NASA TECHNICAL NOTE

NASA TN D-7895

NASA TN D-7895

GROWTH DEFECTS IN THICK ION-PLATED COATINGS

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • JANUARY 1975

1. Report No. NASA TN D-7895	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle GROWTH DEFECTS IN THICK ION-PLATED COATINGS		5. Report Date January 1975
		6. Performing Organization Code
7. Author(s) Talivaldis Spalvins		8. Performing Organization Report No. E-8130
		10. Work Unit No. 506-16
9. Performing Organization Name and Address Lewis Research Center, National Aeronautics and Space Administration, Cleveland, Ohio 44135		11. Contract or Grant No.
		13. Type of Report and Period Covered Technical Note
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration, Washington, D.C. 20546		14. Sponsoring Agency Code
15. Supplementary Notes		

16. Abstract

Industrial ion plating conditions were selected to deposit metallic coatings such as copper, gold, and chromium >2 micrometer thick on metal and glass substrates. The surface finishes of 304 stainless steel, copper, and brass were utilized with mechanically and electrolytically polished surfaces. Nodular growth occurred in these coatings during ion plating as revealed by scanning electron microscopy. Surface irregularities such as scratches, steps, ledges, and so forth are responsible for outward growth, the typical cone type, whereas surface contaminants and loosely settled foreign particles are responsible for lateral growth; namely, the extreme localized surface outgrowths. These defect crystallographic features create porosity in the coatings when subjected to stresses and strains.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Coatings Surfaces Deposition method	Unclassified - unlimited STAR category 26 (rev.)

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
Unclassified	Unclassified	11	$3.00

* For sale by the National Technical Information Service, Springfield, Virginia 22151

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SUMMARY

Industrial ion plating conditions were selected to deposit metallic coatings such as copper, gold, and chromium >2 micrometer thick on metal and glass substrates. The surface finishes of 304 stainless steel, copper, and brass were utilized with mechanically and electrolytically polished surfaces. Nodular growth occurred in these coatings during ion plating as revealed by scanning electron microscopy. Surface irregularities such as scratches, steps, ledges, and so forth are responsible for outward growth, the typical cone type, whereas surface contaminants and loosely settled foreign particles are responsible for lateral growth; namely, the extreme localized surface outgrowths. These defect crystallographic features create porosity in the coatings when subjected to stresses and strains.

INTRODUCTION

In areas where thin metallic films (<1 μm) are utilized (microminiaturization, lubrication, corrosion, decoration, or simply as strike coats), ion plating offers the highest degree of adherence. This exceptionally strong adherence is attributed to the ionization of the evaporant and subsequent acceleration of the ions to the specimen which generate a graded interface. The exact reaction mechanism for the interfacial formation is not established. However, the basic controlling factors are the sputter etched surface, the kinetic energy, and the amount of the ionized evaporant which contribute to the penetration effect and the surficial heating effect, and consequently accelerate diffusion and facilitate surface reactions.

Since the deposition rates of ion plating are high, possibly up to 250 000 Å (0.001 in.) per minute, recent interest has generated in the industrial community to deposit thick coatings or deposits. With the advent of thick ion plated deposits, the structural and morphological growth during the plating process becomes of great practical importance. It is known that during evaporation, sputtering, or ion plating, the deposition parameters, such as substrate temperature, rate of deposition, pressure, and so forth, will affect the microstructure (grain size). It has also been shown that during electroplating (ref. 1), electroless plating (ref. 2), vapor deposition (ref. 3), and sputtering (ref. 4), various defect crystallographic growth features occur. Extreme localized surface growth are initiated by preferential nucleation at irregularities or imperfections. As a consequence, these nodules grow at an accelerated rate extending above the matrix surface. It is important to recognize these crystallographic features, since they become increasingly more disastrous as the coating thickness increases. The nodules are weakly bonded in the matrix and they have a tendency to fall out, especially under stress, thus generating porosity. It has not been reported in the literature to date as to how surface topography affects crystallographic growth defects in thick ion plated coatings.

