

FAILURE INVESTIGATION OF BOILER TUBES

A C O M P R E H E N S I V E A P P R O A C H



PARESH HARIBHAKTI

P. B. JOSHI

RAJENDRA KUMAR



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Preface

Power plants are the backbone of industrial development for most countries and their failures impact economic growth. When failures or forced shutdowns in power plants occur, they are often due to boiler failure, and particularly failure of boiler tubes. The many causes of boiler tube failures include overheating, creep, erosion, corrosion, fatigue, manufacturing and material defects, and operational issues. Boiler tube failures lead to unscheduled shutdowns, increased maintenance and repair costs, reduced plant load factors, and loss of available power. To prevent interruptions in the supply of power, it is critical to investigate the root cause of boiler tube failures and the resultant forced outages and to develop remedial measures for preventing the recurrence of similar failures in the future. Such investigations are also aimed at assessing the remaining life of the boiler tubes.

We have long-standing experience in the field of metallurgy and materials technology, failure investigations, remaining life assessment, and reviewing fitness for service of industrial plants and equipment, including power plants. We have performed a large number of failure investigations of boiler tubes and have made effective recommendations of remedial measures in problem solving for power and utility boilers. An attempt has been made in this book to share our knowledge and expertise in failure investigation of boiler tubes, for the benefit of user industries.

For non-metallurgists, a chapter has been devoted to basics of material science, metallurgy of steels, heat treatment, and structure-property correlation. Without adequate knowledge of physical metallurgy fundamentals of steels and related materials, understanding the mechanisms of boiler tube failure is almost impossible. A chapter on materials for the manufacture of boiler tubes deals with composition and application of different grades of steels and high-temperature alloys currently in use as well as future materials to be used in supercritical, ultra-supercritical, and advanced ultra-supercritical thermal power plants. A comprehensive discussion on different mechanisms of boiler tube failure is the heart of the book. A large number of case studies based on actual failures from the field have been cited along with photographs and microstructures in order to facilitate the discussion of the underlying theory behind the respective failure mechanisms. Chapters dealing with the role of advanced material

characterization techniques in failure investigation and the role of water chemistry in tube failures are key contributions to the book.

This book will help not only the novice but also practicing engineers in the operation and maintenance departments of power plants, boiler tube manufacturers, research and development personnel concerned with power plants, academicians, and students. This book will not make plant personnel experts in analysis of boiler tube failures; however, it will certainly increase their awareness, and help them effectively communicate with specialists and experts from failure investigation agencies as well as with their own management. For academicians and research and development personnel, it will act as a valuable ready reference.

Finally, we have great pleasure in acknowledging the support and encouragement received from the Indian power industry, users of industrial boilers, and allied organizations. Our special thanks to the management of the power plants for whom we have performed failure investigations, for permitting us to use the data, especially in writing the case studies.

We would like to thank the editorial and production staff at ASM International, especially Karen Marken, senior managing editor, for her guidance and valuable contribution at various stages of manuscript preparation.

We are grateful to the late V.K. Bafna, founder of the TCR Group of companies, for his vision and relentless efforts in building a world-class investigation center. We would also like to thank our colleagues at TCR Advanced Engineering, Vadodara, India, for their support in preparation of the manuscript for this book.

P.U. Haribhakti
P.B. Joshi
Rajendra Kumar

About the Authors



Mr. P.U. Haribhakti

Paresh Haribhakti is the managing director of TCR Advanced Engineering Pvt. Ltd. in Vadodara, India (a TCR Engineering Services partner company), director of TCR Arabia, Dammam, and global technical consultant to the TCR group of companies. Mr. Haribhakti is a graduate in metallurgical engineering and has a master's degree in materials technology from The Maharaja Sayajirao University of Baroda, Vadodara, India. With more than two and half decades of experience in the field of metallography, microstructural evaluation, and failure investigation, Mr. Haribhakti has been instrumental in solving

more than 4000 industrial problems. He has investigated approximately 400 cases of boiler tube failures. He has expertise in areas such as failure investigation, remaining life assessment and fitness for service, and material development and import substitution for power plants, fertilizers, chemical and petrochemical complexes, the oil and gas industry, and other engineering and manufacturing industries. He is a member of the Institution of Engineers (India), Institute of Indian Foundrymen, Indian Institute of Metals and Indian Institute of Welding, and ASM International.



Dr. P.B. Joshi

Dr. P.B. Joshi, the former professor and head of the department of metallurgical and materials engineering of The Maharaja Sayajirao University in Baroda, Vadodara, India, has more than 30 years of teaching and research experience and five years of industrial experience. His areas of teaching and research have been physical metallurgy, alloy steels, failure analysis and material selection, material characterization, and powder metallurgy. He has published papers in more than 60 journals of national and international repute. He has worked as principal investigator/co-investigator and chief

coordinator on various research projects funded by the Government of India. He authored a book, *Materials for Electrical and Electronic Contacts*,

with Professor P. Ramakrishnan of IIT, Mumbai, India. The book was jointly published by Oxford & IBH Publishers, New Delhi, and Science Publishers, USA, in 2004. Currently, he is working as a consultant to TCR Advanced Engineering Pvt. Ltd., Vadodara.



Dr. Rajendra Kumar

Dr. Rajendra Kumar earned his Ph.D. from the University of Sheffield (United Kingdom), and started his career as a member of the teaching faculty at IIT, Kharagpur and Banaras Hindu University, Varanasi, India. He was honored with the Commonwealth Visiting Professorship at the University of Austin, Birmingham, United Kingdom during 1979 to 1980. He also served as scientist director at National Metallurgical Laboratory, Jamshedpur, India, and director of Regional Research Laboratory, Bhopal, India. Dr. Kumar has been intimately connected with the thermal power sector in India as well as abroad. He was the expert coordinator for a national level project for improving the plant load factor for power boilers sponsored by the Central Board of Irrigation and Power, India. He was a member of a committee appointed by the government of India formulated for drafting the VIII Plan proposal for research and development in the thermal power sector. He was invited by the United Nations Commission for Science and Technology to prepare a scenario for decentralized thermal power generation to reduce global warming. He has served as an expert to the boiler industry and power plants in India for more than three decades. He is the author of two books, *Operation and Maintenance of Steam Power Boilers*, published in 2008, and *Physical Metallurgy of Iron and Steel*, published in 1969.

CHAPTER 1

Introduction to Boiler Technology

1.1 Introduction

A boiler is an enclosed vessel in which water is heated to produce hot water, steam, superheated steam, or any combination of these under pressure by the application of heat. The necessary heat is produced by burning solid, liquid, or gaseous fuel under a controlled supply of air in the combustion chamber of the boiler. Thus, the boiler is an appliance to convert the chemical energy in fuel into thermal energy to generate steam or hot water. The steam or hot water so produced is then circulated out of the boiler for end use for power generation, or in various manufacturing processes for the captive supply of steam/heat. In projects such as refineries, petrochemical plants, paper mills, food and pharmaceutical industries, and the textile industry, boilers are used for power generation and/or for providing process steam and process heat.

1.2 Classification of Boilers

Because the areas of application of boilers are very diverse, there is a need for their classification. Functionally, two main categories of boilers are utility boilers and industrial/commercial/institutional (ICI) boilers. Utility boilers are used in thermal power plants to produce steam at a constant rate. Utility boilers are very large in size and work with pulverized coal, fuel oil, or natural gas at high pressure and temperature to produce high-pressure, high-temperature, superheated steam for power generation. On the other hand, ICI boilers have markedly different purposes and applications. Industrial boilers are used for producing hot water or steam for industrial process applications including food processing, paper production, chemical processing, petrochemicals and refining, and the textile and allied industries. Commercial boilers provide steam and/or hot water for

commercial establishments such as hotels, restaurants, office buildings, and apartments. Institutional boilers are used in establishments such as hospitals, schools, colleges, and government buildings to provide steam, hot water, and/or electricity. ICI boilers are flexible in terms of their ability to produce steam output and are generally designed with regard to the plant space limitations. In general, ICI boilers work at much lower annual operating loads than typical utility boilers.

1.2.1 Utility Boilers

There are different forms of utility boilers based on the method used for fuel combustion. Utility boilers with different combustion arrangements (Ref 1.1) include:

- Tangentially fired boilers: The air-fuel mixture is introduced into the furnace from the four corners of the furnace, tangentially.
- Wall-fired boilers: Multiple burners are located along a single wall or on opposite walls of the furnace.
- Cyclone-fired boilers: The air-fuel mixture is burned in horizontal cylinders.
- Stoker-fired boilers: The fuel is combined in relatively thin layers on top of a grate.
- Fluidized bed combustion boilers: A fluidized bed of sand particles is used under atmospheric conditions for efficient combustion.
- Pressurized fluidized bed combustion boilers: Similar to fluidized bed combustion, but at pressure greater than atmospheric and with higher efficiency.

1.2.2 Industrial Boilers

Industrial boilers are normally identified by the method of heat transfer and the combustion system utilized. Based on the mode of heat transfer, there are two types of industrial boilers: watertube and firetube boilers. Further discussion on each one of them is covered in succeeding paragraphs. On the basis of the combustion system, industrial boilers may be grouped as burner- or stoker-type boilers.

Further classification of the boilers may be done based on the fuel used, working pressure and temperature, firing practice, draft method, size and capacity, method of fabrication, and portability.

Criteria on which the boilers may also be classified (Ref 1.2) include:

- Horizontal, vertical, or inclined boiler based on the axis of the boiler
- Method of firing, variables being horizontal firing, vertical firing, down shot firing, front and rear wall firing, and tangential firing
- Externally or internally fired boiler based on whether the fire is inside or outside the shell. In other words, a boiler is classified as a *firetube*

or *watertube* boiler based on the relative location of the water and fuel inside or outside the tube.

- Single tube or multitube boiler based on the number of tubes in fire-tube boilers
- Boilers can be classified as natural circulation, forced or controlled circulation, combined circulation, and once-through types.
- Heat source as coal-fired or solid fuel-fired, oil-fired, gas-fired, or lignite-fired boilers. Electric boilers use resistance- or immersion-type heating elements.
- They are also classified as subcritical, supercritical (SC), and ultra-supercritical (USC) boilers. The basic difference between the three types is the operating temperatures and pressures. Subcritical boilers operate below the critical point of water (374.15 °C and 22.1 Mpa, or 705.45 °F and 3.21 ksi), whereas SC and USC boilers operate above the critical point. Supercritical and USC boilers are characterized by the absence of a steam drum, which is normally present in subcritical boilers.
- Stationary or portable boiler
- Based on the method of fabrication as shop-assembled, field-erected, and package boilers. Shop-assembled boilers are built from a number of individual parts or subassemblies. After these parts are aligned, connected, and tested, the entire unit is shipped to the site in one piece. Field-erected boilers are too large to be transported as an entire assembly. Hence, they are constructed at the site from a series of individual components.

1.3 Types of Boilers

Various types of boilers used throughout the world for power and steam generation are discussed (Ref 1.3, 1.4).

1.3.1 Firetube Boilers

A typical example of a firetube boiler is a locomotive boiler. In this type of boiler, the combustion gasses pass through tubes that are surrounded by water. The basic design of a firetube boiler consists of a series of straight tubes that are housed inside a water-filled outer shell (i.e., on the tube side there are hot combustion gases, whereas on the shell side there is water). The tubes are submerged in water so that the hot combustion gases can pass through the tubes several times, thereby transferring their heat across the tube walls to the water filling the outer shell. As a result of this, the water in the shell heats up, boils, and finally transforms to steam. Firetube boilers are generally used for relatively small steam capacities and applications involving low to medium steam pressures. Figure 1.1 shows a cutaway view of a firetube boiler.

