Nitridation processes of titanium for biomedical protheses

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Abstract

Titanium and some its alloys represent the better metallic materials with high biocompatibility useful to realise many biomedical prostheses and implants. Special fix and movable titanium based prostheses are found in Dentistry and Orthopaedy, such as dental implants, knee and hip articulation anchorages.
The functionality and the average lifetime of such devices can be improved by the nitridation processes of titanium. The nitridation increases the mechanical strength and the chemical inertia and reduces the surface wear of the material.
Thermal nitridations of Ti and Ti-6Al-4V alloys have been performed at temperatures between 300°C and 1100 °C as a function of the time. Moreover, the ion implantation of nitrogen ions at 100-300 keV energy and high doses, up to about 10^{17} ions/cm^2, followed by thermal annealing at 500 °C, has been employed with success to reduce the surface wear and friction of movable prostheses and to increase their biocompatibility.
Treated surfaces have been characterised by different physical analysis techniques, such as AES, XRD, RBS and SEM.

Riassunto

Il titanio e alcune sue leghe rappresentano i migliori materiali metallici con alta biocompatibilità utilizzabili per impianti e protesi biomediche. Molte applicazioni in Odontoiatria ed Ortopedia riguardano protesi fisse e mobili, così come gli impianti dentali e gli ancoraggi di ginocchio e di anca.
Il processo di nitrurazione del titanio può essere usato per migliorare la funzionalità dei dispositivi protesici ed aumentare la loro vita media. La nitrurazione aumenta la robustezza meccanica e l'inerzia chimica e riduce l'usura della superficie del materiale.
Processi di nitrurazione termica di Ti e di lega Ti-6Al-4V sono stati eseguiti a temperature tra 300 °C e 1100 °C in funzione del tempo. Inoltre, l'impiantazione ionica con ioni azoto a 100-300 keV di energia, 500 °C di temperatura, e ad alte dosi, fino a 10^{17} ions/cm^2, è stata impiegata per ridurre l'usura e la frizione di superfici di protesi mobili e per migliorare la loro biocompatibilità.
Le superfici trattate sono state caratterizzate con differenti techiche di analisi fisica, quali AES, XRD, RBS e SEM.

INTRODUCTION

Titanium and its biocompatible alloys are successful used in many special biomedical applications, such as in Dentistry and Orthopaedy [1, 2]. These metals are destined mainly to implants and prostheses subject to high mechanical and chemical stresses. Titanium and its alloys, in facts, are resistant to strains, wear and corrosion [3]. A special interest is devoted to Ti, TiO_2 and Ti-6Al-4V alloys (Ti containing 6% Al and 4% V) which have high biocompatibility, high Young modulus, high chemical inertia and a mass density similar to that of the cortical bone. Such metals are used to build up hip anchorages, knee prostheses, vertebral spacers, dental implants, etc. [4]. Tab. 1 reports a comparison between some physical characteristics of the cortical bone, titanium, titanium alloys and some interesting titanium compounds. The TiN and TiC compounds have a high hardness and mechanical strength and can be used to improve some prosthetic devices.

A special attention is devoted to the surface properties of biomaterials because they play an interesting role in the prosthesis functionality and in their lifetime inside the human body. The surfaces can be reactive, to promote the bone growth, inert, to stop the ion release in the biological environment, hard and polished, to facilitate the friction with other surfaces. To reaches these aims, the surfaces can be covered by thin bioceramic films, such as hydroxyapatite and calcium phosphate compounds, to promote the cellular growth [5]; can be physically processed, such as oxidised, nitrided or carbided, to increase the chemical inertia with respect to the external biological environment and to increase their hardness [6]; can be mechanically or chemically polished to reduce the friction coefficient during the movement against another surface [7].

