

# High-Temperature Corrosion of Engineering Alloys



**George Y. Lai**

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# **High-Temperature Corrosion of Engineering Alloys**

To my parents, my wife Mei-Huei, and my daughter Christine

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# Preface

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Working for a major superalloys and high-performance alloys producer, I constantly receive telephone calls from various companies seeking technical consultation. Most of those calls are concerned with materials selection for applications in high-temperature, corrosive environments. Many questions are related to processes in traditional industries such as heat treating, metallurgical processing, refining and petrochemical processing, chemical processing, fossil power generation, etc. Many others, however, are related to emerging industries such as waste incineration and resource recovery, coal gasification and advanced energy conversion, fluidized-bed combustion, etc.

Most high-temperature corrosion problems encountered in industry can be attributed to the following modes of corrosion:

- Oxidation
- Carburization and metal dusting
- Nitridation
- Halogen corrosion
- Sulfidation
- Ash/salt deposit corrosion
- Molten salt corrosion
- Molten metal corrosion

Surprisingly, there has not been a single book covering up-to-date data for all these corro-

sion reactions, where engineers can find solutions to their high-temperature corrosion problems. There are a number of books on corrosion; however, they deal primarily with aqueous and low-temperature corrosion, only briefly touching on high-temperature corrosion. There are also several books on oxidation. These books, discussing mainly mechanistic aspects of oxidation, are excellent for researchers, but provide little engineering data to help engineers make informed materials selection decisions.

The purpose of this book is to provide materials engineers with extensive, up-to-date high-temperature corrosion data pertinent to "real" industrial problems. The book covers primarily engineering data, with some discussion of fundamental aspects of corrosion reactions. The focus is mainly on commercial alloys. Thus, engineers can use the data to select a viable alloy that is commercially available for immediate application. It is my hope that readers will find the book useful for solving material problems caused by high-temperature corrosion.

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George Y. Lai  
Carmel, Indiana  
July 1990

# UNITS

Chemical compositions of alloys are all in weight percent unless otherwise noted. Compositions of gases are all in volume percent unless otherwise noted. Other units and their conversions used in this book are:

|                    |   |                           |
|--------------------|---|---------------------------|
| mpy                | = | mils per year             |
| mm/y               | = | mm per year               |
| 1 mil              | = | 0.001 in.                 |
| 1 mil              | = | 0.0254 mm                 |
| 1 mm               | = | 39.4 mils                 |
| 1 in.              | = | 25.4 mm                   |
| 1 $\mu\text{m}$    | = | 0.001 mm                  |
| 1 m                | = | 1000 mm                   |
| 1 nm               | = | $10^{-9}$ m               |
| 1 nm/h             | = | 0.00876 mm/y = 0.345 mpy  |
| 1 g                | = | 1000 mg                   |
| 1 g/m <sup>2</sup> | = | 0.1 mg/cm <sup>2</sup>    |
| 1 in. <sup>2</sup> | = | 6.4516 cm <sup>2</sup>    |
| 1 dm               | = | 10 cm                     |
| 1 atm              | = | 14.7 psi                  |
| 1 atm              | = | 101,356.5 Pa              |
| 1 Pa               | = | $9.87 \times 10^{-6}$ atm |
| 1 bar              | = | 0.9869 atm                |



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# Introduction

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High-temperature corrosion plays an important role in the selection of material for construction of industrial equipment—ranging from gas turbines to heat treating retorts. The principal modes of high-temperature corrosion frequently responsible for equipment problems are:

- Oxidation
- Carburization and metal dusting
- Nitridation
- Halogen corrosion
- Sulfidation
- Ash/salt deposit corrosion
- Molten salt corrosion
- Molten metal corrosion

The industries that face these high-temperature corrosion problems include:

- Aerospace and gas turbine
- Heat treating
- Mineral and metallurgical processing
- Chemical processing
- Refining and petrochemical processing
- Ceramic, electronic, and glass manufacturing
- Automotive
- Pulp and paper
- Waste incineration
- Fossil fuel power generation

- Coal gasification
- Nuclear

Oxidation is the most important high-temperature corrosion reaction. In most industrial environments, oxidation often participates in the high-temperature corrosion reaction, regardless of the predominant mode of corrosion. In fact, alloys often rely upon the oxidation reaction to develop a protective oxide scale to resist corrosion attack such as sulfidation, carburization, and ash/salt deposit corrosion.

