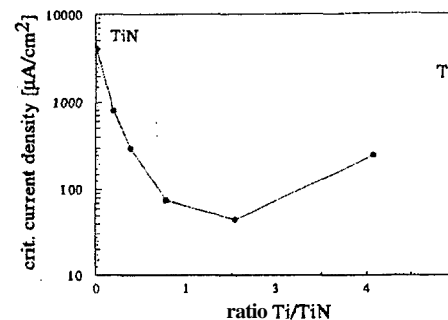


Figure 8: The critical current density for iron dissolution (a measurement of the amount of corrosion) in saturated acetic acid solution for carbon steel samples coated with different TiN/Ti multilayers, as a function of the thickness ratio between the individual TiN and Ti layers. The thickness ratios of the TiN/Ti multilayers were determined by fitting the RUMP simulations of the Rutherford backscattering spectra using the 1/1 N/Ti stoichiometric ratio as determined by nuclear reaction analyses (from Reference 11).

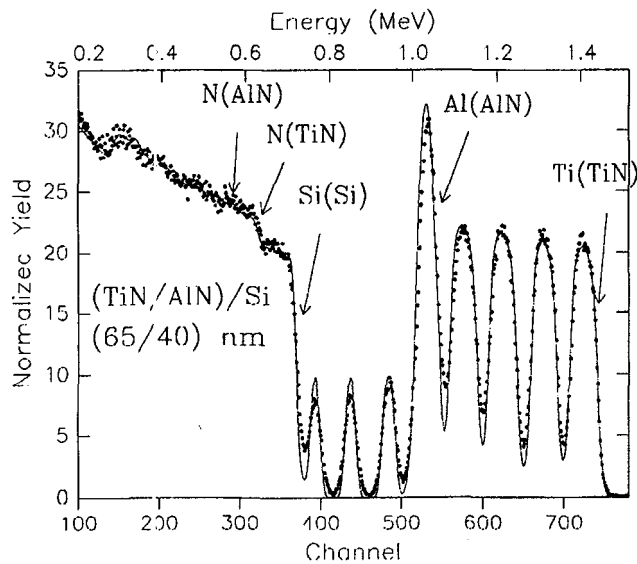


Figure 9: Rutherford backscattering spectrum of 2.0 MeV incident α -particles (normal incidence, 165° detection) from a 65/40 nm TiN/AlN multilayer deposited by reactive sputtering onto silicon substrate. The solid line is the simulation of the spectrum with the RUMP program using the TiN and AlN thicknesses given above and the 1/1 N/Ti and N/Al ratios as measured by combined Rutherford backscattering and $^{14}\text{N}(d,\alpha)$ nuclear reaction. The arrows indicate the energy edges of Ti and N in the outermost TiN layer, Al and N in the outermost AlN layer and of Si in the silicon substrate.

VI. Ion Beam Assisted Deposition Coatings

The use of energetic heavy ion beams to bombard the growing film simultaneously to reactive titanium nitride deposition, which is usually called ion beam assisted deposition (IBAD), represents another emerging method to improve the performance of the coatings in titanium nitride technology. The ion beam (usually Ar^+ or N^+ of energies in the typical range of 1 to 20 keV) is used initially for sputter cleaning of the substrate prior to evaporation; afterwards the electron-beam evaporation is started and the film grows under partial or continuous bombardment with ions^[12,13]. The effect of IBAD on the adhesion of titanium nitride coatings is shown in Fig. 10 by comparison with conventional coatings^[14]. The development of sources for intense large-area ion beams has brought IBAD into a stage of industrial use and several companies making fine metallurgical components are already using this coating method.

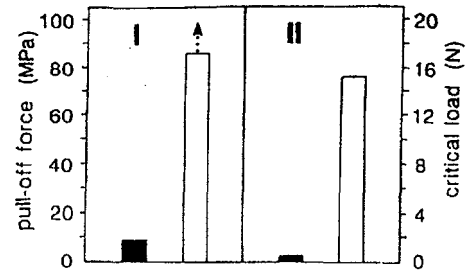


Figure 10: Adhesion measurements made by pull-off test (I) and scratch test (II) of TiN film coatings on steel: (full line bars)- evaporated films and (empty line bars)- films deposited by IBAD (from Reference 13).

