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R. Winston Revie, Series Editor

CÉSAR A. C. SEQUEIRA

# HIGH TEMPERATURE CORROSION

FUNDAMENTALS AND ENGINEERING



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# **High Temperature Corrosion**

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# **High Temperature Corrosion**

## **Fundamentals and Engineering**

**César A. C. Sequeira**

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**WILEY**

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*Dedicated to  
Maria Elisa,  
my eternal wife*

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# Preface

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The science and engineering of gas–solid, liquid–solid, and solid–solid processes, which can involve high temperature reactions with oxygen, sulfur, nitrogen, carbon dioxide, water vapor, molten sulfates, chlorides, carbonates, vanadates, fluorides, etc., has evolved greatly over the past 50–60 years. Numerous symposia and colloquia have been held on the subject and have been widely attended by researchers from all over the world. One of the many factors enabling advancement of our understanding of the field is the creation and evolution of new, sophisticated instruments and techniques that allow a better analysis of scale compositions and structures.

The numerous details of high temperature corrosion (HTC) have led to thousands of publications over the years and to the writing of only relatively few books on the subject. Moreover, the early books suffered from lack of extensive data on various metals and alloys, the nonexistence of good experimental equipment, and an emphasis on materials that were important in the era in which the books were written. Many universities now have courses on oxidation and other forms of HTC, but the availability of texts continues to be limited. The following books have been very useful:

- N. Birks, G.H. Meier, and F.S. Pettit, *Introduction to the High-Temperature Oxidation of Metals*, Cambridge University Press, Cambridge, UK (2006).
- E. Fromm, *Kinetics of Metal-Gas Interactions at Low Temperature – Hydriding, Oxidation, Poisoning*, Springer-Verlag, Berlin, Germany (1998).
- A.S. Khanna, *High Temperature Oxidation and Corrosion*, ASM International, Materials Park, Ohio, USA (2002).
- P. Kofstad, *High Temperature Oxidation of Metals*, John Wiley, New York, USA (1966).
- P. Kofstad, *High Temperature Corrosion*, Elsevier, London, UK (1988).

- G.Y. Lai, *High-Temperature Corrosion and Materials Applications*, ASM International, Materials Park, Ohio, USA (2007).
- S. Mrowec, *Defect and Diffusion in Solids*, Elsevier Science Publications, London, UK (1980).
- M. Schütze, *Protective Oxide Scales and Their Breakdown*, The Institute of Corrosion, John Wiley, Chichester, UK (1997).
- M. Schütze and H.J. Grabke, eds., *Metal Dusting, Carburization and Nitridation*, EFC 41, Woodhead Publishing Ltd., Cambridge, UK (2006).

The main differences between the present book and the competitive books listed above are:

- None of them cover most of the HTC types (e.g. oxidation, sulfidation, nitridation, molten salts, fuel-ash corrosion,  $H_2S/H_2$  corrosion, molten fluoride/HF corrosion, carburization).
- Many books on HTC concern fundamental studies of material-gas processes. In other words, aspects related to diffusion in HTC oxidation are well treated, but the books provide little engineering data to help engineers make informed material selection decisions.
- The present book covers fundamental science and engineering of HTC, in a balanced way, so that an academic researcher or PhD student or an engineer in industry will find it of interest.
- The present book includes up-to-date information accompanied by more than 1500 references, 80% of which cover the last 25 years.
- The present book includes details on systems of particular engineering importance at this time, namely, on the corrosion of high temperature fuel cells, and nuclear power plants.

- The present book includes an up-to-date summary of experimental methods, many of which have not been covered in earlier books.

The current book has 20 chapters, whose contents are briefly described hereafter.

The first chapter begins to examine historical aspects of the development of HTC. Then, the three key components of the corrosion phenomena frequently encountered in high temperature industrial processes are summarized. In the following sections, materials and their design for use at high temperatures, common and not so common hostile environments at high temperature, and the barriers (films, scales) that separate the material and environment and that, in many situations, are necessary to develop the desired corrosion resistance are presented. HTC occurs behind walls as high temperature processes are usually shielded from their environment. However, it can be lifetime and performance determining in a number of everyday examples, its minimization requiring a proper understanding of the underlying principles of corrosion, which involve plant engineering, metallurgy, chemistry, materials science, system design, or failure analysis. So, the academic and industrial impacts of HTC form the themes of the following sections. In this context, corrosion economics, safety, environment damage, and corrosion management are aspects of particular concern.

Basic high temperature phenomena that require attention are changes in dimensions, microstructures, mechanical properties, and other topics under the heading of physical metallurgy. It is no longer possible to neglect the metallurgical aspects of the corrosion problem. Imperfections in an essentially perfect structure, solidification, alloys, iron and steel, deformation and recrystallization, and fracture and fatigue are described in Chapter 2. It is expected to provide an introduction to physical metallurgy primarily intended for undergraduate students at universities and polytechnics, but, additionally, industrial technicians or engineers will be aided in identifying their in-plant corrosion problems. Seventy-three figures fully support the text, illustrating the fundamental points.

An important tool analysis of HTC problems is equilibrium thermochemistry, which, although not predictive of kinetics, allows to ascertain which reaction products are possible, whether or not significant evaporation or condensation of a given species is possible, the conditions under which a given reaction product can react with a condensed deposit, etc. This standard method of thermochemical analysis is commonly used in metallurgical equilibria involving reactions between a gas and a solid as a function of temperature, and the complexity of the ambivalent oxidation usually dictates that the thermochemical analysis be represented in graphical form. Chapter 3 deals with six types of thermochemical diagrams: Ellingham diagrams,

integral free energy–concentration diagrams, vapor species diagrams, stability diagrams for one metal/two nonmetals, 2D stability diagrams for two metals/one nonmetal, and phase stability diagrams for two or more metals. The subject of thermodynamics (or phase equilibria) of metal-fused salt systems in high temperature corrosive environments has been treated in a manner exactly analogous to aqueous solutions by the formation of Pourbaix, i.e. plots of electrode potential (oxidizing potential) versus basicity, being treated in this chapter by constructing and properly detailing an oxidizing potential basicity diagram for iron in molten sodium sulfate.

The lattice of an actual crystal always contains imperfections or defects. Important properties of the crystal, such as diffusion of ions, result from the existence of defects, and, as a consequence, mass transport in the scale formed by oxidation can be explained on the basis of its defect chemistry and crystal structure. An understanding of reaction mechanisms in HTC requires a precise knowledge of defect structures in solids. The growth of a compact or a porous scale, as well as its structure, is largely determined by the presence of the lattice defects. This is analyzed in Chapter 4 on lattice defects in metal compounds. The considered topics include point defects and defect structures, defect reactions and relevant examples, defect equilibrium constants and their significance for defect reaction including electronic imperfections.

Besides its scientific interest, diffusion is of enormous practical relevance for industry and life, ranging from steelmaking, growth of oxide scales, sintering, and high temperature creep of metals to oxide/carbon dioxide exchange in the human lung. Chapter 5 is confined to diffusion in condensed matter, namely, in metals, binary alloys, and oxides. Emphasis is on very basic fundamental aspects, the contents being roughly characterized by the headings general theory of diffusion, diffusion coefficients, Matano–Boltzmann analysis, Kirkendall effect, Darken analysis, factors influencing diffusion, impurity diffusion in metals, grain boundary diffusion in metals, diffusion in solid oxides, morphology of reaction products, and measurement of diffusion parameters. The chapter includes many references for readers at the forefront of the subject; it is primarily intended for graduate students and corrosion scientists.

Many studies from both theoretical and experimental viewpoints and fundamental approaches made along the last 70 years suggested, with sufficient credibility, electrochemical mechanistic models for the observed corrosion at high temperature. Thus, the chemical reactions established at solid–solid, solid–liquid, and solid–gas interfaces during the growth of corrosion products can be visualized as oxidation–reduction electrode processes; in other words, it is acceptable that high temperature oxidation, sulfidation, halogenation, nitridation, carburization, and molten salt

corrosion are processes of electrochemical nature. In Chapter 6, basic aspects of traditional electrochemistry, solid-state electrochemistry, and molten salt electrochemistry are described to show how HTC can be further understood and mitigated. Headings include electrochemical nature of molten salt corrosion, the single potential of an electrode, equilibrium diagrams, the Tafel relationship, corrosion potential– $pO^{2-}$  relationship, electrochemical polarization and monitoring, electrochemical nature of metal oxidation, usefulness of electrochemical cells, current–potential measurements on solid electrodes, simple concepts of oxide semiconductors, conduction processes in ionic solids, and common solid-state electrochemical situations. The chapter is primarily intended for graduate students and corrosion scientists.

Oxidation is an important HTC phenomenon. Metals or alloys are oxidized when heated to elevated temperatures in air or in highly oxidizing environments, such as combustion atmospheres with excess air or oxygen. Many metallic components are subject to oxidation in engineering applications. Starting in 1933, a number of very significant contributions to the theory of oxidation of metals in alloys were published by Wagner, which still form the most comprehensive theoretical basis even in today's discussion of the mechanisms of HTC. There have been quite a number of other pioneering papers in the field that can, however, not be quoted here due to space limitations. Chapter 7 summarizes the main factors for determining the nature and extent of gas–metal reactions that are of paramount importance to understand the subject. In this context, the following topics are analyzed: thermodynamic considerations, kinetic considerations, defect structures, compact scale growth, multilayered scale growth, oxidation resistance, and oxidation of engineering materials. Recent hot topics such as metallurgical factors affecting alloy oxidation, early stages of oxidation and the nature of metal–oxide interface, secondary effects during oxidation in dry environments, and accelerated degradation in the presence of molten oxidants are also underlined in this chapter. The information is primarily intended for students and industrial scientists and engineers.

Hot combustion atmospheres derived from fuels containing sulfur, as in superheaters, heat exchangers, gas turbines, etc., are a source of concern due to the interaction between metals and alloys and hydrogen sulfide, sulfur dioxide, sulfur trioxide, or elemental sulfur itself. Interaction with sulfur dioxide (and/or trioxide) may produce scales consisting of the oxides alone, or oxide plus sulfide, or even sulfate, but, in Chapter 8, the reactions that led to the formation of sulfide scales on metals and alloys only will be considered. The chapter is mainly confined to a brief theoretical consideration of the sulfidation behavior of metals and alloys, discussing the basic phenomena

involved in the process. Accordingly, first, an overall picture of the sulfidation process is given, which is more amplified in three further sections concerning the kinetics of sulfidation of metals, the sulfidation behavior of alloys, and the defect structure of metal sulfides.

Chapter 9 deals with carburization and metal dusting. Carburization involves the formation of internal carbide precipitates, occurring in the cracking tubes used in ethylene and other olefin plants, in the heat treatment of components associated with carburizing furnaces, and for reformer tubes used in the steam reforming of natural gas. Metal dusting is a catastrophic carburization that occurs at temperatures of 430–900 °C when a process gas stream consists primarily of  $H_2/CO$  and  $CO_2$  along with some hydrocarbons with high carbon potentials. This chapter describes the mechanisms of carburization and metal dusting and poses practical problems, discussing solutions, on the alloy resistance to carburization and metal dusting. It is a valuable informational resource for industrial scientists and engineers.

