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Ion Implantation as A New Surface Treatment Technology

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Ion implantation is a new technique (presently used commercially in the semiconductor industry) for treating the surface of metals that has shown a potential for producing orders of magnitude improvement in wear and corrosion applications. Improvements in the surfaces of optical elements and novel optical components may also be possible through use of the process. The objective of the present study was to assess the value of ion implantation in applications of interest to the Department of Defense and the National Aeronautics and Space Administration. Because the application of ion → over

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The report begins with a very brief summary of the Committee's principal conclusions and recommendations. These subjects are discussed at greater length in Chapter 10, the last chapter of this report.

Chapter 1 introduces the subject of ion implantation by describing its use in the semiconductor industry and comparing requirements for the treatment of metals and semiconductors. Chapters 2 and 3 deal with existing knowledge concerning the improvement of the mechanical and corrosion characteristics of metal surfaces by ion implantation. Chapter 4 discusses the application of ion implantation to the modification of optical properties of materials. Chapter 5 compares ion implantation with ion plating, which is emerging as another useful surface treatment technology.

Chapter 6 discusses pulsed annealing, a newly discovered technique for modifying a surface after ion implantation. Chapter 7 illustrates how implantation of one metal species into another can be used to explore the metallurgy of novel systems, even though the alloys formed may eventually be produced by more conventional means. Chapter 8 briefly discusses the unsatisfactory state of available methods for accurately predicting the location of implanted ions in a substrate. Chapter 9 concerns the equipment required to practice ion implantation. As mentioned, Chapter 10 gives the committee's conclusions and recommendations in some detail.

The references are intended to be illustrative and are only a sample of the literature of the field. The proceedings of recent conferences provide surveys of ongoing activities in ion implantation, and a short bibliography of these is appended.

ION IMPLANTATION AS A NEW SURFACE TREATMENT TECHNOLOGY

Report of

Committee on Ion Implantation and
Competing New Surface Treatment Technologies

NATIONAL MATERIALS ADVISORY BOARD
Commission on Sociotechnical Systems
National Research Council

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The project that is the subject of this report was approved by the Governing Board of the National Research Council, whose members are drawn from the Councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the Committee responsible for the report were chosen for their special competence and with regard for appropriate balance.

This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, National Academy of Engineering, and the Institute of Medicine.

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ABSTRACT

Ion implantation is a new technique (presently used commercially in the semiconductor industry) for treating the surface of metals that has shown a potential for producing orders of magnitude improvement in wear and corrosion applications. Improvements in the surfaces of optical elements and novel optical components may also be possible through use of the process. The objective of the present study was to assess the value of ion implantation in applications of interest to the Department of Defense and the National Aeronautics and Space Administration. Because the application of ion implantation to metallurgy is very new, little definitive information is available. The general feeling of this committee is that the results reported are promising enough to justify a vigorous pursuit of the knowledge that will permit a full evaluation of the more promising possibilities, and perhaps, a realization of the application of ion implantation to improve components.

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SUMMARY

Ion implantation has become a useful part of semiconductor processing technology. Exploratory studies of the effects of ion implantation on such surface properties of metals as hardness, wear, and corrosion have discovered cases in which remarkable beneficial effects can be produced.

Recommendations

1. Ion implantation has shown a potential for producing significant improvement in rates of wear and corrosion of metal components. It is recommended that a task force in the Department of Defense identify applications in which surface properties do not meet DoD needs and evaluate the possible use of ion implantation in such cases.

2. Ion implantation is likely to be most economically feasible when applied to small components. The application of ion implantation to the improvement of metal cutting tool life deserves special attention. A variety of new alloying additions should be tried.

3. In the field of corrosion, there are also many opportunities for the study of alloying additions that cannot be added by conventional metallurgical techniques. Thus, further work should be done on previously unexplored alloying additions.

4. It is difficult to base generalizations and predictions upon the existing knowledge because the atomistic phenomena that are responsible for the effects are often not well understood. Research aimed at unraveling the mechanisms that underlie known beneficial effects of ion implantation in metals should be undertaken.

5. An adequate understanding of the atomic phenomena that cause the observed improvements in properties would be greatly accelerated by the involvement of university departments of metallurgy in the needed research. Access to ion implantation equipment is likely to be

a barrier to the participation of university departments in implantation metallurgy. Funding arrangements that insure access to ion accelerators by university departments of metallurgy should be favorably considered.

6. Experimental and theoretical research to increase the reliability of predictions of the range and distribution of implanted ions is desirable.

7. There are opportunities to conserve materials in short supply by replacing bulk alloys and electroplated coatings with ion implanted layers. Quantitative estimates of the potential impact of ion implantation on requirements for critical materials are needed.

8. Ion plating is a technology largely complementary to ion implantation. The coatings produced by ion plating are conventional in composition and structure, and do not raise the pressing basic issues that are encountered in ion implantation metallurgy. Outstanding questions concern the mechanisms that produce the good adherence of plated layers and that control the microstructure of the coating. Research oriented towards understanding the factors that are responsible for the excellent adhesion and that determine the microstructure of ion plated coatings should be undertaken.

Chapter 1

INTRODUCTION: MODIFICATION OF MATERIAL PROPERTIES OF ION IMPLANTATION

Ion implantation is the process of introducing alloying elements into a host material by accelerating them to a high energy (at least tens of kilovolts) and allowing them to strike the surface of the host. The impinging atoms penetrate into the substrate material to a depth of 0.01 to 1 micron, depending on the atomic number and energy of the atom, and create a thin alloyed surface layer on the substrate. The process differs from others such as electroplating in that it does not produce a discrete coating; rather, it alters the chemical composition near the surface of the base material.

In recent years, the electronics industry has made increasing use of ion implantation as a method of doping semiconductors. Since the number of ions implanted is determined by the charge transferred to the substrate and their depth distribution by the incident energy, ion implantation has greatly improved the controllability and reproducibility of certain semiconductor device processing operations. In addition, ion implantation processes do not require the high temperatures needed to introduce impurities by diffusion, so that limitations arising from the changes produced in materials by high temperatures are eased. Ion implantation is also used in electronics to change the magnetic properties of substrates used for magnetic bubble devices.

The advantageous use of ion implantation in semiconductor processing has led to the development of safe, reliable, easy-to-operate equipment for performing implantations and has led to wide availability of accelerators for implantation research. As might be expected, the existence of equipment and people experienced in ion implantation techniques has led to studies of implantation into many materials other than semiconductors. Such experiments have shown that the properties of surfaces with regard to such phenomena as friction, wear, fatigue, and corrosion can be changed by ion implantation and have uncovered exciting possibilities for improving the functional capability of materials in a variety of applications. However, few of these possibilities have been explored in enough detail to verify that a useful new technology might develop. Furthermore, the results obtained are frequently so unusual and unexpected that they defy explanation in terms of simple atomistic models. Thus, metallurgical and solid-state theory is not a complete guide to what may be expected in the future.

Nevertheless, one can be confident that research on novel applications of ion implantation will continue and grow. The striking changes in properties that can be achieved, combined with the advantages of ion implantation, as compared with alternative methods of treating surfaces, guarantee lasting interest in the topic. The following advantages can be cited for ion implantation:

- A variety of ion species can be implanted with the same basic apparatus. Almost all elements of the periodic table have been implanted.
- Ion implantation is a low-temperature process. It can often be added to the end of a production line without affecting existing operations.
- The surface of finished products can be treated without introducing significant dimensional changes and without changing bulk properties.
- The process is easily controlled through the electrical signals applied to the accelerator.
- Novel nonequilibrium structures and metallurgical phases with properties that cannot be duplicated in bulk material can be produced at the surface.
- Ion implantation creates no problems of disposal of waste products, as does electroplating.
- The absence of a discontinous interface between the implanted surface layer and the bulk leads to excellent adhesion of the implanted layer.

In addition to these potential advantages of the application of ion implantation to technology, the preparation of nonequilibrium phases offers new opportunities for metallurgical research. Even in the absence of engineering applications, these basic studies can be expected to continue.

Some phenomena that are encountered in implanted layers and that can play a role in the production of unusual properties are as follows:

- As mentioned, new metallurgical phases with previously unknown properties can be formed. In certain cases, such as heavy implantations of tantalum in copper or phosphorous in iron, amorphous or glassy phases can be formed.
- If the implanted atoms are mobile, inclusions and precipitates can be formed. For example, implanted argon and helium atoms are insoluble in metals and may form bubbles.

- The composition of a surface layer can be changed by differential sputtering caused by the implanted ions.
- Damage and high concentrations of lattice defects, resulting from atomic displacements produced by the incident atoms, can change the chemical reactivity and mechanical hardness of a treated surface.
- Implantation can enhance the diffusion of impurities already deposited in a substrate, presumably through the motion of the high concentrations of lattice defects produced by the incident ions.
- Cooperative effects of two implanted species can occur; for example, implantations of both molybdenum and sulfur into steels seem to have an effect similar to lubrication with MoS_2.
- Surface layers, either contaminants or deliberately deposited layers, can be driven into the substrate by impinging atoms.
- Surface layers with conventional (in the sense that they are the same as in bulk material of the same composition) chemical, optical, magnetic, and mechanical properties may be produced.

