The 31st William Blum Lecture
Presented at the 77th AESF Annual Convention (SUR/FIN 1990)
in Boston, Massachusetts
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The Application of Engineering Principles to the Practice of Electroplating

by
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ABSTRACT

The application of fundamental principles of mass transfer and electrode kinetics to the practice of electroplating is presented. Specific examples, including pulsed plating of alloys, through-hole plating and the deposition of composite materials, are discussed.

Electroplating of metals and alloys has been practiced in industry since the second half of the last century. However, the application has always involved a great deal of empiricism. It is only during the past two decades that a rational approach based on sound engineering principles has been developed. The basic and practical aspects of electroplating are presented, and the applications of these principles to three research projects are illustrated.

Fundamental and practical considerations in electroplating

The basic aspects of electroplating include mass transfer, electrode kinetics and structure of electrodeposits. These considerations have mutual influences on one another and cannot be studied independently. For instance, mass transfer determines the surface concentration of the metal ion, which, in turn, affects the rate of the plating process, as well as the structure of the electrodeposit.[1] Also, it is well known that the kinetics of the plating process depend on the structure of the electrodeposit.[2]

The practical aspects of electroplating involve current and/or metal distribution, deposit composition during alloy plating, and physical properties of the electrodeposits. For simple metal plating with a 100% current efficiency, the current and metal distribution are identical. The normal goal in plating is to achieve a uniform distribution of the metal regardless of the geometry of the system. A successful prediction of current and/or metal distribution in a given system depends primarily on the ability of the electroplater to rationally analyze the mass transfer and kinetics of the plating process. For alloy plating, it is also important to control the deposit composition in order to achieve the desired physical and chemical properties. The deposit composition can be estimated only if the transport, as well as the thermodynamics and kinetics, of the complex plating process is known.

Physical properties of electrodeposits are of paramount importance. Unfortunately, correlations between deposit structure and plating process variables are usually empirical although there has been considerable progress in this field during the past decade.

Applications of engineering principles to electroplating

An engineering analysis of an electroplating process is based on the phenomenological theory of transport processes in the electrolyte and the kinetics of the reaction at the solution-cathode interface. The fundamental transport equations in dilute

electrolytes were discussed in detail by Newman.[3] Applications of these equations have followed two main courses. At low current densities, where the change of the metal ion concentration near the cathode is negligible, the current distribution follows Ohm's law and the solution potential is governed by the Laplace equation.[4] Under these conditions, the current distribution depends only on the geometry of the system if the electrode reaction is reversible. The result is known as the primary current distribution. On the other hand, if the reaction proceeds at a finite rate,[5,6] the current distribution (known as the secondary current distribution) depends on parameters in addition to geometrical factors, including the dimension of the cathode, the conductivity of the plating solution, and the kinetics of the cathode reaction. The smaller the cathode, the higher the solution conductivity; and the more irreversible the cathode reaction, the more uniform the current and/or metal distribution. This is the basis of an observation made by the author[7] that in the absence of a leveling agent, a plating system with a uniform microcurrent distribution has a nonuniform macrocurrent distribution.

At a high current density, the mass transport of the reacting ion becomes rate controlling. The current density is proportional to the concentration gradient of the reacting ion at the electrolyte-cathode interface.[3] An important parameter is the Nernst diffusion layer thickness, which is a function of the degree of agitation and the physical properties of the plating solution. The more intense the agitation, the thinner the diffusion layer. In a stirred system, the diffusion layer thickness typically ranges from 10 to 100 µm. A relatively uniform current distribution results on a macro-surface profile as a result of the uniform diffusion layer thickness over the profile, whereas the local variation of the diffusion layer thickness over a micro-surface profile is responsible for the poor microcurrent distribution. These conclusions have been verified by experimental observations.[7]

Recent research projects

Pulse plating of alloys

Pulse plating implies that the applied current consists of a series of repetitious, on-off, square-wave currents. Mass transfer in pulse plating was analyzed by the author[8] using a Nernst diffusion model for a rotating-disk electrode system. This model was subsequently improved by Viswanathan, *et al.*[9] by taking into account rigorous convection while retaining the uniform accessibility condition suggested by Levich.[10]

