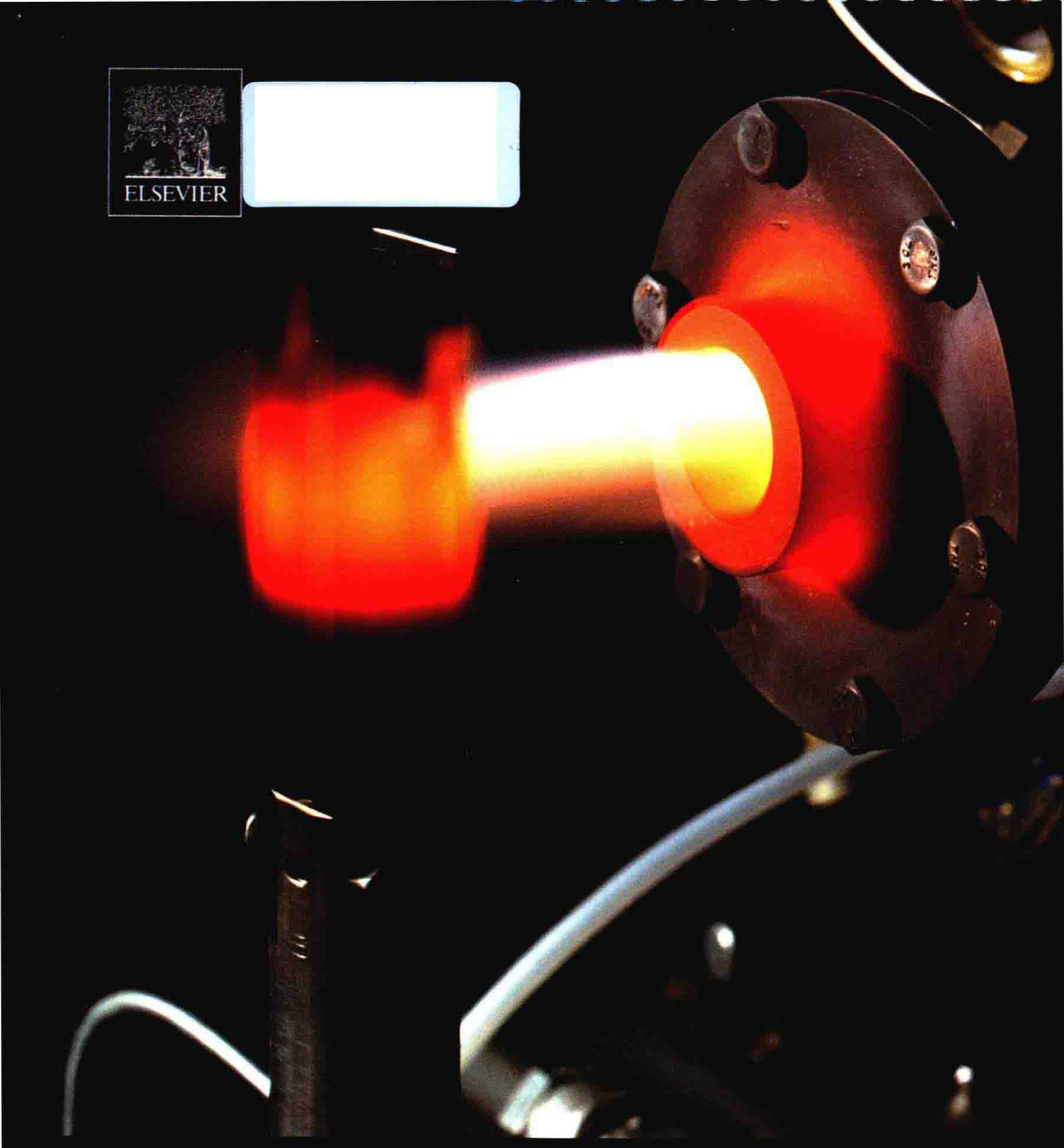

DAVID J. YOUNG

HIGH TEMPERATURE OXIDATION AND CORROSION OF METALS

SECOND EDITION

High Temperature Oxidation and Corrosion of Metals

Second Edition

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High Temperature Oxidation and Corrosion of Metals

