Preface

We live in an interesting time for materials scientists and engineers, when new advanced technology gives us the ability to control structure and properties at the micro- and nanoscale, and when new experimental discoveries in biology give us the insight of how materials and tissues in living nature achieve their remarkable properties. At this interface, the new fields of advanced, nanostructured, smart, functional, and biomimetic materials have emerged. This book describes this new and expanding area of materials that have the ability for self-organization, including self-healing, self-lubricating, and self-cleaning properties. Self-healing is the ability of a material to repair damage, such as a crack or void. Most living organisms can repair minor or moderate damage in their tissues. This ability is a result of a complex hierarchical organization of biological systems. A living tissue has many mechanisms sometimes acting simultaneously and complementing each other, which implement partial or complete self-repair, and this can be a complicated process with many stages. Most artificial or engineered materials do not have the ability for self-healing and tend to deteriorate irreversibly with time due to wear, fatigue, creep, fracture, corrosion, erosion, and other modes. Degradation and wear limit the lifespan of devices, and can cause a catastrophic failure leading to economic loss and even to the loss of human lives. Therefore, deterioration is a significant problem in many areas of engineering. For this reason, creating self-healing artificial materials has always been a dream of engineers.

Recent advances in nanoscience and technology, biotechnology, and other areas have enhanced our ability to control the structure of materials at various scale levels, from the macroscale down to the nanoscale and the atomic and molecular levels. It is becoming possible to build micro- and nanostructured materials as well as to create complex hierarchical structures. Because of these advances, it is now possible to design and synthesize certain artificial self-healing materials. While the area of self-healing materials is still emerging, most progress has been made with polymeric materials, concrete, and some ceramics. The area of self-healing cracks has been around for some time, and many concepts of self-healing materials are borrowed from it; however, considerable improvement is required before these materials can be widely used. Certain advances have been made with metallic self-healing materials, but the field remains in its infancy due to numerous problems that must be overcome to create successful self-healing composite alloys.

Strictly speaking, there are two types of self-healing: autonomous and nonautonomous. While autonomous self-healing implies no external intervention at all, nonautonomous healing implies certain human intervention, for example, heating a material to initiate the repair process. Most self-healing systems suggested so far use some kind of healing agent, often a liquid or a solid with a low melting point, embedded into the matrix of the composite material. When activated either by the deterioration process itself or by an external intervention such as heating, the agent is released and seals the void or crack by solidifying or through a chemical reaction. Another approach involves incorporation of shape memory alloy fibers in metallic matrices. The shape memory alloys stretch when subjected to tensile stress leading to cracks in the matrix. Upon heating the composite, the shape memory alloys shrink to the original length, compressing the crack and shutting the crack closed. Liquation of matrix at crack surfaces due to heating causes the compressed crack surfaces to weld to each other sealing the crack.

Since living nature often provides solutions that are superior to human technology, many scientists are trying to learn from nature and mimic its approaches to engineering problems. Mimicking nature for engineering applications is called biomimetics or bionics. While a true biomimetic approach would imply mimicking and copying the mechanisms used in living nature, a less extreme approach considers nature a source of inspiration for an engineer leading to so-called "bio-inspired" systems and materials. In most situations nature's solutions cannot be mimicked directly, so an adjustment for engineering applications is required. Several ideas have been suggested for biomimetic self-healing, including an artificial vascular system that provides circulation of a healing liquid to the damaged area or nanoparticles serving as artificial leucocytes loaded with a healing agent that stream to the crack or void.

The surface is the most vulnerable part of most engineering components. Not surprisingly, most deterioration – such as wear – occurs at the surface of a body or at the interface between contacting bodies. For this reason, in this book we pay special attention to self-healing and self-organization processes that occur at the interface. One important area of study is self-lubrication. Most technical systems with sliding parts require lubrication to reduce friction and wear. A system that provides low friction and wear without external lubrication is called a self-lubricating system, and a material that can be used in such a system is called a self-lubricating material.

