ADVANCED COATING MATERIALS

Edited by
Liang Li and
Qing Yang

Scrivener Publishing

WILEY

Advanced Coating Materials

Scrivener Publishing
100 Cummings Center, Suite 541J
Beverly, MA 01915-6106

Publishers at Scrivener
Martin Scrivener (martin@scrivenerpublishing.com)
Phillip Carmical (pcarmical@scrivenerpublishing.com)

Managing Editors: George Mishra and Anshuman Mishra

Advanced Coating Materials

Edited by

Liang Li and Qing Yang

Scrivener
Publishing

WILEY

This edition first published 2018 by John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, USA and Scrivener Publishing LLC, 100 Cummings Center, Suite 541J, Beverly, MA 01915, USA
© 2019 Scrivener Publishing LLC
For more information about Scrivener publications please visit www.scrivenerpublishing.com.

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise, except as permitted by law. Advice on how to obtain permission to reuse material from this title is available at http://www.wiley.com/go/permissions.

Wiley Global Headquarters
111 River Street, Hoboken, NJ 07030, USA

For details of our global editorial offices, customer services, and more information about Wiley products visit us at www.wiley.com.

Limit of Liability/Disclaimer of Warranty
While the publisher and authors have used their best efforts in preparing this work, they make no representations or warranties with respect to the accuracy or completeness of the contents of this work and specifically disclaim all warranties, including without limitation any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives, written sales materials, or promotional statements for this work. The fact that an organization, website, or product is referred to in this work as a citation and/or potential source of further information does not mean that the publisher and authors endorse the information or services the organization, website, or product may provide or recommendations it may make. This work is sold with the understanding that the publisher is not engaged in rendering professional services. The advice and strategies contained herein may not be suitable for your situation. You should consult with a specialist where appropriate. Neither the publisher nor authors shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages. Further, readers should be aware that websites listed in this work may have changed or disappeared between when this work was written and when it is read.

Library of Congress Cataloging-in-Publication Data

ISBN 978-1-119-40756-0

Cover image: Pixabay.Com
Cover design by Russell Richardson

Set in size of 11pt and Minion Pro by Exeter Premedia Services Private Ltd., Chennai, India

Printed in the USA

10 9 8 7 6 5 4 3 2 1

Contents

Preface

Coatings is an area with great variety which has developed to be a quite significant technique for protecting existing infrastructure from corrosion and erosion, maintaining and enhancing the performance of equipment, and providing novel functions such as smart coating. In recent years, coating techniques entered an age of rapid development, greatly benefiting the medical device, energy industry, automotive and construction industries.

The mechanisms, usage, and manipulation of cutting edge coating methods are the focus of this book. Not only are the working mechanisms of coating materials explored in great detail, but also craft designs for further optimization of more uniform, safe, stable, and scalable coatings.

A group of leading experts in different coating technologies were invited to summarize the major developments in their discipline, demonstrate their main applications, identify the key bottlenecks, and prospects for the future. Their efforts are reflected in this book, *Advanced Coating Materials,* which broadly covers the coating techniques, including cold spray, plasma vapor deposition, chemical vapor deposition, sol–gel method, etc., and their significant applications in microreactor technology, super(de)wetting, joint implants, electrocatalyst, etc. Numerous kinds of coating structures are addressed, including nanosize particles, biomimicry structures, metals and complexed materials, along with the environmental and human compatible biopolymers resulting from microbial activities. This book divides the collection of diversified topics related to coating materials into three parts: (1) Materials and Methods: Design and Fabrication, (2) Coating Materials: Nanotechnology, and (3) Advanced Coating Technology and Applications.