The hip prosthesis, for example, shows a critical zone at the friction contact between the femoral head and the acetabular cup (see Fig. 1). Such surfaces are submitted to high dynamical stresses due to the continuum friction which produces wear and debris release. Recent investigations suggest to use a disk of polyethylene at high molecular weight (UHMWPE), placed between the metal femoral head and the ceramic acetabular cup, which acts such as a cousin reducing the surfaces friction [8]. However, also this recent configuration shown a limited lifetime and it does not assures a debris loss stop around the prosthesis with the time. Similar problems arise for other movable prostheses, such as the knee and elbow articulations.

In this paper the physical processes of titanium nitridation useful to passive the surface, giving them high hardness and low friction, increasing the prosthesis functionality and biocompatibility, are presented. Two possible processes will be discussed: the traditional thermal nitridation, using a furnace at high temperature under nitrogen flux, and the innovative ion implantation of nitrogen ions at high doses.

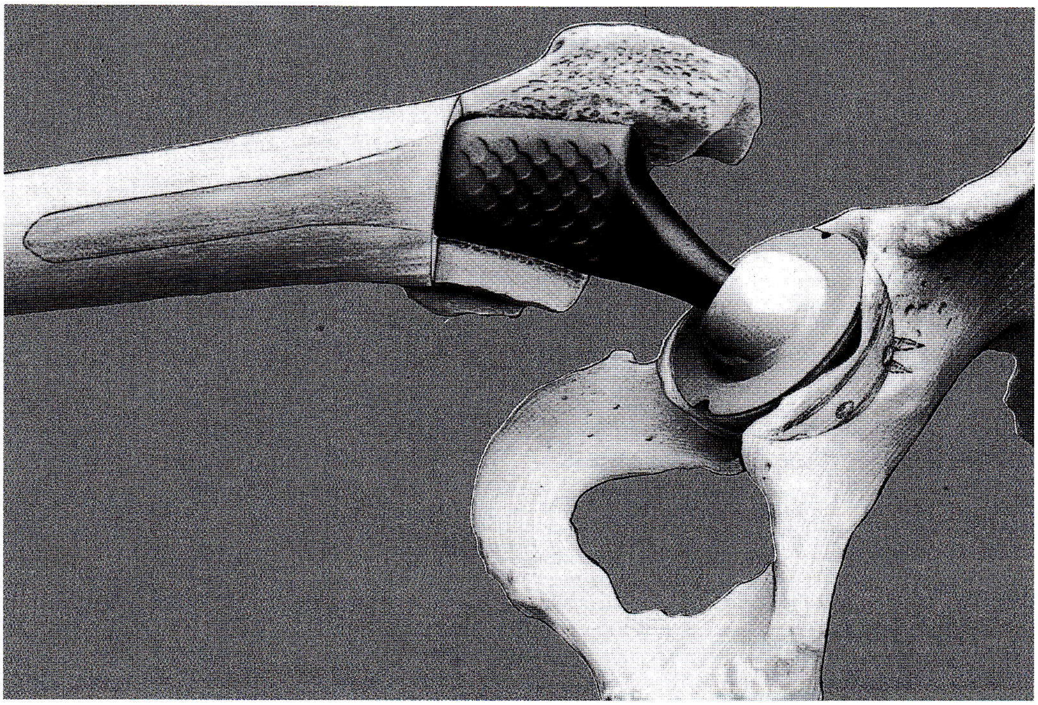

Fig. 1: Hip prosthesis anchorage showing the titanium femoral head, the acetabular cup and the intermediate UHMWPE polymer cup used to reduce the contact friction.

MATERIALS AND METHODS

The materials used in this study were α-phase Ti and α+β phases Ti-6-Al-4V slabs. Generally the sample dimensions were 2 cm^2 surface and 1 mm thickness.

Thermal nitridations were performed in a furnace at temperatures ranging between 300 °C and 1100 °C, in nitrogen flux, with annealing times ranging between 15 min and 6 hours.