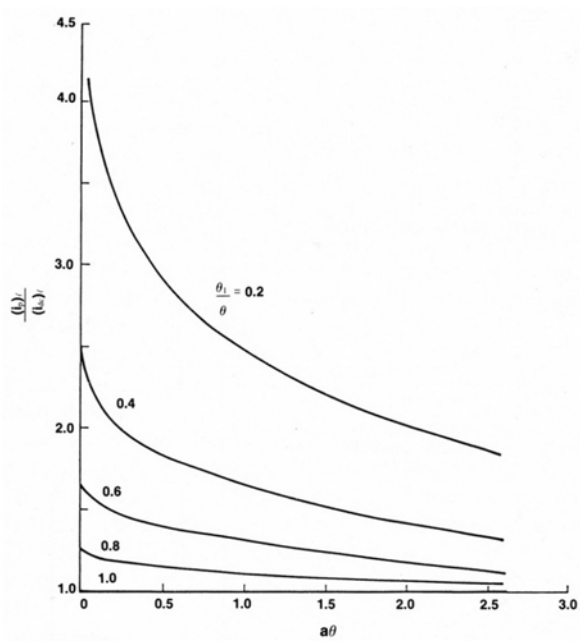

Figure 1 - Instantaneous limiting current density in pulsed plating.[8]

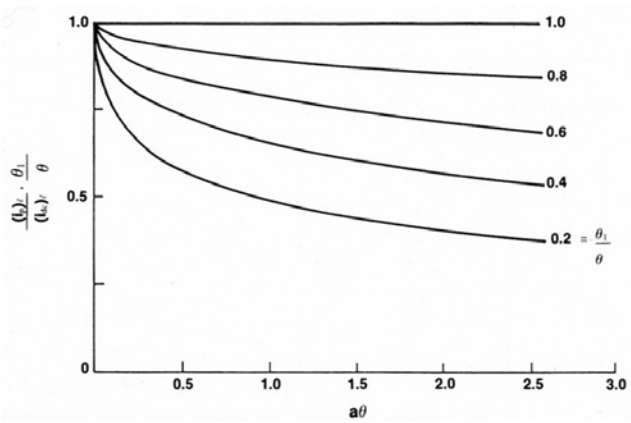

Figure 2 - Average limiting current density in pulsed plating.[8]

In pulse plating, it can be demonstrated that the system generally approaches a periodic-state after a few cycles. If the pulsed current density that causes the lowest surface concentration of the cation to reach zero is defined as the instantaneous limiting current density, its value can be obtained by solving the transport equations. Results on the ratio of the instantaneous limiting current density to that under DC plating conditions as functions of duty cycle and time are shown in Fig. 1. The ratio of the average limiting current density to that in dc plating is shown in Fig. 2. It is clear that the smaller the duty cycle, the higher the instantaneous limiting current density. This is reasonable, since, at small duty cycles, more time is allowed for the recovery of the cation inside the diffusion layer. However, all instantaneous limiting current densities, regardless of duty cycles, asymptotically approach those of DC plating at long times. It is very important to note that the average limiting current density is always lower than that in DC plating. The results have been confirmed in a number of systems.[8,9]

The previous approach has been extended to the plating of Sn-Pb alloy by Cheng.[11] This problem was solved numerically; and a typical result is shown in Figs. 3 and 4. Figure 3 shows the surface concentration of Sn and Pb ions, and Fig. 4 illustrates the periodic-state current densities of the two species. The ratio of the averaged individual current density over an entire cycle is equal to the molar ratio of the two species in the alloy deposit. In Cheng's study,[11] the theoretical and experimental results agree to within 97%.

