1 INTRODUCTION

Materials science is the scientific discipline that probes the relations among structure, composition, synthesis, processing, properties, and performance in material systems. Eight major U.S. industries rely heavily on materials science: aerospace, automobile manufacturing, biomaterials, chemicals, electronics, energy, metals and telecommunications. Together these industries employ seven million people and account, for sales of $1.4 trillion (1)(2). A recent report of the National Research Council notes that advances have come in all eight industries from improved instrumentation, better controls on composition of products and expanded use of computers in modeling behavior of materials. According to the report: "The field of materials science and engineering is entering a period of unprecedented intellectual challenge and productivity. Scientists and engineers have a growing ability to tailor materials from the atomic scale upward to achieve desired functional properties" (1)(3). The field of materials science has grown to a major and distinct field since its origin in the 1940's. It is advancing at a revolutionary pace and is now generally recognized as being among the key emerging technological fields propelling our world society into the twenty-first century (4).

There are excellent texts on the general topic of materials science and a comprehensive 6000 page source of information consisting of eight volumes containing 1580 materials science topics(5). Originally published in 1986, this encyclopedia set has already been supplemented with two additional volumes (113 topics, 653 pages, in 1988, see reference 6; and 130 topics, 832 pages, in 1990, see reference 7) attesting to the continued expansion of materials science.

Since the purpose of this book is to relate materials science and electrodeposition some brief history is in order. The 1949 text by Blum and Hogaboom (8) presents some of the principles of materials science even though it was not so named at that time. The book contains a number of photographs of structures of electrodeposits and data on properties. In the 1960's Read extended this coverage by showing the remarkable range of structures and properties that can be achieved by electrodepositing a given metal in a variety of ways (9,10). In more recent times (1982 and 1984) Weil introduced the topic of materials science of electrodeposits disclosing how the principles of materials science can be used to explain various structures of electrodeposits and how these structures influence properties (11,12). As Weil stated: "The understanding that has been gained is to a great extent responsible for changing plating from an art to a science" (11). Safranek's treatises on properties of deposits (1974 and 1986) are also very valuable resources (13)(14). These two volumes contain property data from over 1000 technical papers.

COMMENTS ON ELECTRODEPOSITION

Electrodeposition is an extremely important technology. Covering inexpensive and widely available base materials with plated layers of different metals with superior properties extends their use to applications which otherwise would have been prohibitively expensive (15). However, it should be noted that electroplating is not a simple dip and dunk process. It is probably one of the most complex unit operations known because of the unusually large number of critical elementary phenomena or process steps which control the overall process (16). An excellent example is the system model from Rudzki (Figure 1) for metal distribution showing the interrelation of plating variables and their complexity (17). Figure 2 is a simplified version summarizing the factors that influence the properties of deposits. Electrodeposition involves surface phenomena, solid state processes, and processes occurring in the liquid state, thereby drawing on many scientific disciplines as shown in Table 1 (15).

FACTORS AFFECTING COATINGS

It has been suggested that three different zones; 1) the substrate interface, 2) the coating, and 3) the coating-environment interface have to be considered when protecting materials with coatings (18). These, plus a fourth zone- the substrate, are covered in sequential fashion in the following chapters. Figure 3 shows these zones along with the titles of the chapters.