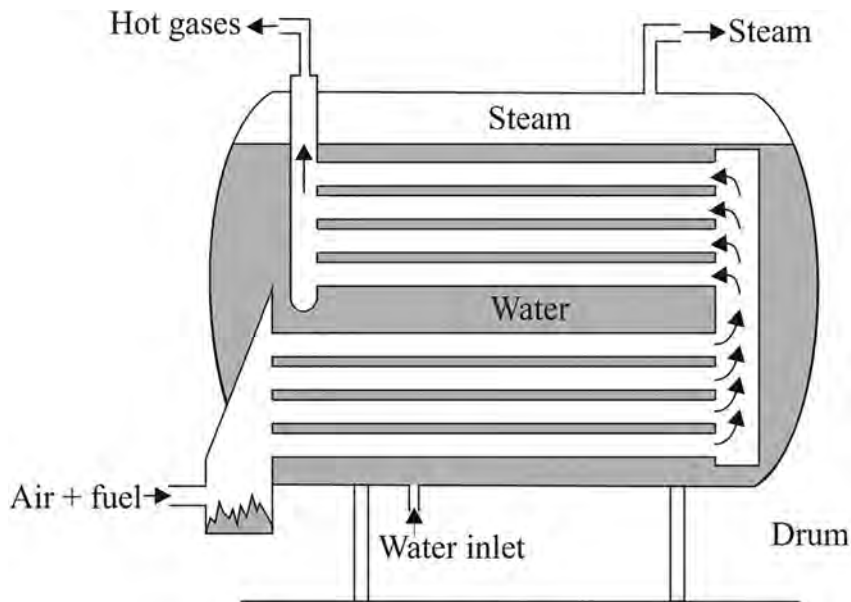


Fig. 1.1 Schematic showing basic principle of a firetube boiler

1.3.2 Watertube Boilers

Watertube boilers are designed to circulate hot combustion gases around the outer surface of a large number of water-filled tubes. In other words, on the tube side there is water, whereas on the shell side there are hot combustion gases. In watertube boilers, the fuel is combusted in a central chamber (furnace, bed, or grate) and the combustion gas transfers heat energy, through radiation and convection, to the water circulating through the tubes. The water tubes are connected to a steam drum at the top and one or more lower drums (also known as a mud drum) at the bottom. The necessary heat is produced by means of fire in the combustion chamber as shown in the schematic (Fig. 1.2). The circulated water is heated by the combustion gases and converted into steam at the vapor space in the steam drum.

Almost any solid, liquid, or gaseous fuel can be burned in a watertube boiler. Commonly used fuels include coal, oil, natural gas, and biomass. These boilers can be used under forced, induced, and balanced draft conditions so as to offer higher thermal efficiency. The only concern is that the water must be treated to improve the water quality, which incurs additional expenditure.

1.3.3 Electric Boilers

Electric boilers are used as an efficient source of hot water or steam. They are available in ratings from 5 to over 50,000 kW. Heating is ensured by

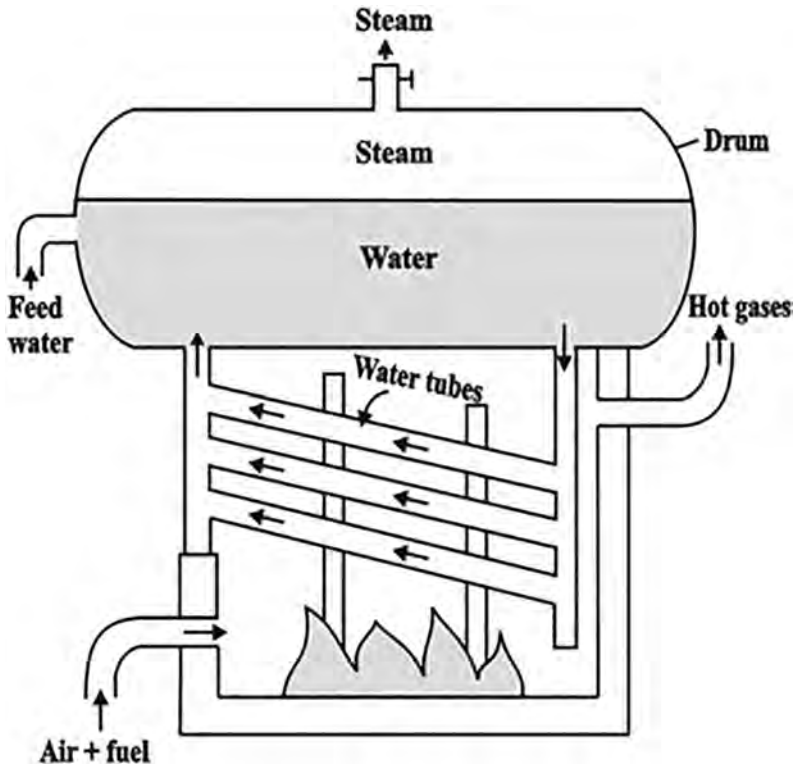


Fig. 1.2 Schematic showing basic principle of a watertube boiler

means of resistance or immersion heaters. They are much cleaner in operation than firetube and watertube boilers.

1.3.4 Packaged Boilers

Packaged boilers are small, self-contained boiler units. Packaged boilers can be either watertube or firetube, and they are generally of the shell type with a firetube design so as to achieve high heat transfer rates by both radiation and convection. They are installed with a large number of small-diameter tubes offering good convective heat transfer with a forced or induced draft system. The small size of the combustion chamber and high heat release rate impart higher thermal efficiency levels to package boilers compared with other boilers.

The major benefits of using packaged boilers are compact design, short installation time, and low installation cost.

1.3.5 Fluidized Bed Combustion Boilers

In principle, a fluidized bed combustion (FBC) boiler is one in which a fire bed is produced by means of finely divided solid particles, such as

silica sand, through which an evenly distributed stream of air or fluidizing gas is passed upward such that the sand particles remain in suspension. Fluidization improves mixing of fuel and air. When the initial velocity of the fluidizing medium (i.e., air or gas) is low, the sand particles are undisturbed. However, as the air velocity increases, a stage is reached when the individual particles are suspended in the air stream, forming a bed called a *fluidized bed*.

With further increase in air velocity, there is vigorous turbulence resembling bubble formation in a liquid. The solid particles within the bed start behaving as bubbles in a boiling liquid and assume the appearance of a fluid, known as a *bubbling fluidized bed*. Depending on the velocity of the combustion air, the layer acquires different types of fluid-like characteristics such as the fixed bed, bubbling bed, circulating bed, and turbulent bed.

If the sand particles in the fluidized state are heated to the ignition temperature of coal, and coal is injected continuously into the bed along with the introduction of air for combustion from the bottom of the bed, the coal will burn rapidly, forming a combustion bed. Fluidized bed combustion takes place at about 850 to 950 °C (1560 to 1740 °F). Because this temperature is below the ash fusion temperature, melting of ash and associated problems are avoided.

Fluidized bed combustion has several advantages over the conventional firing system (Ref 1.4):

- Compact boiler design
- Permits use of many different types of fuels including coal, biomass, rice husk, bagasse, and other agricultural wastes. Inferior-quality fuels containing a high concentration of ash, sulfur, and nitrogen can also be used. Natural gas or fuel oil is used primarily as a start-up fuel to preheat the fluidized bed.
- Higher combustion efficiency
- Lower combustion temperature because of a high coefficient of heat transfer due to rapid mixing in the fluidized bed leads to lower NO_x emissions
- Reduced emission of other noxious pollutants such as SO_x by desulfurization during combustion

Fluidized bed combustion boilers can be further grouped as atmospheric or pressurized units.

In atmospheric fluidized bed combustion (AFBC) boilers, the fuel, such as coal, is crushed to a size of 1 to 10 mm (0.04 to 0.4 in.) and is fed into the combustion chamber. Atmospheric air, which acts as both the fluidization air and the combustion air, is then delivered at pressure and flows through the bed after being preheated by the exhaust flue gases. The energy so

produced is utilized in heating the water circulating through the tubes located within and above the fluidized bed so as to produce steam. Atmospheric fluidized bed boilers are also known as *bubbling bed boilers*. Figure 1.3 shows an AFBC boiler.

Atmospheric FBC boilers are further divided into bubbling fluidized bed combustion (BFBC) and circulating fluidized bed combustion (CFBC) units; the fundamental difference between these two is the fluidization velocity. In the BFBC type, because the velocity of the air is low, the medium particles are not carried above the bed. The fluidizing velocity is lower than the terminal velocity of individual bed particles. The combustion in this type of boiler is generated in the bed.

The CFBC boiler incorporates a cyclone filter to separate solid material from the hot flue gases that leave the exhaust of the furnace. The solids from the filter are recirculated into the bed, hence the name. In the CFBC type, the velocity of air is high, so the medium-sized particles are carried out of the combustor. Here, the fluidizing velocity exceeds the terminal velocity of individual bed particles. The carried particles are continuously captured by a cyclone installed in the outlet of the combustor and sent back to the bottom part of the combustor to combust unburned particles. This helps to ensure full combustion.

A pressurized fluidized bed combustion (PFBC) boiler is a variation of FBC technology that is meant for large-scale coal burning applications. In a PFBC boiler, a compressor supplies forced draft air, which improves the combustion efficiency. The PFBC system can be used for cogeneration or combined cycle power generation.

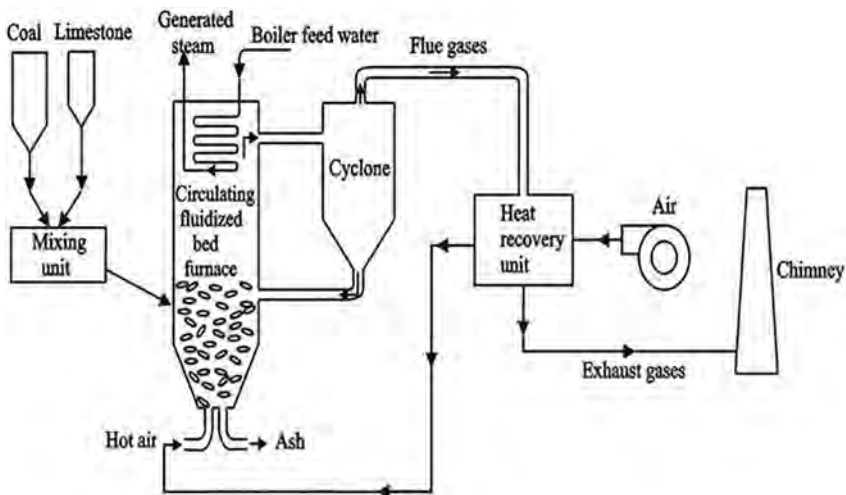


Fig. 1.3 Schematic diagram of a fluidized bed combustion boiler

1.3.6 Oil- and Gas-Fired Boilers

Both oil- and gas-fired boilers use controlled combustion of the fuel to heat water. Oil-fired boilers are used for heating water for domestic and industrial applications. In this type of boiler, the oil is mixed with air and burns by means of a burner to produce heat. The heat of the flame created by burning the oil and air mixture is directed over coiled copper pipe through which the water is flowing, such that the water flowing through the copper coils is heated by conductive heat transfer.

Natural gas boilers employ either atmospheric burners (also known as natural draft burners) or forced draft burners. Both types of boiler can be used for combustion of oil as well as gas because they have some common properties; both contain practically no moisture or ash, and both produce the same amount of flue gas during combustion.

1.3.7 Waste Heat Boilers

The operational efficiency of a boiler is measured by the percentage of the fuel input energy that is eventually delivered as useful heat output. Major sources of heat loss from steam boilers are the flue gas, blow down, and radiation to the boiler's surroundings.

