

## PROJECT ADMINISTRATION DATA SHEET

☒ ORIGINAL ☐ REVISION NO. \_\_\_\_\_  
Project No. E-18-506 (05044-0A0) ~~XXXX~~ GIT DATE 6/5/85  
Project Director: R. F. Hochman School/Unit Mat. Engineering  
Sponsor: DHHS/PHS/NIH/NIDR

Type Agreement: Grant No. 5T32-DE07053-10Award Period: From 7/1/85 To 6/30/86 (Performance) 9/30/86 (Reports)Sponsor Amount: This Change Total to DateEstimated: \$ \_\_\_\_\_ \$ 101,166Funded: \$ \_\_\_\_\_ \$ 101,166Cost Sharing Amount: \$ N/A Cost Sharing No: N/ATitle: Dental Materials Science

## ADMINISTRATIVE DATA

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## RESTRICTIONS

See Attached NIH Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval – Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of \$500 or 125% of approved proposal budget category.

Equipment: Title vests with GIT

## COMMENTS:

No funds may be expended after 6/30/86.

Continuation of E-19-532

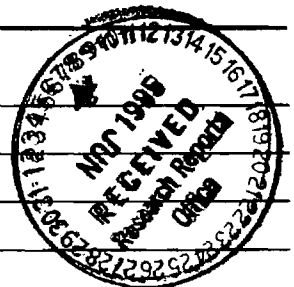
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SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

Date 6-4-87

Project No. E-18-506

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Includes Subproject No.(s) N/A

Project Director(s) Robert E. Hochman

~~XXX~~ / GIT

Sponsor DHHS/PHS/NTH/NIDR

Title Dental Materials Science

Effective Completion Date: 6/30/87

(Performance) 6/30/87

(Reports)

Grant/Contract Closeout Actions Remaining:

☐ None

☒ Final Invoice or Final Fiscal Report

☐ Closing Documents

☐ Final Report of Inventions

☐ Govt. Property Inventory & Related Certificate

☐ Classified Material Certificate

☐ Other \_\_\_\_\_

Continues Project No. E-19-532

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## I. Summary

Dental materials training at Georgia Tech has been in progress for over twenty years as a result of funding of two different, but consecutive, training programs. During that time, more than 60 people have been trained which includes DDS's, PhD's, predoctoral students, as well as "Materials Research Training" for dental students in the summers of the late 60's and early 70's. A large number of dental students, DDS trained dentists, as well as predoctoral and postdoctoral physical scientists have received a broad range of basic materials training as well as training applied specifically to dental materials. The studies have led to 15 theses and 48 research publications. A more detailed report of the training to date is presented in Section II, entitled "Background of Dental Materials Training at the Georgia Institute of Technology." This Section includes theses titles, a list of the publications, as well as a listing of a large number of the trainees, for example, Marek (PhD); Okabe (PhD); Reese (DDS); Love (DDS); Fred (DDS) (summer programs) just to name a few.

To provide the best people to further the understanding and development of more reliable and new restorative dental materials, a well planned and dedicated research and training program is necessary. The proposed program is designed to achieve this through a blend of:

- a) fundamental classroom and laboratory instruction,
- b) supplemental training through seminars and short courses,
- c) interaction with dental school environment and practicing dentists,
- d) research training problems utilizing the latest research tools in studies closely related to dental restorative materials needs.

Postdoctoral trainees will be selected from DDS's and PhD's with indicated interests in the area. DDS trainees will be, and have been, solicited from across the entire country.

The proposed continuation training program will be conducted by an extremely competent staff in the School of Materials Engineering at Georgia Tech. All have stature nationally and several are recognized internationally. Academic and research strength ranges from basic materials, structure-property correlations to special research techniques (Auger, ESCA, SIM's, FIM, SEM, STEM, x-ray diffraction, neutron diffraction, etc.) and corrosion research. Training can be in ceramics, polymers and composites as well as metallurgy. All of these areas are vitally important to achieving advances in dental materials.

Extensive facilities in all phases of modern materials research are available to trainees. Recent equipment expansion has furthered the surface and structure analysis, mechanical property, measurement and corrosion research. The trainee will have all the most modern and sophisticated facilities available for their research training.

The proposed program is designed to provide maximum training by giving proper academic direction and counseling as well as direction to the trainee research to achieve the greatest contribution to the student's growth. All of this has been designed for a critical number of trainees to achieve superior results with a minimum of personnel costs. The proposed training program, the staff, the facilities and the experience, coupled with dental schools interaction, provides the best guarantee that the trainees on this program will develop the background necessary to contribute to dental materials research.

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## II. Background of Dental Materials Training at the Georgia Institute of Technology

## A. Review - Past Trainees

The initial dental materials program at Georgia Tech started in July of 1963 under the direction of the present program director whose involvement in medical-dental materials started in 1957. As the program developed it broadened from strictly graduate training to include postdoctorals, and for a period of time training of dental students in the summer. Its major function was to provide the trainees with a strong background in metallurgy, ceramics and polymers, plus training in the use and application of new research tools and techniques as applied to the research of dental materials problems. As the program developed, more and more interplay between dental and physical science oriented personnel occurred. It is obvious that in addition to the trainees on the program, a large number of Tech staff in Engineering, the Physical Sciences and the Biological Sciences have become much better acquainted with basic dental material problems and the requirements of dental materials research. Broadening of the dental base of the program has resulted through contacts with the Emory Dental School, the Dental School of the Medical College of Georgia and a cooperative program with Dr. Marek, with Dr. Mahler at Oregon, and Dr. Okabe at Baylor.

The work of our trainees to date has resulted in 14 theses and more than 40 papers on dental-medical materials research. For a time period in the late 1960's and early 70's, more than 25 dental students were trained in special summer research training programs. These studies resulted in a number of special projects which received not only local awards, but two projects were finalists in National Table Clinics, with the work of two trainees DDS's, Fred and Aubrey, receiving a second nationally in 1968. Some of the more prominent trainees who have been trained in dental materials and are engaged in direct or related dental material research at Georgia Tech are:

Dr. M. Marek, PhD - Associate Professor of School of Materials Engineering,  
Georgia Institute of Technology

Dr. T. Okabe, PhD - Professor and Chairman of the Department of Dental Materials,  
Baylor College of Dentistry

Dr. L. D. Love, DDS - Professor, Temple University Dental School

Dr. K. J. Bundy, PhD - Associate Professor, Department of Biomedical Engineering,  
Tulane University

Dr. S. Fred, DDS - One time NIDR staff member (now in practice)

Dr. S. Reese, DDS - Assistant Professor of Operative Department,  
Emory University School of Dentistry

Dr. R. J. Mitchell, PhD - Assistant Professor of Restorative Dentistry,  
Dental School of University of Kentucky

Dr. F. M. Butler, DDS - part-time staff member at Emory University and  
Georgia Tech Staff

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Dr. S. Frieman, PhD - Senior Research Scientist, National Bureau of Standards,  
Gaithersburg, Maryland

Dr. A. Villastrigo, DDS - A trainee went to dental school after training at  
Georgia Tech, now a part-time professor at the  
Dental School of University of Texas

Dr. B. Carter, PhD - Research Scientist II, School of Materials Engineering,  
Georgia Institute of Technology

Dr. Saghana B. Chakraborty, PhD, MD - Medical Intern University of Miami

Dr. S. I. Meletis, PhD - Assistant Professor, University of California-Davis

In addition, four other trainees on the program are still actively engaged in  
materials research that can relate to dental-medical products. They are:

Dr. J. W. Koger - Senior Research Metallurgist  
Oak Ridge National Laboratory

Dr. E. L. Ling - Products Research Laboratories,  
St. Joseph Mineral Corporation

Mr. J. C. Caron - Texas Instruments,  
Dallas, Texas

Mr. J. A. Quintal - Martin-Marietta, Aero Space,  
Denver, Colorado

Mr. F. J. Topolski - Western Electric-Bell Telephone Laboratories,  
Atlanta, Georgia

## B. Present Trainees

At this time, there are two predoctoral candidates, Mr. Charles Dervenis and  
Mr. K. Kim and two postdoctorals, Dr. Marlon Jackson (DDS) and Dr. Ali Erdemir.  
The latter is just initiating his postdoctoral program with the completion of his  
thesis and the receipt of his PhD degree this quarter. A short description of the  
program for each trainee is included below.

Postdoctorals

Dr. Marlon Jackson (DDS) is now in his second year of training. His program  
was interrupted for a year allowing him to recover from a serious automobile  
accident. Dr. Jackson received his DDS from the Emory University Dental School in  
June, 1983, and started a postdoctoral program dealing first with obtaining a  
background in basic materials. Since he has returned he has also initiated a  
research program studying the various aspects of surface modification on wear and  
friction behavior of dental cutting materials and the potential of surface  
modification for use in restorative applications. It is also planned to provide  
him teaching experience by utilizing his background in the dental-biological areas  
to provide classroom lectures and general information about clinical dentistry to  
the nondental trainees. At present, he is also working with the Grant Director in  
developing a project which will lead to an AADR paper to be submitted for consideration  
for the 1987 AADR meeting.

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Dr. Ali Erdemir will be joining the program on receipt of his PhD this quarter. Dr. Erdemir has been involved in the use of surface modification through ion plating and ion implantation to produce new and unusual surface properties for materials. Through this study, titanium nitride ion plating, has resulted in improved friction and wear characteristics, in some instances more than an order of magnitude (10 times). In addition, further studies on the corrosion resistance of titanium nitride has shown unusual features for possible exploitation as a highly biocompatible material in the oral environment, whether it be saliva, gingiva or bone structure. It can easily be conceived that some of this work may also lead to methods of treating dental implants to obtain much greater biological attachment and interaction.

#### Predotorals

Mr. Charles Dervenis is presently working in the area of corrosion fatigue of materials and alloys leading towards a Master of Science Degree in Metallurgy. The importance of this work is showing the variation of mechanical and structural behavior on the corrosion fatigue life of alloys, of particular potential is information to be related to in vitro applications. At the same time, Mr. Dervenis is also broadening his background into the dental-biological background.

Mr. K. Kim is a permanent resident of the United States and plans to remain in this country. He is presently working on the aspects of ion implantation in improving surface properties of materials. His work to date has shown the potential to produce stable iron boride surface structures in materials which lead to improved corrosion and wear resistance. Mr. Kim is also being groomed to develop his dental-biological knowledge and his appreciation of the applications of biomaterials in these areas.

#### C. Potential Trainees

Both Mr. Dervenis and Mr. Kim will soon be completing their predoctoral program and I plan to work with one of them to continue on to the PhD. In addition, several other new graduate students, one a minority, is being considered for the potential open-slot in the program. In the postdoctoral category, both Dr. Jackson and Dr. Erdemir will continue on to complete their two or three years training on the program before following a career development award or other research training and then go into related professional careers. For the open-slot for a postdoctoral, we have been actively soliciting DDS's in hope of keeping approximately a ratio of two DDS's to one PhD for a majority of the program. At present, we have two applicants, one who has a DDS degree from Athens, Greece and is certified to practice in this country. This applicant is a lady who is interested in dental materials research. She is a permanent resident of the United States and is qualified to participate in this program. The other is a young dentist from Montgomery who received his DDS through the University of Alabama Dental School and in contact with the people there, has developed interest in dental materials. He is interested in coming to Georgia Tech to follow a program of research and development in dental materials.