More recently a strong effect of the angle of incidence of the ion beam during IBAD on the hardness and corrosion properties of the coatings was found. X-ray diffraction and transmission electron microscopy studies have shown that the crystal orientation of the titanium nitride films made by IBAD change with the angle of incidence of the ion beam and an effort is being put forward now to optimize this angle for excellent hardness and corrosion protection^[15]. Fig. 11 illustrates the hardness and aqueous corrosion dependence on the angle of impact of the ion beam.

We have used the $^{14}\text{N}(d,\alpha)$ nuclear reaction and RBS of α -particles to characterize the single-layered TiN and multilayered TiN/Ti coatings deposited by IBAD in order to study the possible causes of this dependence on the impact angle of the performance of the coatings. Fig. 12 shows the RBS spectra for TiN coatings deposited at ion beam impact angles of 15° and 55° with respect to the substrate normal. Using the film thicknesses as measured by RBS and tallystep and the nitrogen concentrations measured by the $^{14}\text{N}(d,\alpha)$ nuclear reaction we have established the Ti/N ratios, namely 1/0.9 for an incidence angle of 15° and 1/0.8 for an incidence angle of 55° . The RUMP simulations of the RBS spectra shown in Fig. 12 are consistent with these stoichiometric ratios. So, from the point of view of IBA the main differences in the titanium nitride films deposited by IBAD at these two different bombardment angles are the different compositions (probably due to the dependence of the preferential sputtering on the bombarding angle) and the different film thicknesses which were unexpected since a deposition time compensation due to the dependence of the sputtering rate on the bombarding angle was tried to be made. A common feature which is clearly visible from the comparison between the experimental and simulated spectra is the pronounced mixing induced by the ion beam at

the film-substrate interface; this mixing is certainly one of the most important reasons for the enhanced adherence of IBAD deposited titanium nitride coatings.

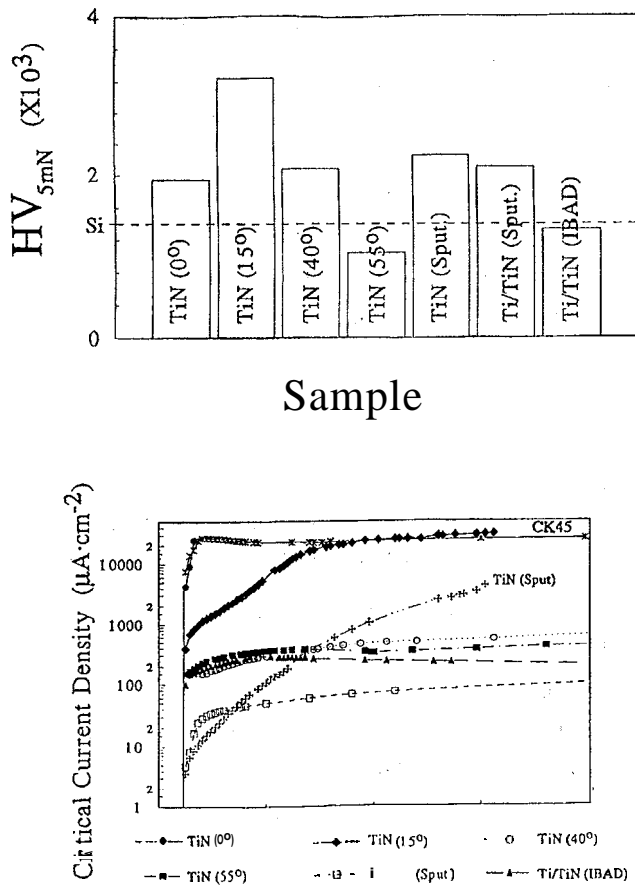


Figure 11: Vickers Hardness and critical current densities for iron dissolution of carbon steel samples coated with titanium nitride films deposited by IBAD at several different incidence angles of the Ar^+ beam during deposition. The results for multilayers deposited by reactive sputtering and by IBAD are also shown (from Reference 15).

