8

POROSITY

INTRODUCTION

Voids (pores) are generally formed in thin films irrespective of the film preparation method (electrodeposition, evaporation, or sputtering) as long as the deposition process involves a phase transformation from the vapor to the solid state. These voids can be extremely small (approximately 10Å) and high in density (about $1 \times 10^{17}/cm^3$)(1-3).

Porosity is one of the main sources of discontinuities in electroplated coatings; the others are cracks from high internal stresses and discontinuities caused by corrosion or subsequent treatments such as wear of deposits after plating as shown in Figure 1 (4,5). In most cases porosity is undesirable. Pores can expose substrates to corrosive agents, reduce mechanical properties, and deleteriously influence density, electrical properties and diffusion characteristics. As discussed in the chapter on diffusion, pores formed as a result of heating (Kirkendall voids) can noticeably reduce adhesion of a deposit.

Porosity in a sacrificial coating such as zinc on steel is not too serious since in most environments zinc will cathodically protect steel at the bottom of an adjacent pore. However, for a noble metal, similar porosity may be problematic. A special significance of porosity is that it permits the formation of tarnish films and corrosion products on the surface, even at room temperature. In the electronics industry, which utilizes the largest quantity of gold coatings for engineering purposes, porosity is a major concern because of its effect on the electrical properties of plated parts (6). Porosity in cadmium deposits, which is desirable for purging hydrogen codeposited during plating, can result in rapid postplating embrittlement due

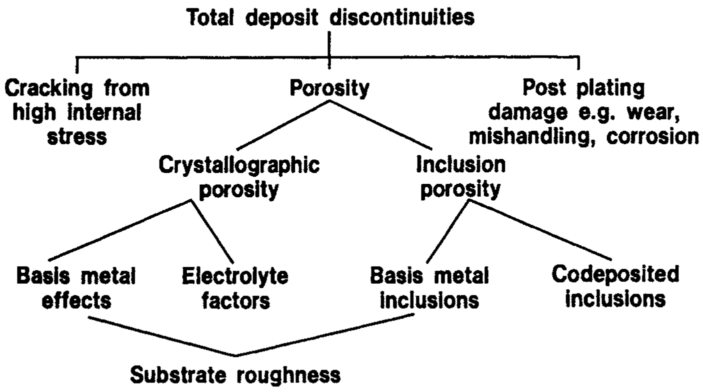


Figure 1: Causes of discontinuities in electroplated coatings. Adapted from Reference 4.

to the lack of a barrier to hydrogen reentering the steel during exposure of the plated part to corrosive environments (7,8).

Depending on the method of formation of the coating, the pore can be filled with air or foreign matter such as gases, fluids, solids, etc. For example, analysis of electrodeposits reveals small amounts of many constituents from plating solutions easily explained by solution filled cavities of small pores but difficult to account for otherwise. Outgassing measurements on electrodeposited gold films revealed that the major constituent in voids in these coatings was hydrogen gas (4,9).

INFLUENCE ON PROPERTIES

Any material (coatings, castings, powder metallurgy consolidated alloys, etc.) containing pre-existing porosity or voids is subject to property degradation. The tensile behavior of materials with pre-existing porosity is characterized by large decreases in both strength and ductility with increasing porosity level, since ductile fracture in engineering alloys is most often the result of the nucleation and link-up of voids or cavities (10). Figure 2 reveals that both powder metallurgy Ti-6Al-4V and chemically pure Ti suffer a decrease in yield strength as well as tensile ductility with increasing porosity level. Three percent porosity in cast, high-purity copper, which reduces the density from 8.93 to 8.66 gm/cm^3 drops the reduction-in-area at 950°C from 100% to 12% (11). Porosity introduces two factors which reduce macroscopic ductility. First, the presence of pores acts to concentrate strain in their vicinity and to reduce the macroscopic flow stress. Secondly, the nonregular distribution of pores results in paths

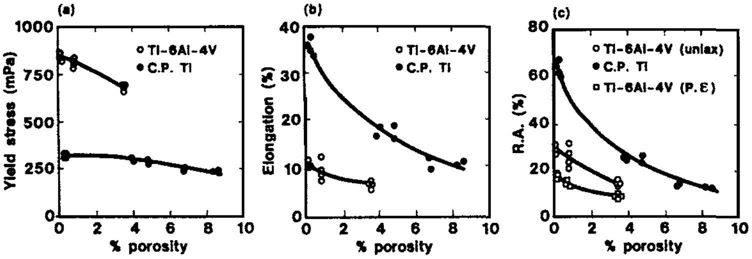


Figure 2: The influence of porosity on (a) the yield stress, (b) the elongation to failure, and (c) the percent reduction in area for chemically pure titanium and Ti-6Al-4V. Adapted from Reference 10.

of high pore content which are preferred sites for flow localization and fracture (10).

Table 1 shows the influence of porosity on various mechanical and physical properties of thin films (1). Point defects such as pinholes laid down during deposition and generated during thermal cycling may act as starting points for severe film cracking at high temperature. Tests carried out on evaporated coatings of chromium, copper and nickel showed that cracks radiated from pinholes in the films. This effect was attributed to stress concentration in the neighborhood of the pinhole (12). Pre-existing

Table 1: Effects of Voids on the Properties of Thin Films*

Properties	Effects of Voids
Mechanical properties	Ductility decrease Hydrogen embrittlement Creep resistance Reduced elastic modulus Decrease in adhesion(interfacial void)
Electrical properties	Resistivity increase
Corrosion properties	Reduced corrosion resistance (through-pores)
Dielectric properties	Dielectric constant

*From reference 3.

voids, along with hydrogen, are responsible for the reduced ductility of electroless copper deposits (13). This is discussed in more detail in the chapter on hydrogen embrittlement. Chromate coatings on copper and nickel-phosphorus films prepared by electrodeposition also contain a high density of voids with a structure similar to that of a crack network. The presence of these voids contributes significantly to brittleness in these films (14,15).

