MECHANICAL TESTS OF CO - ION IMPLANTED ZIRCONIUM OXIDE 316 L STAINLESS STEEL SUBSTRATES

A Thesis Submitted to the
Graduate School of Natural and Applied Sciences of
Dokuz Eylül University
in Partial Fulfillment of the Requirements for
the Degree of Master of Science in Mechanical Engineering, Material Sciences
Program

By
Halit DOĞAN

August, 1996
İZMİR

M. Sc. THESIS EXAMINATION RESULT FORM

We certify that we have read this thesis and that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.-

Prof. Dr.Ahmet ÖZTARHAN
(Advisor)

Prof. Dr. Tevfik AKSOY
(Committee Member)

Prof. Dr. Kazım ÖNEL
(Committee Member)

Approved by the
Graduate School of Natural and Applied Sciences

Prof. Dr. Macit TOKSOY
Director

ACKNOWLEDGMENTS

I would like to thank Professor Dr. Ahmet ÖZTARHAN for his supervision and generous help.

I also wish to thank Professor Dr. Ian G. BROWN (Lawrence - Berkeley Laboratory, U.S. Plasma Application Group Leader.) for doing Zr + O ion implantation of 316 L Stainless Steel substrate.

My special thanks are given to Professor Dr. Ali Fuat ÇAKIR for the permission of using their research facilities and Professor Dr. Eyüp Sabri KAYALI, Associate Professor Dr. Mustafa ÜRGEN for their advice and their research assitance for their technical assistance.

My special and collective thanks, Professor Dr. Tevfik AKSOY, Professor Dr. Kazım ÖNEL, Professor Dr. Ahmet ÇAKIR, Dr. Ümit CÖCEN for their available discussion and advice.

I acknowledge with pleasure HİPOKRAT A.Ş. for supplying and preparing the samples for this work.

I am greatly indepted to my parents for their continued encouragement and support over the years.

Finally, to my wife, with gratitude and affection, who made the completion of this thesis possible.

ABSTRACT

The tribological properties such as surface hardness, friction and wear have been studied for 316 L Stainless Steel substrates which were co - ion implanted with Zirconium and Oxygen ions by I. G. BROWN using new modified version of MEVVA technology (Developed by BROWN et. al.).

It is found that the wear resistance for 316 L Stainless Steel substrates implanted with Zirconium and Oxygen ions increased quite alot.

It is concluded that the increase in surface microhardness and the decrease in friction coefficent of 316 L Stainless Steel substrates play an important role in improving the wear resistance, and the relationship between relative wear volume and relative microhardness is correlated for Zr and Oxygen co - ion implantation.

ÖZET

316 L kalite Paslnmaz Çelik üzerinde , Ian G. BROWN tarafindan geliştirilen; yeni yüzey işlemi gerçekleştiren MEVVA teknolojisi kullanılarak, Oksijen ve Zirkonyum iyonları ile implantasyon yapılmış ve bu implant malzemenin yüzey sertliği, sürtünme ve aşınma gibi tiribolojik özellikleri incelenmiştir.

Zirkonyum ve Oksijen iyonları ile implante edilmiş 316 L kalite Paslanmaz Çeliğin aşınma direncinin oldukça arttığı bulunmuştur.

316 L Paslanmaz Çeliğin yüzey mikrosertiğindeki artma ve sürtünme katsayısındaki düşme aşınma direncini artırmakta önemli bir rol oynar ve relatif aşınma hacmi ile relatif mikrosertlik arasındaki münasebet Zirkonyum ve Oksijen implantasyonu ile doğrudan alakalıdır.

CONTENTS

Page

Chapter One

INTRODUCTION

Chapter Two
EXPERIMENTAL STUDY

Chapter Three
CONCLUSIONS

LIST OF TABLES

LIST OF FIGURES

CHAPTER ONE
INTRODUCTION

1. Surface Modification of Materials by Ion Beams

Ceramic materials are being used much more widely in engines and as hard - facings on metals. Although, they are very hard, they tend to be used in situations in which lubrication is diffucult or impossible and there is severe risk of abrasion. Moreover, friction coefficients can be very high and this can cause surface de - cohesion due to the tensile stress in the wake of a sliding contact. For these reasons treatment that will increase hardness still further, improve fracture toughness and lower friction are very desirable. All these can be done by ion implantation. Some of these works are describted by G. DEARNALEY (Hochman & Legg, 1988, p.3).

So far, to our knowledge, there has been no study with co - ion implantation of Zr and O atoms on Stainless Steel surfaces.

1. 1. History of Ion Implantatiın

The process of ion implantation was introduced about 30 years ago for the doping of silicon crystals. A few years later, around 1970, there began the first systematic investigations of the modification of metals and alloys in order to improve their resistance to wear and corrosion. It was shown to be possible to take advantage of the low temperature, non-equilibrium nature of the process and to exceed normal solubility limits. Some of the research programs exploited the versatility of ion implantation in order to prepare specimens for comparative studies of their oxidation or corrosion behavior, thus using it as a valuable research tool. By 1975, it was possible to initiate a program aimed at the industrial application of a non-analyzed beam of nitrogen ions, and the first implanted designed to this purpose was constructed in 1976. Progress to a much larger (2.6 m) facility took place in 1985 and it became possible to demonstrate the economic benefits of scale-up. Developments of much more powerful ion sources have further extended the potential for industrial applications of gaseous and metallic ion beams. The combination of coating and ion implantation for ion beam assisted deposition and diamond-like carbon deposition has provided additional versatility. Future trends and prospects will be discussed, including the opportunities for plasma based methods of ion implantation. (Dearnaley, 1994, p.7)

1.2. Ion Implantation Process

Metal ion implantation is the process of altering surface properties by bombarding with high-energy metal ions. Because the process does not produce a coating, dimensions and bulk properties of the part remain unchanged, and implanted surfaces have no problems with adhesion, residual stress, or poor microstructure.

To understand ion implantation, one can consider an analogue with what happens when a concrete wall is peppered with bullets from a machine gun: The front surface of the wall is partially removed by the bullets. In the 0same way, when metal ions traveling at high velocity hit a surface, they remove part of the surface. The amount of material removed depends on the size and energy of the ions, but it is generally insignificant - less than 0.1 µm.

However, the wall is also filled with bullets in the region close to the surface, and to a depth dependent on the mass and velocity of the bullets. In the same way, the surface of a material struck by an ion beam contains metal ions. Unlike the bullet analogy, the implanted metals can combine chemically with the surface material, forming a zone whose chemistry and structure differ from the rest of the workpiece. This zone, as depicted in **Fig. 1**, is also on the order of 0.1 µm (4 µin.) deep. Despite the very shallow depth of this implanted zone, it contributes to improved surface performance.

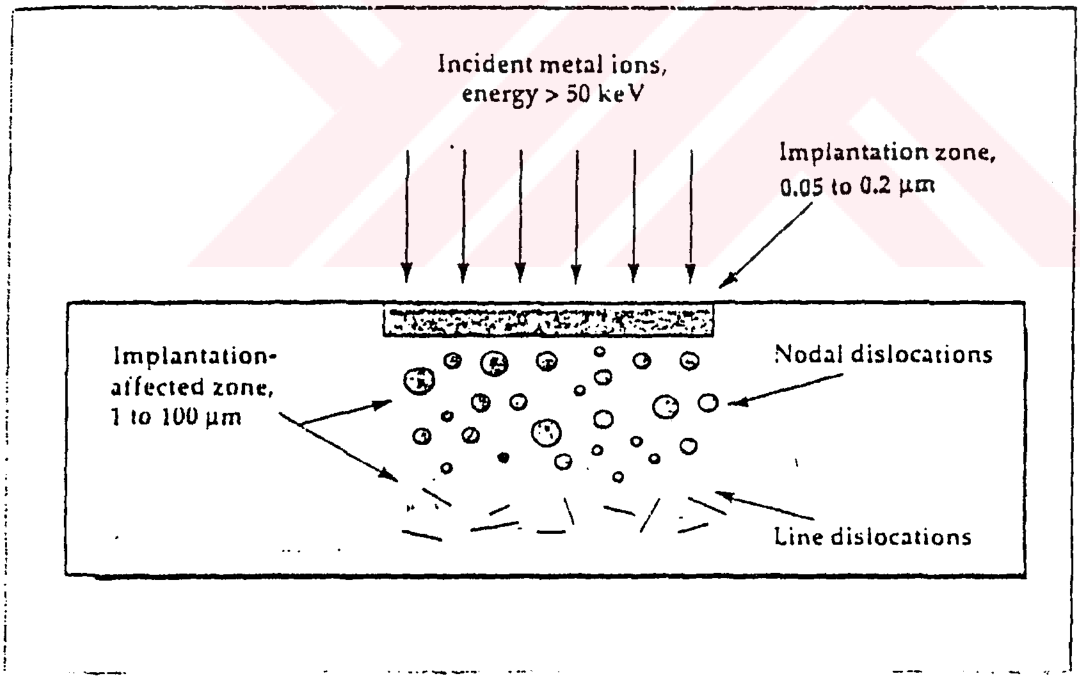


Figure 1. Implanted zone on workpiece is shown.

The wall is also damaged. If the bullets are -22 caliber, say- the damage is rather minimal beyond the implantation zone of the bullets, but may extend quite deeply into the wall. If the bullets are large, the damage beyond the implantation zone is very extensive.

