INTRODUCTION TO THE HIGH-TEMPERATURE OXIDATION OF METALS

A straightfoward treatment describing the oxidation processes of metals and alloys at elevated temperatures. This new edition retains the fundamental theory but incorporates advances made in understanding degradation phenomena. Oxidation processes in complex systems are dicussed, from reactions in mixed environments to protective techniques, including coatings and atmosphere control. The authors provide a logical and expert treatment of the subject, producing a revised book that will be of use to students studying degradation of high-temperature materials and an essential guide to researchers requiring an understanding of this elementary process.

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Professor Neil Birks

This book is dedicated to one of its coauthors, Professor Neil Birks, who passed away during the preparation of the second edition. Neil was an accomplished researcher and educator in a number of fields including high-temperature oxidation, corrosion, erosion, and process metallurgy. He was also a good friend.

Neil's legacy to science and engineering is well established in his scholarly publications and the numerous students he mentored. It is our hope that this book will complete that legacy.

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Preface

Few metals, particularly those in common technological applications, are stable when exposed to the atmosphere at both high and low temperatures. Consequently, most metals in service today are subject to deterioration either by corrosion at room temperature or by oxidation at high temperature. The degree of corrosion varies widely. Some metals, such as iron, will rust and oxidize very rapidly whereas other metals, such as nickel and chromium, are attacked relatively slowly. It will be seen that the nature of the surface layers produced on the metal plays a major role in the behaviour of these materials in aggressive atmospheres.

The subject of high-temperature oxidation of metals is capable of extensive investigation and theoretical treatment. It is normally found to be a very satisfying subject to study. The theoretical treatment covers a wide range of metallurgical, chemical, and physical principles and can be approached by people of a wide range of disciplines who, therefore, complement each other's efforts.

Initially, the subject was studied with the broad aim of preventing the deterioration of metals in service, i.e., as a result of exposing the metal to high temperatures and oxidizing atmospheres. In recent years, a wealth of mechanistic data has become available. These data cover a broad range of phenomena, e.g., mass transport through oxide scales, evaporation of oxide or metallic species, the role of mechanical stress in oxidation, growth of scales in complex environments containing more than one oxidant, and the important relationships between alloy composition and microstructure and oxidation. Such information is obtained by applying virtually every physical and chemical investigative technique to the subject.

In this book the intention is to introduce the subject of high-temperature oxidation of metals to students and to professional engineers whose work demands familiarity with the subject. The emphasis of the book is placed firmly on supplying an understanding of the basic, or fundamental, processes involved in oxidation.

In order to keep to this objective, there has been no attempt to provide an exhaustive, or even extensive, review of the literature. In our opinion this would increase the factual content without necessarily improving the understanding of the subject and would, therefore, increase both the size and price of the book without enhancing its objective as an introduction to the subject. Extensive literature quotation is already available in books previously published on the subject and in review articles. Similarly the treatment of techniques of investigation has been restricted to a level that is sufficient for the reader to understand how the subject is studied without involving an overabundance of experimental details. Such details are available elsewhere as indicated.

After dealing with the classical situations involving the straightforward oxidation of metals and alloys in the first five chapters, the final chapters extend the discussion to reactions in mixed environments, i.e., containing more than one oxidant, to reactions involving a condensed phase as in hot corrosion, and the added complications caused by erosive particles. Finally, some typical coatings for high-temperature applications and the use of protective atmospheres during processing are described.

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Introduction

The primary purpose of this book is to present an introduction to the fundamental principles that govern the interaction of reactive gaseous environments (usually containing oxygen as a component) and solid materials, usually metals, at high temperatures. These principles are applicable to a variety of applications, which can include those where oxidation is desirable, such as forming a resistive silica layer on silicon-based semiconductors or removing surface defects from steel slabs during processing by rapid surface oxidation. However, most applications deal with situations where reaction of the component with the gaseous atmosphere is undesirable and one tries to minimize the rate at which such reactions occur.

The term 'high-temperature' requires definition. In contrast to aqueous corrosion, the temperatures considered in this book will always be high enough that water, when present in the systems, will be present as the vapour rather than the liquid. Moreover, when exposed to oxidizing conditions at temperatures between 100 and 500 °C, most metals and alloys form thin corrosion products that grow very slowly and require transmission electron microscopy for detailed characterization. While some principles discussed in this book may be applicable to thin films, 'high temperature' is considered to be 500 °C and above.

In designing alloys for use at elevated temperatures, the alloys must not only be as resistant as possible to the effects produced by reaction with oxygen, but resistance to attack by other oxidants in the environment is also necessary. In addition, the environment is not always only a gas since, in practice, the deposition of ash on the alloys is not uncommon. It is, therefore, more realistic in these cases to speak of the high-temperature corrosion resistance of materials rather than their oxidation resistance.

The rate at which the reactions occur is governed by the nature of the reaction product which forms. In the case of materials such as carbon the reaction product is gaseous (CO and CO_2), and does not provide a barrier to continued reaction. The materials that are designed for high-temperature use are protected by the formation of a solid reaction product (usually an oxide) which separates the component and atmosphere. The rate of further reaction is controlled by transport of reactants through this solid layer. The materials designed for use at the highest temperatures are ones which form the oxides with the slowest transport rates for reactants (usually α-Al_2O_3 or SiO_2), i.e., those with the slowest growth rates. However, other materials are often used at lower temperatures if their oxides have growth rates which are 'slow enough' because they may have better mechanical properties (strength, creep resistance), may be easier to fabricate into components (good formability/weldability), or are less expensive.

In some cases, the barriers necessary to develop the desired resistance to corrosion can be formed on structural alloys by appropriate composition modification. In many practical applications for structural alloys, however, the required compositional changes are not compatible with the required physical properties of the alloys. In such cases, the necessary compositional modifications are developed through the use of coatings on the surfaces of the structural alloys and the desired reaction-product barriers are developed on the surfaces of the coatings.

A rough hierarchy of common engineering alloys with respect to use temperature would include the following.

- Low-alloy steels, which form M_3O_4 (M = Fe, Cr) surface layers, are used to temperatures of about 500 °C.
- Titanium-base alloys, which form TiO_2, are used to about 600 °C.
- Ferritic stainless steels, which form Cr_2O_3 surface layers, are used to about 650 °C. This temperature limit is based on creep properties rather than oxidation rate.
- Austenitic Fe–Ni–Cr alloys, which form Cr_2O_3 surface layers and have higher creep strength than ferritic alloys, are used to about 850 °C.
- Austenitic Ni–Cr alloys, which form Cr_2O_3 surface layers, are used to about 950 °C, which is the upper limit for oxidation protection by chromia formation.
- Austenitic Ni–Cr–Al alloys, and aluminide and MCrAlY (M = Ni, Co, or Fe) coatings, which form Al_2O_3 surface layers, are used to about 1100 °C.
- Applications above 1100 °C require the use of ceramics or refractory metals. The latter alloys oxidize catastrophically and must be coated with a more oxidation-resistant material, which usually forms SiO_2.

The exercise of 'alloy selection' for a given application takes all of the above factors into account. While other properties are mentioned from time to time, the emphasis of this book is on oxidation and corrosion behaviour.