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## D. Research - Theses and Publications

The research on the training programs, of course, is principally designed for training, however, the work has also yielded significant results in many areas. Some of the principal contributions have been in the understanding of corrosion and biocompatibility in the oral environment, particularly of dental amalgam and implants; the basic diffusion and reaction kinetics in dental materials; and the use of ion implantation to improve the fatigue and corrosion resistance of dental alloys which provides the possibility of low cost, high compatible, crown, bridge and implant materials. This research has resulted in 14 theses and more than 30 papers directly or indirectly related to the research on the training programs to date. A partial list of these publications is provided below:

## 1. Theses

- a) Lozier, Jay S., "Sulfide Tarnishing of Metals." M.S. in Metallurgy (Dental Materials)
- b) Pike, Richard A., "Zirconia Induction Furnace - For Melting High Temperature Alloys." M.S. in Ceramics (Dental Materials)
- c) Crooks, Roy E., "The Influence of Microstructure on the Ductility of Alloys." Ph.D. in Metallurgy (Dental Materials)
- d) Averette, D. F., "The Relationship Between Corrosion and Mechanical Properties of Dental Amalgam." Ph.D. in Metallurgy (Dental Materials)
- e) Biloft, Peter B., "The Effect of Porosity on Corrosion of Dental Amalgam." M.S. in Metallurgy (Dental Materials)
- f) Butler, M.F., "Bacteriostatic Effects of Corrosive Products from Metals Applicable to Dental Materials for the Purpose of Decay Prevention." M.S. in Metallurgy (Dental Materials)
- g) Villastrigo, A.C., "Tarnishing of Dental Gold Alloys." M.S. in Metallurgy (Dental Materials)
- h) Quintal, J.A., "The Effect of Ion Implantation on Dental-Medical Alloys." M.S. in Metallurgy (Dental Materials)
- i) Chien, K. H., "The Effect of Ordering on Low Cycle Fatigue of  $\text{Cu}_3\text{Au}$ ." Ph.D. in Metallurgy (Dental Materials)
- j) Love, L.D., "Corrosion Characteristics of Dental Amalgam." M.S. in Metallurgy (Dental Materials)
- k) Topolski, F.J., "The Effect of Ultrasonics on the Physical and Mechanical Properties of Metals." M.S. in Metallurgy (Dental Materials)
- l) Horne, E.W., "Order Strengthening in Equiatomic Copper-Gold." M.S. in Metallurgy (Dental Materials)
- m) Caron, J.C., "The Effect of High Condensing Pressures and Ultrasonics on the Hardness of Dental Amalgams." M.S. in Metallurgy (Dental Materials)



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- n) Freiman, S. W., "Diffusion of Mercury into Silver-Tin Dental Alloy ( $\text{Ag}_3\text{Sn}$ ) Including the Effect of Ultrasonic Energy." M.S. in Metallurgy (Dental Materials)
- o) Koger, J. W., "A Study of the Kinetics of the Mercury Reaction with the Silver-Tin Dental Alloys." M.S. in Metallurgy (Dental Materials)

## 2. Major Papers Presented and Published

A list of the major papers delivered in relation to the Georgia Tech dental materials program follows.

- a) "In Vivo and in Vitro Studies of the Stress Corrosion Cracking Behavior of Surgical Implant Alloys," K. J. Bundy, M. Marek, and R. F. Hochman, J. Biomed. Mater. Res., 17:467-487 (1983).
- b) "Low Temperature Diffusion of Copper in the Alpha-1 and Beta-1 Phases of Dental Amalgam," S. B. Reese, R. F. Hochman, and M. Marek, Annual Session of the AADR, Los Angeles, 1980.
- c) "The Effect of Fluoride on the Corrosion Behavior of Dental Amalgam," P. M. Soni, R. F. Hochman, and M. Marek, Annual Session of the AADR, Los Angeles, 1980.
- d) "An Electrochemical Test for the Evaluation of Sulfide Tarnishing of Dental Alloys." In "Corrosion and Degradation of Implant Materials: Second Symposium," M. Marek, ASTM STP 859 (A. C. Fraker and C. D. Griffin, Eds.), ASTM, Philadelphia, PA, 1985, pp. 167-178.
- e) "The Effect of Tensile Strain on Corrosion of Dental Amalgam," D. F. Averette and M. Marek, J. Dent. Res., 62:842-845 (1983).
- f) "Corrosion of Dental Materials." In "Aqueous Corrosion and Passive Films," M. Marek, Treatise on Materials Science and Technology, Vol. 23 (J. C. Scully, editor), pp. 331-394, Academic Press, 1983.
- g) "Acceleration of Corrosion of Dental Amalgam by Abrasion," M. Marek, J. Dent. Res., 63:1010-1013 (1984).
- h) "Creep of the Matrix Phases of Dental Amalgam as a Function of Composition," D. F. Averette and M. Marek, Annual Session of the AADR, Los Angeles, 1980.
- i) "Surface Modification by Ion Processes - An Emerging Technology," R. F. Hochman, Proceedings of ASM Conference on "The Applications of Ion Plating and Implantation to Materials," June 1985 (In Press).
- j) "Techniques for Analysis of Ion Plated and Implanted Surfaces," W. B. Carter, Proceedings of ASM Conference on "The Applications of Ion Plating and Implantation to Materials," June 1985 (In Press).
- k) "The Corrosion Properties of Ion Plated, Implanted and Amorphitized Metal Surfaces," R. F. Hochman, M. Marek, and H. J. Kim, Proceedings of ASM Conference on "The Applications of Ion Plating and Implantation to Materials," June 1985 (In Press).

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- l) "The Friction, Wear and Corrosion Properties of Ion Plated TiN," W. Alina, R. F. Hochman, and A. Erdemir, Proceedings of ASM Conference on "The Applications of Ion Plating and Implantation to Materials," June 1985 (In Press).
- m) "Corrosion Wear Properties of Ion Plated TiN Films," E.I. Meletis, A. Erdemir, and R. F. Hochman, Proceedings of ASM Conference on "The Applications of Ion Plating and Implantation to Materials," June 1985 (In Press).
- n) "Corrosion Behavior of Surface Films on Boron-implanted High Purity Iron and Stainless Steels," H. J. Kim, W. B. Carter, E. I. Meletis, and R. F. Hochman, Materials Science and Engineering, 69 (1985) 297-301.
- o) "A Study of the Corrosion Behavior of TiN Films," A. Erdemir, W. B. Carter, E. I. Meletis, and R. F. Hochman, Materials Science and Engineering, 69 (1985) 89-93.
- p) "Ion Plating," R. F. Hochman, 9th Edition ASM Handbook, Volume 5.
- q) "Ion Implantation," R. F. Hochman, 9th Edition ASM Handbook, Volume 5.
- r) "A Study of Fatigue and Corrosion Fatigue of Surgical Implant Materials and Ion Plated and Implanted Materials," R. F. Hochman and M. Marek. Proceedings of the First World Biomaterial Conference, Vienna, Austria, April 8-12, 1980.
- s) "The Effect of Sodium Fluoride on the Corrosion Behavior of Dental Amalgams," R. F. Hochman, P.M. Soni and M. Marek. Published on Conference Microfilm Proceedings, AADR, 1980 Annual Conference, Los Angeles, CA, March 20-23, 1980.
- t) "Low Temperature Diffusion of Copper in  $\alpha_1$  and  $\beta_1$  Phase of Dental Amalgam," R. F. Hochman, S. Reese and Marek. Published on Conference Microfilm Proceedings, AADR, 1980 Annual Conference, Los Angeles, CA, March 20-23, 1980.
- u) "Comparison of the Accuracy of Denture Bases by a Non Parametric Method," P. Soni, Journal of Oral Rehabilitation B (1), 35-39 January 1979.
- v) "An Analysis of In Vivo and In Vitro Biomaterials Properties and Service Characteristics of Orthopedic Implants," R. F. Hochman, M. Marek and K. Bundy. Trans. 11th Int. Biomat. Symp. 3, 126, 1979.
- w) "Bacteriostatic Effects of Pure Metals," R. F. Hochman, K. J. Bundy, and M. F. Butler, J. Biomed. Mat., in press.
- x) "Solution Chemistry of Crevices and Stress Corrosion Cracks," R. F. Hochman and M. Marek and J. G. Rinker, Proceedings of the 6th International Congress on Metallic Corrosion, ICME Australia, 1978, pp. 445-461.
- y) "Material Failure in Medical-Dental Devices," R. F. Hochman - SAMPE, Quarterly, Jan. 1978, pp. 28-33.

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- z) "Mechanism of Crevice Corrosion of Dental Amalgam," M. Marek and R. F. Hochman, Paper presented to the 53rd Session of the IADR, London, April 1975 (DMG microfilm).
- aa) "In Vitro Corrosion of Dental Amalgam Phases," M. Marek, T. Okabe and R. F. Hochman, Paper presented to the 1975 General Session of the AADR, New York, April 1975 (DMG microfilm).
- bb) "In Vitro Corrosion of Dental Amalgam Phases," M. Marek, T. Okabe and R.F. Hochman, Accepted for publication, Journal of Biomedical Materials Research. Based in part on the preceding paper.
- cc) "Auger Analysis of Surface Films on  $\text{Ag}_3\text{Sn}$ ," H.E. Grenga, J.L. Carden, T. Okabe, R. F. Hochman, J. Biomed. Mater. Res., Vol. 9, pp. 207-211 1975.
- dd) "Amalgamation Reaction on Mercury-Plated Dental Alloy ( $\text{Ag}_3\text{Sn}$ )," T. Okabe, R. F. Hochman and L. O. Sims, J. Biomed. Mater. Res., Vol. 9, pp. 221-236 1975.
- ee) "Tracer Diffusion of Silver and Tin in a Dental Alloy ( $\text{Ag}_3\text{Sn}$ )," T. Okabe, R. F. Hochman and M.E. McLain, J. Biomed. Mater. Res., Vol. 8, pp. 381-392 1974.
- ff) "A Study of Simulated Stress Corrosion Crack Tip Electrochemical Reaction," R. F. Hochman, R. Piccinini, M. Marek and A.J.E. Pourbaix, Proc. of Conf. on Localized Corrosion, NACE 1974.
- gg) "Passivity of Dental Amalgam," M. Marek and R. F. Hochman, paper presented at the TMS-AIME/IMD and ASM/MSD Session, 1972 Materials Engineering Congress, Cleveland, Ohio, 1972.
- hh) "A Study of Localized Corrosion Cell Reactions," M. Marek and R.F. Hochman, Proceedings of the 1973 NACE Corrosion Science Symposium.
- ii) "Crevice Corrosion in Dental Amalgam Restorations," M. Marek, M.F. Butler and R.F. Hochman, paper presented at the 51st Session of the IADR, Washington, D.C., 1973.
- jj) "The Corrosion Behavior of Dental Amalgam Phases as a Function of Tin Content," M. Marek and R.F. Hochman, paper presented at the 51st Session of the IADR, Washington, D.C., 1973.
- kk) "Advances in Dental-Medical Implant Materials," Plenary Lecture, 65th Meeting European Federation of Corrosion, Dubrovnik, Yugoslavia, April 18, 1972, Published in Conference Proceedings and CEBELCOR Report.
- ll) "Corrosion Behavior of Amalgam Electrodes in Artificial Saliva," M. Marek and R. F. Hochman, Proceedings, 50th Meeting of IADR, March 23, 1972, Las Vegas, Nevada.
- mm) "Kinetic Factors in Amalgamation of Dental Alloy," T. Okabe, R.F. Hochman and M.E. McLain, Proceedings 50th Meeting of IADR, March 23, 1972, Las Vegas, Nevada.

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Hochman, Robert F.