Waste heat recovery steam generators (HRSGs) use the heat from exhaust gases from combustion processes of gas turbines and diesel engines, or from hot exhaust air from industrial processes, to produce hot water or steam. Waste heat recovery boilers are generally conventional watertube boilers. Here, the heat from the hot exhaust gases from gas turbines or any industrial process equipment is recovered by passing them over a set of parallel tubes through which the normal water (ambient temperature) flows. The heat transfer across the tube walls ensures vaporization of water and in turn its transformation to steam, which is then collected in a steam drum for subsequent end use as heating or processing steam. Efficiency of heat transfer can be further improved by using finned tubes instead of tubes with plain surfaces. The water can be circulated through the tubes a number of times for better results. If the waste heat in the exhaust gases is insufficient for generating the required amount of process steam, auxiliary burners may be used. The black liquor recovery boiler is a classic example of a waste heat recovery boiler.

1.3.8 Black Liquor Recovery Boilers

Recovery boilers were first invented in the early 1930s and play a key role in the kraft process of pulping. Kraft recovery boilers (also known as BLRBs) are used to efficiently convert wood chips into paper in pulp and paper mills. The wood chips are first cooked in an aqueous solution (known as white liquor) in a digester for manufacturing pulp. The digested pulp is then separated from the residual liquor, which is relatively dilute in nature

with a solid concentration of about 15%. Multistage evaporation converts “white liquor” to “black liquor,” where the concentration of solids is raised to 70 to 75%. The black liquor consists of more than 50% organic matter, wood lignin, and inorganic compounds, and includes mainly sodium and sulfur compounds.

Black liquor recovery boilers perform a dual function. First, they recover the valuable cooking chemicals used in the pulp digester, and second, they produce steam that can be used to generate electricity or for heating purposes in the kraft process. There are two main sections in a BLRB: the fire side, or furnace, where the black liquor is burned, and the heat transfer section, where steam is produced. Accordingly, in the furnace part of a BLRB, the spent cooking chemicals in the black liquor are burned to recover the inorganic salts (mainly sodium and sulfur compounds) while simultaneously generating steam through the combustion of the organic matter in the liquor in the heat transfer section. During the process, inorganic solids such as sodium sulfate, sodium sulfide, sodium carbonate, sodium chloride, and sodium hydroxide are melted on the furnace bed. Combustion of black liquor under reducing conditions converts sulfur compounds to sulfides and recovers the inorganic chemicals in molten form. For example, sodium sulfate is converted to sodium sulfide. The total sulfur in black liquor amounts to about 6%. The black liquor as a fuel has a very low calorific value as compared with conventional fossil fuels, and also has very high ash content.

In a BLRB furnace, the black liquor is introduced through a spray into the lower part of the furnace along with air for combustion. The black liquor is thus atomized to form small droplets to enable complete combustion. The size of the droplets is controlled in order to avoid their carryover to the upper portions of the furnace where they may otherwise deposit on the tubes. Such carryover deposits are particularly found in the superheater section, and may consist of soot, ash, and slag. Deposits decrease the boiler efficiency by reducing heat transfer. The heat transfer surfaces are therefore required to be periodically cleaned using air, steam, water, or mixtures thereof. On account of the very nature of this fuel, BLRBs suffer from various forms of fire-side corrosion, erosion-corrosion, and erosion related problems. The fact remains that black liquor fly ash is not as abrasive as the fly ash produced from combustion of coal in power boilers.

1.4 Operation and Working Principle of Utility or Power Plant Boilers

The fuels used in large utility or power plant boilers include fossil fuels (coal, oil, and natural gas), nuclear fuels (uranium and, sometimes, plutonium), and renewable biomass (wood, straw, and manure). Though each type of fuel has its own advantages and limitations, coal is the most

commonly used fuel. Coal-fired boilers using pulverized coal as the fossil fuel dominate the electric power industry, even today.

Unless otherwise specified, a power plant based on coal-fired boilers belongs to the category of subcritical boilers.

1.4.1 Conventional or Subcritical Boilers

Conversion of water to steam involves transition from a liquid to a gaseous state; this is associated with a substantial increase in volume. The volume of one unit mass of steam at atmospheric pressure is sixteen hundred times that of water, because the atoms and molecules in steam are spaced further apart from one another than those in water. Therefore, when water is converted to steam in a closed vessel, the pressure of the steam formed will increase. This is the underlying principle on which a boiler works.

The three stages in conversion of water to steam are (Ref 1.5):

1. Heating the water from room temperature (i.e., cold condition to boiling point or saturation temperature by addition of sensible heat). Further addition of sensible heat is ensured by preheating the high-pressure boiler feed water using extracted heat from the steam recycled by the low-pressure turbine.
2. Boiling of water at saturation temperature to produce steam as a result of addition of latent heat.
3. Heating steam from saturation temperature to a higher temperature, called the superheated temperature, to improve plant efficiency.

As shown in Fig. 1.4, the important components of the boiler are burners, the combustion chamber, the steam drum, heat exchangers such as waterwalls, and economizers. Finely ground coal is mixed with air and fed to the burners, where it ignites to form a fireball in the combustion chamber. The combustion takes place at 1300 to 1700 °C (2370 to 3090 °F) and the heat generated is transferred to the feedwater that flows through the waterwall tubes that form the walls of the furnace. The feedwater consists of condensate or condensed steam returned from the processes and make-up water (i.e., treated raw water), which comes from a source such as a river, reservoir, or lake. For higher boiler efficiencies, an economizer preheats the feedwater using the waste heat in the flue gas. A mixture of water and steam is formed in waterwall tubes as a result of heat transferred by the fireball in the combustion chamber/furnace. This mixture then moves up into the steam drum located at the top end of the boiler, as it has a lower density than the water flowing through downcomers. The liquid water and steam are separated in the steam drum. The separated liquid water is then recirculated to waterwall tubes through downcomers. The downcomers and the waterwall tubes form the two legs of a water

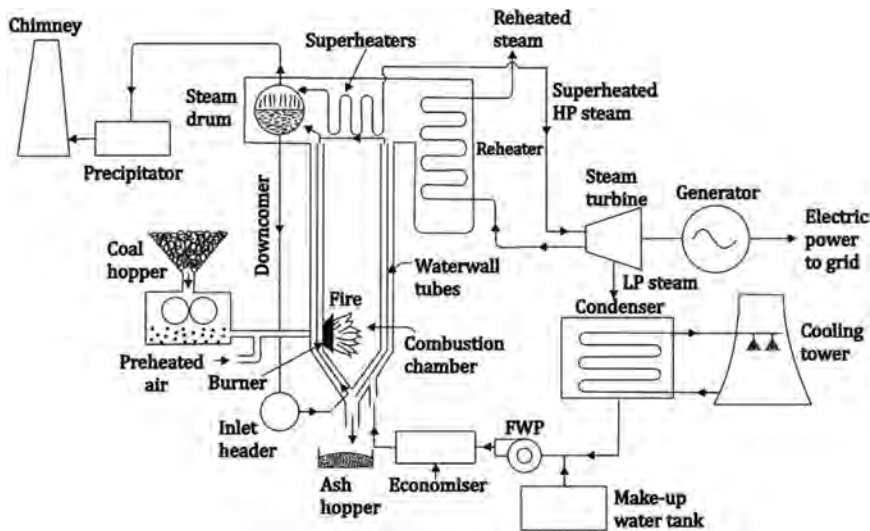


Fig. 1.4 Schematic showing working principle of a boiler

column. The steam collected in the upper half of the steam drum is separated and fed to primary and secondary superheaters to further raise its temperature and pressure. In the secondary superheaters, steam comes across the hot gases exiting the top of the boiler and is heated to its final temperature and pressure before leaving the boiler. The typical temperature and pressure of the final superheated steam are 530 to 570 °C (990 to 1060 °F) and up to 175 bar (2.5 ksi). This steam is then fed to a high-pressure steam turbine to drive a generator, which produces electricity. Steam exiting the high-pressure steam turbine is called *cold reheat*. It is reheated in the reheater tubes and sent back to the low-pressure steam turbine for improving the thermal efficiency of the process. By the time the flue gases exit the boiler, most of their energy is transferred to water in the boiler. Finally, the hot gases are cleaned up before they are sent to a stack, to control pollution.

1.4.2 Advanced Boiler and Power Plant Technologies

Pulverized coal-fired boilers are the most commonly used technology in thermal power plants, based on many decades of experience. This technology is well developed, and there are thousands of units around the world. However, conventional coal-fired plants operate at very low plant efficiency (typically 35 to 38%), making power generation very expensive. Additionally, they are one of the largest sources of air pollution. Emissions such as CO₂, SO₂, NO_x, and dust particles due to burning of fossil fuels are some of the largest contributors to global climate change. Studies reveal

that improvement in the plant efficiency, apart from lowering the cost of electricity production, results in significant reduction in CO₂ emission as well. One way to increase the efficiency of a steam power plant is to increase steam pressure and temperature, and this has been the basis of development of SC, USC, and advanced USC (A-USC) boilers.

1.4.2.1 Supercritical, Ultra-Supercritical, and Advanced Ultra-Supercritical Boilers. A conventional or subcritical boiler is characterized by a maximum operating pressure of 19 MPa (2.8 ksi). Under this condition there is a nonhomogeneous mixture of water and steam in the evaporator (i.e., waterwall tubes) and thus the boiler design requires a steam drum to separate steam from water before it is fed to the superheater and then to the turbine. However, in the supercritical (SC) condition for any system, there is no distinction between its liquid and gaseous states. Thus, for water in the SC state, there is no clear distinction between liquid water and steam, and the system behaves as a homogeneous fluid (dry steam) with homogeneous properties.

Subcritical steam boilers operate at relatively low pressures such that water boils first and is then converted to superheated steam. At SC pressures, water is heated to produce superheated steam without boiling. Incidentally, water reaches this state at a pressure above 22.1 MPa (3.21 ksi) and a temperature of 374.15 °C (705.45 °F). These are the critical temperature and pressure for water (called the critical point of water), and at the critical point of latent heat (enthalpy of steam minus enthalpy of water), they become zero. In physical terms, at this pressure, water transforms to steam spontaneously.

Thus, if the operating pressure in the evaporator part of the boiler is in excess of 22.1 MPa, such a boiler is referred to as an SC boiler. In this type of boiler, cycle fluid does not exist as two phases, liquid water and steam, so there is no question of separation of steam from water. Therefore, SC boilers do not have any steam drum. The heat-absorbing surface is one continuous tube that the water and steam generated in the furnace waterwalls pass through only once; such boilers are called *once through boilers*. The underlying difference in functioning between subcritical and SC once-through boilers is demonstrated in Figure 1.5; there is no recirculation of water in a SC boilers as there is in the case of a subcritical boiler.

As previously mentioned, the efficiency of plants using a subcritical boiler is around 35 to 38%, and increases in plant efficiency lead to reduction in coal consumption and in the level of emission of noxious gases in the environment. Advancements in boiler technology over the past several decades have therefore been mainly focused in the direction of increasing plant efficiency, which can be achieved by raising the operating steam pressure and temperature beyond the critical point of water. This increases the efficiency of the Rankine steam cycle used in power generation. Based on the operating steam temperatures and pressures, there

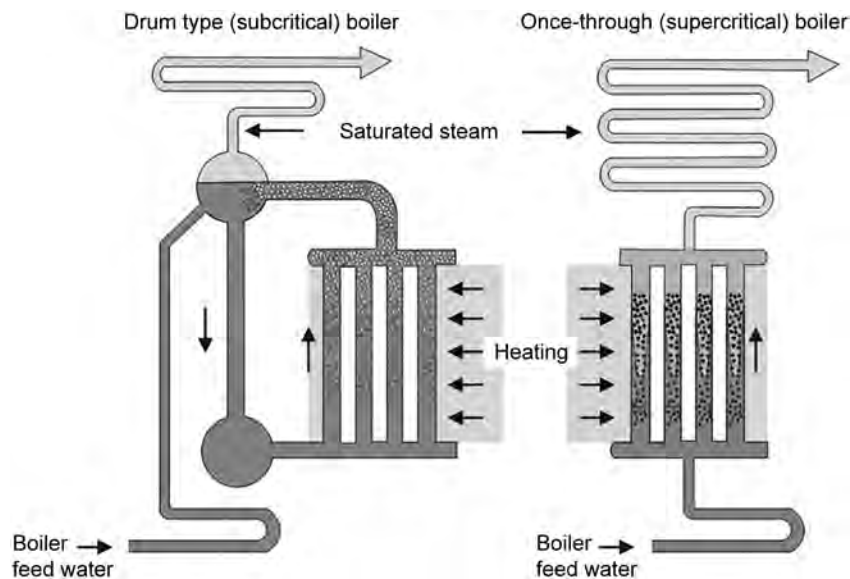


Fig. 1.5 Difference in functioning between subcritical and supercritical boilers

are four types of pulverized coal boilers, namely subcritical, SC, USC, and advanced ultra-supercritical (A-USC) boilers. Table 1.1 gives the classification of various types of boilers on the basis of their operating temperature and pressure and the plant efficiency they offer (Ref 1.6).

