

N O T I C E

THIS DOCUMENT HAS BEEN REPRODUCED FROM
MICROFICHE. ALTHOUGH IT IS RECOGNIZED THAT
CERTAIN PORTIONS ARE ILLEGIBLE, IT IS BEING RELEASED
IN THE INTEREST OF MAKING AVAILABLE AS MUCH
INFORMATION AS POSSIBLE

NASA Technical Memorandum 82630

Ion Plating for the Future

(NASA-TM-82630) ION PLATING FOR THE FUTURE
(NASA) 9 p HC A02/MF A01 CSCL 11F

N81-25189

G3/26 Uclas
26515

Talivaldis Spalvins
*Lewis Research Center
Cleveland, Ohio*

Prepared for the
Twenty-fourth Annual Technical Conference
of the Society of Vacuum Coaters
Dearborn, Michigan, May 12-14, 1981



NASA

ION PLATING FOR THE FUTURE

by Talivaldis Spalvins

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

ABSTRACT

The ion plating techniques are classified relative to the instrumental set up, evaporation media and mode of transport. Distinction is drawn between the low vacuum (plasma) and high vacuum (ion beam) techniques. Ion plating technology is discussed at the fundamental and industrial level. At the fundamental level, the capabilities and limitations of the plasma (evaporant flux) and film characteristics are evaluated. And on the industrial level, the performance and potential uses of ion plated films are discussed.

INTRODUCTION

A cursory survey of the literature reveals that since the ion plating technique was first reported in 1964, it has been referred by a variety of terms such as vacuum ion plating, ion vapor deposition, reactive ion plating, bias sputtering, ion evaporation, ion beam plating and so on. Consequently, it can be concluded that the high degree of ion plating diversifications which exist in instrumental set ups and evaporation media are responsible for the many new terms that have been generated to designate a particular system more specifically. The extensive variation in the instrumental set ups and requirements has precluded the manufacture of a standard ion plating unit in volume production. Each laboratory or industrial operation uses its own unit construction with its own specialized instrumental features to best meet its requirements.

The activity and interest in ion plating has primarily developed at two levels: the industrial or technological and the fundamental or laboratory. At the industrial level, ion plating has proliferated into many areas in which other coating techniques have not been successful. For instance, ion plating technology is well established in the aerospace and aircraft industry for the application of tribological coatings to reduce friction and wear and protective coatings to resist corrosion and oxidation. The technique is used on a production scale to aluminize aircraft components for corrosion protection. It is suitable also for rack coating of large components and barrel coating for a large number of small steel fasteners.

The industrial interest in ion plating stems from the unique features which it offers: (1) the high energy flux of ions and energetic neutrals which contribute to the excellent adherence and (2) the high throwing power which is responsible for the three-dimensional coverage which have been widely discussed (refs. 1 to 3).

On the fundamental or laboratory level, there is a noticeable trend toward improving and understanding the energetics of the evaporant flux. Increased energizing of the process generally leads to improved film adhesion, favorable film morphological growth, higher film density, and reduced residual stresses in the film. To control the film properties and establish the optimum plating conditions it is important to understand the plating

E-884

ORIGINAL PAGE IS
OF POOR QUALITY

environment, which is extremely complex. Further, it is important to have a control of the evaporation flux in terms of the kinetic energy and ionization efficiency. The objective of this paper is to classify the numerous ion plating techniques and discuss and evaluate their potential in terms of plasma and coating characteristics.

Ion Plating Technology

The different versions of the ion plating process in existence may be classified as to the media, evaporation source and mode of transport into two categories: (1) low vacuum (plasma) and (2) high vacuum (ion beams) as shown in Fig. 1. The low vacuum (plasma) technique is essentially the original technique which utilizes the diode dc glow discharge, where ion plating has to take place at pressures above 5 mTorr for the discharge to be self sustaining. The plasma techniques can be further subdivided as to the evaporation source and evaporation media selected. The evaporation sources which have been used are resistance, electron beam, induction heating, reactive evaporation and sputtering targets (magnetron). Each evaporation source has its advantages and disadvantages and the trend has been to select a specific evaporation source to meet the requirements for the end product in terms of coating performance and economic considerations.

