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APPLICATIONS OF ION BEAM TECHNOLOGY

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I. INTRODUCTION

The purpose of this contract was to identify new potential applications of ion beam technology. In order to achieve this goal, several steps were taken. Several literature searches were performed during the course of the contract period. These included both computer searches and searches of appropriate abstract journals. A list of some of the more useful references found is contained in the bibliography of this report. The bibliography is separated into major topics to aid the reader who may be interested in pursuing a specific subject further. In accordance with the original proposal, expert consultants were contacted to discuss various aspects of this study. In addition, persons in industry and academia were contacted to discuss and evaluate applications specific to their needs. In many cases, these contacts proved to be excellent sources of new ideas.

In Table 1 we list all of the personnel that have been connected with this grant (excluding NASA personnel) in any technical capacity, along with their affiliation and interests. The wide variety of contacts listed reflects the wide variety of fields to which ion beam technology can be beneficially applied. These applications are described along with some indication of economic impact where appropriate in the sections which follow.

II. WIRE ADHESION IN STEEL BELTED RADIAL TIRES

Improvements in the construction of steel belted radial tires would have far reaching consequences both from safety and economic points of view. The tire industry produced approximately 193 and 183 million passenger car tires in 1977 and 1978 (Automotive News, 4/25/79), and a

Table 1. PERSONNEL

I. Principal Investigators

Edward Gelerinter Professor of Physics	Nathan Spielberg Professor of Physics

II. Consultants

1. Roy B. McCauley, Professor
   Department of Welding Engineering
   Ohio State University
   Columbus, Ohio 43210

   Interests include applications of ion beam technology to various types of welding and bonding, and structures of surface depositions.

2. A.L. Berlad, Professor
   Department of Mechanical Engineering
   SUNY at Stony Brook
   Stony Brook, New York 11794

   Interests include high temperature energy utilization, combustion, effusive and diffusive membranes.

III. Industrial and Academic Contacts (chronological)

1. Mr. Robert Paine
   Brush-Wellman, Inc.

   Welding and brazing of beryllium.

2. Mr. Jerome Pichert, Operations Manager for X-Ray Products
   Amperex Electronic Corporation

   Welding and brazing of beryllium.

3. Dr. David A. Benko, Research Chemist
   Goodyear Tire & Rubber Company

   Construction of steel-belted radial tires

4. Dr. A.C. Maurer
   Universities Space Research Association

   Applications to membranes in artificial pancreas.

Table 1 (continued)

5. Dr. William Chick
   Jocelyn Research Laboratory
   Harvard University

   Applications to membranes in artificial pancreas.

6. Professor Edwin R. Haering
   Department of Chemical Engineering
   Ohio State University

   Activation of platinum for catalysis.

7. Dr. Jim Burrington
   Standard Oil of Ohio

   Ion beam technology applications to catalysis.

8. Mr. Michael C. Chervenek, Director of Research
   Hydro-Carbon Research, Inc.
   Trenton, New Jersey

   H-Oil process--Desulfurization.

9. Dr. R.K. Grasselli
   Standard Oil of Ohio

   Ion beam applications to catalysis.

10. Dr. M. Dowell
    Union Carbide Parma Technical Center

    Applications of ion beam technology to carbon technology.

11. Mr. Bob Cornish and Mr. Dwight Witte
    Timken Company

    Applications of ion beam technology to improvement of wear properties of roller bearings.

12. Dr. W.J. Choyke
    Westinghouse Research Labs

    Ion beam modifications of metal surfaces.

13. Dr. L. Rubin
    Resource Systems, Inc.

    Silver-palladium foils for hydrogen membranes.

Table 1 (continued)

14. Dr. Edward A. Fletcher
    Department of Mechanical Engineering
    University of Minnesota

    Effusive and diffusive membranes.

15. Mr. B.A. Free
    Comsat Research Laboratories

    Multiple pinhole ion imaging.

16. Mr. Charles Twardy
    Oriel Corporation
    Stamford, Connecticut

    Interference filters.

17. Dr. Ted Kuwana
    Department of Chemistry
    Ohio State University

    Implantation of metals on surfaces for the study of electron transfer interactions.

18. Mr. Larry Stelmack
    Acton Research Laboratories
    Acton, Massachusetts

    Protective coating to optical elements used in lasers.

19. Dr. Don P. Koistinen
    GM Research Labs
    Physics Department
    Warren, Michigan

    Deposition of carbides on sheet metal.

