Effects of Nitrogen Ion Implantation on Microhardness and Surface Roughness of Ti-6al-4v Eli Medical Alloy

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Abstract. Total Knee Replacement has been under development for over 50 years. Its primary objectives are for normal articulation of a diseased joint, to relieve pain and restore function. Over the years three main surgical types of alloys have been used: 316L stainless steel, titanium and cobalt-chrome based alloys. Titanium, despite its superior biocompatibility, closest to bone’s Young’s modulus and lack of nickel in its composition, has poor resistance to wear. This major disadvantage of titanium alloys is the reason for which their use in load bearing prostheses is limited. Various methods of surface modifications have been investigated in order to improve wear performance by improving mechanical and tribological properties of medical grade titanium alloys. In this work, the effect of nitrogen ion implantation on micro-and nano-hardness and surface roughness of medical grade titanium alloy (Ti\textsubscript{6}Al\textsubscript{4}V ELI) has been investigated, and compared to those of unimplanted Ti\textsubscript{6}Al\textsubscript{4}V ELI, cast and wrought CoCrMo alloys. Due to the formation of a smooth and hard nitride layer on the surface of the ion implanted Ti\textsubscript{6}Al\textsubscript{4}V ELI alloy significant improvement in micro- and nano-hardness was achieved. This hardened layer is thought to improve the wear resistance of Ti-based alloys and hence can maximise their use for more demanding prosthetic applications.

1. Introduction
Optimum design of a load bearing prosthesis must consist of carefully engineered geometry to restore natural biomechanics of the joint with adequate choice of materials used in the design. Typical knee replacement prosthesis involves three components: femoral component, tibial tray and polyethylene insert. The metal components are the femoral and tibial easily seen in a radiograph whereas the polyethylene insert is not visible in an x-ray image. The design of the total knee implant, as a working system, is very complex and many factors have an effect on its performance. Despite many efforts made by engineers and designers, there are plenty of failure modes due to which implants need revising. Various authors have investigated the failure modes of the total knee replacement and reported [1-3] that long term failures of the total knee occur mainly due to polyethylene wear, infection, instability and aseptic loosening.

Over the last 5 decades three main surgical types of alloys have been used in total knee replacement (TKR) namely: 316L stainless steel, titanium and cobalt-chrome-molybdenum based alloys. The latter is currently the most popular choice for the metal components of THR due to its superior mechanical properties, high wear and corrosion resistance with good biocompatibility. There are two main shortcomings of the cobalt-chrome alloys: their relatively high stiffness which can cause stress shielding of bone and the presence of nickel in their composition. Titanium alloys, on the other
hand, do not contain nickel and their Young’s are much lower (almost half) than cobalt-chrome alloys. The main disadvantage of titanium alloys is their wear susceptibility, for which their use in load bearing prostheses is limited. Some patients, however, suffer from nickel sensitivity, and therefore cobalt-chrome based prostheses must not be used in those patients. DePuySynthes orthopaedics supports those patients with customised implants portfolio, which include surface engineered titanium knee prostheses.

The field of materials and surface engineering is very broad. Surface modifications have found their application in numerous technological fields, including medical technologies. Ion implantation has been developed primarily as a process for doping semiconductors, but shortly after its use in other industries, it has been applied also in the improvement of prosthetic components. It has therefore been proposed as a method of improving mechanical and tribological properties of titanium medical grade alloys. So far, the literature has reported significant improvements in hardness, wear and corrosion resistance following ion implantation, specifically with nitrogen ion implantation. Reported test results have been very positive, however, there is some question in the conclusiveness of some tests and the validity of many test comparisons made, due to questionable and variable test conditions used. As long as providing evidence of positive effects of ion implantation do not pose problems, quantifying the level of improvement and comparing it with other results is proved to be difficult due to variability in ion implantation processes used in such studies.

The purpose of this study is to perform realistic tests with conclusive results using the standard ion implantation process specified and used on a regular basis by DePuySynthes International, and to attempt to compare our results with those obtained by previous investigators, therefore to make a meaningful assessment of the effects of nitrogen ion implantation on microhardness and surface roughness of medical grade titanium alloy, namely Ti6Al4V ELI.

2. Aims
The purpose of this study was to investigate the effects of nitrogen ion implantation on microhardness and surface roughness of medical grade Ti6Al4V ELI as compared to those of unimplanted Ti6Al4V ELI, cast and wrought CoCrMo alloys.