The term "self-lubrication" has been used for more than two decades, and it refers to several methods and effects that reduce friction or wear. Among these methods is depositing self-lubricating coatings that are either hard (to reduce wear) or with low surface energy (to reduce adhesion and friction) or have a crystal structure, which facilitates formation of protective layers on the surface. Besides coatings, self-lubrication can mean the development of metal, polymer, or ceramic-based composite self-lubricating materials, often with a matrix that provides structural integrity and a reinforcement material that provides low friction and wear.

Many nanocomposites which exhibit very low friction and wear have become a focus of this research, as well as numerous attempts to include nanosized reinforcement, carbon nanotubes, graphene, and fullerene C_{60} molecules in a variety of matrices and with lubricants. Simple models assume that these large molecules and nanosized particles serve as "rolling bearings" that reduce friction; however, it is obvious now that the mechanism can be more complicated and sometimes may involve self-organization. For example, dynamic self-organization is thought to be responsible for self-lubrication in experiments at atomic resolution conducted with atomic force microscopy and other high-resolution techniques involving TEM. A different approach involves a layer of lubricant that is formed in situ during friction due to a chemical reaction. Such a reaction can be induced in situ by mechanical contact, such as, a copper protective layer formed at a metallic frictional interface due to the selective transfer of Cu ions from a copper-containing alloy (e.g., bronze) or from a lubricant. A protective layer can be formed with a chemical reaction of oxidation or a reaction with water vapor. For example, a self-lubricating layer of boric acid (H_3BO_3) is formed as a result of a reaction of water molecules with a B_2O_3 coating. Another type of self-lubricating material involves lubricant embedded into the matrix, or sometimes, inside microcapsules that rupture during wear and release the lubricant. Surface microtexturing provides holes and dimples that would serve as reservoirs for lubricant and can be viewed as another method of providing self-lubrication. We should mention that self-lubrication is observed in many biological systems, and that the term "self-lubrication" is also used in geophysics where it refers to abnormally low friction between tectonic plates that is observed during some earthquakes.

Friction has been traditionally viewed as a process that leads to irreversible energy dissipation and wear. Today it is clear that friction can also lead to self-organization. This is because frictional sliding is a nonequilibrium process which involves numerous nonlinear effects. In particular, due to positive feedback, even a steady frictional system can be driven away from equilibrium by various tribochemical processes as well as mechanical and thermal effects such as thermoelastic instabilities. In that case, the steady state loses its stability, and the system reaches a limiting cycle with so-called secondary structures formed that can reduce friction and wear. It was shown since the 1980s that many dynamic effects associated with frictional sliding, avalanche, landslide, and earthquake formation deal with so-called self-organized criticality.

Self-cleaning is another phenomenon related to self-organization at an interface. Leaves of many water-repellent plants, such as the lotus, have the ability to emerge clean even from dirty water. This is due to the special microstructure of their surface. Such a microstructure leads to superhydrophobicity (contact angles with water greater than 150°). The phenomenon of roughness-induced superhydrophobicity and self-cleaning is called the lotus effect. Due to advances in surface microstructuring of materials it became possible to create artificial biomimetic surfaces that use the lotus effect. There is a great need for such nonadhesive and self-cleaning materials and surfaces, especially for small devices. With the decreasing size of a device, the surface-to-volume ratio grows, and surface forces, such as friction and adhesion, tend to dominate over volume forces. Therefore, adhesion is a challenging problem for small-scale applications, while the lotus effect provides a promising way of designing nonadhesive surfaces. In many senses superhydrophobicity is similar to self-lubrication as the former leads to the reduction of friction between water and a solid surface due to surface micro- and nanostructuring, whereas the latter leads to the reduction of friction between two solid surfaces due to microstructuring or surface modification.

While the conventional lotus effect provides the ability to repel water and contamination particles which tend to be washed away with the repelled water, it is important also to be able to repel organic liquids, such as oils. This is a much more difficult task because organic liquids have much lower surface energy than water. The ability to repel organic liquids is called oleophobicity, and significant progress has been made in achieving roughness-induced oleophobicity. Synthesis of micro- and nanocomposites with engineered structure and reinforcement presents a great opportunity for creating self-cleaning materials.

One of the most remarkable features of biological systems is the hierarchical organization of their structure. Hierarchical structure allows them to achieve flexibility and optimization of desired properties. Not surprisingly, hierarchical organization and multiscale structure play a prominent role in the area of biomimetic materials. Hierarchical structures are found at the surface of a lotus leaf, a water strider leg, bird feathers, a gecko toe, and fish scales. These structures play a prominent role in self-cleaning.