IV. Other Personnel

Ms. J. Felber performed computer and library searches to obtain and classify relevant literature.

large percentage of these were radial ply tires. Radial tire use by commercial vehicles is also increasing. For instance, Pirelli projects that 63% of light commercial vehicles and 90% of heavy commercial vehicles will have radial tires as original equipment by 1982 (Garrett, 1978). The risks associated with defective tires have been written about in both the public and scientific press (Unione and Erdman, 1977). Unione and Erdman estimate that 2 to 85 fatalities and 150 to 5,900 accidents per year are due to manufactured defects. Approximately 2 to 3% of the tires will be returned to a manufacturer for warranty adjustment. One can then get an estimate of the economic effect of radial tire failure by making a few conservative estimates. Suppose each adjustment is approximately $10 and 50% are radial tires. Then the total of these adjustments is the order of 20 to 30 million dollars per year.

The problems associated with steel belt adhesion have been a subject of some research (Van Ooij, 1979). To understand the problems, one must first understand the manufacturing process. In the current process, steel wires are first electroplated with brass (60 to 70% Cu) and then drawn through dyes to achieve a brass layer thickness of 0.1 to 0.3 microns. A multistranded wire is then formed and this is bonded to the rubber during the vulcanization process. During this process a surface layer of Cu_xS forms, with $x \approx 1.95$ (one finds that rubber in contact with the metal is more vulcanized than the bulk). The Cu_xS is found to be necessary for adhesion of the belts. One finds poor bonding between ZnS and the rubber. During the life of the tire, copper atoms migrate toward the wire surface to form Cu_yS where $y \approx 1.5$. This Cu_yS is of a different crystalline phase compared to the original Cu_xS and adhesion failure results due to stress concentration associated with the formation of occlusions, dendrites, sharp edges between different crystal shapes, etc. The role of the zinc component of the brass is to control the formation of the various sulfides of copper Cu_yS. If one has too much Zn, then Cu_xS does not form during vulcanization and poor adhesion results. If one has too little Zn, the Cu_yS will continue to form as copper atoms migrate toward the surface and in-service tire failure will result. The thickness of the brass layer limits the total number of copper atoms available for migration. In addition, if the brass coating is nicked as the wires are drawn through the dyes, then the exposed steel will corrode leading to adhesion failure.

The problem apparently is one of putting thin uniform coatings of copper or brass onto the steel wires before they are twisted together to form multistranded belts. Ion beam technology is well-suited to sputtering accurately controlled thin layers of metal. Lewis Research Center has performed and is continuing to perform some experiments in conjunction with Dr. D.A. Benko of the Goodyear Tire and Rubber Company. After the steel wire is Cu coated at Lewis using ion beam sputtering, an adhesion test is performed at Goodyear. The wires are inserted into a mold containing rubber and the system undergoes a standard vulcanization. The pull-out force is measured with an Instron machine and the results are compared with those from wire processed by current techniques. Samples are subjected to various treatments prior to the pull-out test. Preliminary results on monofilament samples indicated that it is desirable to continue these studies with multifilaments. At the time of this writing, multifilament samples were being processed at Lewis Research Center.

If this effort proves successful, it will have a large economic impact. The increased use of radial tires has made it necessary for the tire manufacturers to plan to build new plants for radial tire production. Ion beam sputtering facilities could easily be incorporated in these plants, so that there is a possibility of relatively early adoption of this process if the laboratory tests prove its feasibility.

III. CARBON FIBERS AND COMPOSITES

Carbon fiber and composite technology uses are increasing dramatically. Currently, most of these fibers are imported from Japan, but companies such as Union Carbide, Hercules, Avco Corp., Celanese, and Hetco are (or will be) producing the fibers. The projected fiber market growth rate is 30 to 40% during the next decade (Aviation Week and Space Technology, 2/12/79). These fibers are finding uses as parts of composites that are useful in automotive applications (Materials Engineering, 3/79; Modern Physics, 4/79; Ward, 1979), aerospace applications (Shepler et al, 1979; Design News, 6/19/78), and manufacturing applications, especially those involving the handling of hot components (Kerr, 1978). The carbon fibers have the advantages of forming injection molded plastic composites that are stiffer than steel and yet are considerably lighter (Krause, 1979). They have the disadvantage of being more expensive. The cost should come down somewhat with improved volume production. Reduction of operating costs may offset the initial cost increase. In high technology applications, the superior strength to weight ratio along with the ability to perform aeroelastic tailoring makes carbon composites extremely desirable.