Ion implantations of N^+ ions were performed at the 400 keV implanter of the Physics Department of Catania University. Ions were accelerated at energies between 100 and 300 keV, the current densities were 1 $\mu A/cm^2$, and the used total doses ranged between 10^{15} and 10^{17} ions/cm^2.

The sample holder can be heated and some nitrogen implants were thermal assisted at 500 °C, in a vacuum of 10^{-6} torr.

The processed surfaces were physically characterised by Auger electron spectroscopy (AES), Rutherford backscattering spectroscopy (RBS), X-ray diffraction (XRD), electron induced X-ray emission (EIXE) and scanning electron microscopy (SEM).

RBS and AES have permitted to measure the nitrogen content and its depth profile in the titanium. Nitrogen profile by ion implantation was controlled both by RBS analysis, using 2.0 MeV helium beam, and by AES, using 5 keV argon to sputter the sample surface. RBS experimental analyses were compared with the TRIM simulations, a computerised program of Ziegler [9]. The nitrogen content in titanium was measured by Auger spectroscopy using the positive N-KLL peak at 379 eV superimposed to the Ti-LMM negative peak (background)[10].

XRD was employed to investigate on the crystalline phase modifications produced by the nitridation processes of the starting materials.

EIXE and SEM have permitted to study the surface morphology of the samples, the nitridation uniformity and the surface composition. The hardness and wear of investigated samples were tested by a Vickers measurements instrumentation, using a diamond point with 10 g mass, and by a 5 g indenter for very surface scratch tests, respectively.

RESULTS

Fig. 2a shows a comparison between some RBS spectra of thermal nitrided of pure Ti. The alpha particles backscattered at 165° angle from N and Ti have energy of 630 keV and 1439 keV, respectively. Their yield depends by the element amount in the irradiated sample. Increasing the process temperature and/or the annealing time the sample becomes more rich in nitrogen content and the nitride layer diffuses in depth.

The growth kinetics of the nitride layers, which thickness increases with the temperature and the time, was determined by RBS analysis. Fig. 2b shows the nitride thickness growth as a function of the annealing time at 600 °C and 800 °C temperatures and for Ti and Ti-6Al-4V. A fast kinetics is obtained for pure titanium while a slower kinetics is obtained for the Ti-6Al-4V alloys. Results indicate that in both cases