The objective of this investigation was to determine by scanning electron microscopy (SEM) the defect crystallographic growth features formed in ion plated metallic coatings on copper, brass, and 304 stainless steel surfaces with various surface finishes. The experimental plating conditions which were selected in this study are the conditions generally used in industrial ion plating.

APPARATUS AND PROCEDURE

The ion plating apparatus used in this study is shown in figure 1. The substrate to be coated is the cathode of the high-voltage dc circuit. The coating material is placed in a tungsten boat about 10 centimeters below the specimen. Below this is the anode, the circular metal plate mounted on ceramic stands, to be isolated from the deposition apparatus. The plating conditions used during this study, are those most commonly used in commercial ion plating. A negative potential of 3 to 5 kilovolts was applied to the specimen, with a current density of 0.3 to 0.8 milliampere per square centimeter in 20 microns of argon. Before evaporation, the substrate was sputter etched at the aforementioned conditions for about 10 minutes.

The substrates used were 2- by 2- by 0.025-centimeter copper, brass, and 304 stainless steel sheets with different surface finishes. The metal sheet specimens were mounted on a circular stainless steel disk (6.25 cm in diameter and 1.25 cm thick) and the bulk temperature was monitored by a Chromel-Alumel thermocouple embedded in the disk. The surface finish was prepared by being (1) ground on a 600-grit emery paper with a resultant surface finish of 22.5×10^{-2} micrometer (9 μin.); (2) polished with diamond paste 2×10^{-2} micrometer (1 μin.); and (3) electropolished. The surface finishes after metallographic polishing were measured by Talysurf. The metals evaporated were copper, gold, and chromium. The thickness of the ion plated coatings were 2 micrometers or more.

Following ion plating the specimens were examined by SEM.

RESULTS AND DISCUSSION

A section of a commercially ion plated integrated circuit with step coverage of 1-micrometer-thick metal film is shown in figure 2. It is obvious from this micrograph that the coating does not have a smooth, uniform growth pattern but shows dome-shaped projections above the surface which are characteristic of nodular growth.

Surface Finish Effects on Nodular Growth

When chromium was ion plated on 304 stainless steel with a 22.5×10^{-2}-micrometer (9-μin.) surface finish, nodular growth was very pronounced along the edges of the scratch marks as seen in figure 3(a). When copper was ion plated on a 304 stainless steel surface (22.5×10^{-2} μm), typical nodular growth of the cone type is seen in figure 3(b), and a more complicated structural growth feature is shown in figure 3(c). At these higher magnifications a distinct surface geometrical structure is revealed. The crystallites are of a prismatic (needle) type profile and are oriented in the direction of the evaporation source. These coatings show distinct separations between the crystallites and even more pronounced separation between the nodule and the matrix.

When gold and copper were ion plated on 304 stainless steel surfaces which were polished with diamond paste, the surfaces were practically free of scratch marks; however, nodular growth appeared randomly. The structural features as seen in figure 4 have a more complicated structure, more of the extreme localized growth type, rather than the typical cone type. To illustrate the formation of extreme localized growth features from foreign body sites on the surface, a few silicon carbide particles were sprinkled over the 304 stainless steel polished surface and ion plated with copper. Figure 5 shows a typical complex growth feature which was nucleated from a foreign particle. These complex crystallographic features are nucleated preferentially by surface contaminants (embedded particles from polishing) or from foreign body sites, rather than from surface microirregularities.

Finally, electropolished copper and brass surfaces with resultant surface finishes of about 0.5 microinch were ion plated with copper. The surface morphologies are shown in figure 6. The nodular growth still appeared randomly, but the size of the nodules was considerably smaller. A typical coating surface morphology is shown in figure 6(a). Apparently a deeper scratch mark which was still present after mechanical polishing and electropolishing acted as a line of nucleation sites and as a result a highly concentrated nodular growth pattern is shown along the defect line in figure 6(b).

