

# High-Temperature Corrosion and Materials Applications

**George Y. Lai**



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**To my grandsons Spencer and Wesley**



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# Preface

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Since the publication of my book *High-Temperature Corrosion of Engineering Alloys* about 17 years ago, there has been a tremendous increase in the publications of high-temperature corrosion data and the emergence of new, challenging high-temperature corrosion and materials problems faced by several industries. Once thought to be a mandane fuel, household garbage under combustion produces a very hostile environment in a waste-to-energy boiler, thus resulting in high wastage rates for the waterwalls of the boilers. The waterwall steel tubes could be corroded through in less than 12 months of service for many boilers. For coal-fired boilers, NO<sub>x</sub> emissions are required to be reduced to comply with the Clean Air Act Amendments of 1990. The combustion of coal was then changed from a conventional firing with excess air with production of undesirable NO<sub>x</sub> to a staged firing by the substoichiometric combustion (i.e., combustion with insufficient oxygen) in the lower furnace followed by introduction of adequate air from overfire air ports at a higher elevation to complete the combustion process, thus significantly reducing the amount of NO<sub>x</sub> produced in the emission. The consequence of the staged firing is the significant increase in the waterwall tube wastage rates, which may increase from approximately less than 0.25 mm/yr (10 mpy) under the traditional firing with excess air to a rate of up to 2.54 mm/yr (100 mpy) for many boilers. As a result of the staged firing under reducing conditions in the lower furnace, some supercritical units have experienced higher tube-wall temperatures, thus staged firing likely to be responsible for another waterwall tube problem—circumferential cracking. In the pulp and paper industry, black liquor recovery boilers has also been experiencing tube corrosion and cracking issues during this time period.

As a metallurgical and corrosion consultant in recent years, I have been heavily involved in determining the root causes of various boiler tube failures related to waste-to-energy boilers, coal-fired boilers, oil-fired boilers, and black liquor recovery boilers. My extensive failure analysis experience with these failed boiler tubes and my visits to some of these plants have provided me with a better understanding of plant operating conditions and associated failure problems. In-depth discussions on the materials problems related to these boilers are presented in this book.

One common problem but less understood in the industry is erosion/corrosion. Component failures under particle-laden gas streams are often thought to result from erosion. In fact, many of those failures should have been attributed to erosion/corrosion. For example, steam soot blowers are often used in boilers to remove fly-ash deposits from boiler tube surfaces. The damages on the tubes are often referred to as soot-blower erosion in the boiler industry. However, the soot-blower erosion, in fact, is primarily caused by erosion/corrosion. Chapter 8 is devoted to erosion and erosion/corrosion phenomena. The subject of the effect of stresses (or strains) on the aqueous corrosion, such as stress-corrosion cracking, is very well known in the industry. Unfortunately, the similar subject on the effect of stresses (or strains) on the high-temperature corrosion is not well known in the industry. Alloys can develop preferential corrosion penetration under tensile stresses (or strains) in certain aggressive environments, such as sulfidizing environments, at elevated temperatures. Applied stresses (or residual stresses), under certain conditions, can cause components made of certain alloys to suffer brittle, intergranular cracking when exposed to intermediate temperatures. This phenomenon is often referred to as reheat cracking, relaxation cracking, or strain-age cracking. Both of these stress-related subjects are included in Chapter 14, “Stress-Assisted Corrosion and Cracking.”

Materials problems due to oxidation, carburization and metal dusting, nitridation, halogen corrosion, sulfidation, hot corrosion, molten salt corrosion, and liquid metal corrosion and embrittlement still abound in the industry. Some of these chapters are greatly expanded due to tremendous increases in technical publications. The book also includes an “old” subject—hydrogen attack. The phenomenon

is related to the reaction of carbon steel with atomic hydrogen at elevated temperatures to form methane gas in the steel, thus resulting in the formation of microfissures and eventually leading to rupture failures of steel components. With “old” engineers gradually retiring, new engineers may not be familiar with this “old,” but important, subject. This can occur in refinery vessels exposed to high-pressure, high-temperature hydrogen as well as in boiler tubes due to heavy waterside corrosion.

The purpose of the current book is to provide engineers with extensive, up-to-date technical data pertinent to “real” materials problems and issues in the industry. The book covers primarily engineering data, with brief discussion of thermodynamic aspects of the corrosion reactions. Brief discussion of the plant process along with its operating conditions is also provided to help readers to better understand the possible corrosion reactions. The focus is mainly on commercial alloys. The effect of alloying elements is also included in the discussion. The data may also provide a useful trend, thus allowing engineers to make a more informed materials selection. Most data reported in this book were generated from laboratory testing. In many industrial systems, plant operating conditions are generally quite complex; it is rather difficult to use laboratory tests to simulate the plant conditions. Furthermore, operating conditions may vary from plant to plant even for the same processing system. In situ field testing or field trials of candidate alloys in the operating plant provides the best way of obtaining corrosion information that can be reliably used for final materials selection for the particular plant of interest. Nevertheless, it is my hope that readers will find the book useful in helping them to address materials problems in current plants or to anticipate materials issues in future plants.