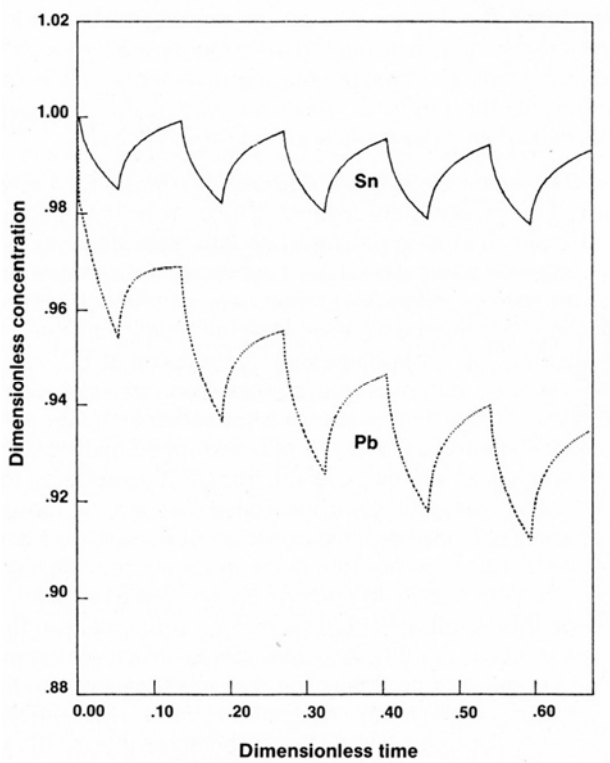

Figure 3 - Surface concentrations of Sn and Pb ions in pulsed plating.[11]

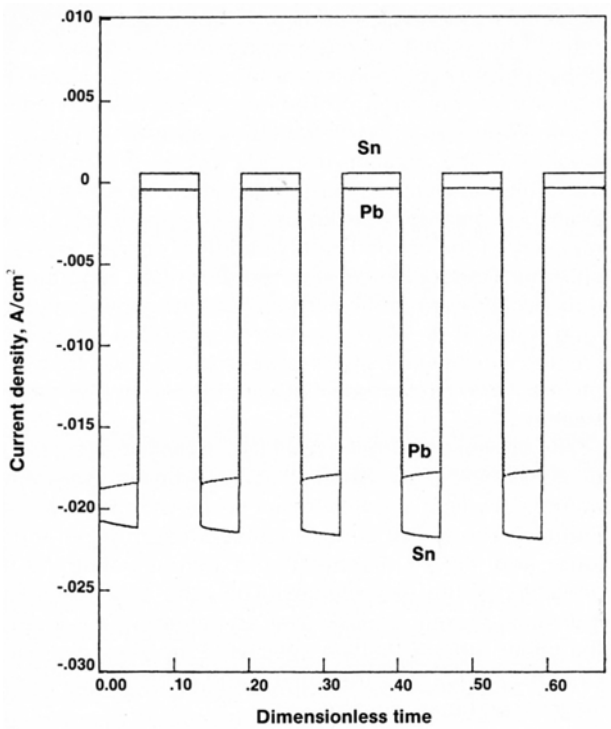

Figure 4 - Partial current densities during pulsed plating of Sn and Pb.[11]

Through-hole plating

Pesco[12] studied through-hole plating of copper under both DC and pulsed conditions, as well as in quiescent and flow systems. The geometry of the system is shown schematically in Fig. 5. Theoretical calculations revealed that when electrolyte flow is absent, the maximum average current density possible within through-holes is much less than 1 mA/cm^2, and the current distribution is highly nonuniform at high-aspect-ratio through-holes. Higher average current densities are possible when flow is induced.[13] However, the current distribution remains nonuniform for high-aspect-ratio holes. It is, nevertheless, possible to make the current distribution more uniform by applying periodic current reversal. Figure 6 shows that when mass transfer is neglected, the current distribution in pulse plating is less uniform than that in DC plating, whereas periodic reversal of current

leads to considerable improvements in the uniformity of the deposit.[14] A similar conclusion has been reached when mass transfer effects are included.