Ion implantation must be compared with other methods of treating surfaces. Treatments such as carburizing and nitriding involve diffusion of impurities into a material at high temperatures. Such processes can easily provide a deeper penetration of the impurity than does ion implantation, and are indispensable when deep penetration is required. On the other hand, the high temperature required by diffusion processes can cause changes in the bulk of the substrate and may require finishing of the part after heat treatment to achieve precise dimensional control.

Ion implantation should not be confused with ion plating. The latter process applies a coating with negligible penetration into the substrate due to the applied voltage. A more detailed comparison of ion plating with ion implantation is given in Chapter 5 of this report.

Application of coatings by such means as electroplating and evaporation also has many uses. Adhesion of the coating to the substrate and inclusion of contaminants at the interface can be problems with these methods. The absence of a sharp interface is a basic advantage of ion implantation and reduces susceptibility to the same problems.

Naturally, useful conventional processes will not be easily displaced. Ion implantation requires expensive tooling and provides only low rates of material deposition. It is not likely to replace other methods except in high-value applications where more conventional processes are unsatisfactory.

Some of the limitations of ion implantation may be seen by comparing the semiconductor and metallurgical applications of the technique.

For electronic applications, including not only doping of semiconductors but also integrated optics and magnetic bubble devices, a single planar surface is implanted. Metallurgical applications will often require implantation of all exterior surfaces of a part and thus mechanical manipulation of substrates in the implanter. Certain portions of the surface of complex shapes may be inaccessible to the line-of-sight capability of particle accelerators. Thus it appears that ion implantation with anything resembling conventional equipment will not be applicable to surfaces such as the interior of gun barrels, for example.

Implantations in semiconductors are almost always intended to produce volume concentrations of less than 0.1 atomic percent, and are frequently aimed at concentrations of less than one part per million. Nonsemiconductor applications are more likely to require concentrations of percents. The number of ions implanted per unit area is called the fluence. Thus, semiconductor applications call for fluences in the range of 10^{12} to 10^{16} per cm^2, whereas metallurgical applications will require fluences of 10^{14} to 10^{18} per cm^2. Equipment intended for nonsemiconductor implantations will have to deliver high beam currents.

In semiconductor applications, the workpiece into which ions are implanted is no larger than a wafer, an area of less than 100 cm^2. Areas of this magnitude are encountered in metallurgical applications--for example, a ball bearing or a lathe tool--and such applications may allow early penetration of ion implantation into technologies other than semiconductors. Other potential applications, such as enhancement of corrosion resistance, may involve areas of many square meters. Indeed, one can think of possible applications, such as inhibiting corrosion of a large structure, that require treatments of several thousand square meters. A new kind of tooling would obviously be required to utilize ion implantations in the potential large-scale applications.

High homogeneity is sought in semiconductor applications; that is, the concentration of the implanted species should not vary by more than a few percent over the surface of a wafer. Metallurgical requirements on homogeneity will probably be far less stringent.

The implantation of ions into semiconductors is usually patterned; that is, some areas of the substrate are covered by a mask that stops the incident ions before they enter the substrate. Blanket applications are more likely to be encountered in metallurgical applications, which thereby are freed of the use of masking technology.

A doped layer in which the implanted atoms are locally in an equilibrium phase is usually desired in semiconductor implantations. Thus, implantation into semiconductors is usually followed by a high temperature annealing treatment, which removes radiation damage through diffusion of lattice defects to defect sinks and recyrstallization of disturbed regions. Metallurgical implantations, on the other hand, are often oriented toward production of a nonequilibrium surface layer and avoid the annealing step.

The most promising nonelectronic applications of ion implantation appear to be in the areas of improving hardness or wear resistance, and decreasing susceptibility to corrosion. Other important nonsemiconductor applications, such as modifying the properties of magnetic films for bubble devices and integrated optics, have much in common with semiconductor applications. They involve patterned implantation of planar surfaces and areas in the semiconductor wafer range. Other optical applications are based on the ability of ion implantations to reduce the deterioration of metallic mirror surfaces.

A further motivation for the exploitation of ion implantation in certain alloy systems is the reduction of national reliance on foreign sources of metallic elements. The case of chromium has received particular attention [NMAB (1), and Covino, et al (2)]. For example, about 10^7 Kg of chromium is used annually in electroplating (1). Since ion-implanted layers will be hundreds or even one thousand times thinner than electroplated layers, this use of chromium might be substantially reduced by replacing plating by ion implantation. The treatment of finished parts by ion implantation may offer opportunities to displace bulk alloys of chromium in applications where electroplating is unsatisfactory because of the dimensional changes that it causes. However, it must be remembered that ion implantation is not likely to be applied to structures of very large size and the thin implanted layers may not be functionally equivalent. Quantitative estimates of the potential impact of ion implantation on the use of critical materials are needed.

In addition to its use in improving the properties of surfaces in applications, ion implantation has been used as a research tool for exploring the effect of alloying additions on surface properties, even if it is intended that the alloy be prepared in some other way in a production process.

Interest in applications of ion implantation exists throughout the world. As in the United States, applications in the rest of the world have centered on semiconductors. British workers at the Atomic Energy Research Established (AERE) at the Harwell Laboratory in Britain have led in the exploration of implantation to improve the mechanical properties of metals, and have attracted attention to nonelectronic applications. The British have also been in the forefront of work on corrosion. However, the United States leads in research on the metallurgical phenomena that underlie the desirable effects that can be produced. The discovery of laser annealing of ion-implanted surfaces is credited to workers in the USSR.

Studies of the metallurgical applications of ion implantation in the United States have been concentrated in university and federally-funded and government laboratories. Applied laboratories in industry and government will become increasingly involved as the capabilities of the technique for solving particular problems become better known. Indeed, the potential for impact on products is at least as great in metallurgical applications as it has been in semiconductor applications, where ion implantation is a step in the manufacture of over $1 billion worth of products each year. The cutting tool industry is of comparable magnitude. An improvement in tool life would be reflected in a reduced cost to DoD of many components.

No discussion of ion implantation would be complete without mention of the analytical tools that enable those in research and development laboratories to explore the atomistic nature of the phenomena involved. The determination of the positions of atoms after they have been implanted and after various kinds of treatment and use is an essential part of the optimization of processing parameters and techniques, of analysis of unsatisfactory performance, and of prediction of ultimate utility. The tools that have proved most useful in studying implanted species are nuclear backscattering (the reflection of energetic light atoms impinging on a surface), and sputtered-ion mass spectroscopy (SIMS). Nuclear backscattering can determine not only the depth of implanted ions but also their location in the lattice in single crystals. SIMS apparatus has a very high sensitivity and can follow the distribution of implanted atoms through a wide range of concentration.

This report is devoted to a more detailed discussion of the possibilities mentioned and this committee's evaluation of their potential.

Chapter 2

HARDNESS AND WEAR

Extremely interesting reports of improvements in the hardness and wear resistance of steel and carbide components as a result of implantation with nitrogen have been published by workers at the Harwell Laboratory of the United Kingdom Atomic Energy Research Establishment [Hartley (3,4) and Dearnaley (5)]. The published work shows:

1. Improvements in life by a factor of 4 are typical [Dearnaley (5)] for steel components such as paper and rubber cutting tools, metal forming tools, and taps for plastics. A similar increase is found in cemented tungsten carbide wire drawing dies.

2. The benefits of ion implantation on wear may persist to a depth 10^3 times that of the implanted layer thickness. The implanted atoms are apparently transported into the metal as the tool wears.

3. Volumetric wear rates of a nitriding steel are improved by two orders of magnitude by nitrogen implantation at light loads, but the improvement drops steadily at higher loads.

These marked and persistent improvements are attractive, but entirely empirical. Thus, there is currently no way to predict behavior or be reasonably sure that the optimum results for a given system have been achieved. A very fine nitride precipitate is suspected to play a role in the implanted steel [Longworth and Hartley (6)]. The beneficial effects in cemented tungsten carbides, or the persistence of this benefit to depths much deeper than the initial implanted layer, could be due to a similar precipitate in the metallic matrix.

These phenomena have obvious potential applicability to two other areas: metal cutting tools and bearings. A good deal of expense is associated with the replacement of these components necessitated by wear, so the cost of ion implantation may be justified. As the advantages of ion implantation are somewhat different in the two cases, they are discussed separately. A further subject, fatigue, which is related to the mechanical properties of surfaces, is also considered.

A. CUTTING TOOLS

Cutting tools used for machining modern high-strength materials used on aircraft and other weapon systems are a high recurring cost item for machining operations. The U.S. market for cutting tools of steel and carbide has been estimated at $900 million per year [Dearnaley (5)]. Because of the amount of amount of machining done per year, improving wear life of cutting tools is economically important.

Grinding, milling, turning, and broaching are major metal removal operations. Cutting tools used for these operations include end mills, taps, reamers, drills, and lathe tools.

