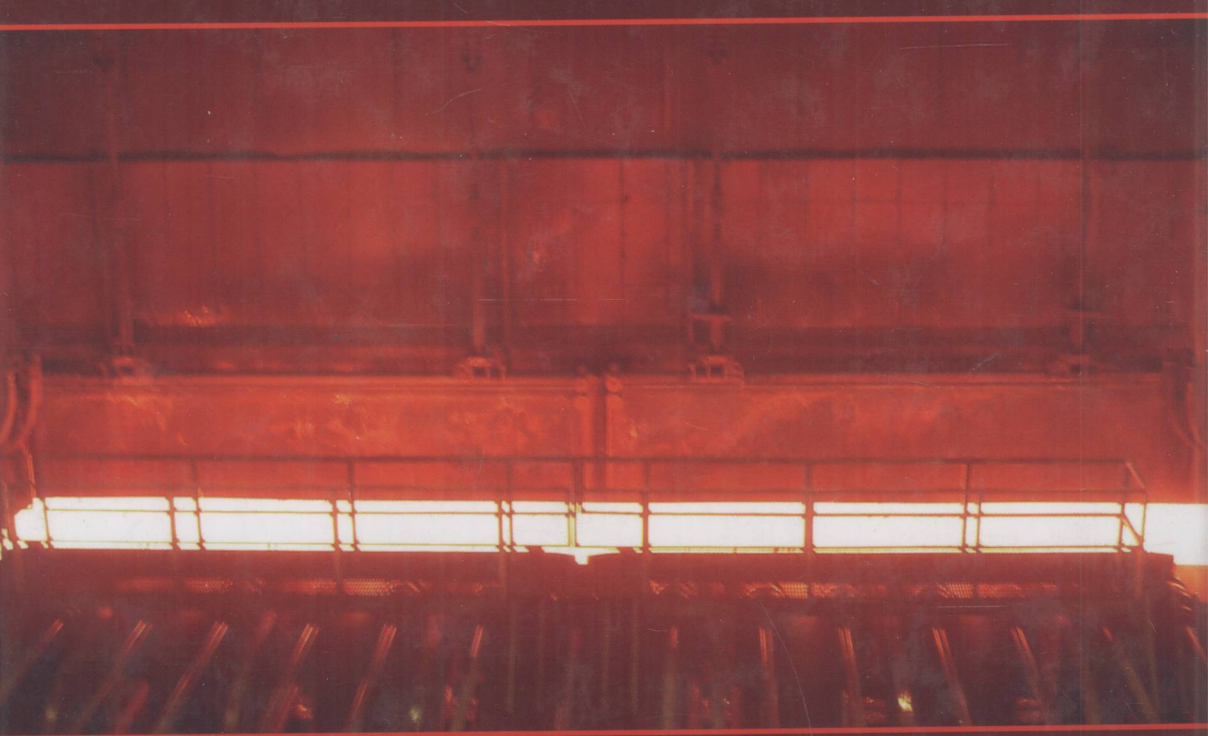


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# HIGH TEMPERATURE OXIDATION AND CORROSION OF METALS



DAVID YOUNG

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By  
DAVID JOHN YOUNG



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# **HIGH TEMPERATURE OXIDATION AND CORROSION OF METALS**

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**ELSEVIER CORROSION SERIES**

Series Editor: Tim Burstein

*Department of Materials Science and Metallurgy, University of Cambridge,  
Cambridge, UK*

**VOLUME 1: High Temperature Oxidation and Corrosion of Metals –**  
by David John Young



## PREFACE

Almost all metals and alloys of technological interest oxidize and corrode at high temperatures. However, the nature of the reaction products and the rates at which metal surfaces are degraded vary widely, and a capacity for prediction is highly desirable. This book is concerned with providing a fundamental basis for understanding the alloy–gas oxidation and corrosion reactions observed in practice and in the laboratory. Its purpose is to enable the prediction of reaction morphology, kinetics and rate as a function of temperature and the compositions of both alloy and gas.