In the same way, the metal ion bombardment "damages" the near surface of the material. However, whereas bullet damage is harmful in that it weakens the wall, metal ion "damage" enhances properties in that it creates nodal dislocations that suppress crack propagation. This dislocation network has been found to contribute to increased hardness, wear resistance, and corrosion resistance. The bombardment also causes line dislocations, but these have not been found to produce any effects on surface performance. While the combined depth of these two dislocation zones, together referred to as the "implantation affected zone" can be as deep as 100 μm (0.004 in.) or more, the maximum effective depth is on the order of 60 μm. (0.0025 in.). Again, as in the bullet analogy, heavier ions have greater effect; therefore, heavy metal ions are valued above light ions such as nitrogen.

Metal-ion implantation is very versatile tool for improving the surface properties of materials. It is clearly shown in **Table 1.** In addition to processing almost any material, minimal pre - treatment is required - no need for acid etching, polishing, grinding, sand blasting, or heat treating. Because surface dimonsions do not change, masking is usually not needed.

Table 1. Characteristics of metal ion implantation.

Treatable Materials	All metals, carbides, ceramics, cermets, and glasses; most plastics and composites; some organic materials (seeds).
Applications	Wear resistance; hardness; friction reduction; corrosion / oxidation resistance; optical properties; fatigue life enhancement; hydrogen embrittlment reduction.
Pre-treatment	Cleaning only - no acid etching, masking, poishing, grinding, sand blasting or heat treating required.
Limitations	Connat build - up part; line - of - sight to 45°
Process environment	Vacuum, on the order of 10^{-5} Torr; process temperature below 150 °C
Post - treatment	None - no heat treatment, machining, polishing, etc.
Quality control	X - ray fluorescence.
Environmental effects	None - no hazardous effluents, gas or liquid.
Cost considerations	Capital costs high, operating costs low, material usage very low.

Four factors make the process particularly attractive:

- Dimensions do not change, so tight tolerances in the treated parts can be maintained.

- Process temperature is usually under 150°C, so thermal post treatment is normally not required.

- No hazardous wastes are generated.

- For most metals, the implanted dose may be measured using simple X - ray fluorescence equipment, making quality control simple.

However, metal - ion implantation does have some limitations. The most obvious one, .ion implantation is a line- of- sight process, so that complex objects must be manipulated in the beam, and the insides of holes with a depth - to - diameter ratio of greater than unity cannot be treated. Clearly, it cannot be used for renewing worn parts.

1. 3. Ion Beam Effects onto Material

The energetic ions penetrate into the substrate surface and interact with the substrate material **(Fig.2.)** by changing the composition and structure of the near surface region. Changes in composition result in the formation of second phases (carbides, nitrides) and solition hardening. The collision cascade produced by the incoming energetic ion displaces on the order of 1000 atoms from their lattice positions. In covalently bonded materials and in certain composition ranges of alloys, these displacements do not anneal out and the crystal structure in the surface region remains in a highly disordered amorphous state. This structure is analogous to that produced in rapidly solidified alloys and results in changes in both the deformation behavior and reactivity of the surface. The metastable compositional and structural changes produced in the surface by ion implantation are frequently observed to be stable under operational conditions.

Some advantages of ion implantation are:

a) Flexibility in that any element can be introduced into any substrate,

b) There are no thermodynamic constraints such as the requirement of an elevated temperature for diffusion or initiation of a chemical reaction,

c) No refinishing or reheat - treating of the part is required since the ion implantation can be performed at or near room temperature,

d) There is no change in dimensional integrity of the part, no shape distortion and no need for final finishing or polishing of the components, and

e) there is no discrete interface to fail since implantation occurs below the original surface. (Hochman & Legg, 1988, p. 37)

Implementing the metal - ion implantation process requires three: a source of metal ions, a means of making the ions travel very rapidly, and a vacuum chamber in which to carry out the process; these is that the process must be carried out in a vacuum

The lack of a viable source of metal ions kept the technology, from full commercial use many years. The reason for this is economic. In the absence of a high - power ion source, metal -ion implantation is extremely expensive, because it requires a beamline ion implantation system. The ion source produces both the implantation ions (chromium, titanium, zirconium) and another species such as chlorine, which is needed to bring the metal into a vapor phase. These two ion species are separated using a procodure that is based on the principle that ions of different momenta have different radii of curvature in a magnetic field. The separation process is expencive, not very reliable, and permits only a limited beam current (throughput of implanted material).

A more advanced approach is direct ion implantation, as shown schamatically in **Fig. 3**. The ion source is a muli - aperture type such as those developed in the nuclear fusion program to heat plasmas. The metal ions are produced directly, eliminating the need for a separator magnet and associated equipment.

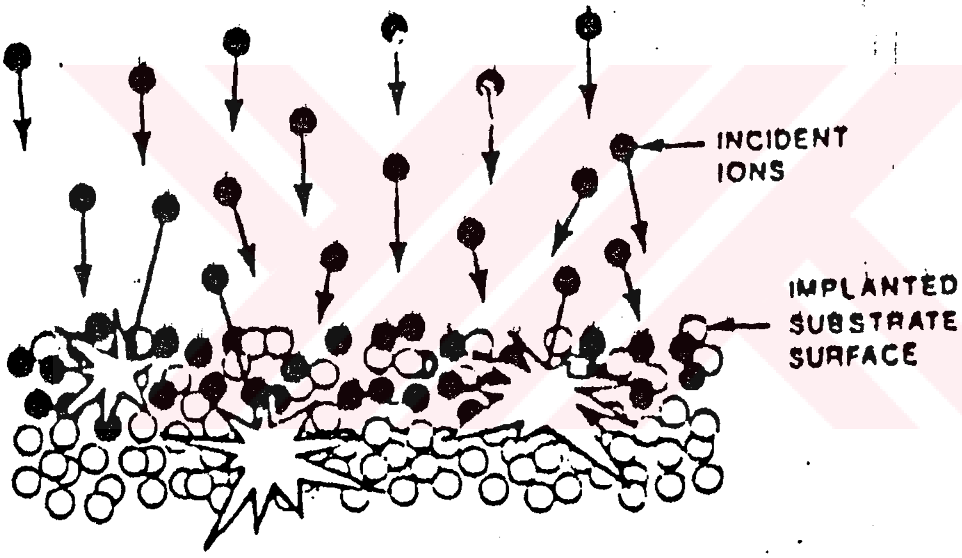


Figure 2. Ion beam effects onto material.

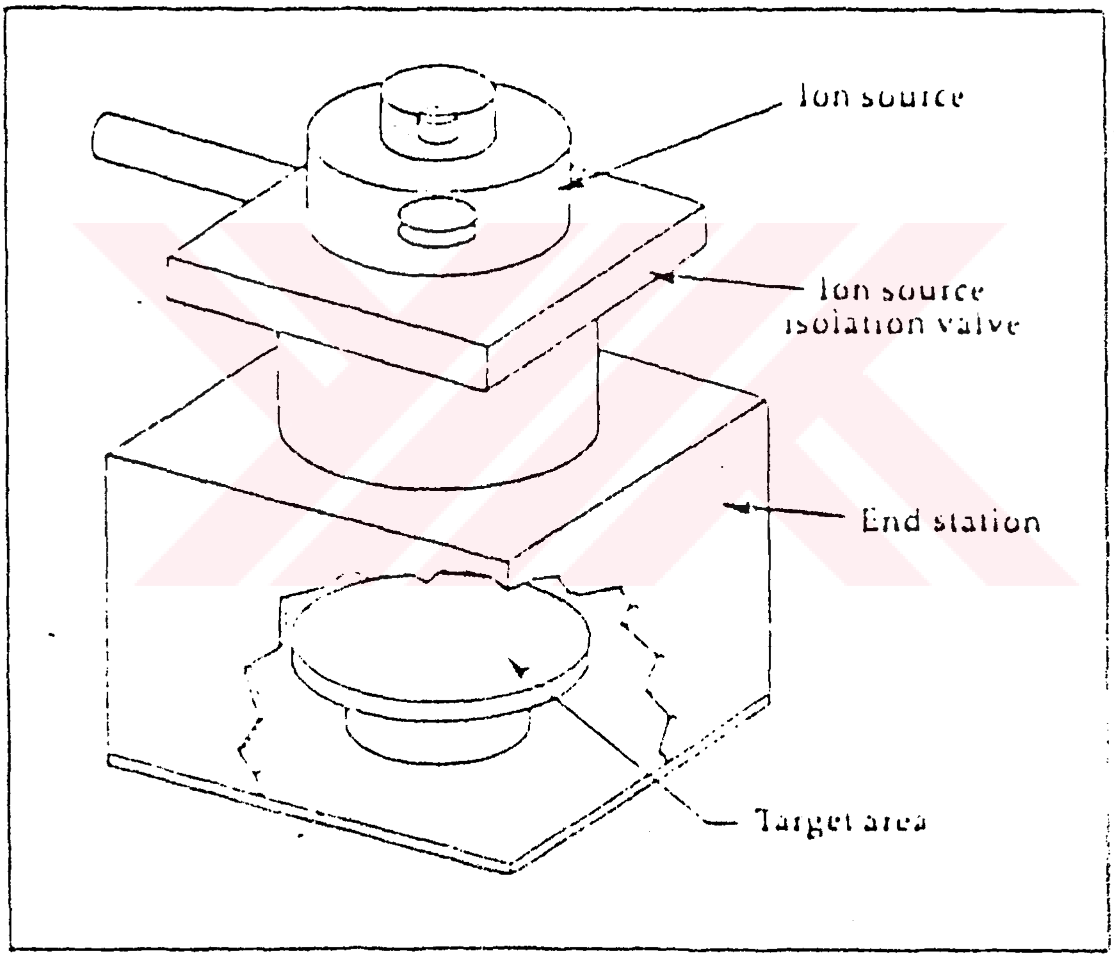


Figure 3. Advanced approach of direct ion implantation is shown.

