

# METALLURGICAL APPLICATIONS OF ION IMPLANTATION: A REVIEW

J. ADEWUYI AKINTUNDE

(Received 27 April 2000; Revision accepted 14 January, 2001)

## ABSTRACT

Ion implantation technology plays an important role in different fields of solid materials modification and materials' synthesis for specific applications and has become an established industrial technique particularly in the developed countries. In this paper, applications of ion implantation technique in the field of metallurgy covering areas such as corrosion protection, friction and wear resistance, surface hardness and synthesis of engineering material are reviewed, to be able to see the relevance of the technique in the iron and steel industry in Nigeria in terms of economic and social benefits. The review touches on the fundamentals of ion implantation in materials, which highlight the unique features or capabilities of the technique that are being exploited for metallurgical applications, and its limitations.

It has been highlighted how the corrosion resistance, wear resistance and hardness of a variety of pure metals and commercial grade engineering alloys (e.g. bearing steels, stainless steels, aluminium alloys, etc) have been improved significantly by implantation of suitable impurity elements, resulting in longer wear lifetime, while low friction metal and alloy surfaces, and other technologically important engineering materials have been produced by ion implantation. The possible mechanisms for the observed effects of ion implantation on the characteristics of the engineering materials are briefly discussed

**Keywords:** Ion implantation, metallurgy, applications, engineering materials.

## INTRODUCTION

If engineers are to adapt engineering materials for society's needs, they must consider the performance of all classes of materials that are potentially useful to the society during a period of extended service.

Ideally, every engineering material should retain its initial characteristics when in service. For example, it is desirable that aluminium alloy used in aircraft industries and steel used in shipbuilding should maintain their high corrosion-resistance in the atmosphere and seawater respectively. However, service conditions may modify materials and may therefore fail unless their alterations (i.e. property modifications) are anticipated and included in the original design. Engineering materials that fail in service must have had their structures altered (Svensson and Johansson 1993). Therefore, metallurgists and materials engineers must pay attention to structure-property-performance relationship. This has led to the search for other methods of materials preparation and processing outside the familiar conventional metallurgical methods. Ion implantation technique has been identified and proved to be very useful for either avoiding or solving many of the metallurgical problems in alloy production and material property modifications (Dearnaley et al, 1973).

Ion implantation, a low temperature and non equilibrium doping process is a versatile technique of making controlled changes to the properties (mechanical, magnetic, electrical, optical, etc) of most solid materials because it makes it possible to introduce into them in a controlled manner, a wide range of

atomic species. The technique has been successfully used in electronic industries to mass produce semiconductor devices and integrated circuits. (Akintunde, 1997).

Ion implantation is carried out when atoms of the desired doping elements are ionized and accelerated through a fairly high electrical potential (~20-400kV or ~1 - 5MV) towards a solid material (e.g. metal or alloy) which the ions strike and enter by virtue of their kinetic energy (or momentum). After the energetic ions come to rest and equilibration has occurred, the implanted atoms can be in a position to modify the properties of the solid substrate.

More than 1000 ion implanters (ion accelerators) operating in the low and medium-energy range ( $\leq 400$  keV) and high energy range (~ 1 - 5MeV) are in operation worldwide for solid materials' surfaces modification. The design of ion implantation systems vary from one to another and indeed depends on applications. The detailed set up and operations of ion implantation accelerators are well documented in the literature (Thomae, 1990; Ryssel and Glawischnig, 1983 )

In the last four decades, the main trends in the application of ion implantation technique in the field of metallurgy are to synthesize, modify and control materials' properties by substituting traditional thermal processing with ion implantation of a broad variety of energetic heavy or light ions depending on applications. By changing the chemistry, structure and properties of a thin surface layer by ion implantation, it is possible to modify materials behaviour in areas such as corrosion, friction and wear resistance, lead-

ing to the development of technologically important engineering materials.

The aim of this paper is to review the applications of ion implantation technique in the field of metallurgy, along with its limitations in order to highlight useful practical results obtained on engineering materials' technology. The fundamentals of ion implantation of solids in the energy range KeV to MeV, covering the fundamental physical processes occurring during ion-solid interactions and the associated phenomena like lattice disorder, e.t.c are briefly discussed and the unique features of the technique that are being exploited for the development of important engineering materials and improvement of materials behaviour for specific applications are highlighted. The possible mechanisms for the observed improvement in the properties of ion implanted solid materials are briefly discussed.

## FUNDAMENTALS OF ION IMPLANTATION

In ion implantation energetic ion impinging on a solid target will penetrate a certain distance before coming to rest inside it, as a result of loss of energy mainly by two mechanisms (Murarka and Peckerar, 1988). One mechanism is the nuclear collisions (i.e. elastic collisions of ion with target nuclei). This is nuclear stopping. The other one is the electronic interactions (i.e. excitation or ionisation of atoms by inelastic collisions with the ion). This is called electronic stopping. The depth at which the ion comes to rest is characteristic of the ion energy and mass, and atomic number of both ion and target atoms. The two energy loss processes, can be regarded to a good approximation as independent processes, so that the energy (E) loss per unit path length of the ion (x) [i.e the total stopping power  $(dE/dx)_{total}$  of the target] is given by the sum of the two contributions: nuclear stopping and electronic stopping [Ryssel and Ruge, 1986]

$$\text{i.e. } (dE/dx)_{total} = (dE/dx)_{nuclear} + (dE/dx)_{electronic} \text{ eV/cm....1.}$$

The essential features of the complicated calculations of the nuclear and electronic stopping terms from theoretical considerations are available in the literature (Ryssel and Ruge, 1986; Lindhard et al, 1968). Nuclear stopping is the principal stopping mechanism at keV energies, whilst electronic stopping dominates at MeV energies.