Many cutting tools are made from heat-treated high-speed steel. High-speed steel is a high carbon steel alloyed with tungsten, chromium, and vanadium. Molybdenum or cobalt can also be used to increase strength. An increase in the tool life of high-speed steel can be obtained by a nitriding process. Many other cutting tools are made from high-strength steels coated with either tungsten carbide, titanium carbide, or a ceramic material. In some cases, the cutting edge is provided by cementing or mechanically fastening a carbide insert to the high strength steel tool.

In the application of ion implantation to cutting tools, carbon or nitrogen ions would be implanted in the edge surfaces of the tool. Depths of penetration of over 100 nm can be achieved with current techniques. The implanted carbon or nitrogen forms a shallow hardened layer that has been shown to provide good resistance to mild wear [Dearnaley and Hartley (7)]. If successful, the use of implantation to improve tool life would have the following advantages:

- It is a low-temperature process resulting in negligible distortion.
- Dimensional tolerances are unaffected.
- Any element can be applied to any metallic substrate.

The last is an important advantage and greatly broadens the scope of elements and combinations of elements that could contribute to improved tool life. Hartley has stated [Hartley (4)], "For example, the diffusion of Fe into Co, largely by a grain boundary mechanism, is known to occur during the machining of iron. Gregory (Ref. 8 of this Report) has proposed, from a series of experiments on Armco iron, that the controlling process during carbide wear is the leaching out of Co from the tool into the workpiece. Thus by implanting a mutually insoluble species such as Cu into the surface of such a tool, interdiffusion could be reduced with a corresponding increase in tool or die lifetime."

Known disadvantages of ion implantation for cutting tools are:

- The hardened layer is very shallow.

- The process is line-of-sight.
- It is a high-technology process requiring skilled labor.
- Target (substrate) manipulation is needed for cutting tool shapes.

Most cutting tools are used in applications in which wear rates are very high, therefore, the effectiveness of the shallow implantation naturally causes skepticism. Some work has shown that implanted ions migrate inward during wear. The migration may occur so as to place the implanted atoms in a region where they can be most effective. Implanted atoms have been reported to be transported to thousands of times their original depth, and still dominate surface behavior [Dearnaley (5)].

The remaining disadvantages must be addressed through equipment development. The use of high voltages to increase depths of penetration also deserves to be explored and is within the scope of existing ion beam technology.

B. BEARINGS

Two aspects of ion implantation that have been mentioned make its application to bearings especially attractive. Dimensional changes accompanying its application to a finished product are only a few microinches. Thus, the customary supplier of a part can be used and no modification of the final process or use is needed. Also, the smooth transition between implanted surface layer and bulk reduces problems of surface layer spalling.

Preliminary results bear out this promise. The main published work here comes from the Naval Research Laboratory [Hirvonen (9)]. Injecting nitrogen into hardened steel ball bearings decreased the wear rate by a factor of two. Much more striking changes in hardness and wear rate come from putting a surface layer on softer metals. For example, boron injected into beryllium surfaces of precision gas-gearing components significantly increases the surface hardness, and is currently being evaluated as an alternative to applying a hard oxide layer, which sometimes has poor adherence.

Friction is intimately related to wear but has not been as thoroughly studied. It is clear that ion implantation can be used to reduce friction in at least two ways. Hartley has shown that the frictional force between a tungsten carbide ball and a case hardened steel surface was decreased by implanting the steel with tin, or with molybdenum and sulfur in the ratio of 2S/Mo [Hartley, et al (3)]. A less quantitative, but practically more important, observation also stems from the work at Harwell. It has been found that implanted drawing dies not only wore longer but provided a better surface on the drawn product, thus implying less friction between the die and the drawn rod [Dearnaley (7)].

C. FATIGUE

Nitrogen ion implantation has been found to increase the fatigue life of a rotating carbon steel beam at loads less than 90 percent on the yield stress and does not change it at stresses above the yield stress [Wen-Wei Hu, (10)]. Hartley has also reported an improvement by a factor of eight to ten in the fatigue lifetimes of nitrogen-implanted titanium stainless steel and maraging steel [Hartley (11)].

These promising results seem consistent with current understanding of the mechanisms of fatigue failure. Fatigue cracks start at a surface, and there is a close connection between surface hardness and fatigue life. Compressive stresses due to the presence of additional implanted ions may also play a role in the suppression of crack initiation. It is difficult to assess the potential in this area, except to note again that the effects reported by Hartley (11) seem quite significant.

Chapter 3

CORROSION AND OXIDATION

A. CORROSION AND ION IMPLANTATION

The production of corrosion-resistant materials by alloying is well established, though frequently not well understood [Dearnaley (12) and Grant (13)]. Two factors seem to be most important: the nobleness or electrochemical potential of the alloy components and the durability and defect properties of protective films that are formed. For example, the incorporation of a galvanically more noble element will lead to reduced corrosion. Elements like chromium, nickel, titanium, and aluminum depend for their corrosion resistance upon a tenacious surface oxide layer called the passive film. The stable and compact passive films formed by these elements provide improved corrosion resistance. Thus, alloying additions which give rise to better passive films are beneficial and can be used to produce corrosion-resistant alloys.

Alloying elements added for the purpose of passivation must be in a solid solution. The potential of ion implantation is important, since restrictions deriving from equilibrium phase diagrams frequently do not apply (i.e., concentrations of elements beyond the limits of equilibrium solid solubility might be incorporated). This could, in fact, lead to heretofore unknown alloyed surfaces which are extremely corrosion resistant.

Ion implantation is likely to play a role in enhancing corrosion resistance only in selected cases where bulk alloy additions are unsatisfactory. Such cases might arise: if the desired alloying elements degrade a desirable property of the substrate, such as fatigue life or electrical conductivity; if the expense of preparing the desired alloy is large; or if no appropriate bulk alloy is known; and, if, in addition, other methods of surface treatments are unsatisfactory. Further, however, ion implantation is playing an important role in corrosion science, in the study of the atomistic mechanisms involved in corrosive reactions.

Work on the effects of ion implantation on corrosion has concentrated on ferrous alloys and titanium. The presence of chromium in iron leads to the formation of a stable, tenacious oxide. Oxidation occurs by diffusion of oxygen through the protective film; diffusion through the oxides is slow.

Chromium alloys, stainless steels, are usually prepared in bulk form. The same effect can, however, be produced by implanting Cr into the surface of pure iron [Ashworth, et al (14) and Sartwell, et al (15)]. Sartwell, et al verified that the enhanced corrosion resistance of iron implanted with Cr or Ni is not a result of radiation damage, but is, in fact, a result of the alloying addition.

Cases are, however, known in which radiation damage does affect corrosion. The generation of vacancies and interstitial atoms, and the inducement of stress are possible sources of alteration of corrosion behavior by ion implantation. Thus, self-ion bombardment of copper [Rickards and Dearnaley (16)] and nickel [Goode (17)] result in marked enhancement of their oxidation rates.

An important study of ion implantation for improving oxidation resistance of ferrous alloys has been reported by Antill, et al (18). These workers based their study on the established fact that alloy additions of yttrium and rare earths improve the scaling resistance of iron and nickel-based alloys [Tripathi and Antill (19) and Antill and Peakall (20)]. Experiments were conducted on yttrium implanted into austenitic stainless steels and a ferritic stainless steel. In both steels, yttrium as a bulk alloy addition has been found to improve both oxidation resistance and oxide adherence. The rates of oxidation of the implanted austenitic steel was comparable to yttrium-alloyed steels, confirming the view that improvement in corrosion resistance is the result of the implanted alloying addition.

The above conclusion was further verified by implantation of niobium and krypton at the same energies. These experiments were carried out to study the effects of radiation damage. In both cases, little effect of the implantation was observed. The improvement in yttrium implanted material must be associated with yttrium itself and caused by a mechanism similar to that operative when yttrium is present as a bulk alloying addition. It is believed that yttrium increases the adherence of the protective oxide.

On the other hand, yttrium implantation into a ferritic 15 Cr-4 Al iron alloy showed no pronounced influence on oxidation resistance [Antill, et al (18)]. The differing effects for the implantation of yttrium in austenitic steel with those on the ferritic alloy are probably due to different mechanisms of oxidation. The austenitic steel forms a protective oxide film based on chromium, and oxidation proceeds by cation diffusion, which allows yttrium to remain in a position near or at the oxide/metal interface where (despite spalling of the outer scale) it can exert a beneficial influence. Though the 0.2 μm implanted depth is lost, the beneficial effect nevertheless persists. Oxides on the ferritic alloy may grow with an appreciable contribution from anion diffusion which would result in the implanted species being incorporated into the oxide layer and lost by oxide spalling.

The implantation of tantalum into iron provides an example of the use of an alloy that does not exist as an equilibrium phase to retard corrosion [Ashworth, et al (21)]. Tantalum is ordinarily insoluble in iron. It has been found that the oxide that forms on the Ta-implanted surface is equal in resistance to aqueous corrosion to that which forms on chromium-containing iron, and is unusually persistent, presumably due to a preferential removal of iron atoms during the corrosion process.