1. 4. Industrial Applications of Ion Implantation

Here, the industrial applications of ion implantation that lie outside the field of microelectronic are given. Nitrogen and certain metallic ion species are being implanted into metals and ceramics on an ever increasing scale, primarily for improving their resistance to wear or corrosion. Both mass analyzed and non - analyzed systems have been designed for industrial use, with large and versatile work chamber facilities, in some cases capable of treating workpieces up to 1.5 tonnes in weight and 1.3m. in diameter.

In parallel with this has been a development of pulsed ion implantation from a nitrogen plasma and initial results appear very promising. Various combinations of hard and soft vacuum coating processes and ion implantation has been investigated, within the broad concept of ion assisted coating. Such coatings cen be very hard, corrosion resistant and may have low coefficients of friction.

Some of the questions will undoubtedly be economic, and the cost of relatively sophisticated ion beam methods of surface treatment has proved a powerful incentive to the development of more cost - effective equipment, more powerful ion sources, and new machine concepts. These are reviewed in the present paper.

Others may concern the acceptability of ion implantation alongside very many other methods that are available for surface treatment. A few comments will be made here, but this will be a useful topic for discussion by the conference participants. Since the technical progress in recent years has been quite rapid, it will be useful to look at present - day trends in order to have some indication regarding the potential for industrial applications to be made in the future. This may indicate how effective is the coupling between driving forces (i.e. from needs) and technological development.

Finally, it will be necessary to assess what are the principal markets for ion beam technology, once we can presume that it is developed to a point of economic viability, and is acceptable to customers. Once again, it is hoped that useful ideas can be generated during discussion at the conference, but some conclusions from previous surveys will be presented here.

Leading markets for the application of nitrogen ion implantation in metals include:

- Tools for injection molding of plastics.
- Biomedical components, especially hip and knee prosthesis.
- Motor racing crankshafts.
- Industrial knives.
- Precision rollers.
- Punches in steel and hard metal.
- Tungsten carbide PBC drills.
- Extrusion dies.
- Bearings.

Besides their extensive and growing use in research on materials science, versatile ion implanters have a number of potential industrial applications, besides those that are already being exploited:

- Improvement of pitting corrosion resistance in steel bearings by implantation of Cr^+;

- Improvement of wear resistance by implantation of Ti$^+$, Ta$^+$, Nb$^+$ etc. Together with the introduction of carbon;

- Improvement of wear resistance by Y$^+$ and possibly other oversized species, in association with an interstitial element;

- Modification of the surface chemistry of ceramics, eg. by elimination of chemo - mechanical effects;

- Preparation of low - friction ceramic surfaces, eg. by implantation of elements that will from lubricious oxides;

Formation of high electronic conductivity paths in polymers eg. by implantation of Cu$^+$;

- Introduction of elements that will facilitate bonding or joining of difficult materials such as ceramics or intermetallics;

- Improvement of oxidation and spalling resistance in stainless steel used for nuclear fuel cladding by implantation of Y$^+$ or rare earth elements;

- Potential modification of thin film superconductors to enhance or to diminish T in defined areas;

- The introduction of luminescent centers, especially transition elements, into optical materials used as phosphors, lasers, optical fibers etc;

- The introduction of ferro - magnetic elements into the surface of films for high density information storage;

- The implantation of elements that will tailor the opto - electronic or ocousto - electric properties of materials for specific devices.

It should be noted that these applications are either in high - cost materials, in which the added value per unit area is high, or else they are in critical parts (bearings, fuel - cladding etc.) used in costly systems for defense, nuclear or bio - medical applications. In such cases the integrity of ion implantation is of considerable importance.

It is also a useful feature that, by virtue of using a directed ion beam, it is possible to define the area of ion implanted surfaces by various masking techniques. There seems to be great potential for combining non - mechanical techniques of changing the topography of material surfaces, eg. by ion milling, by laser ablation etc. because in this way one can achieve microstructures with controllable properties. Optical applications, in which the refractive index is definable both in depth and or lateral dimensions comparable with with the wavelength, or surface acoustic wave devices, in which the topography and the composition can be varied on the required scale, come easily to mind. If a prediction is permissible for this "blue sky session" it is, perhaps, that ion implantation will be combined with 'nanotechnology' or the micro - control of topography to create new, high value devices. There are, after all, not many methods that provide the degree of precision and versatility in modifying material composition as can ion implantation. The history, during the 20th century, of the use of materials has demonstrated a consistent trend towards greater sophistication, for example in microelectronics. While this industry has so far led the other fields, it is reasonable to expect that the expertise will spread into optical and micro - mechanical areas of application. (Hochman & Legg, 1988, p.63)

1. 5. Examples of Improved Production Tools

1. 5. 1. Punching / Forming Metal Sheets

- Forming / cutting punches and dies working very thin sheets or tin can material **(see Fig. 4)**. The tool material is mostly AISI D2, Vanadis 4 (Uddeholm) steel, AISI A2 and AISI M3 steel. Tool failure is caused by seizing and mild abrasive wear. The tools are delicate high tolerance tools, most of which are rather large. They are implanted locally on the critical areas with nitrogen ions. As a result of ion implantation the tools last 5 to 10 times longer or even more. Although extended tool life is obtained, resharpening of the punches / dies may in some cases be necessary. However, resharpening is normally done from the top, and the implanted layer on the punch / die sides is left untouched. The companies have observed that extended tool life is still obtained after several resharpening operations.

- Draving dies made of Vanadis 4 or AISI D2 steel. These tools work without labrication on lecquered thin sheets. They are subjected to abrasive wear, and to some extent seizing occurs. On an average, the tools normally last around 3 weeks. After nitrogen implantation, tool life is increased to more than six months.

- Draving ring made of AISI M2 steel for drawing very thin sheets of stainless steel. Without ion implantation severe seizing took place. After N^+ implantation, over 600000 items could be drawn without problems.

- Steel punches made of AISI M2 steel for punching holes in aluminium. Without ion implantation substantial amounts of adhesive wear and material pick-up was inevitable. N^+ implantation resulted in superior performance, reduced material pick-up, and less use of lubricants.

- Knives made of AISI D2 steel for shearing / cutting aluminium. Material pick-up would stop the production at 80000 cuts. After implantation the tool can make up to 800000 cuts before repolishing is needed.

- CrN-PVD coated punches for punching aluminium. N^+ implantation results in reduced adhesive wear, and the consumption of lubricants is reduced. Tool life is enhanced about 10 times when compared to CrN coating alone.

- TiN-PVD coated punches for forming sheet metal. C^+ implantation results in reduced friction and improved slide of the work material.

1. 5. 2. Plastic Forming

- TiN coated steel parts for plastic moulds. N$^+$ implantation improves the slip of the plastics.

- An example from LEGO System Ltd. In **Fig. 5** is shown field test results from plastic moulds which are subjected to corrosive attack near the air outlets. During the process the plastic emits aggressive gases which attack the hardened steel moulds locally at the air outlets. The life of injection moulds which are subjected to corrosive attack can be enhanced by Cr$^+$ implantation at the air outlets, typically by 3 to 4 times. However, in the present example tool life is enhanced by as much as 12 - 13 times by chromium ion implantation.

- In another example from LEGO System Ltd. nitrogen implantation of gates in injection moulds resulted in reduced abrasive wear, and tool life was enhanced by 3.5 times.

1.5.3. Other Work Materials

- Steel knives for cutting meat. N$^+$ implantation results in life improvement by a factor of 4 - 5.

- Precision knives for cutting plastic / paper labels. N$^+$ implantation gives marked improvement in performance and higher product quality.

- Knives for cutting rubber. N$^+$ implantation results in 7 times life improvement.

- Stainless steel knives for cutting foam rubber. N$^+$ implantation results in 3 times life improvement.

1. 6. Ion Implantation Compared To PVD, CVD And PCVD

Ion implanted, PVD, CVD and PSVD treated surfaces posses quite different properties, and the treatments are performed at different process temperatures. Each treatment has its advantages and disadvantages and each has its particular fields of applications.

CVD coating of tools and components gives a wear resistant surface layer normally made of 3 - 10 μm thick TiN and TiC (Hirvonen, 1984, p.621). Because of a high process temperature (about 1000°C) thermal diffusion results in a mixed interface between coating and substrate giving a very good adhesion between coating and substrate. For tools made of hardened steel, new hardening and tempering procedures must be applied after the CVD process due to the high process temperature. Thus, alterition of tool shape and dimensions must be taken into account, as well as some alteration of the surface finish by increased roughness.

PCVD is a relatively new way of producing CVD coatings at lower process temperatures (Sprint, 1995, p.126) The process is very similar to standard CVD processes, but due to the presence of a plasma in the process gases the parts to be coated need only be heated to around 450 - 550°C. The typical coatings produced are the same as standard CVD. PCVD processes are also used to create diamond or diamond-like carbon (DLC) coatings.

PVD is a common denomination for several different but somewhat similar processes where tools and components are coated whit wear resistant layers typically made of 2 -3 μm thick TiN, TiAlN, TiCN, or CrN (Rebenne, 1994, p.64). The process temperature is normally about 400 - 500°C. At DTI Tribology Centre, however, a process is used (Kavata, 1992, pp.54-55) where the process temperature is usually kept about 300 - 350°C, but in some cases as low as about 200°C. PVD coatings do not have an intermixed interface as mentioned for CVD. The adhesion of PVD coatings can therefore often be a limiting factor when compared to CVD.