Nuclear collisions cause the deflection or scattering of incoming ion leading to changes in its trajectory and displacement of the target atoms from the lattice sites, provided the energy transferred ( $\Delta E$ ) to a target atom is greater than the binding energy of a lattice site (i.e. atomic displacement energy). The target is said to suffer radiation damage or lattice disorder. Each freed atom moves through the target as a second projectile i.e primary "knock-on" (recoiling nucleus) resulting in the formation of a Frenkel pair (Ziegler et al, 1985) (a vacancy and the displaced atom) in the crystalline target. If both the ions and the primary "knock-ons" are sufficiently

energetic, they can create more Frenkel pairs, which in the extreme makes surface layers amorphous.

The total number of atoms displaced by an incoming ion is given by the equation

$$N_d \cong E_n/2 E_d \text{.....2}$$

where  $E_n$  [ =  $\int (dE/dx)dx$  ] is the total energy loss of a particle in primary and secondary nuclear collisions, and  $E_d$  is the displacement energy of a lattice atom.

In amorphous solids and for ion energies above a few keV, the implanted atomic profiles are approximately Gaussian and can be described by the following equation [Lindhard et al, 1968 and Ziegler et al, 1985] which ignores ion channeling effects i.e.

$$n(x) = N_p \exp [ - (x-R_p)^2 / 2 (\Delta R_p)^2 ] \text{.....3}$$

where  $n(x)$  is the ion concentration as a function of depth,  $R_p$  is the projected range or the average depth of implanted ion;  $\Delta R_p$  is the projected straggle, and  $N_p$  is the peak ion concentration at  $x = R_p$ .

Theoretical values of  $R_p$  and  $\Delta R_p$  are used to estimate ion implantation depth for a given ion energy or vice versa for the desired surface modification or solid material synthesis.

Below are the major unique features of ion implantation technique that are exploited in metallurgical surface modification and material synthesis.

- i A wide range of atomic species can be implanted directly into solid materials of interest, because most of the useful impurity atoms can be ionized, accelerated through an electrical potential to a precise energy, mass analysed to reject unwanted ion species, and scanned uniformly across the materials. The above holds even for atomic species which are not miscible with the substrate atoms. In conventional alloying, in which one atomic species is dissolved in another under thermal equilibrium, the choice of atomic species (i.e. alloying species) is limited by chemical solubility and reactivity. Infact comparatively very few atomic species are capable of being incorporated in another by the high temperature because of their low diffusion coefficients.
- ii Because ion implantation is a non-equilibrium process, normal atomic diffusion rates and their solid solubility limits can be readily exceeded in ion implanted layers and the Gibbs phase rule violated. This is because implanted impurity atoms can remain in metastable sites in the substrate lattice and concentrations above the solubility limit will redistribute deeper into the substrate during subsequent heat treatments.
- iii There is no change in the physical dimensions of the substrate material ( i.e work - piece)

during ion implantation, unlike in alloying process. This is desirable in metallurgy, and for industrial applications..

- iv Ion implantation process is basically a clean process because the energetic ions are mass analysed to separate unwanted atomic species (i.e. contaminants) from the ion beam before they hit the target material. In conventional alloying, contaminants may be incorporated under high temperature into the alloy along with the desired alloying species.
- v Ion dose and energy of the implanted impurity atoms, and substrate temperature can be independently selected to control and obtain with remarkable predictability, the implanted impurity concentrations and distributions (i.e. implanted atoms profile shape) in the substrates over a wide range of doses that could be suitable for the desired application.
- vi Ion implantation of selected areas of the target material is possible by using masks of suitable materials to mask off areas which do not require the impurity atoms. This may be very useful for special metallurgical applications where selective material surface modifications are needed.
- vii The surface properties of the implanted surface layer can be optimized, leaving the bulk properties of the target material unchanged.
- viii Ion implantation can be used to create an intimate atomic mixture of controlled composition, without many of the limitations of conventional alloying like thermodynamic constraints. Thus the method can be used to develop new engineering materials by ion beam synthesis, the physical properties of which are dependent on the implanted species.
- ix Ion implantation technique lends itself to automation, because direct monitor and precise control of ion beam dose, energy and uniform spatial distribution of implanted ions are done by ion beam current, accelerating voltage and scanning system. Therefore large scale processing of special engineering materials is possible.

#### CORROSION PROTECTION USING ION IMPLANTATION TECHNIQUE

Prevention of metallic corrosion is a major metallurgical problem (Higgins, 1993). Steels rust away due to lack of adequate protection. Metals corrode when exposed to the atmosphere. The mechanisms of corrosion, viz: "dry" corrosion or oxidation and "wet" corrosion or electrolytic action are documented in the literature (Higgins, 1993).

The presence of very small concentrations of certain impurities in metals and alloys has been observed to modify their corrosion characteristics (Dearnaley et al 1973). These impurity elements tend to promote the formation of a passive film within the surface region of the alloys. Conventional thermal alloying technique (Coudurier et al 1978) used to incorporate the required one or more impurity elements

into steels to improve their corrosion resistances [Clayton and Wang 1983], was regarded to be unsuitable for the following reasons.

- i. The dimensions of the work-piece (metals/alloys) can change under thermal alloying.
- ii. The existing bulk properties of the work-piece may be altered by thermal alloying.
- iii. Solubility of the passivators in the host material and the formation of secondary phases, carbides, intermetallic compounds are the major constraints in thermal alloying.
- iv. Contaminants may be incorporated into the work piece along with the desired impurity elements during thermal alloying, because of the high temperatures involved.

Therefore, preferred method of minimizing or preventing corrosion is to insulate surfaces from the corrosive medium by

- i. corrosion - resistant coatings [e.g. paints, varnishes, metallic films like tin coatings used in canning industries]
- ii. passive surface films [e.g. a thin chromium oxide film on stainless steel surface which restricts corrosion, highly insulating films of yttria-stabilized zirconia (YSZ) on structural materials to restrict the oxygen transport rate to the metal surface. (Kim and Andresen 1998)].