Implantation of titanium with a buried layer of palladium to produce a peak concentration of 5 atomic per cent 250 Å below the surface leads to superior resistance to corrosion by sulfuric acid. The low Pd concentration layer at the surface is rapidly etched away. However, the Ti atoms are removed more rapidly than Pd atoms, so that the concentration of Pd at the surface eventually rises to 20 per cent and the rate of attack becomes very low, less than 10^{-3} times the rate on the surface of unimplanted titanium.

Dearnaley, et al (22) implanted many different species into titanium and zirconium. In these materials, bombardment with self ions had no effect on oxidation resistance and showed that radiation damage did not play a role. However, the corrosion effects could be correlated with the atomic properties of the implanted species in foreign atom implants. Those implants which decorate certain preferred paths in the oxide give rise to greater corrosion resistance so that oxidation in titanium was inferred to proceed by the migration of titanium along such paths. These implants were identified as those which: have a large heat of formation of an oxide, such as barium or cesium; and, have a large ionic size, such as rubidium or cesium. Similar experiments with zirconium substrates showed correlation of the oxidation behavior with ionic size only. Favorable species were found to have ionic radii lying between 80 percent and 100 percent of that of Zr^{+4}. This is interpreted as showing that replacement of zirconium by a somewhat smaller atom relieves stress in the zirconium oxide, thereby, reducing cracking and mechanical rupturing of the oxide [Smeltzer, et al (23)].

Sputtering effects during implantation have not yet received much attention. However, sputtering can lead to a rougher surface, providing active sites for dissolution reactions. In multicomponent systems, where sputtering rates will be different for the various components, a preponderance of one component will be produced on the surface, which would be expected to affect corrosion reactions.

B. SUMMARY

The chemical and atomistic bases of the effects of ion implanted species on corrosion have been more extensively investigated than the mechanisms causing changes in mechanical properties. The factors involved in changing corrosion resistance have been described in some detail to provide examples of the complexity of the phenomena that may be encountered. It can be seen that the ingredients of a successful passivation process are quite varied. Unexpected effects may occur and generalizations are not always a useful guide. It has been suggested that various mechanisms in addition to those that have been mentioned here may play a role in enhancing corrosion resistance. It is clear that considerable process development and extensive field testing will be required to demonstrate the applicability of ion implantation for enhancement of corrosion resistance in each particular case.

Chapter 4

OPTICS

Changing the composition of materials changes their optical properties. Thus, indices of refraction and optical absorption constants can be altered by ion implantation [Brown (24) and Townsend (25)]. Implantation can also be used to improve the mechanical and corrosive properties of optical components. However, very little has been done to investigate these possibilities beyond demonstrations that the effects exist. Thus, the committee's comments consist almost entirely of speculation concerning potential developments.

The application of ion implantation to optics is here divided into two parts. The first, integrated optics, refers to the formation of optical elements such as waveguides and lenses in a thin planar layer by patterning the implantation. The second part is a discussion of the possibility of using ion implantation to improve such individual components as filters, windows, and mirrors.

A. INTEGRATED OPTICS

Integrated optics may be loosely defined as the processing of light signals in insulating and semiconductor materials. In conventional electronic devices, the signals are carried by metal conductors. In integrated optics, the signals are guided within light pipes. A variety of optical components, such as prisms, lenses, directional couplers, and reflectors can be fabricated in thin films. In addition, electro-optical devices that can generate, switch, and detect light are known. Thus, it is possible to think of optical information processing systems embodied in thin film form on a chip containing many components. It is not possible to say with confidence that such integrated optical chips will ever play a useful role in electronic systems. One may, however, think of possible advantages that such a system might possess as compared to conventional semiconductor integrated circuits. Optical components are likely to be less sensitive to ionizing radiation than electrical components. Optical interconnections might turn out to be more reliable than electrical interconnections.

Most important, however, integrated optics is a way to provide the electro-optical interfaces that convert electrical to optical (and vice versa) signals that are needed to utilize optical fibers. Transmission of information in the form of light passing through an optical fiber is an existing technology which can carry signals the length of an aircraft or a ship, and as in commercial operation carrying signals between telephone switching centers. There is a demonstrable weight saving vis-a-vis copper wires, which is of importance in aircraft and missiles. Security is enhanced by fiber transmission lines and optical communications in general. It is extremely difficult to tap such communication lines.

Optical and electro-optical devices can be made by more standard procedures such as thermal diffusion, ion exchange, sputtering, and epitaxy. However, following the experience with semiconductors, we can anticipate that the control and reproducibility provided by the ion implantation process will be advantageous, especially as levels of integration increase.

Despite the fact that this field has received a lot of attention during the last decade, it is roughly at the same state of development as semiconductor technology in the early 1960s. For a few discrete optical devices, the standard techniques work well enough. However, if the same level of complexity is to be achieved with integrated optics as now exists in semiconductor integrated circuitry, the traditional techniques will not be adequate. It is likely that ion implantation will have to play an important role in the next generation of integrated optical components.

B. FILTERS, MIRRORS, AND WINDOWS

Large numbers of optical filters, mirrors, and windows are used under all sorts of severe environmental conditions for everything from gun sights to satellite surveillance devices. In the near future, laser detection, communication, and weapons will continue to require better and more specialized forms of these components. The various effects that increase hardness and corrosion resistance may be applicable. Inhibiting the tarnishing of metal mirrors is a result of ion bombardment. There is a great need for protection of infrared (IR) and ultraviolet (UV) transparent windows from atmospheres and micro-meteorite deterioration. Implants can be very shallow and yet provide mechanical protection for the window.

Ion implantation may also have a role in the improvement of the optical properties of filters, mirrors, and windows. More selective filters can be made due to greater control of chemical doping by implantation. Multilayer filters could be produced inside of an element rather than on the surface by a set of deposited films, as is presently done. This might lead to more stable and more erosion-resistant filter stacks.

Chapter 5

ION PLATING

Ion plating is another surface treatment process that has recently attracted a great deal of attention [Spalvins (26) and (27)]. Ion plating also possesses many advantages as compared to conventional coating techniques. Therefore, although the present study has concentrated on ion implantation, it is appropriate to compare this process with ion plating. There are superficial similarities between these two processes, but there are also striking differences. Thus, each method is likely to find its own regime of application.

Ion plating is carried out in a gaseous electrical discharge in which the substrate to be plated is the cathode. The discharge is created by an applied potential of 500 to 5000 volts. The primary component of the gaseous environment is usually an inert gas, most often argon. Atoms of the material to be plated are introduced into the gas by evaporation from a heated source. A fraction of the atoms injected by evaporation are ionized before striking the substrate. The small portion of the energetic ions and the large portion of energetic neutrals of the evaporant are drawn to the cathode by the electric field and scattering effects. Deposition rates can approach 25 μm/min, but are commonly only about a tenth of this amount.

The essential difference between the two techniques is that the energy of impinging ions is of the order of 100 kilovolts in ion implantation, causing the ions to penetrate some 1000Å into the substrate, and thereby forming an alloy of implanted species and host species. In ion plating, atoms arrive at the surface with energies of only a few hundred volts and penetrate no more than a few lattice constants into the substrate. Thus, ion implantation produces an alloyed surface layer whose composition varies continuously with depth because of the rather broad distribution of the ranges of the implanted ions, while ion plating produces a coating, the composition of which is independent of the nature of the substrate.

A comparison of ion implantation and ion plating in terms of specific features that are important in applications is as follows:

- Surface alloys formed by ion implantation grade continuously into the substrate; there is no sharp interface, and problems of separation of surface layer and substrate are not likely to arise. Ion plated coatings are, however, also exceptionally adherent as compared to conventional coating methods. The excellent adherence is a result of sputter cleaning of the substrate by the discharge, which removes any oxide or other layers that may impair adherence, and interdiffusion of coating and substrate, which is enhanced by heating produced by the discharge and the production of vacancies near the surface of the substrate by the energy of the deposited ions.

- The independence of the composition of the deposited layer and the substrate and the good adherence means that unusual materials combinations can be formed. For example, metals can be plated on plastics and ceramics can be plated on metals. No comparable combinations can be produced by ion implantation. The complete control of the composition of the deposited layer that can be achieved in ion plating also permits layered coatings to be produced. For example, plating a thin layer of aluminum on steel has been found to improve the adherence of a subsequent plating of Al_2O_3.

- Ion implantation depends on line-of-sight access to the surface to be treated. Ion plating has good "throwing power," which means that the atoms to be deposited are scattered by the discharge gas and can enter and deposit in reentrant shapes and deposit on various facets of a substrate simultaneously.

- Ion plating can also be carried out in a reactive gas to produce coatings formed by the reaction of an evaporated species with the gas. For example, titanium nitride has been deposited in this way.

- Ion plating and ion implantation are generally applied to provide similar functional capabilities, that is, to improve hardness and wear resistance, to protect against corrosion, or to reduce friction.

- Ion plating is more readily applied to large work-pieces and to the simultaneous treatment of an assemblage of substrates than is ion implantation, at least in contemporary equipment. Plating equipment is likely to be less costly than implantation equipment. Deposition rates are faster in ion plating, and the thickness of a coating is not limited by penetration of the substrate, as it is in ion implantation, so that coatings a mil or more in thickness may be applied by ion plating.

