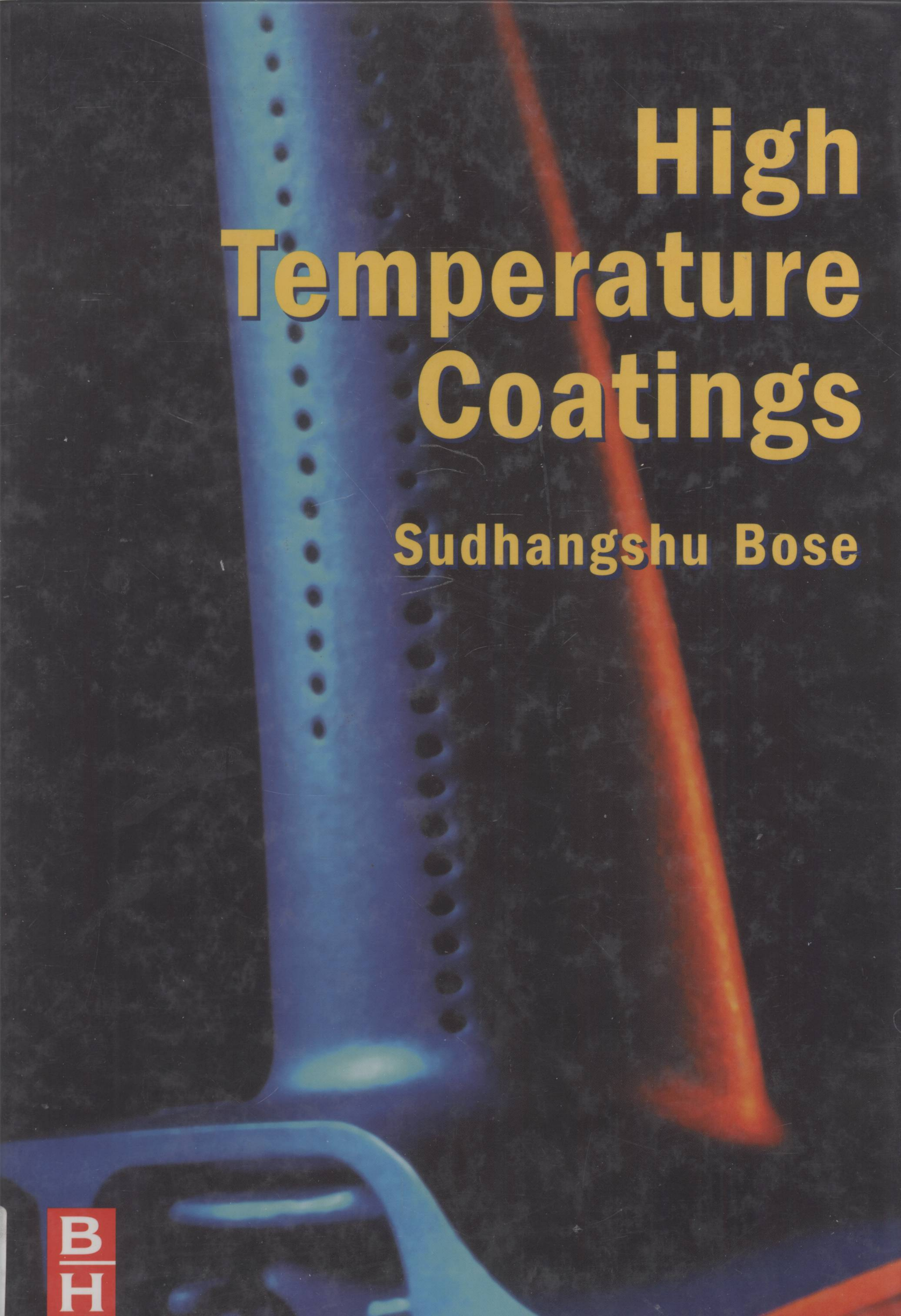

High Temperature Coatings

Sudhangshu Bose

High Temperature Coatings

Sudhangshu Bose

ELSEVIER

AMSTERDAM • BOSTON • HEIDELBERG • LONDON
NEW YORK • OXFORD • PARIS • SAN DIEGO
SAN FRANCISCO • SINGAPORE • SYDNEY • TOKYO