Normally the surface finish is unaltered by PVD, but for highly polished surfaces some minor increase in micro roughness may be observed, depending on the PVD technique applied.

In Denmark surface treatment of machining tools like drills, mills and inserts is primarily made by PVD or PCVD / CVD. In most cases such tools are subjected to rather severe wear, and in such cases ion implantation may not be the most efficient treatment when compared to PVD and PCVD / CVD, due to the shallow depth of the implanted layer. There are exceptions to this, but due to the relatively small dimensions of such machining tools it is often difficult to perform ion implantation on selected areas on these tools which make ion implantation relatively expensive in these cases.

A rough comparison of the different treatments, a kind of ranking between them is given in **Fig. 6**. The figure should only be used as a rough guide, and in several cases there are exceptions to the shown ranking and classification. However, put very generally , ion implantation is a very gentle, safe treatment specially suited for delicate tools. When dealing with more severe wear situations, however, the shallow depth of the implanted layer may be a limiting factor to the use of ion implantation.

But in many applications where tools are subjected to adhesive and / or mild abrasive wear the treatment has proved to be second to none, also pricewise.

Figure 4. Examples of improves tools.

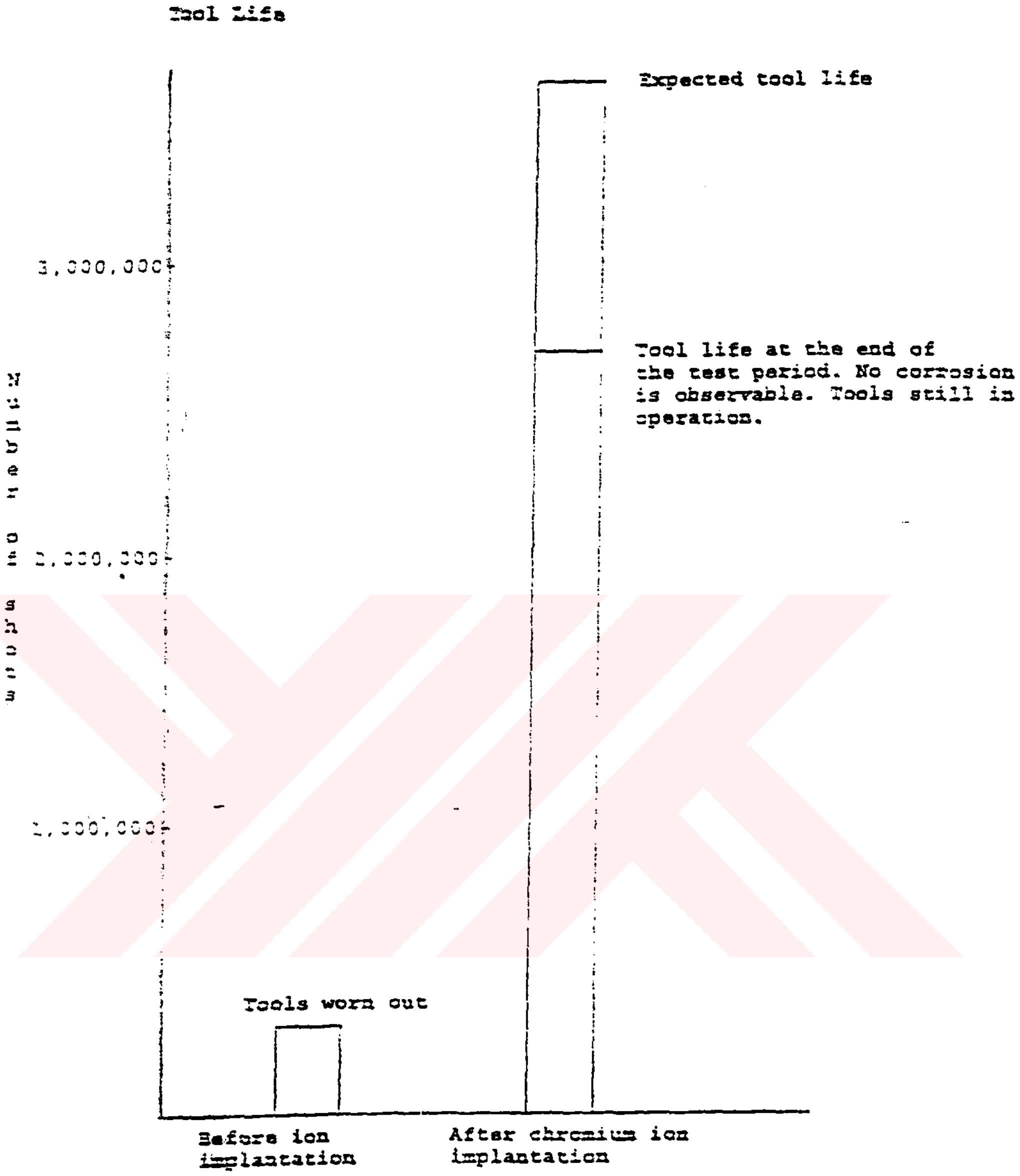
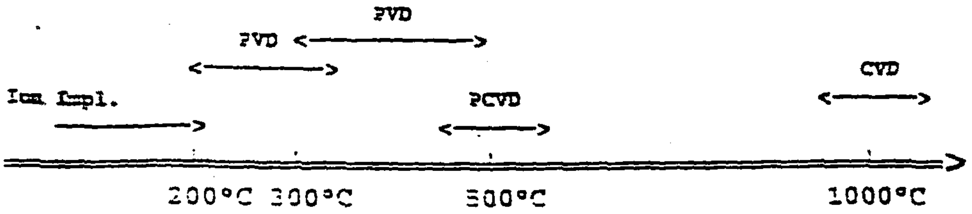


Figure 5. Plastic mould failure is shown.



b)

Ion Impl. PVD PCVD CVD

No influence on surface finish, tool shape and dimension.	Increasing influence on surface finish, tool shape and dimension.

c)

Ion Impl. PVD PCVD CVD

Adhesive wear. Mild abrasive wear. Corrosion.	Adhesive wear. More severe abrasive wear. Corrosion (limited)	Severe abrasive wear. Tools subjected to very large forces.

d)

Ion Impl.	PVD PCVD	PCVD CVD
Rather large punches/dies and draw dies for rather thin metal/steel sheet.	Machining tools, drills, mills and inserts.	Machining tools. Inserts.
	Rather small punches/-dies for sheet/plate and stainless steel.	Deep drawing tools for sheet/plates in stainless steel.
Plastic moulds.	Draw dies.	
Cutting tools for plastics, rubber, paper and meat.	Parts of plastic moulds	

Figure 6. A rough comparison of the different treatments, a kind of ranking between them.

1. 7. Production of Energetic Ion Beams

Ion implantation can be divided into three major stages. They comprise: production of positive ions through gaseous ionization; acceleration and mass selection; and ion beam shaping.

To form the positive ions, a gas is introduced into a chamber where it is ionized by electrons emitted from a hot filament. Producing an ion beam from gaseous elements is quite straight-forward. However, obtaining a metallic ion beam requires sophisticated and specialized equipment. Producing chromium ion beams may involve decomposition of volatile chromium compounds. More commonly, chlorine gas is introduced into the ion source chamber, which is lined with chromium metal. The chlorine reacts with chromium to form chromium chloride, which in turn is volatilized by the intense heat of the filament. The positive ions are extracted from the ion source and accelerated to a mass - separating magnet and mass - defining aperture, which select only one ion species (chromium). The resulting isotopically pure ion beam is then focused and accelerated to its final energy - up to 200 keV.

Finally, the ion beam is directed toward the work - piece by a series of specialized electrostatic and magnetic lensing elements. The magnetic quadruple lenses are used to focus the beam to small dimensions suitable for raster scanning. The electrostatic scan plates are then used to scan the beam over an area of up to 20 x 20 in. The parts to be treated are attached to a water - cooled fixture and manipulated to receive uniform treatment (SIOSHANSI, 1988, pp.42-46)

An ideal source for such intense ion beams and therefore, quick ion implantation is the cathodic arc source. A cathodic, or vacuum arc, is generated when an arc is struck between two electrodes in a vacuum. The electrons exit the cathode from a site that is approximately 1 µm.in diameter. The current needed to sustain the arc is on the order of 100 amperes. As a result, the current density at the cathode is so high that the cathode itself evaporates at the exit site. The metal vapor is rapidly ionized in the intense electron flow, and forms an extremely pure plasma of the cathode metal.

In 1984, Brown et al. , working at Lawrence Berkeley National Laboratory, developed an ion source based on this principle. Termed MEVVA (Metal Vapor Vacuum Arc). (Treglio & et al, 1995, p.29)

CHAPTER TWO

EXPREMENTAL STUDY

2.Tribological Properties of Ion-implanted Steels

For 10 years, ion implantation in metals has been applied to fundamental studies of physical, chemical and mechanical properties in surface layers such as composition, structure, hardness, wear and corrosion. In order to perform these research studies, many types of element have been implanted in a variety of metals, and many results have shown that ion implantation in metals results in significant modification of the surface properties (Hirvonen, 1980, p.18)

Tribology is the study of the friction, lubrication and wear of engineering surface layers including the theories of surface interactions; it is therefore interdisciplinary, covering physics, chemistry, materials science and mechanics. The majority of the investigations on ion-implanted surface layers have concerned hardness, friction and wear properties, which will be closely related to each other (Bowden & Taber, 1964, p.13)

In this study, the effect of ion implantation with ZrO_2 in low carbon 316L Stainless Steel on hardness, friction and wear properties is studied. The implanted element was ZrO_2 and unimplant 316L Stainless Steel; the hardnesses and friction coefficients for both of implant and unimplant steels were measured and their relationship is discussed.