The first part of the book, 'Materials and Methods: Design and Fabrication', describes the most promising approaches illustrated in coating techniques, with Chapter 1 broadly covering the adaptation of new coating techniques by explaining the science behind the molecular precursor method. Information regarding 3D cold spray modeling in an advanced coating process is covered in Chapter 2. The effects of laser process parameters (HLPP) on alloy characteristics are described in Chapter 3 and Chapter 4 focuses on physicochemical properties and electrocatalytical reactivity in oxygen transfer reactions, suggesting that oxidative degradation of organic substances is likely due to an increase in the amount of strongly bound oxygen-containing species on the electrode surface. Chapter 5 discusses nuclear fuel durability enhancement by using polycrystalline diamond (PCD) coating protection, which has been found by nuclear reactor research to be appropriate for prolonging the lifetime of nuclear cladding, and consequently enhancing nuclear fuel burnup as a passive element for nuclear safety. High-performance WC-based coatings for narrow and complex geometries are well defined in Chapter 6.

The topics in the second part of the book, 'Coating Materials: Nanotechnology', are related to dimensional properties of coating materials. The role of nanotechnology in paints and coatings is discussed in Chapter 7, which is representative of the recent technology enhancements which show an astonishing influence of dimensions on antimicrobial properties. Chapter 8 explains anodic oxide nanostructures and theories of anodic nanostructure self-organization (growth mechanism of oxide film). Next, in Chapter 9, the potential prospects of nanodiamond, epoxy, and important epoxy/ND hybrids for coatings and their significant applications are discussed. Nano-dimension coatings are an important coating technology that offer significant benefits for electrocatalytic applications in nanostructured metal–metal oxides, as described in detail in Chapter 10.

The last part of the book, 'Advanced Coating Technology and Applications', mainly focuses on the use of advanced coating technologies in applications of utmost significance to future advancements in the field. Chapter 11 describes solid-phase microextraction coatings based on tailored materials (e.g., molecularly imprinted polymers), which are found to be a significant contributor to the field. The focus of Chapter 12 is the effect of laser processing on hardening of titanium alloy. Engineering involved in scalable fabrication of super(de)wetting coatings is described in Chapter 13, along with prospects and guidelines for the upgraded development. In Chapter 14, some of the widely used polymers are discussed in detail and further research is suggested that can lead to their modification as coating materials for biomedical applications.

This book is written for readers from diverse backgrounds across nanotechnology, biomedical engineering, chemistry, physics, engineering, medical, environmental, and materials science fields. Since it offers a comprehensive view of innovative research in advanced coating materials and their technological importance, the book will be of benefit to scientists, researchers, and technologists in advanced coating materials; those in industrial sectors intending to fabricate materials employing state-of-the-art techniques; and students of PhD, master's and undergraduate-level courses on surface materials processing, properties, and applications of multidisciplinary subjects.

The editors would like to thank the International Association of Advanced Materials, the eminent authors for their contributions to this book as well as the efforts of the publishing team.

Editors
Liang Li, PhD
Qing Yang, PhD
July 2018

Part I

MATERIALS AND METHODS: DESIGN AND FABRICATION

1

The Science of Molecular Precursor Method

Hiroki Nagai and Mitsunobu Sato*

Department of Applied Physics, School of Advanced Engineering, Kogakuin University, Tokyo, Japan

Abstracts

The metal complexes are used in various applications such as catalysts, luminescent materials, and medicines. In 1996, one of the authors, M.S., focused on the thin-film fabrication of various metal oxides and phosphate compounds, using coating solutions involving stable metal complexes of industrially available multidentate ligands. This is the molecular precursor method (MPM). The method is based on the facile preparation of coating solutions involving the metal complex anions and alkylammonium cations. The stability, homogeneity, miscibility, coatability, and other characteristics of the coating solutions are practical advantages, as compared to the conventional sol–gel method. This is because metal complex anions with high stability can be dissolved in volatile solvents by combining with appropriate alkylamines. Furthermore, the resultant solutions can form excellent precursor films through various coating procedures including spin-coating. The precursor films obtained by the coating process on various substrates should be amorphous, just as with the metal/organic polymers in the sol–gel processes; otherwise, it would not be possible to obtain the resulting metal-oxide or metal-phosphate thin films spread homogeneously on substrates by heat treatment. The advantages of the molecular precursor solutions will be also explained through detailed results of thin film fabrication in this chapter.