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Foreword

The depletion of the first edition print run and an enormous increase in published research on high-temperature corrosion have combined to make a second edition of this book desirable. Recent work on mass transport in alumina and, more generally, on oxide grain boundary diffusion has contributed improved clarity to our understanding of how protective alumina and chromia scales behave. Similarly, new investigations into water vapour effects on scaling processes have expanded and refined our knowledge, although a simple, coherent picture remains elusive. These contributions, and several others, have been drawn upon in updating the original text.

Two new topics have been added, reflecting the large body of published research now available and the technological developments which drove that work. Chapter 10 treats corrosion by carbon dioxide, an important issue if CO_2 is to be captured from combustion gas streams. In addition, the thermal properties of carbon dioxide, along with its pressure-volume-temperature characteristics, make it attractive as a heat transfer and working fluid. For these reasons, it is a candidate for use in nuclear reactors and concentrated solar thermal power generation. Unfortunately, it is also corrosive to a variety of alloys.

A new Chapter 12, *Corrosion in Complex Environments*, is concerned with the corrosion phenomena arising from the presence of ionic melts and volatilising halides. Interest in these topics has arisen out of the much increased use of both biomass and municipal waste as fuels for thermal power generation. The resulting flue gases and deposits can be remarkably corrosive, and boiler operating temperatures are strictly limited as a result.

As in the first edition, I have tried to acknowledge important contributions to our understanding made by many researchers, and I apologise for any omissions. The second edition has benefited from colleagues around the world who have offered hospitality and/or generously gave expert commentary: Brian Gleeson (University of Pittsburgh), Daniel Monceau (INPT-CIRIMAT, Toulouse), Bruce Pint (Oak Ridge National Laboratory), Joe Quadakkers (Forschungszentrum, Jülich), Michael Schutze (Dechema, Frankfurt) and Jim Smialek (NASA, Lewis). Rectifying an important omission from the first edition, I thank my wife and family for their support and remarkable forbearance.

David J. Young
December 2015

analysis. The lengthy Chapter 2 reviews the thermodynamic, kinetic and mechanical theories used in this book. It also contains tabulated data and refers to Appendices on alloy composition and diffusion.

After these preliminaries, the book is arranged in a sequence of chapters reflecting increasing complexity, which equates with greater system component multiplicity. An analysis of the reaction between pure metals and single oxidant gases is followed by a discussion of metal reactions with mixed oxidant gases and then, in Chapters 5–7, an examination of alloy reactions with a single oxidant. Much of this discussion is based on the early work of Carl Wagner, which still provides a good conceptual framework and, in several cases, a useful analytical basis for quantitative prediction. However, as will be shown, increasing system complexity is accompanied by a weakening in theoretical completeness. The problems arise from multicomponent effects and from microstructural complexity.

Consider first the effect of increasing the number of alloy components. A steady-state reacting system consisting of a binary alloy and a single oxidant can be modelled in a two coordinate description of both thermodynamics and diffusion kinetics, provided that temperature and pressure are constant. Substantial thermodynamic and diffusion data is available for many such systems, and this is used in developing diffusion path descriptions. Increasing the number of alloy components leads, however, to chemical and structural interactions among them, rendering the experimental problem much less tractable, and diagrammatic representation impossible. In the absence of the requisite extensive thermodynamic and diffusion data, the Wagner theory cannot be applied. Instead, higher order alloys are discussed from the point of view of dilute addition effects on the behaviour of binaries.

Wagner's theory is based on lattice diffusion. However, the transport properties of slow-growing oxides are largely determined by their grain boundaries and, in some cases perhaps, microporosity. Additional alloy components can affect both the oxide grain size and the diffusion properties of the grain boundaries. A description of these phenomena is, at this stage, largely empirical.