2. 1. The Methods of Wear Test

Wear is a complex process involving parameters that can be altered by several orders of magnitude depending on the dominant mechanisms and their interactions with the environment. Ion implantation has a particular role to play in the science and technology of wear. Unexpected benefits which result from the shallow depths of treatment not only can improve the wear resistance but also may lead to a new understanding of the wear process. (Institute of Physical and Chemical Research), Hirosawa 2-1, Wako, Saitama-ken , 1994, p. 12)

Wear is defined in ASTM G 40 as: "Damage to a solid surface, generally involving progressive loss of material...." This statement recognizes the practical importance of surface damage and surface alteration in in affecting, possibly, the function of a tribological component, particularly for systems designed with close tolerances in critical areas. In many mechanical systems, certain contact surfaces are manufactured with close control over surface roughness and finish.

In a large proportion of reports that contain wear measurements, one finds the wear amount reported in volume units, for example, mm^3 . This better enables a comparison of wear among materials having different densities, and also permits easy calculation of linear wear allowances. In some cases, it is actually necessary to directly measure wear volume. This generally occurs when the worn region is very irregular or unsymmetric in shape, or when high accuracy in the result is needed.

2.2. Ultra Microhardness Test Method

Measurement of microhardness and interpretation of the results of these measurements for ion-implanted layers is a complex problem in view of the fact that the indentor often pesses through the the implanted layer under minimum loads (1-20g). Thus the depth of penetration of implanted ZrO in Stainless Steel 316L with E=100 keV does not exceed 200 nm, while the depth of penetration of the diamond indentor during a study of microhardness reaches 1.5 μm for a Vickers pyramid but below 1.5 μm for ultra microhardness test indentation (Komorow, 1979, pp.11-13)

Hardness is one of the most important surface properties of materials, and we can measure it simply by means of conventional Vickers or Knoop hardness testers. The indentation made by the hardness testers, however, penetrates through most implanted layers even at lower normal loads because these implanted layers are of submicron thickness (i.e. they have a thickness of the order of the ion range).Therefore, it is difficult to measure precisely the hardness of implanted layers; the hardness measured as a function of normall loads will give us an average hadness, and it approaches the value of the implanted layer at lower loads.(Iwakı, 1986, p.12)

2. 3. Preparation of Samples

Pin on disk has been used for wear tests. 50 mm diameter and 4 mm thick disks were made of 316 - L Stainless Steel were used. One side of these disks were co - ion implanted with ZrO_2 ,

Pins of 2 mm and 4 mm diameter and 20 mm length were used. Only one side of these pins were also co - ion implanted with ZrO_2. Co - implantation means simultaneous ion implantation of two different species. Co - implantation of this kind is new technique, not much has been done or reported in the literature yet. This new technique has been developed used by Ian Brown in Lawrence Berkeley Laboratory and the samples were co - implanted with Zr and O_2 by his group.

According to their data:

Co - implantation of Zr and O_2.

Extraction voltage 40 kV.

Background oxygen gas pressure (in main vessel): 1.5×10^{-4} Torr

Mean ion charge states; Zr, 1.9; O, 0.67

The ratio of Zr:O ions (particles) in the beam was 0.6; (cf 0.5 for ZrO_2), 0.6 implies about $ZrO_{1.7}$.

The dose was about 5×10^{16} cm^{-2} for Zr.

The colour of ZrO_2 implanted 316 L Stainless Steel samples is dark (purplish) blue.

Implanted and unimplanted pins and disks were put in glass containers filled with aseton and cleaned in ultrasonic cleaner. Therefore, surfaces of samples were free of grease and dust etc.

2. 4.. Friction Tests

Pins and disks were placed in Plint and Partners TE 79 computer controlled test equipment **(see Fig. 7)**. The load can be varied between 0.1 N to 20 N and the speed of disk can be controlled between the values of 0.01 m/s and 1.6 m/s. Before the experiments, necessary calibration and centering were done. 1 N load, 200 mm/sec. tangential disk velocity and 300 m total wear distance are set, for the track location of 8 mm from the disk centre. ZrO_2 implanted 316 L Stainless Steel and unimplanted 316 L Stainless Steel disks were used against ZrO_2 implanted pins for the friction tests. Track length of 300 m was completed after 35 minute.

The results of coefficent of friction for the ZrO_2 implanted and unimplanted 316 L Stainless Steel are shown on **Fig. 8, 9**. From these figures, coefficient of friction was found to be 0.1 for ZrO_2 implanted 316 L Stainless Steel and 0.6 for unimplanted 316 L Stainless

Steel disks, The results showed that the coefficient of friction for 316 L Stainless Steel decreased by a factor 6 when implanted with ZrO_2.

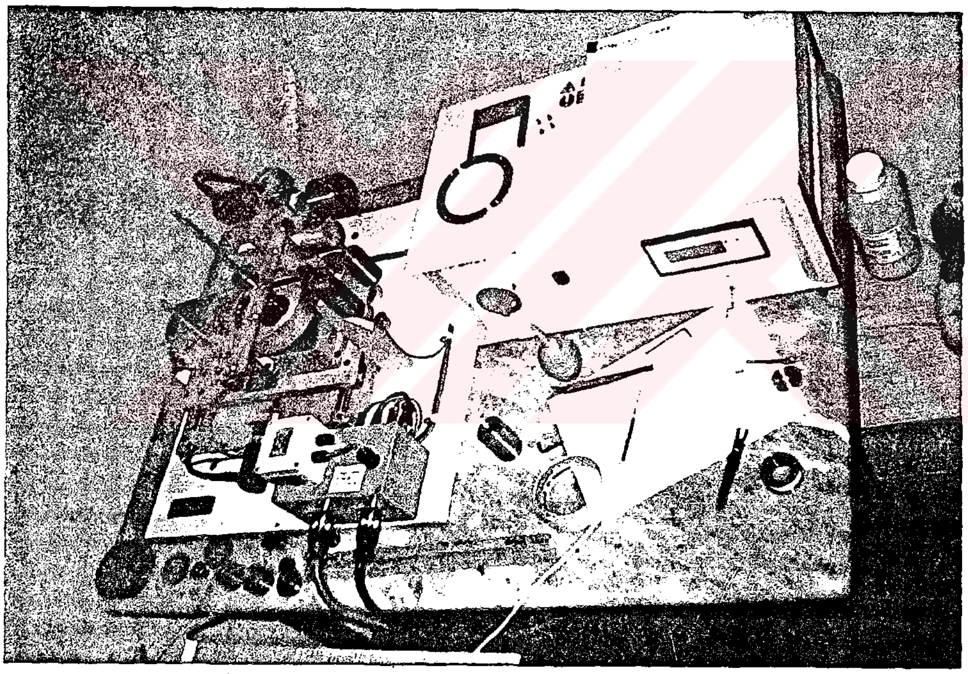


Figure 7. Computer controlled wear and friction test equipment.