- Like ion implantation, ion plating does not involve high-temperature treatment of the workpiece. Thus, if the thickness of the coating is not too great, finishing of the workpiece after ion plating can also be avoided.

- The coatings deposited by ion plating are well-known materials, available in bulk form. Their properties, when deposited by ion plating, present few surprises, in comparison to the wealth of new phases and unexpected phenomena that are encountered in ion implantation. Thus the development of new ion plating applications is likely to be more straightforward and faster than the realization of metallurgical applications of ion implantation. The factor that has attracted recent attention to ion plating is the very good adhesion between incompatible substrates and coatings that can be obtained as compared to other coating techniques. The sources of the excellent adhesion are not fully understood and present a challenge to research. The grain of crystalline coatings affects the properties of the coatings in significant ways, and the factors that affect it deserve study.

Chapter 6

LASER ANNEALING

Semiconductor applications of ion implantation require that the implanted specimens be annealed at a high temperature to produce electrical activity of the implanted species. Indeed, highly reproducible annealing procedures are an essential element of semiconductor implantation technology, and much attention has been devoted to the development of suitable methods of annealing. It has recently been found that satisfactory annealing can be obtained by irradiation of the implanted surface with a pulse of light produced by a high-power laser (28). The irradiation heats, and may melt, a thin layer at the surface of the semiconductor, which then recrystallizes epitaxially on the substrate with no trace of the radiation damage produced by the implantation. Similar effects can be produced by pulsed electron irradiation and by scanning the specimen with a continuous (not pulsed) laser beam. These recently discovered possibilities have not yet been applied in production processes.

Laser annealing nicely complements ion implantation in that it affects only a surface layer approximately equal to the depth of typical implantations, leaving the bulk of the specimens unaltered. Even though annealing may not be required in many metallurgical applications, the availability of laser annealing provides an additional degree of flexibility in the structure of the implanted layer and promises to extend the scope of applicability of ion implantation. The technique is still in its infancy and much remains to be discovered.

The application of pulsed annealing to implanted metals is an obvious path to explore. Such exploration is only beginning. The point to be recognized is that laser annealing provides a way to change the state of a material after it has been implanted. For example, an amorphous material can be converted to the crystalline state or it may be possible to achieve precipitation hardening of a surface with an implanted species.

Laser or other pulsed annealing is also a method of surface treatment in its own right; that is, without being preceded by an ion implantation step. The heated layer at the surface cools rapidly, leaving a quenched surface which might have properties different than those of the bulk.

Chapter 7

IMPLANTATION METALLURGY AS A DEVELOPMENT TOOL

Ion beam techniques can be used to obtain fundamental parameters useful in the development of improved alloys. Although this application does not properly fall into the category of surface treatment, it is discussed here because the laboratory facilities and scientific know-how needed to interpret and evaluate ion implantation as a surface treatment are identical to those needed to apply the technique to alloy development.

The concept is to use ion implantation to form a thin layer of the particular alloy composition of interest. Then, under subsequent thermal treatment, one observes the evolution of the concentration vs. depth profiles in order to obtain key fundamental kinetic and equilibrium parameters [Myers (29)]. Specific uses of this technique in conjunction with alloy development programs would be to determine diffusivities and solubilities, or the phase diagrams for multiple-component systems, at relevant temperatures. Such data could then be used to aid in determining the appropriate alloy additions, processing temperatures, and times for the development of a predictive capability for diffusion-controlled aging processes. A second area of application is the investigation of particular degradation mechanisms and ways in which certain alloy additions can improve system compatibility.

The technique can best be illustrated with two examples. First, consider the implantation of Cu into Be to concentrations of ~ 20 at. % [Myers and Smugeresky (30)]. Subsequent heat treatment at 400°C allows the implanted Cu to migrate. Since the local solid solubility is exceeded, the Cu rapidly precipitates within the high concentration-implanted layer and the diffusion of the copper into the underlying α-Be can be observed via the diffusion tail by use of ion backscattering. An example of the concentration vs. depth profile obtained in this way is shown in Figure 1. The shape of the diffused tail follows the expected complementary error function and can be used to determine the diffusivity. The intersection of the diffused tail with the two-phase precipitated region provides a measure of the solid solubility. As shown in Figures 2 and 3, the solubility and diffusivity can be determined quite accurately in this way and at temperatures much lower than could be achieved by conventional metallurgical techniques [Myers and Smugeresky (30) and Myers, et al (31)]. In applications

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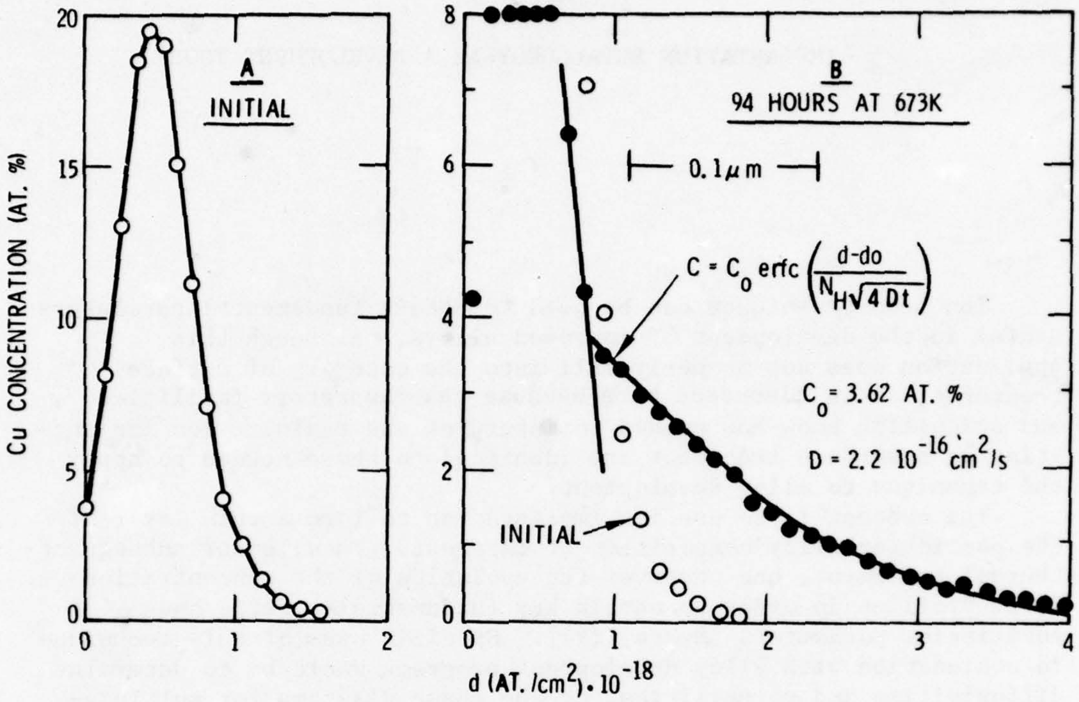

FIGURE 1 Concentration vs. depth profile determined by ion backscattering for Cu implanted in Be before and after heat treatment at 400°C. From Myers and Smugeresky (30).

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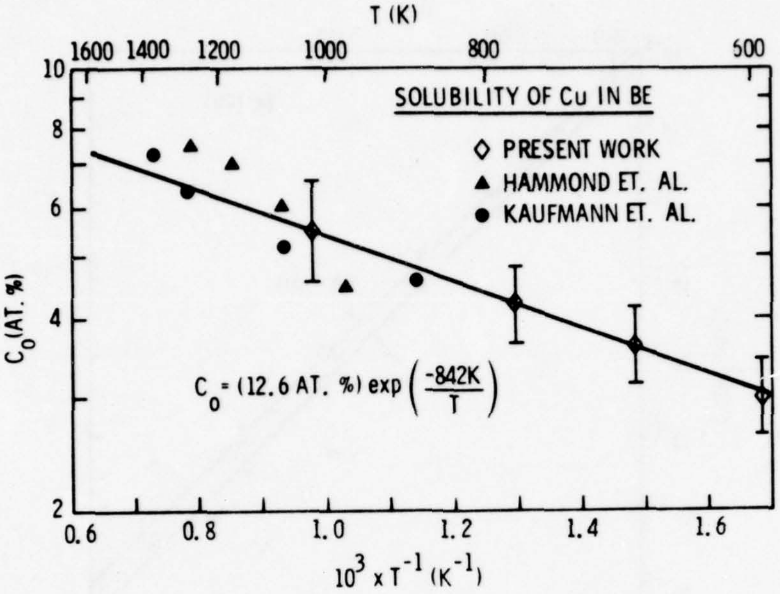

FIGURE 2 Solubility vs. reciprocal temperature for Cu in Be as determined from implanted microalloys (present work) and by conventional metallurgical techniques. From Myers and Smugeresky (30).