Keywords: Molecular precursor method, stability, homogeneity, miscibility, coatability, functional thin films

---

**Corresponding author*: lccsato@cc.kogakuin.ac.jp

Liang Li and Qing Yang (eds.) Advanced Coating Materials,
(3–28) © 2019 Scrivener Publishing LLC

1.1 Metal Complex

Metal complexes (coordination compounds) are one of the most important chemical compounds and form the basis of coordination chemistry. Coordination chemistry is being considered a science only after the formulation of the coordination theory proposed by A. Werner [1, 2]. After Werner, enormous metal complexes were obtained, characterized, and widely applied. Especially, their syntheses, structures, and properties have been investigated.

Metal complexes consisted of a central metal atom (ion) and ligands connected to the metal atom. The combination of metal atom and ligand produces the coordination sphere, which is formed by coordination bonds having donor–acceptor interactions. A coordination bond is mostly formed as a result of the overlapping of atomic orbitals (AO) of ligands, filled with electrons and/or vacant AO of the central metal atom. Lewis acid can form a new covalent bond by accepting a pair of electrons, and Lewis base can form a new covalent bond by donating a pair of electrons. The fundamental Lewis acid–base theory is described by a direct equilibrium, leading to the complex formation as follows.

$$\mathrm{M} + :\mathrm{L} \rightleftarrows \mathrm{M}:\mathrm{L}$$

Thus, the coordination (donor–acceptor) bond between the central metal (M) and each joining group (ligand, L) is formed by the electron pair. The conventional theory by Lewis made a considerable contribution in understanding the reaction with participation of Lewis acids and bases.

The HSAB (Hard and Soft Acids and Bases) principle is one of the important theories for coordination chemistry, formulated by Pearson in 1963 [3]. The following three statements are the basis of HSAB.

1. Chemical reactions, in particular complex formation, can be classified as acid–base ones; the resulting products can be examined as complexes of the type Lewis acids and bases.
2. All acids and bases can be divided into hard, soft, and/or intermediate.
3. The HSAB principle itself is the following: the acid–base reactions take place in such a way that hard acids prefer to be connected with hard bases, meanwhile soft acids react with soft bases.

The classification of HSAB is summarized in Table 1.1.

Table 1.1 HSAB classification of metal and ligand.

	Metal	**Ligand**
Hard	H^+, Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Mn^{2+}, Al^{3+}, N^{3+}, As^{3+}, Cr^{3+}, Co^{3+}, Fe^{3+}, Si^{4+}, Sn^{4+}, BF_3, $AlCl_3$, CO_2	H_2O, OH^-, F^-,SO_4^{2-}, PO_4^{3-}, $CH_3CO_2^-$, RO^-, Cl^-, ClO_4^-, NO_3^-, ROH, NH_3, RNH_2
Borderline	Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Sn^{2+}, Sb^{3+}, Bi^{3+}, Rh^{3+}, Ir^{3+}, SO_2, NO^+, Ru^{2+}, Os^{2+}, R_3C^+, $C_6H_5^+$	$C_6H_5NH_2$, C_5H_5N, N_3^-, Br^-, NO_2^-, SO_3^{2-}, N_2
Soft	Ag^+, Cu^+, Au^+, Tl^+, Hg^+, Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}, Pt^{4+}, Tl^{3+}, RS^+, I^+, HO^+, I_2, Br_2, ICN,	R_2S, RSH, RS^-, I^-, SCN^-, R_3P, CN^-, RCN, CO, C_2H_4, C_6H_6, H^-

The HSAB principle emphasizes the preference for hard–hard and soft–soft interactions, and the highest thermodynamic stability of complexes formed as a result is achieved.

The rows shown below indicate that the hardness of the elements (donor atoms in ligands) decreases from left to right:

$$N > P > As > Sb, O > S > Se > Te, F > Cl > Br > I$$

Ligands with N, O, F, Cl donor atoms containing a combination of these elements are hard bases according to Pearson. On the contrary, containing elements further to the right are soft bases. The hardness and softness of acids depend considerably on the oxidation number of the metal center.