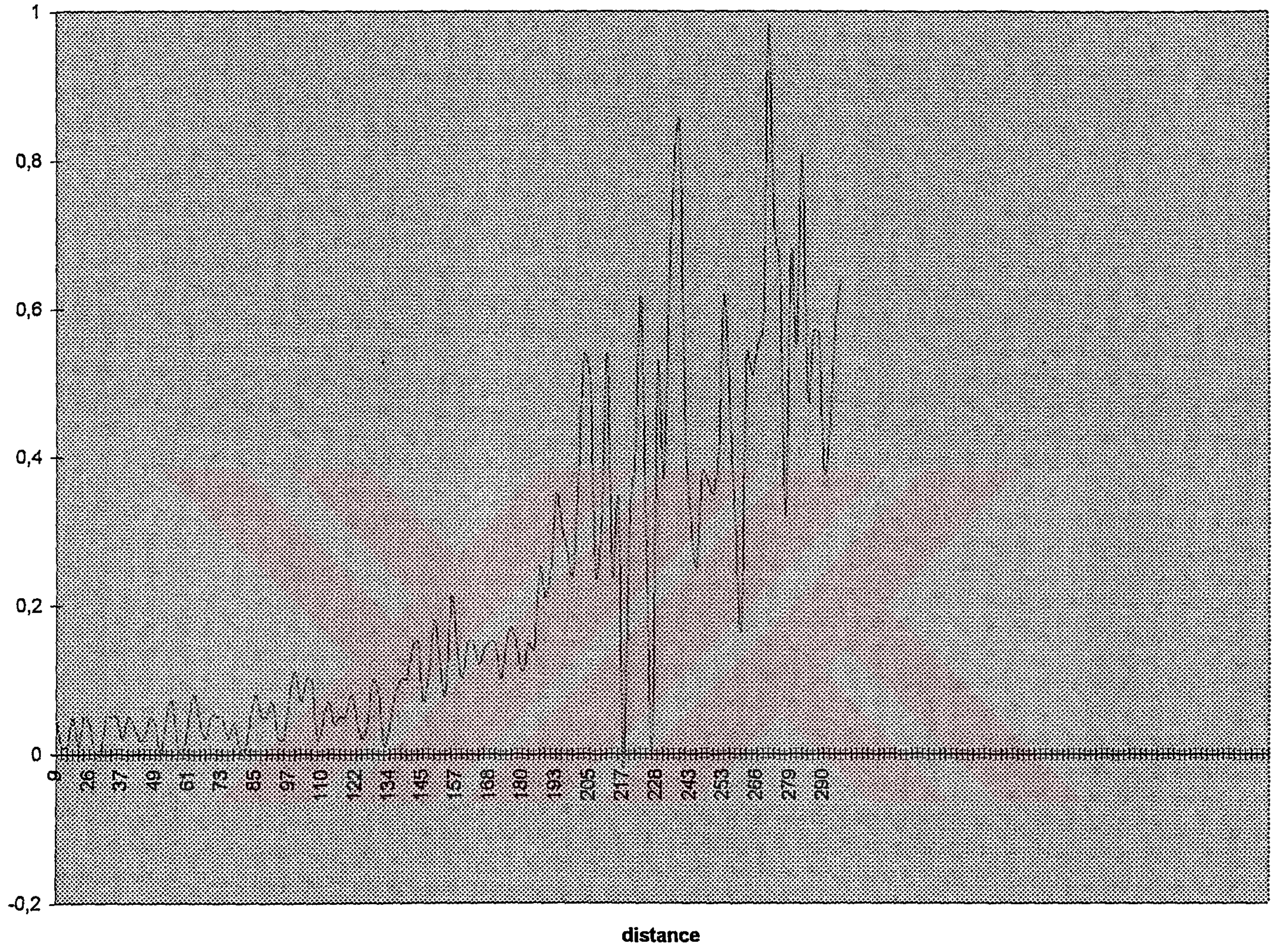


Figure 8. For ZrO_2 implanted 316 L Stainless Steel, friction values graph.

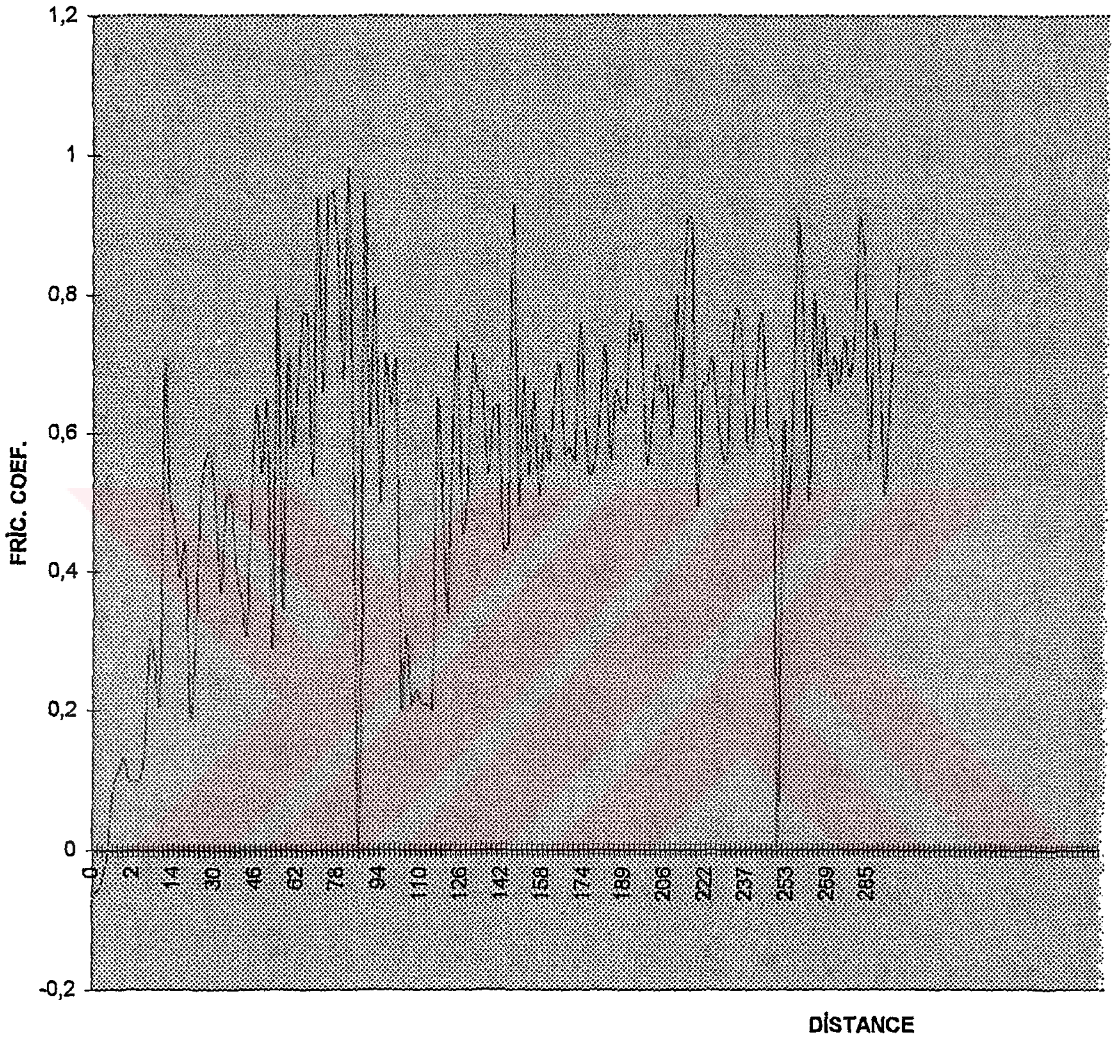


Figure 9. For unimplanted 316 L Stainless Steel, friction values graph.

2. 5. Wear Tests

Implanted and unimplanted disks, which were subjected to wear, were pleaced on Mahr Perthen S 8P Perthometer Profilometer and wear track profiles were obtained. These are shown in **Fig. 10.**

Wear volumes were estimated from the wear track profiles for implanted and unimplanted samples. In order to calculate the wear volumes, width and depth of wear track profiles were measured from the graphs are shown in **Fig. 11, 12.** It is estimated that wear volume of unimplanted 316 L Stainless Steel sample is 1.192 mm^3 and wear volume of ZrO_2 implanted 316 L Stainless Steel sample is 0.19 mm^3. As the results showed, the wear resistance of 316 L Stainless Steel is increased aproximately 6 times when implanted with ZrO_2. Pictures of wear track for implanted and unimplanted 316 L Stainless Steel samples are shown **Fig. 13,14.**

Figure 10. Wear volume profilometer test equipment.

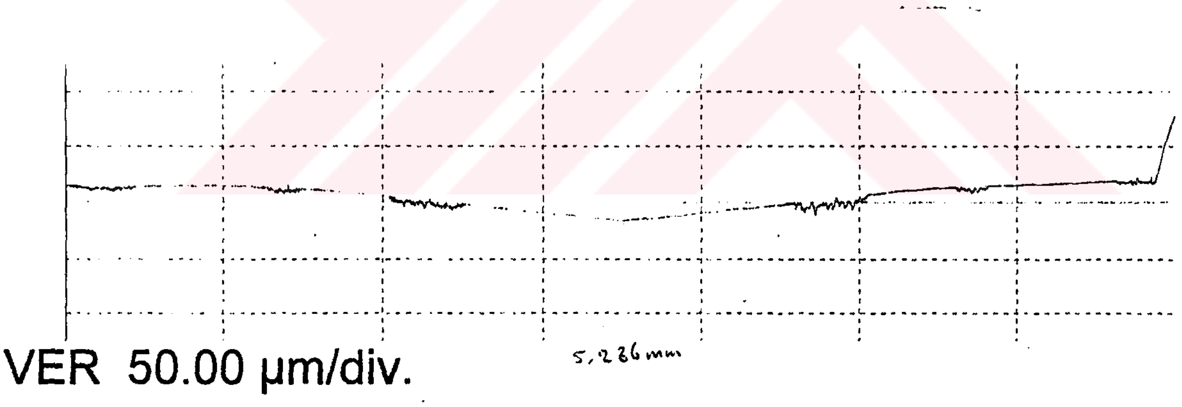


Figure 11. For implanted sample, wear track profilometer graph.

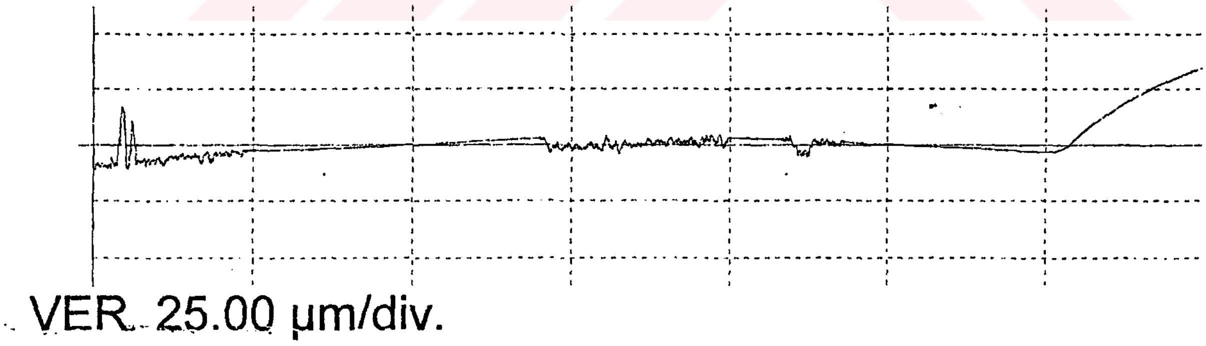


Figure 12. For unimplanted sample, wear track profilometer graph.