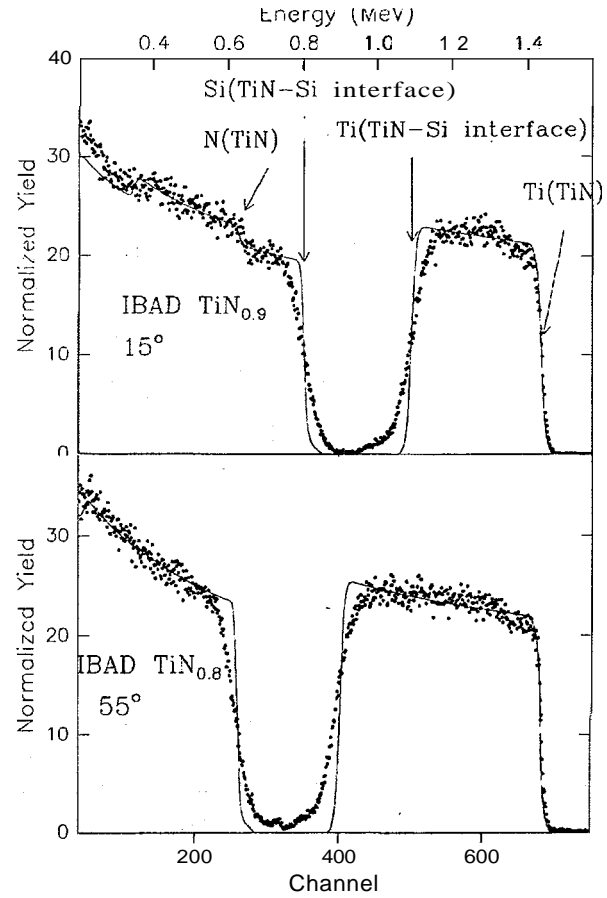


Figure 12: Rutherford backscattering spectra of 2.0 MeV incident α -particles (normal incidence, 165° detection) from titanium nitride films, deposited by IBAD onto silicon substrates at two different angles of incidence of the Ar^S ion beam during deposition (15° and 55°). The simulations of the spectra (solid lines) were performed with the RUMP program using the 0.9 and 0.8 N/Ti ratios for 15° and 55° incidence angles, respectively, as determined by the $^{14}N(d,\alpha)$ nuclear reaction and the thicknesses measurements by RBS, and calculating the curves without considering the straggling. The arrows indicate the energy edges of Ti and Ni in the films and the Ti and Si edges at the TiN-Si interface. The strong disagreement between the simulated spectra (solid line) and measured spectra around the TiN-Si interface reveals the pronounced intermixing that occurs due to IBAD processing.

The same kind of analyses were made in TiN/Ti multilayers deposited by IBAD. The RBS spectrum from a 50/80 nm TiN/Ti multilayer is shown in Fig. 13. The RUMP simulation shown in the figure evidences several of the consequences of IBAD deposition in this case: i) the strong mixing at the film-substrate interface; ii) the also very pronounced mixing between the individual TiN and Ti layers; and iii) the very strong departure from a 1/1 stoichiometry in the TiN layers and the strong contamination with N of

the pure Ti layers. In summary we notice from Fig. 13 that IBAD deposition of TiN/Ti multilayers has originated a graded composition material, which can be controlled to give origin to new and highly desirable properties^[16].

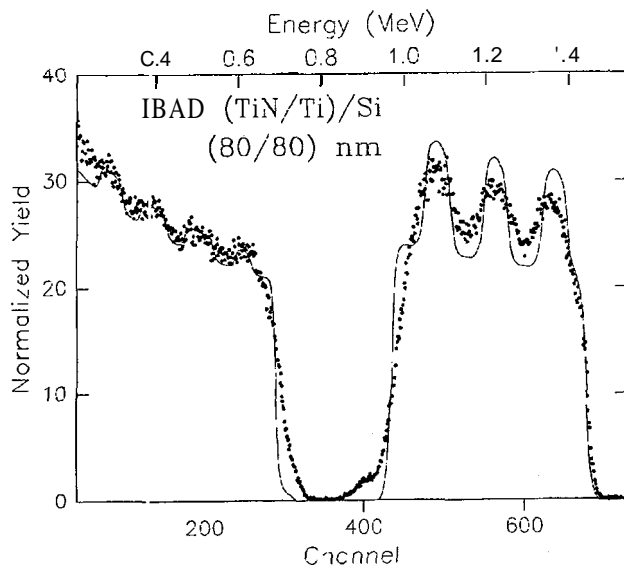


Figure 13: Rutherford backscattering spectrum of 2.0 MeV incident α -particles (normal incidence, 165° detection) from an approximately 80/80 nm TiN/Ti multilayer deposited by IBAD. The simulation of the spectrum with the RUMP program was made using the above mentioned thicknesses for the individual TiN and Ti layers and a 1/1 N/Ti ratio, evidencing the strong departure of the actual average stoichiometry of the individual layers from the one used in the simulator, as well as the strong intermixing of the individual layers composing the multilayer caused by the ion bombardment during deposition.