However, the problems with these methods are mainly the interfacial corrosion beneath such coatings. Ion implantation method with its unique features as stated above is used to avoid such metallurgical problems discussed above. However, limitations to surface alloying by ion implantation are the depth of penetration of implanted ions which is relatively small and makes the implanted layers very useful in relatively non-abrasive environment, because of the fact that the maximum implant concentration is determined largely by sputtering processes and in some cases by radiation enhanced diffusion.

The method of ion implantation is an accepted technique of corrosion protection for some specialized applications. Generally, it has been used to modify the corrosion behaviour of both pure metals and commercial grade engineering alloys [Clayton and Wang, 1983; Wang et al, 1979, and Al-Saffar et al, 1980] either through modification of the substrate by radiation damage or chemical effects which alter the electrochemistry of the surface reactions. The aqueous corrosion resistance of bearings made from M50 and AISI 52100 steel (i.e. fully hardened martensitic steels) was improved by ion implantation (Wang et al 1979). These bearings are used for the construction of military aircraft propulsion systems, in which the precise dimensions of the bearings must be maintained;

hence the need to use ion implantation technique. Measurement of localized corrosion resistance of M50 steel implanted with Cr, Mo, Ti, Cr + Mo ions, done by carrying out anodic polarization (Moreland and Rowland, 1977) in deaerated 0.1M NaCl pH 6 buffer solution [Clayton and Wang 1983] showed that each ion implanted provides self-passivity and higher breakdown potentials indicative of greater resistance to localized corrosion. Localized corrosion resistance of AISI 52100 steel also improved appreciably using similar ion implantation treatments.

It has been observed that not all impurity elements improve corrosion resistance. From the study of the effects of ion implantation on the general corrosion behaviour of 304SS steel in 0.5M  $H_2SO_4$ , and the pitting behaviour in 0.1M NaCl solution, it was observed that implantation of Ar, Ti, and Si ions at 20keV into the steel at doses of  $10^{17}$  ions/cm<sup>2</sup>, had no significant effect on corrosion behaviour, unlike the implantation of Ta, W and Mo which enhanced passivation significantly. This is not unexpected as each of these elements are major passivators, and were therefore probably incorporated into the passive film. Steel 304SS amorphized by implantation of phosphorus ( $1 \times 10^{17}$  p<sup>+</sup> ions/cm<sup>2</sup>, 40keV) showed enhancement in passivity compared with the virgin 304SS steel, and pitting resistance attributable to phosphorus implantation [Clayton and Wang, 1983]

The influence of nitrogen ion implantation on the corrosion behaviour of pure Titanium was studied in 70%  $H_2SO_4$  solution [Masahiko et al, 1999]. For nitrogen ion doses  $< 1 \times 10^{17}$  ions/cm<sup>2</sup>, corrosion resistance increased with ion dose. For ion dose =  $5 \times 10^{17}$  ions/cm<sup>2</sup>, the corrosion resistance decreases, though it is still larger than that of pure Ti. Under X-Ray diffraction (XRD) examination, Ti<sub>3</sub>N formed when ion dose is greater than  $5 \times 10^{16}$  and for ion dose equal to  $1 \times 10^{18}$  ions/cm<sup>2</sup>, both Ti<sub>2</sub>N and TiN formed. Post implantation aging at 673K largely increases the corrosion resistance, with enhanced precipitation of Ti<sub>2</sub>N.

Implantation of tantalum ions of doses  $5 \times 10^{14}$  and  $2 \times 10^{15}$  ions/cm<sup>2</sup> into pure iron specimen was found to improve the corrosion resistance of pure iron. The corrosion resistance of tantalum implanted iron is similar to that of conventional Fe-4.9at%Cr Alloy. (Ashworth et al, 1977).

Potential-time measurements on pure Al and 7075-T6 aluminium alloy implanted with 20KeV,  $1 \times 10^{17}$  Mo<sup>+</sup> ions/cm<sup>2</sup>, showed significant improvement in both general and localized corrosion resistance [Al-Saffar et al, 1980]. A single phase solid solution of Al and Mo in the pure Al sample was reported, despite the fact that Mo is virtually insoluble in Al under normal alloying conditions.

The influence of implantation of silicon, molybdenum and cerium ions at 150keV, in the dose range ( $1 \times 10^{14}$  and  $1 \times 10^{15}$  cm<sup>-2</sup>) on the oxidation behaviour of a 18 Cr 8Ni stainless steel [Perez, et al 1998a] and 0.80%Cr - 0.40% Mo heat resistant 13 CrMo44 ferritic steel [Perez et al 1998b] was studied in air for 144 hours under isothermal conditions at 1173K and 973K respectively. Using Auger Electron

Spectroscopy (AES), Scanning Electron Microscopy (SEM), Energy Dispersive Spectrometry (EDS), and X-Ray Diffractometry (XRD) techniques to characterize the implanted surfaces and the corrosion products formed, it was observed in the case of 18Cr8Ni steel, that the implanted Si and Ce significantly improved protection against oxidation of the alloy by enhanced Cr transport, while Mo gave rise to an accelerated oxidation due to the formation of volatile MoO<sub>3</sub> species. In the case of 13CrMo44 steel, silicon enhances selective oxidation of Cr and a more protective oxide scale was found to grow. However, Ce<sup>+</sup> caused cracking and spalling of the oxide layers formed at high temperature.

Generally, ion implantation of metals causes an increase in the atomic density of the implanted surface layers by introducing radiation damage and adding further ions. These combined to produce compaction of the surface layer. The compaction "case hardens" the surface, closes any microcracks and locks in the surface grains. The compaction also reduces the number of surfaces or crack sites suitable for chemical attack. In this way corrosion resistance of the metal is enhanced.