The term “oxidation” is used in a generic sense, for any chemical reaction which increases the metal oxidation state by forming a compound such as an oxide, sulfide, carbide, etc. Alloy oxidation reactions can be conceived of as occurring in three stages. Initially, all alloy components in contact with a hot gas are likely to react simultaneously. Subsequently, thermodynamically more stable compounds replace less stable ones, and a state of near equilibrium is locally approached. The reacting system can then be modelled as a series of spatially adjacent local equilibrium states which vary incrementally in reactant chemical potentials. During this stage, the reaction morphology and composition distribution are invariant with time. Ultimately, this “steady state” is lost, and all reactive alloy components are consumed in a final breakdown stage.

Successful alloys are those which evidence lengthy periods of slow, steady-state reaction. For this reason, considerable emphasis is placed on analysing the underlying local equilibrium condition and testing its applicability to particular metal or alloy-oxidant systems. When an alloy–gas reaction is at steady state, the constant composition profile developed through the reaction zone can be mapped onto the system phase diagram as a “diffusion path”. Frequent use is made of these paths in understanding reaction product distributions and in predicting, or at least rationalizing, reaction outcomes.

Analysis of the alloy oxidation problem requires a multidisciplinary approach. Physical metallurgy, materials science and physical chemistry provide the tools with which to dissect alloy phase constitutions and their transformations, oxide properties and chemical kinetics. Deliberate emphasis is placed on the use of chemical thermodynamics in predicting oxidation products and describing solid solution phases. Equal attention is paid to the detailed understanding of defect-based diffusion processes in crystalline solids. The introductory Chapter 1 indicates how these various disciplines can contribute to the 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 relevant to diffusion. Appendix A lists representative alloy compositions.

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 co-ordinate description of both thermodynamics and diffusion kinetics, provided that temperature and pressure are constant. Substantial thermodynamic and diffusion data are available for many such systems, and these are 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. In the absence of the requisite extensive thermodynamic or 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. 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 sulfur and carbon-bearing gases. The very rapid diffusion rates involved in sulfidation and carburization 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 generally 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 non-equilibrium 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-based alloys, whereas cobalt-based 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 “pestring” (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 apologize 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 (University of Pittsburgh), Jack Kirkaldy (McMaster University), Daniel Monceau (CIRIMAT, Toulouse), Toshio Narita (Hokkaido University), Joe Quadackers (Forschungszentrum, 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.

D.J. Young  
August 2007



## GLOSSARY OF SYMBOLS

Greek symbols	Explanation for symbol
$\alpha$	Coefficient of thermal expansion
$\alpha$	Enrichment factor for metal in internal oxidation zone
$\alpha$	Ferrite, body-centred cubic metal phase
$\delta$	Deviation from stoichiometry in oxide
$\delta$	Thickness of gas phase boundary layer
$\eta_i$	Electrochemical potential of component i
$\eta_g$	Viscosity of gas
$\gamma$	Austenite, face-centred cubic metal phase
$\gamma$	Surface tension, free energy per unit surface area
$\gamma_i$	Activity coefficient of component i
$\lambda$	Interplanar distance, jump distance
$\lambda$	$x/t^{1/2}$ , for parametric solutions to Fick's equation
$\mu_i$	Chemical potential of component i
$\nu$	Stoichiometric coefficient in chemical reaction or compound
$\nu_g$	Kinematic viscosity of gas
$\nu_{iv}$	Kinetic frequency term
$\nu_p$	Poisson's ratio
$\psi$	Electrostatic potential
$\rho$	Density
$\sigma$	Mechanical stress
$\theta$	Fraction of surface sites
$\xi$	Extent of reaction
$\xi$	Mole fraction of oxide BO in solid solution $A_{1-\xi}B_\xi O$
$\epsilon_c$	Critical strain for mechanical failure of scale or scale-alloy interface
$\epsilon_{ik}$	Wagner interaction coefficients for solute compounds i and k
$\epsilon_{OX}$	Mechanical strain in oxide

