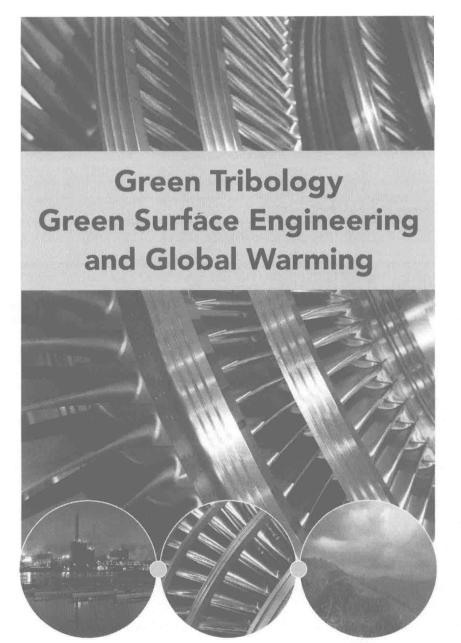


Green Tribology
Green Surface Engineering
and Global Warming



Ramnarayan Chattopadhyay





Ramnarayan Chattapadhyay



ASM International® Materials Park, Ohio 44073-0002 asminternational.org Copyright © 2014 by ASM International® All rights reserved

No part of this book may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise, without the written permission of the copyright owner.

First printing, July 2014

Great care is taken in the compilation and production of this book, but it should be made clear that NO WARRANTIES, EXPRESS OR IMPLIED, INCLUDING, WITHOUT LIMITATION, WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE, ARE GIVEN IN CONNECTION WITH THIS PUBLICATION. Although this information is believed to be accurate by ASM, ASM cannot guarantee that favorable results will be obtained from the use of this publication alone. This publication is intended for use by persons having technical skill, at their sole discretion and risk. Since the conditions of product or material use are outside of ASM's control, ASM assumes no liability or obligation in connection with any use of this information. No claim of any kind, whether as to products or information in this publication, and whether or not based on negligence, shall be greater in amount than the purchase price of this product or publication in respect of which damages are claimed. THE REMEDY HEREBY PROVIDED SHALL BE THE EXCLUSIVE AND SOLE REMEDY OF BUYER, AND IN NO EVENT SHALL EITHER PARTY BE LIABLE FOR SPECIAL. INDIRECT OR CONSEQUENTIAL DAMAGES WHETHER OR NOT CAUSED BY OR RESULTING FROM THE NEGLIGENCE OF SUCH PARTY. As with any material, evaluation of the material under end-use conditions prior to specification is essential. Therefore, specific testing under actual conditions is recommended.

Nothing contained in this book shall be construed as a grant of any right of manufacture, sale, use, or reproduction, in connection with any method, process, apparatus, product, composition, or system, whether or not covered by letters patent, copyright, or trademark, and nothing contained in this book shall be construed as a defense against any alleged infringement of letters patent, copyright, or trademark, or as a defense against liability for such infringement.

Comments, criticisms, and suggestions are invited, and should be forwarded to ASM International.

Prepared under the direction of the ASM International Technical Book Committee (2013–2014), Margaret Bush, Chair.

ASM International staff who worked on this project include Scott Henry, Senior Manager, Content Development and Publishing, Karen Marken, Senior Managing Editor; Sue Sellers, Editorial Assistant; Madrid Tramble, Manager of Production; and Kate Fornadel, Senior Production Coordinator.

Cover images: Counterclockwise from the top—Enlarged image of small steam turbine (courtesy of Alstom); Stora Enso pulp and paper mill, Oulu, Finland (courtesy of Estormiz); Detail of nuclear steam turbine (courtesy of Alstom).

Library of Congress Control Number: 2014932926 ISBN-13: 978-1-62708-064-4 ISBN 10: 1-62708-064-3 SAN: 204-7586

> ASM International® Materials Park, OH 44073-0002 asminternational.org

Printed in the United States of America

Preface

Leonardo da Vinci's main concern in his work as an engineer and inventor was with friction and its effect during movement of his simple mechanical designs. Friction continued to dominate studies of mechanical systems for the next three centuries. Wear of materials became an important subject in the mid-20th century. It was Peter Jost's report in 1966 that gave a big boost to the subject of *tribology* (a name coined by Jost). It transformed the discipline from a study of mere friction to the study of friction and wear of industrial equipment and machinery. The effects of wear bleed billions of dollars each year from the industrial economy.