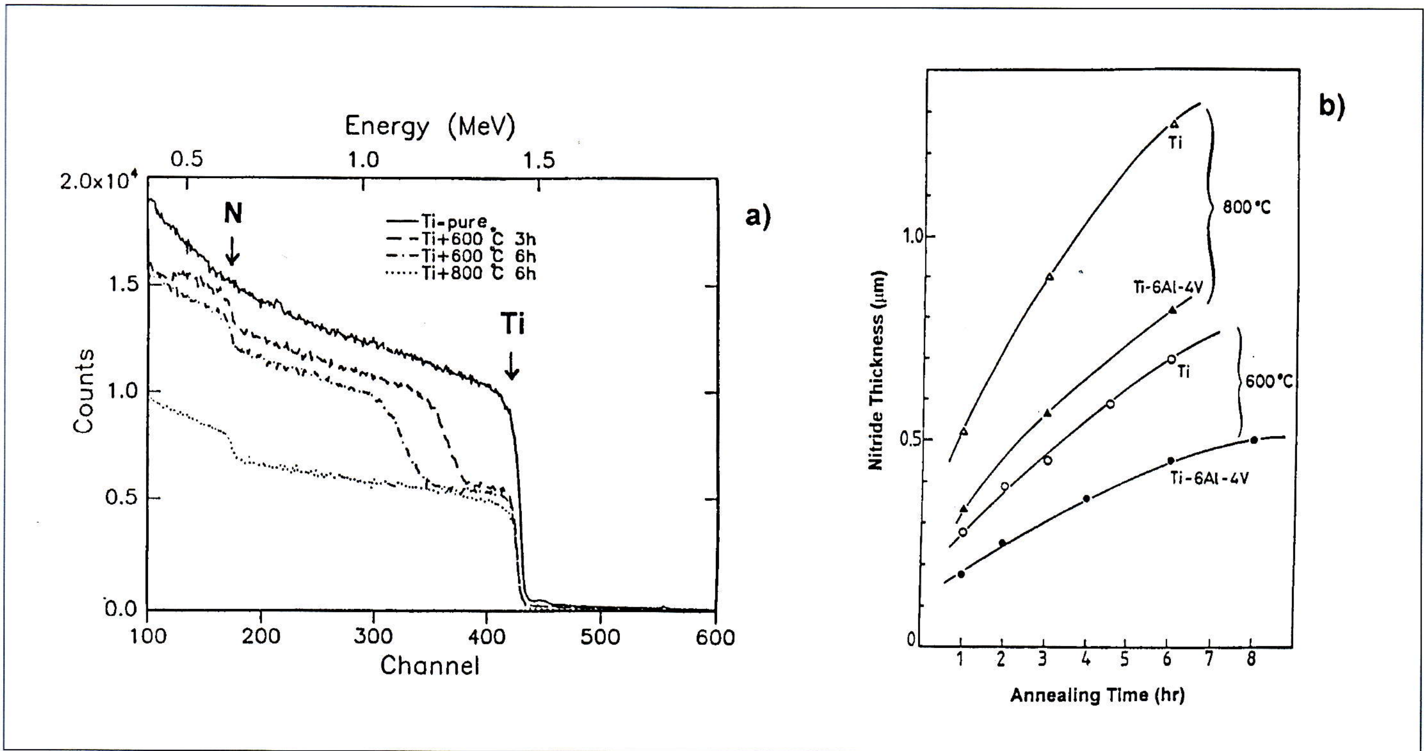

Fig. 2: RBS spectra relative to different processes of thermal nitridation (a) and obtained nitride thickness as a function of the annealing time for two different temperatures and materials (b).

the nitride thickness depends on the diffusion length of nitrogen in the material, according the following relation:

$$L = \sqrt{D(T)\,\Delta t} \qquad (1)$$

where L is the nitride thickness, D(T) is the diffusion coefficient of nitrogen in titanium at T temperature and Δt is the annealing time. The experimental diffusion coefficient of nitrogen in pure titanium is 5×10^{-13} m²/s and 5×10^{-12} m²/s at 600 °C and 800 °C, respectively, in good agreement with literature data [11]. The ~~diffusion~~ coefficient in the alloy is about one order of magnitude lower with respect to pure titanium.

At temperatures lower than about 1000 °C the grown phase is Ti_2N, containing 66% atomic Ti and 33% N. At higher temperatures the grown phase is TiN, containing 50% Ti and 50% N, according literature [12]. RBS analysis, confirmed by TRIM simulations, have indicated that at high temperatures, higher than 900 °C, the N/Ti ratio may reaches the value 1.8. This last result is due to nitrogen absorption at the interstitial sites, grain boundary and defect sites, i.e., to nitrogen not chemically bonded to titanium. The TiN stoichiometry corresponds, in facts, to the maximum nitrogen solubility in titanium, as confirmed by XRD diffraction analysis of nitrided titanium at 1100 °C.

