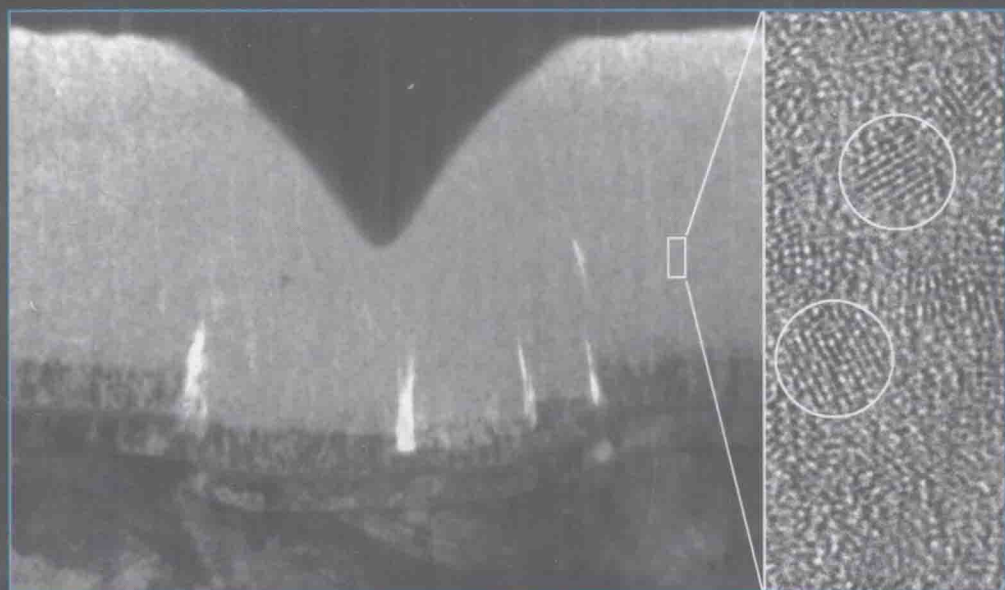


NANOSTRUCTURE SCIENCE AND TECHNOLOGY
Series Editor: David J. Lockwood

Nanostructured Coatings



Edited by
Albano Cavaleiro and Jeff Th. M. De Hosson

Nanostructured Coatings

edited by

Albano Cavaleiro

Universidade de Coimbra
Pinhal de Marrocos, Coimbra, Portugal

and

Jeff Th. M. De Hosson

University of Groningen
Groningen, The Netherlands

 Springer

Albano Cavaleiro
Depto. Eng. Mecanica
University de Coimbra
Pinhal Marrocos
Coimbra 3030 Portugal
albano.cavaleiro@dem.uc.pt.

Jeff Th. M. De Hosson
Department of Applied Physics
University of Groningen
4 Nijenborgh
Groningen 9747 AG
The Netherlands
j.t.m.de.hosson@rug.nl

Cover Illustration: Cross-sectional transmission electron micrograph of a nc-Ti/a- C:H nanocomposite coating after nanoindentation (Yutao Pei, Damiano Galvan, Jeff Th. M. De Hosson, University of Groningen, The Netherlands)

Library of Congress Control Number: 2006925865

ISBN-10: 0-387-25642-3

ISBN-13: 978-0387-25642-9

Printed on acid-free paper.

© 2006 Springer Science+Business Media, LLC

All rights reserved. This work may not be translated or copied in whole or in part without the written permission of the publisher (Springer Science+Business Media, LLC, 233 Spring Street, New York, NY 10013, USA), except for brief excerpts in connection with reviews or scholarly analysis. Use in connection with any form of information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed is forbidden.

The use in this publication of trade names, trademarks, service marks, and similar terms, even if they are not identified as such, is not to be taken as an expression of opinion as to whether or not they are subject to proprietary rights.

