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**NASA**

# ION PLATING FOR THE FUTURE

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## 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

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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  $0.5 \text{ mA/cm}^2$ ; pressure  $2 \times 10^{-2}$  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  $\mu\text{m}$ .

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, Cr<sub>2</sub>C<sub>3</sub>, Cr<sub>2</sub>Si<sub>3</sub>, 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.

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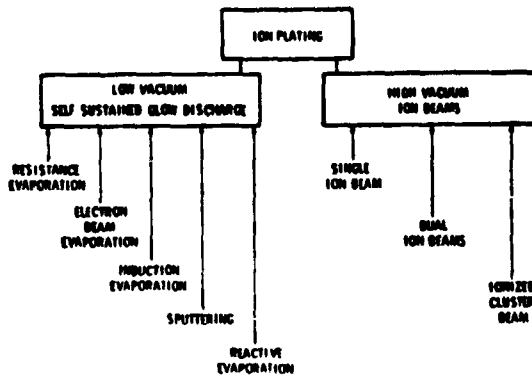


Figure 1. - Classification of ion plating as to media, evaporation source and mode of transport.

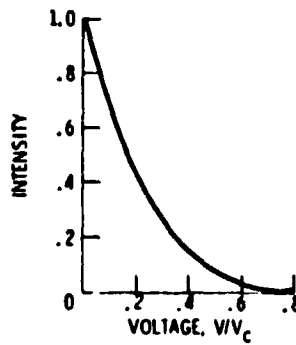
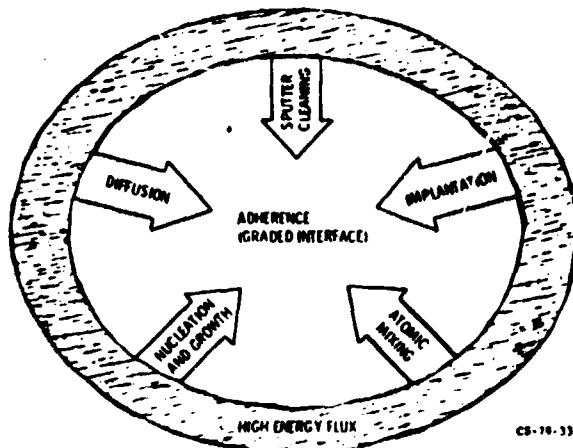


Figure 2. - Typical argon ion energy distribution in a diode discharge, where  $V_c$  is the cathode fall potential.



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



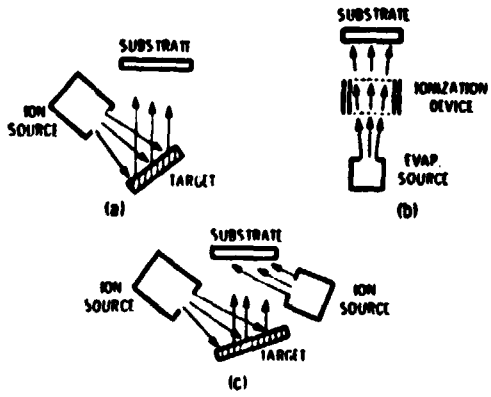


Figure 4. - Ion beam deposition techniques.

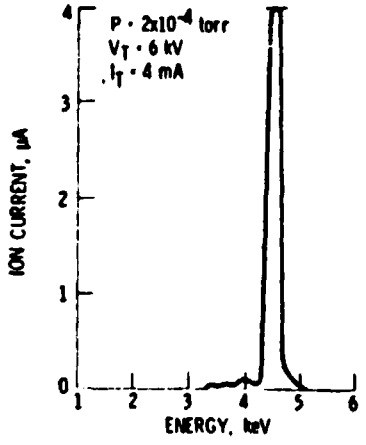


Figure 5. - Energy distribution of argon ions from a fine beam saddle-field ion source.

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