The thermal process at high temperature of Ti-6Al-4V alloy strongly modifies the surface composition. At 1100 °C aluminium and vanadium segregate at the metal surface producing high roughness and darkening of the metallic surface. Depth profiles both of nitrogen thermal diffused and of ionic specie implanted in titanium were determined by AES spectrometry. Fig. 3a shows the nitrogen profile thermally diffused in pure Ti at 600 °C for 8 hours (a). The nitrogen content is almost constant at the surface and decreases about exponentially for depth higher than 0.7 mm. Fig. 3b shows the nitrogen implanted in titanium at 300 keV energy and at room temperature. The ion implantation process permits to introduce nitrogen ions at 4200 Å depth in a layer about 2000 Å width. This layer width can be increased through an implantation process thermal assisted. Due to the thermal effect of implants performed, for example at 500 °C, the nitrogen diffuses and its chemical bonding to the titanium is favourites. The nitrogen content in the implanted layer depends on the ionic dose. An implantation of 10^{17} ions/cm^2 corresponds to a layer containing about 10% nitrogen. Moreover, modulating the ion energy it is possible to increase the depth and the width of the nitrided layers. Multiple implants of 100, 200 and 300 keV, at the same doses, permit to introduce almost uniformly the nitrogen from the surface up to 4200 Å. Nitrogen ions have been introduced energetically in the titanium structure producing a damage of the α-phase structure. Partial damage (more than 70%) can be removed by the thermal implantation at 500 °C in vacuum.

The nitrogen implantation of Ti-6Al-4V alloy induces a vanadium and aluminum surface depletion, as reported in Fig. 3c, which become more evident as the N ion dose increases. This results is in agreement with literature [13] and suggests that a chemical improvement of the material biocompatibility occurs. In facts, the eventual surface release of aluminum and vanadium ions (toxic species) may be strongly reduced. This is due both to the depletion induced by the implantation process and to the TiN layer formation which acts such as a chemical barrier for the ion end electron release. Fig. 3c does not shows the oxygen and carbon elements present significantly at the sample surface.

The XRD analysis have detected the crystalline structures of nitrided layers grown on titanium. The starting pure titanium has a α-phase with a hexagonal structure and reticular parameters 2.95 Å and 4.68 Å. At about 900 °C this structure undergoes a volume contraction of 34%, converting in to β-phase, a cubic centred faces (ccf) crystalline structure with a reticular parameter 4.25 Å, as confirmed by XRD diffraction analysis. Fig. 4 compares two XRD spectra relative to the thermal Ti nitrided at 800 °C for 3 hours (a) and