Ultra-supercritical boilers work at SC pressure of >22.1 MPa (typically around 27 MPa, or 3.9 ksi) with a steam temperature of 565°C (1050°F) or more and plant efficiency around 40 to 42%. Advanced ultra-supercritical coal-fired power plants are characterized by an inlet steam temperature to the turbine of 700 to 760°C (1290 to 1400°F), with average metal temperatures of the final superheater and final reheater running as high as about 815°C (1500°F). A-USC plants can offer a plant efficiency of up to 47%.

Further discussion on SC power plant technology is given in Chapter 2, *An Overview of the Functioning of a Thermal Power Plant*, in this book.

Table 1.1 Typical data on boiler operating parameters versus efficiency

Type of boiler	Steam pressure and temperature	Typical plant efficiency, %
Subcritical	<22.1 MPa, 538°C , (3.2 ksi, 1000°F)	35.0–38.0
Supercritical	24.7 MPa, 538 – 565°C , (3.6 ksi, 1000 – 1050°F)	38.0–40.0
Ultra-supercritical	27 MPa, 565 – 625°C , (3.9 ksi, 1050 – 1155°F)	40.0–42.5
Advanced ultra-supercritical	>30 MPa, above 700°C , (4.4 ksi, above 1290°F)	42.5–47.0

1.4.2.2 Integrated Gasification Combined Cycle Technology.

Gasification of pulverized coal in a conventional coal-fired plant coupled with a combined cycle process has emerged as an alternative to achieving higher plant efficiency. This novel approach, known as an integrated gasification combined cycle (IGCC), is a technology that uses a gasifier to transform pulverized coal under a given set of pressures and temperatures into a synthesis gas termed *syngas*. The gasification process involves a reaction between pulverized coal particles and oxygen and/or steam to produce syngas. The syngas so produced mainly consists of hydrogen and carbon monoxide, besides certain impurities. The syngas is subjected to cleaning to remove impurities such as sulfur. The cleaned syngas is fired in a combustion gas turbine that drives a generator to produce electricity. The waste heat from the gas turbine is recovered by passing the hot exhaust gases of the gas turbine through an HRSG to produce steam. The resultant steam is further used to drive a second steam turbine-generator set to produce electricity.

The burning of gas in a gas turbine not only produces power but also hot exhaust gases that, when routed through an HRSG, yield steam for running a steam turbine to produce power; the process is termed a *combined cycle*. Figure 1.6 shows the block diagram of an IGCC process.

In an IGCC process, the thermal efficiency can be extended to approximately 50–60%. Instead of coal, other carbon-based materials such as diesel or natural gas may also be used as fuel. When natural gas is used as a fuel to produce syngas, the process is called a natural gas combined cycle (NGCC).

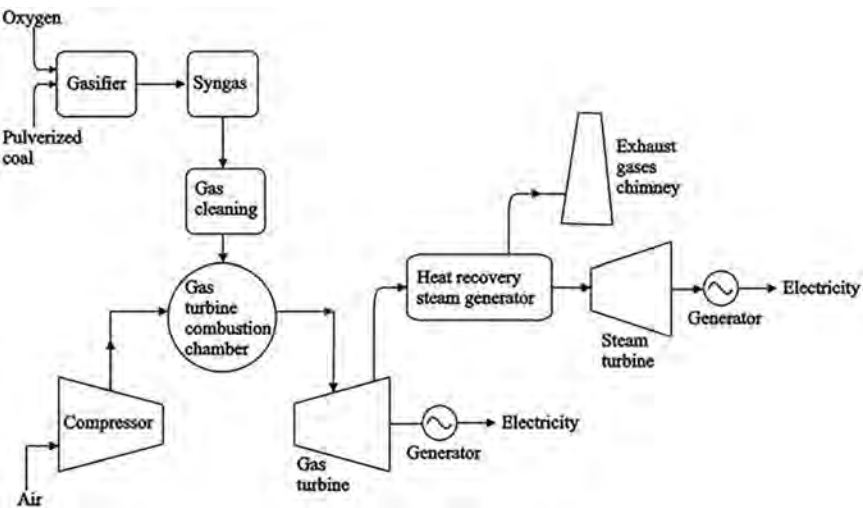


Fig. 1.6 Block diagram of integrated gasification combined cycle process

1.4.2.3 Cogeneration/Combined Heat and Power. *Cogeneration*, also known as combined heat and power (CHP), may be defined as the simultaneous production of electrical and thermal energy from a single fuel. The basic principle of a cogeneration system is that if the waste heat from one process is utilized in the production of the other, a substantial improvement in energy efficiency can be achieved. For example, the waste heat (i.e., heat discarded from a conventional power generation unit such as a steam turbine) is recovered and subsequently utilized as thermal energy for applications such as space heating and cooling, water heating, or industrial process heat. The two main components of any cogeneration facility are a power generator and a heat recovery system. As a result of the CHP approach, it becomes possible to ensure an overall system efficiency of between 50 and 70%. Thus, there is a significant improvement over the efficiency of a fossil-fuel-fired power plant, whose average efficiency is approximately 35%. Cogeneration also leads to reduced energy costs and reduced greenhouse gas emissions. The underlying basic principle of cogeneration is shown in Fig. 1.7.

As shown in the schematic, a heat source (i.e., a boiler) converts water to high-pressure steam. The high-pressure steam is further heated to the boiling temperature and then most frequently superheated to a temperature above the boiling temperature. This high-pressure superheated steam is fed to a steam turbine, where the thermal energy of the steam is utilized to rotate a turbine. The turbine in turn drives a generator to produce electricity, which is then supplied to a plant utility or grid. Waste heat in the form of low-temperature, low-pressure steam at the exit end of the turbine is utilized as hot water or steam for subsequent consumption by an industrial or commercial application. Thus, a CHP plant recovers waste heat and supplies it to local buildings for heating or cooling purposes and thereby improves the process efficiency.

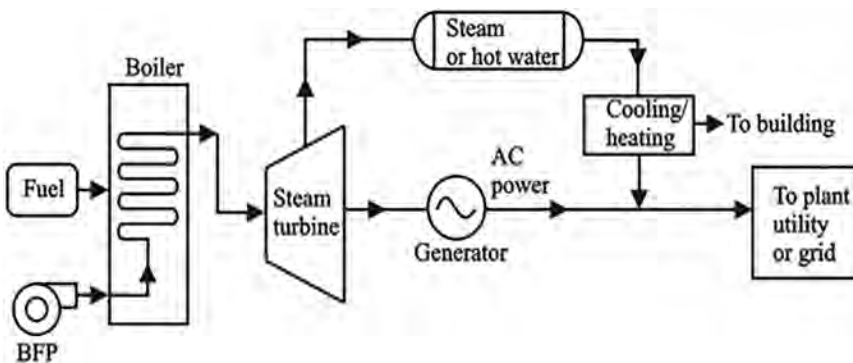


Fig. 1.7 Schematic showing principle of cogeneration using a steam boiler and steam turbine

References

- 1.1 K. Rayaprolu, *Boilers for Power and Process*, CRC Press, 2009
- 1.2 Indira Gandhi National Open University, “Steam Power Plant,” www.ignou.ac.in/upload/Unit-2-58.pdf
- 1.3 S. Teir, Modern Boiler Types and Applications, *Steam Boiler Technology*, Helsinki University of Technology, Espoo, 2002
- 1.4 V. Singh, Boiler Technologies Existing and Emerging Trends, *Power Line*, Vol 8 (No. 3), December 2003
- 1.5 Bright Hub Engineering, “How Does a Coal Power Plant Work?,” www.brighthubengineering.com/power-plants/
- 1.6 M.R. Susta and K.B. Seong, “Supercritical and Ultra-Supercritical Power Plants—SEA’s Vision or Reality?,” POWER-GEN ASIA 2004, p 1–23

CHAPTER 2

An Overview of the Functioning of a Thermal Power Plant

2.1 Introduction

Power is one of the most essential components of infrastructure for sustained economic growth and industrial development of any nation. The sources of fuel for power generation fall under the category of either non-renewable energy sources such as coal, natural gas, oil, and nuclear; or renewable energy sources such as hydro, wind, solar, biomass, geothermal, and marine. Since 1970, the world has seen rapid growth in energy demand, mainly satisfied by fossil fuels. Of about 24.0 trillion kilowatt hours of energy produced globally, approximately 9.5 trillion kilowatt hours are produced by using coal as the fuel. Thus, despite the paradigm shift from conventional to renewable sources of energy over the past few decades, approximately 40% of electricity produced worldwide is still from coal-based thermal power plants. The top three coal-consuming countries are China, the United States, and India, together accounting for more than 70% of the total coal consumption in the world. According to the *International Energy Outlook 2016* (IEO 2016) report, there will be continued increase in total coal-fired electricity generation worldwide from 8.6 trillion kilowatt hours in 2012 to 9.7 trillion kilowatt hours in 2020 and 10.6 trillion kilowatt hours by 2040 (Ref 2.1). Coal-based thermal power plants therefore still have a major role to play in governing the overall global economy.

2.2 How a Conventional or Subcritical Thermal Power Plant Functions

The fossil fuel employed in a steam turbine plant can be pulverized coal (PC), oil, or natural gas. Of all these, coal is most abundant and is widely

used as a fuel for steam turbine plants. A power plant using steam as its working medium works on the principle of the Rankine cycle such that the steam is first generated in a boiler, expanded in the prime mover, condensed in the condenser, and fed into the boiler again.

Figure 2.1 gives a typical layout of a coal-based thermal power plant. Such a plant works on the principle of conversion of chemical energy of the coal into electrical energy. In such units, the electricity is generated by burning of coal to produce steam by boiling water. The steam so produced is expanded through a turbine, which runs a generator coupled to it. The mechanical energy of the turbine is converted into electrical energy. In order to improve the thermal efficiency and overall economy of the process, the steam at the exit end of the low-pressure (LP) turbine is condensed and the condensed water is recirculated to the boiler after preheating. This is a proven technology and there are thousands of units around the world that have adopted it.