In the United States alone, industries annually lose \$200 billion due to wear and \$300 billion due to corrosion. Surface engineering has played a key role in reducing colossal tribological losses. Since the 1970s, tremendous progress has been made in both triboscience and surface engineering to provide innovative solutions for reducing wear loss in advanced equipment and machinery that operate in hostile environments.

I took the assignment, in the late 1970s, to set up an advanced wear-control research center in India. This center was established for a large multinational company, which had a worldwide network providing wear-protection solutions using surface engineering; there was an urgent need for research and development to cater to the fast-growing market needs in India. Life-cycle extension of wear-prone components, beyond the original design life in the given wear (application) environment, by innovative surface-engineering solutions was the primary objective of research at the center. Wear surfacing at the original equipment manufacturing stage led to life-cycle extension of the new component, while repeated resurfacing during maintenance and repair stages extended the life span by several fold. The extended life cycle of vital equipment led to increased productivity and reduced the need to buy new equipment/components. This resulted in savings of billions of dollars for major industries and conservation of nonrenewable mineral resources by billions in tons of metallic resources.

The emphasis was on wear reduction, leading to life-cycle improvement and a consequential gain in conserving natural resources. All of these areas are extensively covered in my first book, *Surface Wear: Analysis, Treatment, and Prevention* (ASM International, 2001). My second book, *Advanced Thermally Assisted Surface Engineering Processes* (Springer, 2004), deals with advanced surface-engineering processes based on innovative heat sources, such as laser, plasma, ion, solar beam, arc, and spark, to minimize wear and extend component life cycles.

The documentary film *An Inconvenient Truth* (2006), featuring former U.S. Vice President Al Gore, increased awareness of the process of global warming and its alarming effects on climate change. The Kyoto Protocol to the United Nations Framework Convention on Climate Change made it mandatory for industries in 132 signatory nations to reduce greenhouse gas emissions; nonsignatory countries such as the United States opted to make voluntary reductions. Burning fossil fuel to generate power is the main source of anthropogenic greenhouse gases. To cater to the needs of a growing population, industries must grow and more energy is needed. In turn, this leads to emission of more anthropogenic greenhouse gas. Efforts to reduce emissions and to slow the pace of global warming have focused primarily on the development of alternative sources of energy.

All of these aspects are discussed in detail in the book *Origin, Significance and Management of Global Warming* (Global Vision Publishing House, India, 2012) that I co-authored with my wife, Mandira (a Ph.D. and professor of geography).

An alternative technoecologically viable option for reducing greenhouse gas emissions is to make industries more energy efficient by minimizing energy losses due to tribological interactions. Green-engineering processes, such as green tribology and green surface engineering, enable efficient conversion of energy from one form to another. Green technologies provide enormous opportunities for limiting global warming within a safe temperature zone and for conserving natural resources.

The emphasis in green tribology and surface engineering is improvement in energy efficiency by reducing energy losses due to wear and friction. Green surface engineering protects the surface against wear and reduces friction. Green tribology and surface engineering extend the life span of critical components in severe wear environments. This leads to improvement in process efficiency, enables component operation in extreme conditions to further increase efficiency, and decreases the carbon footprint of the components. I have attempted to cover all of these areas in this book, with a view to minimizing global warming.

This book is designed to help industries reduce financial loss due to wear and friction and improve productivity and energy efficiency by producing green products with a low carbon footprint. The major emitting industries, such as power plants, transportation, steel, cement, paper and pulp, and machine tool industries, can benefit most by improving energy efficiency. Industries paying for emission in excess of the specified limits should plan to become carbon neutral. This book should be of special in-

terest to manufacturers and suppliers of surface-engineering consumables and equipment; wear-control service centers, including job shops and maintenance and growth shops attached to industries; and corporate (involved in corporate social responsibility). This book can provide valuable guidance to researchers engaged in new green technologies, both in academic institutes and research centers.