Copper was also ion plated on microscope slides (insulators) which were held in a metallic holder. The corresponding surface morphologies are shown in figure 7. Distinct randomly dispersed nodular growth is seen in these micrographs. At the higher magnification the geometrical structures of the crystallites can be resolved, revealing a prismatic structure as seen in figure 7(a). Besides the conical-type nodules, lateral growth types are also formed as seen in figure 7(b).

The scanning electron micrographs illustrate that nodular and extreme localized surface growths have a very strong dependence on the surface topography. Surface defects and irregularities on the macro and micro scale such as scratches, asperities, ledges, contaminants, intercrystalline imperfections between growing crystals and other coating growth defects are the sources for preferential nucleation and growth. These irregularities are the initial high points with a high energy concentration for preferential nucleation and growth. At these points an accelerated growth occurs in respect to the matrix growth. It appears that the nodular growth rate is surface controlled, therefore not changing the crystallographic profiles significantly. Nodular growth of the cone-type structure observed from these micrographs is predominantly outward in growth. The pronounced geometrical differences in the profiles between nodules (simple or fused) as opposed to extreme localized surface outgrowth (complex configurations) may originate from the type of the nucleation source. Surface irregularities such as scratches, ridges, or steps might lead to a nodular growth of the typical parabolic (conical) type. However, the dimensions of the individual or fused nodules stemming from each nucleus depend on the size and spacing of the various nucleation sites.

On the other hand surface impurities or other foreign matter (possibly from grinding or polishing) settled on the surface may lead to extreme localized surface outgrowths of unusual geometrical shapes which are of lateral growth in nature. In addition to the surface finish and contaminant effects on the nodular growth during deposition, the plating conditions, especially plasma instabilities, may also lead to unstable growth conditions. It has been inferred that plasma itself may act as an additional effective nucleation source; however, at the present time this phenomenon is only of scientific curiosity (ref. 5).

Effects of Mechanical Forces on Nodules

When mechanical forces such as bending are exerted on the coating or deposit, these crystallographic features have a tendency to be ejected, thus leaving pores. Typical pore formation left in a 2-micrometer-thick chromium coating after the substrate was bent only once is shown in figure 8. These defects in crystallographic growth (fig. 8) are loosely bonded in the matrix and, as a result, under stresses and strains easily fall out. Porosity of a coating is thus related to the structure and varies with the nature and the state of the substrate finish. Consequently the degree of substrate perfection is the primary cause for porosity in thick coatings and deposits.

SUMMARY OF RESULTS

The objective of this investigation was to determine by scanning electron microscopy (SEM) the defect crystallographic growth features formed in ion plated metallic coatings on copper, brass, and 304 stainless steel surfaces with various surface finishes. The experimental plating conditions which were selected in this study are the conditions generally used in industrial ion plating; the following results were obtained:

1. Nodules and extreme surface outgrowths are formed in ion plated coatings.
2. Surface irregularities such as scratches, ledges, steps, and so forth are responsible for outward growth cone-type configurations. Surface contaminants or settled foreign particles are responsible for lateral growth-extreme localized surface outgrowths.
3. Nodular growth can be reduced by improving the surface smoothness.
4. Nodules are sources for porosity in coatings and deposits, since stresses and strains can easily eject the nodules, leaving voids.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, November 22, 1974,
506-16.