Butterworth-Heinemann is an imprint of Elsevier

Butterworth–Heinemann is an imprint of Elsevier
30 Corporate Drive, Suite 400, Burlington, MA 01803, USA
Linacre House, Jordan Hill, Oxford OX2 8DP, UK

Library of Congress Cataloging-in-Publication Data
Bose, Sudhangshu.
High temperature coatings/Sudhangshu Bose.
p. cm.
ISBN-13: 978-0-7506-8252-7 (hardcover : alk. paper)
ISBN-10: 0-7506-8252-3 (hardcover : alk. paper) 1. Refractory coating.
2. Heat resistant materials. I. Title.
TS695.9.B67 2007
671.7′3—dc22
2006035922

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

ISBN 13: 978-0-7506-8252-7
ISBN 10: 0-7506-8252-3

For information on all Butterworth–Heinemann publications visit our Web site at www.books.elsevier.com

Printed in the United States of America
07 08 09 10 11 10 9 8 7 6 5 4 3 2 1

High Temperature Coatings

This book is lovingly dedicated to my wife Juthika and our two sons, Krishnangshu and Jayanta. They allowed me the luxury of not attending to many chores for the excuse of becoming a book author.

About the Author

Dr. Sudhangshu Bose is a Fellow and Manager at Pratt & Whitney, the manufacturer of Gas Turbine and Rocket Engines. He is also an Adjunct Professor at the Hartford, Connecticut campus of Rensselaer Polytechnic Institute, Troy, New York. He holds a Ph.D in Materials Science and Engineering from University of California, Berkeley, having previously obtained B.Sc (Honors) and M.Sc in Physics from Ranchi University, Ranchi, India. Dr. Bose has taught undergraduate and graduate level courses in Physics and conducted research in Materials Characterization by x-ray diffraction prior to completing the doctoral degree. For the last twenty-nine years at Pratt & Whitney and its sister divisions, Dr. Bose has conducted and managed research and development in advanced materials and processes including oxidation and corrosion in fuel cells and gas turbine engine, catalysis, high temperature coatings, superalloys, intermetallics, and ceramic matrix composites. He holds 14 patents and continues to teach high temperature alloys and coatings courses within Pratt & Whitney and at Rensselaer.

Preface

The idea of a book on high temperature coatings arose out of a need for teaching material for a semester long course for engineering students. Additionally, it would provide a resource of reference material for practicing professionals. It took the author several years during his forays into teaching to assemble the material in a balanced and logical format.

High temperature coatings belong to a technologically important, economically lucrative, intellectually fertile, and fast evolving field. It encompasses basic understanding of materials, principles of physical metallurgy and ceramics, environmental interactions, processing sciences and manufacturing techniques. There is a wealth of information available on various aspects of these coatings. However, the information is dispersed in myriads of technical journals, conference proceedings, handbooks, book chapters, published reports from the manufacturers in the industry, and users of coatings, as well as from National Laboratories and other organizations in a host of countries. The author had the fortune to have access to many of these resources, in addition to his own continuing experience in the aerospace industry spanning over a quarter of a century.

For the users of this book, a rudimentary knowledge of physics and chemistry is assumed. The fundamental concepts, which cover thermodynamic and kinetic principles as well as phases and phase diagrams, are described in the first two chapters. Basic understanding of structural alloys used in high temperature processes and equipment, notably gas turbine engines, which require high temperature coatings, is introduced in a separate chapter. Environmental interactions including oxidation and high temperature corrosion are discussed in Chapters 4 and 5. Metallic coatings for protection against oxidation and corrosion are covered in Chapter 6 in reasonable detail including processing, characterization, and properties. A number of processes traditionally used in the electronic industry to deposit thin films have been included because of their unique characteristics and slow but progressive adaptation to deposit thicker coatings in special cases. Thermal Barrier Coatings (TBC) for thermal protection are addressed in Chapter 7. For better flow and ease of understanding, this chapter is physically separated into three sections starting with an introduction in the beginning, plasma sprayed TBC in the middle, and Electron Beam TBC at the end, together with the literature references for the whole chapter. Non destructive inspection, coatings repair, and coating experience in the field are treated in the last three chapters. Extensive references are given for the readers to consult the original sources.