GOOD ASPECTS ABOUT POROSITY

There are occasions where porosity is desired in a coating. Pores in anodized aluminum provide the opportunity to provide a wide range of colors when they are sealed to eliminate the path between the aluminum and the environment, and pores in phosphoric acid anodized aluminum provide for adhesion of subsequent deposits. Porous chromium deposits from specially formulated solutions provide for improved lubricating properties while microporous chromium deposits, produced by plating over a nickel deposit which contains codeposited multitudinous fine, nonconducting particles, result in uniform distribution of corrosion attack of the nickel (16). Porous electroforms for applications such as perforated shells used in vacuum forming procedures or for fluid retention have been produced (17-19). One technique involved addition of graphite particles to a nickel plating solution. The graphite particles adhered to the deposit and generated channels 50-100/μm in diameter which were propagated through the nickel for 2.5mm or more (17). Another approach involved codeposition of nonconducting powders with the nickel and by decomposing the powders at a low temperature after plating, horizontal as well as vertical porosity was achieved (18).

CLASSIFICATION OF PORES

Kutzelnigg suggests that pores may be broken down into two main categories, transverse pores and masked or bridged pores (20). His pictorial descriptions of the various types of cavities are shown in Figure 3 and the following information is extracted from his comprehensive article on porosity (20). Transverse pores may be either of the channel type (Figure 3a) or hemispherical (Figure 3b) and extend through the coating from the basis metal to the surface of the deposit. They may be oriented perpendicular (Figures 3a,b) or oblique (Figure 3c) to the surface or may have a tortuous shape (Figure 3d). Masked or bridged pores do not extend through the coating to reach the surface but either start at the surface of the basis metal and become bridged (Figure 3e) or start within the coating and become bridged (enclosed pores) (Figure 3f). A pit is a surface pore which does not become masked or bridged (Figure 3g). They may be hybrids (Figure 3h), or give rise to blisters (Figure 3i). Cracks may be regarded as pores much extended in a direction parallel to the surface, but they can also be divided into transverse cracks, enclosed cracks and surface cracks (Figures 3j, 3k, 3l).

A combination of channel and spherical pores is shown in Figure 3m and the influence of substrate defects in Figures 3n, 3o, and 3p. Chemical attack after deposition (Figure 3q), incomplete coverage of the deposit (Figure 3r), and defects due to inclusions (Figures 3s and 3t) are other examples of pores (20).

CAUSES OF POROSITY

Porosity, together with structure and many other properties of an electroplated coating, reflects the effects of: 1) nature, composition and history of the substrate surface prior to plating; 2) composition of the plating solution and its manner of use; and 3) post plating treatments such as polishing (abrasive or electrochemical) wear, deformation, heating and corrosion (21).

A pore may arise in several ways: 1) irregularities in the basis metal; 2) local screening of the surface to be coated; 3) faulty conditions of deposition; and 4) damage after plating. The first two may be attributed to inadequacies of prior processing such as cleaning, pickling, rolling, machining, heat treating, etc. (20). Number three is related to the ability of the plating process to adequately cover the surface through the conventional steps of nucleation and growth. If lateral growth can be promoted in place of outward growth of the deposit, coverage is faster and therefore more effective at lower thickness (22,23,24), as will be shown later in this chapter.

Figure 1 shows that porosity is caused by either inclusions (inclusion porosity) or by misfit of crystal grains (crystallographic porosity). Inclusion porosity arises from small nonconducting areas on the substrate which are not bridged over during the early stages of deposition. Crystallographic porosity arises from structural defects caused by either the basis metal or electrolyte factors (4).

At low deposit thickness, porosity of electrodeposited films is largely controlled by the surface condition and characteristics of the underlying substrate. This condition persists up to a limiting thickness, after which the properties of the film itself, primarily crystallographic properties, determine the rate of pore closure (22). Typically, porosity drops

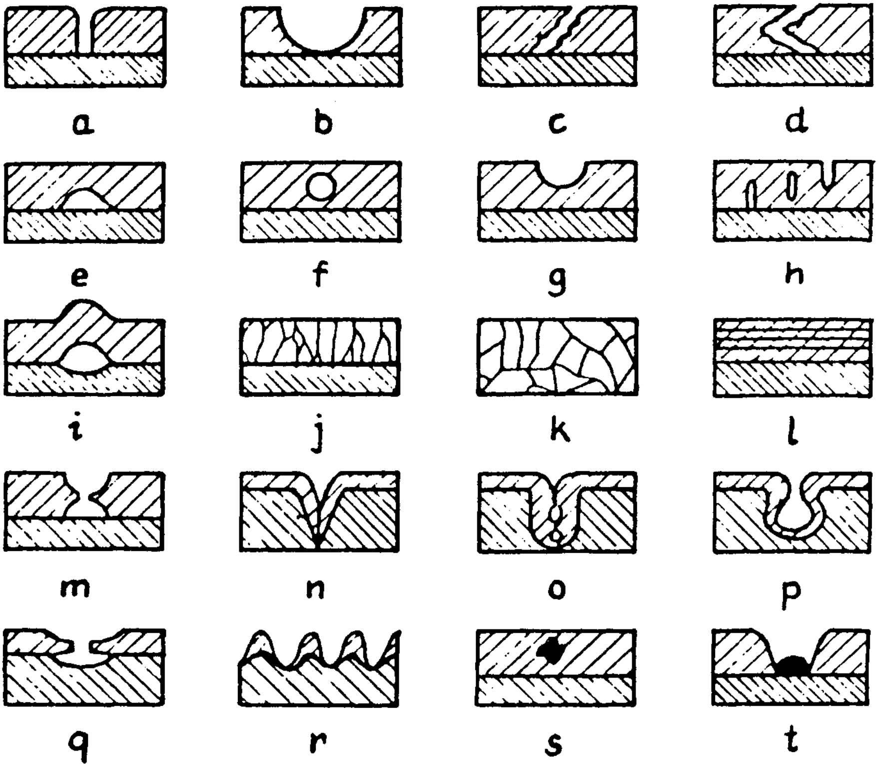


Figure 3: Types of pores or cavities. From Reference 20. Reprinted with permission of the American Electroplaters & Surface Finishers Society.

a Transverse pore oriented perpendicular and extending through the coating from the basis metal channel pore.

b Same as a) but this pore is hemispherical.

c Transverse pore extending through the coating in an oblique fashion.

d Transverse pore extending through the coating in a tortuous fashion.