Coal is brought to a power station by any of three modes of transportation: roadways, railways, or ships. It is then stored in the form of large piles on site. From there the coal is transported to a crusher house with the help of conveyor belts. Ferrous materials in the form of iron particles, nuts, bolts, and small pieces of wire that come along with the coal as impurities are removed by means of magnetic separators before the coal is subjected to crushing. In a crusher, the coal is crushed to small pieces of about 20

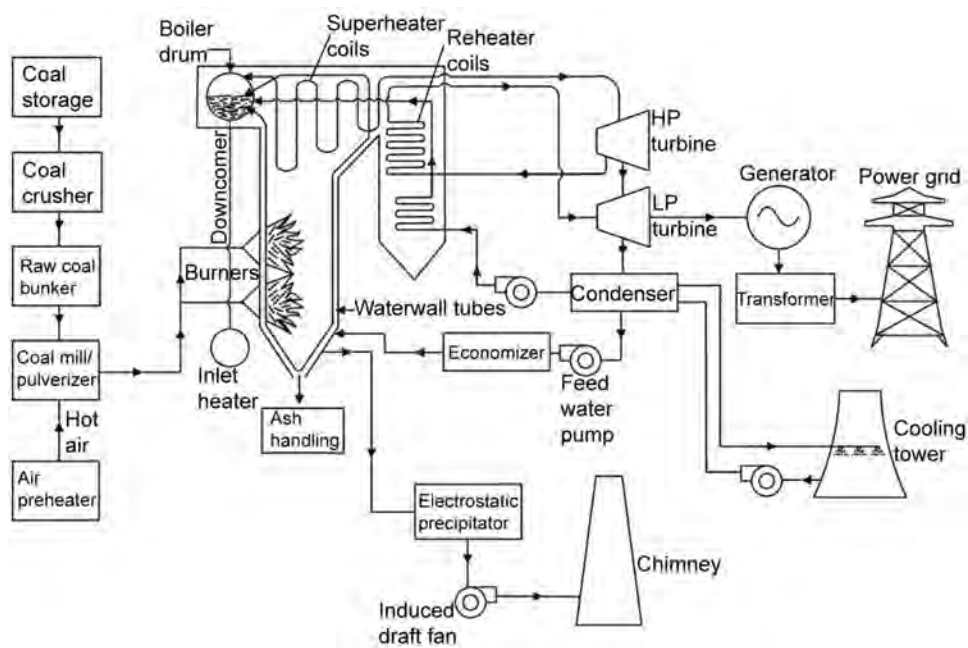


Fig. 2.1 A typical layout of a coal-based thermal power plant

to 25 mm (0.8 to 1 in.). From the crusher house, the coal is either stored in dead storage yards, which supply the coal in case of coal supply bottle-necks, or in live storage in a raw coal bunker in a boiler house. Raw coal from this bunker is subsequently fed to the coal mill or pulverizer, which reduces it to a very fine powder (~200 mesh), so as to facilitate its complete combustion during the combustion process. A portion of the primary air is heated by means of heat from the flue gases and then mixed with cold air as per the requirements of the PC. Normally the temperature is maintained at 60 to 70 °C (140 to 160 °F). The fine, powdered coal is carried to the boiler in coal pipes by high-pressure (HP) hot air.

The boiler is a device used for production of steam for power generation. A boiler is a rectangular furnace typically about 15 m (50 ft.) on a side and 40 m (130 ft.) tall. Its walls are lined with a network or web of HP steel tubes known as waterwalls or waterwall tubes, filled with water and about 55 to 65 mm (2 to 2.5 in.) in diameter. The pulverized coal-hot air mixture is air-blown into the furnace through burners located at corners or along the walls, as per the specific design of the boiler, and is ignited. The residence time of coal particles in the boiler is typically two to five seconds. The combustion of coal takes place at a temperature of around 1300 °C (2370 °F), so as to form a large fireball at the center. Radiation from the fireball heats the water that is circulating through the waterwall tubes located along the periphery of the boiler. The water circulating through these tubes absorbs heat and is transformed into steam. The steam, being lower in density than water, moves upward into the boiler drum. The boiler drum is a large cylindrical vessel that functions as the storage container and feeding point for the water. It also acts as the collection point for the water-steam mixture. There are two sets of pipes attached to the boiler drum, one called risers and the other known as downcomers. The water-steam mixture moves upward through the risers, whereas the downcomers carry the water from the boiler drum to the inlet headers at the bottom of the waterwalls. From these headers, the water rises through the waterwalls of the furnace where some of it is turned into steam, and the mixture of water and steam then re-enters the steam drum. As mentioned earlier, the water-steam mixture that is developed within the waterwall tubes has lower density than the water in the downcomers. This density difference helps in natural circulation of water from the boiler drum, through the downcomers into the waterwall tubes, and back to the drum. Steam, being lighter than water, moves up in the boiler drum and is collected at the upper half of the drum. The steam so formed is then separated from the remaining water inside the boiler drum located at the top of the furnace. The separation of steam from the mixture of water and steam occurs in three steps using different steam separators and dryers, such as cyclone separators (primary separators), secondary separators, and screen dryers (final separators). The dry steam is then fed to the superheater coils in a superheater.

Exhaust gases from the boiler are drawn by an induced-draft fan through an electrostatic precipitator and then vented off through the chimney stack.

Most modern boilers have superheaters and a reheater arrangement. A superheater is a component of a steam generating unit in which steam, after it has left the boiler drum, is heated above its saturation temperature. The steam from the drum passes to the superheater coils placed in the flue gas path. The superheater coils may consist of one or more stages of tube banks arranged to effectively transfer heat from the flue gases. Here, steam picks up extra energy from hot flue gases flowing outside the tubing. Its temperature is now raised above the saturation temperature to a maximum value typically in the range of 530 to 570 °C (985 to 1060 °F) and pressure is raised to about 175 bar (2.5 ksi). This is ensured by making the saturated steam pass through the low-temperature superheater, platen superheater, and final superheater, respectively, for superheating.

The superheated steam from the final superheater then goes to the turbine. Steam turbines have been used predominantly as prime movers in all thermal power stations. The turbine generator consists of a series of interconnected steam turbines and a generator on a common shaft. There is an HP turbine at one end, followed by intermediate-pressure (IP) and LP turbines, and the generator. As steam moves through the system and loses its pressure and thermal energy, it expands in volume, requiring increasing diameter and longer blades at each successive stage to extract the remaining energy. Superheated and pressurized steam is first allowed to expand in an HP steam turbine, which causes rotation of the turbine shaft. The outlet steam from the HP turbine is reheated and made to expand through an IP turbine and then through an LP turbine. Thus, the mechanical energy generated due to rotation of the turbines is converted into electrical energy in the generator. During the journey of hot steam from the HP turbine to the LP turbine, its temperature and pressure both gradually fall.

A bank of turbines is connected to the generator on a common shaft for generation of electricity. The electricity generated is stepped up to 220 KV with the help of step-up transformers and supplied to various substations through a power grid.

In order to improve the thermal efficiency of the process, the steam from the exhaust of the HP turbine is sent back to the boiler for reheating and thereafter returned to the IP turbine. A reheater section consists of coils and tubes heated by hot flue gases flowing outside the tubes. The reheater coils in the flue gas path reheat the returned steam. The steam after reheating is used to rotate the IP turbine, where the heat is converted to mechanical energy through rotation of the turbine shaft. The reheated steam is at a much lower pressure than the superheated steam but its temperature is the same as that of the superheated steam. Final reheated steam temperatures are normally in the range of 560 to 600 °C (1040 to 1110 °F) and the pressure is about 45 bar (0.65 ksi).

Low-pressure steam leaving the turbine, which is a little above its boiling point, enters the condenser, where it condenses back to water. A condenser is a shell-and-tube-type heat exchanger (or surface condenser) installed at the outlet of every steam turbine in thermal power stations. The condensers are heat exchangers that convert steam from its gaseous to liquid state (i.e., water). In doing so, the latent heat of steam is given out inside the condenser. The condenser tubes are held at a low temperature by the flow of cooling water. This creates a near vacuum-like condition inside the condenser chest.

The water used in the condenser for condensation of the steam is sent to cooling towers for cooling. The cooling tower is a semi-enclosed building-like device for evaporative cooling of water by contact with air. Water acts as the heat-transfer fluid during the cooling process. It gives up heat to atmospheric air and gets cooled. The resultant cooled water is recirculated through the system, affording economical operation of the process. More specifically, the hot water coming out from the condenser is fed to the tower on the top and allowed to trickle in the form of a thin ribbon or water droplets. The countercurrent flow of air from the bottom of the tower or perpendicular to the direction of water flow ensures effective cooling. After cooling, the water is again sent to the condenser with the help of a circulating water pump. Thus, the role of cooling towers is to lower the temperature of the water leaving the condenser tubes.

The condensed water from the condenser, after preheating, is pumped to the economizer by means of a boiler feed pump. Flue gases coming out of the boiler carry a lot of heat. The economizer is a horizontal continuous-type counterflow heat exchanger. The function of the economizer is to recover some of the heat from the heat carried away in the flue gases up the chimney and utilize it for heating the feedwater to the boiler. The economizer is placed in the passage of flue gases in between the exit from the boiler and the entry to the chimney. It consists of a large number of small-diameter, thin-walled tubes placed between the two headers. Feedwater enters the tubes through one header and leaves through the other. The flue gases flow outside the tubes, usually in a counterflow. The use of an economizer results in savings in coal consumption and improvements to boiler efficiency. The preheated water from the economizer is finally sent to the boiler drum, whereas the heat carried out with the flue gases, coming out of the economizer, is further utilized for preheating the air before supplying it to the combustion chamber.

2.3 How Supercritical and Ultra-Supercritical Thermal Power Plants Function

The efficiency of conventional fossil fuel or coal-fired power plants is mainly governed by the steam temperature and pressure at which they

operate, and efforts are being made worldwide to increase plant efficiency. Besides enhancement in plant efficiency by reducing coal consumption, it is also essential to protect the environment by minimizing the emission of CO₂, other environmentally unfriendly gases such as NO_x and SO_x, and particulates. An increase in steam temperature above 700 °C (1290 °F) and pressure beyond 22.1 MPa (3.2 ksi) in a steam turbine increases the efficiency of the Rankine steam cycle used in power generation, thereby decreasing the amount of fossil fuel consumed and the emissions generated (Ref 2.2).

During the past fifty years, steam parameters of fossil-fuel-fired power plants all over the world have been gradually mounting. For instance, during 1950–1960, the operating steam pressure was 16.7 MPa (2.4 ksi), with superheater and reheater temperatures around 537 °C (1000 °F) each (represented as 16.7 MPa/537 °C/537 °C). That was the era of subcritical boiler technology. From the early 1960s until the middle of the 1970s, power plants experienced a transition from subcritical to supercritical technology with typical new steam parameters being 24.7 MPa/565 °C/593 °C (3.6 ksi/1050 °F/1100 °F). With further advancements in the materials for high-pressure, high-temperature applications, the operating parameters reached 28 MPa/593 °C/593 °C (4 ksi/1100 °F/1100 °F) by the late 1980s, the beginning of the era of supercritical boilers. Developments in heat/creep-resistant materials such as highly alloyed stainless steels and nickel-based superalloys made it possible to reach operating pressures exceeding 38 MPa (5.5 ksi) and temperatures beyond 700 °C (1290 °F). This gave birth to new technologies, known as ultra-supercritical and advanced ultra-supercritical technology (Ref 2.3). These new technologies have been in development since approximately 2010.

Thus, over the years there has been a gradual evolution in the technology of coal-fired power plants—from conventional or subcritical to supercritical and ultra-supercritical technology—that operate at increasingly higher temperatures and pressures so as to achieve higher efficiencies than conventional and subcritical units, with a significant reduction in CO₂ emission. One might wonder what is so critical about supercritical and ultra-supercritical power plant technology. The answer is that there is nothing critical. The term supercritical is a thermodynamic expression describing the state of a substance where there is no clear distinction between the liquid and gaseous phases (i.e., they are a homogeneous fluid) (Ref 2.4). As shown in Fig. 2.2, water reaches this state at a pressure above 22.1 MPa (3.2 ksi) and temperature equal to 374.15 °C (705.50 °F). This means that above this pressure and temperature, the system reaches a supercritical state. Not only this, but there is no surface tension in a supercritical fluid, as there is no liquid or gas phase boundary.