Obviously, the author benefited immensely from the work of many of the pioneers from the past and the present. One such individual is Dr. Bill Goward. The author is deeply grateful to Dr. Goward for his thoughtful review and constant guidance during the writing of the book. Professors Fred Pettit of University of Pittsburgh, Professor David Clarke of University of California, Santa Barbara, Professor Maury Gell of University of Connecticut, and Dr. Bob Miller of NASA Glenn Research Center, all of whom are prolific contributors to the knowledge base in the field of high temperature coatings, were very kind to review parts of the manuscript and provide suggestions for improvement. My special appreciation goes to Professor Ernesto Gutierrez-Miravete of Rensselaer, Hartford for his encouragement.

Elsevier's Joel Stein has been of immense help from the very beginning of this project, providing advice, encouragement, and the words of wisdom of a seasoned editor. I owe him my sincere thanks. Special thanks are also due to Shelly Palen of Elsevier for her editorial help and to Julie Ochs for her superb production of the manuscript.

The author has made every effort to correct inaccuracies and acknowledge the original sources including authors and publishers. He regrets any omissions.

My appreciation goes to the following sources and copyright owners for their permission to use excerpts, data, figures, tables, and art works:

Elsevier, John Wiley & Sons, Inc., Springer, Taylor and Francis, Maney Publishing, Blackwell Publishers, The Minerals, Metals, and Materials Society (TMS), American Society of Materials (ASM) International, The American Ceramic Society, American Society of Mechanical Engineers (ASME) International, American Institute of Physics, Science and Technology Letters, Annual Reviews, National Association of Corrosion Engineers (NAC), The Electrochemical Society, Praxair Technologies, Sulzer-Metco, Professor Jogender Singh (Pennsylvania State University), Drs. Jim Smialek and Bob Miller, both of NASA Glenn Research Center, Dr. Thomas Strangman of Honeywell, Department of Energy, United State Airforce, and the National Aeronautic and Space Administration.

Finally, I am thankful to Pratt & Whitney for permission to use examples from its collection of coatings, coated engine hardware, publications, and the photo of a turbine blade which appears on the cover of this book.

SUDHANGSHU BOSE

Manchester, Connecticut, USA
Sudhabose@gmail.com
2007

Table of Contents

Chapter 6

Chapter 7

Chapter 8

Chapter 9

Chapter 10

Chapter 1

INTRODUCTION

1.1 HIGH-TEMPERATURE ENVIRONMENT

A large number of industrial processes operate in very aggressive environments characterized by high temperature, increased temperature gradients, high pressure, large stresses on individual components, and the presence of oxidizing and corroding atmosphere, as well as internally created or externally ingested particulate material, which induces erosion and impact damage. A few representative examples of such processes are shown in Fig. 1.1 (Stroosnijder et al., 1994). Machines include aircraft gas turbine engines, steam turbines, industrial gas turbines, coal conversion, petroleum refining, and nuclear power generation. The generation of large amounts of heat and associated high component temperature lie at the heart of all of these processes. For example, in jet engines, fuel is mixed with highly compressed air and the mixture ignited. As a result of the heat generated, the air expands and works on the turbine to rotate it. The turbine in turn forces the compressor to rotate, which compresses the incoming air. The exiting exhaust gas creates thrust for propulsion. The gas temperature in modern gas turbine engines could well exceed 1650°C (3000°F) in the turbine section, with cooled parts reaching temperatures as high as 1200°C (2200°F). In coal gasifiers, coal reacts with steam at high temperatures to convert it into usable gas, which can be transported by pipelines and fed directly into processing plants. Process temperatures could be as high as 1650°C (3000°F) with component temperatures reaching 1090°C (2000°F). Process temperature is also high in petroleum refining as well as nuclear power generation. In petroleum refining, crude petroleum is catalytically cracked at high temperatures and fractionated into usable petroleum products such as liquid petroleum gas, gasoline, kerosene, diesel, heavy oils, plastics, asphalt, and coke. In nuclear power plants the heat from controlled fission of fuel elements, such as uranium and thorium, is used to produce steam, which is in turn fed to turbines to generate electrical power.

All these processes require materials of construction with high-temperature capability under load to meet performance and durability requirements. During operation, the structural materials of individual components degrade. In addition to fatigue and creep damage of structurally loaded components, the materials undergo oxidation, corrosion, and erosive wear. Typical temperatures seen in some of the industrial processes are compared in Fig. 1.2, benchmarked against melting points of some basic structural materials.