e Masked or bridged pore-starts at the surface of the basis metal but does not reach the surface of the deposit.

f Masked or bridged pore-starts within the deposit and becomes bridged (enclosed pore).

g A pit-which does not reach the surface of the basis metal (dead end pore).

h A hybrid-a bridged pore in contact with the base, an enclosed pore, and a surface pit.

i Bridged pores located on the surface of the base metal and originally filled with electrolyte may give rise to "blisters" if the deposit is locally lifted by the pressure of hydrogen generated by interaction of the basis metal and the solution. Blisters may also be produced by rubbing poorly adherent deposits (or heating them).

j Cracks-may be regarded as pores much extended in a direction parallel to the surface. Cracks may also be divided into transverse cracks, enclosed cracks, and surface cracks. They may further be gross, small, or submicroscopic. An extreme case of the last type are the boundaries of the crystallites building up in the deposit.

k The most common examples of cracks is represented by the pattern seen in bright chromium deposits at large magnification.

l Stratifications which may be better understood as lamellar discontinuties. In general these discontinuities differ in composition from the main part of the deposit.

m A combination of channel type and spherical pores.

n Example of porosity obtained with a V notched substrate.

o Example of porosity obtained with a U notched substrate.

p Another type of trouble may arise from pores in the basis metal, e.g., a casting or powder compact part. Though the deposit itself may be free of pores, the resulting pocket filled with electrolyte is the cause of trouble known as blooming out.

q Chemical attack after deposition.

r Incomplete coverage of the surface due to poor macro- or micro-throwing power of the solution (also applies to n and o).

s A defect due to an inclusion-finely dispersed oxide, hydroxide, sulfide, basic matter or as adsorbed organic compounds.

t Another defect due to an inclusion-carbon particles from overpickled steel, residues of polishing compounds, etc.

exponentially with thickness as shown in Figure 4 (23).

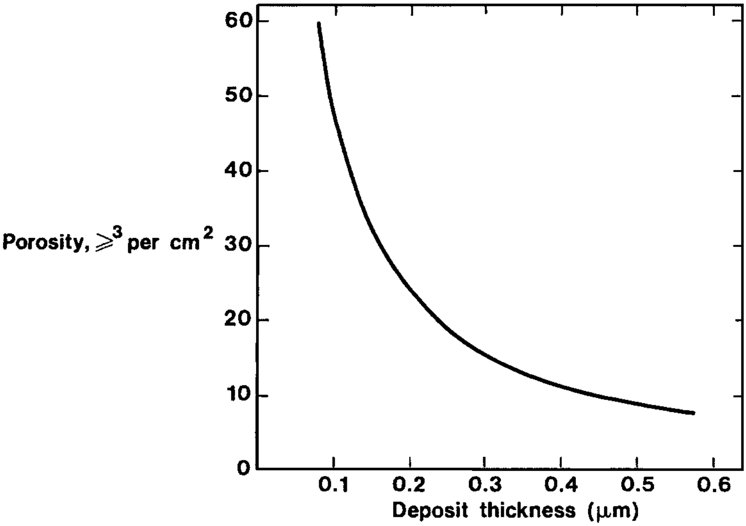


Figure 4: Variation of coating porosity with thickness for electrodeposited chromium. Adapted from reference 23.

An example of the sensitivity of porosity to substrate and deposition parameters is illustrated in Figure 5 which shows three distinct phases for electrodeposited, unbrightened gold on a copper substrate: substrate dominated, transition, and coating dominated. For very thin gold coatings (less than about 1μm), substrate texture controls coating porosity. At greater thicknesses, the slope of the porosity-thickness curve is controlled by parameters relevant to the deposit itself. Between these two regimes is a sharp, well marked transition region in which the porosity of the deposit falls extremely rapidly. The thickness at which this sharp transition occurs varies with the deposit grain size. The form and position of the porosity-thickness plots are affected by the deposit grain size, the crystallographic orientation and the ratio of nucleation rate to rate of grain growth, which, in turn, controls the average grain size of the deposit at any given thickness (22,24,25).

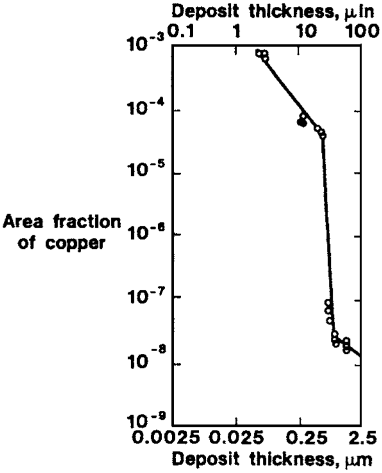


Figure 5: Porosity versus deposit thickness for electrodeposited unbrightened gold on a copper substrate. Adapted from Reference 22.

FACTORS RELATING TO THE SUBSTRATE

The surface of a substrate has small areas with the property of initiating pores which are referred to as pore precursors (26). These precursors prevent fusion of crystals and as the coating thickens a pore is generated. Inclusions of slag, oxides, sulfides, polishing abrasive, dirt, subscale oxide, and particles settling on the substrate from the plating solution, are pore precursors (21).

Substrate surface roughness has a noticeable influence on porosity. This is shown in Figures 6 and 7 for pure acid citrate gold plated directly on OFHC copper discs (Figure 6) and OFHC copper discs with a nickel underplate (Figure 7). The data clearly show a large increase in porosity with roughness. Rough surfaces have a true area greater than the apparent area (Figure 8). Therefore, it is quite possible that at least some of the increase in porosity on rough substrates compared to the porosity on smooth substrates is due to a difference in average true plate thickness. Garte proposed a roughness factor ratio to help explain this (27):

$$R\ (\text{roughness factor}) = \frac{\text{True Area}}{\text{Apparent Area}}$$

If the plating thickness, T, is determined by a weight per unit (apparent) area method, as most methods are, then

$$T = \frac{\text{Weight}}{\text{Apparent Area}} \times \frac{1}{\text{Density}}$$

$$\text{Therefore: True Thickness(t)} = \frac{\text{Measured Thickness (T)}}{R}$$

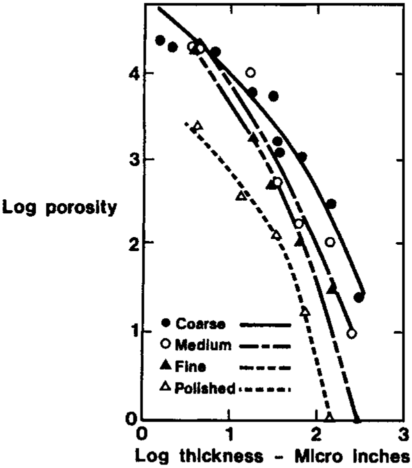


Figure 6: Relationship between porosity-thickness-roughness for acid citrate gold on OFHC copper. Adapted from Reference 27.

