Preface

Almost all metals and alloys of technological interest oxidise and corrode at high temperatures. However, the nature of their 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 composition 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, sulphide, carbide, etc. Alloy oxidation reactions can be conceived of as occurring in three stages. Initially, all reactive components of an alloy in contact with a hot gas are likely to react simultaneously. Subsequently, more thermo-dynamically 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 a steady state, the constant composition profile developed through the reaction zone can be mapped onto the relevant 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 rationalising, 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 trans-formations, 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 un-derstanding of defect-based diffusion processes in crystalline solids. The intro-ductory 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 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.

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David J. Young
August 2007

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