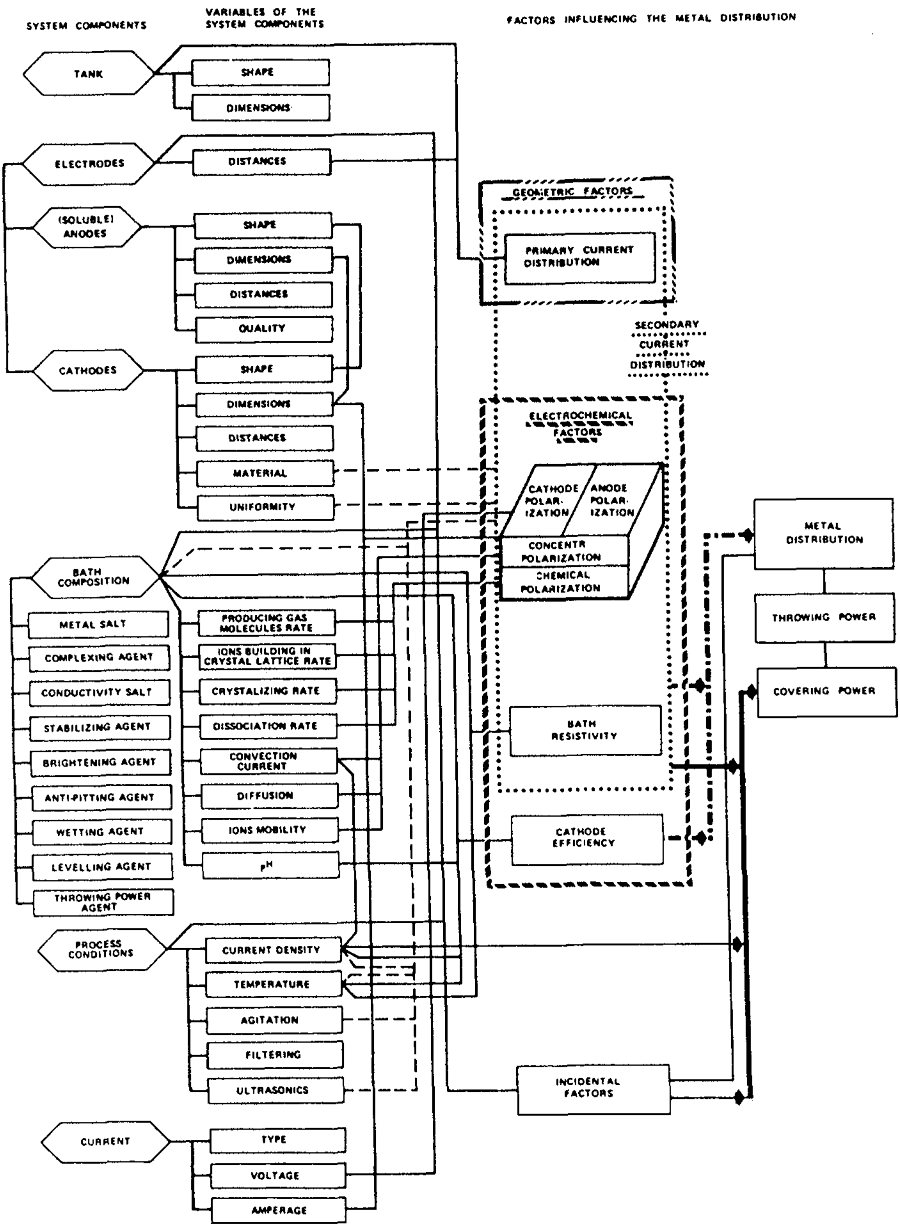

Figure 1: System model illustrating metal distribution relationships. From Reference 17. Reprinted with permission of ASM International, Metals Park, Ohio.

System components	Factors influencing metal distribution	Electrodeposit
Tank		
Electrodes	Geometric	Metal distribution
Solution composition	Electrochemical	Composition
Process conditions	Incidental	Structure
Current		Properties

Figure 2: Metal distribution relationships in electrodeposition.

Table 1: Interdisciplinary nature of Electrodeposition*

Discipline	Involvement
Electrochemistry	Electrode processes
Electrochemical engineering	Transport phenomena
Surface science	Analytical tools
Solid state physics	Use of quantam mechanical solid state concepts to study electrode processes
Metallurgy and materials science	Properties of deposits
Electronics	Modern instrumentation

* From Reference 15.