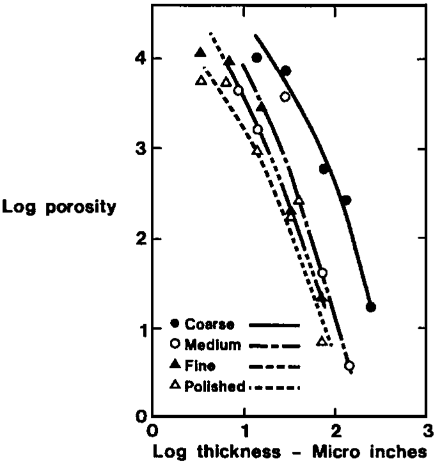


Figure 7: Relationship between porosity-thickness-roughness for acid citrate gold on OFHC copper with a nickel underplate. Adapted from Reference 27.

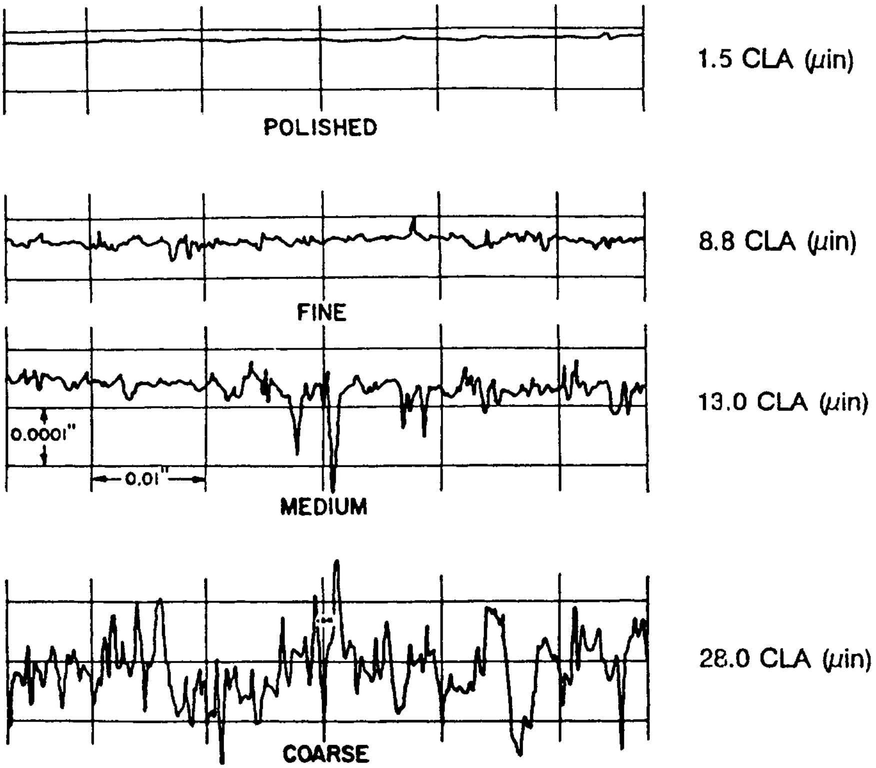


Figure 8: Diamond stylus profilometer tracings of specimen surfaces. Original magnification: 5000× vertically, 100× horizontally. Reprinted with permission of The American Electroplaters & Surface Finishers Soc. From Reference 27.

These geometric considerations show that the true average thickness is the apparent thickness reduced by a factor R. This is strictly true for vary thin deposits, but becomes less important for thicker plates (27). The direction of the change as a function of thickness depends on the microthrowing power of the solution, and is therefore, specific to the type of solution used (28). Some roughness factors for metals abraded in various ways are presented in Table 2.

Surface roughness also influences mean thickness and spread. An example is shown in Figure 9 for 2.9µm (115/µin) of gold deposited on coarse 0.75µm (30µin) CLA, and polished 0.04µm (1.5µin) CLA, OFHC copper. The data represented by the open circles show that on the polished substrate, 1% of the surface had plate thinner than 2.6µm (101µin), while 99% of the plate was thinner than 3.2µm (127µin). The curve for the rough substrate has a lower mean value and also a larger spread. Its extreme areas are considerably thinner than the thinnest parts of the deposit on the smooth

Table 2: Some Roughness Factors from the Literature

Metal	Treatment	Roughness Factor
Copper	#320 grit paper	4.2
Copper	#800 grit paper	3.5
Stainless steel	#320 grit paper	2.7
Stainless steel	#800 grit paper	2.0
Aluminum	#320 grit paper	3.1
Aluminum	#800 grit paper	2.2
Gold	Coarse crocus	2.5-2.7
Gold	Fine crocus	1.7
Gold	2/0 machine paper	2.6-3.0
Gold	1/0 machine paper	3.7
Gold	2/0 emery cloth	6.0
Aluminum	Mill rolled	3.1
Aluminum	#600 Alundum	2.1
Aluminum	#120 Aloxite	3.0
Aluminum	#240 Aloxite	3.4
Aluminum	#0 paper	9.3
Aluminum	#2/0 paper	17.6
Aluminum	#3/0 paper	19.9

* From reference 27.

surface. For example, 1% of the deposit on the smooth surface is less than 2.6μm (101μin) thick, while for the rough surface 1% of the deposit lies below 1.2μm (47μin). Both had the same apparent thickness of deposit (26). The roughness factor for the coarse surface derived from the deposit thickness measurements was computed to be 1.4 and this agreed with a value of 1.4 using a bent wire to conform to the surface profile (27).

