31st William Blum Lecture

The Application of Engineering Principles To the Practice of Electroplating

By Huk Y. Cheh

The 31st William Blum lecture was presented at SUR/FIN® '90 Boston—International by Dr. Huk Y. Cheh, recipient of the 1989 AESF Scientific Achievement Award.

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 percent 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.’ 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’ 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 inter face.[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 pm. 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.’

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’ 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]

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]

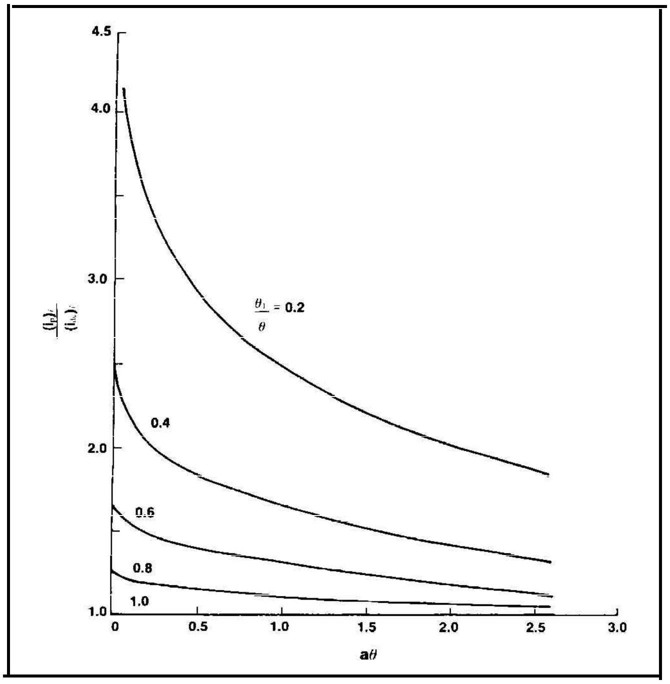

Fig. 1—Instantaneous limiting current density in pulse plating.’

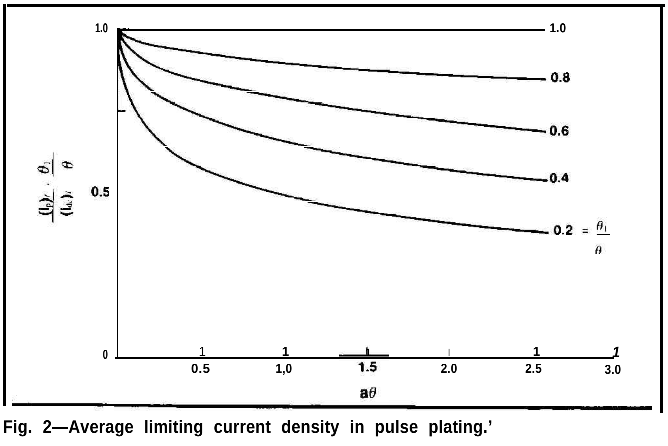

Fig. 2—Average limiting current density in pulse plating.’

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 percent,

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

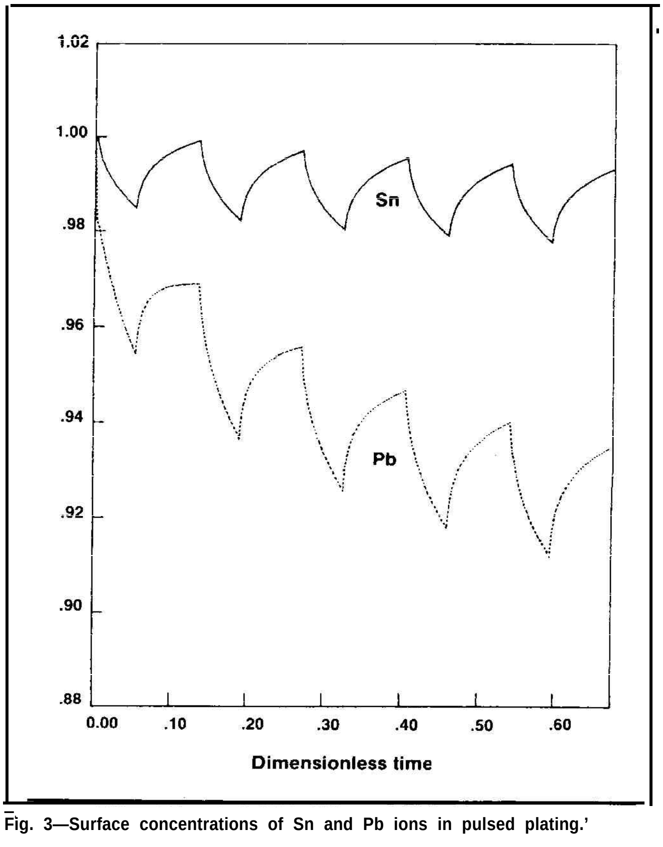

Fig. 3—Surface concentrations of Sn and Pb ions in pulsed plating.’