Ion beam etching may find uses in roughing the surface of carbon fibers or cloths to improve adhesion when they are glued or epoxied to plastic film to form composites. Preliminary experiments have been performed at Lewis on carbon cloth (woven carbon fibers) supplied by Dr. M. Dowell of Union Carbide Parma Technical Center. It was found that it is apparently possible to roughen the surface of the carbon without seriously affecting the tensile strength. More experiments are needed to evaluate tensile strength and wetting properties of samples of the appropriate geometry. There are indications that it may be possible to process the materials as cloth rather than yarn if these tests indicate that we have sufficiently improved the properties of the surface.

This is an application where the relatively low energy and high current capabilities of the instruments at NASA Lewis prove to be an advantage. A large sample can be exposed and the lower energy of the beam causes the integrity of the fibers to remain intact. In view of the varied uses of carbon fibers and the favorable projection on production increases, this may well turn out to be an extremely important application of ion beam technology.

IV. APPLICATIONS TO COLD WELDING, BRAZING, AND FABRICATION OF MATERIALS

Cold welding is a welding process in which the materials to be joined and any additional "filler" materials used to facilitate making the joint are all kept below their normal melting points. The joint is made by diffusion of atoms across the parting surface and by recrystallization of grains across the surface. It is usually necessary to remove oil, grease, and oxides from the surfaces of the material to be welded. It is usually also necessary to apply fairly high pressures to the mating surfaces both to increase the intimacy of contact of the surfaces and to increase the amount of grain refinement in the material next to the surface. This latter is akin to the beneficiation of material properties attained in normal hot forge welding of materials. In many applications, the material to be joined needs still to be heated to enhance diffusion rates. For example, beryllium is heated in some cases to as high as about 1500°F (830°C), in order to obtain a satisfactory joint within a reasonable length of time (Bosworth, 1972).

There are also applications in which ultrasonic techniques are used to "fret" the mating surfaces against each other while the appropriate pressure is applied. This serves to break up the oxide layers at the surface and presumably to generate local heat at the interface. Thus a number of applications have been described involving ultrasonic welding of aluminum and of titanium alloys in aircraft access doors (Devine and Vollmer, 1978), of aluminum wire to copper lugs for electrical connections, and of ultrasonic soldering of aluminum tubes in heat exchangers (Graff, 1977). In the soldering application, it is not necessary to apply pressure since the solder (if properly chosen) wets the mating surfaces. However, in the other applications, it is necessary to apply substantial pressure to effect a satisfactory joint. For some applications, the resulting deformation of the base metals (sometimes resulting in thickness reduction of as much as 60%) is not acceptable.

At NASA-Lewis Research Center there has been a substantial effort directed at cold welding, using the ion beam to properly clean the mating surfaces. Promising welds have been achieved using only pressure, and no heating, between strips of nickel and copper. However, at the vacuum conditions achievable in the experimental set-ups at Lewis, it has been necessary to carry out the actual welding technique within a short time of the cleaning techniques. Evidently enough oxides form even at those conditions (about 10^{-6} torr) to hinder the cold diffusion process.

The incorporation of an ultrasonic component capability in the apparatus at Lewis Research Center should be extremely useful in that it would make it possible to break up oxides which form in the interval between ion beam cleaning and the actual welding operation. The fretting action of the ultrasonic process makes it possible to deliver energy directly to the mating surfaces, and should make it possible to reduce the necessity for large deformation of the weldments in order to maintain intimate contact.

A particular application, which should be of some significance for aerospace uses, is to the welding and brazing of beryllium. Because of its particularly high strength-to-weight ratio and its good ablation properties, beryllium has been the subject of extensive study for aircraft structures. At one time, there was also an active program studying the use of beryllium in nuclear fuel rod assemblies. Thin beryllium windows are also quite significant in a number of applications involving x-rays: x-ray tubes, x-ray detectors of various types, various x-ray scattering chambers. Beryllium fabrication and its incorporation within various structures and devices is sufficiently costly and of a sufficiently high technology nature to warrant the use of sophisticated techniques. Present techniques and previous efforts in joining beryllium also illustrate some of the advantages and difficulties of diffusion welding beryllium.

Ordinary fusion welding of beryllium has yielded rather poor results in terms of problems with cracking in the fusion zone. Brazing of beryllium (with silver or titanium based brazing alloys) is hampered by intergranular penetration of the brazing compound in the base metal in the heat affected zone. This particular problem sets a lower limit on the thickness of beryllium windows (about 0.3 mm), which can be reliably brazed in an x-ray tube production facility. Diffusion welding at elevated temperatures and pressures has met with some limited success in a research project where one inch square foils were bonded to each other, leading to laminated structures which developed strengths, in tension across the joints, approaching that of the base metal (Heiple, 1972).