Chapter 10 gives a brief review on nitridation, a process that results in the formation of nitrides in a material. It results from exposure to reducing high temperature environments with high nitrogen activity. Since nitrides are inherently hard, brittle phases, nitridation can produce local or widespread loss of material strength and possible metal wastage. In the present review, information on nitridation mechanisms and nitridation in industrial media will be found.

Halogens and many halogen compounds are very corrosive. Hence, materials for containing and handling halogens and corrosive halogen compounds must be selected with particular care. In Chapter 11, oxidation and corrosion theories are applied to the problems of destructive metal and alloy halogenation. Metal–halogen and alloy–halogen reactions and many laboratory studies are reviewed.

The effect of water vapor on the oxidation behavior of metals and alloys at high temperature has been summarized in many recent reviews. Hydrogen is also a gas that causes serious industrial problems, particularly in refinery vessels and other high temperature equipment, many times associated with water and/or water vapor. Steels, carbon, and Cr–Mo steels, low-alloy steels, and other materials can suffer hydrogen attack or hydrogen damage at high temperature, which results in rupture failures of steel components and/or microfissures in boiler tubes and other industries. The purpose of Chapter 12 is to provide a brief discussion of the corrosion reactions involving  $H_2$  and/or  $H_2O$ , which are a really important subject of HTC. At first, particular attention is given to the concept, mechanism, detection, and prevention of corrosion by hydrogen; hydrogen damage in coal-fired boilers and petroleum refining is shown to be a serious issue when the water chemistry is not properly controlled under normal operating conditions. In the

subsequent section, the corrosion by water vapor is considered. The kinetics and mechanisms of oxidation are analyzed by using concepts of solid-state chemistry focused on the themes of proton incorporation, volatility of metal hydroxides, and plasticity of oxide scales. The chapter is primarily intended to graduate students and industrial scientists and engineers.

Interest in the use of molten or fused salts in industrial processes is being accelerated by the increasing demand for the production of refractory metals, actinides, lanthanides, and transition and light metals by processes involving fused salts, by the use of molten salts in high temperature batteries and fuel cells, and also by the novel chemical engineering techniques that have been developed in the nuclear energy industry. Chapter 13 focuses on key aspects of molten salt corrosion processes and on corrosion data useful in selecting high temperature materials. Corrosion processes, thermodynamic diagrams, corrosion rate measurements, test methods, electrochemical studies on fluorides, chlorides, nitrates/nitrites, hydroxides, carbonates, vanadates, and sulfates, as well as prevention of molten salt corrosion, are the considered topics.

The corrosion behavior of metals, alloys, and ceramics in liquid metals is a complex problem involving simple dissolution (chemical corrosion), electron transfer processes (electrochemical corrosion), physical erosion (when there is a swift flow of melt relative to the surface of the solid), fouling, embrittlement, and stress corrosion, and these phenomena have a real impact on many industrial applications. Chapter 14 discusses several types of corrosive attack of materials by liquid metals, namely, simple dissolution, alloying between liquid metal and solid metal, intergranular penetration, impurity reactions, temperature-gradient mass transfer, and concentration-gradient mass transfer. Then, interactions of important engineering materials with molten aluminum, zinc, lead, lithium, sodium, magnesium, mercury, and other metals are reported.

Many very important engineering systems operating at high temperatures (650–1100 °C) involve contact of metallic or ceramic materials with combustion product gases or other oxidizing gases containing inorganic impurities, namely, gas turbines, steam generators, incinerators, and numerous petrochemical process vessels. As the gases are cooled, corrosive fused salt films may condense on the hardware to generate an accelerated degradation known as hot corrosion. A wealth of literature exists on the kinetics of hot corrosion and on the resulting microstructures. The solubilities of oxides and their dependencies on melt basicity and oxygen activity constitute important information to interpret hot corrosion mechanisms. Chemistry, electrochemistry, phenomenology, and experimental work all aid in the interpretation of hot corrosion of metals. In Chapter 15, the hot corrosion of gas turbines is particularly studied. The gas turbine engine is described, and its main

materials and corrosiveness are noted. Early studies of the phenomenon and the alloy–Na<sub>2</sub>SO<sub>4</sub> reactions are reviewed. The mechanisms of hot corrosion, with particular reference to acidic and basic fluxing, are analyzed. Hot corrosion of gas turbine alloys, methods of evaluating hot corrosion, and its prevention are subjects also discussed.

High temperature fireside corrosion is best outlined by admitting the presence of molten or semi-molten deposits. Obviously, corrosion is affected by transport processes across deposits and by reactions occurring at gas-deposit interfaces and deposit-metal surfaces. The presence of a molten phase is a sufficient prerequisite to stimulate both transport processes and heterogeneous reactions, providing a more intimate contact between metal and corrodents. An additional factor is the presence of SO<sub>3</sub>, which, besides stabilizing the physical state of deposits, enhances corrosion by increasing the metal oxide solubility in the molten phase and, acting as oxygen carrier, by increasing the oxidizing power of deposits. It is the aim of Chapter 16 to briefly delineate mechanisms, remedies, materials problems, and other current views related with this field of coal-ash corrosion, oil-ash corrosion, and vanadic corrosion, which is encountered in coal-fired boilers, oil-fired boilers, and waste incinerators. The chapter also includes a brief summary of industrial experience on fireside corrosion in Denmark, Germany, Holland, the United Kingdom, and Japan.

Chapter 17 covers a large number of surface analytical and electrochemical techniques used for HTC science and engineering. The surface analytical techniques provide the necessary information on the surface chemical composition, structure, topography, defects, and mechanical and electronic properties, in close relationship with the kinetic data on corrosion that are obtained by electrochemical techniques. Topics are focused on testing equipment and monitoring, optical microscopy, thermogravimetry, spectroscopy, diffraction techniques, electron microscopy, electron spectroscopy and ion scattering, surface microscopy, optical spectroscopy, nondestructive inspection techniques, traditional electrochemical methods, nontraditional electrochemical methods, and combined electrochemical methods. Well-established techniques such as AES, TEM, and EIS and many newer techniques such as GDOES, FTIR, solid-state voltammetry, ellipsometry, electrochemical quartz crystal microbalance, and electrochemical noise analysis are discussed. Extensive references and 80 figures aid the study of this essential subject. The chapter is of primary interest to university students and researchers, industrial scientists, and engineers.

There are many measures to protect the materials against their degradation at elevated temperatures, but the great stringent requirement of high temperature strength and corrosion resistance is a composite system in which

mechanical strength is achieved by alloy development and corrosion resistance by surface coating or surface modification. Corrosion and oxidation protective coatings work by forming a thin oxide barrier on the surface, which is extremely thin, able to reform the oxide coat should some of it become damaged due to cracking, spallation, etc. Chapter 18 briefly deals with diffusion, overlay and thermal barrier coatings, and processes for their application, which are available for protection. These include chemical vapor deposition, pack cementation, out-of-pack cementation, physical vapor deposition, plasma spraying, high velocity oxygen/fuel, and other coating processes. Brief considerations on coating degradation and present and future applications are also described.

Among the various industries in which HTC is a widespread problem, the energy arena involving (i) the study of processing and properties of high temperature materials and (ii) the experimental observations to predicting behavior, from scientific principles to engineering design and from atomic scale models to performance while in use, constitute the aim of Chapter 19 as described for two types of energy technologies: advanced energy conversion sources, and more precisely, high temperature fuel cells, and nuclear power plants. The first section presents the operating principles of a molten carbonate fuel cell (MCFC) and then analyzes corrosion issues in the anode materials, cathode materials, electrolyte and matrix, wet seal, bipolar current collectors, and hardware materials. Future directions of MCFCs are also included. The second section deals with the solid oxide fuel cell, describing the cell and concentrating on the interconnect-related corrosion issues, and protective coatings for metallic interconnects. The third section describes direct carbon fuel cells (DCFCs), giving particular attention to the various types of DCFCs, and their corrosion issues. The last section moves to the theme of nuclear power plants.

The nuclear renaissance is highlighted, as well as recent nuclear reactor types. Advanced materials for nuclear reactors, and corrosion in nuclear applications, are also discussed.

Chapter 20, the last chapter, is a collection of case histories or practical solutions adapted from recent literature on practical and fundamental problems that have been analyzed and subsequently solved using relatively innovative approaches. The following seven cases are examined: making stainless steels, corrosion protection of turbine blades, oxidation of silicides for VLSI application, naphthenic acid corrosion in petrochemical plants, oxidation of ceramic matrix composites, shell corrosion of rotary cement kilns, and corrosion in a linear alpha olefin plant. These solutions span a wide range of industrial problems frequently encountered in a variety of high temperature environments.

It is the experience of the author that the material in this book can serve as a basic textbook for a two-semester MSc course. It provides enough information for the students to understand the underlying principles of HTC and to carry out some laboratory work when the instructor is posing more practical problems, then discusses solutions, refers some of the extensive references contained in the book, and teaches basic techniques as described in Chapter 17. Any industrial scientist or engineer whose work involves material selection, system design, process operations, or failure analysis will find this book to be a valuable educational and information resource.

The author has received his education in universities in Europe and North America and has a combined experience as teacher and researcher in the fields of corrosion and electrochemistry of over 40 years. The present book is a product of this experience.

*Lisbon, August 2017*

CÉSAR A. C. SEQUEIRA

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*Lisbon, August 2017*

CÉSAR A. C. SEQUEIRA

# Chapter 1

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## Introduction

### 1.1 Definition of High Temperature Corrosion

The term *corrosion* has its origin in Latin. The Latin term *rodere* means “gnawing” and *corrodere* means “gnawing to pieces.” The term *high temperature* means always temperatures high enough that water, when present in the corrosive environment, will be present as the vapor rather than the liquid. In contrast to room temperature corrosion, high temperature corrosion (HTC) is characterized by high rates of the formation of corrosion products and strong material degradation.

The subject of HTC is capable of extensive investigation and theoretical treatment. It is normally found to be a very satisfactory subject to study. The fundamental treatment covers a wide range of materials science, chemical, and physical principles and can be approached by people of a wide range of disciplines who, therefore, complement each other's efforts. The subject of HTC is also of considerable engineering interest, because there are many traditional and engineering industries that face HTC problems.

It is rather interesting to start this introduction by examining the main historical aspects of the developments of HTC.

### 1.2 Historical Development

The attainment of high temperatures has been important in the development of civilization for many centuries. Fired ceramics, extraction of metals from their ores, and the development of casting, forging, and the optimization of metal properties by heat treatment are all high temperature processes of considerable antiquity. However, the high temperatures were contained by refractories, and in use most metals saw only modest temperatures. This began to change with the industrial revolution. The first heat engines introduced at the end of the eighteenth century were large steam pumps to remove water from deep mines, and these operated at fairly low temperatures. However, the

desire for improved efficiency pushed boiler temperatures progressively higher, first to develop engines for power production in factories and then for locomotives. Today, the main steam temperatures in advanced utility boilers are about 650 °C, with the outer surface of the heat exchangers in contact with the combustion gases perhaps 50 °C higher. In Europe, Japan, and the United States, plans are now afoot to raise the main steam temperature to perhaps as high as 800 °C.