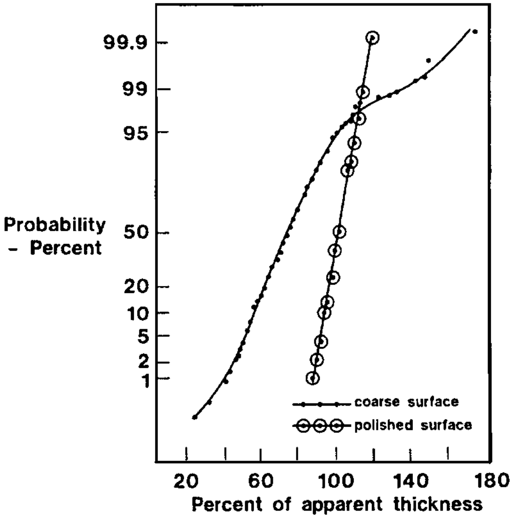


Figure 9: Distribution of thickness measurements made on acid citrate gold plated on coarse and polished OFHC copper. Average thickness—115 microinches. Adapted from Reference 26.

INFLUENCE OF PLATING SOLUTION AND ITS OPERATING PARAMETERS

The porosity in a coating varies with: 1) the concentration of all salts in the solution; 2) the presence of addition agents; 3) the accumulation of aging byproducts; 4) the form of current and the current density used for deposition; 5) the degree of agitation; and 6) the temperature of the solution. Extensive investigations for nickel, copper, gold, cobalt, tin and tin-nickel have verified these general effects which are reviewed in an excellent article by Clarke (21). Figure 10 shows the influence of pulse plating for unbrightened gold on copper. The same three phases that are present for non-pulse plated gold (substrate dominated, transition and coating dominated) are evident but they are displaced downward (22,29).

METHODS TO REDUCE POROSITY

A. Underplates

A convenient and often very effective way to modify the substrate and reduce porosity is to use an underplate. Figure 11 shows that

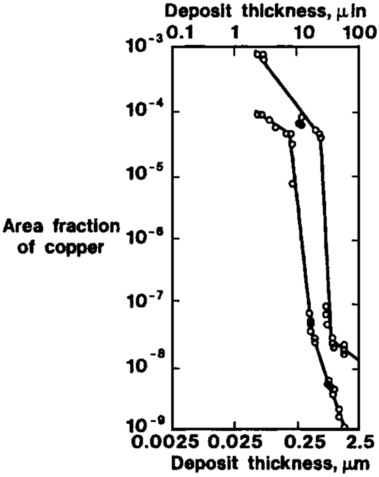


Figure 10: Porosity versus deposit thickness for pulse plated gold on a copper substrate. The curve for an unbrightened gold deposit on a copper substrate (top) is shown for comparison (Also see Figure 5). Adapted from Reference 22.

a sharp reduction in gold plate porosity is achieved with copper underplate of sufficient thickness (26). Another example is Figure 12 which shows the reduction in porosity brought about by using a pure soft gold underplate for a cobalt-hardened gold (30). The curve marked "old" shows the results obtained from a solution which had been replenished several times, while the curve marked "new" is for a fresh solution. The curve marked "duplex" shows results for both solutions with a strike deposit of 13μm. The horizontal dashed line indicates an arbitrary acceptable porosity level for the nitric vapor test used to assess porosity.

B. Crystallographic Orientation

The chapter on structures contains some discussion on crystallographic planes and directions in crystal lattices. Morrissey and his coworkers (22,24,25) effectively utilized this type of information to demonstrate that covering power and rate of pore closure of bright gold deposits on copper are related to the crystallographic orientation of the deposits. The following is extracted from their work.

Gold crystallizes in a face centered cubic structure wherein the most densely packed planes are (111) followed by (200) and then (220) planes. If atoms were added at a constant rate to a crystallite with these

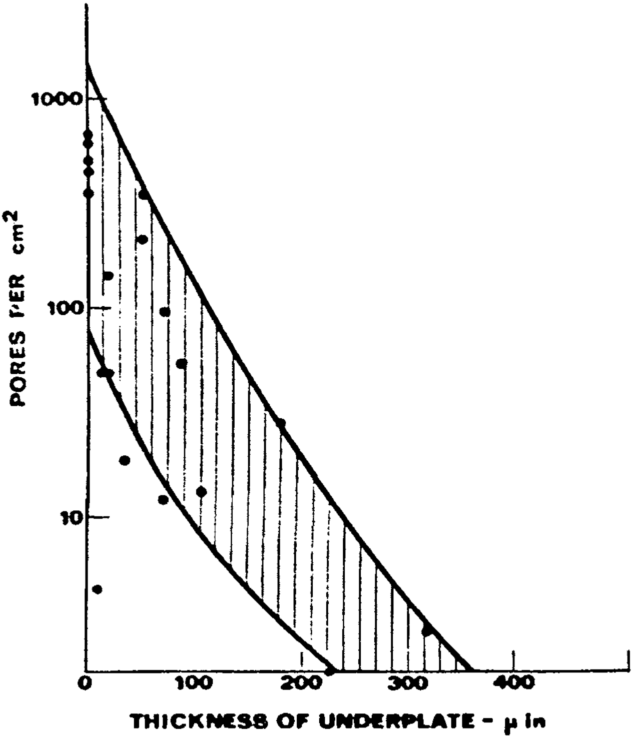


Figure 11: Porosity of 30 microinches of acid citrate gold plated over various thicknesses of acid sulfate copper underplate on OFHC copper substrate. From reference 26. Reprinted with permission of The American Electroplaters & Surface Finishers Soc.

exposed faces, the (111) face would grow at the slowest rate and the (220) face at the fastest rate. Therefore, an electrodeposit with a strong (111) orientation with respect to its surface has its slowest growing crystal planes in the plane of the substrate. This will tend to cause it to grow outward at a much faster rate than it does laterally. By contrast, a deposit with a (220) orientation has fast growing crystal planes in the plane of the substrate so it will tend to grow laterally at a faster rate than outward from the surface (24). Some porosity-thickness results for a series of highly oriented gold deposits on copper, shown in Figure 13, verify these statements. One observation is that the covering power of the various gold deposits decreases with decreasing closeness of atomic packing (111) > (200) > (220). The reason for this is that nucleation on a (111) face lays down more gold atoms than on a (200) or (220) face of equal area. Another observation is that the