The HSAB conception has been widely used to explain various coordination modes in the complexes of di-and polydentate ligands. The solvent nature can be also an important factor. The most favorable conditions to control the localization mode of a coordination bond with participation of ligands containing hard and soft donor atoms are created when complex-formation reactions are carried out in aprotic nonaqueous solvents.

Ligands, as the main part of metal complexes, are the object of a great deal of attention in coordination and organometallic chemistry. The reaction control should be emphasized among the reaction conditions of competitive complex formation. It is necessary to take into account that it is possible to determine, and frequently predict, the direction of the electrophilic attack to the donor atom of di- and polyfunctional donors (ligands) only in the case when the thermodynamically stable products are formed under conditions of kinetic control.

Thus, the thermodynamic stability of complexes is discussed, when the bond between the metal and di- and polydentate ligands is localized in the place of primary attack on the donor atoms by the electrophilic reagent, without further change of coordination mode in the reaction of complex formation.

1.2 Molecular Precursor Method

In 1996, one of the authors, M.S., focused on the thin-film fabrication of various metal oxides and phosphate compounds using the stable metal complexes [4–54]. This is the Molecular Precursor Method (MPM), which is one of the chemical processes used for thin-film fabrication. In those days, most of the researchers in the field of thin-film formation by chemical processes preferred to use rather unstable metal complexes. It is easy to imagine the capability of polymers to form "films" because we use polymer films every day. In fact, well-adhered precursor films involving metal ions can be formed on various substrates by coating the solution dispersing the produced oligomers and polymers including metallic species provided by hydrolyzing the unstable metal complexes. These results led us to believe for a long time that only the oligomers and polymers can form precursor films, but the stable metal complexes having a discrete molecular weight would not be useful in the fabrication of such thin films. The MPM was a challenge to this central belief.

The MPM, pertinent to coordination chemistry and materials science including nanoscience and nanotechnology, has been used to fabricate various high-quality thin films with appropriate film thicknesses. As a result, the MPM represents a facile procedure for thin-film fabrication of various metal oxides or phosphates, which are useful as electron and/or ion conductors, semiconductors, dielectric materials such as In_2O_3, ZnO, $LiCoO_2$, $Li_3Fe_2(PO_4)_3$, TiO_2, Cu_2O, Co_3O_4, $SrTiO_3$, ZrO_2, SiO_2, $BaTiO_3$, and $Ca_{10}(PO_4)_6(OH)_2$. The MPM aims to develop many functional materials by surface modification of various substrates including glasses, metals, and ceramics, through chemical fabrication of thin films. One of the features related to this method is the low-cost manufacture involving the chemical process, which can save both resource and production energy.

1.3 Counter Ion (Stability)

The appropriate alkyl groups in the used amines play an essential role. This principle of the MPM is absolutely different from that of the conventional sol–gel method, which needs and uses the mixture of oligomers and polymers for the identical purpose. Amino group itself is usually very reactive, forming simple salts with metal complex anions. The stability of these salts is dependent on the basicity of amine and pH in the used solvent. Most of these salts are rather soluble in both water and aprotic organic solvents. Additionally, the presence of the ligands in metal complex anions and alkylammonium cations in the precursor films generally affects the properties of resultant thin films, as expected. It is very interesting that the thermal reactions between them and metallic species are quite sensitive to the reaction conditions during heat treatment for fabricating the final thin films.