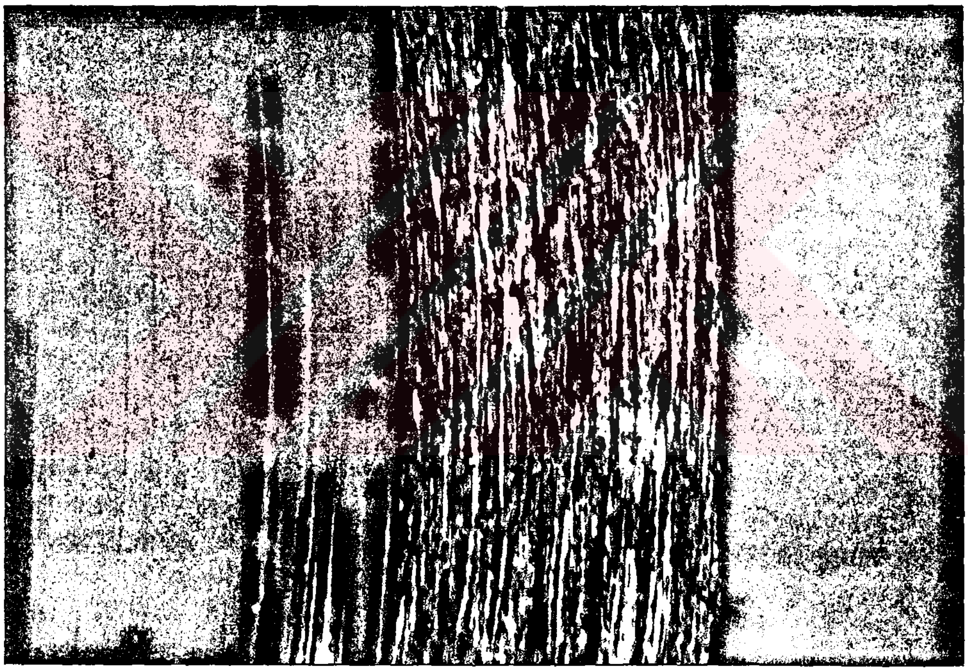


Figure 13. Picture of wear track for implanted 316 L Stainless Steel sample is shown.

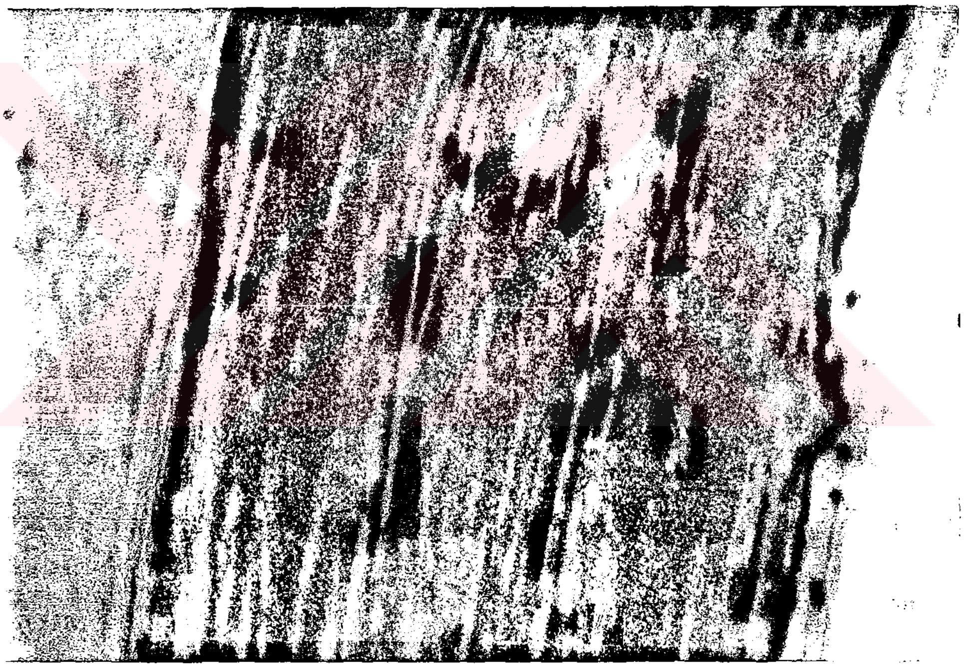
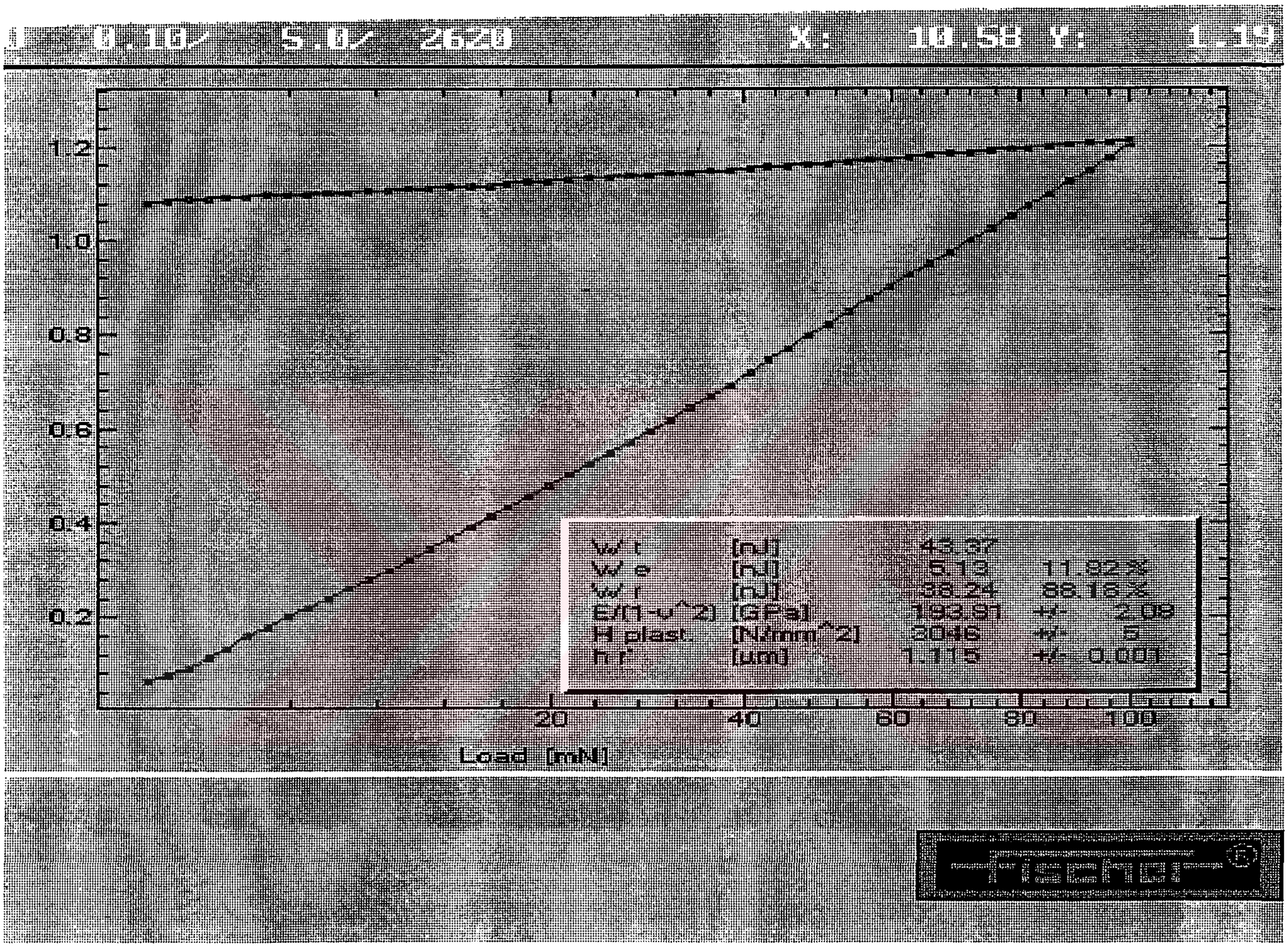


Figure 14. Picture of wear track for unimplanted 316 L Stainless Steel sample is shown.