- nn) "Amalgamation Reaction of Tin, Silver and Dental Alloys (Ag<sub>3</sub>Sn)," T. Okabe, F. Ling and R.F. Hochman, J. Biomed. Mater. Res., Vol. 6, pp. 553-573, 1972.
- oo) "Crystallography and Kinetics of Stress Corrosion Cracking of Type 316 Stainless Steel Single Crystals," M. Marek and R.F. Hochman, Vol. 27 No. 9, Sept., 1971, NACE, Houston, Texas.
- pp) "Review of Metal Base Dental-Medical Implant Materials," R.F. Hochman, presented April 16, 1970, Clemson University, Proceedings, Materials for Implant Dentistry, to be published.
- qq) "Fatigue Properties of Implants," R.F. Hochman, presented at National Meeting, AIME, February 1969, New York, N.Y.
- rr) "High Strength Amalgams Produced by Changing the Fracture Characteristics with Different Condensing Methods," R.F. Hochman and J.C. Caron, Presented March 21, 1968, Houston, Texas, Proceedings of the 1968 IADR Meeting.
- ss) "Improved Properties of 316L Stainless Steel Implants by Low Temperature Stress Relief," R.F. Hochman and L.M. Taussig, Presented by R.F. Hochman at the joint ASM-ASTM Symposium on Orthopedic Materials, Detroit, Michigan, published by J. of Materials, Vol. 1, No. 2, ASTM, June 1966.
- tt) "The Kinetics of the Mercury Reaction with Silver-Tin and the Effects of Ultrasonics of this Reaction," R.F. Hochman, J.W. Koger and S.W. Freiman, presented by R.F. Hochman at the Proceedings of the Meeting of the IADR, July 1965, Toronto, Canada.
- uu) "The Effect of Ultrasonic Energy on Diffusion and Sintering," R.F. Hochman, S.W. Freiman and R.M. Gray, presented by R.F. Hochman, June 23, 1965, at an International Conference on Sintering and Related Phenomena, published.
- vv) "Metals in the Human Body," R.F. Hochman, Metals Review, Vol. XXXVII, No. 8, August 1964, American Society for Metals, Cleveland, Ohio.

This list represents only the major presentations and publications and does not include numerous presentations and lectures to technical, dental and medical groups by members of the program staff and trainees, and a particular series of presentations by R.F. Hochman on "Advances in Dental-Medical Materials," at more than twenty meetings across the country.

## III. Proposed Training

## A. Objectives

The requirements for restorative dental continues to require improved and more reliable dental restorative materials. A number of reports in the past several years has pointed out this basic requirement to dental health which will be with us for well past the year 2000. To achieve this type of improvement in materials, requires strong basic training in materials engineering and physical sciences which must come from areas with broad physical science and engineering programs with the unique and sophisticated facilities, only possible in such programs. With this training the student may easily adapt his knowledge to the problems associated with dental materials. It is also important that those trained in the pure physical science and engineering atmosphere be introduced to the problems in the real world of dentistry at a point early in their training. To achieve this, the proposed program can be best summarized in the following short statement of training objectives.

- a) Strong academic and laboratory instruction in fundamental materials research.
- b) Effective supplemental training through seminars, short courses and special laboratory instruction in specialized or advanced materials research areas.
- c) Continuing interaction with dental schools and practicing dentists on their problems and requirements.
- d) Develop a basic research problem or theses study for each trainee to utilize a broad range of knowledge and techniques on a problem that can relate to dental materials.
- e) Arrange special dental orientation program for non-dental trainees to stimulate and challenge their interests in the field.

To pursue this program the training starts with the selection of the trainee, followed by his academic program, including dental orientation for non-DDS trainees, and culminating in the trainees research training project.

## B. Trainee and Trainee Selection

In predoctoral selection two major points will be stressed: one, a good academic background, and two, a strong interest in the dental-medical materials and the bio-engineering areas. Since the re-establishment of our dental materials training program we have now reached a point where predoctoral applications have exceeded available space and postdoctorals in non-DDS fields also exceeds our requirements. However, we are showing a preference to any DDS with a qualified background because of their greater dedication to the field. However, it is also obvious with trainees such as Dr. Marek, Dr. Okabe, Dr. Bundy, Dr. Meletis, Dr. Mitchell, etc., that significant contributions by non-DDS's are and will be made. The program should have a selection ratio of one out of every two or three interested candidates. This will result in a high retention of the graduated trainees in the dental-medical area. In fact, the possibility of retention is far more than it was when the first training grants in dental materials were conceived in the early 1960's, due most probably to more publicity of the area as well as more information on careers in biomaterials education and research. This awareness on the part of prospective graduate students has been manifested in much greater interest in biomaterials on the part of prospective graduate students. In addition, a number of minority students have expressed interest, and Marlon Jackson, DDS, is presently a trainee in this program.

Postdoctoral trainees will be selected from two sources, Ph.D.'s and Sc.D's in metallurgy and materials and DDS's. It is planned to have at least one, hopefully two, DDS's on the program at all times. The materials postdoctoral will be a choice from

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several candidates we have each year. Because of our background in biomaterials a number of new doctorals, wishing to broaden their knowledge in research in this area, apply to us. This, plus our own Ph.D.'s with biomaterials interests, will provide an excellent selection for postdoctoral trainees.

The DDS postdoctoral prospects may come from several sources. The first will be through our interaction with our area dental schools (Emory and Georgia); the second through our personal contacts with other dental schools, not only in relation to new graduates, but particularly those schools with young staff, they may wish to broaden in dental restorative materials; and finally through selective advertizing to prospective and graduated DDS's, the latter is accomplished through a special brochure. Since the normal postdoctoral program is 2 to 3 years in length, recruitment of 2 or 3 DDS postdoctorals (during the 5-year program) should not be a difficult accomplishment, particularly based on the recent DDS interest. It would also be extremely effective in DDS recruiting as well as general DDS training if the very successful summer dental student training programs in dental materials be reinstituted.

### C. Academic Training

The academic training, as a result of the flexibility in our graduate programs, can have a range of course requirements depending on student-preceptor decisions. Although the major consideration is the academic and research training of the DDS postdoctoral, it is possible for most DDS's to achieve a MS, by fulfilling the normal requirements for academic and research training on the program. There are many permutations possible so only the three most probable programs are presented below. It must be understood that these programs are not inflexible and several variations in each category are possible.

#### 1. Predoctoral - MS or PhD candidate.

Requirements: Math: Through Differential equations  
Physics: Through Basic College Physics  
Chemistry: Through Physical Chemistry  
Materials: Min. of 5 hours for non-material disciplines  
and 25 hours for material BS degrees.

#### Course Requirements (Credits are in quarter hours):

Met. 4421 - 3 hrs - Nonferrous Metallography  
Met. 4422 - 4 hrs - Ferrous Metallography  
Met. 4423 - 3 hrs - Metallurgical Fabrication  
Met. 4441 - 3 hrs - Physical Metallurgy  
Met. 4445 - 3 hrs - Electron Microscopy  
Met. 4446 - 4 hrs - X-ray Metallography  
Met. 4491 - 3 hrs - Corrosion  
Met. 6005 - 2 hrs - Dental-Medical Materials  
Met. 6091 - 3 hrs - Advanced Corrosion  
Met. 7051 - 3 hrs - Advanced Mechanical Met.  
Met. 7081 - 3 hrs - Metallurgical Thermodynamics  
Met. 7085 - 3 hrs - Metallurgical Kinetics  
Met. 8001 - 2-3- 3 hrs - Seminar  
ChE. 4450 - 3 hrs - Polymers  
CerE. 3080 - 2 hrs - Survey of Ceramics  
Dental orientation program - minimum of 4 weeks

For the M.S. a Theses Research Problem completes the program. The Ph.D. trainee must complete at least 20 more hours of advanced materials courses, a 15 hour minor in a related field, plus a high level, indepth, publishable thesis research study.

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2. Postdoctoral DDS

Requirements: Math: Through calculus or take special Tech Math  
Course 1710

Physics: College Physics or Special Physics  
Course 3003

Chemistry: Physical chemistry or Special Physical  
Chemistry Course 4741

Materials: 5 hours or Metallurgy 3301

Course Requirements:

Met. 4421 - 3 hrs - Nonferrous Metallography  
Met. 4422 - 4 hrs - Ferrous Metallography  
Met. 4423 - 3 hrs - Metallurgical Fabrication  
Met. 4441 - 3 hrs - Physical Metallurgy  
Met. 4445 - 3 hrs - Electron Microscopy  
Met. 4446 - 4 hrs - X-ray Metallography  
Met. 4491 - 3 hrs - Corrosion  
Met. 6005 - 2 hrs - Dental-Medical Materials  
Met. 7081 - 3 hrs - Metallurgical Thermodynamics  
Met. 7085 - 3 hrs - Metallurgical Kinetics  
Met. 8001 - 2-3 - 3 hrs - Seminar  
ChE. 4450 - 3 hrs - Polymers  
CerE 3080 - 2 hrs - Survey of Ceramics

A reserach problem or with completion of the above course requirements a thesis which would qualify the trainee for a Master of Science degree in Metallurgy and Materials.

3. Materials Postdoctoral

Special dental training orientation of 4 weeks minimum duration plus a selection of at least 20 hours of advanced course work in metallurgy, polymers and ceramics. Applicable courses in chemistry, physics, and mathematics with the training directors approval, are also possible. A partial list of courses is provided below:

Met. 4464 - Nondestructive Testing  
Met. 6014 - Electrometallurgy  
Met. 6025 - Powder Metallurgy  
Met. 6033 - High Temperature Metallurgy  
Met. 6091 - Advanced Theory of Metallic Corrosion  
Met. 7041 - Advanced Physical Metallurgy I  
Met. 7045 - Advanced Electron Microscopy I  
Met. 7046 - Advanced Electron Microscopy II  
Met. 7051 - Advanced Mechanical Metallurgy  
Met. 7052 - Advanced Dislocations and Strengthening Mechanisms I  
Met. 7053 - Advanced Dislocations and Strengthening Mechanisms II  
Met. 8100 - Special Topics in Advanced Physical Metallurgy  
Ch.E. 6751 - Polymer Science and Physical Properties II  
Ch.E. 6753 - Surface Science and Technology Laboratory  
Ch.E. 4004 - High Temperature Thermodynamics  
Cer.E. 4053 - Technical Ceramics  
Cer.E. 6030 - Crystal Structure of Materials  
Cer.E. 6031 - Crystal Structure of Materials

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## D. Research Training

The major aspect of the theses, or the research problem of a trainee is the performance of original work to develop the fundamental understanding of basic research and research techniques. The research, will of course be on a dental material related problems, but since training, and not the application of the research, is of paramount importance, the results may not be readily applicable to clinical evaluation. Some studies can be, and will be turned over to dental school clinicians, others will require further study and applied developments.

After the predoctoral has been on the program for approximately 6 months, and had the opportunity to observe the various areas of thesis research, meetings with the program director and possible preceptors are arranged to initiate preliminary studies and literature review. This should be completed at the end of another quarter and the trainee will then initiate preliminary research studies. He will have then had approximately three quarters to develop laboratory skills to be productive.

Postdoctoral, DDS's will follow a similar time table to allow for academic and laboratory training for a sufficiently indepth approach to a research problem or an MS thesis study in materials. Postdoctorals in materials science are expected to pick a problem in the first quarter and be well into its development in the second quarter of residence. A brief review of five possible broad areas of research study are presented here and ten more specific research ideas are also listed.

## 1. Research Areas

## a) Corrosion Research

Our research in corrosion has evolved into a program of national and international significance. Even with the advances in the understanding of the corrosion characteristics of dental amalgam, its influence on the actual life of amalgam restorations has still not been thoroughly evaluated. The amalgam corrosion tests developed here at Georgia Tech has shown that much is still not known of the oral compatibility of dental restorative materials. The relationship between corrosion and micro-structure is necessary not only in amalgam, but in other cast and wrought restorative materials. In addition, the characterization of corrosion and cytotoxicity bears further investigation and the biological responses to materials must necessarily be examined. Tests utilizing impressed current to increase the corrosion rate can provide accelerated tests for study of these phenomena. New materials being used for orthopedic implantation should be examined for stability in the oral environment. In addition, the great potential for the use of ion plating and implantation for improving the surface characteristics involving fatigue and corrosion resistance will be studied.

## b) Surface Modification (Ion Plating and Ion Implantation)

Work over the last few years in our program at Georgia Tech has indicated improved fatigue resistance, improved corrosion characterization and most recently a unique wear improvement in various ion plated or implanted systems.