The introduction of the internal combustion engine in the late nineteenth century introduced the need for materials capable of operating for long times exposed to high temperature combustion gases without noticeable surface damage, in particular the exhaust valves, which are difficult to protect by cooling. Again, as part of the drive for higher efficiencies and higher specific power outputs, the idea of supercharging was introduced, and the most common method was the turbocharger. The conditions to which the small turbocharger rotor was exposed resulted in the development of a class of castable high temperature alloys, of which Co–10% Ni–35% Cr–7, 5% W–0.5% C is an example. The introduction of electricity as a major energy source at the beginning of the twentieth century led to the development of electric heating for industrial systems, and the problems of producing a wire capable of forming a radiant heater with a surface temperature of the order of 850 °C became a major challenge, which was solved by the development of Ni 20% Cr alloys, which can be drawn into wires, but which have adequate creep strength and good oxidation resistance at the desired use temperature.

The next major challenge was the introduction of the aviation gas turbine in 1940 in Germany and the United Kingdom, and this continues to be the pacing technology for the development of high temperature alloys to this day. For this application, it becomes difficult to reconcile alloy design demands for adequate high temperature mechanical properties and those for adequate corrosion resistance, and this has led to a separation of these functions. An alloy with good mechanical properties and perhaps marginal



corrosion resistance is protected by the application of a coating that has excellent corrosion resistance but marginal mechanical properties. A further complication is that the turbine inlet temperatures have now risen to over 1350 °C, while the intrinsic strength capability of the best alloys currently available hardly exceeds 1000 °C. This is handled by cooling the hot components, but the formation of the cooling passages places further demands on the castability of the high temperature alloys.

All of these high temperature applications of metals and alloys demand materials that have a variety of properties such as strength, toughness, fatigue resistance, creep resistance, formability, and not least resistance to degradation by reaction with the environment. Essentially all potential metallic materials are unstable in these high temperature environments, and the various oxidation processes are highly exothermic. The only reason it is possible to have materials that can be used at all is that the reaction product – the oxide – forms a “protective layer” on the component surface, and it is the ways in which this is possible that form the basis of the science of high temperature oxidation and corrosion resistance. Here, the term oxidation is associated with corrosion because in most aggressive high temperature environments, oxidation often participates in the HTC reactions, regardless of the predominant mode of corrosion. In fact, alloys often rely upon the oxidation reaction to develop a protective scale to resist corrosion by other forms of high temperature attack, and so it can be said that oxidation is the most important HTC reaction but, strictly speaking, high temperature oxidation is only one type of HTC.

The first paper that expressly addressed high temperature oxidation was that by Gustav Tammann in 1920. He enumerated the “parabolic law,” i.e. the rate of oxidation of metal decreases as oxide layer thickness increases. In 1922 he established the logarithmic law of oxidation of metals. However, the first paper that lays out the basics of the problem as we know it was that by N.B. Pilling and R.E. Bedworth in 1923. They defined “high temperature” as that at which the transport of the reactive components through the protective layer was the principal determinant of the reaction rate (as opposed to the situation in aqueous corrosion processes at close to ambient temperatures). They showed that under these circumstances it could be expected that the rate of reaction would diminish as the protective scale thickened, leading to a “parabolic rate law.” They also highlighted the problems associated with forming an adherent crack-free protective oxide layer on the oxidizing surface because of the volume changes associated with the oxidation process. The discussion to this seminal paper shows that others were thinking along similar lines at the time. Six years later, Leonard B. Pfeil introduced the concept of movement of metal outward rather than oxygen inward into the oxide layer, and in 1934 Portevin, Pr  tet, and Jolivet

carried out extensive studies on the oxidation of iron and its alloys. At the same time, the discovery that oxides contained lattice defects and that the transport processes within them are determined by the motion of these defects allowed a more quantitative approach. This was recognized by Carl Wagner, who produced an important body of work over the course of the next twenty years largely defining how we now look at the basic theory of the bulk transport processes in oxides. Of significance was the derivation of Wagner’s equation by Hoar and Price in 1938. In recent years, however, the recognition that in many cases the transport processes involve short-circuit paths, such as grain boundaries, has introduced further complications into this elegant picture.

The problem of the integrity of the protective oxide was not part of Wagner’s contribution, and its practical solution for the high temperature alloys that were developed for the applications mentioned above was discovered essentially by accident in the early 1940s. It was found that very small amounts of what are now called “reactive elements” added to the alloys introduced a remarkable improvement in the apparent integrity of the protective oxide, particularly in its resistance to thermal cycling. The reasons for this effect are still a matter of considerable debate.

Other important contributions in the 1939–1948 period were those of Cabrera and Mott, postulating that oxide film growth is controlled by ions jumping from site to site over intervening energy barriers. Mott’s theory was then highly criticized by Karl Hauffe that performed significant work on the oxidation of alloys. During the 1920–1940 period, other relevant studies on oxidation at high temperature deserve reference: these are the interference method of obtaining thickness of oxide films (Tammann 1920–1926), the spectroscopic method to obtain thickness of oxide film (Constable 1927), and the X-ray and electron diffraction methods to study oxide films (Finch Quarrell 1933).

The earliest treatments of oxidation problems considered simple systems, with a single oxidant (usually oxygen) and a pure metal, although in practice high temperature-resistant materials were always alloys. More recently, approaches such as in multicomponent diffusion theory have been applied, and the growth of oxides on polyphase materials has been analyzed. These approaches have been greatly assisted by the development of modern characterization techniques.

In recent years, the problem of HTC in relatively complex environments, such as mixed gases with low oxygen activities but significant carbon or sulfur activities, or environments in which molten alkali salts may be deposited on the alloy surface, has become of much greater importance. Theoretical models for some aspects of these situations have been developed, but they are still not fully understood. Many challenges still exist!

In view of the practical importance of this area, and the intellectual problems it presents, it is not surprising that an enormous amount of published literature on fundamentals and engineering of HTC has been produced. Research activities, case histories, practical solutions, etc. have been published over the last 50 years by well-known scientists and engineers, whose names can be listed below:

|                  |                 |                 |                  |
|------------------|-----------------|-----------------|------------------|
| C.B. Alcock      | B.K. Gupta      | J.R. Nichols    | J. Stringer      |
| A. Atkinson      | M.G. Hocking    | E.J. Opila      | J.B. Wagner, Jr. |
| J. Bénard        | B.E. Hopkins    | F.S. Pettit     | D.P. Whittle     |
| N. Birks         | A.S. Khanna     | B.A. Pint       | G.C. Wood        |
| N.S. Bornstein   | P. Kofstad      | J.W. Quadakkers |                  |
| M.A. Decrescente | O. Kubaschewski | A. Rahmel       |                  |
| F. Gesmundo      | G.Y. Lai        | R.A. Rapp       |                  |
| B. Gleeson       | E. Lang         | M. Schütze      |                  |
| J.A. Goebel      | G.H. Meier      | J.L. Smialek    |                  |
| G.W. Goward      | S. Mrowec       | K.E. Stern      |                  |
| H.J. Grabke      | K. Natesan      | K.N. Strafford  |                  |

Clearly, the list is by no means exhaustive, and there are an extensive number of other international authorities from leading academic and nonacademic organizations that have provided novel and relevant aspects on HTC. All this experience has been extremely rich to the current state of knowledge on HTC.

### 1.3 High Temperature Corrosion Phenomena

Failure of construction elements in high temperature applications can be due to interaction of the environment with the material, resulting in loss of protection and subsequent accelerated degradation, or to accidental overheating due to poor process control. Both oxidizing and reducing environments can exist at high temperature, and both can lead to HTC. Depending on the oxygen activity of the environment, one or other mode of HTC may predominate. Apart from oxidation, which is the most predominant

HTC reaction, sulfidation, carburization, hydrogen attack, halide attack, and molten salt and molten metal attack are also important modes of HTC. More peculiar phenomena such as metal dusting, hot corrosion, green rot, *black plague*, pesting, phase changes, etc. can occur during high temperature service, which can be responsible for component failures.

During exposure of high temperature-resistant materials, in many cases a *scale* is produced from corrosion products that protects the underlying metal against further attack. If the integrity of the film is impaired by blistering, shear cracking, or flaking of the scale or if the scale is dissolved or volatilized, the corrosive atmosphere has free access to the metal surface and corrosion will continue in some cases with very high rates of corrosion.

It is clear from the preceding considerations and those from Section 1.2 that the HTC system is mainly composed of a material at high temperature, an aggressive or hostile environment, and a film or scale that is the corrosion product of the material–environment interaction. It is necessary to understand both the characteristics of each key component of the HTC system and the interactions between the components. This is really the main objective of this book. In the next sections, beginning considerations are described about materials and their design for use at high temperatures, common and not so common hostile environments at high temperature, and the barriers (films, scales) that separate the material and environment and that in many situations are necessary to develop the desired corrosion resistance. These three key components of the HTC system, which are more frequently encountered in various industrial processes, are summarized schematically in Figure 1.1.

### 1.4 High Temperature Materials

The operation of materials in high temperature application involves unusual constraints not seen in other application.

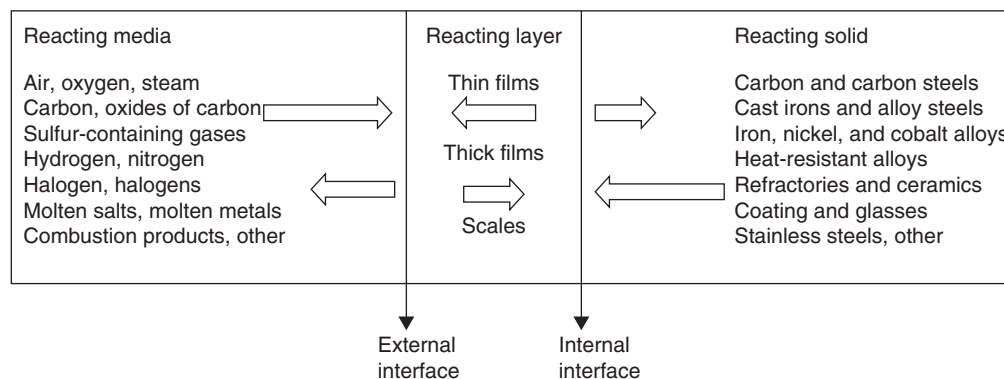


Figure 1.1 Key components of the HTC system.

High melting point, high Young's modulus, good creep resistance and high temperature strength, and microstructure stability at high temperature are requirements of the mechanical properties of the material that need to be met. Additional criterion for material selection at high temperatures is to meet the requirements of the chemical properties of the material. These include materials with very low rates of corrosion at the temperature of interest, or that form thin, slow-growing scales that are impervious to the environment, or that form protective scales strongly resistant to the aggressive environment. In many situations, the material cannot be tailored to meet simultaneously the structural capability requirement to carry load and the requirement for corrosion resistance. The overall protection requires the use of coatings that provide barriers between the alloys and the outer environment.

