Metallurgical and Ceramic Protective Coatings

Edited by
KURT H. STERN

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Contents

1

Introduction

Kurt H. Stern

1.1 PROTECTIVE COATINGS

Modern technology has placed increasing stresses on the material used for a variety of technological uses. Both the uses and the stresses have probably grown at a greater rate than the number of materials that can be used to meet them. This is particularly true for structural materials which are almost entirely metallic. Although much has been done by producing new alloys with improved properties, there is a limit to the protection that can be afforded by this means alone. For this reason coatings have played an increasing role in protecting the structural metals from stress.

1.2 STRESSES

Stresses can conveniently be classified into a few types.

1.2.1 Wear

Wear occurs when material is removed from a surface by abrasion, i.e. the moving of one surface over another which, in severe cases, may result in detachment of the coating, and by erosion, the loss of material from the impact of high velocity particles.

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1.2.2 Chemical attack

This may occur both in the gaseous and liquid phase, particularly at high temperatures, and includes attack by ambient oxygen. Corrosive liquids include acids and bases, molten salts and slags, i.e. molten oxides and silicates. Chemical attack may include a combination of these, such as occurs in marine gas turbines when ambient oxygen, droplets of sea salt and sulfur impurities in the fuel combine to form molten sodium sulfate which attacks the metallic turbine blade coating.

1.2.3 High temperatures

Structural materials may undergo undesirable changes when their temperature is raised, such as mechanical weakening or increased susceptibility to other kinds of attack. One approach to this problem is the application of thermal barrier coatings which reduce the substrate temperature. Another is the use of ablation coatings which reduce the surface temperature of space vehicles reentering the earth's atmosphere by removing excess heat as the heat of vaporization of the coating material.

1.3 SELECTION OF COATING MATERIALS

The types of materials used for coatings are relatively few – metals and a few classes of inorganic (ceramic) compounds (oxides, carbides, borides and nitrides) singly or in combination. Note that many useful coating materials, such as paints and plastics, are not mentioned here because this book deals with stresses which are too severe for them.

In selecting a coating material it is necessary to consider the uses to which it will be put. Factors to be considered include:

(a) the properties of the coating material itself – its melting point, hardness, vapor pressure, density and thermal expansion coefficient;
(b) the resistance of the coating material to the attack expected;
(c) the compatibility of the coating and substrate over the temperature range of the expected application. This includes the minimizing of thermal stresses, by matching thermal expansion coefficients, and the provision of good coating–substrate adhesion. Some interdiffusion may be desirable, but an excessive amount, such as may occur with silicon plating at high temperatures, may only lead to bulk diffusion and alloy formation; and
(d) the cost. Ultimately whether or not a particular coating will be used depends on the trade-off between the benefits to be gained and the additional cost to be incurred. When the application is critical, and the consequences of failure disastrous, higher costs are usually justified, particularly when there exists no reasonable alternative. However, cost is always a 'moving target' since a great need frequently leads to improvements in existing methods and the development of new ones.

It has recently been argued [1] that the rapid introduction of tribological coatings will require closer cooperation between coating experts and mechanical engineers if a new coating is to be successfully introduced. Coating experts use the following parameters to identify a new coating; coating method, composition, thickness, hardness, coating–substrate adhesion and friction and wear data, e.g. pin-on-disk. The following information is required by the mechanical engineer to design a coated machine element: Young's modulus, Poisson's ratio, thermal expansion coefficient, thermal conductivity, density, specific heat of both coating and substrate and information on residual stresses to assess the overall stress level exhibited by the coated body.

The authors point out that the information produced by the coating expert is largely useless to the designer. Coatings will only be introduced if the elements needed in design analysis are furnished together with the coating.

1.4 METHODS OF APPLICATION

New methods for applying coatings, improvements in existing methods, and new applications have proliferated in recent years, driven by technological need. As Bunshah [2] has pointed out, there is no unique way to classify these methods, which may, for example, be classified as vapor vs. condensed phase, chemical vs. physical, or atomistic vs. bulk.

Most of the coating methods are described in journal articles and conference proceedings which leave the nonspecialist potential user with a bewildering number of choices with which he is probably not equipped to deal. Books, which might be expected to take a broader view, are in short supply. Prominent among current books is the volume edited by Bunshah [2] which deals largely with vapor phase methods and the recently published book on ceramic films and coatings edited by Wachtman and Haber [3], which includes both protective coatings and coatings for electronic and optical applications. Note that both of these books are multiauthor, in recognition of the fact that no single individual can be intimately familiar with all the curently used methods for applying coatings.

1.5 ELECTROPLATING – AN EXAMPLE OF A TECHNOLOGY

The electroplating of metals from solutions, nearly always aqueous and at ambient temperature, has its roots in the work of Faraday, who enunciated the fundamental laws bearing his name, laws which relate the quantity of electrical charge passed between the electrodes in solution and the quantity and valence of material deposited. Long before more modern methods of depositing coatings were developed, many of the principles relevant to electroplating, such as the thermodynamics of electrode potentials and the kinetics of diffusion and the movement of ions under an applied field in solution, as well as their discharge at the electrode surface, had been worked out.