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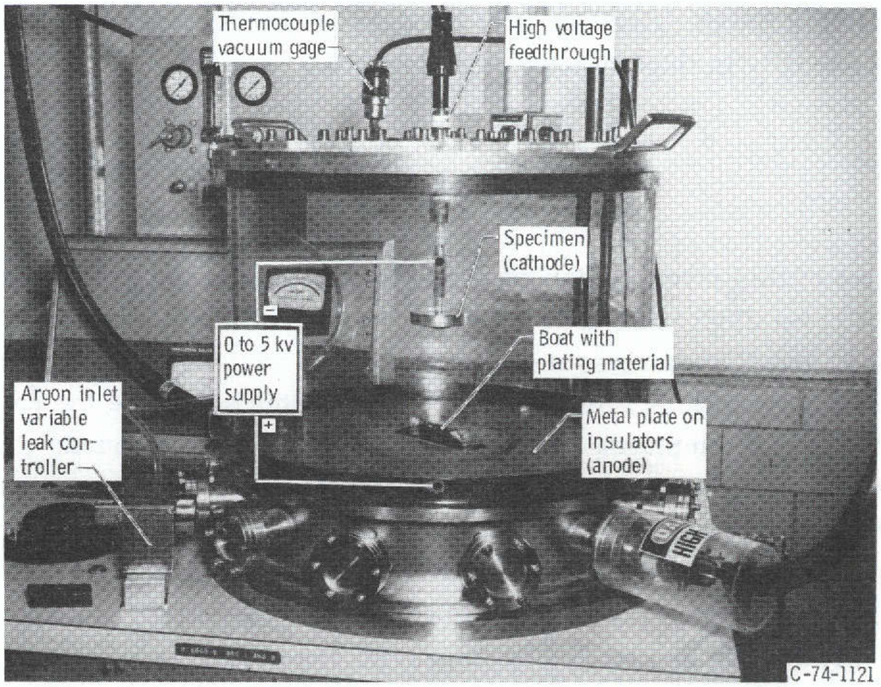


Figure 1. - Ion plating chamber.

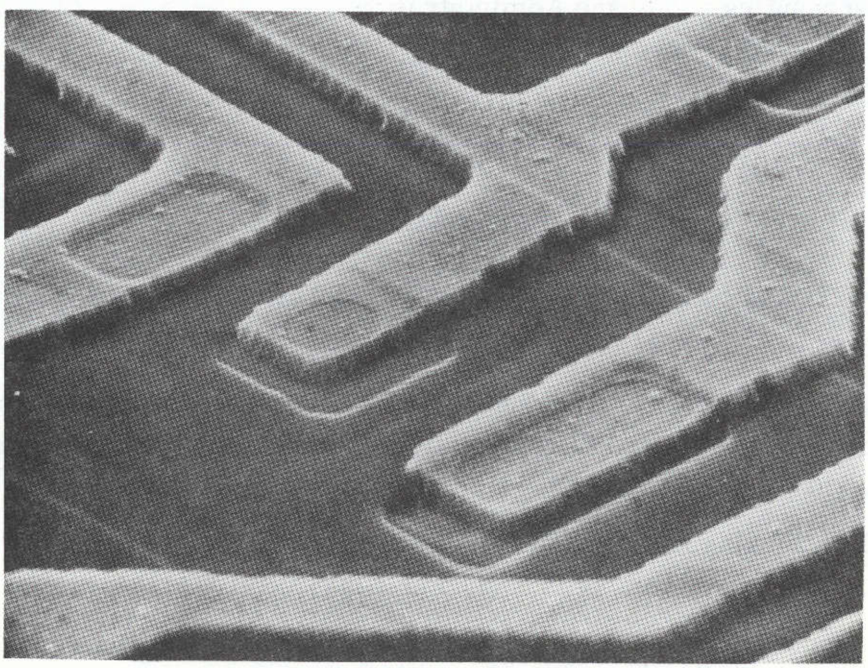
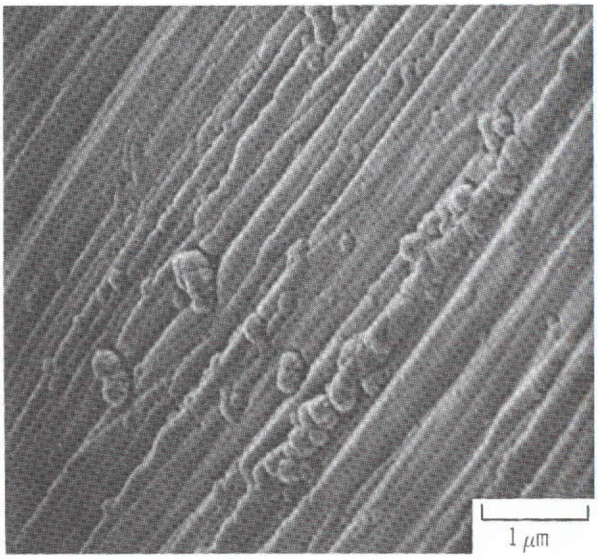
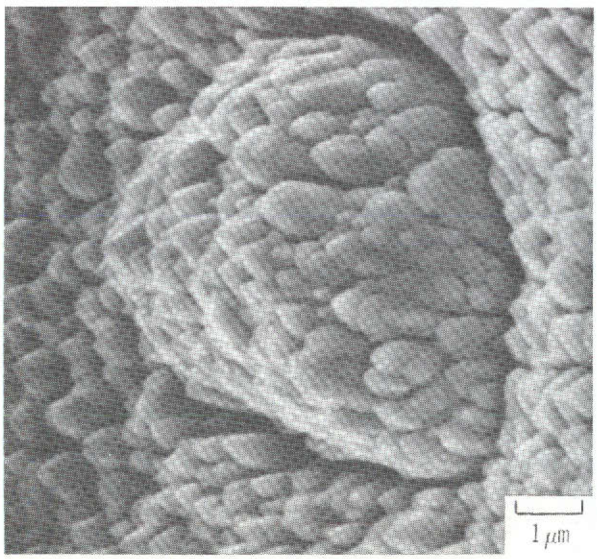