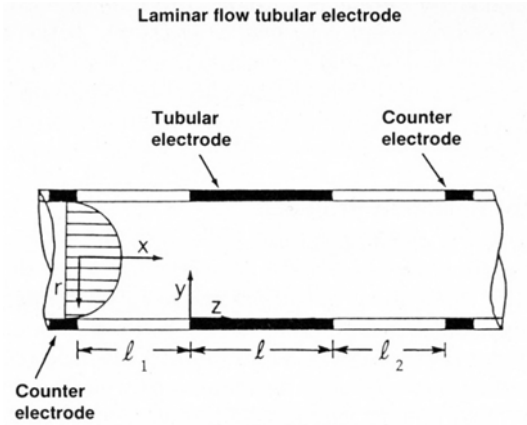

Figure 5 - Schematic diagram of through-hole geometry

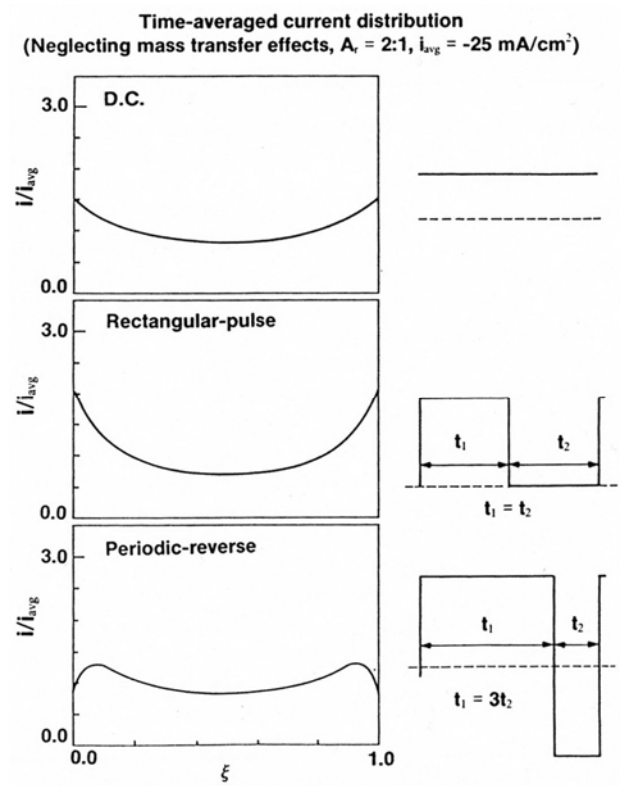

Figure 6 - Current distribution in DC, pulsed and periodic current reversal plating.[14]

Co-deposition of colloidal particles in metal deposition

One of the most rapidly advancing fields is the manufacture and application of composite materials. Metal deposits with interspersed particulates have been designed to retard corrosion, increase strength of materials, and reduce friction. Valdes[15] conducted a fundamental study on the co-deposition of monodispersed, submicron-sized, polystyrene latex particles and copper from an acid sulfate solution. The system is shown schematically in Fig. 7. An extensive theoretical analysis was performed that included particulates, as well as metal ion transport. In addition to a pure mass transport controlled case, two kinetic models were used to complete the modeling - one based on a non-electrochemical theory (the surface force boundary-layer approximation, SFBLA) and one based on the inclusion of charge transfer effects (the electrode-ion-particle electron transfer model, EIPET). An experimental investigation was also carried out to measure the rates of particle incorporation and metal deposition on a rotating-disk electrode. Theoretical and experimental results are shown in Fig. 8. The particle Sherwood number is directly proportional to the rate of particle incorporation and the particle Peclet number represents flow conditions in the system. It is seen here that the SFBLA model agrees well with experimental findings. These results can be translated into a prediction of the volume fraction of particles in the composite film as a function of applied current density and flow conditions. This result is shown in Fig. 9, where D_a is a chemical rate constant for the SFBLA model, and p represents the physical characteristics of the copper-polystyrene latex particles system.

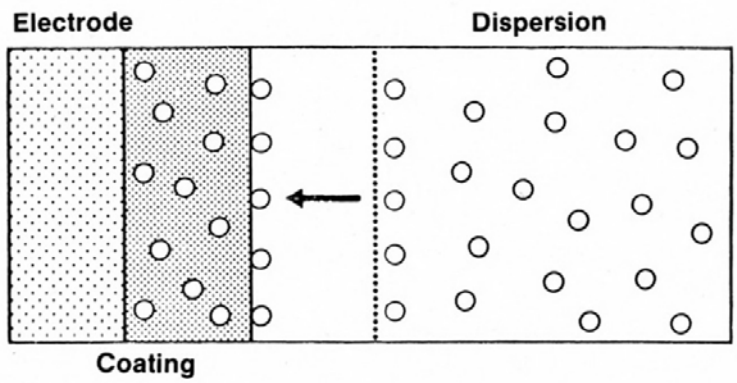

Figure 7 - Schematic diagram for co-deposition of particulates and metal.[15]