#### PRODUCTION OF LOW - FRICTION AND WEAR RESISTANT METAL SURFACES BY ION IMPLANTATION

Friction and wear of metal or metallic alloy surfaces cause a loss of surface materials. The conventional method of reducing friction and wear is to apply fluids (e.g oil) or solid (dry) lubricants (e.g paints, coatings, etc) to the metal or alloy surfaces. Moreover, under dry lubrication, wear-resistant metal surfaces can be obtained using the methods of case hardening, alloying, and plating. Although a reasonable measure of success has been achieved using these conventional treatments of metal or alloy surfaces, some problems that have been identified are;

- i. Lubricants may cause undesirable chemical changes in the engineering material surfaces since frictional forces can induce changes in metal surface temperature leading to various chemical reactions with the surrounding atmosphere.
- ii. Under high temperature conditions, solid lubricants with their low vapour pressure, which are applied as thin coatings with some form of binders often peel off or we have accumulation of soft wear debris.
- iii. Under certain conditions/environments, fluid lubricants containing sulphur may degrade to tarnish copper, forming copper sulphide. The tarnished copper surface makes copper tubes tear during drawing in the factory.

Because of the problems enumerated above, surface modification by implantation of foreign atoms was tried and found to reduce friction and wear of metal surfaces depending on the type of foreign atoms used. (Pope et al, 1984).

The effects of dual implantation of Titanium ( $90 - 180 \text{ keV}$ ,  $2 \times 10^{15} \text{ Ti}^+ / \text{mm}^2$ ) and Carbon ( $30 \text{ keV}$ ,  $2 \times 10^{15} \text{ C}^+ / \text{mm}^2$ ); and Nitrogen ( $2 \times 10^{15} \text{ N}^+ / \text{mm}^2$ ,  $50 \text{ keV}$ ) into 440C stainless steel, on the friction and wear were investigated (Pope et al, 1984) using pin - on - disc configuration. The results are shown in figure 1. Friction coefficients were measured continuously and steady state values reached near the end of 1000 unidirectional cycles were considered. Wear was determined after 1000 cycles by measuring the mean Maximum Wear Depth (MWD)

defined as the distance from the original surface to the deepest part of the profile. In a nutshell, their results showed that dual implantation of Ti and C into 440C stainless steel reduced friction coefficients by  $\sim 40\%$  for loads  $\leq 600\text{g}$ , and wear by  $>80\%$ , compared to unimplanted 440C steel, for Hertzian stresses as large as  $2900 \text{ Mpa}$  ( $\sim 800\text{g}$ ). The amorphous layer produced by these dual implant is believed to reduce friction and wear. Implantation of  $2 \times 10^{15} \text{ N}^+ / \text{mm}^2$ ,  $50 \text{ keV}$  into 440C steel reduces friction slightly ( $25\%$ ) for Hertzian stresses  $< 1840 \text{ Mpa}$ ,

TABLE 1. IMPROVEMENTS IN WEAR LIFETIME OBTAINED BY NITROGEN IMPLANTATION  
[ Hirvonen 1984 ]

APPLICATION	MATERIAL	LIFETIME INCREASES, ADDITIONAL BENEFITS
Scoring Die for Aluminium Beverage Can Lids	D2 Tool Steel	3X
Forming Die for Aluminium Beverage Can Bottoms	D2 Steel	Lowered wear
Wire Guides	Hard Cr Plate	3X without significant wear
Finishing Rolls for Cu Rod	H-13 Steel	Negligible wear after 3X normal lifetime; Improved surface finish of product
Paper Slitters	1.6% Cr 1% C Steel	2X
Punches for acetate sheet	Cr-plated steel	Improved product
Taps for phenolic resin	M2 high speed steel	Up to 5X
Tool inserts	4% Ni 1% Cr Steel	Reduced tool corrosion by 3X
Forming Tools	12% Cr 2% C Steel	Greatly reduced adhesive wear
Fuel injectors and metering pump	Tool steel	$> 100\text{X}$ in engine tests
Plastic Cutting	Diamond tools	2X - 4X lifetime
Hip joint prostheses	Ti / 6Al / 4V	100X in laboratory tests
Printed Circuit Board Drills	WC - Co	3X, Lowered smearing with 50% lower operating temperature, reduced breakage
Dental Drills	WC - Co	2X - 3X, significantly lower cutting force required
Punch and die sets for sheet steel laminations	WC - Co	4X - 6X, improvement remains after resharpening
Precision punches for electronic parts	WC - 15% Co	Greater than 2X.
Swagins dies, press tools for wheels	WC - Co	2X
Dies for copper rod	WC - 6% Co	5X throughput, improved surface finish
Dies for steel wire	WC - 6% Co	3X
Sheet steel chopper blades	WC - Co	Greater than 3X, reduced chipping
Injection molding nozzle, molds screws, gate pads for glass and mineral filled plastics	Tools steels and hard Cr plated steels.	4X - 6X
N into thermally nitrated steel molds	Tool steels	Combination better than either process alone
Profile Hot Die for plastic extrusion	P-20 Tool steel	4X

NB: 2X means two times

which disappeared for loads  $\geq 400$ g. However, nitrogen implantation provides little or no reduction in wear. It seems that any hard nitride particles produced by nitrogen do not modify the hardness of 440C steel significantly. (figure 1.)