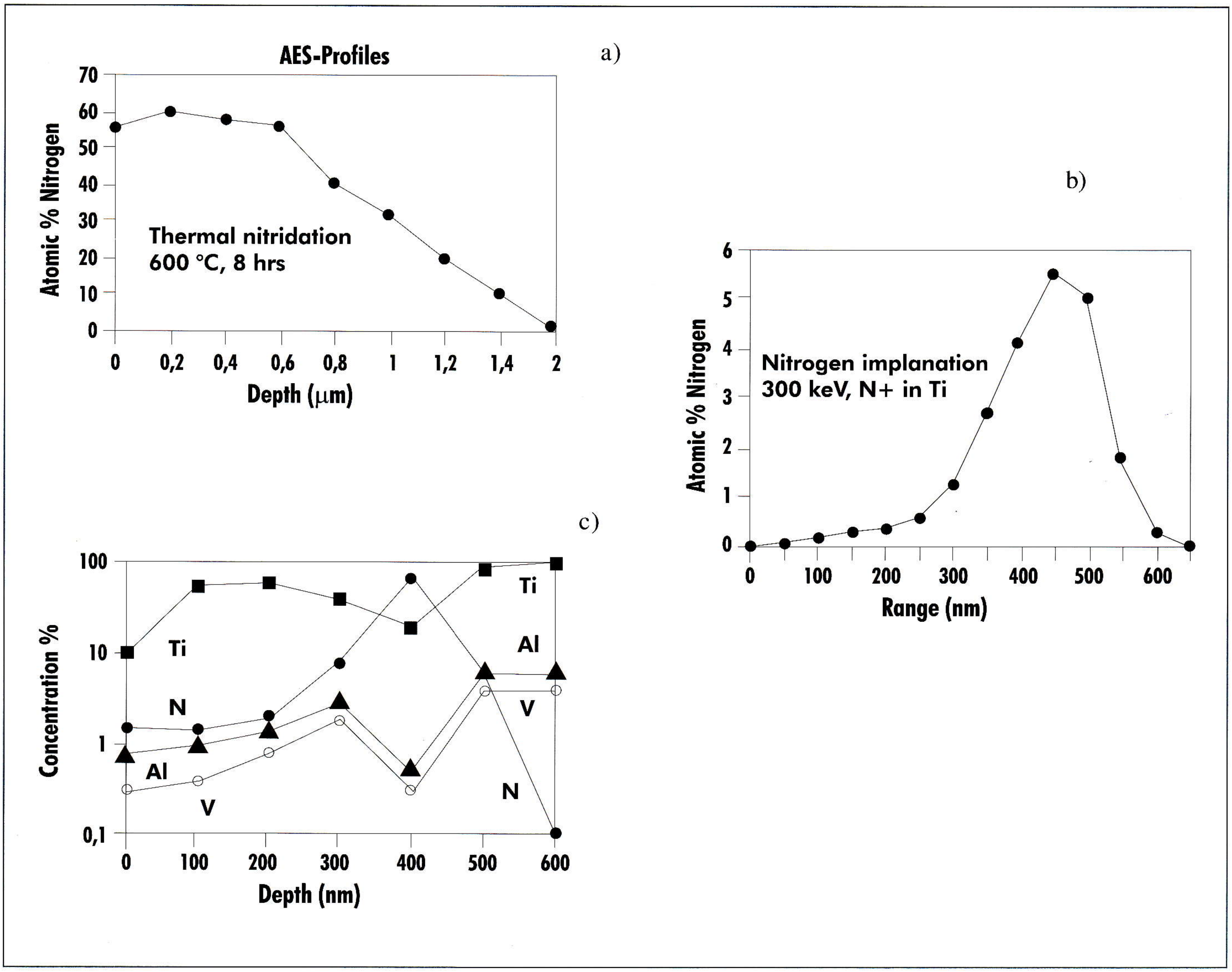

Fig. 3: AES depth profiles for thermal diffused nitrogen (a) and implanted nitrogen in pure titanium (b) and in Ti-6Al-4V alloy (c).

1000 °C for 6 hours (b), respectively. The upper spectrum shows a partial nitridation of the titanium because the diffraction peaks are due both to nitrided surface layers and to un-nitrided bulk. The lower spectrum shows a thicker titanium nitrided layer.

The Vickers hardness measurements in thermal nitrided Ti samples are reported in Fig. 5. It is possible to observe a significant hardness increase vs the nitrogen content in the Ti_xN_y stoichiometry. The N/Ti ratio was changed by the annealing temperature and was measured by RBS analysis. The initial Ti hardness is 280 Kg/mm^2. It increases of about 4.5 times at the Ti_2N stoichiometry, obtained by an annealing at 400 °C, and of about 7 times at the TiN stoichiometry, obtained by an annealing at 1100 °C. Results are in agreement with literature [14]. The measured hardness concerns only the sample surface and it is referred to a layer thickness lower than 10 µm. This layer was probed with 10 g diamond point pressing for 10 s on the sample. This probe was too weight to measure the surface hardness of ion implanted layers because they are perforated by the probe. In order to have further information about the surface hardness and wear resistance, some scratch tests were performed on thermal and ion implanted samples. They were performed with 5 g probe (diamond point) scratching the material surface. The scratches were observed at the SEM and their depth were compared at different nitridation processes. Fig. 6 shows a comparison between the scratch in pure titanium submitted to a thermal nitridation at 1000 °C, 6 hrs (a) and in a nitrogen implantated titanium surface at 300 keV, 10^{17} ions/cm^2 (b). In these experimental conditions the scratches seems to be comparable, indicating a significant hardness increase in both cases. The Fig. 6 c shows the surface roughness of the starting titanium and demonstrating that a polishing procedure it is need to reduce the surface friction coefficient. Obtained results, concerning hardness and wear of nitrided layers of pure titanium, were very similar to those obtained nitriding the Ti-6Al-4V biocompatible alloy.