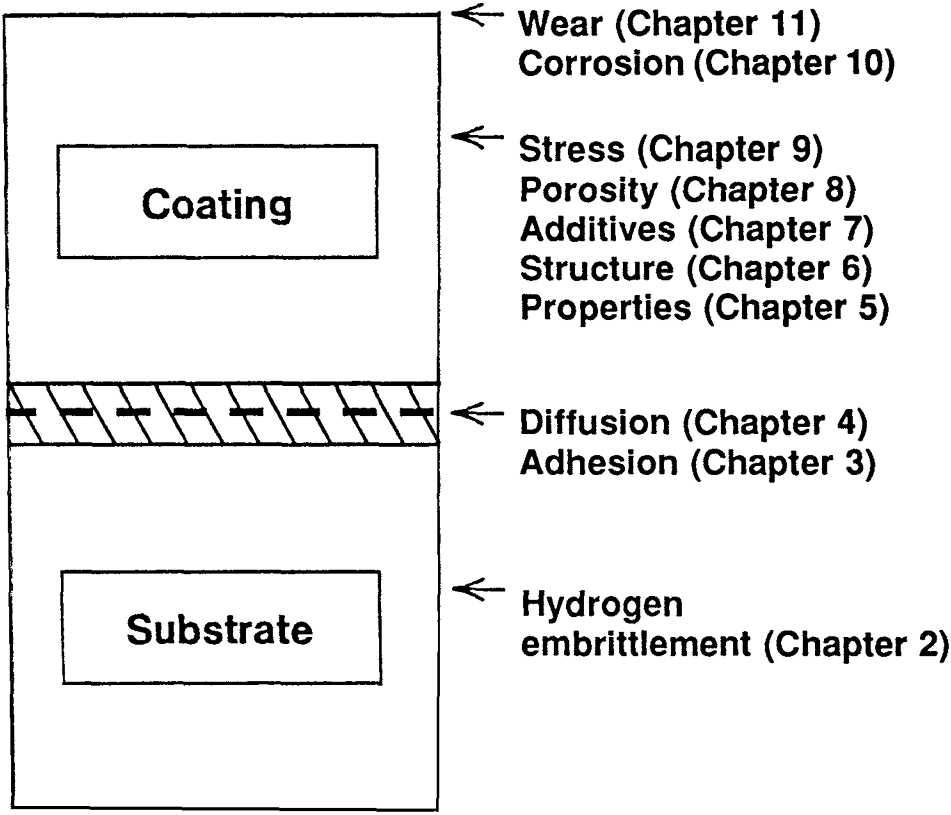

Figure 3: Important criteria when selecting coatings. This also is a listing of the following chapters in this book starting with HYDROGEN EMBRITTLEMENT and proceeding through to WEAR.

First is the substrate where potential hydrogen embrittlement effects are of concern. The second zone is the basis metal interface where adhesion of the coating and interdiffusion between the coating and substrate are of importance. The third zone is the coating itself where composition and microstructure determine properties and factors such as stress, phase transformations and grain growth exert noticeable influences. The final zone is the environmental interface where the interaction of the coating in its intended application has to be considered in terms of corrosion and/or wear.

Clearly, many of the items are important in more than one zone. For example; porosity and/or stress in the substrate (rather than just in the coating) can noticeably influence coating properties; porosity can noticeably affect corrosion resistance and tensile properties; hydrogen embrittlement is a factor not only for substrates but also for some coatings; and diffusion of codeposited alloying impurities to the surface can noticeably affect wear and corrosion properties. For reasons such as these, many of the topics are discussed interchangeably throughout the book.

The chapter on HYDROGEN EMBRITTLEMENT concentrates heavily on steels since these substrates are particularly susceptible to damage by hydrogen. This chapter also covers permeation of hydrogen through various protective coatings, hydrogen embrittlement of electroless copper deposits and hydrogen concerns as a result of chemical milling.

The importance of ADHESION is discussed in the next chapter and this topic is broken down into four categories; interfacial adhesion, interdiffusion adhesion, intermediate layer adhesion and mechanical interlocking. A variety of quantitative tests for measuring adhesion are discussed and then a methodology is presented for use when confronted with difficult-to-plate substrates. Processes that have been used to provide adhesion of coatings on difficult-to-plate substrates are discussed and supported with quantitative data. The relatively new approach of combining physical vapor deposition with electroplating which offers considerable promise for obtaining adherent bonds between coatings and difficult-to-plate substrates is also covered. Other techniques such as interface tailoring, alloying surface layers with metals exhibiting a high negative free energy of formation, use of partial pressure of various gases during deposition, reactive ion mixing and phase-in deposition are also discussed.

DIFFUSION, which is the attempt of a system to achieve equilibrium through elimination of concentration gradients, can result in degradation of properties and appearance. Diffusion mechanisms are discussed with particular emphasis placed on Kirkendall voids which can lead to loss of adhesion. Diffusion is influenced by the nature of the atoms, temperature, concentration gradients, nature of the lattice crystal structure, grain size, amount of impurities and the presence of cold work (19). An effective way to minimize or eliminate potential diffusion problems is the use of barrier coatings. In some instances, diffusion can benefit coating applications. Examples include deposition of alloy coatings and diffusion welding which utilizes diffusion to produce high integrity joints in a range of both similar and dissimilar metals.