There have also been more recent developments. Many of these developments are scattered in the journal literature and have not yet found their way into books for the general technical reader.

A recently introduced method for improving the properties of electroplated coatings is the pulsed reversed current (RC) technique [4]. The cathodic curent is periodically interrupted by an anodic pulse which briefly redissolves some of the just deposited coating. This introduces two more parameters into the plating process: the pulse frequency v and the duty cycle $T/(T + T')$, where T is the (cathodic) deposition time and T' is the (anodic) dissolution time. Obviously $T > T'$. Optimizing RC conditions can lead to improvements in coating smoothness, and texture, somewhat comparable to the use of organic brighteners.

Another technique which has recently received increased attention is the electrodeposition of layered alloy coatings, usually called cylic multilayered (or compositionally modulated) alloy coatings (CMA). Although the technique goes back to early work by Brenner [5], it was more recently revived and extended by Cohen, Koch, and Sardi [6] who showed that layered coatings of Ag–Pd could be plated from a single bath by periodic alteration of current or potential. Spacings of less than 100 nm were achieved. Subsequently, spacings of Cu–Ni alloys as small as 0.8 nm were achieved by Yahalom and Zadok [7]. As poined out by Lashmore and Dariel [8], electrodeposition presents, in principle, several advantages over vapor phase methods for the production of layered alloys. Among them is the strong tendency for the coating to grow epitaxially and thus form materials with a texture determined by the substrate; the process is inexpensive and can easily be scaled up for plating large parts; and it is carried out at room temperature, avoiding coating–substrate diffusion.

These alloys have been of interest for their mechanical, electrical and magnetic properties [9]. In the context of this book the interest is in mechanical properties. It has been shown [10] that CMAs exhibit increased fracture strength, as much as three times that of the constituent metals, and enhanced wear performance in both dry sliding and in lubricating conditions.

Much remains to be learned about CMAs – which alloys can be plated, optimization of the plating parameters and relation of the coating characteristics, such as layer spacing, to the properties of interest, but it is already clear that work in this field is worth pursuing.

Although the editor wished to include a chapter on electrodeposition in the present volume, he was unable to find anyone willing to write it. It is interesting that the most recent book on electroplating written by a single author is the monumental two-volume *Electroplating of Alloys* by Brenner [5], which includes historical background, basic principles and a thorough discussion of all the alloys that could be plated from aqueous solution. Brenner was chief of the Electrodeposition Section at the National Bureau of Standards (now NIST, the National Institute of Standards and Technology) who devoted his entire career to this field. There are very few recent books. Frederick Lowenheim's *Modern Electroplating* [11] is an excellent multiauthor text, published in 1974, which covers both general principles and includes chapters on all the important metals and many alloys. The recent book by Dini [12], although it has 'electroplating' in its title, deals primarily with the properties of the plated coatings, such as porosity, stress, corrosion and wear, rather than with methods for plating metals and alloys.

The current situation, that of rapidly expanding scientific and technical fields that no single person can master, as well as the increasing demands placed on scientists, particularly in technology, has probably mitigated against broad, single-author books. The trend seems to be toward multiauthor books, but even they require an editor to organize them. The present book is a good example. I was recently asked to write an entire book on coatings, but found this well beyond my competence, though I agreed to write some chapters related to molten salt electroplating. Urged to serve as editor, I spent six months learning about coatings and trying to decide what should be in the book. Thus I must take whatever responsibility attaches to the selection of topics.

1.6 PLAN OF THIS BOOK

The purpose of the present volume is to explore in detail several methods, primarily carried out in the condensed state, which have not been reviewed recently. Although the emphasis is on the condensed state, some of the methods cannot be classified unambiguously. For example, although pack cementation is carried out by packing articles to be coated into a container, surrounded by a powdered mixture, the actual formation of a corrosion-resistant layer occurs by gas phase transport from the powder to the metal.

The methods also differ widely in the degree to which they have become technologically established. Thus, pack cementation is a currently used industrial method, with relatively little basic science still to be done. On the other hand, the electrodeposition of refractory metals and compounds is almost entirely in the basic research phase, and is included because it has the potential for giving rise to a useful technology.

In addition to the chapters on coating methods, chapters on coating corrosion and the measurement of coating adhesion have also been included. Coating corrosion is a serious problem at high temperatures in corrosive atmospheres, and much effort has gone into reducing it. Coating adhesion is of great importance in preventing the removal of a coating from a substrate by mechanical stresses.

The book begins, because of the editor's interest, with three chapters on electrodeposition from molten salts. Refractory metals, because of their desirable properties, had been the object of interest for a long time until many futile efforts showed that hydrogen overvoltage problems prevented