Environments are frequently classified, in terms of oxygen activity, as either “oxidizing” or “reducing.” An oxidizing atmosphere is an environment that contains molecular oxygen ( $O_2$ ), such as air or a combustion atmosphere with excess “free” oxygen. Oxygen activity in this case is very high and is controlled by the concentration of molecular oxygen. A reducing atmosphere is generally produced by combustion under stoichiometric or substoichiometric conditions with no excess oxygen. The oxygen activity is very low in this case and is controlled by  $CO/CO_2$  or  $H_2/H_2O$ . The reducing atmosphere is generally more corrosive for many corrosion modes, such as sulfidation, carburization, nitridation, and ash/salt deposit corrosion.

When an environment has a high sulfur ac-

tivity (or sulfur potential), the corrosion reaction will more likely be dominated by sulfidation. The reaction will also be influenced by oxygen activity. Lowering the oxygen activity tends to make the environment more sulfidizing, resulting in increased domination by sulfidation. Conversely, increasing the oxygen activity generally results in a less sulfidizing environment. The reaction is then increasingly dominated by oxidation. Thus, sulfidation is controlled by both sulfur and oxygen activities.

Carburization behaves in a similar fashion. The reaction is controlled by both carbon and oxygen activities. Lowering the oxygen activity tends to make the environment more carburizing, and vice versa. Nitridation is the same in that the reaction becomes more severe when the environment is reducing.

In halogen corrosion, oxygen activity influences the reaction differently. For example, high-temperature corrosion in chlorine-bearing environments is generally attributed to the formation of volatile metallic chlorides. Oxidizing environments cause some alloys with high levels of molybdenum and tungsten to suffer significantly higher corrosion rates, presumably by forming very volatile oxychlorides. Reducing environments often are less corrosive. Nevertheless, the reaction is controlled by both halogen and oxygen activities.

Many industrial environments may contain several corrosive contaminants that tend to form ash/salt deposits on metal surfaces during high-temperature exposure. These ash/salt deposits can play a significant role in the corrosion reaction. "Hot corrosion" for gas turbine components is a good example. Sulfur from the fuel and NaCl from the ingested air may react during combustion to form salt vapors, such as  $\text{Na}_2\text{SO}_4$ . These salt vapors may then deposit at lower temperatures on metal surfaces, resulting in accelerated corrosion attack. In fossil-fired power generation, ash/salt deposits are also very common because of sulfur and vanadium in the fuel oil, particularly low-grade fuels, and alkali metals, chlorine, and sulfur in the coal. The accelerated corrosion due to ash/salt deposits in

this case is frequently referred to as "fuel ash corrosion." Both hot corrosion and fuel ash corrosion are generally believed to be related to liquid salt deposits, which destroy the protective oxide scale on the metal surface. Waste incineration generates very complex ash/salt deposits, which often contain sulfur, sodium, potassium, chlorine, zinc, lead, phosphorus and other elements. Ash/salt deposits are common in waste heat recovery systems for industrial processes, such as aluminum remelting operations and pulp and paper recovery boilers, and are also common in calcining operations for various chemical products. This mode of corrosion is referred to as "ash/salt deposit corrosion."