The strength ranges of a few potential materials of construction for high-temperature processes as a function of temperature are shown in Fig. 1.3 (Meetham, 1988). Properties of many of these engineering materials such as tensile, creep, and fatigue strength are generally optimized for maximum load-carrying capability, with less emphasis on the environmental resistance. As an example, turbine blades for jet engines are made of precipitation-strengthened nickel base superalloys, the precipitates being the gamma prime phase in a gamma phase matrix. One of the constituents of the alloys is aluminum, which participates in the formation

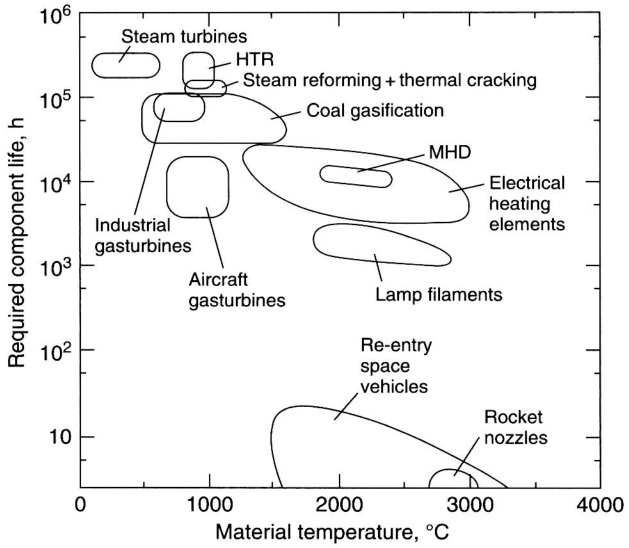

Figure 1.1 High-temperature processes with component temperatures and required lives (M. F. Stroosnijder, R. Mevrel, and M. J. Bennett, The interaction of surface engineering and high temperature corrosion protection, *Materials at High Temperatures*, 1994, 12(1), 53–66). Reprinted with permission from Science and Technology Letters.

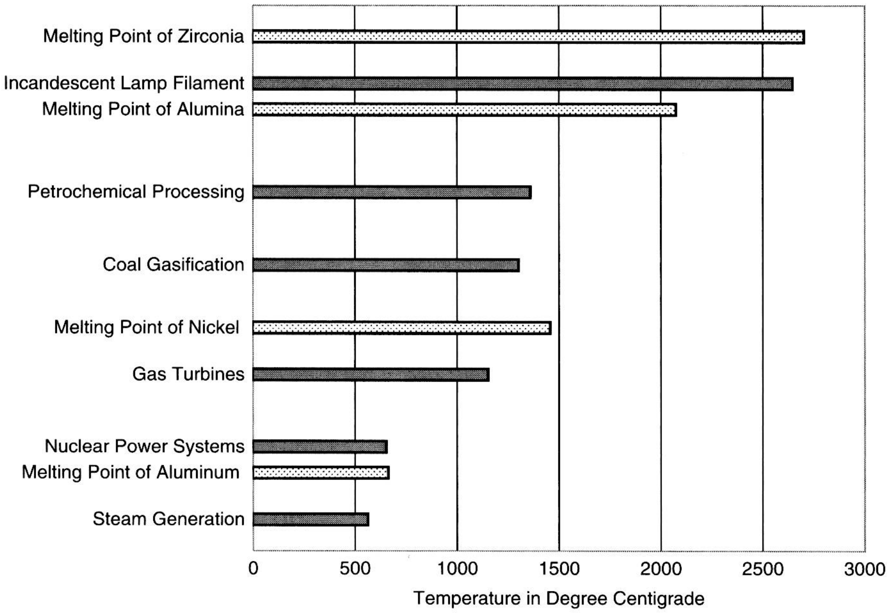

Figure 1.2 Typical temperatures for some industrial processes.