A rough hierarchy of common engineering alloys for high temperature service would include the following:

- Low-alloy steels, which form  $M_3O_4$  ( $M = Fe, Cr$ ) surface layers, are used to temperatures of about  $500^\circ C$ .
- Titanium-based alloys, which form  $TiO_2$ , are used to about  $600^\circ C$ .
- Ferritic stainless steels, which form  $Cr_2O_3$  surface layers, are used to about  $650^\circ C$ . 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  $850^\circ C$ .
- Austenitic Ni–Cr alloys, which form  $Cr_2O_3$  surface layers, are used to about  $950^\circ C$ , which is the upper limit for oxidation protection by chromia formation.
- Austenitic Ni–Cr–Al alloys, aluminide, and  $MCrAlY$  ( $M = Ni, Co, \text{ or } Fe$ ) coatings, which form  $Al_2O_3$  surface layers, are used to about  $1100^\circ C$ .
- Applications above  $1100^\circ C$  require the use of ceramics-, nickel-, and cobalt-based superalloys or refractory metals. The latter alloys oxidize catastrophically and must be coated with a more oxidation-resistant material, which usually forms  $SiO_2$ .

Although most engineering alloys are known by their popular names that were derived from their trade names, all alloys have very specific names or numbers. One of the most important designations is the unified numbering system (UNS) number. Other designations such as ASTM, SAE, ASME, AWS, etc. are also widely used to designate wrought products, castings, and weld filler metals. Cross-references between the different specifications of the American, British (BSI), Japanese (JIS), and German (DIN) systems are published (Bringas 1993).

In many respects, the behavior of a material reflects its chemical nature, particularly the dominant type of

chemical bonding that holds its atoms and molecules together. Chemical bonds fall into two categories, primary and secondary.

The primary bonds involve some type of transfer of electrons, from one atom to another. Due to this transfer, some atoms become positively charged, and some become negatively charged. The atoms with opposite charge are then attracted to each other, producing primary bonds that are very strong. There are three different *primary bonds*: *metallic*, *ionic*, and *covalent*. Metallic bonding is nondirectional, and so it allows ready movement of dislocations, producing the ductile behavior that is characteristic of metals. Covalent bonding is highly directional, leading to the brittle behavior that is characteristic of many ceramics.

The *secondary bonds* cause attractions even when there is no overall charge. Neutral atoms or molecules may have a dipole, a distribution in charge within the atom or molecule. These dipoles provide for bonding between neutral atoms or molecules when a positive dipole on one molecule is attracted to the negative dipole on an adjacent molecule, producing a secondary bond. Water molecules have permanent dipoles, and the resulting bonds are called *hydrogen bonds*. Even molecules without permanent dipoles may develop temporary distributions in charge, which produce *van der Waals bonds*. Both types of secondary bonds are much weaker than the primary bonds, and the van der Waals bonds are weaker than the hydrogen bonds. These bonds are especially important in organic polymers, including wood.

A material whose chemistry is dominated by primary bonds is strong and stiff, while a material dominated by secondary bonds is weak. Thus, it is important to consider the chemical composition and bonding in engineering materials in order to gain a general understanding of the mechanical properties, strength, and stiffness. Deterioration of materials often involves specific chemical reactions with constituents in the environment, so the chemical composition is also important in order to understand the durability of these materials.

There is one other aspect of a material that influences its behavior: this is the *microstructure*. Microstructure refers to the way that individual constituents are arranged inside the material. A material may be porous or dense. A constituent may be small or may be large and easily recognized without the assistance of a microscope. Likewise, a constituent may be well dispersed throughout a material or may be clustered. The microstructure of a material often depends on how the material was processed, whether cooled from a molten state or formed by some chemical reaction between a solid and a liquid. The microstructure itself often depends on the chemical composition. Some compounds occur with characteristic shapes reflecting the arrangement of atoms into crystalline patterns, while others have no regular atomic arrangement.

To understand the properties of engineering materials for high temperature application, it is important to consider their chemical composition and their microstructure.

Chapter 2 provides an introduction to physical metallurgy that begins with a discussion of the structure and metals followed by a discussion of mechanical properties including strengthening mechanisms. The remainder of this section begins with a classification of high temperature materials and then discusses some of the materials more relevant to our interest, including their chemical properties and briefly reviewing the specifications and operational requirements imposed on them for high temperature service. High temperature coatings are discussed in Chapter 18.

### 1.4.1 Classification of Materials

The technically relevant materials can be classified into two groups – metallic materials and nonmetallic materials. As a further useful classification, metallic materials can be subdivided into ferrous metals and nonferrous metals. The ferrous metals can be classified into steel and cast iron. Iron–carbon alloys with a carbon content lower than 2% are defined as steels, and iron–carbon alloys with more than 2% carbon are known as cast iron. According to DIN EN 10027 (1992), steel alloys can be subdivided on the basis of application or chemical composition or quality groups, i.e.:

- Structural steels (normal and high strength).
- Steels for heat treatment and surface hardening.
- Stainless steels.

- Free cutting steels.
- Tool steels.

An example of a typical classification based on different applications is presented in Table 1.1. While plain carbon steels and steels with a total alloying content of up to 12% are not generally selected for resistance to HTC (the material choice is largely dictated by cost, ease of fabrication, and mechanical properties), they are often required to operate in high temperature aggressive environments. For instance, the power generation, refuse incineration, and chemical process industries use many miles of low-alloy steel heat exchanger tubes. Hence, the high temperature oxidation properties of low-alloy steels are often important in determining component life.

Nonferrous metals include nickel, cobalt, titanium, zirconium, refractory metals (tungsten, molybdenum, tantalum, and niobium), etc. Refractory metals can withstand temperatures for extended periods of time in excess of 1000 °C, but they cannot be used above 1200 °C without oxidation protection, because their oxides melt and even vaporize much below the metals' melting temperatures. Nickel and cobalt are the major elements of superalloys, materials widely used in critical regions of jet engines and gas turbines, because they contain elements for solution hardening and dispersion hardening that increase their load-carrying abilities at high temperature.

Temperature-resistant nonmetallic materials are called refractories and/or technical ceramics. Some properties of typical manufactured nonmetallic high temperature materials are given in Table 1.2.

**Table 1.1** Classification of steel grades DIN EN 10027 (1992)

| Steel grade  | Characteristics, example  | Quality grade             |
|--|---|---------------------------|
| <i>Structural steels for the building trade, bridge construction, vehicle and mechanical engineering</i> |   |                           |
| Structural steels (DIN EN 10025)   | Unalloyed and low-alloy C steels, yield strength 180–360 MPa, S235JR, S355JR (A516 Gr. 65/70)   | Basic steels              |
| High-strength structural steels (DIN EN 10113–2/3)   | Micro-alloyed steels (Ti, Nb, V, B, Zr), yield strength 460–960 MPa. S460 N or S460 M (ASTM A63.3, Gr. E). S690 V (ASTM A517 Gr. F)   | Quality steels            |
| <i>Steels for heat treatment</i>   |   |                           |
| QT steels (DIN EN 10083–1/3)   | Mn/CrMo/V-alloyed steels with 0.2–0.6% C, high strength, C45E (ASTM A576 Gr. 1045) 42CrMo4 (ASTM A434 Class BB)   | Quality steels            |
| <i>Steels with special properties</i>  |   |                           |
| Low temperature steels (DIN EN 10028–4)  | Ni-alloyed steels with excellent toughness between –60 and 195 °C, 10Ni14, X8Ni9  | Alloyed high grade steels |
| Stainless steels (DIN EN 10088–1/3)  | 12% Cr steel, austenitic stainless steel, duplex stainless steel X3CrNiMo13–4 (A182 Gr. F 6 NM) X20Cr13 (A276 Type 420) X2CrNi19–11 (A182 Gr. F 304L) X2CrNiMoN22–5 (A182 Gr. F 51) | Alloyed high grade steels |
| Heat-resisting steels (DIN EN 10095 draft)   | Cr/Ni/Al/Si-alloyed steels, high temperature application 800–1100 °C, X10CrAlSi7, X10CrAlSi25, X10CrNiTi18–10, X15CrNiSi25–21   | Alloyed high grade steels |

**Table 1.2** Some properties of typical manufactured nonmetallic high temperature materials

| Material                | Specific heat at 1000 °C (cal/g/°C) | Coefficient of thermal expansion at average RT–1000 °C (°C × 10 <sup>6</sup> ) | Thermal conductivity at 800 °C (cal/cm <sup>2</sup> /cm/°C/s) | Total emissivity at 800 °C (%) | Electrical resistivity at 600 °C (Ω cm)          |
|-------------------------|-------------------------------------|--|---|--------------------------------|--|
| Silica glass            | 0.30                                | 0.5  | 0.006   | 70                             | 10 <sup>6</sup> –10 <sup>7</sup>                 |
| Alumina (dense)         | 0.30                                | 8.5  | 0.016   | 45–60                          | 10 <sup>9</sup> –10 <sup>11</sup>                |
| Silicon carbide (dense) | 0.30                                | 4.5  | 0.09–0.17   | 86                             | Semiconductor<br>very dependent<br>on impurities |
| Graphite                | 0.45                                | 2–5  | 0.1–0.25  | 86–90                          | 6–20 × 10 <sup>-4</sup>                          |

### 1.4.2 Cast Irons

When *cast iron* is exposed to high temperature under oxidizing conditions, oxidation of the metal results, with the formation of a surface scale. In addition, the dimensions of the component become distorted. Although such dimensional changes can occur also in inert atmospheres or in vacuum, the evidence available suggests that this “growth” is frequently associated with oxidation, and accordingly it is appropriate to consider it as an aspect of the corrosion of the iron.

Components designed for high temperature duty may either remain at a steady high temperature for their entire life or, as more commonly happens, may undergo cyclic variation between a minimum temperature, often room temperature, and a maximum temperature. The maximum temperature involved may be either above or below the critical temperature range of the iron. This is the range within which the transformation between ferrite or pearlite and austenite occurs, and for the majority of unalloyed irons, it may be regarded as being 700–850 °C.

Conditions of cyclic reheating are more severe than conditions of steady high temperature, and cyclic reheating through the critical range is particularly liable to cause excessive growth of the iron.

Generally, the studies that have been carried out suggest that growth of up to 40% by volume can occur within the first 40 hours of cyclic reheating to 900 °C with a frequency of 1–4 hours/cycle, while subsequent cycling produces growth at a rate rarely exceeding 20% increase in volume in 100 hours. The rate of growth that develops increases with increase in temperature and possibly also with increase in frequency of cycling. Although the fact that a 60% increase in volume may occur after only 140 hours of cyclic reheating suggests that unalloyed iron is totally unsuited for such applications, iron is in fact extensively used under such conditions, e.g. furnace doors and fire bars. This may be partly because these applications involve cycling frequencies lower than those that cause the very high rates of growth mentioned, but undoubtedly a major fact determining the use of unalloyed cast iron for such duties is its cheapness, which outweighs

the superior growth resistance of more highly alloyed and more expensive irons.

At temperatures below the critical range, much less growth occurs, rarely exceeding 3% for 100 hours of cycling reheating. Here too the rate of growth depends on the temperature and the frequency of cycling. At temperatures below 400 °C, growth becomes negligible for most irons, while below 350 °C it is negligible for all irons. This threshold is probably related to the marked decrease in strength that occurs when irons are heated above 400 °C, which results in the component being more easily distorted by the development of the internal volume changes. Clearly, unalloyed irons have a very considerable usefulness up to about 700 °C, and even in a steam plant, where dimensional stability is important, there is a case for the use of unalloyed iron at temperatures up to 400 °C.