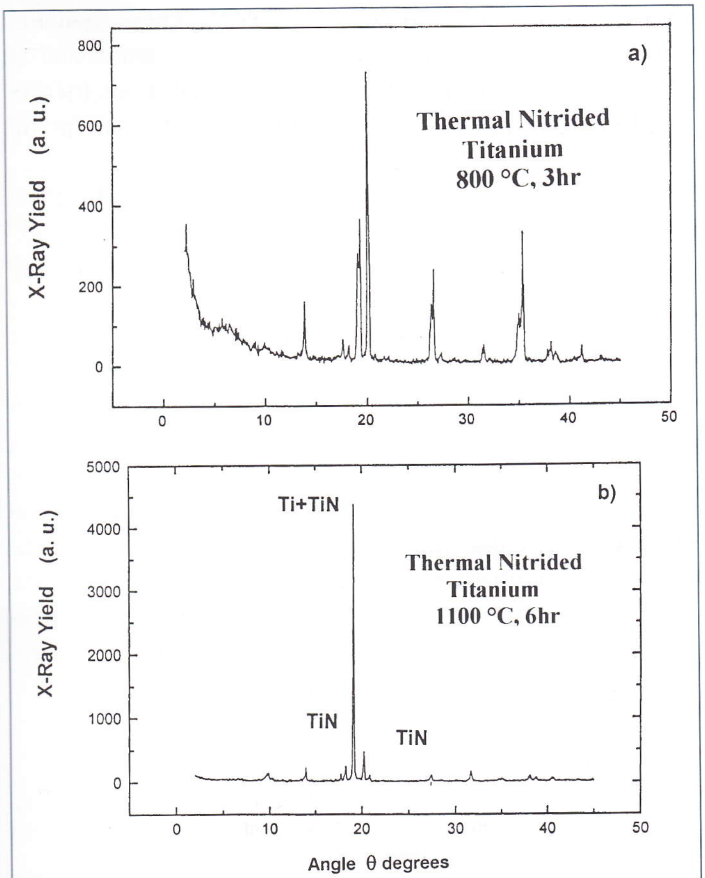

Fig. 4: XRD spectra on nitrided titanium at 800°C, 3 hrs (a) and at 1100 °C, 6 hrs (b).

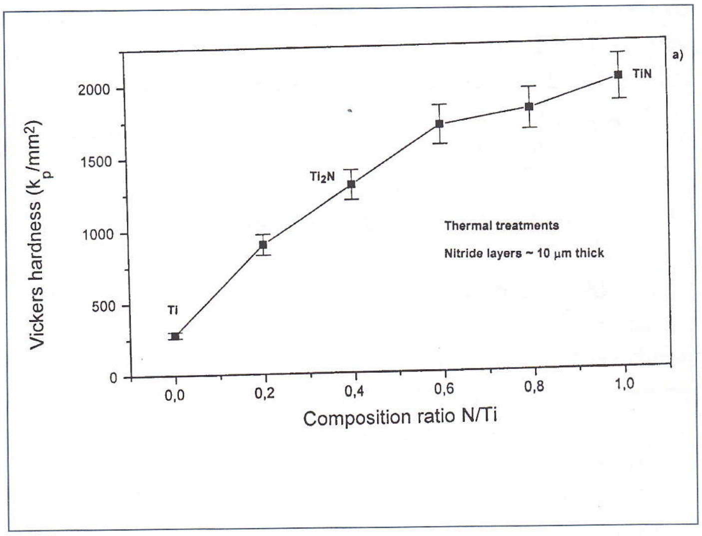

Fig. 5: Vickers hardness as a function of the N/Ti atomic ratio (thermal nitridation).

a) b) c)