I gratefully acknowledge the help and support that I have received from various sources. Further, I wish to thank various authors and publishers for permitting the use of their data and diagrams in this book.

My thanks to Scott Henry (ASM International) in getting the book proposal approved. In addition to editing, Karen Marken (ASM International) has helped and guided me in the whole process of completing the manuscript in the shortest possible time. It would not have been possible to publish this book without her complete involvement in the project. A special thanks to Karen and the ASM International staff including Kate Fornadel and Liz Marquard.

I am grateful to Professor Joaquin Lira-Olivares, Director of the Surface Engineering Center at Simón Bolíver University in Caracas, Venezuela, for his support in all my earlier projects, including the current one. Thanks are also extended to John Dey for valuable support.

My family has been very supportive during this project. My younger son, Raunak, is an active and enthusiastic supporter of my writing and buys the first copy of each new book. Robin, my daughter in law, has helped me in using library facilities. My elder son, Romik, and grandsons, Ryan and Ronan, are happy to see me writing. Thanks to all of them for their support. Finally, I would like to thank my wife, Mandira, who has given her full support to my book-writing activities. I have spent many long hours engaged in research and writing, and I would not have been able to do it without her support.

R. Chattopadhyay January 2014

About the Author

Dr. R. Chattopadhyay earned B.S. and Ph.D. degrees in metallurgical engineering from the University of London. He is a member of ASM International and the American Welding Society and is a life member of several Indian professional bodies on metal, materials, welding, powder metallurgy, and tribology. He was a fellow of the Institute of Materials, Minerals, and Mining (United Kingdom) and a chartered engineer of the Engineering Council (United Kingdom) for 30 years.



Dr. Chattopadhyay's first assignment was to develop alloy steels at the National Metallurgical Laboratory (India). In the early 1970s, he played a major role in developing the first commercial heats of microalloyed high-strength, low-alloy steels in India.

Highlights of his next job, at Tube Investments of India (Madras), included failure investigation work he conducted at Tube Investments Research Laboratories (Hinxton Hall, Cambridge, United Kingdom), which led to the first-ever product liability case that was won in India.

Dr. Chattopadhyay established a world-class premier research center on wear control at EWAC Alloys Limited (Mumbai), a subsidiary of Larsen & Toubro Limited, in collaboration with Castolin Eutectic (Lausanne, Switzerland). As a founder, he pioneered work on the conservation of non-renewable resources and energy savings for all major industries in India, including aerospace (gas turbine), power (both hydro and thermal), automobile, railway, cement, steel, paper and pulp, and petrochemical.

Dr. Chattopadhyay has presented and published more than 100 research and technical papers at national and international conferences on wear, surface engineering, thermal spray, welding, materials science, and powder metallurgy. He has conducted courses for professional organizations, industries, and academic institutions. He was an examiner of doctoral the-

ses and a member of the faculty selection committee at the Indian Institute of Technology (Bombay).

Dr. Chattopadhyay is the author of *Surface Wear: Analysis, Treatment, and Prevention*, ASM International, Materials Park, OH, USA (2001), and *Advanced Thermally Assisted Surface Engineering Processes*, Kluwer Academic Publishers, Norwell, MA, USA (2004). In 2004, he received an appreciation letter from the President of India, Dr. A.P.J. Abdul Kalam, that cited these two books as "very useful contribution[s] for surface engineering." With his wife (Professor Mandira Chatterjee, Ph.D.) as coauthor, he also wrote *Global Warming: Origin, Significance and Management*, Global Vision Publishing House, New Delhi, India (2012).

Dr. Chattopadhyay received the Jindal Gold Medal from the Indian Institute of Metals for his contribution to the steel industries. In 2006, he also received the title of honorary professor at the Center for Surface Engineering, Simon Bolivar University (Caracas, Venezuela), "for his selfless support and collaboration" in guiding doctoral students. The Tribological Society of India included his name on their list of Eminent Tribologists.