At temperatures below the critical range, an important cause of growth is *graphitization*, i.e. the decomposition of the carbide constituent of pearlite to give ferrite and graphite. Unalloyed irons usually contain up to 0.8% combined carbon, and complete graphitization of this can theoretically result in a volume increase of 1.6%. This value has been confirmed by Gilbert and White (1963) who have shown that ferritizing a fully pearlitic iron gives a linear growth of up to 0.7% (i.e. about 2.1% volume increase). Clearly, the rate of growth due to this mechanism will be controlled by the stability of the carbide in the pearlite, and this will vary with the composition of the iron. The presence of certain elements, notably silicon, decreases the stability of the carbide, while it is stabilized by the presence of other elements, namely, chromium. An iron with a low silicon content and containing some chromium may thus be expected to have good resistance, but since excessive carbide stability can lead to a hard, brittle alloy, there is a limit to the benefit that can be derived from such stability. It should be emphasized that unless large amounts of carbide-stabilizing elements are present in the iron, all that will be achieved is a slower rate of growth; there will not be a decrease in the total growth possible.

Phosphorus appears to have a beneficial effect on the growth rate. At subcritical temperatures, it helps to

stabilize the carbide, while at temperatures up to about 900 °C, the presence of the hard phosphide eutectic network restricts the deformation to which the much more ductile matrix would otherwise be subject. Since the phosphide eutectic melts at about 950 °C, irons containing appreciable amounts of this constituent should clearly not be exposed to this temperature.

Another cause of growth that is of equal importance with graphitization is the penetration of oxides into the metal along the graphite flakes. This presumably takes place because oxidizing gases can be adsorbed on the graphite and so allowed access to the metal/graphite interface. Since the oxides are more bulky than the metal from which they are derived, internal stresses are set up and growth results. As might be expected, the amount of growth due to internal oxidation increases as the graphite content increases and also as the section size increases, since this leads to a coarsening of the graphite. On the other hand, a white iron that contains no graphite is very growth resistant since it does not readily graphitize, nor is it easily penetrated by oxidation. For similar reasons, nodular graphite irons are resistant to growth.

At temperatures above the critical range, the maximum amount of growth due to graphitization may account for less than 10% of the total growth observed. Undoubtedly a large contribution to the total growth is made by the oxidation of the iron, since the stresses set up in the oxide layers by the differences between the expansion of the oxides and the iron during the alternate heating and cooling cycles generate cracks in the scale, which prevent the reaction from ever becoming self-stifling.

All the remarks so far made have been concerned with conditions of cyclic reheating. When an alloy is held at a steady temperature above the critical range, some growth will arise from graphitization, partly offset by the contraction involved in the ferrite–austenite transformation, but most of the growth will be due to oxide penetration.

Work carried out by Gilbert (1959) on irons maintained at 500 °C for 64 weeks has shown that in ordinary unalloyed flake irons, graphitization and oxidation cause roughly equal amounts of growth and that as the carbon content increases, the effect of oxidation becomes more important and the overall rate of growth increases. Nodular graphite irons grow very slowly under these conditions.

Irons designed specifically for good oxidation and growth resistance have highly oxidation-resistant matrices, containing either no carbides at all or very stable carbides, and have critical temperatures either below room temperature or above the maximum temperature anticipated. The alloys most commonly used are Silal, Niresist, Nicosilal, and Fe–30Cr. Details of these irons and their properties are given in Table 1.3. The extremely fine graphite structure present in Silal probably makes a major contribution to its

good heat resistance. However, when Silal is produced with nodular graphite, its heat resistance is further enhanced.

Two other alloys that have been used for their good oxidation and growth resistance are Cralfer (Fe–7Al–0.75Cr) and Fe–14.5Si. The production of the former, however, entails considerable difficulties, while the latter has poor mechanical properties and poor resistance to thermal shock, with the result that neither is extensively used for this purpose today.

### 1.4.3 Unalloyed and Low-Alloy Steels

On a tonnage basis, carbon and *low-alloy steels* are the most widely used engineering materials. An acceptable corrosion rate for a low-cost material such as plain carbon steel is approximately 0.2 mm a year or lower. Otherwise, unalloyed and low-alloy steels must be protected by appropriate methods. The most important alloying element of iron is carbon. The phase diagram of iron–carbon is discussed in Chapter 2.

The mechanical properties of unalloyed and low-alloy steels are determined by their chemical composition, microstructure, and heat treatment. The strength of structural steels, in particular, has been improved continuously in recent decades (Figure 1.2). On the basis of structural steels St37 and St52, new fine-grained structural steels with a yield strength up to 960 MPa (StE 690, StE 960) were developed. In a first step, the alloy content of normal structural steels was increased to furnish greater strength. But this concept was restricted by the requirement of weldability. A higher alloy content commonly reduces weldability, which is expressed by the carbon equivalent (CEV) for structural steel. For arc welding, the CEV must be in the range of 0.35–0.70. With increasing CEV preheating becomes necessary to avoid cold cracking:

$$\text{CEV} = \%C + (\%Mn/6) + ((\%Cr + \%Mo + \%V)/5) + ((\%Ni + \%Cu)/15) \quad (1.1)$$

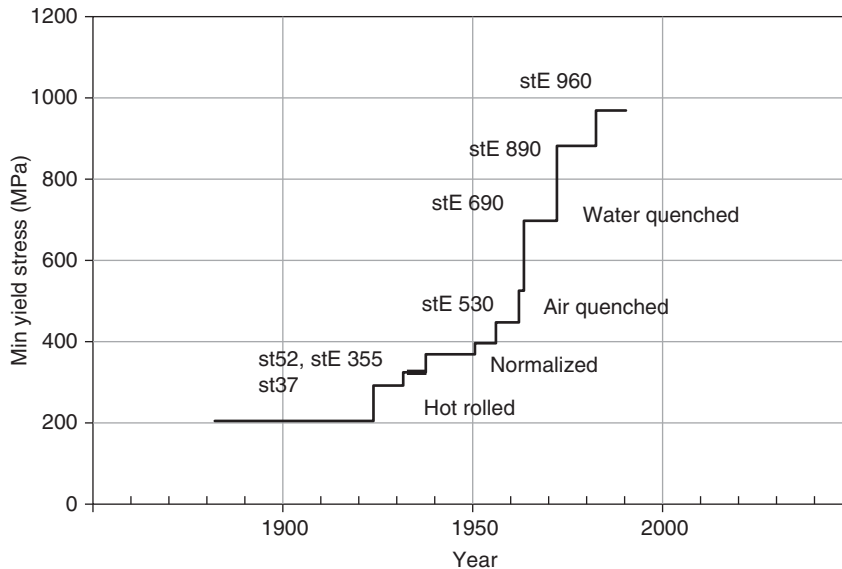
Higher strength and improved toughness was achieved by combined thermomechanical treatment and/or tempering from the hot-forming temperature. Modern high-strength structural steels are micro-alloyed steels containing Ti, Nb, Zr, and B to impart a fine-grained structure. The main applications of high-strength structural steels are pressure vessels, pipelines, and construction of apparatus.

The toughness of steel was also increased by improved ladle and process metallurgy. Most accompanying elements – sulfur and oxygen – can be removed by vacuum ladle treatment (vacuum oxygen decarburization, VOD/argon oxygen decarburization, AOD) and calcium injection into the liquid melting bath, and so the number of nonmetallic inclusions, e.g. sulfides and oxides, in the alloy is considerably reduced. Today, a sulfur content

**Table 1.3** Heat-resisting irons

| Name                  | Composition  |     |      |     |     | Structure   | Mechanical properties                           |                |                            | Critical temperature (°C) | Growth characteristics              |
|-----------------------|--------------|-----|------|-----|-----|---|---|----------------|----------------------------|---------------------------|-------------------------------------|
|                       | Total carbon | Si  | Ni   | Cr  | Cu  |   | Ultimate tensile strength (MN m <sup>-2</sup> ) | Elongation (%) | Hardness (H <sub>B</sub> ) |                           |                                     |
| Silal                 | 2.5          | 6.0 | -    | -   | -   | Fine graphite in silico-ferrite matrix                        | 154   | Nil            | 280                        | >920                      | Nil after 80 × 1 ½ h at 870 °C      |
| Nicrosil <sup>a</sup> | 2.0          | 5.0 | 20.0 | 2.0 | -   | Fine graphite in austenitic matrix with some complex carbides | 216   | 2              | 140                        | <20                       | <1% by length after 240 h at 950 °C |
| Niresist <sup>a</sup> | 3.0          | 2.0 | 20.0 | 2.0 | -   | Fine graphite in austenitic matrix with some complex carbides | 232   | 2              | 150                        | <20                       | <1% by length after 240 h at 950 °C |
|                       | 3.0          | 2.0 | 14.0 | 2.0 | 7.0 |   |   |                |                            |                           |                                     |
| High chromium iron    | 1.5          | 1.0 | -    | 30  | -   | Complex carbides in chromium-ferrite matrix                   | 463   | Nil            | 320                        | >1100                     | <1% by length after 240 h at 950 °C |

<sup>a</sup>These irons may sometimes contain up to 5% Cr, which slightly improves the heat resistance and makes the alloy stronger and harder.



**Figure 1.2** Development of high-strength weldable structural steels.

below 20 ppm and an oxygen content below 30 ppm can be reached.

The formation of calcium–sulfur compounds, in particular, influences the properties of the material. Calcium–sulfur compounds have an increased deformation resistance during hot rolling and remain nearly spherical. In the absence of calcium, injection of manganese sulfides with a very low deformation resistance will normally be obtained. During hot rolling, long banded manganese sulfide inclusions are formed, and this reduces the toughness (lamellar tearing). Spherical nonmetallic inclusions reduce the directionality of notch impact toughness and reduce susceptibility to *hydrogen-induced cracking* (HIC).

Additional alloying elements can influence the stability range of a crystal structure. Austenite is stabilized by the alloying elements Mn, Co, Ni, N, and C; ferrite is stabilized by Cr, Mo, Si, Al, Ti, and Nb. The opening up or shrinking of the  $\gamma$  phase field enables the development of austenitic and ferritic steels. For austenitic stainless steels, Cr, Ni, and Mo are the major alloying elements. It is clear that many of the reported element additions increase the HTC resistance, strength, toughness, microstructural stability, and creep resistance of the substrate alloy.

#### 1.4.4 Stainless Steels

*Stainless steels* are a versatile group of engineering materials. They have good corrosion resistance and good fracture toughness in a wide range of working conditions, such as chemically aggressive environments, cryogenic temperatures, and high temperatures. The strength–toughness ratio of some of the stainless steel grades is unique when compared with other engineering materials. Therefore, the worldwide use of stainless steel is growing about 5% a year within the traditional and new applications.

Stainless steels are iron (Fe)-based alloys, which contain 11–30 wt% chromium (Cr), low carbon (C), and nitrogen (N) content. The presence of chromium in those amounts creates an oxide “passive layer” (spinel) on the surface of the steel, thus protecting the metal against corrosion. Stainless steels can also contain other elements, such as Ni, Mo, Si, Mn, Ti, Nb, and N, which are added for different purposes.