For example, Mo plating or implantation of actual service materials may greatly deter crevice and pitting corrosion phenomena. In addition, it is also plausible to expect further research efforts utilizing both ion implantation and ion plating will produce beneficial effects in relation to the biocompatibility and even potential biological interaction or attachment. It is obvious from the interest generated at recent meetings that there are many potential applications of these processes in dental restorative materials. A summary of these processes and their application is contained in the paper attached as Appendix 1.

c) Surface Studies

It is obvious that a unique and vital consideration of any system in contact with the oral environment is how its surface interfaces with its environment. The surface, having differences in free energy and often a difference in composition, serves as the interface between the environment and the material bulk. In previous work on surfaces of amalgam alloy, oxidation and sulfur tarnish were both found and a unique variation from initially a tin oxide to later a silver sulfide surface was found. This auger work indicates the broad range of studies possible for characterization of not only materials surfaces, but the oral-material interface. Now with the availability of much more sophisticated equipment such as the scanning auger microscope, the scanning ion microscope, and electron spectroscopy for chemical analysis (ESCA), evaluation of surface layers and how the surface changes as a function of exposure to environment is possible. Even evaluation of interaction in the environment on an atomic level is possible. It is planned, as this program proceeds, to have at least one trainee in the area of surface phenomena to characterize the interface between metal-tissue, metal-bone or tooth, and metal vs. saliva.

d) Polymers and Composites

An excellent polymer program has emerged in the Engineering College at Georgia Tech. Close cooperation between the people in our program and the polymer program has been developed. The most noteworthy study to date has been the preliminary work on an adhesive bond to tooth and bone structure as a result of unsaturated hydroxyl bonds. Some material of this type has been synthesized and has shown some of the characteristics desired. It is hoped that someone with a strong chemical background in our program will take this study and develop it into a research program to thoroughly evaluate the potential of this type of system. In addition, studies on the extent of reaction of dental composites can be performed through the evaluation of characteristic viscosity of the system prior to complete reaction. The high viscosity can hinder and possibly prevent completion of the reaction. Model compounds and composites resins can be evaluated calorimetrically in such a study. Also, the characterization of stress relaxation of general adhesive joints is important to the continuing protective nature of dental adhesives and the potential for such studies is available in our program depending on trainee interests.

## 2. Research Ideas

As discussed in the previous section, a broad range of studies are available in the research training program. A more specific list of potential research topics for the trainees is presented below.

- a) In vivo and in vitro corrosion characterization of non-precious alloys.
- b) Ion plating of noble or protective films on the surface of dental restorative alloys.
- c) Correlation of in vitro and in vivo data to evaluate the nature and importance of corrosion in the oral environment.
- d) Surface analysis of implanted materials to evaluate their interaction with the tooth, tissue, and saliva interface.
- e) Alloying and fabrication characterization of potential nonprecious dental restoration alloys.
- f) Ion implantation of noble or anodic film forming elements in dental restorative materials.
- g) Evaluation of the viscosity characteristics of composite resins in relation to their reaction completion potential.
- h) Thermal-mechanical-environmental fatigue of dental restorative materials.
- i) Stress relaxation of adhesive joints.

These are specific interests of preceptors for the program and there are a number of other specific research ideas of interest to these preceptors. This, however, will provide some cross-section of the research studies that may be initiated by trainees on the program.

## E. Dental Interaction

It is obvious from our previous training that basic data and its clinical relevance to the dentist is important to the training of the physical science student. Trainees in the program must be aware of the specific problems and the general nature of dental clinic procedures as well as how to relate to the biological aspects of the problem. It is going to take interaction with dentistry and dental school clinics to answer certain questions of the relevance to dentistry. For example, our projected program with the University of Pacific (Dr. Ryge) is designed to answer to what extent is corrosion responsible for the failure of amalgam restorations and in the marginal areas is some corrosion beneficial because it seals the restoration in the cavity or is this not correct?

With these combined clinical - in vitro studies will answer these questions of the desired level of corrosion resistance for amalgam. Other factors related to mechanical properties, fatigue, creep, etc., all must be related in principal to the dental restoration so that these characteristics can be studied with the actual problems of the dentist in mind. Particularly, now with more and more technician

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involvement with restorations, requiring greater reproducibility, less problems with the human factors are required of dental materials.

The problems cited are only a portion of those requiring interaction with clinical dentistry. Recognizing the strong need for greater interaction of our trainees and staff with the dental environment, the following program to maintain dental coordination will be continued.

1. Meetings during the academic year between the faculty, graduate trainees, postdoctorals on the program, dental school faculty, or other clinical or dental research consultants. This will be coordinated with trainee seminars on their research.
2. It is important that non-dental trainees have specific contact with the dental environment to discuss various problems of biological and clinical relevance, and also serve as observers in clinical restorative work. It is planned to have some formal lectures of a limited nature in basic nomenclature and knowledge of the tooth structure and the general biological characteristics of the mouth. This particular part of the program will be required as special problem studies, now presently designated as Metallurgy 8500 and will be required by all non-dental trainees and postdoctorals involved in the program. It is planned to provide a minimum of 4 weeks exposure of this type to the dental environment, with 20 hours in lectures on various physical and biological aspects of dentistry.
3. Dental and Physical Science Consultants. From time-to-time specific problems will be encountered that require the need of consultants on information from the dental aspect. It is planned, for example, to have dentists from the Medical College of Georgia and Baylor dental schools who have a broad background in the actual clinical problems of restorative materials, spend time reviewing our program to provide an insight to the actual problems observed and work with us in developing, correlating, and publishing joint data on the observations of various basic and clinical studies.
4. Cooperation with the dental schools at Emory and the Medical College of Georgia has been effective, particularly through the efforts of present and past trainees. For example, several joint papers have been presented by Georgia Medical College, Emory and Tech and others are contemplated or already in preparation.

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## IV. Staff and Facilities

## A. Staff

To effectively pursue advanced dental materials training and research requires an excellent well grounded staff in fundamental material science and engineering. The materials staff is composed of vigorous, nationally and internationally recognized personnel. The staff available as trainee preceptors on this program average more than forty publications each, as well as patents, chapters in books, two monograph and editing of three books. This, plus an excellent record of classroom instruction recognized by the ECPD accreditation committee, presents the graduate and postdoctoral trainees with a healthy and challenging training environment. The two major staff preceptors, Dr. R. F. Hochman and Dr. M. Marek have been active in dental-medical materials for a total of 45 years. In addition, Dr. Brent Carter (former postdoctoral trainee), Dr. Stuart Stock and Dr. James Schaffer are younger staff, well schooled in new exciting areas appropriate for dental materials research training. Background of R. F. Hocmman and M. Marek may be found in the section on biographical sketches.

Two additional materials faculty, Dr. Ted Chapman (Ceramics) and John D. Muzzy (Polymers) have dental-medical materials interest and are available as instructors in their specialties and trainee preceptors should a trainee desire to spend his major research activity in their area.

## B. Associate Staff

Assistance and coordination of dental indoctrination will be provided by Dr. Forrest Butler, a past postdoctoral dentist, and an adjunct professor at Georgia Tech.

In addition to those people cited working directly on the program, many additional staff in materials and physical sciences are available, both for the formal training in the classroom and in the supplementation of the student's knowledge through meetings and discussions on techniques in physical science research. A brief list of these additional people who may work closely with the trainees are: Dr. E. E. Underwood, Professor of Metallurgy, internationally recognized for his work on quantative metallography and stereology; Dr. R. A. Young, Professor of Physics and Director of the Solid State Science Division of the Engineering Experiment Station, is well known in the area of crystallographic studies of materials and presently directs a NIDR program in the area of basic structure and structural changes in hydroxy apatite; and Dr. Charles Liotta, Associate Professor in the School of Chemistry, who has a strong background in the area of surface-polymer interactions and development of high strength polymeric materials.

This provides only a partial list of people who may interact with program, however, many other members of the excellent staff of the Institute can become involved in the training and research as it requires their expertise.

## C. Facilities

The Materials School, the basic unit of this training program is housed in the Materials and Chemical Engineering Building. More than 30,000 square feet of research and teaching space is available. The major portion of the engineering polymer program of the Institute and the Ceramic Program are also located in the same building. This space includes laboratories in metallography, electron

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microscopy, x-ray diffraction, mass spectrometry, thermomechanical properties, mechanical testing, heat treating, nondestructive testing, field-ion microscopy, photographic services, etc. In addition, such important research techniques including a number of major new innovations in the study of materials are available to the program in other departments and the Engineering Experiment Station. For example, scanning electron microscopy, microprobe, micromechanical measurements, etc., are all available to the program.

Extensive modern analytical instrumentation is available for surface and bulk characterization of materials. Specialized resources are supported by additional laboratory facilities, including a complex of high-quality, well-equipped, laboratories for fabricating and evaluating materials.

The Materials Analysis Center is equipped with many modern surface science tools, including Scanning Auger microscopy (SAM), electron spectroscopy for chemical analysis (ESCA), angle-resolved Auger spectroscopy and ultraviolet photoelectron spectroscopy (UPS). These electron spectroscopies allow researchers to obtain elemental and chemical composition data from the outer few atomic layers of most solids. In combination with inert gas ion sputtering, they also provide information on composition as a function of depth beneath the surface. The UPS system permits detailed testing of model structures in co-adsorption of two or more species on semiconductor surfaces.

The Center also is equipped with scanning (SEM), transmission (TEM), and scanning transmission (STEM) electron microscopes, as well as an electron microprobe. These electron microscopes allow scientists to obtain high resolution backscattered, latticed, transmitted, and secondary images. They are also used to obtain reflection and transmission electron diffraction patterns. Support facilities include optical microscopes and x-ray analysis systems as well as energy dispersive x-ray spectroscopy, cathodoluminescence and electron beam induced current imaging. The energy dispersive x-ray spectrometer includes color imaging software which provides quantitative and qualitative information about composition and morphology of materials. Optical materials characterization capabilities include a variety of lasers and spectrometers for measuring absorption, reflection and photoconductivity spectra between 0.2 and 40  $\mu\text{m}$ , and modulated reflection and photoluminescence spectra between 0.35 and 5  $\mu\text{m}$ .

The Institute also has an excellent library. It contains one of the finest, most readily accessible technical collections of work in the country which includes over a million volumes of reports and patents. It is one of the 12 libraries designated to receive complete government and industrial research reports service as well as being an AEC depository. In addition, it has a basic collection of most of the major science and technology publications as well as texts and important books in physical, biological, and engineering research and education.

## APPENDIX I

# Ion Plating

By Robert F. Hochman  
Associate Director for Metallurgy  
Georgia Institute of Technology  
and  
D. M. Monox  
Supervisor  
Surface Metallurgy Division  
Sandia National Laboratories

ION PLATING is a generic term applied to atomistic film deposition processes in which the substrate surface and/or the depositing film is subjected to a flux of high-energy particles (usually gas ions) sufficient to cause changes in the interfacial region or film properties. Such changes may be in film adhesion to the substrate, film morphology, film density, film stress, or surface coverage by the depositing film material. The above definition of ion plating refers only to processes that affect the film and/or substrate and does not define either the source of the depositing material or the origin of the bombarding species. The ion-plating technique (U. S. Patent No. 3,329,601, 1967) was first reported in the technical literature in 1964 (Ref 1).

## Process Basics

Ion plating is typically done in an inert-gas discharge system similar to that used in sputter deposition (see the article on sputtering in this Volume), except that the substrate is the sputtering cathode and the bombarded surface often has a complex geometry.