VII. Conclusions

The usefulness of ion beam analyses in characterizing the several different new materials based on titanium nitride films that are being considered to improve the performance of hard coatings has been demonstrated along the present article. The determination of the stoichiometry by the combined use of RBS and NRA was made in multicomponents and multilayered composites, as well as in the films deposited by IBAD. In the case of multilayered coatings the use of RBS and the simulations allowed the determination of the structure of the multilayers, namely the thicknesses and composition of the individual layers. The characterization of the IBAD films by RBS and NRA has addressed not only the thickness, composition and wavelengths of the multilayers but also the interdiffusion occurring at the interfaces of the systems, like the film-substrate interface and the several

interfaces between the individual layers in the case of multilayers deposited by IBAD. In many of the cases discussed above the informations obtained by ion beam analyses are unique in the sense of determination of the concentration of the elements, the resolution of the depth profiles and the nondestructiveness of all the analytical methods used here.

Acknowledgements

The author wants to acknowledge at first Prof. Fernando Lazaro Freire Jr. for sharing the original idea and the many efforts of the PUC/RJ-Porto Alegre cooperation since 1985, together with the many colleagues from Rio de Janeiro and Porto Alegre that participated in the different research programs included in this cooperation. Many of the results presented here were obtained in the framework of this cooperation and can be found in the bibliography here referred.

Acknowledgements are also due to Profs. Gerhard Wolf and Wolfgang Ensinger at the University of Heidelberg, Profs. Juan Carlos Acquadro and Ivette Openheim at the University of São Paulo, and the Groupe de Physique des Solides at the University of Paris for the kind hospitality during the year of 1993.

Last but not least a warmfull thanks is due to Prof. Fernanda C. Stedile for the many suggestions and careful reading of the manuscript.

References

1. Proceedings of the International Conference on Plasma in Surface Engineering, Garmisch, Germany (November, 1992). To be published in Surface and Coatings Technology, Elsevier Publishers (April, 1993).
2. F. L. Freire, B. K. Patnaik, C. V. Barros Leite, I. J. R. Baumvol and W. H. Schreiner, Nucl. Instr. Meth. **B40/41**, 769 (1989).
3. L. R. Doolittle, Nucl. Instrum. Meth. **B9**, 344 (1985).
4. M. Berti and A. V. Drigo, Nucl. Instr. Meth. 201 473 (1982).
5. D. B. Duncan and J. E. Perry, Phys. Rev. **82** 809 (1951). S. E. Hunt and W. M. Jones, Phys. Rev. 89 1283 (1953).
6. O. Knotek, W. D. Münz and T. Leyendecker, J. Vac. Sci. Technol. **A5(4)**, 2173(1987).

7. J. Aromaa, H. Ronkainen, A. Mahiout and S. P. Hannula, *Surf. Coat. Technol.* **49** 353 (1991).
8. I. J. R. Baumvol, F. C. Stedile, W. H. Schreiner, F. L. Freire and H. Schroer, accepted for publication in [1].
9. F. C. Stedile, I. J. R. Baumvol, W. H. Schreiner and F. L. Freire, Proceedings of the International Conference on Surface Analyses with Ion Beams, Namur, Belgium (April, 1993). Accepted for publication in *Vacuum*.
10. R. Hubler, A. Schroer, W. Ensinger, G. K. Wolf, F. C. Stedile, W. H. Schreiner and I. J. R. Baumvol, *J. Vac. Sci. Technol.* **A11(2)**, 451 (1993).
11. R. Hubler, A. Schroer, W. H. Ensinger, W. H. Schreiner, I. J. R. Baumvol and G. K. Wolf, accepted for publication in [1].
12. A. Schroer, W. Ensinger and G. K. Wolf, *Mater. Sci. Engin.* **A140** 625 (1991).
13. G. K. Wolf and W. Ensinger, *Nuc. Instr. Meth.* **B59/60** 173 (1991).
14. G. K. Wolf, *Nucl. Inst. Meth.* **B46**, 369 (1990).
15. R. Hübler L. Alberts and G. K. Wolf, accepted for publication in [1].
16. U. König, *Powder Metallurgy International* 24, 297 (1992).