There are other types of low-melting compounds that can form on the metal surface during the high-temperature reaction. The most common ones include  $\text{V}_2\text{O}_5$ ,  $\text{MoO}_3$ , and Ni-P compounds. These liquid phases can easily destroy the protective oxide scale and result in accelerated corrosion attack. When  $\text{V}_2\text{O}_5$  or  $\text{MoO}_3$  is involved, the attack is referred to as "catastrophic oxidation." When the environment contains phosphorus, high-nickel alloys may react with it to form low-melting Ni-P eutectics, which then destroy the protective oxide scale. The subsequent oxidation or other mode of attack is thus accelerated.

Two other important high-temperature corrosion modes are molten salt corrosion and molten metal corrosion. Oxygen activity may still play an important role in the corrosion reaction for both environments. For example, in a molten salt pot the worst attack frequently occurs at the air-salt interface, presumably because that is where oxygen activity is highest.

The above brief outline describes the important environments and principal modes of high-temperature corrosion encountered in various industrial processes. These are summarized schematically in Fig. 1.1. The figure also illustrates that in each corrosion mode there will be interactions between oxygen activity and a principal corrodent activity.

To deal effectively with the high-temperature corrosion problems associated with processing equipment, the materials engineer

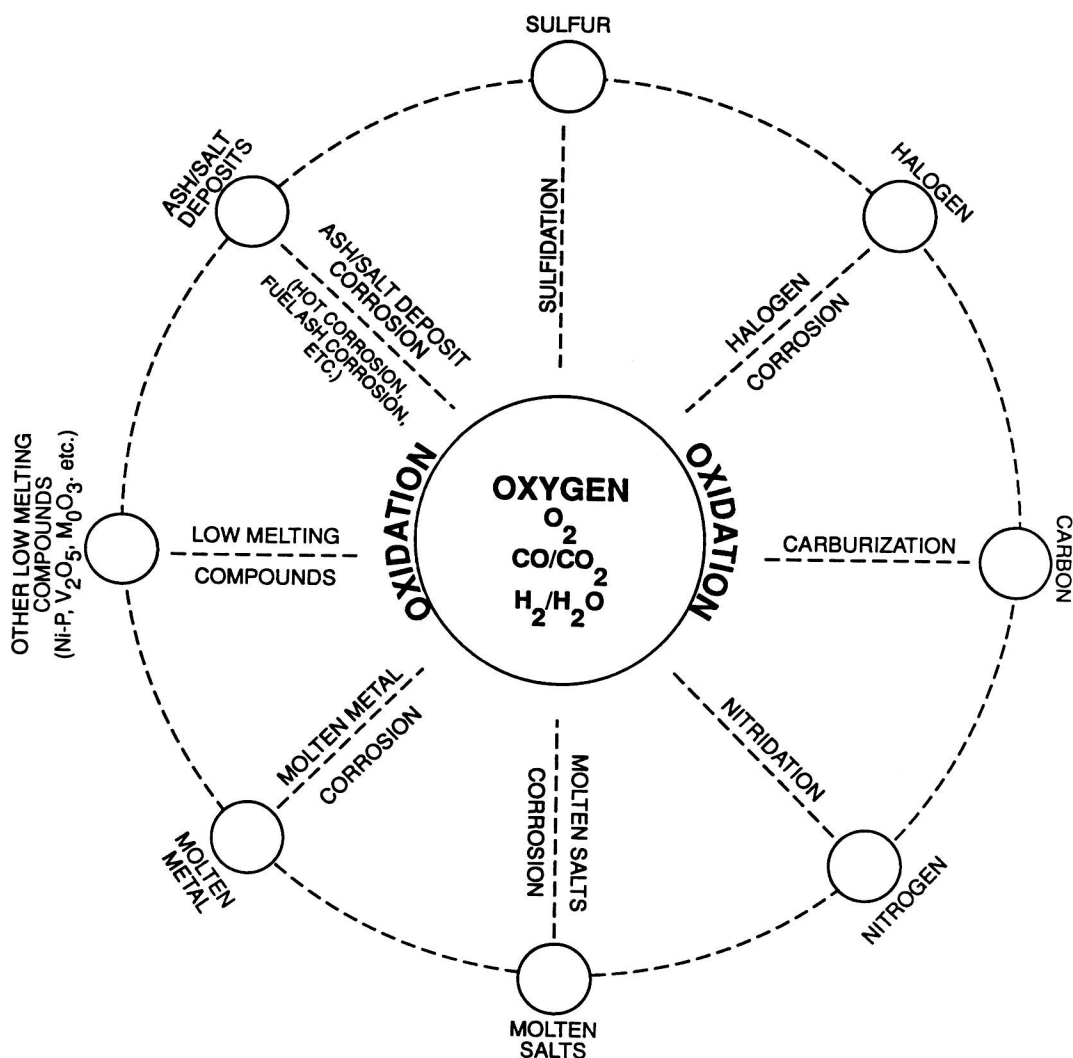


Fig. 1.1 Schematic showing the principal modes of high-temperature corrosion in industrial environments, as well as the interaction between oxygen activity and a principal "corrodent" activity

needs both a strong background in high-temperature corrosion and an extensive high-temperature corrosion database on commercial alloys. Most materials engineers in industry are responsible for a variety of metallurgical issues, such as welding, fabricating, mechanical properties, metallurgical structures, embrittlement, high-temperature corrosion, and aqueous corrosion. They also have to deal with a wide variety of materials, both metallic and nonmetallic. The pressure to solve a production-related corrosion prob-

lem quickly often prevents an extensive literature search of relevant corrosion data.

The purpose of this book is to provide materials engineers with extensive, up-to-date high-temperature corrosion data pertinent to real industrial problems. The book primarily covers engineering data, with some discussions on fundamental aspects of corrosion reactions. Most data are presented to reveal alloy ranking, and thus serve as a guide to materials selection. The effects of alloying elements, temperature, and environmental