Although PROPERTIES are discussed throughout the book, this chapter is included to cover some specifics not covered elsewhere. Topics include tensile property measurements, strength and ductility of thin deposits, the Hall-Petch relationship between strength and grain size, and the influence of impurities on properties. Superplasticity, which refers to the ability of a material to be stretched to many times its original length, is covered since electrodeposition offers some potential in this area.

STRUCTURE is one of the longest chapters in the book and rightfully so since structure is so dominant a factor in materials science. The variety of structures obtainable with electrodeposits are discussed and illustrated, as is the influence of substrate on coating structure. Phase transformations, which can noticeably affect deposit properties, are reviewed for electroless nickel, gold-copper, tin-nickel, palladium and cobalt deposits. Microstructural stability of copper and silver deposits at room temperature is also covered. Texture of deposits is an important structural parameter for bulk materials and coatings and a good illustration of how properties can be tailored for applications such as formability, corrosion resistance, etching characteristics, contact resistance, magnetics, wear resistance, and porosity. Fractals, which offer the materials scientist a new way to analyze microstructures, provide a new tool for studying surfaces and corrosion processes. Some concepts of fractals are presented as are examples of results already obtained with various surfaces.

ADDITIVES are included as a separate chapter because of their extreme importance on the structure and properties of deposits. Some of the folklore regarding addition agents is discussed and examples included illustrating the interesting history of this complex aspect of electrodeposition. Data are presented showing the influence of additives on tensile properties, leveling, and brightening. Typical additive systems used for deposition of a variety of deposits are reviewed as are proposed mechanisms of additive behavior. Control of addition agents via techniques such as the Hull cell, bent cathode, electroanalytical techniques, chromatography and other analytical methods is covered in some detail.

POROSITY is one of the main sources of discontinuities in electrodeposited coatings. It can noticeably influence corrosion resistance, mechanical properties, electrical properties and diffusion characteristics. Items which influence porosity include the substrate, the plating solution and its operating characteristics, and post plating treatments. An effective way to minimize porosity is to use an underplate. Another is to deposit coatings with specific crystallographic orientations which can strongly influence covering power and rate of pore closure. A variety of porosity tests are available for testing coatings and these are discussed in some detail.

STRESS in coatings can also adversely affect properties. A variety of options are available for reducing deposit stress and these include: choice of substrate, choice of plating solution, use of additives and use of higher plating temperatures. A variety of theories have been postulated regarding the origins of stress but none of them covers all situations. Numerous stress measurement techniques are available and they vary from the simple rigid strip technique to sophisticated methods using holographic interferometry.

CORROSION is affected by a variety of factors including metallurgical, electrochemical, physical chemistry and thermodynamic. Since all of these encompass the field of materials science, the topic of corrosion is essentially covered in many places in this book other than this particular chapter. Often it is difficult to separate corrosion from many of the other property issues associated with deposits. When selecting a coating it is important to know its position with respect to its substrate in the galvanic series for the intended application. Besides galvanic effects, the substrate and the interfacial zone between it and the coating can noticeably affect the growth and corrosion resistance of the subsequent coating since corrosion is affected by structure, grain size, porosity, metallic impurity content, interactions involving metallic underplates and cleanliness or freedom from processing contaminants (20). Decorative nickel-chromium coatings developed for automotive industry applications are a good example of use of materials science and electrochemistry to improve corrosion resistance properties.

WEAR, like corrosion, does not fit handily within the confines of a traditional discipline. Physics, chemistry, metallurgy and mechanical engineering all contribute to this topic. A particular feature of electrodeposition that is attractive for wear applications is its low temperature processing and ability to be applied to distortion prone substrates without increasing stress in the composite. Mechanisms of wear are discussed as are some of the more important tests used for evaluating wear characteristics. Coatings that are used for various wear applications include chromium, electroless nickel, precious metals and anodized aluminum. Recent advances include ion implantation of chromium deposits with nitrogen to provide improved wear resistance and codeposition of dispersed particles with electroless nickel. Microlayered metallic coatings also known as composition modulated coatings also offer promise. Although electrodeposited coatings are typically not effective at temperatures above 500°C, composite coatings containing chromium or cobalt particulates in a nickel or cobalt matrix can be effective.

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