In order to understand the concept of supercritical fluids, let us analyze what happens when water is heated. As we go on heating water, the temperature of the water increases until it reaches 100 °C (210 °F). Further

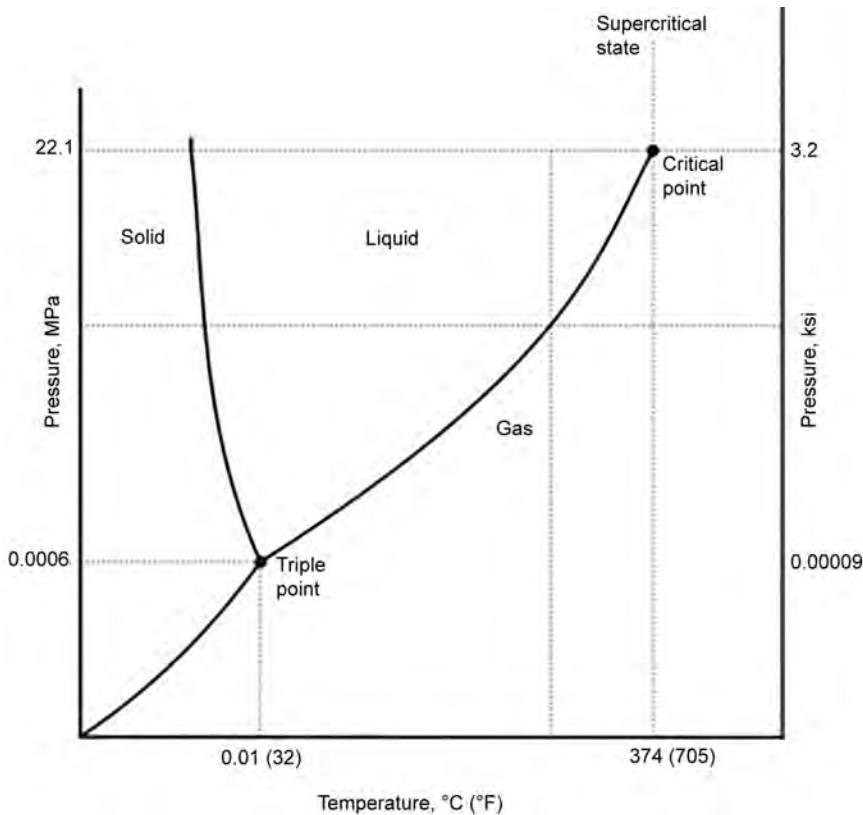


Fig. 2.2 Pressure-temperature diagram for H₂O system

heating does not increase its temperature; instead, water starts boiling and bubbles of steam start to form. The temperature remains constant at 100 °C until all of the water turns into steam. Thus, water absorbs the heat without any change in its temperature. This is known as *latent heat of vaporization*, which is equal to 2256 kJ/kg at atmospheric pressure. A further rise in temperature alone accounts for superheating of the steam. However, if pressure is also increased along with temperature, the boiling point of water increases, and its heat of vaporization decreases. Any further increase in pressure and temperature leads us to a point at which the latent heat of vaporization is zero such that there is no boiling and the water directly turns into steam. This is the critical pressure and the critical temperature for steam which have values equal to 220.6 bar (22.1 MPa) and 374.15 °C, respectively. Figure 2.3 demonstrates the difference in the boiling process between subcritical and supercritical boilers.

The thermal efficiency of a coal-fired power plant is governed by how much energy has been fed into the cycle and is getting converted into electrical energy. In other words, as the electrical output for a given amount

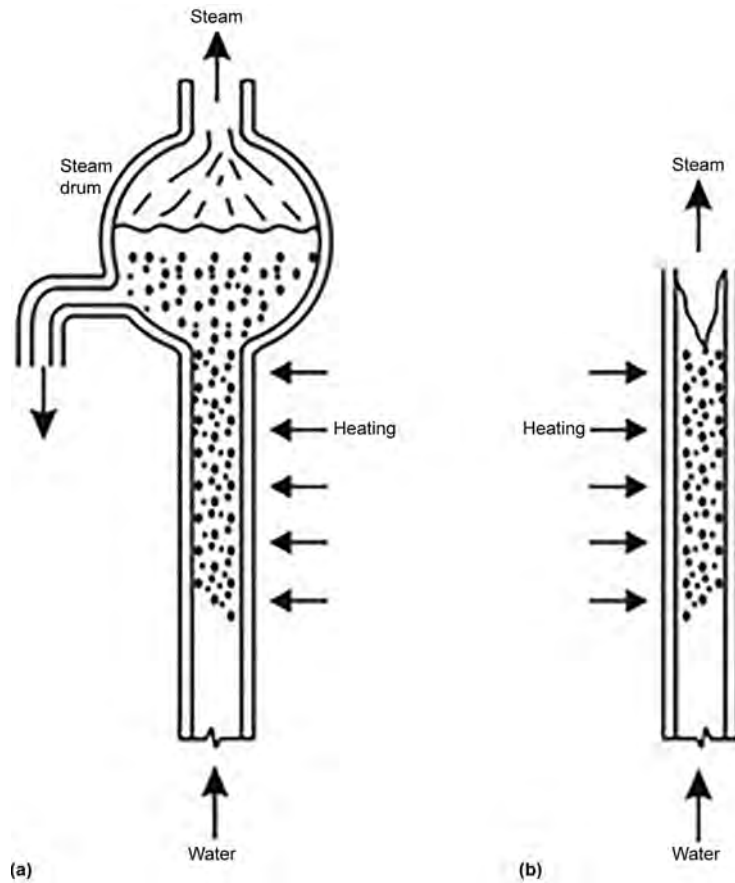


Fig. 2.3 Schematic showing difference in the boiling process between (a) subcritical and (b) supercritical boilers

of thermal energy input increases, the efficiency of the plant increases. With an increase in the temperature and pressure of the steam, thermal efficiency increases. The presently used conventional or subcritical coal-fired power plants typically operate at 170 bar (17 MPa, or 2.5 ksi) pressure and 540/540 °C (1005/1005 °F) superheater/reheater temperature, offering a thermal efficiency of 38%. Supercritical units, operating at 250 bar (25 MPa, or 3.6 ksi) and 600/615 °C (1110/1140 °F), have efficiencies typically in the range of 40%. Likewise, ultra-supercritical units, operating at 300 bar (30 MPa, 4.4 ksi) pressure and 615/630 °C (1140/1165 °F) temperature have efficiency up to 42%. Along the same lines, advanced ultra-supercritical coal-fired power plants around the world are designed with a turbine inlet steam temperature of about 700 to 760 °C (1290 to 1400 °F) and have reached an overall plant efficiency of 47 to 49% (Ref 2.5).

Whether a particular plant cycle is subcritical or supercritical depends on the operating pressure in the evaporator part of the boiler. If the operating

pressure is less than about 220 bar (22.1 MPa), the cycle is subcritical. In this case, a drum-type boiler is used because a nonhomogeneous mixture of water and steam is in the evaporator part of the boiler, and the steam needs to be separated from water in the drum before it is superheated and led to the turbine. Above this value of pressure, the cycle is supercritical because it is a single-phase fluid with homogeneous properties and there is no question of steam being separated from water in the drum. This does not mean that supercritical is just an elevated pressure operation as compared with subcritical. Rather, it crosses the critical point and alters the phase change pattern of working fluid in the boiler. In terms of *once-through* logic, in the case of supercritical units, there is no circulation in waterwalls. All supercritical boilers are of a *once-through* arrangement, meaning that water and steam flow through the boiler circuitry only once. Contrary to this, with drum-type boilers, water and steam recirculate through the furnace enclosure. In subcritical units, the drum acts as a fixed evaporation end point and the furnace waterwalls act as the evaporator. It is not so in the case of supercritical units. The evaporation end point can occur in various levels of the furnace depending on the boiler load. The percentage of superheat in supercritical units is higher than that in subcritical units. Because of this, the furnace tubes act more as superheaters than as waterwalls. This necessitates the use of a higher grade of materials, such as alloy steels, in the furnace. Most supercritical units use once-through technology. Figure 2.4 gives the schematic view of a supercritical boiler plant.

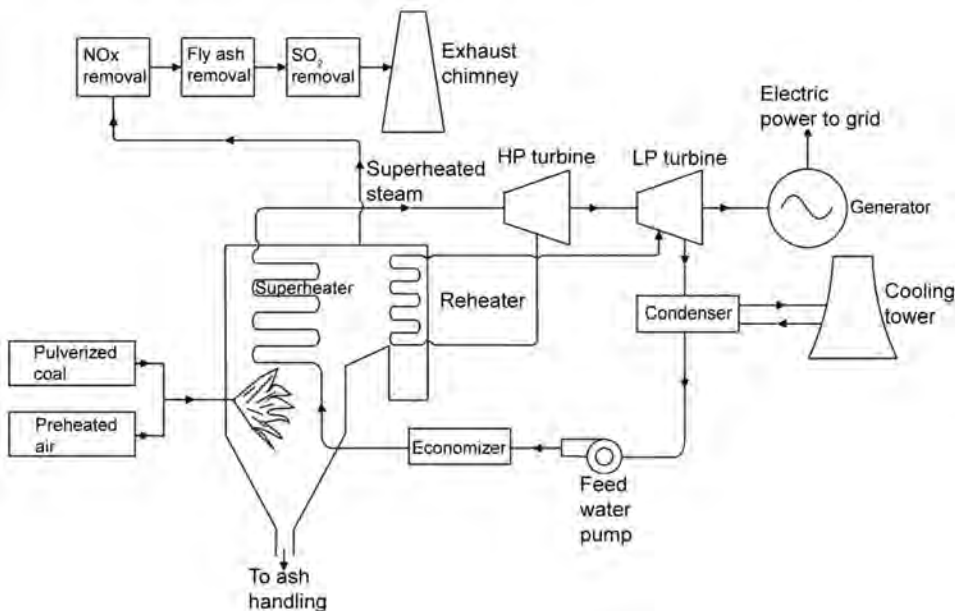


Fig. 2.4 Schematic view of a supercritical boiler plant

It is worth mentioning here that supercritical power plants have been in service for the past six decades, but the technology did not really take off due to materials-related problems from a metallurgical point of view. The most important factor that permits the use of higher and higher pressure and temperature is the availability of materials to withstand these conditions. The rise in operating pressure and temperature has to go hand in hand with developments in metallurgy, and major breakthroughs in this direction have taken place only in the recent past.

Though there is a major difference in the design of boilers used between subcritical and supercritical technologies, the turbines designed for supercritical and ultra-supercritical plants are similar to those for subcritical plants, with the only difference being that special materials are required for the casings and walls to withstand high temperatures and pressures. Materials for advanced boiler technologies are discussed at length in Chapter 4, *Materials for Boiler Tubes*, in this book.

REFERENCES

- 2.1 U.S. Energy Information Administration, “International Energy Outlook 2016,” www.eia.gov/ieo
- 2.2 R. Viswanathan and W.T. Bakker, “Materials for Ultra Supercritical Fossil Power Plants,” Report TR-114750 EPRI, March 2000
- 2.3 M.R. Susta and K.B. Seong, “Supercritical and Ultra-Supercritical Power Plants—SEA’s Vision or Reality?,” POWER-GEN ASIA 2004, p 1–23
- 2.4 I. Paul, “Supercritical Coal Fired Power Plants,” Energy Issues, No. 19, The World Bank, April 1999, p 1–8
- 2.5 G.S. Bindra, “Ultra Supercritical Power Plants,” paper presented at 3rd Thermal Power India, 2009

CHAPTER 3

Metallurgy of Steels and Related Boiler Tube Materials

3.1 Introduction

Materials used for different engineering applications are broadly classified as metallic materials (i.e., metals and alloys), ceramics, or plastics and polymers. The combination of two or more different materials from these three basic groups leads to the formation of materials called composites. Metallic materials include pure metals as well as alloys. Alloys are the combination of two or more metals, or a metal with a nonmetal. Metallic materials have an atomic structure consisting of a core of positive ions surrounded by a number of delocalized electrons such that these electrons are not confined to any particular atom but are free to move anywhere within that solid. On account of this atomic structure, metals and alloys possess good electrical and thermal conductivity, and are non-transparent to visible light (i.e., they are opaque). Besides this they have good strength along with good ductility and toughness and therefore are used in various engineering applications.