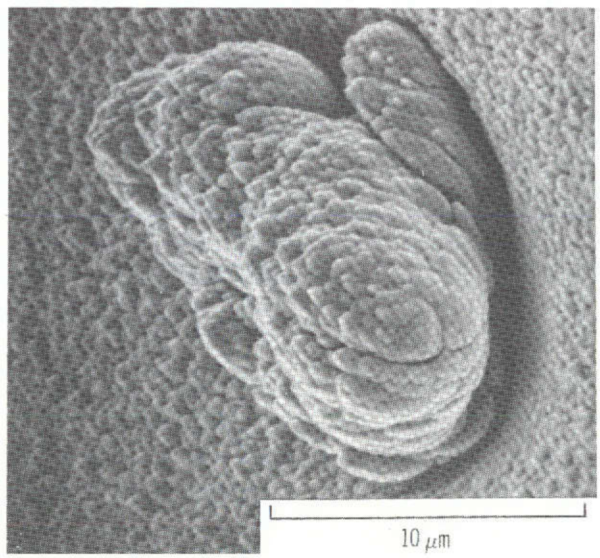
Figure 2. - Section of commercially ion plated integrated circuit. X2000.



(a) Surface view of ion plated chromium.

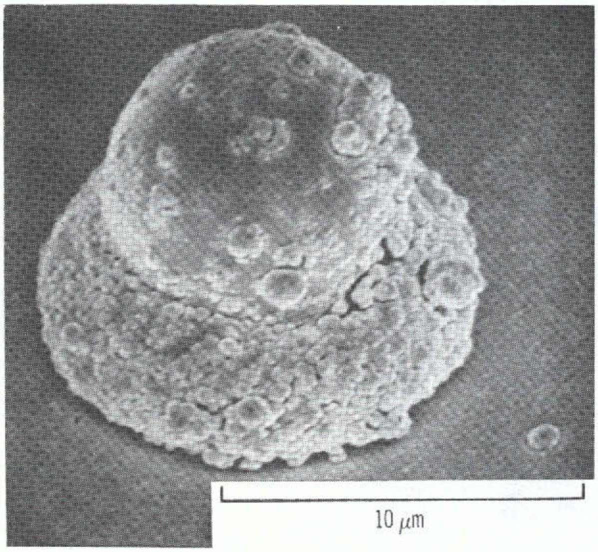


(b) Growth of single nodule.