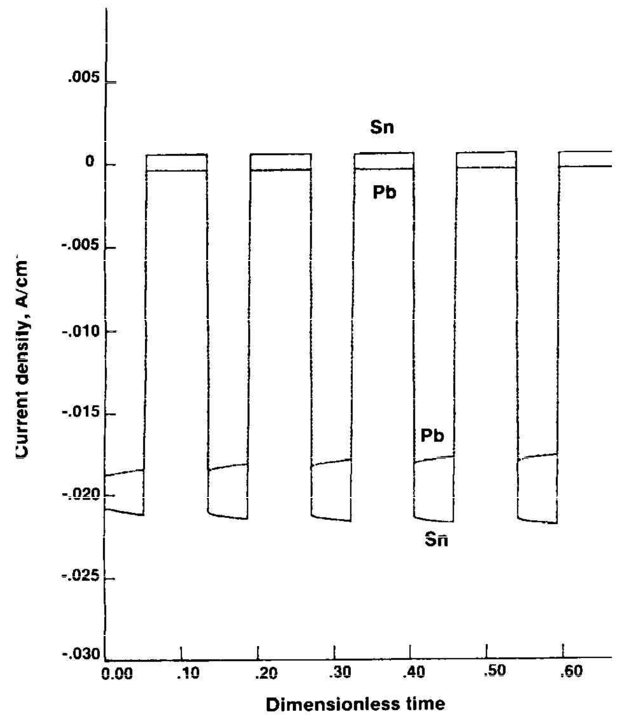

Fig. 4—Partial current densities during pulsed plating of Sn and ph.’

at high-aspect-ratio through-holes. Higher average current densities are possible when flow is induced. ” 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. ” A similar conclusion has been reached when mass transfer effects are included.

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 particulate 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 particulate, 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, El PET). 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

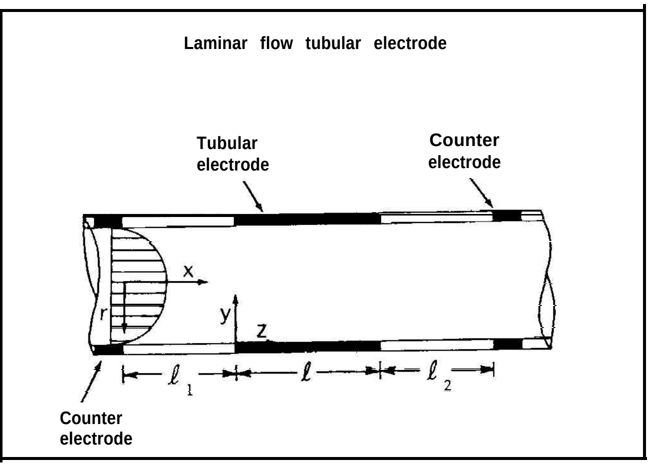

Fig. 5—Schematic diagram of through-hole geometry.[14]

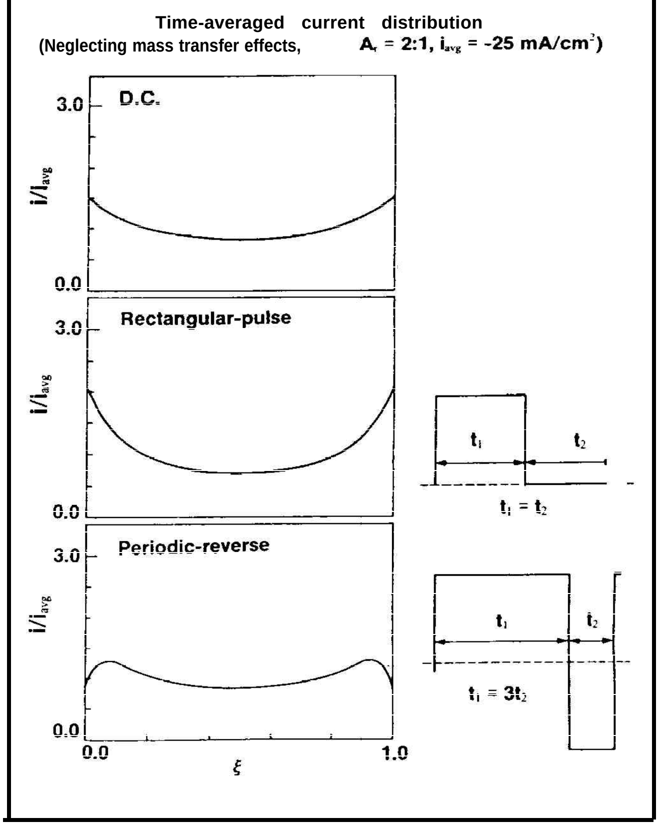

Fig. 6—Current distribution in dc, pulsed and periodic current-reversal plating.[14]