3.1.1 *Structure of Metals*

The properties of a metal are directly related to its atomic structure. When in a liquid state, metals have a highly disordered noncrystalline structure. However, when a molten metal or alloy cools and solidifies to form a bulk solid, it develops a crystalline structure with an ordered arrangement of atoms. In a crystalline solid there is a repetitive or periodic arrangement of atoms over large atomic distances. A crystalline solid consists of small repetitive entities called the unit cell, which act as a basic building block. A unit cell, when translated in three coordinate directions, forms a crystal.

The three common crystal structures found in metals are body-centered cubic (bcc), face-centered cubic (fcc), and hexagonal close-packed (hcp). Most crystalline solids, including metals and alloys, are composed of a large number of small crystals or grains having a variation in the crystallographic orientation from grain to grain. The two neighboring grains are separated by a boundary, called a grain boundary, where there is random arrangement of atoms and some atomic mismatch. Figure 3.1 shows the schematics for a unit cell, a crystal lattice, and a polycrystalline solid having grains and grain boundaries.

3.1.2 Imperfections in Solids

It is assumed that in crystalline solids, a perfect order exists throughout the material on an atomic scale. However, in reality it is not so. All crystalline solids contain a large number of various crystal defects/imperfections, and the properties of the material are strongly influenced by the presence of these imperfections. By definition a lattice irregularity of one

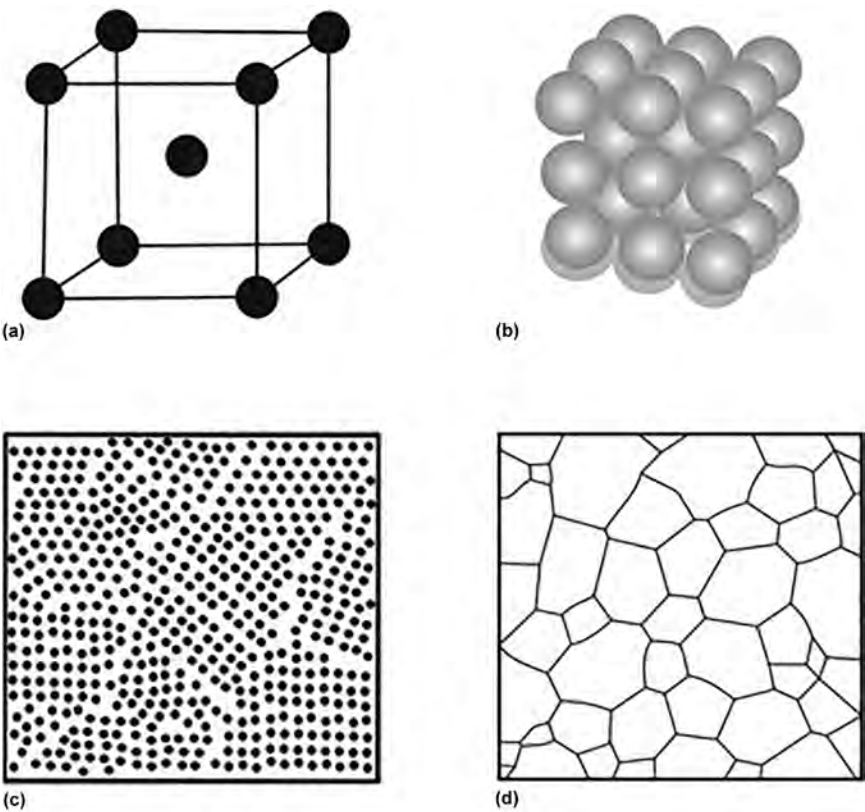


Fig. 3.1 Schematics for (a) a bcc unit cell, (b) a bcc crystal lattice, and (c) and (d) a polycrystalline solid with grains and grain boundaries

or more atomic positions is called a crystal defect or crystal imperfection. These play a major role in governing the properties of a material, in particular having a profound influence on the macroscopic properties. It has become apparent that some defects, when introduced in a controlled way, improve the properties of a material. For example, the strength of a metal or an alloy can be increased by increasing the density of dislocations in it (i.e., the number of dislocations per unit volume). On the basis of their geometry and size, crystal defects/imperfections are classified as point, line, and area defects.

Point defects in metals include vacancies (or vacant lattice sites), self-interstitials (host atoms that occupy interstitial sites), and impurity atoms. A solid solution type of an alloy is formed when impurity atoms are added to a solid. There are two types of solid solutions; substitutional solid solutions and interstitial solid solutions. In the former case, some of the atoms of the parent metal are replaced or substituted by atoms of the alloying metal, whereas in the latter, because the atoms of the parent or solvent metal are significantly larger than the atoms of the alloying or solute metal, the smaller atoms of solute fit into the interstices formed by larger solvent atoms. Figure 3.2 shows schematics illustrating substitutional and interstitial solid solutions in metals.

Another imperfection in solids is called a dislocation. It is a linear defect characterized by misalignment of atoms surrounding it. There are two types of dislocations: edge dislocations and screw dislocations. Typical values for the density of dislocations in a metal in an annealed condition are 10^{10} to 10^{12} per m^2 (Ref 3.1). An edge dislocation causes lattice distortion along the end of an extra half-plane of atoms, whereas a screw dislocation may be looked upon as a spiral planar ramp resulting from shear deformation. Figure 3.3 gives pictorial views of an edge and a screw dislocation.

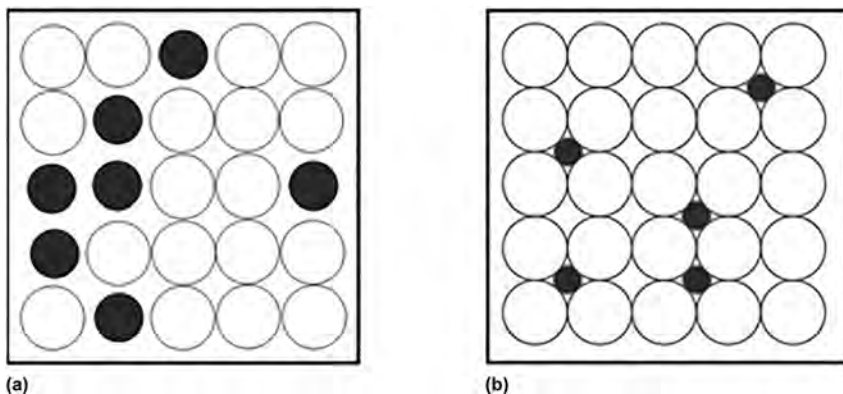


Fig. 3.2 Schematics showing (a) substitutional and (b) interstitial solid solutions

One more category of crystal defect is an area defect, which is an interfacial defect and is commonly known as the grain boundary (Fig. 3.4). This is the boundary separating two grains having different crystallographic orientations in a polycrystalline material. The grain boundaries impede dislocation motion and give rise to strengthening of metals.

3.2 Iron-Carbon Alloys

Metals and alloys can be further classified into two groups: ferrous and nonferrous. Ferrous alloys are those where the major element present is iron, whereas all others can be grouped together as nonferrous alloys. There are three types of ferrous alloys: (1) pure iron with <0.008 wt.% C, which is α -ferrite at room temperature; (2) steels; and (3) cast irons. The

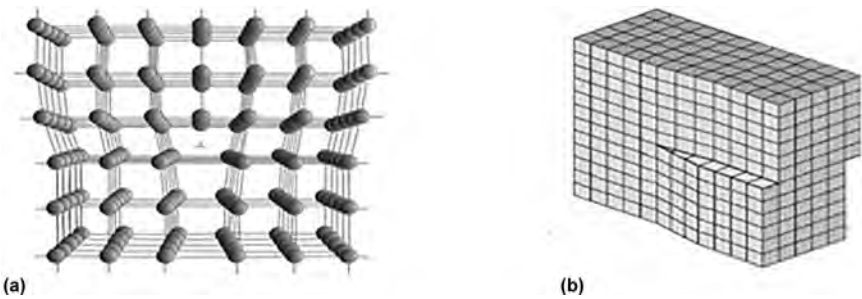


Fig. 3.3 Pictorial views of (a) an edge dislocation and (b) screw dislocation

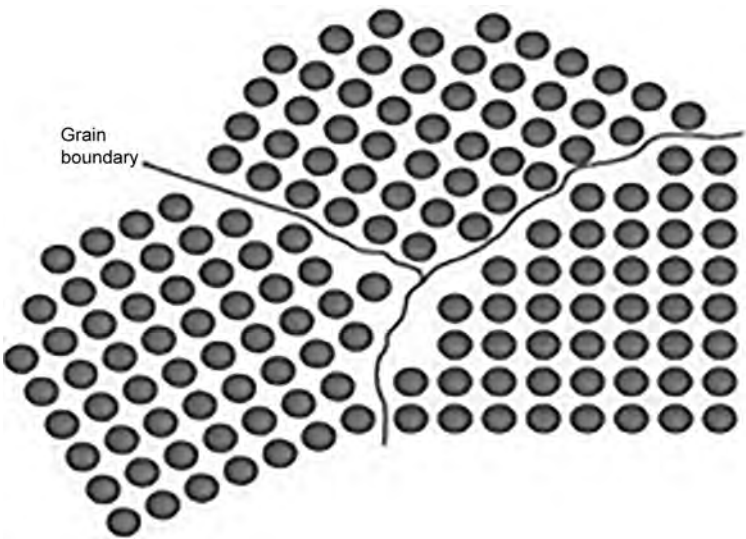


Fig. 3.4 Schematic diagram showing grain boundary

metal iron serves as the basis for some of the most important engineering alloys. But a relatively small amount of iron is used in pure form in comparison with that used in alloys because iron is very soft and has low strength. Carbon is one of the most important elements forming alloys with iron. Even though present in relatively low concentrations, carbon significantly influences the mechanical properties of iron-carbon alloys. A series of alloys have been developed between iron and carbon having percentages of carbon between 0.08 and 6.67% by weight. They are known as steels and cast irons. Alloys of iron and carbon having a maximum of 2.0 wt.% carbon are called steels. An alloy of iron and carbon with 0.8 wt.% carbon is called eutectoid steel; that containing less than 0.8 wt.% carbon is called hypoeutectoid steel; and that having greater than 0.8 wt.% carbon is called hypereutectoid steel.

Alloys of iron and carbon having carbon between 2.0 wt.% and 6.67 wt.% are termed cast irons.

3.2.1 Allotropic Forms of Iron

Pure iron exists in three different allotropic forms, namely delta (δ) iron, gamma (γ) iron, and alpha (α) iron in decreasing order of their transformation temperature. They have the same chemical composition but different crystal structures. Allotropic changes are always associated with a change in crystal structure.