A schematic of a system, typical for many ion-plating operations, is shown in Fig 1. Basically, the ion-plating apparatus is comprised of a vacuum chamber and a pumping system, which is typical of any conventional vacuum deposition unit. There is also a film at-

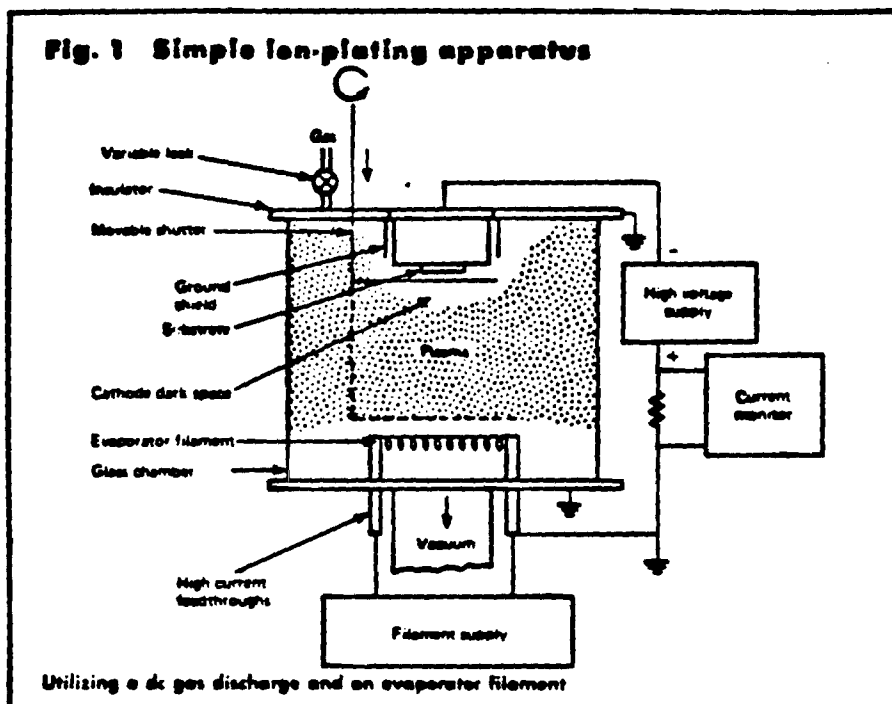
om vapor source and an inert-gas inlet. For a conductive sample, the workpiece is the high-voltage electrode, which is insulated from the surrounding system. In the more generalized situation, a workpiece holder is the high-voltage electrode and either conductive or non-conductive material for plating are attached to it. Once the specimen to be plated is attached to the high-voltage electrode or holder and the boat or filament vaporization source is loaded with the coating material, the system is closed and the chamber pumped down to a pressure in the range of  $10^{-3}$  to  $10^{-4}$  Pa ( $10^{-5}$  to  $10^{-6}$  torr). When a desirable vacuum has been achieved, the chamber is backfilled with argon to a pressure of approximately 1 to 0.1 Pa ( $10^{-2}$  to  $10^{-3}$  torr). The argon influx is controlled by a variable leak valve, and it can be further controlled by a selected closure or a baffle valve between the work chamber and the vacuum system. A potential of -3 to -5 kV is then introduced across the high-voltage electrode (specimen or specimen-holder) and the ground for the system. A glow discharge occurs between the electrodes which results in the specimen being bombarded by the high-energy argon ions produced in the discharge, which is equivalent to direct current sputtering. The argon ion bombardment effectively cleans the specimen surfaces by removing any adsorbed layers or surface contamination. The cleaning step usually

can be completed in a few minutes and provides a clean work surface for receipt of the plating atoms and ions. The coating source is then energized and the coating material is vaporized into the glow discharge. The above process provides the workpiece with a uniform ion bombardment, and gas scattering along with ion deflection gives rise to the effectively high throwing power of this technique and results in uniform coating of even rather intricate variations in surface contour. For a film to form, the deposition rate must exceed the sputtering rate, and ion bombardment may or may not be continued after the interfacial region has been formed.

After the interfacial region has been formed, the coating can continue to be developed at a low rate if bombardment effects on film properties are desired. Film properties may be varied by controlling the substrate potentials and atom/ion bombardment ratio during deposition. The coating may be deposited at higher rates or in a vacuum if ion bombardment effects on film properties are not desired.

For nonconductive workpieces, the bias potential must be produced between anode and the workpiece holder or a conductive screen or similar device held to or around the workpiece. This results in a uniform system for developing the argon plasma, which is the principal source of bombarding ions. A wide variation in the geometries of holders

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and even entire systems has been developed for conductive as well as non-conductive materials, and a system is designed to be generally unique to a specific series of coating workpieces.

### Ionization and Evaporation Sources

Depending on the type of ion plating to be performed and the desired properties of the ion-plated part, a broad range of evaporation or ionization techniques is available. The major evaporation techniques are summarized below.

**Resistance Heating Vaporization.** Either a refractory metal filament holding the metal to be plated or a refractory metal boat containing the material to be plated is used for resistance heating evaporation. This technique is limited to plating materials with a melting temperature of less than 1500 °C (2730 °F). The technique also has limitations when evaporating alloys or compounds, although some difficulties have been overcome by the development of "flash" evaporation.

In flash evaporation, the material to be coated is in powdered form and is fed continuously into a preheated boat. The temperature of the boat is set as high as necessary so as to instantaneously evaporate the least volatile component of the material being used. The constituents of the powder, when coming in

contact with the boat, are vaporized instantly so as to prevent any fractional or partial decomposition of the material. The powdered material is fed into the boat continuously with a continuous flash evaporation reaction. No material should accumulate in the boat and the vapor which is produced from the uniform powder feed should generally provide a surface coating with the same composition as the original material. Parameters to be controlled in flash evaporation are particle size, rate of powder delivery, and preheat temperature of the reaction boat.

**Electron Beam Vaporization.** High melting point materials, with melting temperatures up to 3500 °C (6330 °F), have been evaporated in ion-plating systems by using conventional electron beam guns. The electron beam gun is a principal evaporation source in many experimental and commercial ion-plating systems. However, because of the necessity of a lower vacuum for operation of the electron beam gun, a system utilizing an electron beam must have a conductance baffle to separate the plasma area from the higher vacuum of the electron beam area.

**Sputtering Sources.** Another source for depositing material in an ion-plating system is the use of sputtering targets. The production of the vapor is very similar to the normal sputtering process, with the exception of the higher voltages

used. Some variations in sputtering targets can be achieved so that a broad range of potential ionization sources can be realized.

**Reactive Ion Plating.** In this technique, a reactant gas is introduced into the ion-plating system in controlled amounts. The reactant gas, when introduced into the plasma, undergoes dissociation and ionization of the atoms of the reactant gas molecules. In instances where alloy or compound coatings are desired, the coating composition can be maintained by careful control of the process parameters, particularly the concentration of the reactant gas. This system has been used for deposition of selected nitrides, carbides, silicides, and oxides.

**Radio Frequency (RF) Induction Ionization.** It is possible to introduce a bare induction coil directly into the glow discharge without producing an arc, if the operating frequency has been reduced to about 75 kHz. This can be accomplished by using an induction generator reduced to this level from the more normal metallurgical operating frequency of about 450 kHz. The latter frequency cannot be used in ion plating because severe arcing between the coils through the plasma would occur.

Other lesser used ion sources and ionization techniques include: (a) the promotion of evaporation by high frequency induction heating; (b) the use of electron-emitting filaments to form a triode, ion evaporation system; and (c) the use of an ion beam source similar to that of ion implantation, with the ion accelerated through a suitable acceleration system (vacuum ion plating).

### Process Control

Because there are generally a large number of interactive variables in the ion-plating process, it is often necessary to have more extensive process controls than are used in other vacuum processes. This is particularly true when using reactive gases to form compound coatings. Process variables in ion plating include:

- Precleaning/handling processes
- In-situ predeposition processes
  - Residual contaminants
  - Sputter cleaning parameters
  - Substrate temperature
- Deposition process
  - Substrate temperature
  - Vapor source, atoms unit time

Bombardment process (ions and neutrals)

Species

Energy distribution

Dose rate

• Reactive gas (ions and neutrals)

Species

Energy distribution

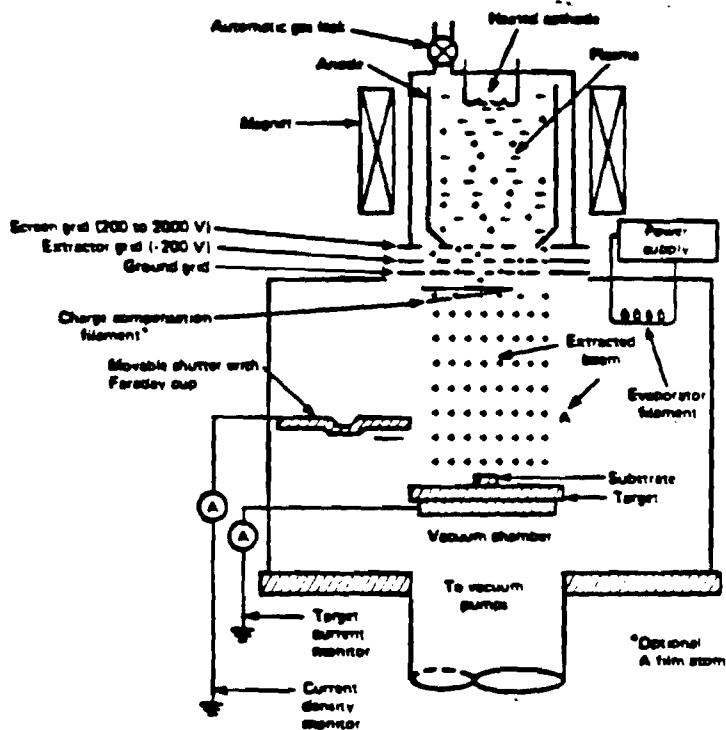
Dose rate

Generally, predeposition and deposition variables are not controlled directly, but rather are reproduced and held constant by controlling process parameters such as cathode current density, cathode voltage, chamber pressure, substrate temperature, fixture geometry, and residual gas contaminants. Recently, the use of vacuum ion plating, where the ion-bombardment source is an ion gun and the substrate is in a moderately good vacuum, has allowed the disassociation of the ion-bombardment parameters from the deposition parameters. This has led to a more controllable process, where the interface and coating properties are very process sensitive. Figure 2 shows such an ion-gun system, using a Kaufman ion source.

Plasma density near the substrate surface is important, and in the direct current glow discharge technique, the plasma density may be highly variable due to the substrate geometry. Figure 3 shows some enhanced plasma sources that increase the plasma density by techniques other than ionization from secondary electrons arising from the ion bombardment, as in the direct current glow discharge technique. In Fig 3(a), (b), and (d), the ionizing electrons are generated by a hot electron-emitting filament. In Fig 3(d), the electron path length is increased by the use of a small magnetic field, and the shape is similar to that of triode sputtering. In Fig 3(c), the secondary electrons emitted by the electron beam evaporation process are extracted toward the positively biased electrode and create ionization in the region above the evaporation hearth.

The most important region in the ion plating plasma is so-called dark space near the cathode. It is in this region that there is the largest potential drop in the plasma. Hence the significance of the dark space in relation to ion plating is that in this region the ions within the plasma will achieve the highest acceleration towards the cathodic target or workpiece. The size of this dark space can be expanded or contracted by increasing or decreasing the pressure of the gas used for forming the plasma.

Fig. 2 Ion-gun ion-plating apparatus



Ion-beam ion-plating system, using a Kaufman ion source and an evaporator filament source

In Fig 1, an electrically conductive substrate was assumed to exist. If the substrate is an electrical insulator, the negative bias may be applied by using a radio frequency (RF) potential, similar to RF sputtering, or a high transmittance grid may be used in front of the substrate surface. An ion-gun system with a neutralizer filament also may be used to electrically bombard insulating surfaces.

**Substrate Temperature.** In a typical direct current diode ion-plating operation, the power input may be several watts per square centimetre. This may lead to a high substrate temperature if the power dissipation ability of the part is poor. Part temperatures may be lowered by improving power dissipation, using pulsed ion bombardment, pre-cleaning to reduce the need for sputter cleaning, or changing the ion-energy spectrum to improve sputtering efficiency. High substrate temperature also can be alleviated by using the supported discharge ion-plating process, where the substrate is at a lower negative potential and the electrons necessary for supporting the discharge come

from an auxiliary heated tungsten filament (Fig 2d).