9 8 7 6 5 4 3 2 1

springer.com

Contributors

Nuno J. M. Carvalho, Department of Applied Physics, Materials Science Center and Netherlands Institute for Metals Research, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Albano Cavaleiro, ICEMS, Mechanical Engineering Department, Faculty of Sciences and Technology, University of Coimbra, Portugal

Thomas Chudoba, ASMEC Advanced surface mechanics GmbH, Rossendorf, Germany

Ming Dao, Massachusetts Institute of Technology, Cambridge, MA, USA

Peter M. Derlet, Paul Scherrer Institut, NUM/ASQ, Villigen, Switzerland

Damiano Galvan, Department of Applied Physics, Materials Science Center and Netherlands Institute for Metals Research, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Abdellatif Hasnaoui, Paul Scherrer Institut, NUM/ASQ, Villigen, Switzerland

Jeff Th. M. De Hosson, Department of Applied Physics, Materials Science Centre and the Netherlands Institute for Metals Research, University of Groningen, Nijenborgh 4, 9747 A. G. Groningen, The Netherlands

P. Eh. Hovsepian, Nanotechnology Centre for PVD Research, Materials and Engineering Research Institute of Sheffield Hallam University, Sheffield S1 1WB, UK

Lars Hultman, Department of Physics and Measurement Technology (IFM), Linköping University, S-581 83 Linköping, Sweden

Adrian Leyland, Department of Engineering Materials, The University of Sheffield, Sheffield, UK

Allan Matthews, Department of Engineering Materials, The University of Sheffield, Sheffield, UK

Christian Mitterer, Department of Physical Metallurgy and Materials Testing, University of Leoben, Franz-Josef-Strasse 18, A-8700 Leoben, Austria

Benedikt Moser, Massachusetts Institute of Technology, Cambridge, MA, USA

W.-D. Münz, Nanotechnology Centre for PVD Research, Materials and Engineering Research Institute of Sheffield Hallam University, Sheffield S1 1WB, UK

J. Musil, Department of Physics, University of West Bohemia, Plzeň, Czech Republic; Institute of Physics, Academy of Sciences of the Czech Republic, Praha, Czech Republic

Ilya A. Ovid'ko, Institute of Problems of Mechanical Engineering, Russian Academy of Sciences, St. Petersburg, Russia

Yutao Pei, Department of Applied Physics, Materials Science Center and Netherlands Institute for Metals Research, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Ruth Schwaiger, Massachusetts Institute of Technology, Cambridge, MA, USA

Helena Van Swygenhoven, Paul Scherrer Institut, NUM/ASQ, Villigen, Switzerland

Bruno Trindade, ICEMS, Mechanical Engineering Department, Faculty of Sciences and Technology, University of Coimbra, Portugal

Stan Veprek, Institute for Chemistry of Inorganic Materials, Technical University Munich, Lichtenbergstr. 4, D-85747 Garching b. Munich

Maritza G.J. Veprek-Heijman, Institute for Chemistry of Inorganic Materials, Technical University Munich, Lichtenbergstr. 4, D-85747 Garching b. Munich

Maria Teresa Vieira, ICEMS, Mechanical Engineering Department, Faculty of Sciences and Technology, University of Coimbra, Portugal

Foreword

Controlling the performance of structures and components of all sizes and shapes through the use of engineered coatings has long been a key strategy in materials processing and technological design. The ever-increasing sophistication of engineered coatings and the rapid trend toward producing increasingly smaller devices with greater demands on their fabrication, properties and performance have led to significant progress in the science and technology of coatings, particularly in the last decade or two. Nanostructured coatings constitute a major area of scientific exploration and technological pursuit in this development. With characteristic structural length scales on the order of a few nanometers to tens of nanometers, nanostructured coatings provide potential opportunities to enhance dramatically performance by offering, in many situations, extraordinary strength and hardness, unprecedented resistance to damage from tribological contact, and improvements in a number of functional properties. At the same time, there are critical issues and challenges in optimizing these properties with flaw tolerance, interfacial adhesion and other nonmechanical considerations, depending on the coating systems and applications.

Nanostructured coatings demand study in a highly interdisciplinary research arena which encompasses:

- surface and interface science
- study of defects
- modern characterization methodologies
- cutting-edge experimental developments to deposit, synthesize, consolidate, observe as well as chemically and mechanically probe materials at the atomic and molecular length scales
- state-of-the-art computational simulation techniques for developing insights into material behaviour at the atomic scale which cannot be obtained in some cases from experiments alone

The interdisciplinary nature of the subject has made it a rich playing field for scientific innovation and technological progress.