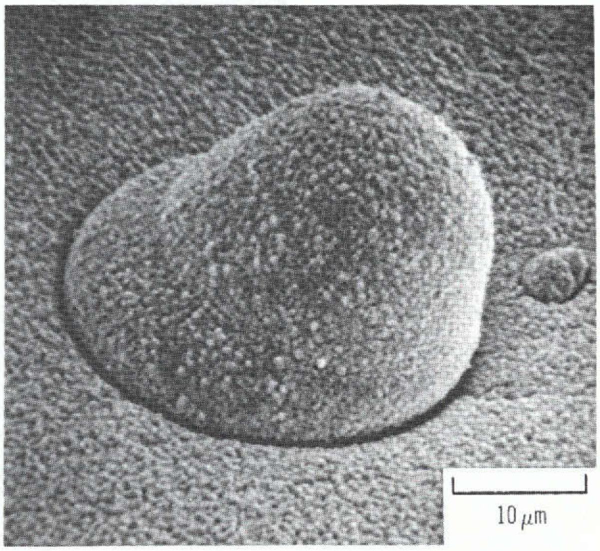


(c) Growth of fused nodules.

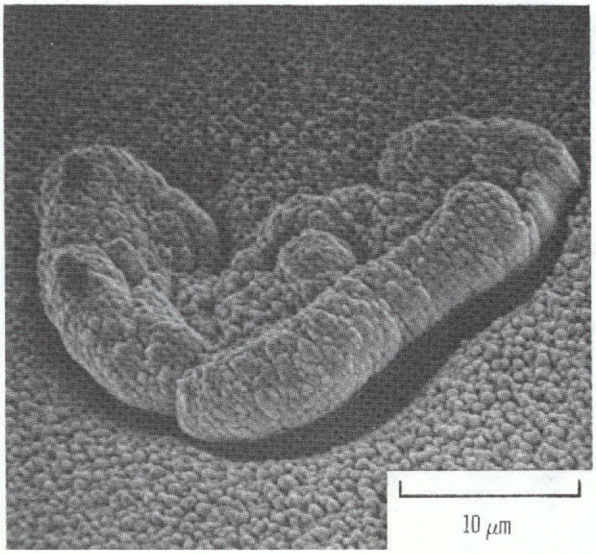
Figure 3. - Surface structure of ion plated chromium and copper on 304 stainless steel surface sanded to 22.5×10^{-2} micrometer (9 μin.).



(a) Step-type nodular growth.



(b) Distorted nodular growth.



(c) Complex surface overgrowth.

Figure 4. - Surface view of ion plated gold and copper on diamond paste polished 304 stainless steel surface ($2X10^{-2}$ μm or 9 $\mu in.$).