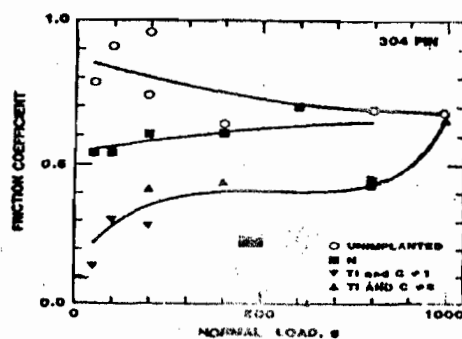
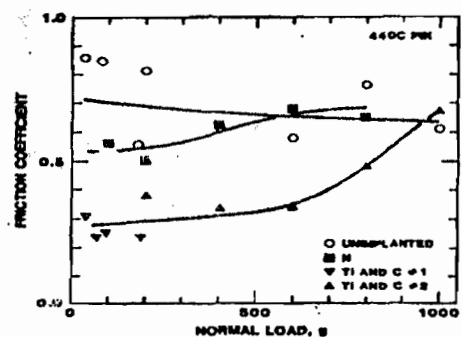
Hartley et al 1973 have also shown experimentally that modification of the wear of steel surfaces is dependent on the type of ions implanted. Selected ion species like  $\text{Sn}^+$ ,  $\text{Pb}^+$ ,  $\text{Mo}^+$ ,  $\text{In}^+$ ,  $\text{Ag}^+$  and  $\text{Kr}^+$ , have been implanted into polished or ground specimen of a case-hardened steel-EN-352 to doses between  $10^{16}$  and  $10^{17}$  ions/cm<sup>2</sup>. Friction, wear and chemical changes were measured as a loaded tungsten carbide ball is driven repeatedly across an implanted surface. Many of the implanted metals produced a reduction in the coefficient of friction of the En 352 steel surface. Krypton (inert gas ions) did not produce a change in the coefficient of friction whilst Pb increased the coefficient of friction because it is believed to be weakly bonded to the surface, so it sheared.

Hard and wear resistant aluminium alloys are very useful in aeronautical and molding industries. Nitrogen implanted into aluminium alloys have been shown to improve the alloys' hardness and wear resistance as the nitrogen ion doses increased [Rodriguez et al 1999]. Post implantation thermal annealing which is meant to improve crystallinity of the implanted layers also enhances the wear resistance and hardness. Ion implantation is a good technique for treating industrial tools, if such tools cannot withstand the high temperatures associated with conventional thermal processing because of possible distortion, or there is a need to avoid dimensional changes of the tools. Hence nitrogen implantation has been used to increase the wear lifetime of Cobalt-cemented tungsten carbide dental drills. Table 1. gives information on other nitrogen implanted industrial tools. ( Hirvonen 1984 ),

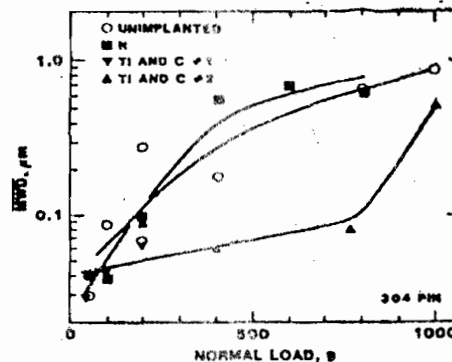
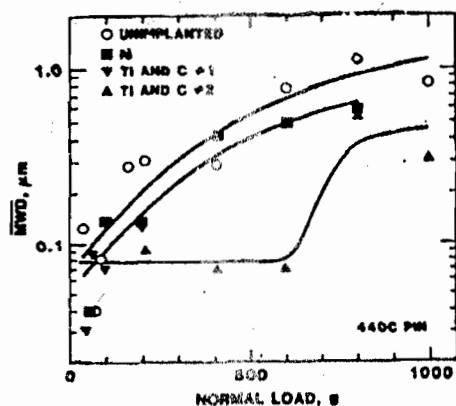
### MATERIAL SURFACE HARDENING BY ION IMPLANTATION

The main goal of design and materials engineers is to create stronger and tougher (i.e hard) engineering materials to enhance their performance and prolong their lifetime when in service. Hardening of engineering materials involves impeding the movement of dislocations by making alterations to the structure on approximately the atomic scale ( Higgins, 1993 ; Grounds, 1974 ). Ion implantation is suitable for creating these impediments to dislocation motion, which take the form of impurity atoms, defects, precipitates, e.t.c.

Low-energy ion implantation is commonly used as a hardening technique to obtain point defects hardening, defect complexes hardening, solid solution hardening due to implanted foreign atoms, and strain hardening. Surface hardness of metals has been significantly increased by low energy nitrogen or carbon implantation ( Bredell and Malherbe, 1985). Hardening mechanism of implanted atoms can be explained as follows: The implanted impurity atoms



(a)



(b)

Figure 1:

- (a) Friction coefficient versus normal load from implanted 400C, the average fluctuation in friction coefficient during one revolution for all tests was  $\pm 0.06$ . (Pope et al 1984)
- (b) MWD versus normal load for implanted 440C stainless steel, with an average coefficient of variation of  $\pm 0.3$  (Pope et al 1984)

reside in the crystalline host matrix either on substitutional or interstitial positions. They produce lattice

distortion when the substitutional atoms are either larger or smaller than matrix atoms or the interstitial atoms are larger than the interstitial sites they occupy. The stress fields associated with these distortions interact with the stress field of a moving dislocation, causing the motion of the dislocation to be impeded. This type of hardening is known as solid solution hardening. Implanted atom induced point defects also harden the material since they impede the motion of dislocations. Defect generation rates by ion implantation are high, and dependent on ion species (ion size), energy and dose. Increase in ion dose can lead to saturation of damage production and enhancement of hardness. The strain fields associated with the defects and implanted atoms also enhance the hardness.

Carbon ions were implanted at high doses ( $\leq 8 \times 10^{18}$  ions/cm<sup>2</sup>) in AISI 440C martensitic stainless steel and Ti6Al4V (Titanium - Aluminium - Vanadium) alloy substrates to form carbon layers without a sharp interface with the substrates (Viviente et al, 1999). From X-Ray photoelectron spectroscopy (XPS) analysis, and for ion dose of  $4 \times 10^{18}$  C<sup>+</sup>/cm<sup>2</sup>, a carbon layer containing more than 85 at %C was formed in the near surface region for both substrates. Surface hardening occurred for all ion implantation conditions for ion doses  $\leq 10^{18}$  cm<sup>-2</sup>. However, for ion doses  $> 10^{18}$  cm<sup>-2</sup>, the stainless steel showed softening.