Single crystals of the metal complex can be obtained from the precursor solution in several cases when the alkyl groups in the alkylamines are sufficiently small, for example, an ethyl group. The model structure of the amorphous precursor films formed on substrates can be examined by means of crystal engineering and based on the crystal structures. For example, an ORTEP view of the precursor complex having the EDTA (ethylenediaminetetraacetic acid) and peroxo ligands linked to the central Ti^{4+} ion is shown in Figure 1.1. The molecular structure was determined by an X-ray single crystal structure analysis of the diethylammonium salt of the complex. The

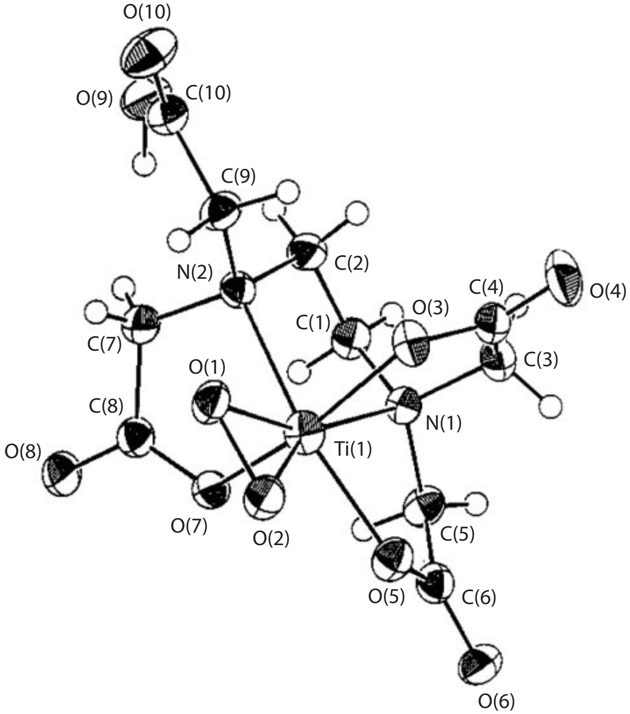

Figure 1.1 An ORTEP view of the precursor complex having the EDTA and peroxo ligands linked to the central Ti^{4+} ion.

single crystals of the identical orange-yellow color could be obtained from a reacted solution of the complex with the diethylamine. The single crystal was $\{(C_2H_5)_2NH_2\}[Ti(O_2)(Hedta)]\cdot 1.5H_2O$; in a monoclinic crystal system, $P2_1/c$ with $a = 8.583(1)$ Å, $b = 6.886(1)$ Å, $c = 36.117(2)$ Å, and $\beta = 92.780(3)°$. The full-matrix least-squares refinement on F^2 was based on 3206 observed reflections that were measured at 250 K by using an imaging plate as a detector and converged with unweighted and weighted agreement factors of R = 0.054 and Rw = 0.061, respectively, and GOF = 1.63. Two Ti–N(edta) bond lengths of 2.307 and 2.285 Å are slightly longer than the bond length of 2.12 Å in the TiN single crystal.

Results indicated that EDTA acts as a pentadentate ligand in the complex, and the peroxo ligand linked to the Ti^{4+} ion has a side-on coordination structure.

1.4 Conversion Process from Precursor Film to Oxide Thin Film

A stable metal complex anion in the precursor solution is dissolved at a molecular level. The metal complex salt in the precursor film must be amorphous before heat treatment in order to fabricate thin films without cracks and pinholes. The alkylammonium cations play an important role in obtaining an amorphous salt in the precursor film. The plausible packing of the metal complex in the precursor film formed on the substrate can be theoretically explained using molecular dynamics and crystal engineering. The shrinkage rate of the film in the vertical direction can be easily estimated from the model structure before heat treatment based on the crystal structure of the metal complex salt, which can be obtained as a single crystal when the alkyl groups in the amines are short enough. The shrinkage rate in the sol–gel method is usually considered to be around 10 times. However, it is roughly estimated to be 10–15 times in the case of MPM, on the basis of the crystal structures (Figure 1.2). Thus, the densification degrees of the precursor films during heat treatment in the process of MPM are similar to those in sol–gel procedures, even though the precursor films involve alkylamines and ligands.

1.5 Anatase–Rutile Transformation Controlled by Ligand

Titanium dioxide, the only naturally occurring oxide of titanium at atmospheric pressure, exhibits three polymorphs, rutile, anatase, and brookite.