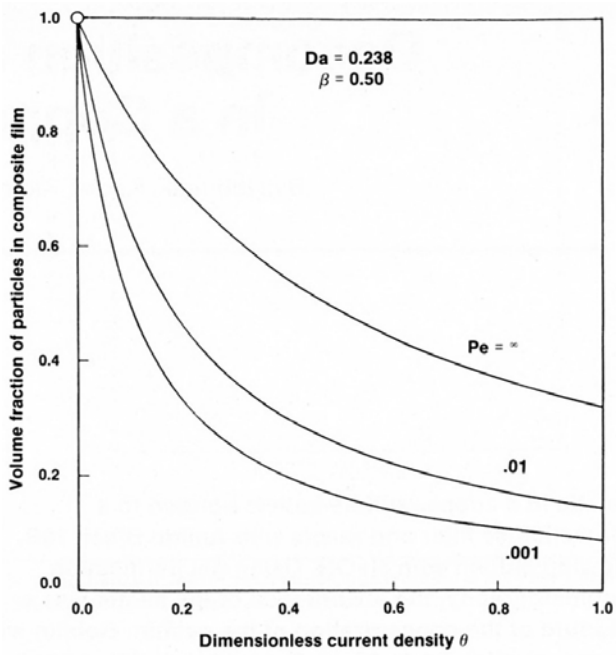

Figure 8 - Rate of particle deposition.[15]

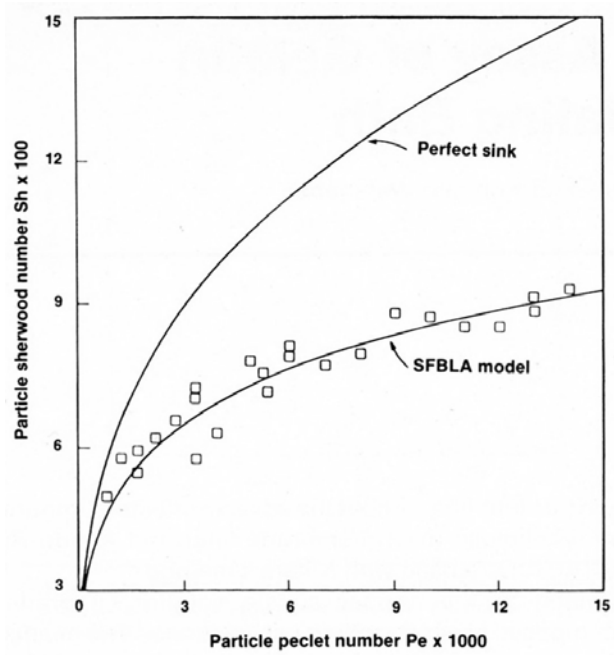

Figure 9 - Volume fraction of particulates in copper deposit.[15]

Conclusions

As technology advances, there is an increasing demand for improved design and control of plating systems to produce deposits with prescribed physical and chemical properties. The application of basic engineering analysis is indispensable to the electroplating of modern materials and processes.

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About the author:

This piece was written at the time Dr. Cheh was announced as the recipient of the 1989 Scientific Achievement Award.

Professor Huk Y. Cheh, of Columbia University in New York, noted for his impressive list of technical accomplishments and tireless service to others involved in electroplating and electrochemical research, has been selected as the 1989 recipient of the AESF Scientific Achievement Award. The award, which is the highest honor conferred by the Society, recognizes an individual who has made outstanding scientific contributions advancing the theory and practice of electroplating and allied sciences, raised the quality of products or processes, or enhanced the dignity of the profession.

Dr. Cheh, a member of the AESF Garden State Branch was born in Shanghai. His career in electroplating and electrochemical engineering began at Bell Laboratories in 1967 after completion of his Ph.D. in electrochemical engineering at the University of California, Berkeley, under the direction of Professor Charles Tobias. In 1970 he joined the chemical engineering faculty at Columbia University, where he became a full professor in 1979 and chairman of the department in 1980. He served as chairman until 1986. In 1982 he was named the Samuel Ruben-Peter G. Viele Professor of Electrochemistry, which is a lifetime appointment.