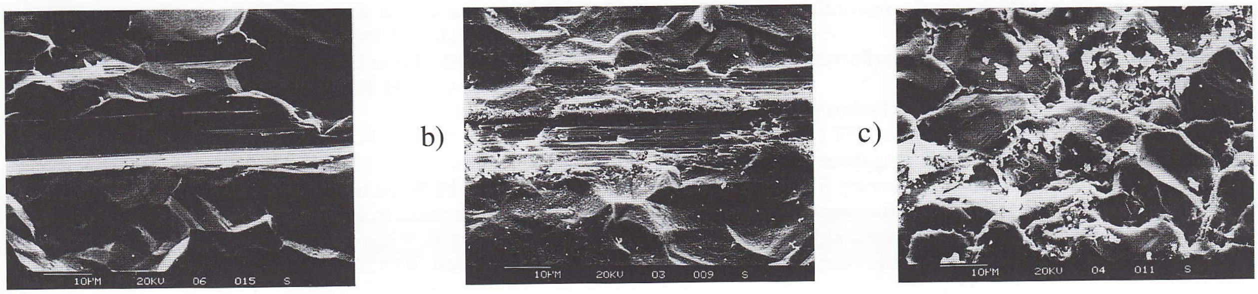

Fig. 6: SEM investigation of the scratch tests on thermal nitridation (a) and nitrogen implantation (b) and as received titanium surface (c).

TABLE 1 - Comparison between some physical characteristic of the cortical bone and of the titanium based biocompatible materials.

Material	Density (g/cm^3)	Young Mod. (GPa)	Hardness (Vickers) (Kg/mm^2)	Tensile strength (MPa)	Compressive strength (MPa)
Cort. Bone	2.2	30	200	100	180
Ti	4.5	118	280	350	500
Ti-6Al-4V	4.4	110	340	900	1600
TiN	5.2	80	2000	400	2000
TiO_2	4.1	300	980	350	900
TiC	4.9	400	3000	450	730

CONCLUSIONS

Titanium nitridations, obtained both by thermal process and by ion implantation, have peculiar properties, showing high density, high hardness, high wear resistance and high chemical inertia. These processing techniques, differently by the coating processes, produce layers very adherent to the underlying material with high mechanical strength useful to prepare biomedical prostheses for load-bearing applications.

Thermal treatments and ion implantation modify the surface properties of biocompatible titanium. At a temperature lower than 1000 °C the Ti_2N phase is grown while at higher temperatures the TiN phase is found. The nitrided depth depends on the annealing time according eq. (1). The kinetic growth of nitride in Ti-6Al-4V alloy is slower with respect that in pure Ti. This behaviour is due to a lower diffusion coefficient of nitrogen in the alloy.

The nitridation process of the Ti-6Al-4V alloy produces a Al and V migration toward the surface with roughness increase. Instead, useful appears the nitrogen implantation of the alloy because it, reducing the Al and V at the surface and producing a nitride layers which stops their migration toward the external biological environment, increases the alloy biocompatibility.

In order to growth a surface useful for biomedical load-bearing applications, such as the hip prosthesis (titanium femoral head), the nitrided layer should have a TiN crystallographic structure with about 100 mm thickness. This thickness should be obtained, for example, using 1100°C temperature, and an annealing time of about 16 min. At this temperature, in facts, the diffusion coefficient is very high assuming the value $D(1100°C) = 10^{-11}\ m^2/s$.

The TiN layers between biological environment and Ti prosthesis act as chemical barrier against the migration of electrons and ionic species giving to the underlayers high chemical stability and protecting the prosthesis bulk material. Moreover, these hard layers reduce the surface wear and the metal debris caused by friction.

In conclusion, the biocompatibility and wear properties of titanium were improved by the nitridation process, mainly by the ion implantation of nitrogen ions. These positive effects could probably be enhanced with development of a better polishing technique and finding methods of extending the penetration depth and the concentration of the nitrogen ions. Further investigations are in progress to improve the functionality and duration of specific prosthesis using the ion implantation technique, as will be presented in a next paper.

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