High energy ion implantation (MeV) makes it possible to produce thick distorted (hardened) layers in which the influences of different defect types and of implanted atoms can be differentiated. Point defects are located within the near surface layer and defect complexes within the buried highly damaged layer. Point defect hardening acts as a second hardening mechanism, in addition to solid solution hardening. 1 MeV,  $1 \times 10^{18}$  N<sup>+</sup>/cm<sup>2</sup> implanted into pure Ti made the peak of the nitrogen concentration to be located at a depth of 0.94  $\mu$ m. This deep implant caused an increase in surface hardness and load-carrying ability of 30% compared to low-energy implants (35-200keV). Also a decrease in the sputtering yield with increasing ion energy has been observed.

## SYNTHESIS OF ENGINEERING MATERIALS BY ION IMPLANTATION.

### Surface alloy formation

Three major reasons for alloying two or more metals are to improve the mechanical properties of metals such as tensile strength, yield point, and hardness; lower the cost and obtain special properties for a particular application. Conventional alloys which involve high temperature treatments are difficult to prepare, and incorporation of dopants is very restricted. Chemical purity of ion implantation method plus the control over the implanted ion distribution in the substrate ensure that many of the metallurgical problems in alloy production are avoided. Thus in ion im-

planted alloys, the choice of dopants is wider, and solid solubilities or atomic diffusion rates normally considered critical in thermal alloying are no constraints using ion implantation. Surface alloys are formed either by direct implantation of the atoms of interest into the substrates or ion beam mixing technique. However, major limitations of ion implantation method for production of alloys, which may make it not to be adequate or appropriate for production of final alloys for general applications are the increase in implantation times with ion dose, depth of penetration which is somehow shallow ( $\sim \mu$ m) and the maximum implant concentration which is determined largely by sputtering processes, and in some cases by radiation enhanced diffusion (R.E.D.) [Liau and Mayer, 1980].

### Alloy formation by direct ion implantation of substrates

Sartwell, et al, 1976 have formed surface binary alloys by direct implantation of low energy (25keV) nickel, chromium and aluminium ions of various doses into polycrystalline iron. The implanted layers heat treated at 500°C are Fe - 6.6 at% Cr., Fe - 13.3 at% Cr, Fe - 18 at% Cr, Fe - 6.6 at% Ni, and Fe - 6.6 at% Al. These alloys possess high corrosion resistance. Many binary alloys like Cu-Ni, Cu-Au were created in single crystalline copper held at room temperature using ion implantation. [Borders and Poate, 1976; Good and Dearnaley, 1976] Some of the dopants (e.g. Au) which are 100% substitutional in Cu. Ion implanted amorphous intermetallic alloys like Ni-Dy (30at%), have also been produced at room temperature [Andrew et al, 1976]

### Alloy formation by ion beam mixing technique

In this technique a film of metal is either evaporated or sputter deposited on the target surface and inert gas ions are implanted through the film to promote inter-diffusion across the film - substrate interface. This technique has been used to obtain surface alloys (e.g Cu - Zn, Cu - Sn) of a broad range of composition by implanting inert gas ions (Xe<sup>++</sup>, Kr<sup>++</sup>, e.t.c) through evaporated or sputter deposited metal films (Zn or Sn) on the substrate (Cu) to promote interdiffusion across the film - substrate interface (Liau, 1980). The thickness of the surface alloy can be increased by repeating the process.

### Superconducting alloys

Development of superconducting alloys using the conventional metallurgical methods can be difficult and time consuming, and there are many problems of solubility and phase stability to contend with. Ion implantation has been used as an alternative method. (Dearnaley et al, 1973)

Ion implantation has been used to synthesize superconducting alloy (Nb<sub>3</sub>Sn). Niobium (Nb) tapes measuring 3mm x 10  $\mu$ m each were bombarded with 100KeV Sn<sup>+</sup> ions to doses such that a mean concen-

tration of 25 at % was implanted to a depth of about 1000Å. A thin surface layer of Nb<sub>3</sub>Sn precipitates was produced in the Niobium which was thermally annealed at 950°C in argon at 360 torr for times up to 20 minutes. Nb<sub>3</sub>Sn is an important superconductor, with a high critical field (>200K<sub>0</sub>), a high current density (>10<sup>6</sup>Acm<sup>-2</sup>) and a high superconducting transition temperature T<sub>c</sub> of 18.5K. Concerning the mechanism responsible for the observed superconductivity, it was believed that either a large concentration of fine Nb<sub>3</sub>Sn precipitates within the Nb surface region would screen the underlying Nb from the penetration of the magnetic field by pinning the flux vortices at the surface to enhance its superconducting properties or a fine distribution of Nb<sub>3</sub>Sn precipitates could carry a superconducting current by a tunneling phenomenon.

Properties of superconducting alloys are generally sensitive to their compositions, and specifically in some cases, the optimum properties occur for a metastable state [Rose-innes and Rhoderick 1969]. In these cases ion implantation technique is capable of producing compositions not attainable by other means, as demonstrated by work done by some investigators on the Pd - H - noble metal superconductors [Stritzker 1974]. One hydrogen (H) per metal atom is needed to obtain a maximum T<sub>c</sub>, a concentration far above the H solubility. This problem, was circumvented by implanting H into the Pd - noble metal alloys at 4K, to obtain concentrations in excess of one H per metal atom. Thus high T<sub>c</sub> ~ 17K was obtained in Pd - Cu alloy.