He has participated actively in AESF over the years, and conducted two AESF-sponsored research projects (numbers 35 and 48). His work on pulsed electrodeposition, particle codeposition, models for linear sweep voltammetry on rotating disk electrodes, and models of current and metal distribution, have been of particular interest to those involved in electrodeposition of electronic and aerospace materials and the electro-analytical techniques necessary for control of such processes. His analyses of pulsed and periodic electrodeposition have provided clear insight into the mass transport and kinetic processes involved in electrodeposition under non-DC conditions. His work has enabled calculation of the maximum deposition rate under pulsed conditions and has eliminated the considerable confusion existing in the literature on this topic prior to his publications. This work is frequently quoted by scientists and engineers involved in this area of research and it has helped lead to the establishment of pulsed electrodeposition as a viable commercial process. Pulsed electrodeposition processes based on the principles developed by Dr. Cheh have also resulted in the development of novel multilayer alloy coatings that exhibit unusual strength. Currently, there are exciting potential applications of these high-strength, light-weight materials in electroformed components of rocket engines.

Dr. Cheh and his students were the first to establish the detailed transport processes and electrokinetic interactions involved in codeposition of colloidal particles and metal ions. This work provides a quantitative prediction of the relative rates of particle and metal deposition. The results have far-reaching consequences in the manufacture of composite materials such as dry lubricant films, necessary for a variety of aerospace applications. Dr. Cheh has applied basic electrochemical engineering principles to current and metal distribution problems in both macro- and microsystems. He has firmly established the concept of macro- and microthrowing powers in industrial processes for electroplating through-holes in printed circuit boards. This insight has led to process optimization and product improvements.

Dr. Cheh has conducted a systematic investigation to extend the application of linear sweep voltammetry to a flow system, the rotating disk electrode, for studying the kinetics of simple and complex electrode reactions. By applying linear and matrix algebra, he and his co-workers have also established a systematic approach to the determination of reaction mechanisms for complex reactions. This has provided a sound theoretical basis for a technique which is now used as a standard for process monitoring and control in the plating industry.

It is noteworthy that Dr. Cheh also conducted early experiments in electrolytic recovery of metals from electroplating wastewaters. In view of the Society's current emphasis on environmental problems, it is clear that he has demonstrated a good vision of the future in his work.

Over the years, Professor Cheh has contributed significantly to a wide variety of research areas outside electrodeposition, which reflect his intense and diverse interests in thermodynamics, kinetics and transport phenomena. For example, he has numerous publications on membrane transport, plasma processing of materials, heat transport processes in the human body, and electrolytic gas evolution. He is both an engineer and a scientist.

His research has resulted in 72 journal articles, 46 presentations, 26 special seminars in the U.S. and the Republic of China (Taiwan), patents, and the successful training of 24 Ph.D. chemical and electrochemical engineers, as well as hundreds of B.S.- and M.S.-level professionals. He has also hosted numerous foreign scientists in his laboratories at Columbia over the past several years.

In recognition of his work and talent, Professor Cheh has received several outstanding honors from other organizations and universities, including the American Society for Metals Merit Award (1960), the American Society of Testing and Materials Student Prize Membership (1960-62), the Society of Chemistry and Industry Gold Key for Merit (1962, London), the University of Ottawa Silver Medal (1962), the University of California, Berkeley, Earle C. Anthony Scholarship (1966), the Phi Lambda Epsilon Honor Chapter of the American Chemical Society Urey Award (1981), and the Electrodeposition Research Award of the Electrochemical Society (1988). He is also listed in Who's Who in America, Who's Who in Engineering, Who's Who in Technology Today, Who's Who in Frontier Science and Technology, and Who's Who in the World.

Dr. Cheh has given his time and talent generously in service to others through his work for the AESF, the Electrochemical Society (ECS) and several other professional organizations. In addition, he is a member of Sigma Xi, the American Institute of Chemical Engineers (AIChE), and the New York Academy of Science. He has served as the Electrodeposition Division editor for the Journal of the ECS since 1977 and routinely serves as a reviewer of research proposals for four major funding agencies, including the National Science Foundation.

At Columbia, Professor Cheh has been a member of 16 university administrative committees and 45 Ph.D. committees, not including those of his own students. He served as a member of the Board of Trustees of Beaver College in Glenside, PA, from May 1984 to October 1987 and is currently a member of the Executive Advisory Board of the Encyclopedia of Physical Science and Technology, published by Academic Press.