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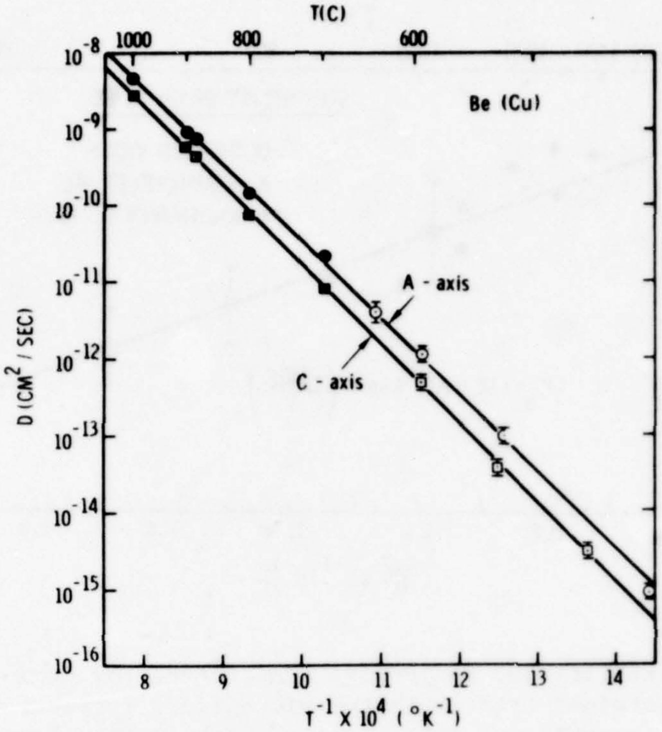

FIGURE 3 Diffusivity vs. reciprocal temperature for Cu in single crystal Be of C and A orientation as determined by ion implantation and ion backscattering techniques (open symbols) and by conventional radiotracer and stripping techniques. From Myers, Picraux, and Prevender (31).

to Cu solution strengthening of Be alloys, this work provided quantitative information on the amount of copper which should be introduced into solution in Be and the equilibration times. The data have been used in selecting Be(Cu) alloys for mechanical tests which have shown significant improvement in yield strength without loss of ductility. Specifically, by adding 0.7 at. % Cu, yield strengths have been increased from 270 MPa to over 370 MPa. Additionally, this implantation approach has been extended to ternary alloy systems such as Be/Fe/Al and used to interpret and predict precipitation effects as a function of residual impurities and heat treatment [Myers and Smugeresky (32)].

A second illustration of the technique is the study [Myers, et al (33)] of how Ti alloy additions to bcc Fe alloys can improve resistance to temper embrittlement by such unwanted impurities as Sb. Transmission electron microscopy analysis of Ti-implanted Fe (even at the highest commercially available purity levels) showed that Ti carbide precipitates formed upon subsequent heat treatment at 600°C. Implanted Sb was found to be strongly trapped in the depth region corresponding to the Ti carbide precipitates, whereas this trapping did not occur in non-Ti implanted Fe. While it was known that Ti-containing steels exhibited reduced susceptibility to temper embrittlement by such impurities as Sb, the mechanism was not known. These implantation metallurgy studies suggest that TiC precipitates in Fe are effective traps for Sb and they were proposed as the contributing mechanism to the reduced temper embrittlement in Ti-containing steels [Myers, et al (33)].

The advantages of the use of implantation metallurgy in conjunction with alloy development is that it allows one to obtain an alloy system by implantation rapidly and for essentially any elements. These microalloy systems can then be used to obtain basic parameters in comparatively short times and with a great savings of money over full-scale alloy fabrication. Additional advantages result from the short distances involved which allow equilibrium to be reached in short times; also the intimate mixture is obtained at the concentration of interest so that unwanted persistent phases are bypassed. These are contributing factors to the complexity of trying to fabricate in bulk quantities a wide range of bulk alloys. Thus, the key factor is that many alloys can be surveyed with a single implantation system and those which appear most promising selected for studies in bulk systems.

An additional advantage is that kinetic and equilibrium data can be obtained at much lower temperatures than is usually possible by such conventional techniques as, for example, radio-tracer detection and stripping for diffusion profiles. Lower temperature data is often quite important, since many processing and aging steps take place at such temperatures at which direct determination of fundamental parameters such as solubility and diffusivity has not previously been possible.

The primary limitation of this approach is that close collaboration between basic and applied people is required. Also a large enough development program is needed to allow the implantation metallurgy and conventional metallurgical techniques to progress hand in hand in an interactive way. This technique does not directly compete with any existing process and is a truly complementary tool to enhance the effectiveness of alloy development programs.

Chapter 8

RANGE AND DISTRIBUTION CALCULATIONS

The interpretation of the effects of ion implantation on the surface properties of metals depends on a knowledge of the location of the implanted ions in the substrate. The distribution of the implanted species is described by their range, R, or average distance of penetration into the substrate, and the scatter, or standard deviation of the penetration distance around the average, ΔR. Both of these quantities depend on the energy of the impinging ions and on the implanted and substrate atomic species. A wide variety of implanted atoms and substrate alloys are of interest in applications. This section discusses the state of the knowledge that is needed to predict the location of implanted ions.

The relation between the ranges of particles in matter and their energy in the energy region from 0 to 10MeV was of great interest to nuclear physicists in the first half of this century. The available data and theoretical treatments were summarized by Bethe and Ashkin [Bethe and Ashkin (34)] in 1951. A widely used method of determining the energy loss rate and the ion range for ions in the energy region commonly used in implantation was published by Lindhard et al [Lindhard, et al (35)] in 1963. Atomic collision theorists made notable strides with the theory in the sixties which were summarized by P. Sigmund (36) in 1973. Ion implantation in the semiconductor industry began to take on an important role in the early seventies and stimulated much work on depth profiling of major dopants in Si and Ge at energies below 200keV. The need of the implantation community led to a number of new works on range projections [Gibbons, et al (37), Brice (38), Winterbon (39)]. Also, two major compilations and extrapolations of energy loss data for the elements were published in the seventies [Northcliffe and Schilling (40) and Ziegler (41)].

The work of Ziegler and Chu (42) in 1974 called attention to the fact that the electronic stopping power of light atoms such as energetic He in targets of varying atomic number (Z) undergoes oscillations as a function of the target Z.

More and Venskytis (43) pointed out that the Northcliffe-Schilling data are based on interpolation from the series (C, Al, Ni, Ag, Au) for which experiments had been performed, and that interpolation from this series is misleading because elements of the series happen to fall near the minima in the oscillations of the energy loss function. Theory is tolerably reliable at very low energies and at high energies (E > 10MeV for light ions). Experimental values of the energy loss function are essential to bridge the gap.

There is need for additional research in both the experimental and theoretical aspects of the ranges of ions in solids. Such information will be of value, not only to the application of ion implantation to metallurgical surface treatments, but also to its application in the semiconductor industry and in the simulation of nuclear reactor radiation damage.

Chapter 9

EQUIPMENT

Two topics related to ion implantation equipment are considered. First, present implanters are designed for semi-conductor applications, and modifications, particularly an increase in the current delivered, will be required for metallurgical production tools. Second, in the development of ion implantation processes a variety of analytical tools will be needed.

A. ION IMPLANTATION EQUIPMENT FOR METALLURGICAL PRODUCTION

Present-day semiconductor ion implanters have the following components:

1. an ion source, which only under rare circumstances emits one specie of ion;
2. a magnetic mass analyzing system to "purify" the beam;
3. an accelerating stage or stages which can bring the particle up to energies of hundreds of kilovolts;
4. a beam scanner or wobbler to obtain beam uniformity;
5. a target chamber which can be instrumented to handle large numbers of planar structures, rotate samples in and out of the beam, and make use of complicated masks; and,
6. electronics which provides readout of mass analysis, beam current, beam profile, and vacuum conditions in the machine and at or near the implantation site.

At the present time, there are between 500 and 600 implanters used throughout the world. The vast majority are used in the preparation of semiconductors. Cost for a state-of-the-art production or research machine with accelerating capability of up to 400 kV is about $300,000. With current technology and a fully operational facility, the cost of an implant for a typical dose used for improving wear or corrosion resistance is estimated to be roughly 30 cents per

cm^2. As production machines will be developed for wear and corrosion applications, it is expected that the cost per cm^2 can be decreased to 5 cents per cm^2 [Dearnaley (5)].

The requirements for equipment for implantation in metals differ significantly from the requirements of semiconductor applications. For the latter applications, ion dose uniformity, reproducibility, and precision are typically held within a few per cent. For applications to metals (e.g., improving wear and corrosion resistance), it appears likely from presently available information that these requirements can be significantly relaxed. Furthermore, semiconductors are extremely sensitive to small amounts of undesired impurity. This is not true of the mechanical properties of metals. Thus the requirements for high vacuum and beam purity could be relaxed significantly. These factors will have to be examined in detail for particular applications, but should allow more flexibility and lower costs in designing production ion implantation machines for metallurgical applications.

It should be stressed that a period of research will be required to ascertain necessary machine requirements for specific applications. However, there should be no fundamental problems in scaling-up present machines.

In addition to implanter scale-up, part handling apparatus will have to be developed for specific applications to allow efficient production. The surface to be treated must be line-of-sight and exposed for the appropriate length of time in a vacuum environment.