3. Materials and Methods

3.1. Sample preparation

Each sample was embedded in Bakelite resin mount; surfaces were grinded and polished to a mirror finish. All samples were supplied by DePuy Orthopaedics International (Leeds, UK). The sample size used in each analysis is listed in Table 1.

|         | Unimplanted Ti6Al4V ELI | Ion implanted Ti6Al4V ELI | Cast CoCrMo | Wrought CoCrMo |
|---------|-------------------------|---------------------------|-------------|----------------|
| Surface roughness | 14                      | 14                        | 6           | 8              |
| Microhardness   | 7                       | 6                         | 2           | 5              |
| Nanohardness   | 7                       | 6                         | 4           | 3              |

3.2. Ion implantation
Ion implantation process involves bombardment of a surface of a material with high energy ionised elemental species [4]. The process is carried out under vacuum and very low pressure. Typical distribution of ions implanted via the ion implantation process (Figure 1) is shown in Figure 2. Ion implantation has been found to be capable of improving surface properties such as hardness and wear resistance, reduced friction, and resistance to chemical attack without affecting bulk properties,
causing dimensional changes or delamination [5]. Two step mass analysed ion implantation techniques were applied for the modification of titanium alloy as follows:

- N\textsuperscript{+} ions, dose: 2x10\textsuperscript{17} ions/cm\textsuperscript{2}, energy: 80keV
- N\textsubscript{2}\textsuperscript{+} ions, dose: 1x10\textsuperscript{17} ions/cm\textsuperscript{2}, energy: 80keV

Figure 1. Schematic representation of the process of ion implantation [6].

Figure 2. Schematic representation of ion implanted layer distribution in the substrate material [7].
3.3. Surface roughness measurement
Surface roughness was measured using Talysurf CCI3000 (Taylor Hobson, Leicester, UK). Three measurements of each sample were taken at different locations across the surface. Ti6Al4V ELI samples were tested prior to and following the ion implantation.

3.4. Vickers microhardness test
Vickers microhardness tests were conducted using the Reichert Universal Camera Microscope “MeF” Microhardness Tester fitted with a diamond pyramidal indenting device. Loads of 5g, 10g, 20g, 30g, 50g, and 80g were used; each indentation was applied for 10 seconds.

3.5. Nano-indentation microhardness test
The nanoindentation testing was conducted using AFM fitted with Berkovich nanoindenter tip. Four different loads were used: 2.5mN, 5.0mN, 7.5mN and 10mN. Measurements were taken at 6 different locations along the surface.

3.6. Results and brief discussion
The surface roughness results (Figure 2) showed an insignificant decrease (p>0.05) in surface roughness for the Ti6Al4V ELI alloy following ion implantation (from 0.036 to 0.035µm). On the other hand, cast and wrought CoCrMo alloys achieved mean surface roughness of 0.026µm and 0.016 µm, respectively (see Figure 2).

![Surface roughness](image)

**Figure 3.** Surface roughness results did not indicate significant change in surface roughness following the ion implantation process.

The microhardness results (Figure 4) showed a significant increase in surface microhardness for the nitrogen implanted Ti6Al4V ELI samples. For each load, improvements in microhardness of ion implanted samples were statistically significant (p<0.05). CoCrMo samples had much higher microhardness with the wrought alloy showing the highest microhardness, as expected.
Figure 4. Vickers microhardness results showing significant increase of microhardness of the titanium alloy following the ion implantation process.

The nanoindentation results (Figure 5) also showed a significant increase in surface microhardness for the nitrogen implanted Ti6Al4V ELI samples. For each tested load, the differences were statistically significant (p<0.05). At 2.5mN load the increase was of 65%. CoCrMo samples were found to be much harder as also seen via microhardness results.

Figure 5. Significant increase of microhardness of Ti6Al4V ELI alloy following ion implantation process showed in the nanoindentation test.
4. Conclusions
It is known that nitrogen ion implantation forms a smooth and hard nitride layer on the surface of Ti-based alloys, and thus as seen in this work, the ion implanted Ti6Al4V ELI samples showed significantly improved microhardness. This hardened layer is thought to improve the wear resistance of Ti-based alloys and hence can maximise their use for more demanding prosthetic applications.

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