There has been reported some indication that microalloying plays a useful role in forming good joints. In particular, it is speculated that certain iron-beryllium compounds are precipitated beneficially at the joint (Bosworth, 1973). One of the problems encountered was that the presence of beryllium oxides inhibited the diffusion of atoms across the mating surfaces. In fact, fractional percentages of oxides were present in the bulk material. This is presumably due to the fact that the bulk material was derived from sintered beryllium powders and therefore the individual grains of beryllium had an oxide coating which further inhibited processes of diffusion and microalloying.

The following uses of ion beam technology therefore need to be explored:

1. The use of ion beam cleaning of mating surfaces of beryllium, or of beryllium and some other metal, to remove surface oxides inhibiting diffusion across the mating surface. The cleaned surfaces are to be joined in vacuum, using ultrasonic welding techniques and a modest application of pressure and temperature.

2. The use of ion beam sputtering of controlled amounts of intermediate materials on the mating surface(s), to facilitate the diffusion of atoms across the interface and the formation of microalloying compounds (Knowles, 1970).

3. The use of ion beam sputtering of controlled amounts of brazing materials, so that enough is available to make the desired joint, but that relatively little excess material is available for intergranular penetration.

A useful test application to motivate and guide studies in this area is to the preparation of thin beryllium window inserts for x-ray tubes for spectroscopy and diffraction. We have been able to establish that real interest exists on the part of at least one x-ray tube manufacturer (Amperex) in exploring this application further.

V. HYDROGEN PRODUCTION, SEPARATION, AND STORAGE USING EFFUSIVE AND DIFFUSIVE MEMBRANES

The current energy shortage has resulted in a search for alternate fuels. One such fuel which has received quite a bit of favorable consideration is hydrogen (Braun, 1979; Berger and Standley, 1978). There are several methods of producing hydrogen each with its own set of advantages and problems. The same is true for the various techniques of storing the hydrogen. Storage of gaseous or liquid hydrogen is both costly and hazardous, so that innovative storage is also a problem. Some of these methods of production and storage will be indicated along with a discussion of the ways that ion beam technology would be useful to the technique.

Hydrogen can be produced from the direct dissociation of water (Ihara, 1978; Fletcher, 1977) or hydrogen bromide (Fletcher, 1979). Rather high temperatures are required for this process. The required energy is obtained from the sun by employing either a solar furnace or solar absorber (Gurev, 1977). The hydrogen can be removed via a selective filter, but rather stringent conditions are placed on such a filter because of the high temperatures at which the decomposition takes place. It has been possible to fabricate effusive membranes of thoria or yttria based on techniques similar to those used in manufacturing gas mantles (Diver and Fletcher, 1977). These have had areas up to about 340 sq. cm, and mesh apertures of the order of 60 to 70 microns, but have been too primitive to permit significant advances, and other membranes need to be developed. Some possibilities for the fabrication of such membranes can be explored with ion beam technology:

1. Sputter deposition of refractory oxides of nitrides on a substrate mesh made from refractory metals such as tungsten or molybdenum. The oxides to be deposited may be thoria, zirconia, or urania. The bare refractory metals would be severely attacked by the water or the oxidizing elements present in the proposed system at the desired high temperatures.

2. Preparation of a suitable mesh by ion beam erosion or milling of thin foils or tubings of iridium. (While iridium is reported to form a highly volatile oxide at high temperatures, there seems to be some preliminary evidence that this oxide would be unstable under the conditions envisaged for this application, and thus the iridium metal will remain resistant to corrosion in this application.)

3. It may also be possible to co-sputter iridium and some plastic compound onto a base metal substrate to give a spongy deposit, decompose the plastic by heating to high temperature, and then dissolve the substrate by a suitable acid, leaving the porous iridium as the membrane material.

4. Perhaps the most promising technique is based upon the use of a multiple pinhole ion lens (Free, 1978) using 50 micron foils that are available off the shelf from Goodfellow Metals, England. If one passes the ion beam through a pinhole (say 50 microns diameter) before allowing it to strike an iridium foil target, then an image of the holes in the

accelerating grid will be cast on the target. The relative size of the image to object (accelerating grid) will depend upon the spacing of the pinhole relative to the target and accelerating grid. In this application, the geometry would be arranged for demagnification (one wants small holes) so that the intensity of the beam would be increased. In fact, it would be increased by the demagnification factor squared. If the foil were left in the beam for some length of time, then a pattern of holes, similar to the pattern of holes in the accelerating grid, would be etched into the foil. Since one desires many holes in the foil, one could use many pinholes causing many patterns to be etched into the foil. The pinhole array might be a 50 micron mesh (this dimension is not critical). Since the intensity of the beam on the mesh is much smaller than that on foil, one would expect the mesh not to etch as fast as the foil. The increase in intensity due to the demagnification will facilitate the etching of the iridium.