2. 6. Ultra Microhardness Tests

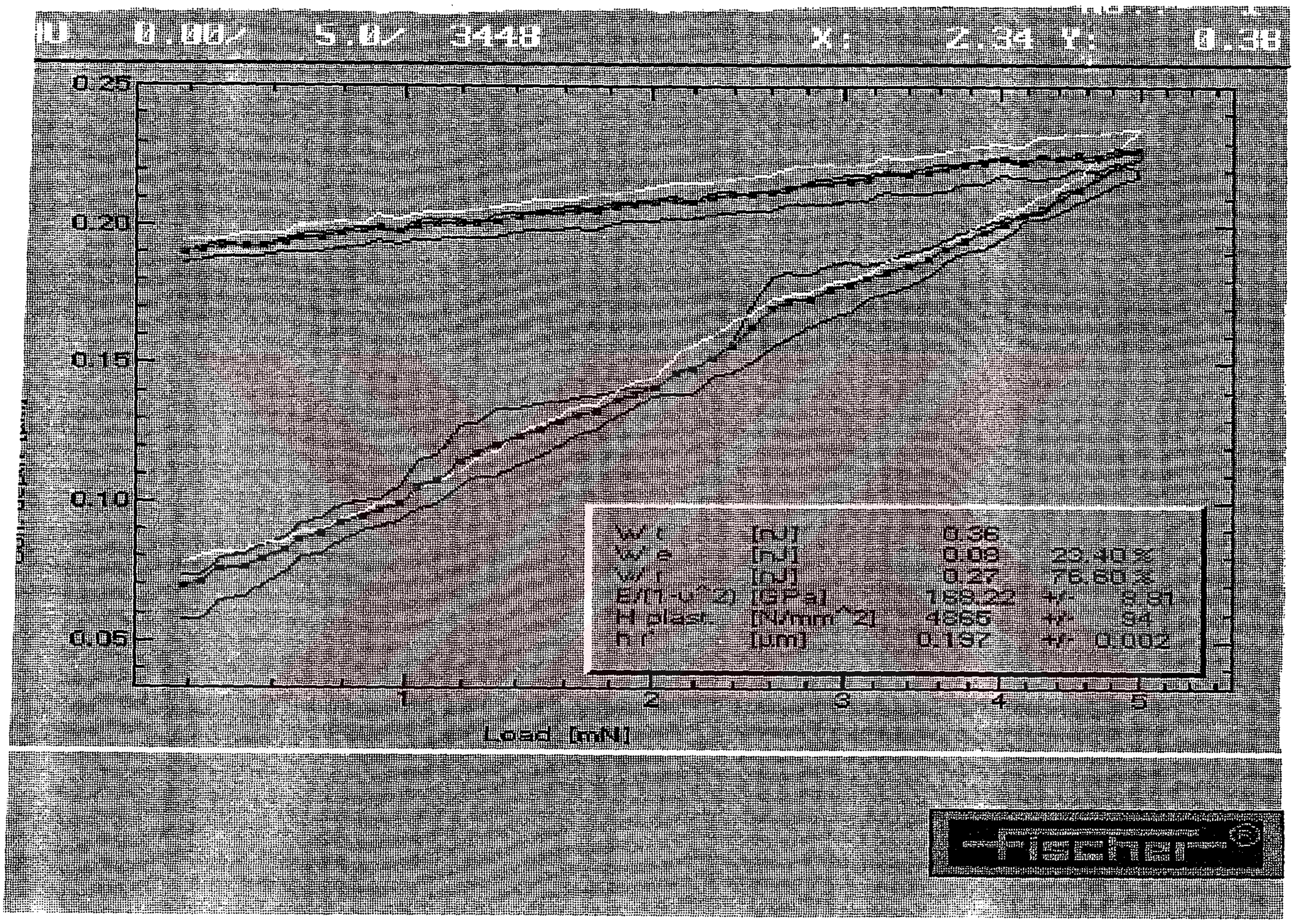
Ultra microhardness of implanted and unimplanted samples were mesured by Fisher HP 100 X - Y PROG Ultra Microhardness Tester equipment. Load can be varied between 0.4 - 1000 mN with various progressing speeds. With these machine, one can measure the microhardness of the implanted surface without being affected by the base material (316 L Stainless Steel). The results are shown on **Fig. 15.16**

The ultra microhardness of ZrO_2 implanted 316 L Stainless Steel sample was found to be 485,6 vickers where as for the unimplanted 316 L Stainless Steel sample it was 304,6 vickers. An increase of 60% was obtained in microhardness when implanted with ZrO_2.



W t	[nJ]	43.37	
W e	[nJ]	5.13	11.82 %
W r	[nJ]	38.24	88.18 %
E/(1-v^2)	[GPa]	193.91	+/- 2.08
H plast.	[N/mm^2]	3046	+/- 5
h r'	[um]	1.115	+/- 0.001

Figure 15. Ultra microhardness result for unimplanted 316 L Stainless Steel sample.



W t	[nJ]	0.36		
W e	[nJ]	0.08	23.40 %	
W r	[nJ]	0.27	76.60 %	
E/(1-υ^2)	[GPa]	188.22	+/-	8.91
H plast.	[N/mm^2]	4865	+/-	94
h r'	[μm]	0.197	+/-	0.002

Figure 16. Ultra microhardness result for implanted 316 L Stainless Steel sample.

2. 7. X - Ray Difraction Test

Philips PW 3710 X test equipment was used to examine the ZrO_2 formation. However, as it is seen in **Fig.17**, because of amorphous structure of ZrO_2 (implanted in 316 L Stainless Steel substrate surface) peaks for Zr and O were not observed.

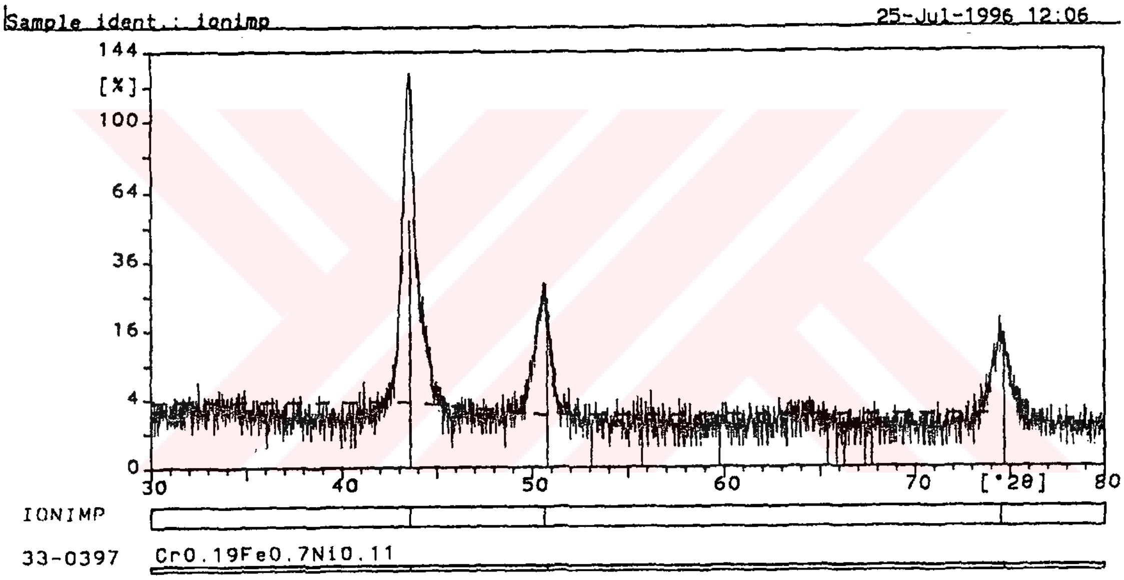


Figure 17. X - Ray difraction result of ZrO_2 implanted 316 L Stainless Steel sample.

CHAPTER THREE

CONCLUSIONS

3.1. General Critics

The objective of the present work was to study the effects of co - ion implantation of ZrO_2 on tribological properties of 316 L Stainless Steel subtrates.

It is found that the decreacse in coefficient of friction is about six times, and an increase in surface microhardress is about 60%. It is believed that the surface amorphisation is responsible for the decrease in coefficient of friction and ZrO precipitate accounts for an increase in surface microhardness.

The increase in surface microhardness and/or decrease in coefficient of friction plays an important role in improving wear resistance and the relationship between relative wear volume and relative hardness is correlated for Zr and O implantation. As indicated above, the wear volume of Zr and O implanted 316 L Stainless Steel substrates was decreased approximately six times compared to the unimplanted 316 L Stainless Steel substrates.

The results of X - Ray difraction measurements (shown in **Fig.17**) suggests that Zr + O implantation on 316 L Stainless Steel substrates has an amorphous structure as there were no peaks for Zirconium and Oxygen. However, there may be a question of whether the implantation has been successfull or not.

The results of I. G. BROWN (private communication) shows that Zr + O implantation was succesfull indeed. He found that ranges in steel are about 175 °A for Zr and 265 °A for O. According to I. G. BROWN, widths of the implanted distributions for Zr (175°A) and for O (265°A) implied that there would be a fairly good overlap of the implanted Zr and O profiles.

I. G. BROWN 's estimation (based on his measurements) gives the ratio of Zr : O ions as 0.6 which implies $ZrO_{1.7} \Rightarrow ZrO_2$ %4 (private communication).

In most cases amorphization by ion implantation appears to occur at low energies and high fluences (40 keV and 10^{17} ion / cm^2) and holding the target at low temperatures.

In this work, 316 L Stainless Steel substrates which were Zr and O ion implanted fulfill the above requirements (see chapter 2).

REFERENCES

1. Hochman & Legg, (1988), Ion Implantation and Plasma Assisted Process, Ion Beam Process p.3, Atlanta,

2. Geoff Dearnaley, 1994, Surface and Coatings Technology , p10

3. Hochman & Legg, (1988), Ion Implantation and Plasma Assisted Process , p. 37

5. Hochman & Legg, (1988), Ion Implantation and Plasma Assisted Process Developments in ion implantation for industrial applications, G. Dearnaley, P63, Atlanta.

6. Hirvonen, (1984), Mater. Res. Soc. Symp. Proc., p.621, Denmark.

7. Dissemination of Ionic Surface Treatment Techonology Among Industries of the Metalurgical Sector, (1994), pp.78-80, Spain.

8. G. Rebenna & G. Bhat, Surface Coating Techonology, (1994), p. 64, Atlanta.

9. K. Kawata, Surface Coating Techonology, (1992), p.604, Georgia.

10. K. Reichelt & X. Jiang, Thin Solid Films, (1990), p.191, Georgia, Atlanta

11. T. Lyendecker & O.Lemmer Wear and Friction Properties of Hard PVD Coatings, (1991), p.175, Denmark