Albano Cavaleiro and Jeff De Hosson have edited an outstanding volume on nanostructured coatings which provides an excellent snapshot of the state-of-the-art in this important topic. They have assembled as contributors to this volume an

impressive group of research teams who have participated in the rapid progress this area has seen in the recent past. The volume provides a very balanced picture of the broad scope of the field, while at the same time capturing the rich details associated with the various topics covered. The community will benefit greatly from the hard work of the editors and authors of this volume, and I expect this volume to have a significant impact on research and practice involving nanostructured coatings.

SUBRA SURESH
Ford Professor of Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts

Acknowledgments

The editors are grateful to the team of experts that took care of the peer-review of the chapters, consisting of Prof. Jorgen Bottiger, Prof. Steve Bull, Dr. Peter Hatto, Dr. Nigel Jenett, Prof. Francis Levy, Dr. Joerg Patscheider, Prof. Jean-François Pierson, Prof. Yves Pauleau, Prof. Carlos Tavares, Prof. Carl Thompson, Prof. Filipe Vaz, Prof. Atul Chokshi, and Prof. Dirk van Dyck.

Contents

1. Galileo Comes to the Surface!	1
<i>Jeff Th. M. De Hosson and Albano Cavaleiro</i>	
1. Introduction	1
2. Coatings	2
3. Challenges and Opportunities	4
3.1. Wear: The Role of Interfaces in Nanostructured Materials	4
3.2. Friction: Size Effects in Nanostructured Coatings	9
3.3. Tribological Properties: The Role of Roughness	16
4. Leitmotiv and Objective	21
Acknowledgments	23
References	24
 2. Size Effects on Deformation and Fracture of Nanostructured Metals	 27
<i>Benedikt Moser, Ruth Schwaiger, and Ming Dao</i>	
1. Introduction	27
2. Mechanical Testing of Nanostructured Bulk and Thin Film Materials	28
2.1. Tensile and Compression Testing	28
2.2. Indentation Testing: Experimental Technique and Computations	30
2.3. Cantilever Bending	33
2.4. <i>In Situ</i> Testing Technique	34
3. Deformation and Fracture Under Microstructural Constraint	34
3.1. Crystalline Materials	34
3.1.1. Microstructure	34
3.1.2. Monotonic Deformation	36
3.1.3. Monotonic Fracture	50
3.1.4. Cyclic Deformation	51

3.2. Amorphous Materials	53
3.2.1. Yield Function	54
3.2.2. Serrated Flow in Bulk Metallic Glasses	56
3.2.3. Stress-Induced Nanocrystallization	57
4. Deformation Under Dimensional Constraint	57
4.1. Yield Stress and Hardening	57
4.2. Cyclic Deformation	63
5. Concluding Remarks	66
References	67
 3. Defects and Deformation Mechanisms in Nanostructured Coatings	78
<i>Ilya A. Ovid'ko</i>	
1. Introduction	78
2. Deformation Mechanisms in Nanocrystalline Coatings: General View	80
3. Lattice Dislocation Slip	82
4. Grain Boundary Sliding	85
5. Rotational Deformation Mechanisms	89
6. Grain Boundary Diffusional Creep (Coble Creep) and Triple Junction Diffusional Creep	93
7. Interaction Between Deformation Modes in Nanocrystalline Coating Materials: Emission of Dislocations from Grain Boundaries	95
8. Defects and Plastic Deformation Releasing Internal Stresses in Nanostructured Films and Coatings	97
9. Concluding Remarks	101
Acknowledgments	102
References	102
 4. Nanoindentation in Nanocrystalline Metallic Layers: A Molecular Dynamics Study on Size Effects	109
<i>Helena Van Swygenhoven, Abdellatif Hasnaoui, and Peter M. Derlet</i>	
1. Introduction	109
2. Atomistic Modeling	111
2.1. Molecular Dynamics	112
2.2. Steepest Descent and Conjugate Gradient Methods	113
2.3. Interatomic Potentials	114