I would like to thank Haynes International, Inc. for allowing me access to its excellent technical library during the course of my writing. Many thanks to Mrs. Amy Russell, Haynes International’s librarian, for her kind help during my literature review for the book. Appreciation is also due to those authors whose works have been discussed and cited in the book. I am especially grateful to my reviewers: Dr. Hira Ahluwalia, consultant; Mr. Roger Anderson, Wheelabrator Technologies, Inc.; Dr. John (Sean) Barnes, DuPont Company; Mr. Jeffrey Blough, First Energy Corporation; Professor Brian Gleeson, Iowa State University; Dr. Peggy Hou, Lawrence Berkeley National Laboratory, University of California at Berkeley; Dr. James Keiser, Oak Ridge National Laboratory; Dr. Dwaine Klarstrom, Haynes International, Inc.; Mr. Larry Paul, ThyssenKruppVDM; Mr. Gaylord Smith, Special Metals Corporation; Mr. Jerry Sorell, consultant; and Mr. Michael Welch, Welding Services Inc. I am also grateful to Mr. Charles Moosbrugger, Ms. Eileen De Guire, and Ms. Madrid Tramble of ASM International for their wonderful assistance. Finally, I would like to thank especially my wife, Mei Huei, for her support.

George Y. Lai  
Carmel, Indiana  
March 2007

# About the Author

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George Y. Lai is a graduate of Taipei Institute of Technology in Taiwan, Virginia Polytechnic Institute (M.S.), Blacksburg, VA, North Carolina State University (Ph.D.), Raleigh, NC, and a post-doctoral fellow at University of California, Berkeley, CA.

He began his high-temperature corrosion research in 1974 at General Atomic Company working on high-temperature gas-cooled reactor research projects specifically on the oxidation, carburization, and friction and wear of alloys and coatings in simulated primary coolant helium environments containing low levels of H<sub>2</sub>O, CO, CO<sub>2</sub>, and CH<sub>4</sub>. He continued his high-temperature corrosion research work at Haynes International (a leading superalloy producer) in 1980 to 1996. During that time, he expanded his high-temperature corrosion research to include oxidation, nitridation, carburization and metal dusting, corrosion by halogen and halides, sulfidation, hot corrosion, molten salt corrosion, and molten metal corrosion. He developed a large database for these eight basic high-temperature corrosion modes that have been responsible for the majority of high-temperature corrosion problems in the industry. In addition, he was involved in developing new high-temperature alloys. He was an inventor of a patent that led to commercial alloy HR-160, and a co-inventor of a patent that led to commercial alloy HR-120. In late 1996, he joined Welding Services Inc., which pioneered the field application technology of a corrosion-resistant weld overlay cladding in boilers and vessels using automatic gas metal arc welding machines. He was involved in the selection and application of weld overlay alloys for corrosion protection against both high-temperature corrosion and aqueous corrosion for the boiler industry, refinery and petrochemical industry, chemical process industry, pulp and paper industry, and steel industry. Since 2000, he has been a metallurgical and corrosion consultant, providing consulting services for materials problems in various industries.

He has published about 100 technical papers and is the author of *High-Temperature Corrosion of Engineering Alloys*, co-editor of three proceedings books, and holds six U.S. patents. He is a Fellow of ASM International.



# Units

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

mpy = mils per year  
mm/yr = mm per year  
1 mil = 0.001 in. = 0.0254 mm = 25.4  $\mu\text{m}$   
1 mm = 39.4 mils  
1 in. = 25.4 mm  
1  $\mu\text{m}$  = 0.001 mm  
1 m = 1000 mm  
1 m = 3.28 ft  
1 ft = 0.305 m  
1 dm = 10 cm

1 nm =  $10^{-9}$  m = 10  $\text{\AA}$   
1 nm/h = 0.00876 mm/yr = 0.345 mpy  
1 g = 1000 mg  
1  $\text{g}/\text{m}^2$  = 0.1  $\text{mg}/\text{cm}^2$   
1  $\text{in.}^2$  = 6.4516  $\text{cm}^2$   
1 atm = 14.7 psi = 101,356.5 Pa = 760 torr =  
760 mm Hg = 406.79 H<sub>2</sub>O  
1 Pa =  $9.87 \times 10^{-6}$  atm  
1 bar = 0.9869 atm



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