Ion beam technology thus could be used to produce an effusive filter capable of withstanding the high temperatures required in the rather efficient thermochemical production of hydrogen. Ion beam evaporation techniques would also be useful in the manufacture of multiple layered solar absorbers (Gurev, 1977) used to heat the water. Thin layers of Si, Si_3N_4, SiO_2, Cr_2O_3, and Ag are required. Since layer thickness is important in this scheme employing an absorber-reflector tandem converter, the accurate sputtering control of ion beam technology would be useful.

A second method of generating hydrogen is by electrolysis of water (Srinivasan and Salzano, 1976; Dubey, 1978). In order for this technique to be competitive with thermal decomposition, it is necessary to find an inexpensive way of generating the electricity required. Wind and solar power are two suggested sources. Since the process takes place at moderate temperatures, some of the diffusive filtering systems discussed below would be useful. Diffusive filters will be discussed in conjunction with the hydrogen storage techniques.

Other techniques of hydrogen production in which diffusive membranes would be helpful involve the generation from hydrocarbons such as methanol or coal (Jonchere, 1976; Leonard and Frank, 1979).

Some of the possible methods of storing hydrogen in various forms include compressed gas, liquid, metal hydrides, and ammonia. The pure gas and liquid are costly to handle, the latter requiring cryogenic techniques, and also pose safety problems. Metal hydrides present a feasible way to store hydrogen. Upon later dissociation into metal and hydrogen, the gas is easily separated from the solid. However, hydrogen recovery requires quite a bit of energy. Ammonia is very valuable in itself and a large part of current hydrogen production goes into its manufacture. However, as the energy situation worsens ammonia will become more valuable as a hydrogen storage system. The technology of making ammonia is well-known. It is also a waste produced in the steel making industry. Low-grade waste heat could be used to form N_2 and H_2 gas and the H_2 removed by a selective filter. Palladium and palladium alloy filters are useful for this purpose (Knapton, 1977; Farr and Harris, 1975) as are iron membranes (Chatterjee, 1978; Grigor'ev and Gorbacher, 1971). Ion beam technology may be useful in improving the performance of these filters.

An alloy membrane could be formed by co-sputtering palladium and silver with good control of thickness and composition of the alloy. If the membrane is to be specifically for NH_3, a monolayer or less of platinum could be sputtered on one surface of the membrane. (Platinum is a specific catalyst for the dissociation of ammonia.) In addition, ion bombardment could be used to change the physical-chemical nature of the membrane. Defects would be introduced which might change the diffusive rate through the membrane.

The surface of the membrane could be textured to greatly increase the surface area. This may increase the hydrogen "alloying" rate and, hence, the diffusion through the membrane. A AgPd foil must have its surface activated before the hydrogen permeation rate becomes significant. (Jewitt and Makrides, 1965) report that argon ion bombardment, a common method for producing clean surfaces for absorption studies, is also useful for activating the surface of a AgPd foil. In particular, they used 300 to 600 ev Ar+ ions to clean and activate the surface. Their experimental results showed that this preparative technique gave essentially the same permeation rates that one would get using other common preparative techniques. Later experimenters (Kishimoto and Hirai, 1977) suggest that surface preparation produced active sites (possibly a kind of surface defect) and these active sites are necessary for high permeation through the foils. In view of the relatively low energies used by Jewitt and Makrides, we feel that the 1 to 2 keV Ar+ ions available at Lewis could be used to clean, produce active surface sites and/or etch the surface of a AgPd foil. If one could successfully etch the surface, then one would have an increased surface that presumably would be activated. Fundamental studies of Pd membranes are required to test the validity of these ideas. These should include *in situ* permeation tests immediately after ion bombardment to get a good measure of treatment effectiveness.

Yttrium and cerium alloys of Pd also show promise as foil materials specific to H_2. For example, hydrogen throughput for some of these alloys are reported to be 50% higher than the conventional Ag-Pd system. Surface oxidation is sometimes a problem, but this is overcome by coating the membrane with 500 Å of Pd (Knapton, 1977). This is also an excellent application for ion beam technology.

In view of the energy problems current and projected, the use of ion beam technology in manufacturing and studying effusive and diffusive filters can reasonably be expected to pay dividends in the future.