Table 1.4 shows some of the major advancements in the history of the industrial use of stainless steels.

Stainless steels can be divided into four main groups according to their microstructure, namely, martensitic, ferritic, austenitic, and austenitic–ferritic steels. Typical compositions for each group are shown in Table 1.5.

Martensitic and ferritic stainless steels have a ferritic microstructure when delivered to customers. The *ferrite* phase that has a body-centered cubic (BCC) crystal structure and the *austenite* phase that exhibits a face-centered cubic (FCC) crystal structure differ significantly from each other with respect to their mechanical properties. The combination of these two phases, present in the austenitic–ferritic (duplex) grades, produces unique mechanical properties such as very high yield strength and excellent corrosion resistance.

The most common austenitic stainless steel is the 18Cr–9Ni (EN 1.430I, AISI 304). In this material, the austenite phase is metastable, which means that it can transform to the martensitic phase by the application of an external driving force, such as strain, or by bringing the material to low temperatures. Another interesting phenomenon exhibited by this steel is that after solidification (casting, welding), the microstructure can contain some percent (0–15%) of delta ferrite, which is the high temperature phase of iron. The reason for this is due to



**Table 1.4** Development of industrial use of stainless steel

| Decade | Industrial use in larger scale  |
|--------|---|
| 1930   | War industry (martensitic steels)   |
| 1940   | Fertilizer industry   |
| 1950   | Petrochemical/wood processing/clothing industry and housekeeping  |
| 1960   | Nuclear power stations (hot water), food industry, hospitals, varied range of consumer goods  |
| 1970   | Environmental control (fuel gas desulfurization, closed circulations, waste water treatment, exhaust tubes), building industry (panels, decoration, roofs, elevators, etc.) |
| 1980   | Offshore technology, new energy technology, cryogenics, architecture, coal gasifying, transportation industry (trains and bus coach, liquid transportation containers)      |
| 1990   | Load-bearing structural components (in building industry)   |
| 2000+  | Automotive structural parts (crash zone), lightweight structures (welded sandwich panels, cold-deformed sheets)   |

**Table 1.5** Composition of stainless steels according to EN 10088-I and corresponding ASTM/AISI grade

| Steel group         | EN     | ASTM   | Composition, wt% according to EN 10088-I |           |           |           |                               |
|---------------------|--------|--------|--|-----------|-----------|-----------|-------------------------------|
|                     |        | AISI   | C, max.                                  | Cr        | Ni        | Mo        | Others                        |
| Martensitic         | 1.4006 | 410    | 0.08–0.15                                | 11.5–13.5 | –         | –         | –                             |
|                     | 1.4028 | 420    | 0.26–0.35                                | 12.0–14.0 | –         | –         | –                             |
| Ferritic            | 1.4003 | —      | 0.03                                     | 10.5–12.5 | 0.3–1.0   | –         | –                             |
|                     | 1.4512 | 409    | 0.03                                     | 10.5–12.5 | –         | –         | Ti: 6x(C + N) ... 0.65        |
|                     | 1.4016 | 430    | 0.08                                     | 16.0–18.0 | –         | –         | –                             |
| Austenitic–ferritic | 1.4521 | “444”  | 0.025                                    | 17.0–20.0 | –         | 1.8–2.5   | Ti: 4x(C + N) + 0.15 ... 0.80 |
|                     | 1.4362 | S32304 | 0.03                                     | 22.0–24.0 | 3.5–5.5   | 0.10–0.60 | N: 0.05–0.20                  |
|                     | 1.4462 | S32205 | 0.03                                     | 21.0–23.0 | 4.5–6.5   | 2.5–3.5   | N: 0.10–0.22                  |
| Austenitic          | 1.4318 | 301LN  | 0.03                                     | 16.5–18.5 | 6.0–8.0   | –         | N: 0.10–0.20                  |
|                     | 1.4301 | 304    | 0.05                                     | 17.0–19.5 | 8.0–10.5  | –         | N < 0.11                      |
|                     | 1.4306 | 304L   | 0.03                                     | 18.0–20.0 | 10.0–12.0 | –         | N < 0.11                      |
|                     |        |        |  |           |           |           | N: 0.12–0.22                  |
|                     | 1.4311 | 304LN  | 0.03                                     | 17.0–19.5 | 8.5–11.5  | –         | Mn: 6.0–8.0, N: 0.15–0.20     |
|                     | 1.4371 | –      | 0.03                                     | 16.0–17.0 | 3.5–5.5   | –         | N < 0.11                      |
|                     | 1.4436 | 316    | 0.05                                     | 16.5–18.5 | 10.5–13.0 | 2.5–3.0   | N < 0.11                      |
|                     | 1.4404 | 316L   | 0.03                                     | 16.5–18.5 | 10.0–13.0 | 2.0–2.5   | N: 0.12–0.22                  |
|                     | 1.4406 | 316LN  | 0.03                                     | 16.5–18.5 | 10.0–12.0 | 2.0–2.5   | Cu: 1.2–2.0                   |
|                     | 1.4539 | NO8904 | 0.02                                     | 19.0–21.0 | 24.0–26.0 | 4.0–2.5   | Cu: 0.5–1.5, N: 0.15–0.25     |
|                     | 1.4547 | S31254 | 0.02                                     | 19.0–21.0 | 24.0–26.0 | 6.0–7.0   | Cu: 0.5, N: 0.4, Mn: 2.0      |
|                     | 1.4652 | S32654 | 0.01                                     | 24        | 22        | 7.3       | –                             |

the fact that the composition of this steel is very close to the composition required to produce the formation of the ferrite phase. By increasing the Ni content in this steel, to approximately 12–14%, the stability of austenite increases, and thus neither *martensite* transformation takes place during deformation nor ferrite precipitation during solidification (Brooks and Thompson 1991).

Figure 1.3 shows the equilibrium diagram for Fe–Cr alloys. In this diagram, it is evident that for chromium contents higher than about 12%, only the ferrite phase is stable up to approximately 810 °C. Another phase present in the *phase diagram* is the sigma phase (45% Cr–55% Fe), which is stable for chromium contents in the range of 10–85% and in the temperature interval of 500–810 °C. In

the chromium range of 0–12%, an austenite loop region appears in the phase diagram between temperatures of 850 and 1400 °C. The size of this austenite loop is strongly influenced by the carbon and nitrogen contents. Figure 1.4, which shows the influence of carbon and nitrogen on the austenite loop, can be used for the evaluation of the microstructure of ferritic stainless steels that are not alloyed with titanium or niobium.

As discussed before, the addition of nickel to stainless steels stabilizes the austenite phase. Figure 1.5 shows the phase diagram for the Fe–Cr–Ni system with contents of 70% and 60%. Iron contents of approximately 70% correspond to grade 18Cr–9Ni, which are the most used stainless steels. In the diagram it is clear that the

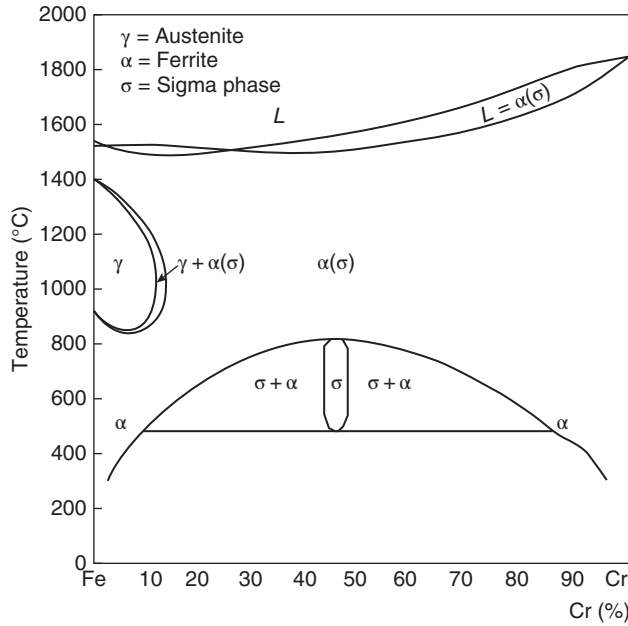


Figure 1.3 Fe-Cr phase diagram (Kubaschewski 1982).

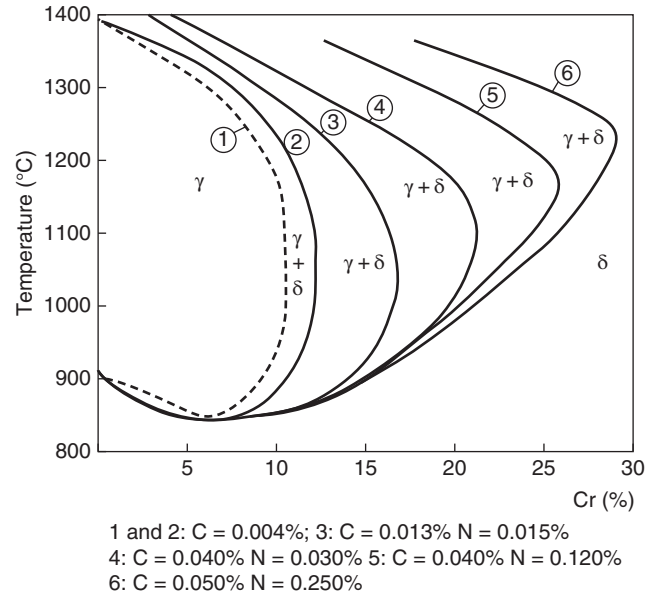


Figure 1.4 Thermal convection loop.

18Cr-9Ni stainless steel begins to solidify as delta ferrite. During cooling to room temperature already in the solid state, delta ferrite transforms gradually to austenite, and at room temperature the stainless steel exhibits a pure austenite phase. During casting or welding, the cooling rates involved are extremely fast, and thus diffusion of carbon and other alloy elements between the delta ferrite and the austenite phase is sluggish, which induces some delta ferrite to remain in the microstructure at room temperature.

The phase diagram at 70% Fe is also very useful to the evaluation of austenitic-ferritic (duplex) steels, in which the composition is typically 22Cr-5Ni-3Mo. For this composition, the microstructure is pure ferritic from the solidus line to about 100 °C. Below 1000 °C the ferritic microstructure partially changes to austenite, and at room temperature austenite/ferrite ratio is about one. The phase diagram at 60% Fe is important for the evaluation of high-alloyed austenitic stainless steels, such as alloys of the type 25Cr-15Ni.