## Beneficial Effects

Ion plating has been used most often to provide good adhesion between a film and a surface. The principal benefits obtained from the ion-plating process are its ability to:

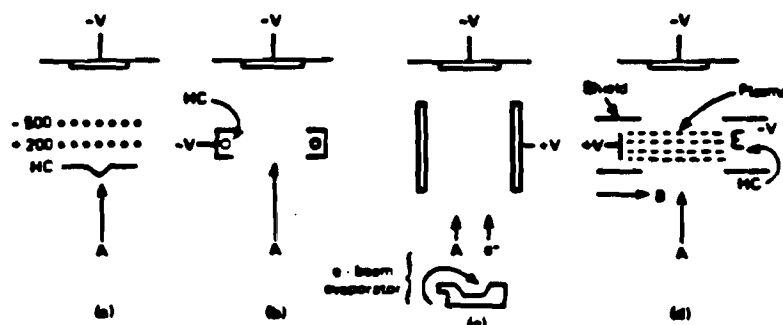
- Modify the substrate surface in a manner conducive to good adhesion and maintain this condition until the film begins to form
- Provide a high-energy flux to the substrate surface, giving a high effective surface temperature, thus enhancing diffusion and chemical reactions without necessitating bulk heating
- Alter the surface and interfacial structure by introducing high defect concentrations, physically mixing the film and the substrate material, and influencing the nucleation and growth of the depositing film

In addition to modifying the substrate surface and influencing the film-sub



## 420/Metallic Coating Processes

**Fig. 3 Enhanced ionization sources used for ion plating**



(a) Hot electron emitting filament with accelerating grid. (b) Electron emitting filament. (c) Positive cylindrical electrode to attract secondary electrons from evaporation hearth; may be used with a magnetic field. (d) Hot cathode magnetically confined plasma. In each configuration, the electrons enhance the plasma density near the surface to be coated. The substrate potential extracts ions from the plasma to bombard the surface. A, atoms from source; B, magnetic field; HC, hot cathode.

strate interface, ion bombardment of the growing film may cause modification of the morphology of the deposited material, changes in the internal stress of the deposited film, or modification of other physical and electrical properties.

In some situations, another advantage of ion plating is the high throwing power, or ability to cover a surface, as compared with that obtained by vacuum evaporation. This high throwing power results from gas scattering, entrainment, and redeposition from the sputtered film surface. This allows coatings to be formed in recesses and areas remote from the source substrate line of sight, thus giving more complete surface coverage than is attained with vacuum processes.

### **Ion-Plating Applications**

Ion plating in production applications is limited, but because of its potential, many applications are becoming apparent with its development. Each independent process requires its own set of processing variables, and therefore, growth has been in new and difficult coating applications rather than in replacing a standard process. A number of typical production applications now in use, as well as a number of potential applications, are given below. It is too early in the development of this process to provide a systematic, overall set of data that can be applied in general to

the technique. Thus, the individual user must evaluate variations in plasma voltage, ionization source, and vacuum pressure within the system before and during the plasma phase and adjust these to his needs. Deposition rates can produce coatings as rapid as 25  $\mu\text{m}/\text{min}$  (1000  $\mu\text{in.}/\text{min}$ ), but generally about 3 to 5  $\mu\text{m}/\text{min}$  (120 to 200  $\mu\text{in.}/\text{min}$ ) is more common. The applications discussed give the potential user an idea of the broad range of applicability of the technique and/or where and how to apply the process.

Processes that are being used commercially include coating of aircraft and spacecraft steel and titanium fasteners. Ion plating was much preferred to other coating processes because of excellent uniformity of thickness, aluminum adhesion, and good throwing power. Fasteners, which were previously coated with cadmium, are now coated with the more compatible aluminum through the ion-plating process. The aluminum coating has excellent uniformity in thickness, strength, and mechanical properties. This aids in the improvement of stress corrosion resistance, precludes embrittlement of cadmium-coated titanium fasteners, and reduces the potential for general corrosion of this type of part. A broad range of steel and titanium fasteners, as well as ion-plated thin-walled stainless steel tubes for interconnect sections of small heat exchangers, can be coated by ion-plated aluminum. When coated

**Table 1 Applications of ion plating**

| Coating material                     | Substrate material             | Use          |
|--------------------------------------|--------------------------------|--------------|
| <b>Optical</b>                       |                                |              |
| Cr .....                             | Plastics                       | ...          |
| In(Sn)O .....                        | Glass                          | ...          |
| TiN .....                            | Plastics                       | ...          |
| ZrC .....                            | Metals                         | ...          |
| <b>Electrical</b>                    |                                |              |
| Pt, Al, Au, Ag ..                    | Si                             | Contact      |
| Al .....                             | GaAs                           | Contact      |
| In(Ga) .....                         | CdS                            | Contact      |
| Cu .....                             | Al <sub>2</sub> O <sub>3</sub> | Contact      |
| Si <sub>3</sub> N <sub>4</sub> ..... | Si                             | Passivation  |
| <b>Mechanical</b>                    |                                |              |
| Au, Ag, MoS <sub>2</sub> ..          | Metals                         | Lubrication  |
| Ti(C, N), Zr (C, N), Cr (C, N) ..... | Metals, carbides               | Wear/erosion |
| Ag .....                             | Be                             | Bonding      |
| Cu .....                             | Ta, W, Nb, oxides              | Bonding      |
| Au-Cr .....                          | Mo                             | Bonding      |
| Pt .....                             | Ti                             | Creep        |
| <b>Corrosion</b>                     |                                |              |
| Al .....                             | U, Ti, steel                   | Gas/liquid   |
| Cr .....                             | Steel                          | Gas/liquid   |
| Al <sub>2</sub> O <sub>3</sub> ..... | Steel                          | Gas/liquid   |
| Si <sub>3</sub> N <sub>4</sub> ..... | Mo                             | Gas/liquid   |
| Cd .....                             | Steel                          | Gas/liquid   |
| Ti .....                             | Steel                          | Gas/liquid   |
| C .....                              | Metals                         | Biological   |
| Ti .....                             | Metals                         | Biological   |
| Ta .....                             | Steel                          | Chemical     |

with aluminum and subjected to 12-month endurance tests, no indication of aluminum flaking, contamination of the system, or indications of corrosion were found.

A series of more unique applications of ion plating include spacecraft telepoint rotors, missile launchers, high strength steel aircraft components, and aircraft actuator door extension springs. A telepoint rotor normally is coated with cadmium when used in the earth's atmosphere but, because cadmium has an extremely high vapor pressure, it cannot be used when exposed to the hard vacuum of space. Ion-plated aluminum was tested along with nickel and gold coatings, which were applied by vapor deposition and electro-deposition. It was shown that the ion-deposited aluminum coatings were superior to all other coatings for this application. Ion-plated aluminum protection for steel springs for aircraft actuator extension springs was another application successfully tested.

Aluminum coating of uranium reactor parts was one of the first applications of ion plating. Investigation of the

process was based on the knowledge that aluminum provides a low neutron cross section, has high thermal conductivity, and has electronegativity close to that of uranium so that galvanic corrosion is minimized. The reactor elements were first cleaned by sputtering, after which the aluminum was ion plated. Deposits of 0.013 mm (0.0005 in.) could be produced in 2 to 5 min. It was further shown that subsequent heating of this deposit layer resulted in UAl<sub>3</sub> providing a thermodynamic stable barrier to any reactor corrosion.

Examples of four different titanium alloys having platinum ion coatings showed improved high-temperature fatigue resistance, oxidation resistance, and cyclic fatigue properties.

**Electroplating.** Application of ion plating is used as a precursor to electroplating or to provide a surface on a metal or alloy not normally compatible with electroplating. Because of the exceptional bonding that occurs, and because the ion plating process ensures a method whereby a prior ion bombardment can produce a clean, generally oxide-free coating, the resultant electro overplate is very effective. For example, the use of ion-plated copper on titanium can serve as the precursor for electrodeposited copper. The prospects of successfully electrodepositing copper directly to titanium is extremely poor, but electroplated coatings to titanium that had a prior ion-plated copper surface showed excellent integrity and overall bonding. This method can be used to produce electroplated coatings on metals that are not normally compatible, such as ion plating of gold onto beryllium oxide gyro rotors used in guidance systems. These individual units were found to be most effectively gold coated using ion plating (Ref 2).

Production of ion-plated titanium carbide and titanium nitride coatings on hardened steel surfaces resulted in a series of patents that have dealt prin-

cipally with the formation of titanium carbide on the surface of a hardened steel (Ref 3). Commercially available meat cutting band saws show a marked increase in life (minimum of three to five times that of normal band saw blades) as well as improved corrosion resistance and cutting characteristics.

The technique involved in ion plating on high-strength plain carbon steels also has the potential for improving many alloy steels used in cutting operations. The voltage used was typically in the neighborhood of 3 to 4 kV for titanium plating. This was followed by carburization at temperatures resulting in the formation of titanium carbide through diffusion. The surfaces had hardness in excess of 1400 HK, with the potential for several hundred points higher with increased carburization.

Improved corrosion-resistant stainless steels for biomedical applications also were reported (Ref 4). The ion plating of titanium and molybdenum on the surface of cold worked stainless steels showed direct improvement of fatigue life and corrosion resistance. The corrosion resistance of cold worked 316 stainless steel was improved most effectively through ion plating of molybdenum. This was the result of the ability of the molybdenum to preclude the initiation of pitting and/or crevice corrosion due to the precipitation of an insoluble molybdenate, as the pH levels occurring in localized corrosion. In addition, marked improvement in fatigue life was found, particularly for the molybdenum ion-plated materials. This included both air and corrosion fatigue.

The technique of ion plating opens up a broad range of new types of surface coatings which, when plated normally, have poor adhesion. Coating of complex shapes, which have been a major problem in both electrochemical and chemical vapor deposition, has been solved because of the excellent throwing power of the ion-plating technique.

The potential for ion plating spans a much broader range than the applications presented, such as corrosion-resistant films, fatigue-resistant films, wear-resistant coatings, low-friction coatings, optical applications, and catalyst surfaces. Table 1 lists some of these applications in more detail. Reference 5 contains a bibliography of ion plating and its applications.

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Bombardment process (ions and neutrals)

Species

Energy distribution

Dose rate

• Reactive gas (ions and neutrals)

Species

Energy distribution

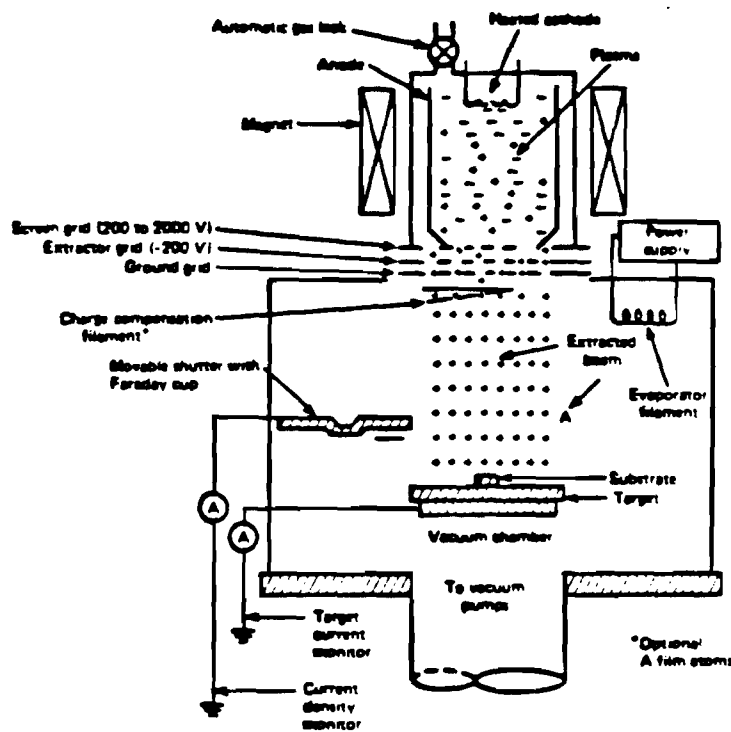
Dose rate

Generally, predeposition and deposition variables are not controlled directly, but rather are reproduced and held constant by controlling process parameters such as cathode current density, cathode voltage, chamber pressure, substrate temperature, fixture geometry, and residual gas contaminants. Recently, the use of vacuum ion plating, where the ion-bombardment source is an ion gun and the substrate is in a moderately good vacuum, has allowed the disassociation of the ion-bombardment parameters from the deposition parameters. This has led to a more controllable process, where the interface and coating properties are very process sensitive. Figure 2 shows such an ion-gun system, using a Kaufman ion source.