The high vacuum (ion beam) techniques are basically performed on the laboratory scale and are conducted in the 10^{-4} to 10^{-7} Torr range. They utilize various ion beams such as single, dual and ionized cluster (Refs. 4 and 5). The advantage of these techniques is that the evaporant flux (the ion beam) can be controlled with respect to the amount of ionized and neutral species, kinetic energy, angle of incidence and other parameters.

Glow discharge considerations. - In a self sustained glow discharge, the ions are produced in the negative glow region and are accelerated across the cathode dark space which forms around the specimen. Almost all of the applied potential is dropped across the dark space, since almost all of the discharge voltage occurs here. Due to gas collisions and charge exchange, the vaporized metal ions are accelerated across the dark space to the substrate where they lose a considerable amount of their kinetic energy through collision transfer to metal atoms. As a result, the incident energy is reduced and the specimen is bombarded by a wide spectrum of ions and energetic neutrals which may have a distribution of energies from thermal up to the voltage applied to the discharge.

A typical ion energy distribution in a diode discharge is shown in Fig. 2. The two glow discharge characteristics, ionization efficiency (percentage of evaporant atoms which are ionized) and the kinetic energy of the evaporant flux have not been resolved and as yet cannot be controlled during ion plating. Recent calculations, based on certain simplifying assumptions have been made and the estimates are, that under typical ion plating conditions (cathode voltage 3 kV, ion current density 0.5 mA/cm^2 ; pressure 2×10^{-2} Torr), the ionization efficiency is less than 1 percent and the ions carry only 10 percent of the energy dissipated while the neutrals carry 90 percent (Ref. 6). Thus, the plating flux consists of a small number of energetic ions and a large number of energetic neutrals. It is also estimated that the average energies of ions and neutrals are in the order of 100 eV.

Since the ionization efficiency under typical ion plating conditions is below 1 percent, various attempts are made to intensify the glow discharge and to increase the bias power density by inserting additional support fila-

ments (triode) (Ref. 7). Using a triode system, it is possible to increase the discharge current by an order of magnitude and vary it independently from the bias voltage on the substrate and also to sustain the discharge at argon pressures as low as 1 μ m.

Evaporation sources. - The range of materials that can be ion plated is predominantly determined by the selection of an appropriate evaporation source and gaseous media. Each evaporation source (mentioned previously) has its advantages and disadvantages and the trend has been to select the specific source in terms of coating performance and economic considerations. The resistance heating sources which utilize refractory boats are generally preferred, because they are comparatively sturdy, inexpensive, reliable and simple to operate. These sources have been basically confined to the elemental metals which have melting temperatures less than 1300° C. When compounds and alloys have to be ion plated, electron beam evaporation is the most preferred technique. Reactive ion plating techniques which achieve reaction of the metal vapor and the reactive gas are primarily of great importance for the formation and deposition of carbides, nitrides, silicides and oxides. By varying the reactant gas concentration, a graded composition region between the substrate and the coating can be formed which contributes to the superior adherence.

Film Characteristics

The excellent film adherence and the unusual ability to withstand interfacial stresses, regardless of film/substrate combination, is attributed to the formation of a graded-fused interface and this is well documented in the literature (Refs. 8 to 10). The exact reaction mechanism which contributes to the formation of such an interface is not fully understood, but the controlling factors are, sputter etched surface, diffusion, implantation, atomic mixing and nucleation and growth characteristics (morphology) as shown in Fig. 3. These factors can act separately or in various combinations, depending on the film/substrate compatibility.