Introduction

The absorption of infrared (heat) from solar beams by carbon dioxide and other greenhouse gases results in warming of the Earth's atmosphere. Carbon dioxide can stay in the atmosphere for 100 years and thus has a high global-warming potential. Anthropogenic (man-made) emissions due to growing industrial activities have resulted in the progressive increase in carbon dioxide. Industries using fossil fuels, such as the power-generation and transport sectors, are major direct emitters of greenhouse gases, mainly carbon dioxide. Other industries using power generated by fossil fuels are indirectly responsible for greenhouse gas emission. Improvements in energy efficiency in all sectors can substantially reduce greenhouse gas emissions.

Green engineering is about overall improvement in energy to negate global warming. Green tribology and surface engineering of materials have become key subjects to improve energy efficiencies in whole spectrums of industries. The loss of material and energy due to wear and friction occurs at the interacting surfaces in equipment and machinery. Surface-engineering techniques have been used to reduce material and energy losses and thus improve energy efficiency.

Recognition of the importance of green or eco-friendly tribology in negating global warming and therefore the possibilities of savings from major changes in ecological balance, climate, environment, and biomes has led to a paradigm shift in current tribological research toward green areas.

Tribology is the science of wear, friction, and lubrication of interacting surfaces in relative motion. Wear and friction result in material and heat loss from the interacting surfaces, thus reducing the efficiency of energy-transformation processes. Green tribological studies on wear, friction, and lubrication aim at improving energy efficiency by reducing wear and frictional losses. The wear coefficients of materials in different wear modes vary over a wide range. Appropriate selection of materials can lead to reduction in loss due to wear. Similarly, the coefficient of friction values vary widely in similar and dissimilar material pairs, thus providing the

opportunity to control frictional heat loss. In bearing applications, selection of polymeric materials within limiting pressure \times velocity ratios results in minimizing energy loss due to frictional heat generation. Wear of ceramic materials is inversely proportional to fracture toughness ($K_{\rm Ic}$) and remains constant over a range of temperatures before a sudden drop at higher temperatures leads to brittle failure. Ceramics for high-temperature applications can be selected according to the temperature range for constant $K_{\rm Ic}$ values.

Wear is not an intrinsic property of the material, and it occurs at the working surface. It is therefore possible to control wear by engineering the surface properties of the solid. The major goal of green surface engineering is to improve energy efficiency by reducing wear and friction loss through modification of surface properties. The surface-modification processes include peening, electroplating, electroless coating, and thermal processing. The four major thermal processes are diffusion of elements (interstitials such as carbon, nitrogen, and boron, and substitutionals such as chromium and aluminum), vapor-phase deposition (physical vapor deposition and chemical vapor deposition), weld overlay (manual metal arc welding, submerged arc welding, laser, plasma-transferred arc, and spark deposition), and thermal spraying (high-velocity oxyfuel, plasma, and cold spray). The coating process is selected on the basis of application requirement.

Reduction in material and energy losses can lead to a substantial increase in working life. Life-cycle assessment in wear processes (abrasion, adhesion, and erosion), fatigue, creep, and fatigue crack propagation with stress intensity (fracture toughness) has been found useful to assess and monitor improvement in the working life of engineering components. Life-cycle improvement of equipment also leads to conservation of material.

It is necessary to find a wear-protection system based on the application requirements. Application-based tribological studies on engineered surfaces in major emitting industries (energy, transport, mining, cement, steel, and paper and pulp) have enabled improved energy efficiency by substantial reduction of wear and frictional losses in these sectors. The amount of energy savings in major applications by green tribological and surface-engineering practices can result in a corresponding reduction of greenhouse gas emission of more than 10% of the current global emission figure. Reduction in anthropogenic greenhouse gas emission by 10% or more will have a significant effect on global warming.