There presently exist prototype implantation machines for treating workpieces for improved lifetimes [Dearnaley (5)]. These are capable of providing higher beam currents than present research machines and can handle samples up to a foot in diameter. In the United States, plans to scale-up implanters for high-volume solar cell production should be examined, since with appropriate ion sources, they may be well suited for nonelectronic part production [Muller, et al (44)].

B. TOOLING FOR A DEVELOPMENT LABORATORY

The basic tools required are an ion implantation facility, an ion beam analysis facility, and conventional microstructural analysis facilities. A high-current ion implanter (current on target greater than 100 μA) is required with sources to produce any metal ions of interest in the development program and give ion energies ranging from ten to over 100keV. The implanted ion beam should be mass analyzed to preserve purity, and provision must be made for sweeping either the beam or the sample to form alloys which are laterally uniform over an area of the order of 1 cm^2. The implantation chamber should provide temperature control at reasonable vacuum levels ($\lesssim 10^{-6}$ Torr).

The ion beam analysis system can be based on a 2 MeV Van de Graaff accelerator. Helium ion or proton beams can be used for determining the dependence of the concentration of impurities on depth by means of ion backscattering for heavier elements and by ion-induced nuclear reactions for light elements (e.g., for oxygen, carbon, and deuterium). Charged particle detectors with the associated electronics, including a multi-channel analyzer, would be required for energy analysis of the backscattered or nuclear reaction products to determine the concentration versus depth [Ion Beam Handbook for Materials Analysis (45)].

Secondary ion mass spectroscopy (SIMS) and sputter Auger systems are possible alternative or additional analysis tools. These latter systems have the advantage of being sold commercially as complete systems. However, they have the disadvantage of requiring calibrations which may be matrix-dependent, and they require destructive layer removal techniques. Microstructural analysis can be obtained using conventional transmission electron microscopy and scanning electron microscopy systems.

Chapter 10

CONCLUSIONS AND RECOMMENDATIONS

Ion implantation is a novel technique for treating the surface of metals. It has shown a potential for producing significant improvement in rates of wear and corrosion. Improvements in the surfaces of optical elements and novel optical components may also be possible through ion implantation.

The beneficial effect of ion implantation on surface properties must be compared to the effects achieved by conventional processes which introduce alloying elements by a variety of means, apply coatings, or mechanically deform the surface. Because of the expense and the novelty of the ion implantation process, its use, at least in the near future, will be confined to applications in which conventional processes have not been able to meet all of the requirements.

It is recommended that the Department of Defense identify applications in which the available surface treatments do not meet DoD needs in the areas of corrosion resistance, wear, hardness, and fatigue. These applications should be examined to determine the potential for employment of ion implantation. Such an effort should be implemented by the constitution of a task force of several persons, preferably at an influential level in DoD. Limitations of ion implantation, including the restrictions to line-of-sight surface treatment and shallow alloying depths, must be taken into account. The limitations have not prevented successful laboratory scale demonstrations, and scale-up to production appears to be straightforward. Thus, an effort to evaluate the use of ion implantation to improve performance should be inaugurated for particular problems. The evaluation must include a study of economic feasibility.

The great diversity of implanted species and the variety of the possible applications offer so many opportunities for ostensibly useful research that it will be possible to pursue only a small fraction of them. The following criteria should be applied to select the most worthy areas.

- Scientific foundation. Does the existing base of metallurgical knowledge suggest that ion implantation might provide a solution to a technological problem? It would be comforting if basic knowledge could be used to

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predict areas in which ion implantations might be usefully employed. Unfortunately, many ill-understood phenomena are encountered, and other factors must be considered.

- Comparison with alternative methods of surface treatment to determine whether ion implantation might offer any unique advantages. This is not always possible, as unanticipated phenomena are frequently discovered in implanted layers.

- Economic Feasibility. Would the additional value of the part outweigh the cost of implantation if a successful development occurred?

- Potential for scale-up to a manufacturing level. Could a laboratory demonstration of a process be translated into a manufacturing process? This would be simpler for small parts.

- Degree of interaction with engineers involved in field use of the product involved. Close interaction is needed to insure that research results are a valid solution to a problem.

- Potential for validating a solution through field testing. Are there opportunities for testing in the environment of intended use?

- Potential for understanding the atomistic and metallurgical basis of a solution to a problem. Are the available analytical tools and the scientific training of the investigators adequate to insure progress toward understanding of the results obtained?

- Is the level of staffing adequate to support operation of the implantation facility and the analytical equipment and to interpret results and guide research towards useful goals?

The obvious criteria of availability of an ion implantation facility and competency of the personnel involved have been taken for granted. A successful effort to evaluate the applicability of ion implantation will require a significant commitment for staffing and tooling. The equipment required would include not only an ion accelerator but also the analytical equipment that enables an analysis of the events that occur on an atomistic scale to be performed. Proper evaluation of data, interpretation of analytical results, and program guidance will call for the involvement of professionals, highly skilled in the metallurgical, physical, and chemical sciences. Five persons, plus generous allocations of capital resources, would be needed to lauch an effective program.

It is further concluded that research aimed at unraveling the complex of microscopic phenomena that underlie the beneficial effects produced by ion implantation of metals is needed. The field lacks the general principles that would enable effects discovered in one system to be optimized and extended to other systems. When technologically important effects of ion implantation are discovered, they should be followed up by scientific investigation of the atomic mechanisms involved.

Especially in the field of wear resistance, where exceedingly complex phenomena are encountered, a careful study aimed at understanding a few model systems would be of substantial benefit in defining the structures sought in a successful application. This would require the collaboration of experts in the areas of ion implantation, transmission electron microscopy, and mechanical metallurgy.

The application of ion implantation to the improvement of metal cutting tool life deserves special attention. A variety of new alloying additions should be tried.

In the field of corrosion, there are also many opportunities for the study of alloying additions that cannot be added by conventional metallurgical techniques. Thus, further work should be done on previously unexplored alloying additions, and analysis of the mechanisms involved. Further, the physics of the damage and sputtering processes should be investigated to determine how these factors influence "alloy-ability" and corrosion behavior. For example, it is possible to obtain amorphous surfaces by implantation [Singhal, et al (46)]. This aspect of metastable phase formation could very well lead to new corrosion-resistant glassy phases; e.g., stainless steel protected by a passive glass coat. Again, investigation of the sources of the unusual corrosion resistance that is found in certain cases is required.

A role for academic science is found in the unraveling of the physical and chemical mechanisms at work in the production of improved surface properties by ion implantation; departments of metallurgy in institutions of higher learning are ideally suited to undertake the basic studies that are needed. Indeed, it is probably safe to say that an adequate level of basic studies will not be achieved without the involvement of academic departments of metallurgy. The principal barrier to the involvement of university departments in ion-implantation metallurgy is likely to be lack of access to the ion accelerators that are required for both implantation and back scattering analysis.

It is, therefore, recommended that efforts to insure access to ion accelerator facilities by departments of metallurgy be inaugurated. Such efforts could take the form either of provision of additional accelerators or of funding arrangements to increase the availability of existing accelerators.

Implantation apparatus intended for metallurgical applications will be significantly different from that commonly used in semiconductor technology. Lower requirements on beam purity will permit relaxation of the need for high vacuum and elimination of the magnetic separator. Lesser demands on uniformity and reproducibility of the dose will also be translatable into reduced equipment cost. On the other hand, higher beam currents to supply larger dosages, ability to handle larger substrates, and ability to mechanically manipulate substrates would be desirable in metallurgical productions tools. On the whole, it appears that the cost per unit area of metallurgical implantations will be substantially less than that of semiconductor implantations. Initial steps toward high-current, low-cost implantation are being taken in the development of silicon solar cells.

There are opportunities to conserve materials in short supply by replacing bulk alloys and electroplated coatings with ion implanted layers. Quantitative estimates of the potential impact of ion implantation on requirements for critical materials are needed.

Various methods of predicting the way in which the depth distribution of implanted ions depends on ion energy and on the composition of the substrate give varying results. A reliable method of calculating these quantities is needed for the analysis and interpretation of experimental results.

REFERENCES

(1) National Materials Advisory Board, Contingency Plans For Chromium Utilization (NMAB-335), National Academy of Sciences, Washington, D.C., 1978.

(2) B. S. Covino, B. D. Sartwell, and P. B. Needham, Jr., "Anodic Polarization Behavior of Fe-Cr Surface Alloys," J. Electrochemical Society, 125: 366-369, 1978.

(3) N. E. W. Hartley, et al in Applications of Ion Beams to Metals, (Eds., S. T. Picraux, E. P. EerNisse and F. L. Vook) (Plenum Press), p. 123, 1973.

(4) N. E. W. Hartley, "Ion Implantation Case Studies," Surface Treatments for Protection, Proc. Institution of Metallurgists, Spring Review Conf., Cardiff, April 1978.

(5) G. Dearnaley, "The Ion Implantation of Metals and Engineering Materials," Transactions of the Institute of Metal Finishing, 56: 25-31, 1978.

