

Preface

The aim of this book is to bring to scientists, researchers, engineers, and students the newest achievements in electrochemically and chemically deposited metals and alloys. This book is to some degree a continuation of our former book *Fundamental Aspects of Electrometallurgy*, although there are significant differences. More particularly, this book is devoted to the surface morphology of deposited metals and/or alloys and offers an in-depth analysis of the influence of the parameters of electrodeposition or chemical deposition of metals and alloys, which could lead to technological advances in industrial settings worldwide. As such, the proposed book may equally attract attention from those working in electrometallurgical or electroplating plants and from members of research departments in industry or academia.

The surface morphology of electrochemically deposited metals and alloys is a very important property and thus may significantly influence their potential applications. Conditions of electrochemical deposition such as electrolyte composition, pH, temperature, stirring, time, deposition overpotential, and current density determine the surface morphology.

The morphology of electrodeposited metals is usually analyzed on the basis of the exchange current density and overpotential for hydrogen evolution. When electrodeposition of metals is characterized by *very large* exchange current densities, at lower overpotentials individual grains or boulders are formed, while at higher overpotentials formation of dendrites takes place. In the case of *large* exchange current densities, spongy deposits and dendrites are produced at lower or higher overpotentials, respectively. Finally, during electrodeposition characterized by *medium and low* exchange current densities, compact deposits are obtained at low overpotentials, while dendrites or spongy deposits are formed at high overpotentials.

A proper analysis of the polarization curves in correlation with the surface morphology could contribute to very important conclusions useful for technological operations in order to produce a metal deposit with the desired properties. Electrodeposition of metals at low overpotentials proceeds under ohmic

control and at higher overpotentials under diffusion control when the process is characterized by the *extremely large* exchange current densities. In the ohmic control regime, granular or regular crystals are deposited, while under diffusion control, different shapes of dendrites are formed. When the electrodeposition of metals is characterized by *large* exchange current densities, diffusion control is observed in the whole range of overpotentials. Therefore, spongy deposits are formed at lower and dendrites at higher overpotentials. For metals where electrodeposition is characterized by *medium or low* exchange current densities, the process proceeds under activation control at low overpotentials. Activation-controlled electrodeposition produces large grains of metal with well-defined crystal shapes. This is observed for overpotentials in the regions of the Tafel linearity. For overpotentials larger than those consistent with Tafel linearity and smaller than those determining the limiting diffusion current density plateau (the mixed activation–diffusion control), the surface morphology is influenced by mass transfer. Compact or uniform deposits of metals are obtained under these conditions. Formation of dendrites is observed at overpotentials inside the plateau of the limiting diffusion current density. For metals where electrodeposition is characterized by *medium and low* exchange current densities, the shapes of dendrites are very different than those produced for metals where the electrodeposition is characterized by the *extremely large or large* exchange current densities. This observation raises many further questions from the fundamental point of view of material science in conjunction with electrochemistry and opens a new window for future studies.

Vigorous hydrogen evolution changes hydrodynamic conditions in the near-electrode layer. In this way the presence of significant hydrogen evolution may strongly affect the morphology of metal deposits. The typical structure obtained in the presence of vigorous hydrogen evolution is honeycomb-like, with holes or pores formed from detached hydrogen bubbles and surrounded by cauliflower-like agglomerates of metal grains. Complexing agents and additives (organic or inorganic) present in the electroplating solutions may also strongly affect the morphology of deposits. The difference in the morphology of electrodeposited metals relative to the one obtained by the electrodepositions from simple salt solutions is caused by the change of the kinetic parameters of electrodeposition due to the effect of additives or complexing agents. The deposition of compact metals and alloys, bright galvanic coatings, and dispersed and powdered precipitates is discussed in detail. Also, the effects of periodically changing currents and/or potentials during the electrodeposition on the morphology and related properties of deposits are thoroughly presented in this book.

All the remarks mentioned above are applicable as well to the electrodeposition of alloys. Using Brenner's classification of alloy electrodeposition, e.g., equilibrium, regular, anomalous, etc., all existing combinations of deposition parameters and their influence on the alloy morphology are analyzed. Interestingly, certain features, which are not recognized in the electrodeposition of pure metals, are observed in the alloy deposition processes. An example includes the *spatiotemporal structures*, which is discussed in this book.

Chemically deposited metals and alloys from aqueous solutions have been significantly less studied than their electrodeposition counterparts. Both chemical deposition, or as frequently termed in the literature *electroless* deposition, and electrodeposition are charge transfer processes and as such can be considered as *electrochemical*. Practically, all metals and/or alloys that can be electrodeposited from aqueous solutions can be deposited by the electroless means using appropriate reducing agents. Electroless deposition of various metals has been widely used in industry since the 1950s. Metals of interest include Ni, Cu, Ag, Au, Pd, and Co. Many alloys of these metals find applications in different industries. Both galvanic and autocatalytic types of electroless deposition in relation with the surface morphology are analyzed in this book.

The electrodeposition portion of this book is written by Popov, Nikolić, and Jović. Chapters 1, 2, and 3 are written by Popov and Nikolić, Chap. 4 is written by Popov, Chap. 5 is written by Nikolić, Chap. 6 is written by Nikolić and Popov, and Chaps. 7 and 8 are written by Jović. The chapter related to the chemical deposition is written by S. Djokić. Chapters 1, 2, 3, 4, 5, 6, 7, and 8 of this book are based on classical studies performed at the Department of Physical Chemistry and Electrochemistry at the Faculty of Technology and Metallurgy, University of Belgrade; Department of Electrochemistry at the Institute of Chemistry, Technology and Metallurgy (ICTM), University of Belgrade; and at the Institute for Multidisciplinary Research, University of Belgrade, Serbia. K. I. Popov, N.D. Nikolić, and V.D. Jović would like to acknowledge contributions and inspiration by Professor A.R. Despić who initiated research in the area of electrodeposition at the University of Belgrade. Popov and Nikolić (Chaps. 1, 2, 3, 4, 5, and 6) are thankful for help from their colleagues Professors M.D. Maksimović, M.G. Pavlović, N.V. Krstajić, B.N. Grgur, P.M. Živković, S.K. Zečević, and B.J. Lazarević. Also they acknowledge contributions from Drs R.M. Stevanović, S.M. Pešić, Z. Rakočević, Lj.J. Pavlović, G. Branković, V.M. Maksimović, and S.B. Krstić, as well as from numerous colleagues and students who participated in their research.

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We hope that the book will be of a particular interest to the individuals or groups dealing with electrochemistry of metals or more specifically with the electrodeposition phenomena in relation with the surface morphology. The research departments in the automotive, aerospace, electronics, energy device, and perhaps in the biomedical fields may find this book as a very useful source in developments of their future programs. Professors and students in the university settings worldwide, when learning, investigating, or lecturing various electrodeposition processes at both undergraduate or graduate levels, will find this book as a very valuable source for their courses and/or projects. We believe that for the university environments, the book can be attractive to the engineering students. Perhaps, chemistry or physics students will find the book as a very useful source in their studies.

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Belgrade, Serbia
Belgrade, Serbia
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Konstantin I. Popov
Stojan S. Djokić
Nebojša D. Nikolić
Vladimir D. Jović

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Popov, K.I.; Djokić, S.S.; Nikolić, N.D.; Jović, V.D.

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