The latter part of the book is concerned with the effects of other corrodents and temperature variations. Chapters 8 and 9 deal with sulphur and carbon-bearing gases. The very rapid diffusion rates involved in sulphidation and carburisation makes them potentially threatening corrosion processes in a number of industrial technologies. Of fundamental interest are the complications arising out of the complex gas-phase chemistries and the sometimes slow homogeneous gas-phase reactions. It becomes necessary in discussing the behaviour of these gas mixtures to consider the role of catalysts, including the alloys in question and their corrosion products. It emerges that not only the gas phase, but also the gas-solid interface can be far removed from local equilibrium. In particular, analysis of the catastrophic 'metal dusting' corrosion caused by carbon-supersaturated gases calls for the use of nonequilibrium models.

The effects of water vapour on oxidation are discussed in Chapter 10. In many respects this is the least well understood aspect of high-temperature corrosion. The reason for the difficulty is to be found in the multiple ways in which water molecules can interact with oxides. Preferential adsorption, hydrogen uptake, lattice defect changes, grain boundary transport property changes, gas generation within oxide pores and scale and scale-alloy interface mechanical property changes need all to be considered.

Finally, the effects of temperature cycling on oxide scale growth are considered in Chapter 11. A combination of diffusion modelling with a rather empirical scale spallation description is found to provide a reasonably successful way of extrapolating data for particular alloys. However, there is a need for development of more predictive descriptions of the relationship between spallation propensity, alloy properties and exposure conditions.

Discussion is focused throughout on developing an understanding of the fundamentals of high-temperature oxidation. Frequent use is made of experimental information on real alloys in order to illustrate the principles involved. However, no attempt is made to survey the very extensive literature which exists for alloy oxidation. Thus most examples considered concern either iron- or nickel-base alloys, whereas cobalt-base alloys are largely ignored. Nickel aluminides are discussed, but other intermetallics are seldom mentioned. The scope of the book is further limited by the exclusion of some particular topics. Examples include 'pesting' (disintegration by grain boundary attack) of silicides, and extensive oxygen dissolution by metals such as titanium and zirconium. No book of manageable proportions can ever be complete, or even fully up to date.

It is remarkable that since the early, very substantial progress made by Carl Wagner and associates in understanding oxidation phenomena, the research effort has nonetheless continued to expand. The reason, of course, is the continuing need to operate equipment at ever higher temperatures to achieve greater efficiencies and reduced emissions. The need to develop suitable materials can be expected to drive even more research in years to come.

Writing this book has been a large task, and its content inevitably reflects my own experience, as well as the ideas and results of others. I have tried to acknowledge important contributions to our understanding made by many researchers, and apologise for any omissions. My own research in this area has benefited from interaction with many talented students, research fellows and colleagues, all acknowledged by direct reference. It has also been sustained in large part by the Australian Research Council, a body to be commended for its willingness to support fundamental research. This book has benefited from colleagues from around the world who offered hospitality and/or generously gave expert commentary as I wrote: Brian Gleeson (Iowa State University), Jack Kirkaldy (McMaster University), Daniel Monceau (CIRIMAT, Toulouse), Toshio Narita (Hokkaido University), Joe Quadakkers (Forschungzentrum, Julich), Jim Smialek (NASA, Lewis) and Peter Tortorelli (Oak Ridge National Laboratory).

Finally, I acknowledge with gratitude and affection the inspiration provided by my mentors and friends at McMaster University, Walt Smeltzer and Jack Kirkaldy.