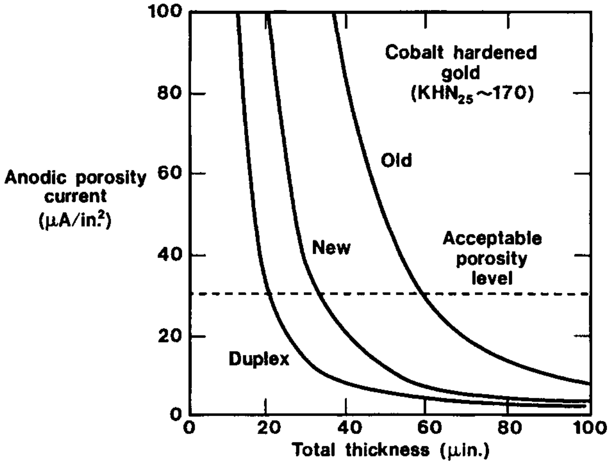


Figure 12: Reduction in porosity achieved by using a pure soft gold underplate for a cobalt-hardened gold. The curve marked "duplex" shows results for both solutions with a strike deposit of 13µm. Adapted from Reference 30.

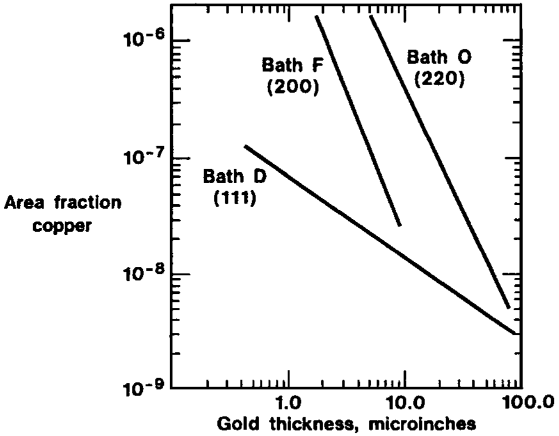


Figure 13: Porosity versus thickness for gold deposits of various preferred orientations. Adapted from Reference 24.

rate of pore closure, which is obtained from the slope of the curve, is greatest for deposits of highest index orientation. Once developed, these high index faces grow laterally at a faster rate than low index faces (24).

Figure 14 shows porosity-thickness results for a highly oriented gold deposit. At 33°C, this deposit shows a high (111) orientation while at 49°C the deposit is (111) preferred, but with appreciable (200) and (220) contributions. The covering power is excellent but the rate of pore closure is slow at 33°C. By contrast, at 49°C the covering power is poorer but the rate of pore closure is quite rapid. By splitting the deposition operation between the two solutions, e.g., nucleating the deposit at 33°C to obtain the best initial coverage, then doing the final plating at 49°C to take advantage of more rapid pore closure, optimum results are obtained in terms of coverage and reduced porosity. This approach has been used in production (24).

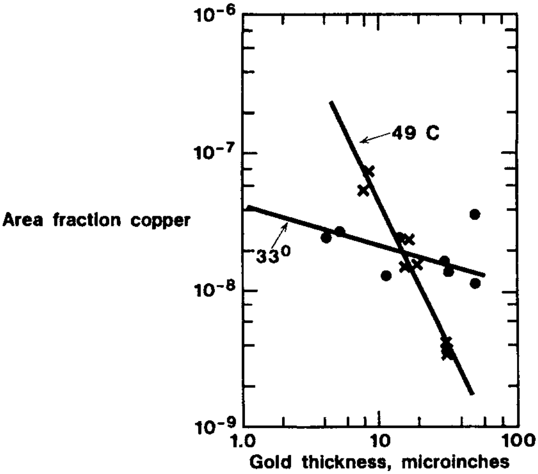


Figure 14: Porosity versus thickness for deposits produced in the same solution at different temperatures. Adapted from reference 24.

C. Deposition Technique—Comparison of Electroplated and Physically Vapor Deposited Films

The porosity of gold thin films depends on the method of deposition. Evaporated and sputtered films are noticeably more porous than plated films. For example, electrodeposits of copper, nickel, and gold developed continuous films at an average thickness of less than 50 Å on copper and nickel substrates, whereas, evaporated films 500 Å or less in thickness were not continuous and showed many holes or channels (31). Figures 15 and 16 show that in two different porosity tests, electrodeposited gold films performed much better than films prepared by physical vapor deposition (32,33).

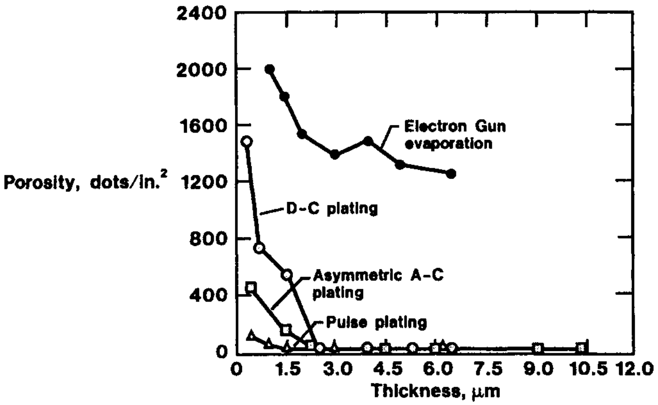


Figure 15: Relationship between porosity and thickness of gold films deposited by electron gun evaporation, asymmetric a-c plating, d-c plating and pulse plating. Substrate material was copper and a nitric acid test was used to measure porosity. Adapted from reference 32.