(6) G. Longworth and N. E. W. Hartley, "Mossbauer Effect Study of Nitrogen-Implanted Iron Foils," Thin Solid Films, 48: 95-104, 1978.

(7) G. Dearnaley and N. E. W. Hartley, "Ion Implantation of Engineering Materials," Conference Proceedings of Ion Plating and Allied Techniques, CEP Consultants, Ltd., Edinburgh, U.K.

(8) B. Gregory, "Surface Interaction of Cemented Carbide Tool Material and Armco Iron," Brit. J. Appl. Phys., 16: 689-695, 1965.

(9) J. K. Hirvonen, "Ion Implantation in Tribology and Corrosion Science," to be published in J. of Vacuum Sci. and Tech., 15: 1662-1668, 1978.

(10) Wen-Wei Hu, C. R. Clayton, H. Herman and J. K. Hirvonen, Scripta Met., 12: 697-698, 1978.

(11) N. E. W. Hartley, "Tribological Effects in Ion-Implanted Metals," Conference on Application of Ion Beams to Materials, September 1975, Coventry, Warwicks., England, Institute of Physics, p. 210-223, 1976.

(12) G. Dearnaley, "The Use of Ion Beams in Corrosion Science," in Applications of Ion Beams to Metals, ed. S. T. Picraux, E. P. EerNisse, and F. L. Vook (Plenum Press, New York), pp. 63-85, 1974.

(13) W. A. Grant, "Surface Chemistry of Ion-Implanted Solids," in Applications of Ion Beams to Materials, 1975, ed. G. Carter, J. S. Colligon and W. A. Grant (The Institute of Physics, London), pp. 127-140, 1976.

(14) V. Ashworth, D. Baxter, W. A. Grant, and R. P. M. Proctor, "The Effect of Ion Implantation on the Corrosion Behavior of Pure Iron II Chromium Ion Implantation," Corrosion Science, 16: 775, 1976.

(15) B. D. Sartwell, A. B. Campbell and P. B. Needham, Jr., Ion Implantation in Semiconductors and Other Materials (Plenum Press, New York), 1977.

(16) J. Rickards and G. Dearnaley, Proc. Conf. on Applications of Ion Beams to Metals, Albuquerque (Plenum Press, New York) p. 101, 1974.

(17) P. D. Goode, Proc. Int. Conf. on Application of Ion Beams to Materials, Warwick, England, 1975.

(18) J. E. Antill, M. J. Bennett, R. F. A. Carney, G. Dearnaley, F. H. Fern, P. D. Goode, B. L. Myatt, J. C. Turner, and J. B. Warburton, "The Effect of Surface Implantation of Yttrium and Cerium Upon the Oxidation Behavior of Stainless Steel and Aluminum Coatings at High Temperatures," Corrosion Science, 16: 729, 1976.

(19) K. C. Tripathi and J. E. Antill, "Influence of Metallurgical Condition and Surface Finish on the High Temperature Oxidation Behavior of Austenitic Stainless Steel in CO_2," Corrosion Science, 10: 273, 1970.

(20) J. E. Antill and K. A. Peakall, "Influence of Alloy Addition of Yttrium on Oxidation Behavior of Austenitic and Ferritic Stainless Steel in Carbon Dioxide," J. Iron Steel Inst., 205: 1136, 1967.

(21) V. Ashworth, D. Baxter, W. A. Grant, and R. P. M. Proctor, "The Effect of Ion Implantation on the Corrosion Behavior of Pure Iron-III Tantalum Ion Implantation," Corrosion Science, 17: 947, 1977.

(22) G. Dearnaley, J. D. Benjamin, W. S. Miller and L. Weidman, "The Use of Ion Implantation in a Comparison of the Thermal Oxidation of Titanium and Zirconium," Corrosion Science, 16: 717, 1976.

(23) W. W. Smeltzer, R. R. Hearing, and J. S. Kirkaldy, "Oxidation of Metals by Short Circuit and Lattice Diffusion of Oxygen," Acta Met., 9: 880, 1961.

(24) W. L. Brown, "New Ion Implantation Areas," Proc. of the 2nd Int. Conf. on Ion Implantation in Semiconductors (Springer, Berlin-Heidelberg), p. 430, 1971.

(25) P. D. Townsend, "Ion Implantation and Integrated Optics," Journal of Physics, E: Scientific Instruments, 10: 197-203, 1977.

(26) T. Spalvins, New Applications for Sputtering and Ion Plating, NASA TM X-73551, May 1977.

(27) T. Spalvins, "Industrialization of the Ion Plating Process," Research/Development, pp. 45-48, October 1976.

(28) Papers Presented at the Materials Research Society Symposium on Laser-Solid Interactions, Boston, November 28-December 1, 1978.

(29) S. M. Myers, "Metallurgy by Ion Implantation," Electro-Chemical Society Symposium on Thin Film Phenomena, October 1977.

(30) S. M. Myers and J. E. Smugeresky, "Low Temperature Solubility of Copper in Beryllium, in Beryllium-Aluminum and in Beryllium-Silicon Using Ion Beams," Met. Trans., 8A: 609, 1977.

(31) S. M. Myers, S. T. Picraux, and T. S. Prevender, "Study of Cu Diffusion in Be Using Ion Backscattering," Phys. Rev., B6: 3953, 1974.

(32) S. M. Myers and J. E. Smugeresky, "Phase Equilibria and Diffusion in the Be-Al-Be System Using High Energy Ion Beams," Met. Trans., 7A: 795, 1976.

(33) S. M. Myers, D. M. Follstaedt, and H. J. Rack, "An Ion Beam Study of Sb Trapping in Fe-Ti-Sb-C Alloys," Appl. Phys., Letters, 33: 396, 1978.

(34) H. A. Bethe and Julius Ashkin, "Passage of Radiations Through Matter," in Experimental Nuclear Physics, Vol. 1, Ed. by E. Segre, (John Wiley & Sons), p. 166, 1953.

(35) J. Lindhard, M. Scharff and H. E. Schiott, "Range Concepts and Heavy Ion Ranges," Danske Videnskab, Selskab, 33, 1963.

(36) P. Sigmond, "Energy Loss of Charged Particles in Solids," in Radiation Damage Processes in Materials, Ed. C. Dupuy (Noordhoff, Leiden), 1975.

(37) J. W. Gibbons, W. S. Johnson, and S. W. Mylroie, Projected Range Statistics, Second Edition (Dowden, Hutchinson, and Ross, Stroudsburg, Pa.), 1975.

(38) D. K. Brice, Ion Implantation Range and Energy Deposition Distributions, Vol. 1 (IFI/Plenum, New York), 1975.

(39) K. B. Winterbon, Ion Implantation Range and Energy Deposition Distributions, Vol. 2 (Low Incident Ion Energies) (IFI/Plenum, New York), 1975.

(40) L. C. Northcliffe and R. F. Schilling, Nuclear Data Tables, A7: 233-463, 1970.

(41) J. F. Ziegler, "He Stopping Powers and Ranges in All Elements," (Vol. 4 of "The Stopping and Ranges of Ions in Matter," "organized" by J. F. Ziegler) (Pergamon Press, New York), 1977.

(42) J. F. Ziegler and W. K. Chu, Atomic Data and Nuclear Data Tables, 13: 463, 1974.

(43) R. M. More and F. J. Venskytis, Radiation Effects, 35: 129, 1978.

(44) J. C. Muller, A. Grub, J. J. Grub, R. Stuck and P. Siffert, Thirteenth Photovoltaic Specialists Conference - 1978 (Institute for Electrical and Electronics Engineers, New York), pp. 711-716, 1978.

(45) Ion Beam Handbook for Materials Analysis, Eds. J. W. Mayer and E. Rimini (Academic Press, New York), 1977.

(46) S. Singhal, H. Herman and J. K. Hirvonen, Applied Physics Letters, 32(1): 25, 1978.

BIBLIOGRAPHY

Proc. Int. Conf. on Ion Implantation in Semiconductors and Other Materials, Yorktown Heights, New York, 1972 (Plenum Press, New York), 1973.

Proc. Int. Conf. on Ion Implantation in Semiconductors and Other Materials, Osaka, Japan, 1974 (Plenum Press, New York), 1975.

Proc. Int. Conf. on Ion Implantation, Reading, England, 1970 (Peter Peregrinus, England), 1970.

Proc. Int. Conf. on Ion Implantation in Semiconductors and Other Materials, (Plenum Press, New York), 1972.

Proc. Int. Conf. on Application of Ion Beams to Metals, Albuquerque, N.M., 1973 (Plenum Press, New York), 1974.

Proc. Int. Conf. on Ion Implantation in Semiconductors and Other Materials, Osaka, Japan, 1974 (Plenum Press, New York), 1975.

Proc. Int. Conf. on the Application of Ion Beams to Materials, Warwick, England, 1975 (Institute of Physics, London), 1976.

Proc. A.V.S. Symposium on Ion Implantation - New Prospects for Materials Modification, T. J. Watson Research Center, Yorktown Heights, N.Y., (American Institute of Physics), 1978.

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