#### USE OF ION IMPLANTATION FOR BASIC RESEARCH IN METALLURGY

Ion implantation has been used to investigate intermetallic alloys and radiation damage at low and high temperatures (Borders, 1976 ; Good and Dearnaley, 1976 ; Robinson and Young, 1976 ). In the low temperature regime (e.g room temperature), ion implantation is used to create and study new metastable phases, which include substitutional solid solutions of immiscible elements, amorphous alloys, and improved superconductors of nonequilibrium compositions, because lack of atomic diffusion at low temperatures makes a metastable condition induced by ion implantation persist. Ion implantation has also been used to study equilibrium alloys in the high temperature regime (e.g 400 - 800°C), where appreciable atomic diffusion occurs over experimental times (Dearnaley et al chap. 6 1973). The atomic diffusion is monitored, and the amount of disorder in the alloy, the substitutional fractions of the solute atoms and their depth are determined using 2 MeV He<sup>+</sup> ion backscattering (RBS) combined with channeling (Chu et al, 1978) and transmission electron microscopy (TEM) measurements. Solid solubilities of the solutes are derived from the measured substitutional fractions, i.e composition versus depth profile of the solutes can be measured. Generally, the results of these investigations have revealed new information about phase diagrams, diffusion rates, and solubility

of solutes in the host matrix.

Implantation and diffusion of copper (100keV, 4-5x10<sup>16</sup>Cu<sup>+</sup>/cm<sup>2</sup>) in single-crystalline Beryllium has been studied (Myers et al, 1974). Concentration versus depth profile up to ~ 2 μm was determined using 2 MeV, He<sup>+</sup> ion backscattering, following isochronal anneals (400 - 650°C) of the copper implanted Beryllium. Comparison of the profile obtained with the Linhard, Scharff and Schiott(LSS) theory (Linhart et al, 1968) showed a strong temperature dependent diffusion rate for copper in Beryllium.

Investigations similar to the one described above have been carried out on binary alloys created at room temperature in single crystal copper [e.g Cu - Au, Cu - W, e.t.c ] (Borders and Poate, 1976 ; Good and Dearnaley, 1976). High substitutionality for many insoluble elements (e.g. W) in copper were obtained.

The suitability or otherwise of many materials and elements in the periodic table for the production of superconductors have been studied (Dearnaley, et al, 1973).

#### CONCLUSIONS

1. This review has highlighted the work done to synthesize alloys and improve the hardness, corrosion, friction and wear behaviour of a variety of commercial grade engineering alloys for special applications by modifying the surface composition and structures using ion beam mixing and direct ion implantation of suitable impurity atoms (e.g. Cr, Mo, Ni, etc).
2. A major limitation to surface alloying by ion implantation is the depth of penetration of implanted ions which is relatively shallow (~μm). This makes the implanted layers very useful in relatively non-abrasive environments for technological applications where modification of surface properties of engineering alloys, without change of the bulk properties or alloy dimensions are very desirable. Examples are steel components such as gears, shafts, e.t.c.
3. Ion implantation is being used as an important research tool in basic research in metallurgy. Implantation is used to incorporate diffusing elements into materials of interest with better precision. Different implanted metal layers are heat-treated to obtain information about atomic diffusion rates, solubility of a solute in the host matrix, phase diagrams etc using Rutherford Backscattering Spectrometry (RBS) combined with channelling technique, and Transmission Electron Microscopy (TEM) measurements.
4. Ion implantation technology lends itself



to automation leading to a large scale processing of engineering materials (e.g. domestic and industrial tools). There is therefore the need to acquire ion implantation technology in iron and steel industries and related establishments in Nigeria, with dedicated ion accelerators (implanters) as the major equipment for commercial utilization. The utilization includes reduced surface friction and improved wear resistance of ion implanted industrial and domestic tools, leading to the extension of their wear lifetimes. Nigeria will then be self-reliant and self-sufficient in the production of high quality corrosion resistant low-friction and wear-resistant commercial grade engineering alloys, metals, etc. A short "return-on-investment time" is expected.

#### ACKNOWLEDGEMENT

The author would like to thank his colleagues at Obafemi Awolowo University, Ile - Ife, for useful discussions and the staff of the Central Library of the Central Research Institute for Physics, KFKI, Budapest, Hungary, for the use of their Library facilities during the author's stay at KFKI as an IAEA Fellow.