conditions on the corrosion behavior of alloys are also discussed, providing information about the alloy's capability in terms of the useful temperature limitation.

The focus is on commercial alloys, including both generic and proprietary alloys. Engineers can thus use the data and information to select a viable alloy that is commercially available for immediate application. These

commercial alloys primarily include carbon and low-alloy steels, stainless steels, and iron-, nickel-, and cobalt-base alloys, including those referred to as high-performance alloys and superalloys. Trademarks for alloys and alloy manufacturers are listed in Appendix 1. The compositions of these alloys are tabulated in Appendix 2.

# 2

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## Methods of Testing and Evaluation

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### 2.1 Laboratory Testing

#### 2.1.1 Introduction

Laboratory testing is important in understanding the behavior of metals and alloys in various corrosive environments. Most of the scientific theories on high-temperature corrosion have been developed through laboratory study. Laboratory testing has also contributed significantly to the wealth of corrosion data that allows engineers to make informed materials selections for various processing equipment.

There are, however, several drawbacks. A laboratory test cannot simulate exactly the operating environment and conditions of a processing system. Another drawback is the relatively short test duration compared to the equipment's design life. Extrapolation becomes necessary to make materials behavior predictions. One major problem with extrapolation is the unpredictability of breakaway corrosion. In many cases, metals and alloys

rely on the formation of protective scales (mostly oxide scales) to resist high-temperature corrosion attack. Although it is generally understood that the protective scale may eventually break down, leading to breakaway corrosion, it is not currently possible to predict the onset of breakaway corrosion. Thus, laboratory tests are often conducted under accelerated conditions (e.g., higher temperatures and/or more corrosive environments) in order to increase the confidence level for the selected alloy. The accelerated test is also frequently used for initial alloy screening to narrow down the viable candidates for long-term tests and/or field trials. Extreme care should be taken if the results of short-term tests and/or accelerated tests are used for life extrapolation.