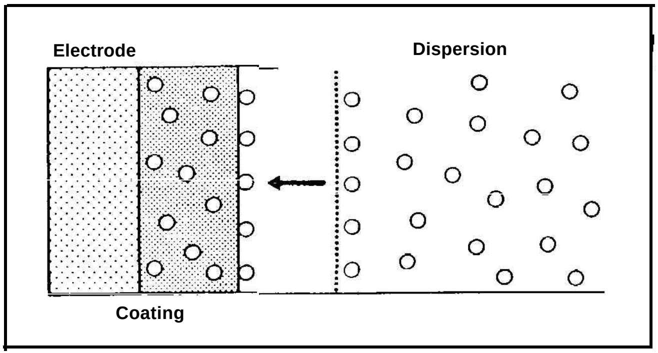

Fig. 7—Schematic diagram for co-deposition of particulates and metal. ”

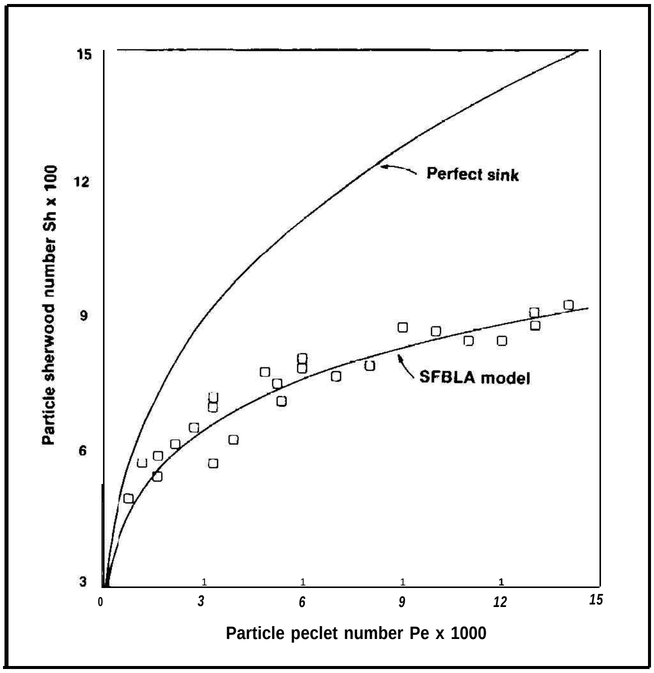

Fig. 8—Rate of particle deposition. ”

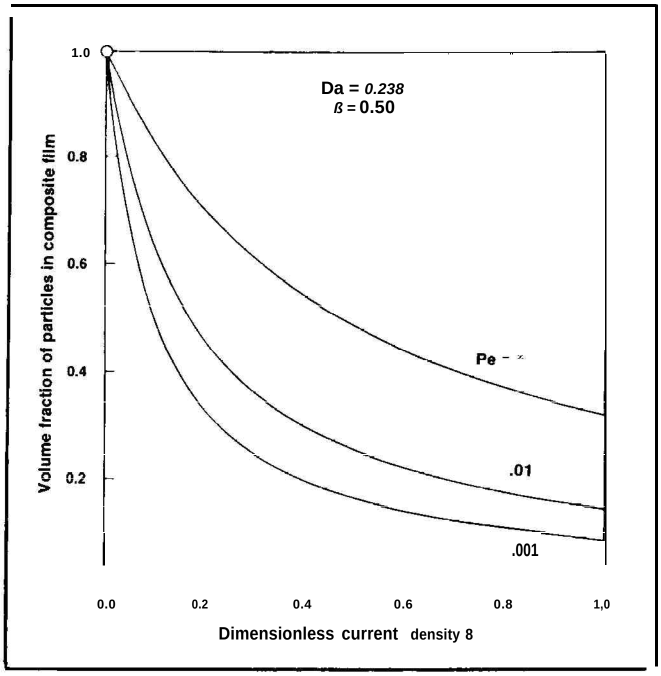

Fig. 9 — Volume fraction of particulates in copper deposit.’

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 Da is a chemical rate constant for the SFBLA model, and ß represents the physical characteristics of the copper-polystyrene latex particles system.

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

Dr. Huk Y. Cheh is a professor of electrochemistry in the Department of Chemical Engineering & Applied Chemistry at Columbia University, New York, NY 10027. His career in electroplating and electrochemical engineering began at Bell Laboratories in 1967 after completion of his PhD in electrochemical engineering at the University of California, Berkeley. In 1970, Dr. Cheh joined the chemical engineering faculty at Columbia University in New York, where he became a full professor in 1979 and chairman of the department in 1980. In 1982, he was named the Samuel Ruben-Peter G. Viele Professor of Electrochemistry—a lifetime appointment.

Through his analyses of pulsed and periodic electrodeposition, Dr. Cheh has provided clear insight into the mass transport and kinetic processes involved in electrodeposition under non-de conditions. His work has enabled calculation of the maximum deposition rate under pulsed conditions and has eliminated considerable confusion on this topic.

Over the years, Dr. Cheh has contributed significantly to a wide variety of research areas outside electrodeposition. He has published numerous papers on membrane transport, plasma processing of materials, heat transport processes in the human body and electrolytic gas evolution. Dr Cheh's research has resulted in 82 journal articles, 26 special seminars in the U.S. and abroad, several patents and the successful training of 30 chemical and electrochemical engineers to the PhD level. He has also conducted two AESF Research Projects (#35 and #48).