2.4. Creation of Nanocrystalline Atomistic Configurations	115
2.5. Atomistic Nanoindentation Simulation Geometry	116
2.6. Atomistic Visualization Methods for GB and GB Network Structure	118
2.7. The Time- and Length-Scale Problem	120
3. The Deformation Mechanisms at the Atomic Level in Nano-Sized Grains Beneath the Indenter	121
3.1. Deformation Mechanisms in nc fcc Metals Derived from Tensile Loading	121
3.2. Atomistic Mechanism under the Indenter	122
3.3. Interaction of Dislocations with the GB Network	126
3.4. The Ratio between Indenter Size and Grain Size	129
3.5. Material Pileup	134
3.6. Unloading Phase	136
4. Discussion and Outlook	138
References	139
 5. Electron Microscopy Characterization of Nanostructured Coatings	 143
<i>Jeff Th. M. De Hosson, Nuno J. M. Carvalho, Yutao Pei, and Damiano Galvan</i>	
1. Introduction	143
2. Description of the Experimental Methodology	146
2.1. Materials	146
2.2. Characterization with Electron Microscopy Techniques	147
2.3. TEM Sample Preparation	160
3. Microstructure of Diamond-Like Carbon Multilayers	162
3.1. DLC Coatings	162
3.2. Coated Systems	163
3.3. Particles Inside an Amorphous Structure	172
3.4. Defect Structure	175
3.5. Mechanisms of Crack Propagation	176
4. Characterization of TiN and TiN-(Ti,Al)N Multilayers	181
4.1. Transition Metal Nitrides	181
4.2. Microstructural Features	184
4.3. Formation and Microstructure of Macroparticles	189
4.4. Nanoindentation Response	192
5. Outlook	199
Acknowledgments	209
References	209

6. Measurement of Hardness and Young's Modulus by Nanoindentation 216

Thomas Chudoba

1. Introduction	216
2. Theory of Indentation Measurements	217
3. Influence and Determination of Instrument Compliance	226
4. Influence and Determination of Indenter Area Function	233
5. Additional Corrections for High-Accuracy Data Analysis	239
5.1. Thermal Drift Correction	239
5.2. Zero Point Correction	242
6. Specific Problems with the Measurement of Thin Hard Coatings	243
6.1. Consideration of Substrate Influence	243
6.2. Sink-In and Pileup Effects	250
7. Limits for Comparable Hardness Measurements	251
8. Young's Modulus Measurements with Spherical Indenters	255
Acknowledgments	258
References	258

7. The Influence of the Addition of a Third Element on the Structure and Mechanical Properties of Transition-Metal-Based Nanostructured Hard Films: Part I—Nitrides 261

Albano Cavaleiro, Bruno Trindade, and Maria Teresa Vieira

1. Introduction	261
2. The Addition of Aluminum to T_M Nitrides	263
3. Ternary Nitrides with T_M Elements from the IV, V, and VI Groups	267
4. The Specific Case of the Addition of Si to T_M Nitrides	270
5. Addition of Low N-Affinity Elements to T_M Nitrides	274
6. W-Based Coatings	275
6.1. The Binary System W-X	275
6.1.1. Chemical Composition and Structural Features	275
6.1.2. Hardness	277
6.2. The Ternary System W-X-N	279
6.2.1. Coatings with the bcc α -W Phase	279
6.2.2. Coatings with the fcc Nitride Phase	283
6.2.3. As-Deposited Amorphous Coatings	288
6.2.4. Achievement of Nanocrystalline Structures from the Crystallization of Amorphous Films of the T_M -Si-N System	290