#### REFERENCES

- Akintunde J.A., 1997. Ion implantation and its applications in GaAs device technology. *Nig. J. Renew. Energy*, 5 (1&2): 70-84.
- Al-Saffar A.H., Ashworth V., Bairamov, Chivers D.J., Grant W.A. and Procter R.P.M., 1980. The effect of molybdenum ion implantation on the general and pitting corrosion behaviour of pure Al and a high strength Al alloy. *Corrosion Sci.* 20, 127-144.
- Andrew R., Grant W.A., Grundy P.J., William J.S., and Chadderton L.T., 1976. Non-Crystallinity of ion irradiated metals. *Nature*, 262, 380-385.
- Ashworth V; Baxter D; Grant W.A., and Procter R.P.M., 1977. Effect of ion implantation on the corrosion behaviour of pure iron: Tantalum implantation. *Corrosion Sci.* 17, No. 12, 947-960.
- Borders J.A. and Poate J.M., 1976. Lattice site location of ion implanted impurities in copper and other fcc metals. *Phys. Rev. B.* 13, 969-979.
- Bredell, L.J. and Malherbe J.B., 1985. Microhardness of a nitrogen implanted layer on mild steel. *Thin solid films* 125, L25-27.
- Chu W.K., Mayer J.W., Nicolet M.A., 1978. Back-scattering Spectrometry, Academic Press, N.Y.
- Clayton C.R. and Wang Y.F., 1983. Modification of the corrosion behaviour of engineering alloys by ion implantation. *IEEE Transactions on Nuclear Science.* NS-30, No. 2, 1752-1755.
- Coudurier L, Hopkins D.W. and Wilkomirsky I., 1978. *Fundamentals of metallurgical processes*, Pergamon Press, New York.
- Dearnaley G, Freeman J.H, Nelson R.S, Stephen J., 1973. Ion implantation. North Holland Publishing Company, Amsterdam. 802pp.
- Good D.K. and Dearnaley G., 1976. Ion implanted surface alloys in copper and aluminium in Carter G, Collins J.S and Grant W.A: *Applications of ion beams to materials* (Inst. Phys. Conf. No. 28, London and Bristol) 196-203.
- Grounds, D.M. 1974. *An introduction to metallurgy*, London Caledonian Press Ltd. Watford, Herts. 54pp.
- Hartley N.E.W., Dearnaley G, and Turner J.F., 1973. Frictional changes induced by the ion implantation of steel in Crowder B.L. (Editor). *Ion Implantation in semiconductors and other materials*. Plenum press. New York. 423-436.
- Higgins, R.A., 1993. *Engineering Metallurgy 6th Edition*. Edward Arnold Press, Sydney. 550pp
- Hirvonen J.K., 1984. Industrial applications of ion implantation. *Material Research Society Symp. Proc.* 27, 621 - 629.
- Kim Y.J. and Andresen P.L., 1998. Application of insulated protective coatings for reduction of corrosion potential of type 304 stainless steel in high temperature water. *Corrosion (Houston)* 54, No. 12, 1012-1017.
- Liau Z.L. and Mayer J.W., 1980. In *Ion implantation V.18: Treatise on material Science and technology*. (Hirvonen, H.K. ed.). Acad. Press. N.Y.
- Linhard J., Scharff M., and Schiott H., 1968. Range concepts and heavy ions ranges. *Dans Matt-Fys. Meddr.* 36(10), 33-46.
- Masahiko Kato, R. Wang, and Kasakejiro Na, 1999. Effects of  $N_2^+$  ion implantation on the corrosion behaviours of pure titanium. *Zairyo*, 48, No. 5, 483-488 (Japan)
- Moreland P.J., and Rowlands J.C., 1977. Technique and instrumentation for polarization resistance measurements. *Corrosion Journal*, 12, No. 2, 72-79.
- Murarka S.P. and Peckerar M.C., 1988. *Electronic materials: Science and Technology*, Academic Press Inc. New York, Chap. 5.

- Myers S.M., Picraux S.T., and Prevender T.S., 1974. Study of Cu diffusion in Be using ion backscattering. *Phys. Rev. B*, 9, 3953-3957.
- Perez F.J., Otero E., Hierro M.P., Gomez G., Pedraza F., De seqovia J.L., Roman E., 1998. High temperature corrosion protection of austenitic AISI 304 stainless steel by Si, Mo, and Ce ion implantation. *Surface coating Technol.* 108-109, 127-131.
- Perez F.J., Otero E., Hierro M.P. Gomez G., Pedraza F., De seqovia J.L., Roman E., 1998. Corrosion protection of 13 CrMo44 heat-resistant ferritic steel by silicon and carium ion implantation for high temperature applications. *Ibid* 121-126.
- Popo, L.E, Yost, F.G, Follstaedt, D.M, Picraux, S.T and Knapp, J.A., 1984. Friction and Wear reduction of 440C stainless steel by ion implantation, *Mat. Res. Soc. Symp. Proc. Vol 27*, pp661 - 666, Elsevier Science Publishing Co. Inc, N.Y.
- Robinson M.T. and Young F.W, 1976 (Nat. Tech. Info. Serv, U.S. Dept of Commerce, Springfield, Va 1976), Rept. on ion implantation and intermetallic alloys No CONF - 751006.
- Rodriguez R.J, Sanz A; Medrano A; Garcia-Lorentz J.A., 1999. Tribological properties of ion implanted aluminium alloys. *Vacuum* 52, Nos 1 & 2, 187-192.
- Rose - Innes A.C. and Rhoderick E.H., 1969. Introduction to superconductivity. Pergamon Press. London. 229pp.
- Rysael H. and Glawischnig H., 1983. Ion Implantation: Equipment and Techniques, Springer-Verlag, Berlin, Heidelberg, New York. 556pp.
- Rysael H. and Ruge J., 1986. Ion implantation, Wiley and sons, New York, chap. 1
- Sartwell, B.D, Campbell, A.B, and Needham, P.B, 1976. Formation of corrosion - resistant surface alloys by implantation of low energy Ni and Cr ions into polycrystalline iron. In ion implantation in semiconductors ed: Chernow F., Borders J.A, and Brice D.K, Plenum Press N.Y and London Pp 201 - 211,
- Stritzker B., 1974. High superconducting transition temperature in the palladium noble metal-hydrogen system. *Z. Physik* 268, 261-268.
- Svensson J.E. and Johansson, L.G., 1993. Laboratory Study of the initial stages of the atmospheric corrosion of zinc in the presence of NaCl: influence of SiO<sub>2</sub> and NO<sub>2</sub>. *Corrosion Sci.* 34, 721-741.
- Thomae R.W., 1990. Recent developments in ion implantation accelerators. *Nuclear Instruments and methods in Phys. Research B50*, 444-454.
- Viviente J.L., Garcia A, Loinaz A, Alonso F, Onate J.I., 1999. Carbon layers formed on steel and Ti alloys after ion implantation of C<sup>+</sup> at very high doses. *Vacuum* 52, 141 -146
- Wang Y.F, Clayton C.R, Hubler G.K., Lucke W.H. and Hirvonen J.K., 1979. Application of ion implantation for the improvement of localized corrosion resistance of M50 bearing steel. *Thin solid films* 63, 11-18.
- Ziegler J.F., Biersack J.P., and Littmark U., 1985. The stopping and range of ions in solids,. Pergamon Press, New York.