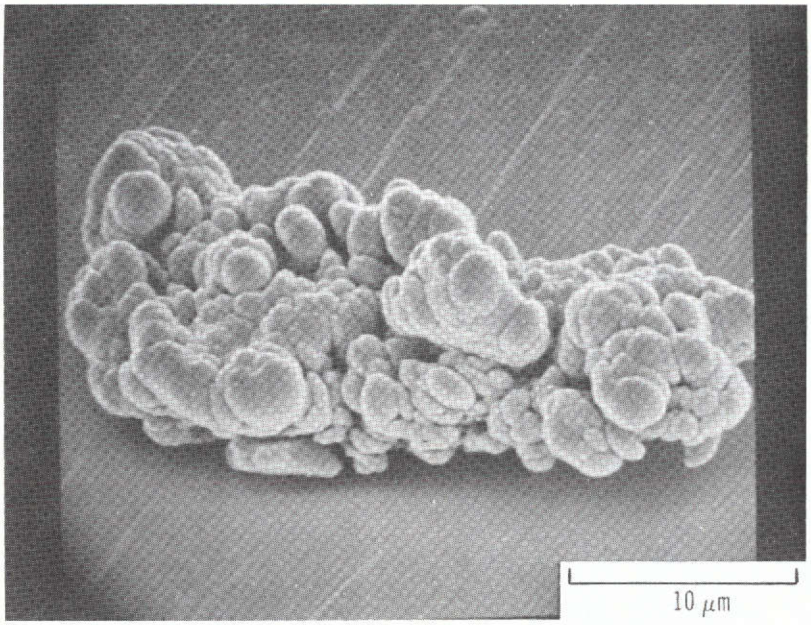
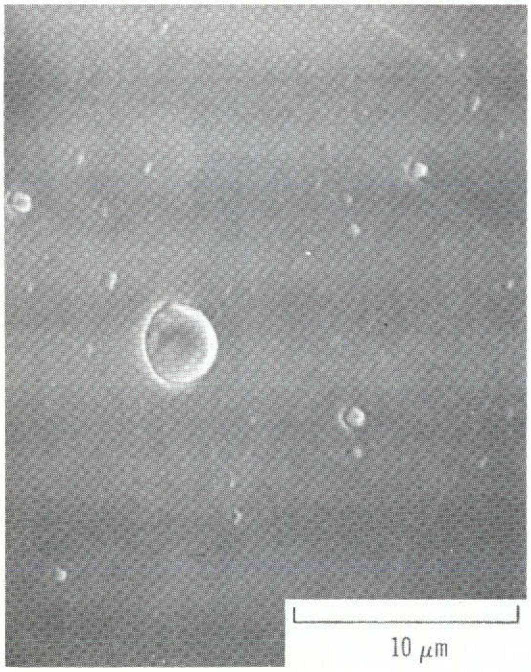
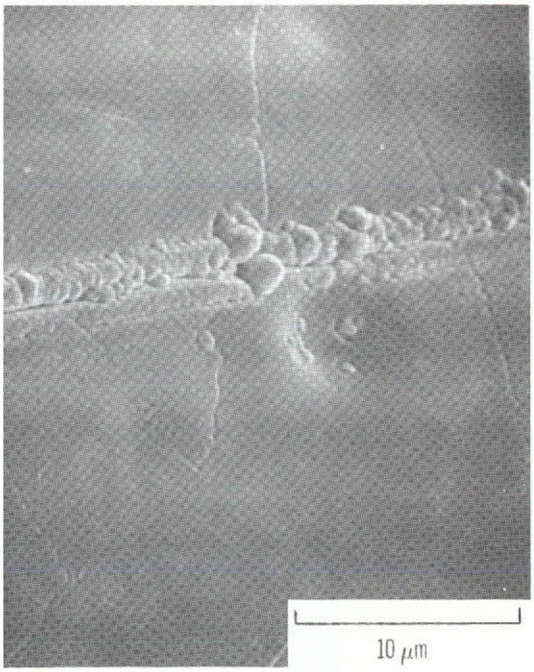


Figure 5. - Surface view of ion plated copper on polished 304 stainless steel surface sprinkled with carbide particles.