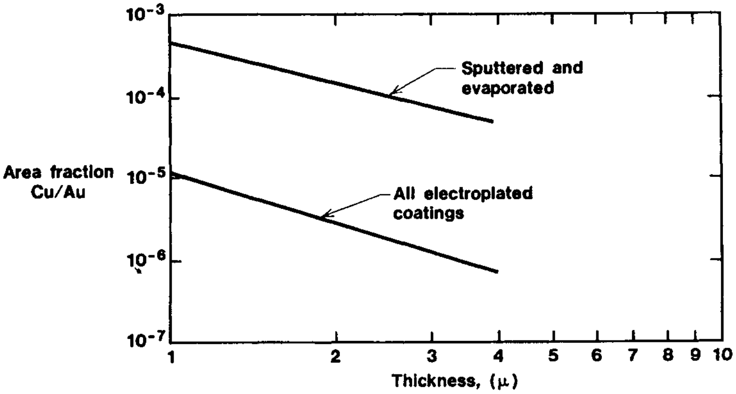


Figure 16: Comparison of porosity of evaporated, sputtered and electrodeposited gold films. Substrate was copper and porosity was measured by an electrochemical test. Adapted from Reference 33.

D. Hot Isostatic Pressing (HIP)

Porosity can be suppressed by hot isostatic pressing (HIP), a heat treatment under high pressure. However, because of the high temperature used, e.g., 550°C under 21 kg/mm^2 (30 kpsi) nitrogen pressure for 2 hours for copper, the process results in grain growth (34). HIP has also been used to suppress Kirkendall porosity formation (35).

POROSITY TESTING

The purpose of this section is to describe porosity tests that have been used. For an extremely comprehensive review on this subject see reference 21; references 1, 36 and 37 also provide good detail. Table 3 lists the various types of porosity tests.

Table 3: Porosity Tests

- Chemical
  - color change
  - chemical analysis

- Gas
  - sulfur dioxide
  - nitric acid vapor

- Electrolytic
  - anodic current plot
  - electrographic printing

- Microscopic
  - optical metallography
  - scanning electron microscopy
  - transmission electron microscopy
    - a - diffraction contrast
    - b - phase contrast

- Density measurements

- Detached Coatings
  - gas flow
  - visual and photographic

Porosity tests may be broken down into four categories:

1. Pore detection tests which make pore sites visible for inspection and counting. This includes detection in situ by producing visible corrosion product, detection by radiography, and examination of coatings detached from their substrate.
2. Porosity index tests which provide a direct numerical measure.
3. Microscopic techniques which permit direct observation of both isolated voids and through pores.
4. Density measurements which provide an indirect measure of both isolated voids and through pores.

A. Chemical Tests

Color tests involve use of a reagent which causes a color change in the presence of corrosion products from the substrate, forming a distinctive spot at each pore. An example of this is the classic ferroxyl test for steel which uses a solution of sodium chloride and potassium ferricyanide (38). Chemical analysis tests rely on quantitative determination of substrate corrosion products by chemical analysis, such as the use of an ammonia- ammonium persulfate solution which attacks a copper substrate but not a gold overcoat, so the amount of dissolved copper is a measure of the porosity of the coating (39).

B. Gas Exposure Tests

Gas exposure porosity tests offer two potential advantages over liquid immersions tests: 1) the gas has a better ability to penetrate small pores, since surface tension effects could inhibit such penetration by bulk liquids; and 2) many gaseous porosity tests simulate pore corrosion mechanisms that may actually occur in service (40). Two gas tests that have been used include the humid, 10% sulfur dioxide test and the nitric acid vapor test (41). The 10% sulfur dioxide test atmosphere is generated by mixing a 50% solution of concentrated sulfuric acid with a 20% (by weight) solution of sodium thiosulfate. The ratio of the sulfuric acid solution to that of the thiosulfate is usually 1:4. The nitric acid vapor test relies on corrosive vapor produced directly from concentrated nitric acid that has been placed in the bottom of the test vessel. This test is limited to gold and platinum coatings (40).

C. Electrolytic Techniques

Electrolytic techniques offer the opportunity for rapid and relatively nondestructive means of determining porosity with high sensitivity (42,43). Ogburn (44) lists three types of electrolytic tests wherein the specimen is immersed in an electrolyte with an auxiliary electrode and a reference electrode: 1) the current is measured while the specimen is made anodic; 2) the anodic polarization curve slope is determined; or 3) a measurement is made of the corrosion potential.

Good examples of the quantitative type of data that can be obtained with electrochemical porosity measurements are shown in Figures 5, 10, 13, 14, and 16, which present corrosion potential measurements made with gold plated copper samples in 0.1 M ammonium chloride electrolyte. The corrosion potential of the sample is related to the exposed basis metal area fraction and this relationship affords a convenient and sensitive means for determining porosity. In addition to use of this test to provide quantitative data for gold on copper (33,42), it has been used for nickel on uranium (45,46) gold on tungsten (47), and tin on steel (48).

Electrographic porosity testing, also referred to as electrography or electrographic printing, involves use of chemically impregnated dye-transfer paper which is pressed firmly against the surface to be examined. Current is passed from the specimen which is anodic to an inert cathode at a fixed current density for a specified time. Cations from the substrate are formed at pores or cracks in the protective coating under the influence of the applied potential. These cations enter the gelatinized surface of the dye-transfer paper and react with appropriate chemicals to form soluble complexes or colored precipitates. Pores appear as colored dots while cracks appear as colored lines on the print (49). This test is quick, reproducible, suitable for on-line testing and provides a print which can saved for future reference (50). A schematic of the test set-up is shown in Figure 17. Table 4 lists chemicals used for various coatings and substrates (51). Some examples of use of electrography to measure porosity of electrodeposited coatings include gold on copper and nickel substrates (50,52) and chromium on various substrates (49). Figures 18a and 18b are electrographic prints of 1.5 μm thick decorative chromium on a nickel and copper plated zinc base die casting illustrating the effect of heat cycling three times to 80°C. Electrography has also been used to detect pinholes in thin dielectric films (53), polymer films on metallic substrates (54,55) and chemically vapor deposited coatings on cemented carbide substrates (56).