#### 2.1.2 Test Methods

The gravimetric method is widely used to study oxidation and other forms of high-temperature corrosion. This test method involves



measuring the specimen's weight as a function of time. Test apparatus that continuously monitors the specimen's weight during testing with a recording balance is very popular in academia for conducting oxidation studies. One such test apparatus (Ref 1) is shown schematically in Fig. 2.1. This particular experimental arrangement has a nice feature that allows the inlet test gas to be preheated to the test temperature in a small tube prior to reaction with the test sample in the reaction chamber. Preheating the inlet test gas is particularly desirable when the test involves a mixture of several gaseous components, be-

cause preheating allows the gas mixture to reach thermodynamic equilibrium prior to reaction with the test sample.

The major advantage of a gravimetric apparatus with an automatic recording balance is the continuous record of the reaction kinetics. It is an excellent way of studying kinetics and mechanisms of a high-temperature corrosion reaction. The disadvantage is that only one sample can be tested each time, so generating comparative data for a number of candidate alloys is a lengthy process. Therefore, the method is not very suitable for generating an engineering database.

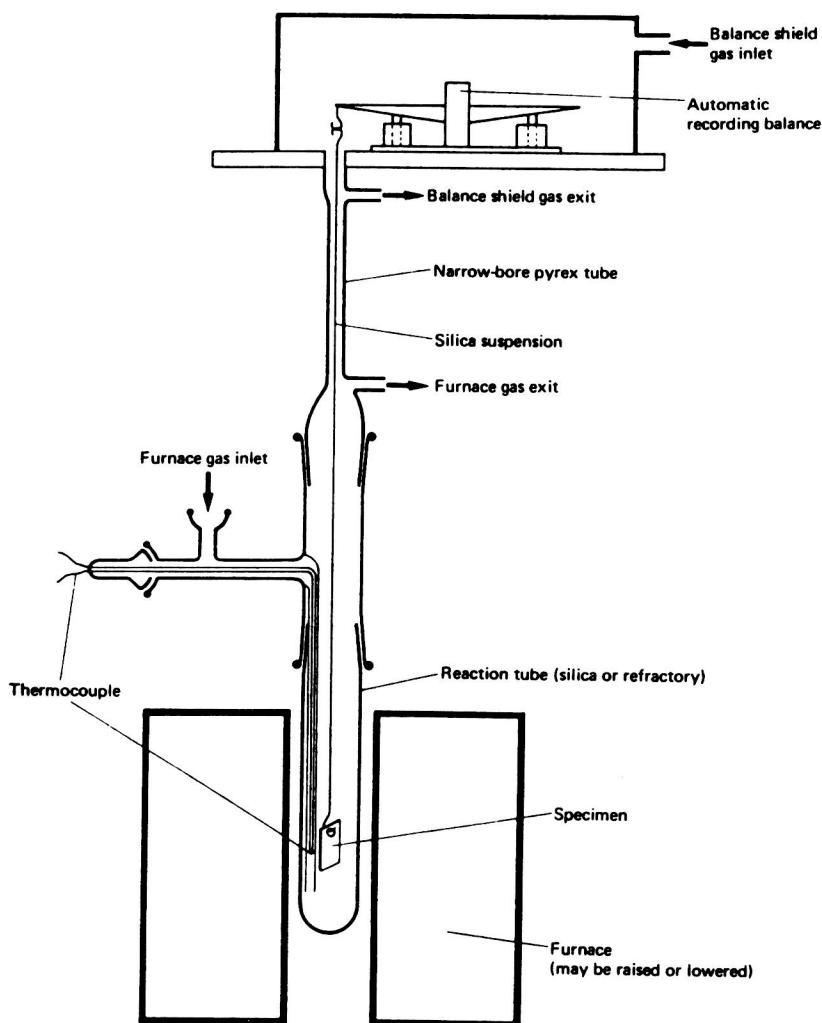


Fig. 2.1 Schematic of a thermogravimetric apparatus with an automatic recording balance for oxidation and other high-temperature gas-metal reactions. Source: Ref 1