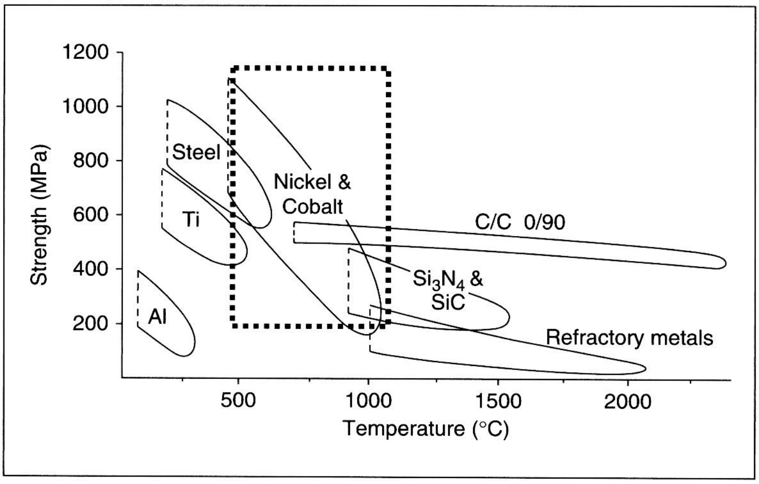

Figure 1.3 Temperature capabilities of classes of materials (G. W. Meetham, Requirements for and factors affecting high temperature capability, *Materials and Design*, 1988, 9(5), 247). Reprinted with permission from Elsevier.

of strengthening precipitates as well as in providing for oxidation resistance. Although higher aluminum content of the alloys increases high-temperature oxidation resistance, it is kept at a level below 6% to maximize creep strength. If such bare alloys are exposed to the environment of high-pressure turbine of modern gas turbine engines, they will degrade fast by several of the processes discussed below.

- *Oxidation*: The alloys do not have adequate levels of such critical elements as Al and Cr to impart oxidation resistance for the life of the parts. Increasing Al, therefore, would apparently be a logical solution to increase oxidation capability. However, a high Al level will lower the melting point of the alloys and their creep resistance, reducing, in turn, the load-bearing capability, a "must have" property of turbine blades and other turbine hardware.
- *High-Temperature Corrosion*: The Cr content of the majority of the alloys used in the turbine section of the gas turbine engine is below the requirement for corrosion resistance. Again, the reason for lower Cr content is to have other critical elements necessary to meet the structural capability requirement to carry load.
- *Heat Damage*: Two of the consequences of high-temperature exposure are oxidation and corrosion, as explained earlier. Additional damages due to cyclic exposure to high temperature in the presence of fluctuating stresses come about by the process of thermal fatigue. The strengthening of the alloys helps to some degree in developing resistance to fatigue cracking. The overall protection against heat damage requires surface treatment of the alloys. For oxidation and corrosion, surface treatment by coatings is the only choice. The coatings provide barriers between the alloys and the outer environment. These coatings can be tailored to meet requirements for environmental resistance, for example, by increased Al and Cr content because they do not need to have load-bearing capability. Chapter 6 addresses oxidation- and corrosion-resistant coatings. An additional avenue to reduce heat damage to the alloys is to lower their temperature without sacrificing the performance of the turbine.

This is addressed for hot components by thermally insulating them. A class of coatings called thermal barrier coatings (TBCs) in combination with active cooling accomplishes this function.

Nondestructive testing of the coating is an essential tool to monitor quality of new coatings and progressive degradation during their use. Understanding of this technologically important area is important.

Repair of coatings is another technologically important area, which also has financial components due to the high cost of coatings and coated hardware.

This book addresses most of the aspects of coatings discussed earlier as a single resource. For better grasp of the subject matter, introductory materials essential to the understanding of the science and technology of coatings are covered in Chapters 2 and 3. Knowledge of how the coatings have fared in the real environment is described in Chapter 10 to tie into the earlier chapters on their processing, structure, and properties.

REFERENCES

Meetham, G. W., Requirements for and factors affecting high temperature capability, *Materials and Design*, 1988, 9(5), pp. 244–252.

Stroosnijder, M. F., R. Mevrel, and M. J. Bennett, The interaction of surface engineering and high temperature corrosion protection, *Materials at High Temperatures,* 1994, 12(1), pp. 53–66.

Chapter 2

FUNDAMENTAL CONCEPTS

Background in the fundamental concepts of thermodynamics, kinetics of reactions, diffusion, crystal structure, phase equilibrium, and phase diagrams of alloys is essential in order to understand the selection, processing, and behavior of high-temperature coatings. These concepts are discussed briefly in this chapter.