Ion plating is essentially an energetic activation technique where not merely the ions, which transfer energy, momentum and charge, but also the high energy neutrals produced by the charge exchange activate the substrate and the growing film in terms of higher activation energy and increased nucleation density. Consequently, the ion plated films differ from the other films such as electroplated, in that it does not produce a discrete coating, rather it alters the chemical composition in the subsurface. The adhesive strength depends not only on the bonding across the interfacial region but also on the microstructure within this region. The graded interface and film morphology is not only responsible for the excellent adherence, but also induces a strengthening effect on the mechanical behavior of the material. The strengthening effects are believed to be due to a structural alteration of the crystal lattice and subsequent effects of dislocation interactions, where the film acts as a barrier to the egress of dislocations near the surface, thus displaying pronounced mechanical strengthening effects such as increased yield, tensile, fatigue and creep strengths. A morphological change from the normally columnar structure to a more dense, equiaxed grain structure is observed. This change gets more pronounced with an increase in ionization efficiency, which means, that it is possible to produce dense, fine grained, equiaxed coatings. Because of the increased nucleation density, fully dense and uniformly-continuous films can be obtained at lower nominal thickness than with other deposition techniques.

Applications and Performance

The ion plating technology is well established in the aircraft and aerospace industry where the durability of rotating or sliding components and structural components are primarily controlled by surface related phenomena such as friction, wear and corrosion. The application of tribological coatings, such as the soft metallic lubricating films (Au, Ag, Pb) and the hard wear resistant coatings (TiN, TiC, Cr₂C₃, Cr₂Si₃, etc.) to prevent mechanical failures at rubbing contacts is well documented (Ref. 11). For instance, the soft metallic lubricating films are used very successfully for spaceborn bearings such as solar array drives, de-spin and pointing mechanisms for antennas. The increased endurance life and the reduced coefficient of friction for the soft metallic films are attributed to improved adherence, the small crystalline size, shape, and the increased cohesive strength of the film. In addition, these films, due to the very small crystalline size, display a continuous film formation at lower nominal thickness which is of great significance in thin film lubrication (Ref. 12). Of the hard refractory coatings, TiN coatings which are synthesized by reactive ion plating are widely investigated because they possess both decorative (gold like appearance) and wear resistant properties.

A production capability is in operation wherein aluminum is ion plated on steel, titanium aircraft fasteners, and large aircraft components (wing skins, landing gears, etc.) to improve corrosion resistance. The strong film adherence and coherence again are responsible for the improved corrosion resistance. Because of the exceptional adherence, ion plated strike coats are being used prior to electroplating on surfaces, which would otherwise be very difficult or impossible to plate. Also, ion plated surfaces are being used to facilitate their joining by conventional soldering and brazing techniques. Due to the high throwing power, porous components can be sealed for vacuum and hydraulic applications. For reclamation purposes, worn out mechanical components can be refinished. The components of the electrically conductive polymers (caprez) can be directly coated in three-dimensions. Other areas of application which are presently being investigated are protective platinum coatings for medical instruments, optical coatings where glass surfaces can be strengthened by compressive glazes, decorative coatings and many other specialized areas.

High Vacuum - Ion Beam Techniques

The plasma techniques have the disadvantage in that the evaporation flux cannot be controlled in a defined manner with respect to the fractions of neutral and ionized species, kinetic energy and incidence angle. Therefore, the investigations of high vacuum ion plating (10^{-4} to 10^{-7} Torr range) are primarily conducted at the fundamental level. Basically, the ion beam techniques introduced a decade ago, utilize an external ionization source (gun) where the evaporated atoms pass near a filament and collide with the emitted electrons or ion beam sputter sources as shown in Fig. 4. The collimated beam is directed to the target in high vacuum environment and can be controlled with respect to the amount of ionization by: (1) selectively maintaining a monoenergetic distribution of ions, (2) combination of ions and energetic neutrals, (3) retarding the fast ions and (4) by special deceleration and filter mechanisms. A typical energy distribution from an ion source is shown in Fig. 5.

The high throwing power due to gas scattering which is always associated with ion plating and is responsible for the three-dimensional coverage. This is almost entirely absent in the high vacuum plating techniques. Therefore, one obtains a line of sight deposition with these latter techniques. Various kinds of ion beam deposition techniques have been investigated, where atomic, molecular or cluster ions have been used with and without neutral particles.