Plasma density near the substrate surface is important, and in the direct current glow discharge technique, the plasma density may be highly variable due to the substrate geometry. Figure 3 shows some enhanced plasma sources that increase the plasma density by techniques other than ionization from secondary electrons arising from the ion bombardment, as in the direct current glow discharge technique. In Fig 3(a), (b), and (d), the ionizing electrons are generated by a hot electron-emitting filament. In Fig 3(d), the electron path length is increased by the use of a small magnetic field, and the shape is similar to that of triode sputtering. In Fig 3(c), the secondary electrons emitted by the electron beam evaporation process are extracted toward the positively biased electrode and create ionization in the region above the evaporation hearth.

The most important region in the ion plating plasma is so-called dark space near the cathode. It is in this region that there is the largest potential drop in the plasma. Hence the significance of the dark space in relation to ion plating is that in this region the ions within the plasma will achieve the highest acceleration towards the cathodic target or workpiece. The size of this dark space can be expanded or contracted by increasing or decreasing the pressure of the gas used for forming the plasma.

Fig. 2 Ion-gun ion-plating apparatus



Ion-beam ion-plating system, using a Kaufman ion source and an evaporator filament source

In Fig 1, an electrically conductive substrate was assumed to exist. If the substrate is an electrical insulator, the negative bias may be applied by using a radio frequency (RF) potential, similar to RF sputtering, or a high transmittance grid may be used in front of the substrate surface. An ion-gun system with a neutralizer filament also may be used to electrically bombard insulating surfaces.

**Substrate Temperature.** In a typical direct current diode ion-plating operation, the power input may be several watts per square centimetre. This may lead to a high substrate temperature if the power dissipation ability of the part is poor. Part temperatures may be lowered by improving power dissipation, using pulsed ion bombardment, pre-cleaning to reduce the need for sputter cleaning, or changing the ion-energy spectrum to improve sputtering efficiency. High substrate temperature also can be alleviated by using the supported discharge ion-plating process, where the substrate is at a lower negative potential and the electrons necessary for supporting the discharge come

from an auxiliary heated tungsten filament (Fig 3d).

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Ion plating has been used most often to provide good adhesion between a film and a surface. The principal benefits obtained from the ion-plating process are its ability to:

- Modify the substrate surface in a manner conducive to good adhesion and maintain this condition until the film begins to form
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In addition to modifying the substrate surface and influencing the film-sub-

# Ion Implantation

By Robert F. Hochman  
Associate Director for Metallurgy  
Georgia Institute of Technology

**ION IMPLANTATION** is the process of modifying the physical or chemical properties of the near surface of a solid by embedding appropriate atoms into it from a beam of ionized particles. The properties to be modified may be electrical, optical, or mechanical, and they may relate to the semiconducting behavior of the material or its corrosion behavior. The solid may be crystalline, polycrystalline, or amorphous and need not be homogeneous (Ref 1).

Ion implantation allows the controlled introduction of one or more species into the surface of a substrate by using high energy ion beams of the species to be introduced. When alternatives such as diffusion coatings or co-evaporation are impractical, ion implantation offers a straightforward and reproducible method for attaining a desired result. Because this is a non-equilibrium process, solubility limits may be exceeded with or without subsequent precipitation. This makes it possible to incorporate any kind of ion without developing a set of diffusion conditions or considering the control of chemical constraints. Ion implantation was initially concerned with the fabrication of semiconductor components. For this application, ions were introduced at a relatively low concentration into the substrate. However, it has been discovered that by introducing large quantities of an implanted species, a broad range of chemical and mechanical properties of substrate material may be modified (Ref 1, 2, 3).

## Capabilities

The use of accelerated electron beams can produce penetrations into a substrate surface on the order of 0.1 to 0.2  $\mu\text{m}$  (1000 to 2000  $\text{\AA}$ ) at 100 kV and with higher accelerating voltages, the potential for depth of penetration is increased. Surfaces may be treated by ion implantation and produce an effective alloyed surface layer where the composition varies as a function of depth. An ion beam implanter, which can provide a range of ion energies, can produce remarkable variations in surface characteristics and for limited depths below the surface. In addition, unique alloys not possible through normal alloying can be produced through this technique. Theoretically, two or more metals, completely insoluble in each other, can be alloyed in this manner. Reactive substances can also be added to the ion beam, which can produce surface and subsurface compounds. Post implant heat treatment can be used to anneal out defective structures or produce surface products with unique characteristics. The equipment necessary for treatments limits the application to high-cost parts where a specific surface is extremely important, or to applications in fail-safe systems where high reliability is necessary. Such reliability can be achieved because of the improved corrosion and fatigue resistance, as well as the much reduced friction and or wear which are characteristic of this process. An ion beam ac-

celerator is illustrated schematically in Fig. 1.

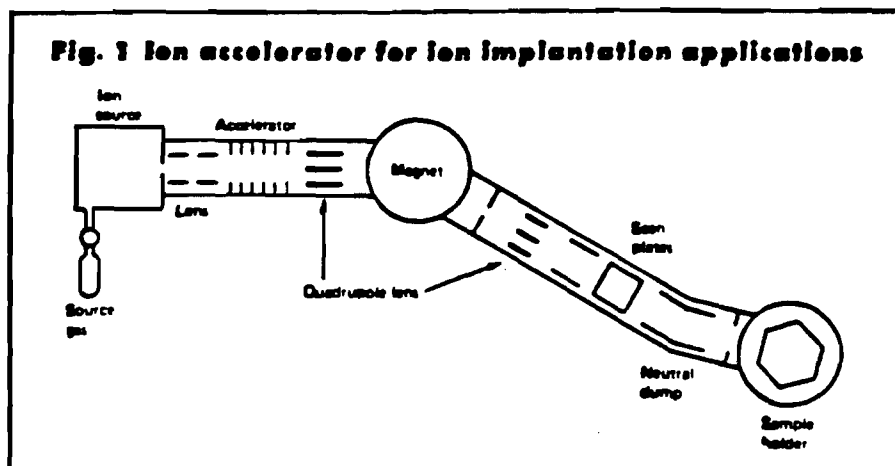
Although relatively thin, an implanted ion layer can alter mechanical and chemical properties significantly. For example, the optimum surface layer thickness for wear resistance under high load conditions can be quite thin, only 2  $\mu\text{m}$  (0.08 mil) for a molybdenum disulfide compound applied in a conventional manner (Ref 4). A conventional lubricating film applied with a binder over an oxide film is not in close contact with the underlying substrate; however, an ion implanted surface is in excellent atomic contact with the substrate.

With the restricted distance ions travel in a substrate, ion implantation cannot be expected to modify bulk properties of materials. Ion implantation is restricted to modification of the outer surface layer and can alter only surface properties significantly.

## Ion Penetration

As an ion beam enters a solid target, it undergoes collisions with free electrons in the target and atom nuclei on lattice sites. Each collision causes a loss of energy, referred to as electronic and nuclear stopping. The relevant parameter is the stopping power,  $dE/dx$ , representing rate of energy loss with distance of penetration. When the energy of an ion falls to about 20 eV, it ceases to move through the solid, becoming trapped by the cohesive force of

Fig. 1 Ion accelerator for ion implantation applications



the material. The distance travelled from the surface to the trapping point is called the total range. In many cases, subsequent motion because of electrostatic forces (ion drift) or thermal diffusion may occur, but these are exceedingly slow mechanisms when compared with the  $10^{-12}$  to  $10^{-16}$  s involved in stopping an incident ion from a conventional ion beam source.

The behavior of a high energy ion, losing energy principally by electronic collisions, is not appreciably influenced by a few atomic layers of contaminant, and conversely the ion does not appreciably alter the surface composition. A slow moving ion, however, losing energy primarily by nuclear collisions, collides with surface atoms. As a result, any contaminant or oxide layers influence the progress of a slow ion, and the surface of the target erodes through sputtering and loss of ions from surface backscattering. Contaminant atoms may also be driven into the substrate, causing an additional, unwanted, implanted species. By ensuring that the substrate targets are atomically cleaned by sputtering, many surface difficulties can be avoided.

**Range.** High energy ions undergo many collisions as they penetrate the substrate. Each collision results in a change in scattering angle, as well as fluctuations in energy loss. A number of statistically related variables are used to describe the probability distribution of penetration depth. A most probable range is defined as  $R_p$ , a median range  $R_m$ , a mean range  $\bar{R}$ , and whenever the distribution shows a definable cutoff, a maximum range  $R_{max}$ .

A projected ion changes directions frequently. The path length of a projected ion is the total range,  $R_{tot}$ . Be-

cause the concern is depth of penetration, not total length of path, a more useful parameter for ion implantation is the projection of total range parallel to the incident ion direction,  $R_p$  (projected range). The total range of a particle entering a target at energy  $E_0$  is simply related to the rate of energy loss by the equation:

$$R_{tot} = \int_0^{E_0} \frac{dE}{-(dE/dx)}$$

Because ion penetration is an inherently statistical process, parameters such as the mean square fluctuation for each of the range parameters given above must also be defined.

**Depth of Distribution.** An implanted species forms a broad layer some depth from the surface. For incoming energies of a few hundred keV, this depth may be in the order of microns, and essentially none of the implanted species appear at the surface. At sufficiently low energies (a few keV), the projectiles come to rest close to the surface, and the scattering of ranges ensures that many of the implanted species lie at the surface itself. By implanting a single substrate with ions of both low and high energies, a uniform depth distribution extending to a few microns can be developed.

Evaluation of the order of magnitude of the quantities involved in ion implantation is important. Table 1 shows the various energies, the projected range ( $R_p$ ), and standard deviation ( $\Delta R_p$ ) of  $Ti^+$  ions implanted into iron at a beam current of  $10 \mu A/cm^2$ . Also shown is a rough estimate of percentage concentration after 10 s irradiation calculated on the assumption that all particles come to rest within  $\pm \Delta R_p$  of the

projected range and neglecting diffusion after the ion has come to rest. The ranges of implanted particles are clearly rather small. Despite this, the implanted region cannot be regarded as a surface layer in the atomic sense because it occupies many atomic layers and, for the higher energy implants, few atoms may be at the surface. The ion implanted surface is defined as a surface in a mechanical sense of hundreds of atomic layers.

**Lattice Damage.** At high ion projectile energies, the principal energy loss mechanism is collision with electrons; at low energies, collisions with substrate nuclei predominate. An energetic ion entering a target workpiece first loses energy by electronic stopping and nuclear collisions predominate only as the ion reaches the end of its range. Lattice damage occurs by displacement of substrate atoms at the end of the incident ion range. Such damage may be removed by subsequent annealing of the implanted material. The properties of ion implanted specimens change because of radiation damage and changes as a result of the implanted species. In ion implanted materials, the location of the implanted species must be determined to understand the effects observed. Experimental work (Ref 5) has provided general formulas that are useful for estimating ion penetration in noncrystalline materials, and this has been refined to include electron shell structure (Ref 6). However, most existing evaluations of energy loss and range are formulated for a single ion entering an undamaged substrate. Although these evaluations are adequate where the implanted species represent only a small concentration in the target, as in the fabrication of semiconductor devices, these analyses have not been modified to treat implantation conditions with large concentrations of implant ions entering a lattice or structure already damaged by impinging ions.