VI. APPLICATIONS TO CATALYSIS

Almost all industrial chemical processes depend upon catalytic enhancement of reaction rates at reduced temperatures. Among major applications of catalysis are petroleum refining and suppression of pollutants in automotive exhausts. These typically involve the passage of fluid or gaseous streams over or through beds containing the catalytic material so that a large area of catalyst is exposed to the stream. The catalyst is often "carried" on the external and internal surfaces of porous beads. It is hard to see how ion beam deposition of catalytic material can be usefully applied in such circumstances, particularly in view of the tendency for "sintering" processes to take place, which reduce the amount of effective catalytic surface area. These processes occur more rapidly at high temperatures.

Two developments have been reported within the past few years, however, which may be able to take advantage of the unique characteristics of ion beam technology. Work at the Johnson-Mathey Research Center (Pratt and Cairns, 1977) has indicated that it may be quite feasible to fabricate substrates for automotive catalytic converters from alloy steel foils of an appropriate composition. These foils are capable of withstanding the operating temperatures of the automotive application, and of coming to the proper equilibrium temperature fairly quickly. With procedures for depositing the catalytic coating on the foils, the overall structure has promise of being more compact and using less catalyst material than present structures. Work at the Alloy Surfaces Company (C & E News, 1977) on the leaching of previously deposited layers which had been diffused into metal surfaces has led to the development of very reactive surfaces, similar to those achieved with Raney nickel. The reactivity is attributed to the development of a very finely porous surface having a very high specific surface area.

It becomes quite clear that a very attractive possibility is the deposition by ion beam sputtering onto the foil of an intimate mixture of catalyst material, e.g., platinum, and some plastic material, after which the plastic material would be boiled off leaving a porous deposit, of high specific area. The foil could then be fabricated into the active material for the catalytic converter. The use of the sputtering technique combined with the deposition onto thin foil makes possible very precise control of the amount of catalytic material, and may lead to substantial economies in the use of platinum for this purpose. Such a structure may also be useful for recovery of the platinum from the surface of converter inserts which had reached the limit of their useful life.

The co-deposition technique can be extended readily to the deposition of several different catalytic materials, so as to make possible the use within one structure of three-way conversion techniques for the suppression of unwanted emissions in automotive exhausts. Such deposition techniques would be useful for other catalytic applications.

In a more straightforward application of ion beam technology, it is apparently well-known in some automotive circles that the presence of platinum on valves and cylinder walls in diesel engines suppresses soot formation. Certainly the preparation of controlled adherent platinum deposits on valves represents an area of reasonable technical certainty.

Some studies indicate that it is not necessary to have full coverage of a surface by the catalytic material in order to obtain suitable behavior.

In fact, agglomeration of the catalyst material reduces the effectiveness of the catalyst (see comment about sintering above). Thus the use of ion implantation techniques may be called for; however, the implantation depth apparently need not be very deep. Thus adaptation of the Lewis apparatus for modest biasing of the substrate, as discussed elsewhere in this report, may suffice for this application.

We have transmitted some glassy carbon substrates from Dr. Ted Kuwana of the Ohio State University Chemistry Department, for the deposition of fractional monolayers of palladium and silver. In order to simulate implantation to a depth within the substrate, it may be desirable to sputter a deposit of carbon on top of the palladium or silver.

Another application to catalytic purposes where ion beam technology may be significant, is in the deposition of small amounts of platinum on ceramic electrochemical and electroresistive devices being developed as exhaust system sensors for feedback loops in microprocessor controlled automotive ignition and carburetion systems.

VII. SPUTTERING, TEXTURING, AND OTHER APPLICATIONS

A. Bearing Surfaces. Obvious applications are the deposition of coatings of thin hard materials with good wear properties, onto materials with poor surface properties, but with good bulk properties in terms of ductility, strength-to-weight ratio, etc. Such deposition could be carried out without having to heat the underlying structure excessively, thereby minimizing distortion. A more subtle application is the deposition of bearing material having a hard component in a soft matrix to reduce the likelihood of seizing. For example, the deposition of Pb-Co, Pb-Cu, or Pb-carbide might be useful. Also, the preparation of a spongy deposit, which could hold lubricant effectively could be carried out by the codeposition of a metal and a plastic, with subsequent boiling away of the plastic.

The preparation of bearing surfaces for subsequent deposition (not necessarily ion beam deposition) of suitable surface materials can be carried out by appropriate direct sputtering of the surface at ion energies which would damage, e.g., introduce a substantial density of dislocations at the surface. These would supply channels for subsequent diffusion of the surface treatment material into the bulk.