6.2.5. Evolution of the Chemical Composition of T_M -Si-N Films During Thermal Annealing	294
6.2.6. Mechanical Properties of T_M -Si-N Coatings after Thermal Annealing	295
7. Conclusion	306
Acknowledgments	307
References	307
 8. The Influence of the Addition of a Third Element on the Structure and Mechanical Properties of Transition-Metal- Based Nanostructured Hard Films: Part II—Carbides	 315
<i>Bruno Trindade, Albano Cavaleiro, and Maria Teresa Vieira</i>	
1. Introduction	315
2. Amorphous Carbide Thin Films Deposited by Sputtering	318
3. Structural Models for Prediction of Amorphous Phase Formation	318
4. Amorphous Phase Formation in T_M - T_{M1} -C (T_M and T_{M1} = Transition Metals) Sputtered Films	323
4.1. T_M -Fe-C (T_M = Ti, V, W, Mo, Cr) Thin Films	323
4.2. W- T_M -C (T_M = Ti, Cr, Fe, Co, Ni, Pd, and Au) Thin Films	327
5. Hardness and Young's Modulus of Sputtered T_M - T_{M1} -C Thin Films	332
5.1. Ternary T_M -C/ T_{M1} -C Systems (T_M = Group VA Metal; T_{M1} = Group VIA Metal)	332
5.2. Other Ternary T_M - T_{M1} -C Systems	335
6. Thermal Stability of Sputtered Amorphous M1-M2-C Thin Films	339
7. Conclusions	342
References	343
 9. Concept for the Design of Superhard Nanocomposites with High Thermal Stability: Their Preparation, Properties, and Industrial Applications	 347
<i>Stan Veprek and Maritza G. J. Veprek-Heijman</i>	
1. Introduction	347
1.1. Possible Artifacts During Hardness Measurement on Superhard Coatings	348
1.2. Requirements on the Thickness of the Coatings	351
2. The Earlier Work	352

3. Superhard Nanocomposites in Comparison with Hardening by Ion Bombardment	355
4. Superhard Nanocomposites with High Thermal Stability	359
4.1. The Design Concept for the Deposition of Stable Superhard Nanocomposites	359
4.2. Properties of the Fully Segregated Superhard Nanocomposites	369
4.2.1. Thermal Stability, "Self-Hardening," and Stabilization of $(Al_{1-x}Ti_x)N$	369
4.2.2. Oxidation Resistance	375
4.2.3. Morphology and Microstructure	378
5. Reproducibility of the Preparation of Superhard, Stable Nanocomposites	381
5.1. The Role of Impurities	381
5.2. Conditions Needed to Obtain Complete Phase Segregation During the Deposition	385
5.3. Conditions Needed to Achieve Hardness of 80 to ≥ 100 GPa	388
6. Mechanical Properties of Superhard Nanocomposites	390
6.1. Recent Progress in the Understanding of the Extraordinary Mechanical Properties	390
6.2. The Resistance Against Brittle Fracture	392
6.3. High Elastic Recovery	393
6.4. Ideal Decohesion Strength	395
6.5. The Future Research Work	396
7. Industrial Applications	397
8. Conclusions	398
Acknowledgments	400
References	400

10. Physical and Mechanical Properties of Hard Nanocomposite Films Prepared by Reactive Magnetron Sputtering 407

J. Musil

1. Introduction	407
2. Formation of Nanocrystalline and Nanocomposite Coatings	408
2.1. Low-Energy Ion Bombardment	408
2.2. Mixing Process	409
2.3. Structure of Films	409
3. Microstructure of Nanocomposite Coatings	413
4. Role of Energy in the Formation of Nanostructured Films	415

4.1. Ion Bombardment in Reactive Sputtering of Films	417
4.2. Effect of Ion Bombardment on Elemental Composition of Sputtered Films	419
4.2.1. Resputtering of Cu from Zr-Cu-N Films	420
4.2.2. Desorption of Nitrogen from Sputtered Nitride Films	420
4.3. Effect of Ion Bombardment on Physical Properties of the Film	421
4.4. Ion Bombardment of Growing Films in Pulsed Sputtering	423
5. Enhanced Hardness	426
5.1. Open Problems in Formation of Nanocomposite Films with Enhanced Hardness	428
5.2. Macrostress in Sputtered Films	428
5.3. High-Stress Sputtered Films	433
5.4. Low-Stress Sputtered Films	434
5.4.1. Effect of Chemical Bonding	434
5.4.2. Effect of Grain Size	436
5.4.3. Effect of Deposition Rate a_D on Macrostress σ	436
5.4.4. Macrostress σ in X-ray Amorphous Films	438
5.5. Concluding Remarks on Reduction of Macrostress σ in Superhard Films	441
6. Origin of Enhanced Hardness in Single-Phase Films	441
7. Classification of Nanocomposites According to Their Structure and Microstructure	443
8. Mechanical Properties of Hard Nanocomposite Coatings	445
8.1. Interrelationships between Mechanical Properties of Reactively Sputtered Ti(Fe)N _x Films and Modes of Sputtering	447
8.2. Effect of Stoichiometry x and Energy E_{pi} on Resistance to Plastic Deformation and Hardness of Reactively Sputtered Ti(Fe)N _x Films	448
9. Trends of Future Development	450
Acknowledgments	453
References	453
 11. Thermal Stability of Advanced Nanostructured Wear-Resistant Coatings	 464
<i>Lars Hultman and Christian Mitterer</i>	
1. Introduction	464
2. Measurement Techniques	465
2.1. Biaxial Stress–Temperature Measurements	466