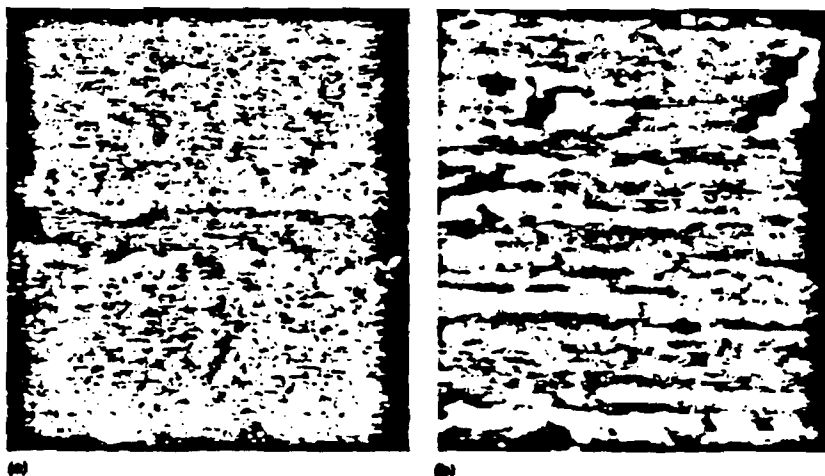
**Channeling.** When ions are directed into a single crystal along a crystallographic path, implants may enter channels between rows of atoms and lose energy only by electronic stopping, penetrating considerably further than in an amorphous sample. The ions cause little radiation damage. However, an ion that does not enter close to the center of a channel undergoes a large angle deviation through collisions with occupied lattice sites and subsequently moves into the crystal in

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**Table 1 Energies, projected ranges, and standard deviations involved in ion implantation**

| Energy, keV | $R_p$ , $\mu\text{m}$ | $R_p$ , Å | $\Delta R_p$ , $\mu\text{m}$ | $\Delta R_p$ , Å | Concentration in 10 a. % |
|-------------|-----------------------|-----------|------------------------------|------------------|--------------------------|
| 10          | 0.0052                | 52        | 0.0029                       | 29               | 3.7                      |
| 100         | 0.0342                | 342       | 0.0166                       | 166              | 0.7                      |
| 1000        | 0.3750                | 3750      | 0.0825                       | 825              | 0.13                     |

**Fig. 2 Wear track of nitrogen implanted and unimplanted titanium disks**



(a) Nitrogen implanted and (b) unimplanted titanium disks after 12 000 revolutions of sliding. Titanium implanted with nitrogen showed a greater improvement in wear resistance than nitrogen implanted iron disks. Flowing grooves are visible only with the aid of a scanning electron microscope (SEM)

a random direction, rapidly coming to rest. A potential for very deep implants exists from the channeling of ions in an oriented structure associated with very little radiation damage. However, channeling usually occurs in only single crystals or high oriented polycrystalline samples and may have very limited technological application.

**Diffusion.** In implanted materials, an important consideration is radiation-enhanced diffusion, first suggested nearly 20 years ago (Ref 7, 8). The distribution of implanted ions is modified by the diffusion of atoms after they have been reduced to thermal velocities. This modification may occur even for species where diffusion does not usually occur at room temperature. The additional vacancies and interstitials created in implantation may far exceed those created thermally, thus excess vacancies may enhance the rate of diffusion at relatively low temperatures. Radiation-enhanced diffusion has also been observed in metals (Ref 9), but the phenomenon is complex and not fully

understood. Radiation damage may induce diffusion of the implanted species and result in a final profile that extends several factors deeper than that expected from a simple ion range calculation.

### Applications of Ion Implantation

The potential of ion implantation was well documented in a recent edited version of a National Material Advisory Board (NMAB) report in the *SAMPE Journal* (Ref 10). The NMAB Committee on Ion Implantation and New Surface Technologies report also succinctly covers the advantages of the process, which are included in the following list:

- A variety of ion species can be implanted with the same basic apparatus. Almost all elements of the periodic table have been implanted
- Novel nonequilibrium structures and metallurgical phases with prop-

erties that cannot be duplicated in bulk material can be produced at the surface. In certain cases, amorphous or glassy phases can be formed

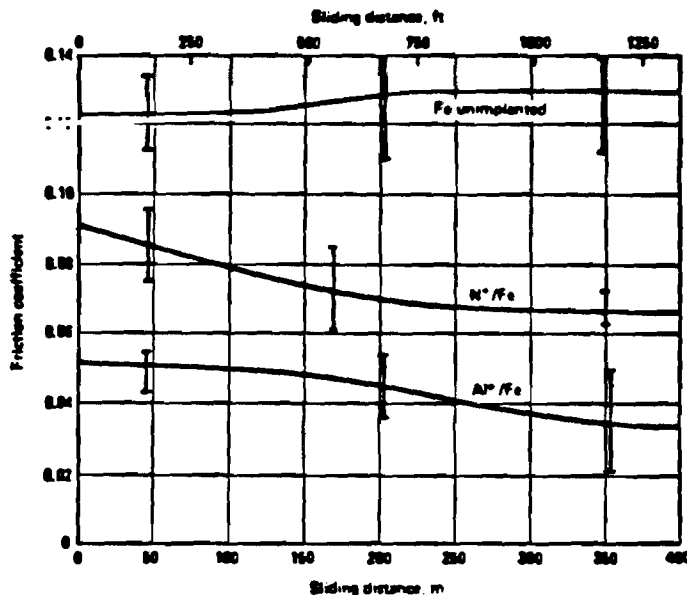
- If the implanted atoms are mobile, inclusions and precipitates can be formed. For example, implanted argon and helium atoms are insoluble in metals and may form bubbles
- Cooperative effects of two implanted species can occur; for example, implantations of both molybdenum and sulfur into steels seem to have an effect similar to lubrication with molybdenum silicide
- 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 absence of a discontinuous interface between the implanted surface layer and the bulk leads to excellent adhesion of the implanted layer
- The process is easily controlled through the electrical signals applied to the accelerator
- Ion implantation creates no problems of disposal of waste products, as does electroplating

**Disadvantages.** These advantages must also be weighed against the known disadvantages of ion implantation. These are:

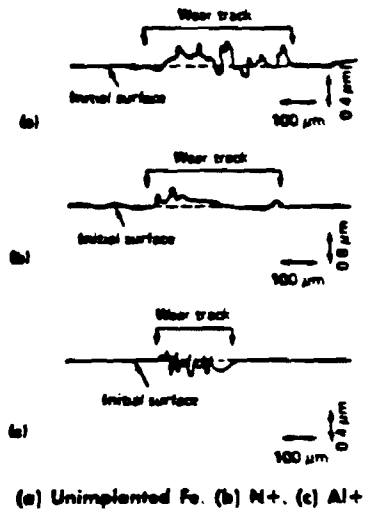
- Shallow surface layer
- Process strictly line-of-sight or beam-line
- Skilled labor and expensive equipment are required for this high technology process
- Necessity for target or substrate to be manipulated in *vacuo* to implant surfaces of varying design
- Study and development of ion sources needed to produce a high beam concentration that is relatively clean
- High maintenance costs of the vacuum system and limitations on the vapor pressure materials to be used

**Major industrial applications of ion implantation** have been in the electronics industry. Ion implantation has served as a useful method for doping semiconductors to produce controllable, homogeneous concentrations of doping agents with excellent reproducibility compared to conventional diffusion processing. The use of ion implantation in the semiconductor industry has led to development of more reliable and more

**Fig. 3 Change in friction coefficient with sliding distance of unimplanted iron, Al+ implanted, and N+ implanted iron systems**



**Fig. 4 Profiles of worn disk surfaces of unimplanted Fe, N+ implanted Fe, and Al+ implanted Fe**



easily operated ion implantation equipment. Ion accelerators have moved out of the laboratory and into industry, and equipment to do a broad range of industrial implants is available or can be easily adapted to a range of new applications without extensive modification.

Potentially fruitful nonelectronic applications involve improved properties and life of metal tools, cemented carbide tools and more recently, ceramic tools; improvements are because of increased surface hardness, and reduced wear and friction. Also, improved aqueous corrosion resistance and improved high temperature corrosion and oxidation resistance can be achieved. Other possible benefits include improved optical properties, unique catalyst surfaces, bonding and adhesion between highly dissimilar materials, and any other process where a unique metallurgical surface or surface alloy is warranted.

**Wear Resistance.** In pin-on disk friction and wear tests of nitrogen and aluminum-implanted iron and titanium, significant reduction in friction and wear of the iron and titanium disks can be attributed to a hard layer formed during the ion implantation process (Ref 11). This hard layer minimizes plowing (see Fig. 2) and subsurface deformation, and reduces the delamina-

tion wear process, which consists of crack nucleation, crack propagation, and the formation of delamination wear sheets. The formation of an alloyed surface via ion implantation produces a substantial change in hardness, which minimizes the friction coefficient. Figure 3 compares change of friction coefficient with sliding distance for unimplanted iron, nitrogen-implanted, and aluminum-implanted iron disks. Figure 4 illustrates the resulting wear profiles of these three disk surfaces.

Several developing industrial applications involving nitrogen-implanted iron have led to improved properties of steel surfaces for tools used in steel forming in the automotive industry (Ref 12). Examples include a steel press tool, which showed an improved performance after nitrogen ion implantation of nearly ten times that of its unimplanted counterpart. A treated forming die resulted in the production of nearly 5000 automobile parts compared to the normal 2000 part life from a similar tool hard faced with electrodeposited chromium. Another example is a ring cutter for tin plate treated by nitrogen ion implantation of a tool steel, resulting in extending the life of the tool by a factor of three. Improved hot rolling dies for nonferrous rod and steel gear cutters were also produced by ion

implanting nitrogen. All of these have shown increased life from 200 to 1000% following nitrogen ion implantation with an ion flux in the neighborhood of  $5 \times 10^{17}$  nitrogen ions/cm<sup>2</sup> ( $3 \times 10^{16}$  ions/in.<sup>2</sup>) with implantation voltages in the neighborhood of 100 keV.

Improved life of nitrogen ion implanted tools is also achieved by injection molds used in plastic production. Injection molding screws and dies have shown marked life increases as the result of ion implantation of nitrogen. Cobalt-cemented tungsten carbide, used for many dies and wear-resistant tools, can be effectively improved by ion implantation of nitrogen and carbon. Wire drawing dies having three to five times the usual lifespan as a result of nitrogen ion implantation treatment have been documented (Ref 12).

Work at the U.S. Naval Research Laboratories (Ref 2) has resulted in improved surfaces for beryllium hardened by boron implantation at energies between 90 and 250 keV. The total dosage of boron ions was approximately  $6 \times 10^{17}$  ions/cm<sup>2</sup> ( $4 \times 10^{16}$  ions/in.<sup>2</sup>).

**Corrosion Resistance.** Improved corrosion and wear resistance of burner tips through which fuel oil and air are injected into oil-fired furnaces in power generating plants has also been achieved (Ref 13). Although nitrogen

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ion implantation was ineffective, cerium implantation significantly reduced the degree of sulfidization attack because of the reaction with the sulfur-rich combustion products. Additional work in the United Kingdom has also shown that stainless steel pumps and valves used in the food processing industry have poor wear resistance characteristics, but these materials have shown a marked reduction in adhesive wear because of nitrogen ion implantation.

Another area that has been considered by several authors and discussed in a paper on thermal oxidation (Ref 13) has been the improvement of turbine blades for jet aircraft engines. The potential for corrosion-resistant coatings, either through reactive ion implantation or through the production of refractory surfaces, is being explored and developed.

In a new and unique application of ion implantation, mercury ions are introduced into aluminum to activate the surface so the material may be used as a sacrificial anode (Ref 14). Once mercury is introduced at the aluminum

surface, an electrode in the presence of oxygen forms a mercury-aluminum (HgAl) amalgam, and then reoxidizes to alumina and mercury with the alumina being nonprotective. This product is being tested as a potentially inexpensive sacrificial anode compared to zinc or magnesium.

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