A number of specimens have been supplied by the Timken Corporation for treatment and subsequent evaluation of wear properties. The treatment here is to be contrasted to the use of ion implantation techniques, demonstrated to give improved surface wear properties. The advantage of ion beam sputtering at Lewis, if the technique proves useful in this application, is the relatively high flux of the ion beam as contrasted to ion implantation apparatus, making possible the treatment of larger items in a much smaller length of time.

B. Titanium Carbide Coatings. Titanium Carbide (TiC) coatings and coated inserts can be used to greatly increase the life of cutting tools, dies, etc. (Sauer, 1974; Bunshah, 1977; Ber, 1971; Persson, 1970). In one particular case, an automotive manufacturer TiC coated a particular die to get a tool life which was increased by a factor of ten. This, coupled with a substantial decrease in downtime, yielded the equivalent of 3 to 4 additional production days per month. Included among the possible applications where TiC coating is useful are cutting tools, punches and dies for stamping sheet metal and drawing tubes and wires, compacting dies for powder metallurgy, cam grooves, and all sorts of sliding surfaces. The list is almost endless.

The properties of TiC coatings that make them useful for these applications are the hardness of the surface, which greatly reduces wear, coupled with a low coefficient of friction to reduce galling and seizing tendencies. Oxidation resistance is good below 750°F, but scaling occurs above 1100°F. The coating process used by Aerobraze Corporation, Eastlake, Ohio, and other companies involves vapor deposition at 1800 to 1900°F. This requires a substrate that will withstand these temperatures. Furthermore, even if the substrate will withstand these temperatures, its hardness and temper will be affected and the part would require rehardening, probably by some form of heat treatment.

Ion beam technology may turn out to be useful to TiC coatings technology. Firstly, there is the possibility of using the beam to preclean the substrate for better adhesion. Secondly, TiC powder (available from Goodfellow Metals) could be used as a sputtering target. This would keep the substrate cooler allowing for the use of lower temperature materials and alleviating the loss of hardness and temper problems. The sputtering rate of TiC needs to be investigated before one can determine the feasibility of this application since typical coatings are 0.0002 to 0.001 inch thick depending on the substrate metal.

In view of the large array of applications for TiC coatings and inserts and the advantages of a cooler process, the possibility of using ion beams to make these coatings should be investigated further.

C. Protective Coatings. There is a particular need for the deposition of protective coatings for optical elements in laser and other optical systems containing corrosive vapors. Among the vapors of concern are fluorine vapors, so that fluoropolymer coatings would be of particular interest. Alternatively diamond-like coatings are also of interest. Both of these have been deposited by ion beam techniques. Because of the necessity of controlling optical pathlengths in these applications, particularly in the ultraviolet region of the spectrum, the coatings need to be 50 ± 5 Å thick. Because of the great control over deposition rates possible with ion beam technology, it is a deposition technique that should be explored for this application. To this end, a number of silica substrates for test depositions have been furnished by the Acton Research Corporation.

We have also looked into the possible advantages that ion beam technology might have for preparation of narrow band-pass ultraviolet interference filters for various analytical and spectral applications. It seems, however, that present deposition techniques give adequate control of thickness of these layers. It is possible that ion beam technology may provide a suitable means of depositing, through co-sputtering, of more suitable filter materials. However, research and development is required to specify materials which would be more suitable than those currently in use.

There have also been instances where the use of coating techniques have been used for carbon filaments which were subsequently formed into brushes for rotating electrical machinery, with considerably improved wear properties. Similarly ion beam implantation has been used for tungsten powders which were later sintered and drawn into filaments. In both these applications ion beam sputtering may be useful for production purposes because of the higher flux as compared with implantation techniques.

D. Ion Beam Texturing. There are some applications where simple ion beam texturing may be useful. For example, the separation of Johanson blocks may be facilitated if the mating surfaces are textured, thereby permitting the introduction of air between the surfaces. Similarly the texturing of bearing surfaces may reduce the likelihood of seizures, particularly if a small amount of lubricant can be retained on the surfaces.

E. Multi-Pinhole Lenses. The use of multi-pinhole lenses for the fabrication of effusive membranes by ion beam erosion of very thin foils is discussed elsewhere in this report (Free, 1978). Here, it is worth pointing out that such lenses can be used to make a large array of images of a particular aperture. Thus if a very regular pinhole array is to duplicate a master x-ray zone plate, the preparation of very large aperture soft x-ray lenses becomes feasible. These would make possible the fabrication of instruments of very large "light-gathering power," which would be of considerable use in various x-ray astronomy experiments carried out from rockets and space vehicles. A considerable amount of stability and freedom from vibration during the fabrication of these lenses would be required, however.