Contents

Preface	. V
About the Author	ix
Introduction	xi
CHAPTER 1 Introduction to Global Warming	1
The Earth's Atmosphere. Greenhouse Gas Effects. Global Warming Potential Global Warming Projection Effects of Climate Change due to Global Warming. Current Emissions Global Emission Patterns. Green Technologies to Reduce Global Warming.	9 10 13 14 16
CHAPTER 2 Green Tribology 2	29
History of Tribology and Green Tribology Economic and Energy Loss due to Wear and Friction Wear of Material Abrasion Adhesion and Friction Erosion Surface Fatigue Wear Corrosion Thermal Wear Wear of Ceramic Materials	31 32 40 51 67 76 79 34

CHAPTER 3 Green Surface Engineering	01
Solid Surfaces and Properties10Green Surface Engineering Processes1Mechanical Surface-Engineering Processes1Electrochemical Processes1Chemical1Thermally Assisted Processes1Vapor-Phase Deposition1Diffusion1Thick-Film Overlays1Special Techniques for Protection against Wear1Summary18	11 12 17 19 20 22 38 48 76
CHAPTER 4 Life-Cycle Assessment	93
Comparative Life Cycle Using Archard's Equation	97 23 30
CHAPTER 5 Tribological Applications	39
Cement Industries 28 Steel Industries 29 Paper and Pulp Industry 29 Applications, Energy Savings, and Reduction in Anthropogenic Emissions 29	44 59 75 80 86 92 97
Today 24	1.0

CHAPTER 1

Introduction to Global Warming

THE PRESENCE OF INCREASING QUANTITIES of anthropogenic (man-made) greenhouse gases in the atmosphere has been found to be responsible for average atmospheric global temperature rise, a phenomenon known as global warming (Ref 1.1). Global warming requires early remedies in order to avoid a drastic change in the climate and the accompanying damaging results. The Fourth Assessment Report (2007) of the United Nations Intergovernmental Panel on Climate Change (IPCC) (Ref 1.2) warns that serious effects of warming have become evident. The Kyoto Protocol, an international treaty that assigns obligations to industrialized countries to reduce greenhouse gas emissions, recommends the "enhancement of energy efficiency in relevant sectors of the national economy" to negate global warming (Ref 1.3). Green engineering efforts to tackle the global warming problem are of recent origin and include triboscience and related surface engineering. These efforts play a significant role in improving the energy efficiency of industrial processes and help in reducing the rate of average temperature increase across the globe.

The Earth's atmosphere (Greek *atmos*, or vapor, plus *sphaira*, or sphere) consists of a mixture of gases. The major constituents (99%) are a mechanical mixture of nitrogen and oxygen. They have little effect on the atmospheric temperature, weather, and climate. The presence of variable quantities, in parts per million level of carbon dioxide, has a significant role in determining the atmospheric temperature.

Absorption of the infrared portion (heat) of the solar beam by carbon dioxide is the main source of heating the Earth's atmosphere. Carbon dioxide can remain in the atmosphere for 100 years, thus increasing the global heating potential over a long period. Nature has perfected the system of retaining the residual quantities of carbon dioxide in the atmo-

sphere. This is done by dynamic cycling through other spheres, such as the biosphere, geosphere, and hydrosphere, thus providing optimum temperatures for sustaining life on Earth (Ref 1.1).

However, excessive emissions by industries in the man-made sphere, that is, the anthrosphere, have resulted in the loss of the dynamic balance, causing a dramatic increase of carbon dioxide in the atmosphere. Charles David Keeling, "father of global warming," studied this fact for decades (Ref 1.4).

Industries using fossil fuels, such as the power-generation and transport sectors, are major direct emitters of greenhouse gases, mainly carbon dioxide. Other industries using power generated by fossil fuels are indirectly responsible for greenhouse gas emission. The energy consumption figures are directly related to the quantities of greenhouse gas emission. Energy efficiency and conservation of energy and material in industries are key instruments to reduce greenhouse gas (GHG) emissions. Green or eco-friendly technology plays a significant role in improving energy efficiency and conservation of resources.

A review of the Earth's atmosphere and how it is affected by carbon dioxide (CO₂) is discussed in this chapter. The potential of global warming and its effects on climate change are also reviewed. The chapter concludes with an introduction to green technologies.

The Earth's Atmosphere

The atmosphere is one of the four spheres, the other three being the hydrosphere, biosphere, and geosphere. Unlike the atmosphere in other planets, the presence of free oxygen, water vapor, and carbon dioxide make the Earth's atmosphere a unique entity for the existence and survival of life on the planet.