Symbol	Explanation for symbol
$A$	Surface area of oxidizing metal
$a_i$	Chemical activity of component i
$a'_o, a''_o$	Boundary values of oxygen activity at metal-scale and scale-gas interfaces
$B_i$	Mobility of species i
$C_i$	Concentration of component i
$C', C''$	Boundary values of concentration at metal-scale and scale-gas interfaces
$D$	Diffusion coefficient
$D$	Grain boundary width
$D_A$	Intrinsic diffusion coefficient for species A

Symbol	Explanation for symbol
$D_{AB}$	Gas phase diffusion coefficient for binary mixture A–B
$D_A^*$	Tracer or self-diffusion coefficient of species A
$D_{ij}$	Diffusion coefficient relating flux of component i to concentration gradient in component j
$\tilde{D}$	Chemical (or inter) diffusion coefficient
$D_B$	Self-diffusion coefficient component B; self-diffusion coefficient for species in grain or phase boundary
$D_L$	Self-diffusion coefficient for lattice species
$D_O$	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
$\bar{G}$	Partial molar 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
$K_n$	Chemical equilibrium constant for reaction number $n$
$k$	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
$k_v$	Vaporization 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
$n_T$	Total number of moles, all species
$N_i$	Mole fraction of component i
$N_{AV}$	Avogadro's number

Symbol	Explanation for symbol
$N_{M, i}$	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
$N_O$	Mole fraction of dissolved oxygen
$N_O^{(s)}$	Mole fraction of dissolved oxygen at alloy surface (solubility at ambient conditions)
$p$	Pressure
$\rho$	$D_A/D_B$ , ratio of metal self-diffusion coefficients in ternary oxide
$P_i$	Partial pressure of component i
$P_T$	Total pressure of gas mixture
$Q$	Activation energy
$q$	Charge
$R$	General gas constant
$r_i$	Rate constant for indicated gas–solid reaction
$\dot{s}$	Entropy source term (time rate of entropy production per unit volume)
$S$	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 co-ordinate
$X_M$	Metal surface recession
$X_{ss}$	Steady-state scale thickness when growth balanced by evaporation
$X^{(i)}$	Depth of internal oxidation zone
$y$	Position co-ordinate for scale–alloy interface relative to the original, unreacted surface location
$\bar{y}$	$z/z_s$ (or $x/X$ ), position within scale normalized to its thickness
$Z$	Effective charge, valence
$z$	Position co-ordinate in reference frame with origin at scale–alloy interface

## ABBREVIATIONS AND ACRONYMS

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
SEM	Secondary electron microscope
SIMS	Secondary ion mass spectrometry
TBC	Thermal barrier coating
TEM	Transmission electron microscope
TGA	Thermogravimetric analysis
TGO	Thermally grown oxide
XRD	X-ray diffraction
YSZ	Ytria-stabilized zirconia

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## The Nature of High Temperature Oxidation

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At high temperatures, most metals will inevitably oxidize over a wide range of conditions. The practical issues of material lifetimes and corrosion protection methods therefore centre around the rate of the oxidation reaction, methods of slowing it and the means for controlling its morphology. Answers to these questions turn out to be rather interesting, involving as they do the need for a fundamental understanding of several diverse aspects of solid-gas reactions. The general nature of the problem can be appreciated from a consideration of some practical examples.

### 1.1. METAL LOSS DUE TO THE SCALING OF STEEL

Carbon steel is produced in prodigious quantities: about  $1.3 \times 10^9$  t worldwide in 2007. Almost all of it is cast into large pieces such as slabs, which are subsequently reheated to around 1,000–1,200°C to be formed into more useful shapes (Figure 1.1). The reheating operation is carried out in direct-fired furnaces where steelworks gases, or sometimes natural gas, are combusted with excess air.