David J. Young
August 2007

Abbreviations and Acronyms

APT	Atom probe tomography
CTGA	Continuous thermogravimetric analysis
CVD	Chemical vapour deposition
EBSD	Electron back scattered diffraction
EDAX	Energy dispersive analysis of X-rays
EELS	Electron energy loss spectroscopy
EPMA	Electron probe microanalysis
FIB	Focused ion beam
IGCC	Integrated gasification combined cycle
ppm	Parts per million (unit of relative concentration)
ppma	Parts per million by atoms
ppmm	Parts per million by mass
PVD	Physical vapour deposition
SAD	Selected area diffraction
SCC	Supercritical CO_2
SEM	Secondary electron microscope
SIMS	Secondary ion mass spectrometry
TBC	Thermal barrier coating
TEM	Transmission electron microscope
TGA	Thermogravimetric analysis
TGO	Thermally grown oxide
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
YSZ	Yttria-stabilized zirconia

$\widetilde{D}$	Chemical (or inter) diffusion coefficient
D_o	Diffusion coefficient for solute oxygen in alloy
$D_{o,i}$	Diffusion coefficient for oxygen along an interface
E	Electric field
E_{OX}	Elastic modulus of oxide
E_A	Activation energy
e'	Free electron
F	The Faraday (96,500 C)
f	Fraction
f_v	Volume fraction
G	Total or molar Gibbs free energy
G_{OX}	Shear modulus of oxide
G_v	Free energy per unit volume
g_{BO}	Volume fraction of internally precipitated oxide, BO
H	Total or molar enthalpy
$h^\bullet$	Positive hole
$i\|S$	Species i adsorbed (bound) to surface site
ioz	Internal oxidation zone
J_i	Flux of component i
K	Chemical equilibrium constant
k	Rate constant
k	Boltzmann's constant
k_c	Parabolic rate constant for metal consumption, corrosion rate constant
k_l	Linear rate constant for scale thickening
k_m	Gaseous mass transfer coefficient
k_s	Surface area fraction of oxide spalled
$k_p^{(i)}$	Parabolic rate constant for internal oxidation
k_p	Parabolic rate constant for scale thickening
k_w	Parabolic rate constant for scaling weight gain
k_v	Vaporisation rate
K_p	Equilibrium constant at fixed pressure
K_{sp}	Solubility product
K_{IC}	Fracture toughness, critical stress intensity factor
L_{ij}	General mobility coefficient, Onsager phenomenological coefficient
L	Length of material over which gas flows
l	Half thickness of alloy sheet
MW	Molecular weight
m_i	Molar concentration of component i
$m^\bullet$, m'	Number of charge units on lattice point defect species
n	Number of moles
N_i	Mole fraction of component i
N_{AV}	Avogadro's number
$N_{M,i}$	Mole fraction of component M at scale-alloy interface
$N_{M,min}$	Minimum mole fraction of component M required to support growth of external MO scale
$N_M^{(o)}$	Mole fraction of component M originally present in alloy
$N_O^{(s)}$	Mole fraction of dissolved oxygen at alloy surface
P	Pressure
p	D_A/D_B, ratio of metal self-diffusion coefficients in ternary oxide
p_i	Partial pressure of component i

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P_T	Total pressure of gas mixture
Q	Activation energy
q	Charge
R	General gas constant
r_i	Rate constant for indicated gas-solid reaction
S	Total or molar entropy
S	Spacing of periodic microstructure
S	Surface site
S_M^X	Species S located on crystal lattice site M, with effective charge X
T	Temperature
t	Time
t^*	Time at temperature in cyclic exposure conditions
U	Total or molar internal energy
U_i	Building unit in crystalline compound
V	Volume
v	Velocity
V_i	Molar volume of phase i
W	Weight
X	Scale thickness
x	Position coordinate
X_M	Metal surface recession
X_{ss}	Steady-state scale thickness when growth balanced by evaporation
$X_{(i)}$	Depth of internal oxidation zone
y	Position coordinate for scale-alloy interface relative to the original, unreacted surface location
y	z/z_s (or x/X), position within scale normalised to its thickness
Z	Effective charge, valence
z	Position coordinate in reference frame with origin at scale–alloy interface

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