The five atmospheric layers—troposphere, stratosphere, mesosphere, thermosphere, and exosphere (Fig. 1.1)—are classified by temperature and pressure. The ozone layer in the stratosphere filters out harmful ultraviolet rays from the solar beam before it reaches the troposphere, the layer closest to the Earth's surface (Ref 1.5).

The pressure drops uniformly across the layers from bottom to topmost layer. The atmosphere is most dense near the surface and thins out with height until it eventually merges with space (Fig. 1.2). The atmospheric temperature varies from one zone to another and also in each zone (Fig. 1.3). Each layer has its well-defined function, leading to the lowest layer just above the Earth's surface (the troposphere), with optimum conditions for survival and growth of man, animal, plants and all other living beings. The weather and climate are directly related to the conditions in the troposphere.

The troposphere is the layer of atmosphere under which we live; it contains 80% of the total mass of the atmosphere. The word *troposphere*

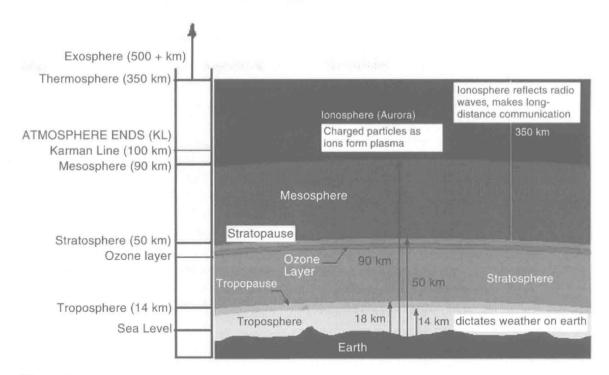


Fig. 1.1 Atmospheric layers above the Earth. Adapted from Ref 1.5

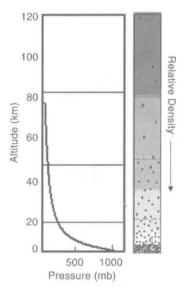


Fig. 1.2 Variation in pressure and density in different atmospheric layers. Source: Ref 1.1

means mixing, reflecting the fact that turbulent mixing plays an important role in the structure and behavior of the troposphere. Weather occurs in this layer. The thickness of the troposphere layer varies at different latitudes and with changing weather conditions. The thickness of the troposphere beginning at the Earth's surface can vary between shallow layers of

7 km (4 miles) at the poles in summer and deeper layers of up to 20 km (12 miles) at the equator.

The two types of gases present in the atmosphere are termed fixed and variable components. The fixed components (Table 1.1) consist mainly of nitrogen and oxygen, together amounting to almost 99%, but play no role in the weather.

The variable components, constituting less than 1% of atmospheric gases, have a greater influence on both short-term weather and long-term climate. The minor gases, such as water vapor, carbon dioxide ($\rm CO_2$), methane ($\rm CH_3OH$), nitrous oxide ($\rm N_2O$), and sulfur dioxide ($\rm SO_2$), absorb the infrared heat emitted by solar beams, thus warming the atmosphere. The variation in water vapor in the atmosphere changes the relative humidity.

These gases can remain in the atmosphere for a long period (100 years or more), creating what is known as the greenhouse effect. These gases are known as greenhouse gases (Table 1.2).

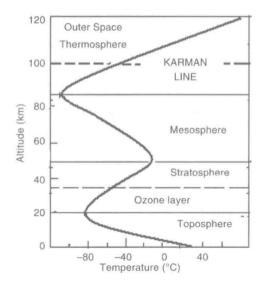


Fig. 1.3 Variation in temperature in different atmospheric layers. Source: Ref 1.1

Table 1.1 Constant components of atmosphere

Gases Percentage, vol%

Gases	Percentage, vol%
Nitrogen	78.1
Oxygen	21.0
Argon	0.897
Neon	bal
Helium	bal
Krypton	bal
Xenon	bal

Note: Proportions remain constant over time and location. Source: Ref 1.1