Porosity testing in a gelled medium is a special form of electrographic testing (electrography) which eliminates many of the disadvantages associated with pressure electrography (50,57). In this test,

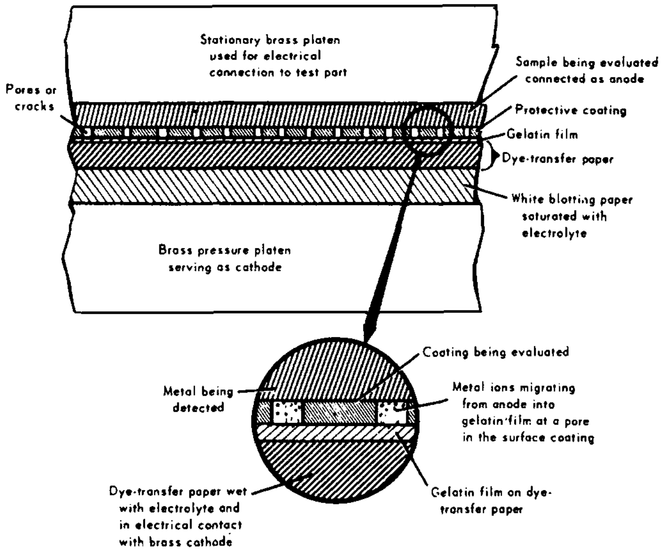
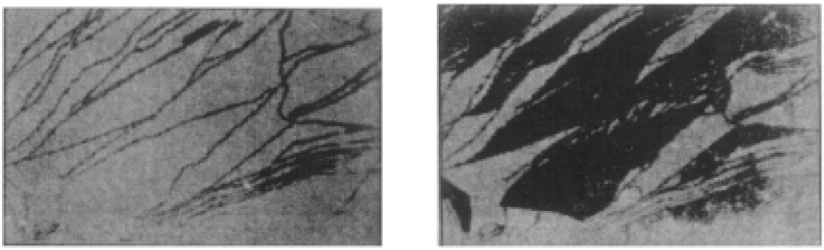


Figure 17: Detail of electrographic printing method illustrating principle of operation. From reference 49. Reprinted with permission of The American Electroplaters & Surface Finishers Soc.



a. Before heat cycling.

b. After heat cycling.

Figure 18: Electrographic prints of 0.06 mil thick chromium on a nickel and copper plated zinc-base die casting illustrating the effect of heat cycling three times to 80°C. From Reference 49. Reprinted with permission of The American Electroplaters & Surface Finishers Soc.

Table 4: Reagents Used In Electrographic Tests

Deposit	Solution
Gold on copper, silver on copper	Potassium ferricyanide(brown spots)
Tin on iron	Potassium ferricyanide(blue spots)
Tin on brass	Antimony sulfide plus phosphoric acid (brown spots)
Gold on nickel	a-Ammoniacal dimethylglyoxime and sodium chloride (red spots), b-Alcoholic dimethylglyoxime and sodium chloride (red spots)
Chromium on nickel	Dimethylglyoxime (pink spots)
Copper on iron	Dimethylglyoxime (deep cherry red spots)
Nickel on steel	Sodium chloride plus hydrogen peroxide (rust spots)
Gold on bronze	Ammonium phosphomolybdate
Nickel on copper or brass	Sodium nitrate solution, developed later with potassium ferricyanide solution plus acetic acid
Tin on lead	Ammonium acetate and potassium chromate
Gold, platinum or iridium on molybdenum	Potassium bisulfate developed later with potassium ferricyanide (dark brown spots)
Zinc or cadmium on steel	Half-normal sodium hydrosulfide (black spots)
Zinc on iron	Potassium ferrocyanide and magnesium sulfate
Deposits on iron or copper anodes	Potassium ferricyanide solution
Deposits on silver anodes	Potassium bichromate solution
Thin polymer films or dielectrics	Benzidine (references 54 and 55)

*Unless otherwise noted all data in this table are from reference 51. Additional details on solution formulations can be found in reference 49.

the specimen is made the anode in a cell containing a solid or semisolid electrolyte of gelatin, conducting salts, and an indicator. Application of current results in the migration of base metal ions through continuous pores. The cations react with the indicator giving rise to colored reaction products at pore sites, and these may be counted through the clear gel. Table 5 lists various electrolyte solutions and their resulting indicator colors. This method is suitable for coatings commonly used on electrical contacts, e.g., gold on substrates of silver, nickel, copper and its alloys, and for coatings of 95% or more of palladium on nickel, copper and its alloys.

Gel-bulk electrography offers a number of advantages over paper electrography: pressure control difficulties are eliminated, special mounting or clamping devices are not required, exposed surfaces of any geometry, even complex shapes can be tested, and the exact location of pores can be observed without having to index a piece of test paper which shows a mirror image of the test part. Also, the gel method appears to be more sensitive in that smaller pores can be detected and current flow is much smaller, reducing the possibility of producing pores by the test procedure (57).

Table 5: Gel Porosity Testing Solutions

Test for	Electrolyte (Aqueous)	Indicator	Indicating Color	Comments
Copper[a]	4% sodium carbonate + 1% sodium nitrate	saturated solution of rubeanic acid in ethanol	dark olive green	also detects nickel, cobalt
Copper	4% sodium carbonate + 1% sodium nitrate	7.5% potassiuim ferrocyanide in water	brown	-----
Nickel[a]	4% sodium carbonate + 1% sodium nitrate	saturated solution of rubeanic acid in ethanol	blue-blue violet	also detects copper,cobalt
Nickel	5% ammonium hydroxide	saturated solution of dimethylglyoxime in ethanol	pink	----------
Silver[ab]	0.2 molar nitric acid	1% glacial acetic + 5% sodium dichromate	red	solution must be free of halogens
Silver[b]	0.2 molar nitric acid	saturated solution of rhodanine in ethanol	red-red violet	solution must be free of halogens

[a] Preferred Test

[b] Not suitable for palladium overplates

* From reference 57

D. Microscopic Techniques

Microscopic techniques, which include optical metallography (OM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), permit direct observation of both isolated voids and through pores (1). Voids intersecting the film surface can be detected by OM and SEM while TEM is more useful in examining both small and large voids which can be isolated inside a film or located on the film surface. With use of the defocus contrast technique (phase contrast) in TEM (58), high density (about $1 \times 10^{17}/cm^3$) very small (approximately 10Å) voids have been found in thin films prepared by evaporation, sputtering and electrodeposition (3). Of interest is that this demonstrates that voids are generally formed in thin films irrespective of the film preparation method as long as the deposition process involves a phase transition from the vapor to the solid state (1).

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