CONCLUSIONS

The only way to properly and effectively utilize ion plating is to understand the basic considerations involved and how they can be applied to solve a specific problem.

At the fundamental level, the plating environment is extremely complex and insufficient information exists concerning ionization efficiency and the kinetic energy of the evaporant flux. High vacuum-ion beam investigations are however narrowing the gap.

On the technological level, the ion plated films offer in terms of adherence, coherence and morphology, the greatest potential. This is already recognized in the aerospace and aircraft industry where ion plating technology has been developed on a production basis.

REFERENCES

1. Mattox, D. M.: Fundamentals of Ion Plating. J. Vac. Sci. Technol., vol. 10, no. 1, Jan. 1973, pp. 47-52.
2. Mattox, D. M.: Sputter Deposition and Ion Plating Technology. American Vacuum Society, 1973.
3. Spalvins, T.: Horizons in Ion Plated Coatings. Met. Finish., vol. 12, no. 6, June 1974, pp. 38-43.
4. Schiller, S.; Heisig, U.; Goedicke, K.: Ion Deposition Techniques for Industrial Application. Proceedings of the 7th International Vacuum Congress and 3rd International Conference on Solid Surfaces, Vienna, Austria, 1977, Vol. 2, pp. 1545-1552.
5. Weissmantel, C.; et al.: Recent Developments in Ion-Activated Film Preparation. Proceedings of a Conference on Ion Plating and Allied Techniques, CEP Consultants, Ltd., Edinburgh, Scotland, 1979, pp. 272-283.
6. Teer, G. D.: Adhesion of Ion Plated Films and Energetics of Deposition. J. Adhesion, vol. 8, no. 4, 1977, pp. 289-300.
7. Higham, P. A.; and Teer, D. G.: Influence of the Deposition Parameters on the Structure of Ion-Plated Chromium. Thin Solid Films, vol. 58, 1979, pp. 121-125.
8. Spalvins, T.: Survey of Ion Plating Sources. J. Vac. Sci. Technol., vol. 17, no. 1, Jan./Feb. 1980, pp. 315-321.
9. Mattox, D. M.: Ion Plating - Concepts and Applications. Proceedings of the 25th Meeting MFPG Engineering Design, T. R. Shives and W. A. Willard, eds., National Bureau of Standards, NBS-SP-487, 1977, pp. 311-323.
10. Walls, J. M.; et al.: Comparison of Vacuum-Evaporated and Ion-Plated Thin Films Using Auger Electron Spectroscopy. Thin Solid Films, vol. 54, 1978, pp. 303-308.
11. Spalvins, T.: Coatings for Wear and Lubrication. Thin Solid Films, vol. 53, 1978, pp. 285-300.
12. Spalvins, T.; and Buzek, B.: Frictional and Morphological Characteristics of Ion Plated Soft Metallic Films. To be published in Thin Solid Films.

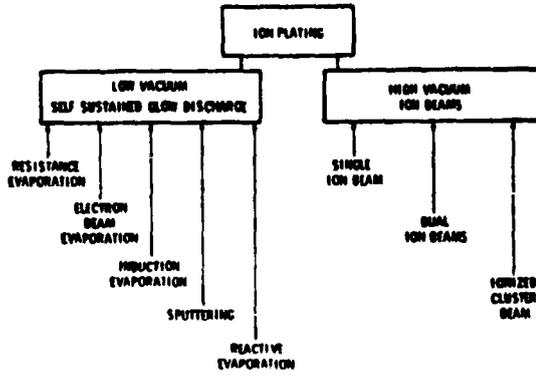


Figure 1. - Classification of ion plating as to media, evaporation source and mode of transport.