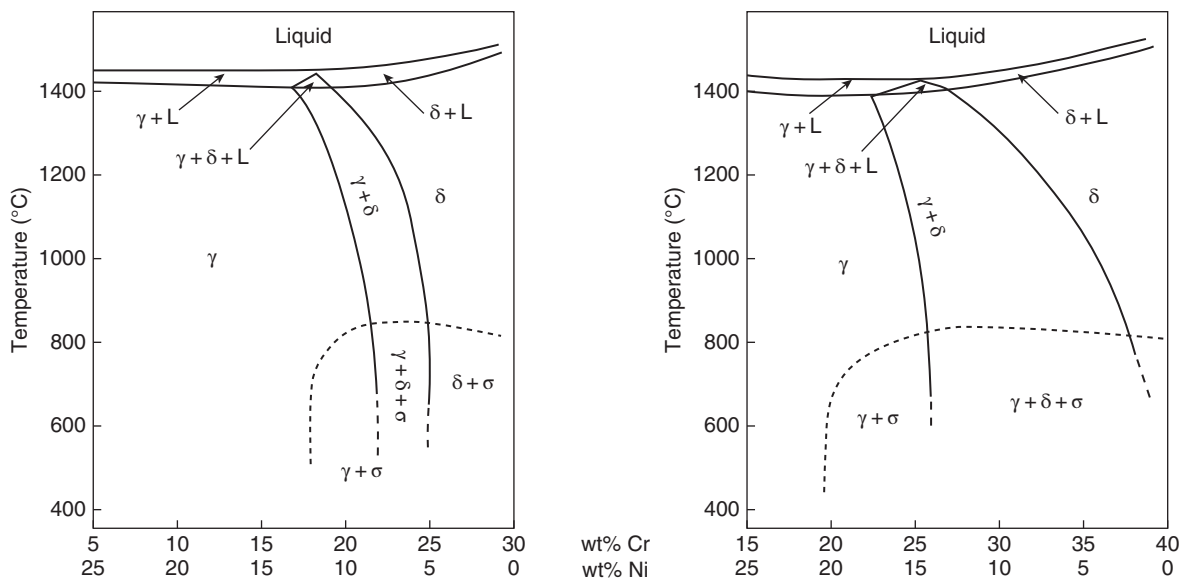
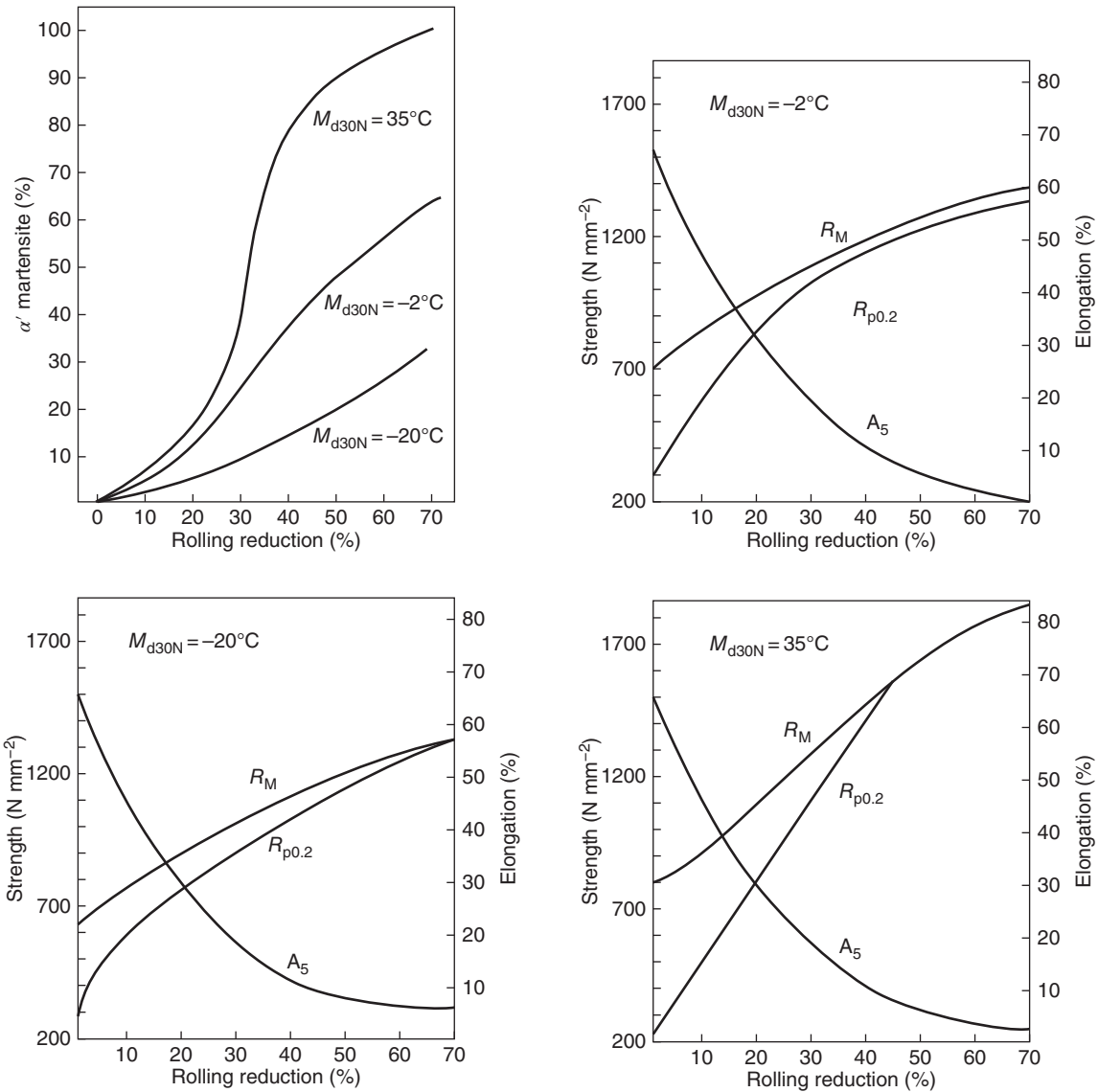


Figure 1.5 Stages in thermal gradient mass transfer.

**Table 1.6** Mechanical and physical properties of stainless steel

| Steel group         | EN     | Tensile test values, EN 10088-2 |                              |                              |                 | Physical properties   |   |
|---------------------|--------|---------------------------------|------------------------------|------------------------------|-----------------|---|---|
|                     |        | $R_{p0.2}$ ,<br>min. 20 °C      | $N\text{ mm}^{-2}$<br>300 °C | $R_m$ ( $N\text{ mm}^{-2}$ ) | $A_{80}$ % min. | Expansion coefficient,<br>20–100 °C ( $10^{-6}\text{ K}^{-1}$ ) | Thermal conductivity,<br>20 °C ( $\text{W mK}^{-1}$ ) |
| Ferritic            | 1.4003 | 280                             | 215                          | 450–650                      | 20              | 10.4  | 25  |
|                     | 1.4512 | 210                             | 180                          | 380–560                      | 25              | 10.5  | 25  |
|                     | 1.4016 | 260                             | 200                          | 450–600                      | 20              | 10.0  | 25  |
| Austenitic–ferritic | 1.4362 | 420                             | (255)                        | 600–850                      | 20              | 13.0  | 15  |
|                     | 1.4462 | 480                             | (290)                        | 660–950                      | 20              | 13.0  | 15  |
| Austenitic          | 1.4301 | 230                             | 110                          | 540–750                      | 45              | 16.0  | 15  |
|                     | 1.4318 | 350                             | 170                          | 650–850                      | 35              | 16.0  | 15  |
|                     | 1.4371 | 300                             | 165                          | 650–850                      | 45              | 16.0  | 15  |
|                     | 1.4436 | 240                             | 127                          | 550–700                      | 40              | 16.0  | 15  |
|                     | 1.4529 | 300                             | 170                          | 650–850                      | 40              | 16.0  | 15  |



**Figure 1.6** The effect of cold rolling reduction on the volume percentage of martensite and the corresponding strength and ductility of austenitic 18/8 stainless steels for different  $M_{d30N}$  values.

Table 1.6 shows some examples of mechanical and physical values for ferritic, austenitic–ferritic, and austenitic stainless steels. As discussed above, during cold deformation, an 18Cr–9Ni austenitic stainless steel transforms partly to martensite. The ability to form martensite during cold working can be expressed as a  $M_{d30N}$  value, which is the temperature at which 30% cold deformation causes 50% of martensitic structure. This can be expressed as Nohara et al. (1977)

$$M_{d30N}(^{\circ}\text{C}) = 551 - 462 \times (\%C + \%N) - 9.2 \times \%Si - 8.1\% \times \%Mn - 13.7 \times \%Cr - 29 \times (\%Ni + \%Cu) - 68 \times \%Nb - 18.5\% Mo + 1.42 \times (\text{grain size ASTM} - 8) \quad (1.2)$$

Figure 1.6 shows the effect of cold rolling reduction on martensite formation and the associated strength and ductility of austenitic stainless steels at different  $M_d$  values. Austenitic stainless steels show a unique combination of strength and ductility in the cold-rolled condition.

Austenitic stainless steels in the cold-rolled condition are also part of the Euro standard 10088-2 and ASTM designation A-666. The Euro standard specifies the strengths as  $R_m$  values, whereas the ASTM designation specifies the  $R_{p0.2}$ ,  $R_m$ , and  $A_5$  values (Table 1.7).

In the production of stainless steel products, good formability is often required. The most common forming types are bending, drawing, and lathe spinning/flow turning. In bending, the bending radius is a critical material parameter. Generally speaking, the following bending radii, shown in Table 1.8, can be used.

**Table 1.7** Cold-worked austenitic stainless steels in the Euro standard EN 10088–2 and ENV 1993–1-4; Eurocode 3 and correspondence to ASTM A-666

| Strength class | EN, yield strength, $f_y$ min. (N mm <sup>-2</sup> ) | ASTM, ultimate strength, $f_u$ min. (N mm <sup>-2</sup> ) | A-666 correspondence |
|----------------|--|---|----------------------|
| C700           | 350  | 700   | 1/8 Hard             |
| C850           | 530  | 850   | 1/4 Hard             |
| C1000          | 750  | 1000  | 1/2 Hard             |
| C1150          | 900  | 1150  | 3/4 Hard             |
| C1300          | –  | 1300  | Full hard            |

**Table 1.8** Minimum bending radius of austenitic and ferritic stainless steels, thickness up to 4.75 mm (Davis 1996)

| Steel grade, AISI  | Minimum bending radius, $t$ = thickness |
|--------------------|---|
| 301, 302, 304, 316 | $\frac{1}{2} t$                         |
| 430, 410           | $t$                                     |

In *drawing*, the strength of the material can be described in the form (true stress–true strain)

$$\sigma = k\varepsilon^n \quad (1.3)$$

where  $\sigma$  is the stress,  $\varepsilon$  is the strain,  $n$  is the strain hardening exponent, and  $k$  is a constant.