2.1 THERMODYNAMIC CONCEPTS

The principles of thermodynamics are used to determine the spontaneity of many chemical and metallurgical phenomena and the direction in which they proceed. A few examples of practical applications of thermodynamics include processes for extraction of metals from ores, formation of alloys, precipitation and grain growth, and degradation of materials in service. In order to understand these processes, a number of thermodynamic parameters need to be defined. The concepts, discussed next, will be specifically helpful in understanding the processes of oxidation and corrosion, phase and microstructure changes of high-temperature coatings, and their interactions with substrate alloys.

Enthalpy

Enthalpy H is the measure of the combination of internal energy E and the product of pressure P and volume V of a system. Thus $H = E + PV$. For example, if the system consists of an inflated balloon made of a thermally insulating rubber, the internal energy is the energy of the gas molecules inside the balloon, and the pressure is that of the ambient atmosphere. If a small amount of heat dQ is added to this system, it will increase internal energy by dE and induce a change in volume dV while the pressure remains constant at P. Thus, $dQ = dE + PdV$. For constant pressure, $dQ = d(E + PV)$, which leads to $dQ = dH$. This relationship indicates that enthalpy is a measure of heat in the system. Change in enthalpy is related to the heat capacity at constant pressure, $(dH/dT)_{\mathrm{p}} = (dQ/dT)_{\mathrm{p}} = C_{\mathrm{p}}$, where dT is the change in temperature. Integration gives

$$H = H_0 + \int C_{\mathrm{p}}\, dT,$$

in which H_0 is a constant and T is temperature in absolute (K) units.

Entropy

Entropy is a measure of the order or randomness of a system. For example, if red and white billiard balls are arranged alternately in an array on a tray, the arrangement is highly ordered with low entropy. If the tray is shaken sufficiently, the arrangement will become randomized, with a red ball as likely to have a red neighbor as a white neighbor. In all processes, entropy maximizes. The quantitative aspect of entropy can be more easily understood with the balloon example. If we add heat dQ to the balloon kept at temperature T, the entropy change is given by $dS = dQ/\mathrm{T} = C_p\ dT/T$. Integration provides $S = S_0 + \int C_p\ dT/T$, in which S_0 is a constant.

Free Energy

Free energy or, more appropriately, Gibbs free energy (after the inventor of the concept, J. Willard Gibbs) is a composite thermodynamic concept involving both enthalpy H and entropy S. It is given by $G = H - TS$. If a small change occurs in a system kept at constant temperature, the resulting free energy change is given by $\Delta G = \Delta H - T\,\Delta S$.

Free energy change determines the direction in which a process such as a chemical reaction proceeds. For example, at constant temperature free energy decrease (ΔG negative) for the reaction $4/3\mathrm{Al} + \mathrm{O}_2 = 2/3\mathrm{Al}_2\mathrm{O}_3$ indicates that the reaction will go from left to right; that is, aluminum will spontaneously oxidize when in contact with oxygen. On the other hand, for the reaction $2\mathrm{FeO} = 2\mathrm{Fe} + \mathrm{O}_2$, the free energy increases (ΔG is positive), which means that the reaction will *not* go from left to right. In other words, iron oxide will not decompose spontaneously into elemental iron and oxygen. However, for the reaction $2\mathrm{Fe} + \mathrm{O}_2 = 2\mathrm{FeO}$, at some temperatures, the free energy decreases (ΔG is negative), which indicates that iron will spontaneously oxidize to iron oxide. Thermodynamics does not predict the rate at which the oxidation or, for that matter, any reaction, proceeds. The rates are controlled by kinetics of the process. Kinetics will be discussed in a later section. Equilibrium is defined as a state of constancy in which changes do not occur over time. For example, in the hypothetical reaction $m\mathrm{A} + n\mathrm{B} = p\mathrm{C} + q\mathrm{D}$, at equilibrium, as many atoms of A and B react to form C and D as the latter two react to reform A and B. In thermodynamic calculations, the absolute values of enthalpy, entropy, and free energy are never known and are seldom required. The calculations are based on changes in these parameters. In order to assess changes, a "standard state" is used as a basis relative to which all changes are measured. The standard state is defined as the state in which the "pure" substance (solid, liquid, or gas) exists at a pressure of 1 atmosphere and temperature of 298°K (25°C). The absolute values of the parameters at standard state are generally indicated with a superscript such as G°.