F. Photovoltaic Devices. The electrical properties of silicon used in solar cells can be drastically changed using the process of ion implantation, which is described elsewhere in this report. In addition, ion beam evaporation may be useful in fabricating antireflection coatings, electrode geometries, etc. (Dey and Scholz, 1977; Landis and Young, 1979). Although NASA would have an interest in solar cells because of their space applications, the large commercial effort on conventional silicon solar cells may preclude NASA from entering this field. However, there is some research ongoing at Kent State concerning an unconventional photovoltaic device which involves a semiconducting layer of Prussian Blue (PB) sandwiched between metallic electrodes. Ion beams may be useful in the construction of this device by cleaning the glass substrate and sputtering metallic electrodes. There has been some interaction between Dr. Neff of Kent State and NASA personnel on this project. This application is very interesting but quite speculative at this point.

PB can also be used as a display material. It is deposited as a film on a platinum or gold electrode. The film is inserted into a KCl solution and can be made to appear colorless, blue or green depending upon the magnitude and polarity of the applied voltage.

VIII. ION BEAM IMPLANTATION

Based on our study of the literature and attendance at the IBMM-80 Conference on Ion Beam Modification of Materials (discussed in our special report dated July 23, 1980), it is quite clear that ion implantation techniques, as contrasted to ion beam sputtering techniques, are extremely useful for the modification of materials. Of particular interest is the demonstrated success in making corrosion and wear-resistant surfaces. These techniques involve the use of ions at energies up to a few hundred keV, although most of the work currently reported is around 100 keV. Even bombarding energies of 20 keV are useful in some cases. Most of the accelerators used for these purposes are current limited, and thus the application of the technique is somewhat restricted. The ion beam sources at Lewis Research Center, on the other hand, are capable of rather high currents, but in their current configuration are limited to accelerating voltages of the order of 2 keV maximum. It is in principle possible to bias the targets negatively to achieve higher energies. Moreover, if multiply ionized ions are used, the bombarding energy will be increased proportionally to the degree of ionization. Manipulation and cooling of negatively biased targets would be somewhat more complex than for grounded targets, but for some applications this may not be a problem. A more serious limitation might be associated with the design of sources for the various ions which it might be desirable to implant.

This limitation can be overcome, for many purposes, by using the technique of "recoil implantation," which is based on one of the mechanisms inherent in ion beam implantation. In this technique, a layer of the desired element for implantation is first deposited, say by normal ion beam sputtering. This layer is then bombarded by high-energy noble gas ions, i.e., Ar+, Kr+, or Xe+, which would transfer energy to the atoms in the deposited layer in a "collision cascade," thereby driving them into the surface of the substrate. Some of the initially deposited material will be sputtered off the surface as well, but this will depend upon such factors as the energy of the incident particles and the angle of the beam. It is also possible to deposit an overcoat over the original deposited layer and bombard through this overcoat to reduce the amount of sputtering. Any excess material can be removed by various stripping techniques or by sputtering at low energies. A further variation of this technique is simultaneous ion beam sputtering and high-energy noble gas bombardment.

IX. CONCLUSIONS

The foregoing sections describe some of the applications of ion beam technology which the principal investigators feel are both interesting and relevant. NASA-Lewis is a unique position to pursue experiments in several of these fields because of the availability of high current beams from its ion generators. Lewis could also access some of the interesting ion implantation applications by biasing the targets as described in the previous section. We suggest that serious consideration be given to this option.

We also suggest continuation of the projects already in progress and the commencement of experiments as indicated in the foregoing discussion.

In particular, the radial tire research should be continued since there is a possibility of solving a problem that has both economic and

and safety implications. The carbon fiber study is important because of the ever increasing use of composites in general and because of the applications to aerospace in particular. The cold welding project has clear aerospace applications. The combination of ion beam cleaning followed by ultrasonic cold welding appears to be particularly promising. The energy shortage makes it important to improve the efficiency of production for our conventional fuels and to produce alternate fuels such as hydrogen. Ion beam applications to catalysis, effusive and diffusive filters, and photovoltaic devices look promising in this area. Perhaps this research could be performed in conjunction with another federal agency such as the Department of Energy. The sputtering and texturing applications have already produced some industrial interest, especially those applications which reduce wear. Some of these could have significant positive economic impact.

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