During the drawing operation of the sheet, three different strains can be defined, namely,  $\varepsilon_1$  (drawing direction),  $\varepsilon_2$  (transverse direction parallel to the surface), and  $\varepsilon_3$  (transverse direction and perpendicular to the surface). These strains can be expressed as follows:

$$\varepsilon_1 = \ln(l/l_0), \text{ where } l_0 \text{ is the initial length of the workpiece and } l \text{ the final length.}$$

$$\varepsilon_2 = \ln(w/w_0), \text{ where } w_0 \text{ is the initial width of the workpiece and } w \text{ the final width.}$$

$$\varepsilon_3 = \ln(t/t_0), \text{ where } t_0 \text{ is the initial thickness of the workpiece and } t \text{ the final thickness.}$$

The strain ratio  $r = \varepsilon_2/\varepsilon_3$  can be calculated from the drawing direction by using  $\varepsilon\varepsilon_1$ . The  $r$  value represents the tendency of the metal sheet for deformation along the width and thickness. Normally, the mechanical properties vary as a function of the direction, and thus drawing properties can be described by the anisotropy parameters  $r_n$  and  $\Delta r$ , where  $r$  values have been measured along the 45° and 90° direction relative to the rolling direction of the sheet:

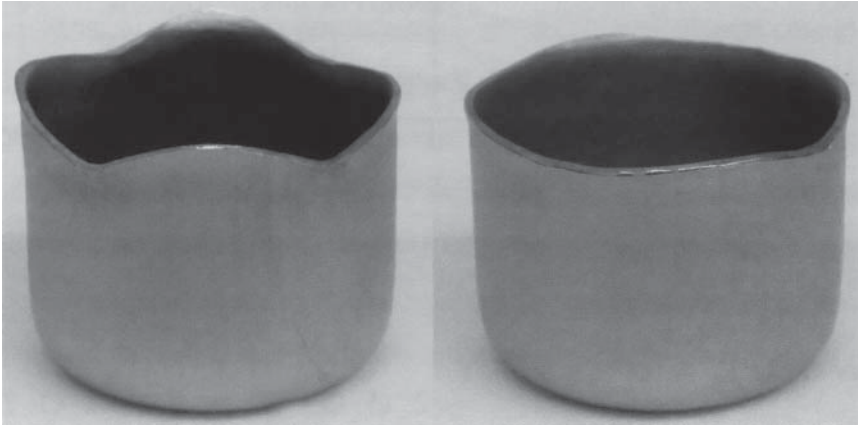
$$\text{Normal strain ratio : } r_n = (r_0 + r_{90} + 2r_{45}) \quad (1.4)$$

$$\text{Planar strain ratio : } \Delta r = (r_0 + r_{90} - 2r_{45}) \quad (1.5)$$

The deep drawability of the material can also be studied with the “Swift cup test” in which the cup, shown in Figure 1.7, is deep-drawn with different initial blank diameters. The largest initial blank (diameter) drawn without cracking specifies the *limiting drawing ratio* (LDR). The planar anisotropy can also be measured with the “Swift cup test.” This factor is called the *earing index* (%), shown in Figure 1.7.

The values for different formability tests are shown in Table 1.9 for the two common stainless steels EN 1.4301 and EN 1.4016. Austenitic stainless steels have higher values of  $n$  than ferritic stainless steels and therefore exhibit better properties during expansion (stretching) ( $\varepsilon_1 > 0$  and  $\varepsilon_2 > 0$ ), whereas ferritic steels perform better in deep drawing because of their high  $r_n$  values. In ferritic stainless steels, the  $r_n$  and  $\Delta r$  very much depend on the crystallographic texture, which is influenced by the rolling and heat treatment procedures.

The *forming* process can be described by forming limit diagrams (FLDs), which show the behavior of materials in two planar strain ( $\varepsilon_1, \varepsilon_2$ ) conditions. Figure 1.8 shows the principal diagram for austenitic and ferritic steels, for which

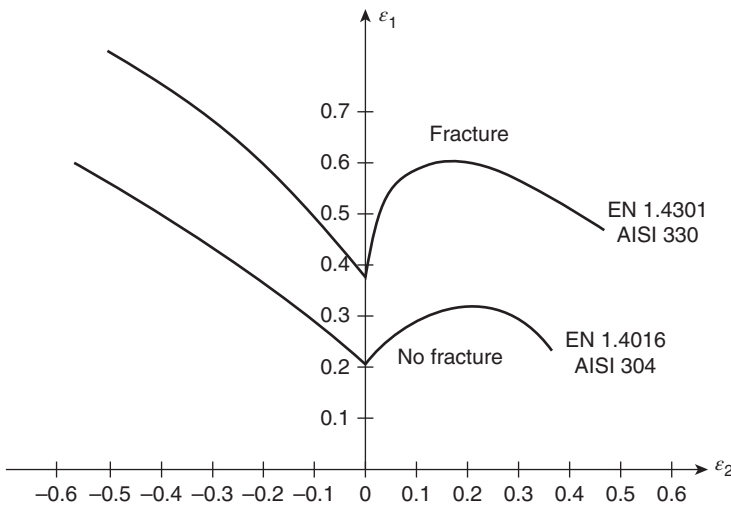


**Figure 1.7** Swift cup test samples with different ear heights.

**Table 1.9** Typical values of formability parameters for austenitic (EN 1.4301) and ferritic (EN 1.4016) stainless steels

| Steel EN | $n$       | $r_n$   | $\Delta_r$ | Earing index (%) <sup>a</sup> | LDR       |
|----------|-----------|---------|------------|-------------------------------|-----------|
| 1.4301   | 0.50–0.70 | 1.0–1.3 | 0.45       | 5–7                           | 2.00–2.05 |
| 1.4016   | 0.20–0.25 | 1.1–1.6 | 0.50       | 8–12                          | 2.05–2.10 |

<sup>a</sup>Swift cup test.



**Figure 1.8** Forming limit diagram (to fracture) for austenitic and ferritic stainless steels.

the limits to cracking can be seen. The left side of the diagram is related to deep drawing ( $\epsilon_1 > 0$  and  $\epsilon_2 < 0$ ) and the right part related to expansion ( $\epsilon_1 > 0$  and  $\epsilon_2 > 0$ ).

Welding is the most common joining method for steels. Adhesive bonding, mechanical joining, brazing, and soldering can also be used to join thin stainless steel sheets. However, most large stainless steel structures, such as tubes, containers, and machines, are typically joined by welding. Arc, resistance, and laser welding are the most common welding methods for stainless steels.

The weldability for stainless steels can be studied with an original *Bystram diagram* (Figure 1.9), which is based

on the well-known Schaeffler diagram (Schaeffler 1949), which shows the expected stable phases in the steel after arc welding. The diagram relates the steel composition to the problems encountered in welding. The most common austenitic stainless steels (1.4318, 1.4301, 1.4404, etc.) have been designed to be in the optimal point of the Bystram diagram.

On the basis of the Bystram diagram, stainless steels can be divided into different categories concerning weldability in arc welding. In martensitic stainless steels and in the ferritic 1.4016 steel, the reason for poor weldability is the formation of the brittle martensite phase in the weld and

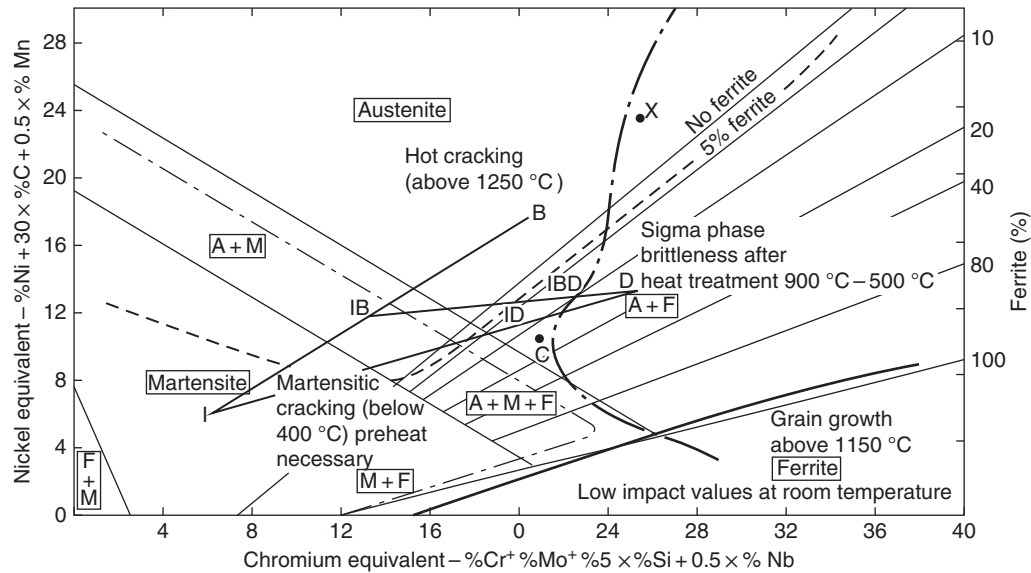


Figure 1.9 Bystram diagram for stainless steels in arc welding (Bystram 1956).

in the base metal heat-affected zone (HAZ). In addition, ferritic stainless steels (1.4512 and 1.4521) can have their ductility and impact toughness at low temperature degraded because of grain growth during welding. Good results have been obtained with the more modern low carbon ferritic steel 1.4003, which exhibits fine dispersed martensite in the microstructure after welding. By limiting the welding energy, low ductile-to-brittle transition temperatures ( $-40^{\circ}\text{C}$ ) have been obtained in the HAZ. In the case of austenitic–ferritic steels, there is some susceptibility to ferrite grain growth and intermetallic phase formation during the welding thermal cycle. Therefore, limited welding energy is needed. On the other hand, austenitic stainless steels have very good general weldability characteristics. However, because of large coefficients of thermal expansion and low thermal conductivity, austenitic stainless steels have a tendency to hot cracking, which can become a problem for good weldability. Therefore, sulfur and phosphorus contents, which increase hot cracking susceptibility, have been often restricted to a maximum of about 0.001% and 0.002%, respectively.

The basic importance of chromium in relation to *passivity* in the resistance of steels to aqueous corrosion is paralleled by its role as the most important alloying element in practice in securing the high temperature oxidation resistance of heat-resisting steels. It is not surprising, therefore, that these two aspects of corrosion resistance developed together, and early investigators of the chromium–iron alloys showed interest in the potential usefulness of these materials for high temperature oxidation resistance. Thus, Hatfield (1927), discussing early studies in France, has indicated that the scaling resistance of Fe–Ni–Cr alloys was appreciated at least as early as 1917.

It can therefore be said that it is the chromium content of the stainless steels that in the main establishes the steels susceptibility to general oxidation/corrosion. Stainless steels are also susceptible to local corrosion, called grain boundary corrosion, which is caused by the precipitation of  $\text{Cr}_{23}\text{C}_6$  along grain boundaries, leading to Cr-depleted zones in the vicinity of grain boundaries. This type of corrosion has nearly been completely eliminated in the modern low carbon steels.

One other severe type of corrosion formed only in austenitic stainless steels is the stress corrosion cracking mechanism, in which fine cracks grow across the microstructure assisted by  $\text{Cl}^-$  ions, stress, and temperatures above  $60^{\circ}\text{C}$ . A typical case is the welded or cold-formed structure when used at high temperatures in water or steam. High nickel stainless steel grades (20% Ni) are not as susceptible as 8–10% Ni grades. Ferritic stainless steels are immune to stress corrosion cracking.

In the United Kingdom the rapidly growing interest in high-alloy steels after World War I coincided with expanding needs of industry for materials of improved strength and oxidation resistance at elevated temperatures. Aeroengine developments, rising steam temperatures and pressures in power production, and the increasing importance of high temperature, high pressure processes in oil-cracking and synthetic chemistry were all contributory factors in the development of heat-resisting steels from the 1920s. Nowadays, the heat-resisting steels are used for a wide range of general engineering and chemical engineering applications where the corrosion resistance, and in some instances strength, of the lower-alloy steels is inadequate. The martensitic steels, because of their lower oxidation resistance, are normally used for the less