Equilibrium Constant

The concept of equilibrium constant is adopted from chemistry and is used in calculations relating to free energy changes. For the reaction $4/3\mathrm{Al} + \mathrm{O}_2 = 2/3\mathrm{Al}_2\mathrm{O}_3$, the equilibrium constant is given by $K = [\mathrm{Al}_2\mathrm{O}_3]^{2/3}/[\mathrm{Al}]^{4/3}[\mathrm{O}_2]$, where [ ] denotes concentration. Note that the concentration is raised to a power equal to the number of molecules (or atoms) participating in the reaction. The free energy change of the reaction at standard state is related to the equilibrium constant through the equation $\Delta G = \Delta G^\circ + RT\ \ln\ K$ where R is the gas constant, "ln" is the traditional symbol of natural logarithm, ΔG is the free energy change in an arbitrary state, and ΔG° is the free energy change involving reactants and products in their standard state. When the reaction is in equilibrium, $\Delta G = 0$. This gives $\Delta G^\circ = -RT \ln K$. The convention used in assessing concentration in reactions defines *pure* materials in either reactants or products as having a concentration of unity. Thus $[Al_2O_3]$ and [Al] are each unity, resulting in $\Delta G^\circ = -RT \ln(1/[O_2]) = RT \ln[O_2]$.

Activity Coefficient

In the foregoing discussion, the concentrations $[Al_2O_3]$ and [Al] each have been taken as unity because they are assumed to be in their standard state as pure solids. However, this assumption is not valid in many instances where Al exists in an alloy or a solution. In such cases the concept called *activity* is used instead of concentration. Thus, for a Ni base alloy containing 6% aluminum, knowing that the initial oxidation product is Al_2O_3, the oxidation reaction needs to be written as $4/3Al$ (alloyed in Ni) $+ O_2 = 2/3Al_2O_3$ with the equilibrium constant $K = [Al_2O_3]^{2/3}/[a_{Al}]^{4/3}[O_2]$, where a_{Al} is the activity of aluminum in the alloy. Because the product oxide is still pure Al_2O_3, its concentration (or activity) is unity. The free energy change is now given by $\Delta G^\circ = -RT \ln K = RT \ln[O_2] + 4/3RT \ln a_{Al}$. This relationship defines activity, which is the "effective concentration" of the species in the alloy. A more complete definition of activity is given by $a_{Al} = P_{Al\ in\ alloy}/P_{Al}$, the ratio of vapor pressure of Al over the alloy divided by the vapor pressure of Al over pure Al (which is its standard state) at the same temperature. The activity of gaseous species is represented by the partial pressure. We therefore replace $[O_2]$ by P_{O2}. The difference between the oxidation of a pure substance and an alloy can be elucidated by the following example of oxidation of Si:

$$\text{Si (pure)} + O_2 = SiO_2,\ \Delta G^\circ = -RT \ln\{[SiO_2]/[Si]\cdot[O_2]\} = RT \ln P_{O2},$$

because $[SiO_2]$ and [Si] are each unity because both the metal and the oxide are pure solids in their standard state;

$$\text{Si (in alloy)} + O_2 = SiO_2,\ \Delta G^\circ = -RT \ln\{[SiO_2]/[a_{Si}]\cdot[O_2]\} = \mathrm{RT} \ln a_{Si} + RT \ln P_{O2},$$

since $[SiO_2]$ is unity because the oxide is pure solid and in its standard state. However, Si is not in its standard state as pure solid but is in the alloy. The concentration is therefore replaced by its activity in the alloy.

2.2 CONCEPT OF KINETICS

Thermodynamic analysis through estimation of free energy changes predicts whether processes such as oxidation, dissolution, precipitation, or grain growth are possible. However, prediction of the rates at which these processes occur is outside the purview of thermodynamics. The principles of "kinetics" determine whether the processes take place at reasonable rates. A simple example of the limitation of thermodynamics is demonstrated by the relationship between diamond and graphite. The reaction C (as diamond) = C (as graphite) at ambient temperature and pressure has associated with it a negative free energy change. Therefore, diamond should spontaneously convert to graphite. However, we know that this does not occur. The underlying reason involves kinetics or rate of the reaction. Each atom in diamond is attached to four atoms at the corners of tetrahedra, whereas in graphite each atom in a plane is attached to three atoms with a weak bond between parallel planes. Thus, conversion from diamond to graphite would need extensive breaking and making of bonds with atomic rearrangement in between, all of which require expense of energy. In absence of this energy, the thermodynamic prediction is therefore not realized.