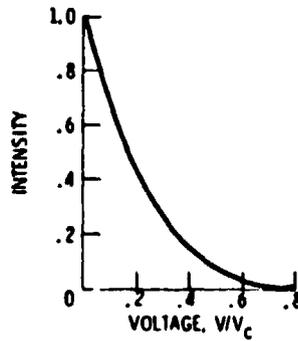
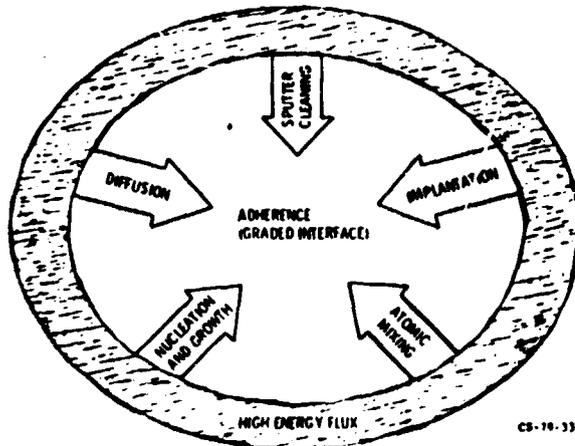


Figure 2. - Typical argon ion energy distribution in a diode discharge, where V_c is the cathode fall potential.



CS-70-3334

Figure 3. - Illustration of the factors which influence adherence and interface formation during ion plating.

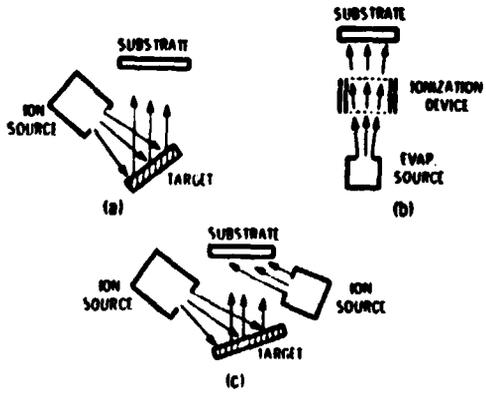


Figure 4. - Ion beam deposition techniques.

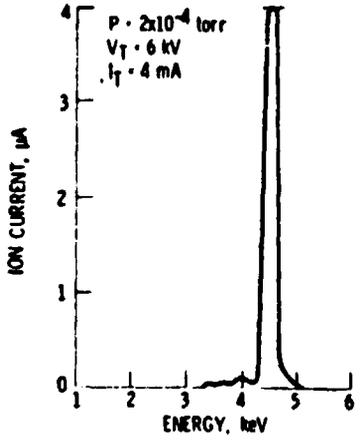


Figure 5. - Energy distribution of argon ions from a fine beam saddle-field ion source.

ORIGINAL PAGE IS
OF POOR QUALITY

1. Report No. NASA TM-82630	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle ION PLATING FOR THE FUTURE		5. Report Date	
		6. Performing Organization Code 506-53-12	
7. Author(s) Talivaldis Spalvins		8. Performing Organization Report No. E-884	
		10. Work Unit No.	
9. Performing Organization Name and Address National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135		11. Contract or Grant No.	
		13. Type of Report and Period Covered Technical Memorandum	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D. C. 20546		14. Sponsoring Agency Code	
		15. Supplementary Notes Prepared for the Twenty-fourth Annual Technical Conference of the Society of Vacuum Coaters, Dearborn, Michigan, May 12-14, 1981.	
16. Abstract The ion plating techniques are classified relative to the instrumental set up, evaporation media and mode of transport. Distinction is drawn between the low vacuum (plasma) and high vacuum (ion beam) techniques. Ion plating technology is discussed at the fundamental and industrial level. At the fundamental level, the capabilities and limitations of the plasma (evaporant flux) and film characteristics are evaluated. And on the industrial level, the performance and potential uses of ion plated films are discussed.			
17. Key Words (Suggested by Author(s)) Ion plating Coatings		18. Distribution Statement Unclassified - unlimited STAR Category 26	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages	22. Price*

National Aeronautics and
Space Administration

Washington, D.C.
20546

Official Business

Penalty for Private Use, \$300

SPECIAL FOURTH CLASS MAIL
BOOK

Postage and Fees Paid
National Aeronautics and
Space Administration
NASA-451



NASA

POSTMASTER: If Undeliverable (Section 158
Postal Manual) Do Not Return