2.2. Differential Scanning Calorimetry and Thermogravimetric Analysis	468
3. Recovery	470
3.1. Single-Phase Coatings	470
3.1.1. Compound and Miscible Systems	470
3.1.2. Pseudo-Binary Immiscible Systems	476
3.2. Multiphase Coatings	477
3.2.1. Nanocomposite Coatings	477
3.2.2. Superlattices	479
4. Recrystallization and Grain Growth	480
4.1. Single-Phase Coatings	480
4.1.1. Compound and Miscible Systems	480
4.1.2. Pseudo-Binary Immiscible Systems	482
4.2. Multiphase Coatings	483
4.2.1. Nanocomposite Coatings	483
4.2.2. Superlattices	486
5. Phase Separation in Metastable Pseudo-Binary Nitrides	489
5.1. Spinodal Decomposition	489
5.2. Age Hardening	493
6. Interdiffusion	495
7. Oxidation	497
7.1. Alloying of Hard Coatings to Improve Oxidation Resistance	497
7.2. Self-Adaptation by Oxidation	499
8. Conclusions and Outlook	500
Acknowledgments	502
References	502

12. Optimization of Nanostructured Tribological Coatings 511

Adrian Leyland and Allan Matthews

1. Introduction	511
2. The Significance of H/E in Determining Coating Performance	513
3. Practical Considerations for Vapor Deposition of Nanostructured Coatings	517
4. Design and Materials Considerations for Metallic-Nanocomposite and Glassy-Metal Films	518
4.1. Background to Metal Nanocomposite Films	518
4.2. Design Considerations	520
4.3. Materials Selection for Nanostructured and Glassy Films	522

5. Examples of PVD Metallic Nanostructured and Glassy Films	526
5.1. CrCu(N) and MoCu(N) Nanostructured Films	526
5.2. CrTiCu(B,N) Glassy Metal Films	528
6. Adaptive Coatings	531
7. Summary	533
References	534
13. Synthesis, Structure, and Properties of Superhard Superlattice Coatings	539
<i>Lars Hultman</i>	
1. Introduction	539
2. Growth of Superlattice Films	540
3. Origin of Superhardening	543
4. Mechanical Deformation and Wear Mechanisms	545
5. Conclusions	551
References	552
14. Synthesis Structured, and Applications of Nanoscale Multilayer/Superlattice Structured PVD Coatings	555
<i>P. Eh. Hovsepian and W.-D. Münz</i>	
1. Aspects of Industrial Deposition of Nanoscale Multilayer/Superlattice Hard Coatings	555
1.1. Introduction	555
1.2. Production Aspects	557
1.3. Arc Bond Sputtering Interface	562
1.4. Main Criteria Defining Superlattice Structure	568
1.5. Texture and Residual Stress	577
1.6. Mechanical and Tribological Properties	583
2. Industrial Applications of Various Nanoscale Multilayer/Superlattice Structured PVD Coatings	586
2.1. Application-Tailored Superlattice Coating Family	586
2.2. Superlattice Coatings Dedicated to Serve High-Temperature Applications	587
2.2.1. Structure and High-Temperature Behavior of TiAlCrN/TiAlYN and TiAlN/CrN Nanoscale Multilayer Coatings	587
2.2.2. Application of TiAlCrN/TiAlYN in Dry High-Speed Cutting Operations	592