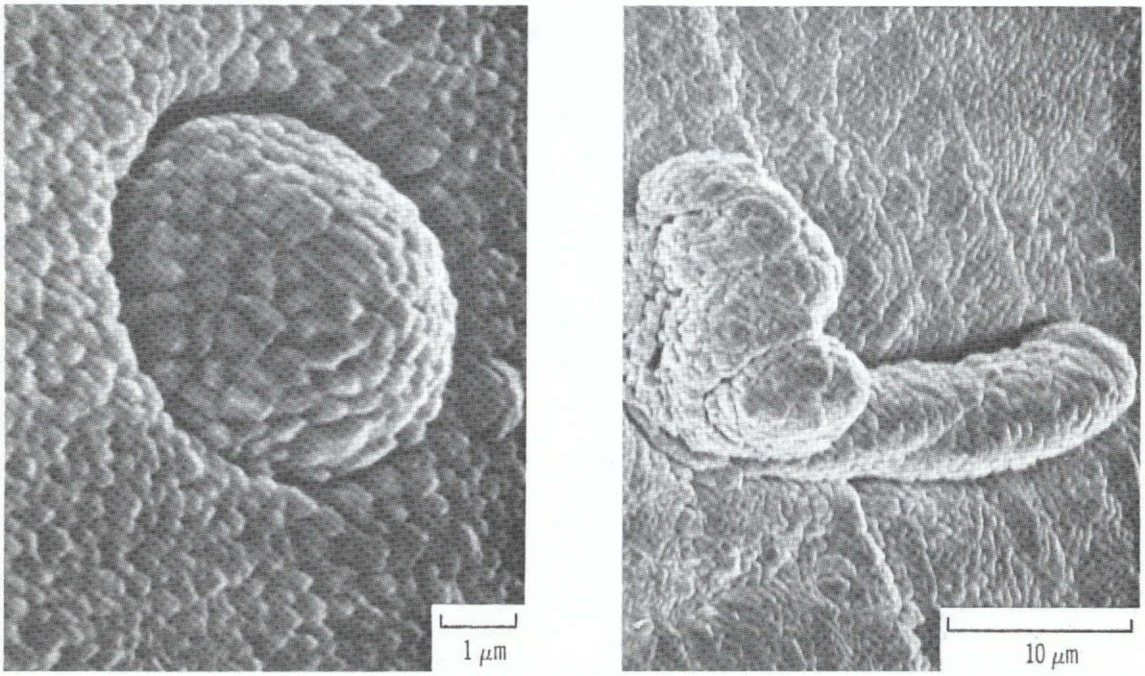


(a) Typical nodules on brass surface.



(b) Nodular growth along a scratch mark on copper surface.

Figure 6. - Surface view of ion plated copper on electropolished brass and copper surfaces.



(a) Conical-type nodule.

(b) Lateral-growth-type overgrowth.

Figure 7. - Surface view of ion plated copper on microscopic glass slides.

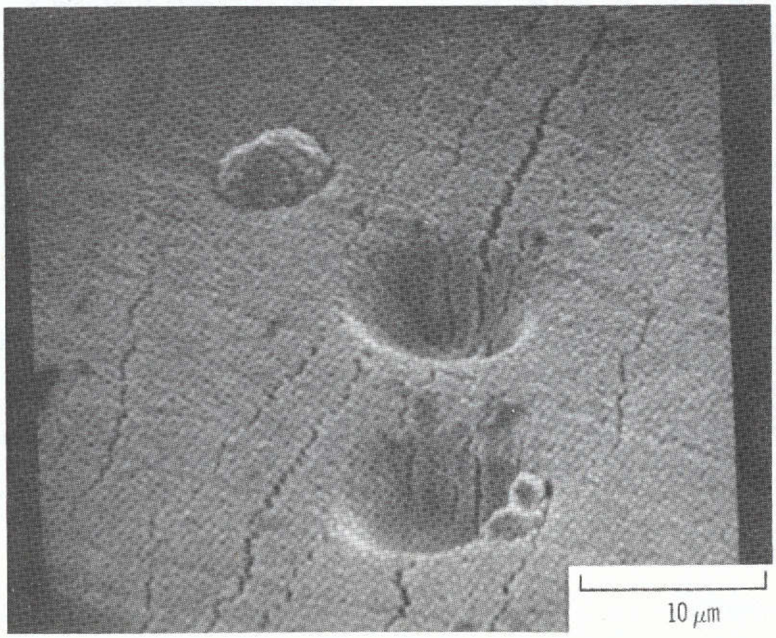


Figure 8. - Surface view after nodular ejection on 304 stainless steel.

NASA-Langley, 1975 E-8130