One of the main tasks of materials science and engineering is to establish structure–property–processing–performance relationships for a given system. However, currently, self-healing, self-lubricating, and self-cleaning materials are designed and produced using the trial-and-error approach since there is no general theory of these phenomena that would relate their quantitative structural characteristics to their self-organizing properties. On the other hand, it can be seen from the above that there are many common features among these phenomena. First, most of them involve macro-, micro-, and nanostructuring. Second, they often involve self-organization. Third, many of these phenomena are observed in living nature. It is, therefore very important to identify common mechanisms in all these processes, and to identify central design themes and structural parameters that control the self-healing, self-lubricating, and self-cleaning properties.

Self-organization became a topic of active theoretical and experimental research in physics and chemistry in the middle of the last century when many self-organizing systems were discovered or investigated, such as the *Bénard cells* in boiling water of the Belousov–Zhabotinsky oscillating chemical reaction. On the other hand, it was understood that self-organization in physical, chemical, biological, and even social systems has many typical features that could be described by the methods of nonequilibrium thermodynamics. Significant results were achieved in understanding self-organization and its relation to nonequilibrium (irreversible) thermodynamics. At the same time many new examples of self-organizing systems in nature and technical applications were found. However, the general principles of self-organization and nonequilibrium thermodynamics in materials have not been applied to the study of self-healing, self-lubricating, and self-cleaning materials. One of the purposes of this book is to close this gap.

The monograph is divided into three parts. The first chapter introduces basic concepts and summarizes several fields of research that are relevant to this multidisciplinary book, so that self-healing, self-lubricating, and self-cleaning materials are reviewed. Our purpose is to discuss very recent experimental findings and emerging design methods in these fields, and at the same time we attempt to provide a significant level of theoretical generalization. We view these three fields as special cases of self-organizing materials and surfaces, and thus we attempt to generalize by applying the methods of nonequilibrium thermodynamics. This is what makes our book different in comparison with similar books in the area. Each of the three parts follows the same logical organization of the material. First, we present currently known basic experimental facts, many of which were discovered in recent years or decades. After that, a detailed theoretical analysis is presented, and additional experimental observations are discussed in light of the theoretical analysis. Finally, practical design considerations for emerging materials and applications are formulated.

The book is intended for research scientists, graduate students, and engineers who want to familiarize themselves with the new and exciting area of self-healing, self-lubricating, and self-cleaning materials and surfaces.

Some of the work presented in Parts I and II of the book was done in support of US Army TARDEC (under TACOM contracts # W56HZV-04-C-0784 and W56HZV-08-C-0716). The material in these sections is also in part based upon work supported by the National Science Foundation under Grant No. OISE – 0710981. The research reported in Chap. 7 was partially supported by the University of Wisconsin-Malwaukee (UWM) Research Growth Initiative grant. The research reported in Chaps. 12 and 13 was partially supported by UWM Research Foundation Bradley Catalyst grant and by NSF IUCRC for Water Policy and Equipment grant. We would like to thank our colleagues from the UWM for their help in preparation and review of the manuscript of this book and very helpful and stimulating discussions: Prof. Ryoichi Amano, Drs. Benjamin Schultz, Jose Omar Martinez-Lucci, and J. B. Fergusson, as well as Messrs. Andrew Ruzek, Vahid Mortazavi, Vahid Hejazi, Mehdi Mortazavi, Anthony Macke, Gonzalo Alejandro Rocha Rivero, Dan Kongshaug, Andrew Braun, Shobhit Misra, Dean Meilicke, and Ms. Katherine Connerton for their help with text preparation.

Milwaukee, WI, USA

Michael Nosonovsky
Pradeep K. Rohatgi

http://www.springer.com/978-1-4614-0925-0

Biomimetics in Materials Science
Self-Healing, Self-Lubricating, and Self-Cleaning Materials
Nosonovsky, M.; Rohatgi, P.K.
2012, XXVI, 418 p., Hardcover
ISBN: 978-1-4614-0925-0