Figure 3.5 shows the cooling curve for pure iron. As shown in this figure, the pure iron isothermally transforms from the liquid to solid state at

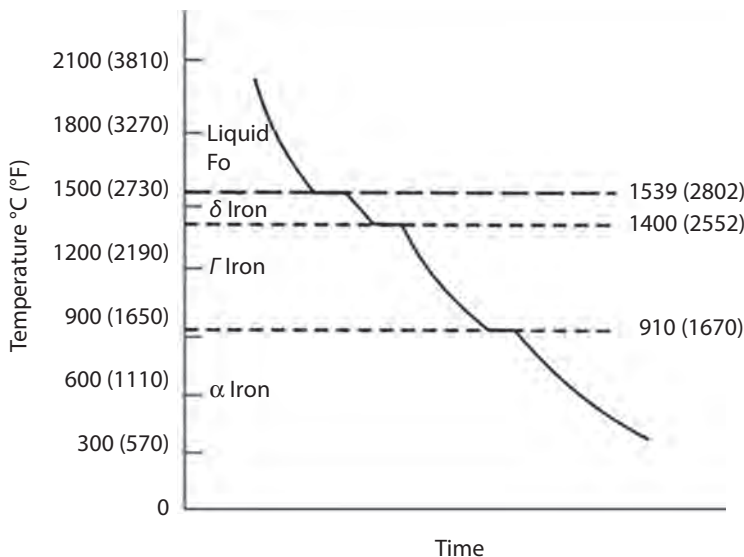


Fig. 3.5 Cooling curve for pure iron

1539 °C (2802 °F). From 1539 to 1400 °C (2802 to 2550 °F) δ -iron is present and has a bcc structure. At 1400 °C, the lattice changes from a bcc to an fcc type. Between 1400 and 910 °C (2802 and 1670 °F), pure iron exists as γ -iron. At 910 °C, the pure iron again transforms to a bcc structure called α -iron, which is stable up to room temperature. Thus, both α - and δ -iron have bcc structures but their lattice parameters are different, whereas the γ -iron has an fcc structure.

Figure 3.6 shows the schematics of bcc and fcc structures of allotropic forms of pure iron.

3.2.2 Iron-Carbon Diagram and Microstructure Development

The behavior of steels can be better understood with the help of a phase diagram known as the iron-carbon diagram. The phase diagram of an alloy is a graphical representation of the distribution of various phases as a function of temperature and overall composition. It represents the equilibrium temperature and composition limits of phase fields and phase reactions in an alloy system. Phase diagrams also provide quantitative understanding of phase transformations and related microstructural changes. A phase is a chemically homogeneous, physically distinct, and mechanically separable region of a material with a given composition and structure (Ref 3.2).

A general understanding of the iron-carbon diagram is essential for engineers, from a material selection (i.e., the choice of steel grade, especially when welding is involved) point of view, for deciding the heat treatment procedure for a given steel, and for understanding the performance of the steel during service under a given set of operating conditions.

Carbon is a nonmetallic element and is soluble in iron in both a solid and liquid state. Because the size of the carbon atom (0.77 Å) is much smaller compared with that of iron (1.24 Å), it occupies a position within

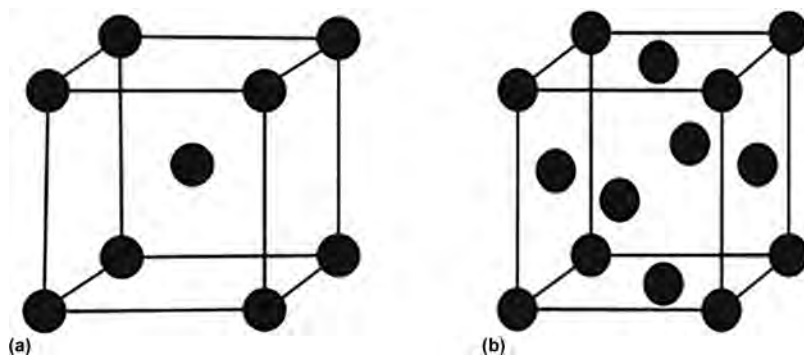


Fig. 3.6 Schematics of (a) body centered cubic (bcc) and (b) face centered cubic (fcc) structures of pure iron

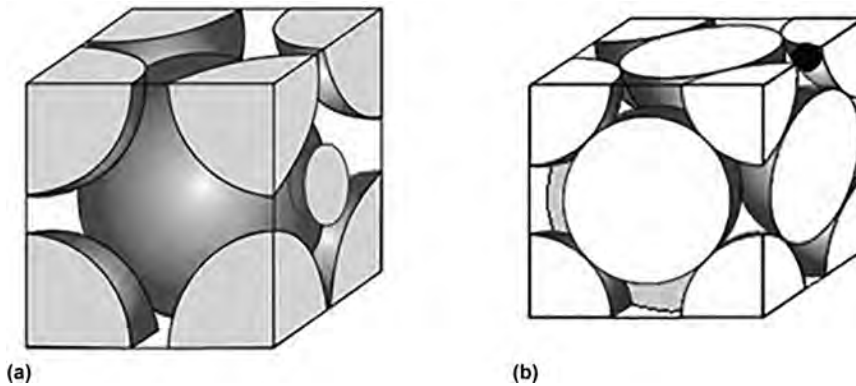


Fig. 3.7 Schematic showing that (a) carbon atoms occupy face center positions in bcc lattice of α -iron and (b) occupy edge center positions in fcc lattice of γ -iron

the interstices formed by iron atoms in the crystal lattice of iron, and the resultant solid solution formed is called an interstitial solid solution. Because the interstitial space between the iron atoms in the fcc lattice of γ -iron is larger than that in the bcc lattice of α -iron, the solubility of carbon in austenite is higher than that in ferrite. Figure 3.7 schematically shows the location of carbon in bcc α -iron and fcc γ -iron lattices.

Thus, besides the melt or liquid phase (i.e., solution of carbon in molten iron) there are four important solid phases in the iron-carbon system, namely δ -ferrite, austenite, ferrite, and cementite.

In the iron-carbon diagram (Fig. 3.8), temperature is plotted on the y-axis, whereas composition in terms of the percentage of carbon dissolved in iron is plotted on the x-axis (Ref 3.3). As shown in this diagram, pure iron melts at 1539 °C (2802 °F). When the percentage of carbon added to iron is increased, the melting point of an iron-carbon alloy gradually decreases such that an alloy of iron and carbon having 4.3 wt.% carbon when heated melts at a temperature as low as 1147 °C (2096 °F). This is the lowest temperature at which any alloy between iron and carbon melts and is called the eutectic point.

As shown in the diagram, the maximum solubility of carbon in bcc α -iron is 0.025 wt.% at 723 °C (1333 °F) and decreases with decreasing temperature to a value of 0.008 wt.% at room temperature. The solid solution so formed is called *ferrite* or α -*ferrite*. It is very soft and ductile and has low strength. *Austenite* is the name given to the solid solution of carbon in fcc γ -iron with maximum solubility equal to 2.0 wt.% at 1147 °C (2096 °F). Thus, the solubility of carbon in austenite is approximately 100 times greater than that in ferrite at 723 °C. Similarly, δ -ferrite is the solid solution of carbon in bcc δ -iron. Carbon and iron also form a metastable

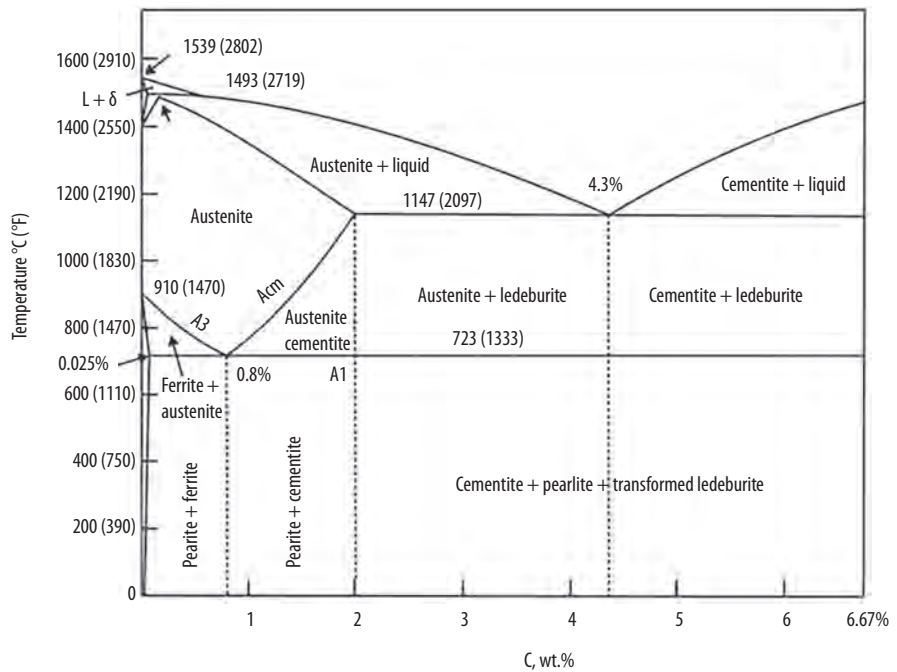


Fig. 3.8 Iron-carbon phase diagram. Source: Ref 3.3

intermetallic compound known as cementite (Fe_3C). Cementite contains 6.67 wt.% carbon by weight. Ferrite and cementite are stable phases at room temperature, whereas austenite is not. Austenite is present only at high temperatures. It is not stable below 723 °C unless cooled rapidly. The crystal structure of cementite is orthorhombic, and it is very hard and brittle.

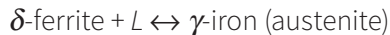
For all practical purposes cementite is stable at room temperature but decomposes very slowly (over a period of several years) into $\alpha\text{-Fe}$ and C (graphite) or rapidly on heating to a temperature of 650 to 700 °C (1200 to 1290 °F). Therefore, in a strict sense, the iron-carbon diagram is not a true equilibrium diagram because cementite is not an equilibrium phase; rather it is a metastable phase and under certain conditions it decomposes to iron and graphite.

Temperatures at which the solid-state transformations in an iron-carbon system take place are called critical points or critical temperatures. For hypoeutectoid steels (i.e., steels containing <0.8 wt.% C), the upper critical temperature (point), A_3 , is the temperature below which on cooling of austenite, ferrite starts to form as a result of ejection of carbon from austenite. In hypereutectoid steels (i.e., steels containing >0.8 wt. % C), A_{cm} is the upper critical temperature, below which cementite starts to form on cooling of austenite as a result of ejection of carbon from austenite. A_1 is the lower critical temperature at which austenite-to-pearlite eutectoid

transformation occurs. Below this temperature, austenite does not exist when the material is slowly cooled.

The iron-carbon diagram shows three horizontal lines each representing an invariant transformation occurring at reaction points having constant temperature and involving three phases. These reactions are known as peritectic, eutectic, and eutectoid reactions.

- *Peritectic reaction* occurs at a peritectic point corresponding to 0.16 wt.% carbon and 1493 °C (2719 °F) temperature.



In general terms, upon cooling one liquid and one solid react to form a new solid, whereas upon heating one solid phase transforms into a liquid phase and another solid.

- *Eutectic reaction* occurs at the eutectic point corresponding to 4.3 wt.% carbon and 1147 °C (2096 °F) temperature.



In general terms, upon cooling one liquid solidifies into two solids, whereas upon heating two solids react to form one liquid phase.

The eutectic mixture of austenite and cementite is known as ledeburite.

- *Eutectoid reaction* occurs at a eutectoid point corresponding to 0.8 wt.% carbon and 723 °C (1333 °F) temperature.



In general terms, upon cooling one solid decomposes into two solids, whereas upon heating two solids react to form one solid phase.

The eutectoid mixture of ferrite and cementite is known as pearlite.

Among these, the one which takes place completely in the solid state is the eutectoid transformation, and this forms the basis for heat treatment of steels. The following discussion pertains to what happens when steel is subjected to heating or cooling across the critical temperature. For the sake of convenience in understanding solid state transformations in steel, only the steel portion of the iron-carbon diagram is reproduced in Fig. 3.9.

For instance, if a hypoeutectoid steel (0.4 wt.% C) is heated below the A_1 temperature and then cooled at any desired cooling rate, there is no change in its microstructure, which remains ferrite and pearlite only. However, if this steel is heated to just above the A_1 temperature, the pearlite will transform to austenite. Here, the eutectoid ferrite and cementite (of pearlite) react at their interface to form nuclei of austenite. Growth of these

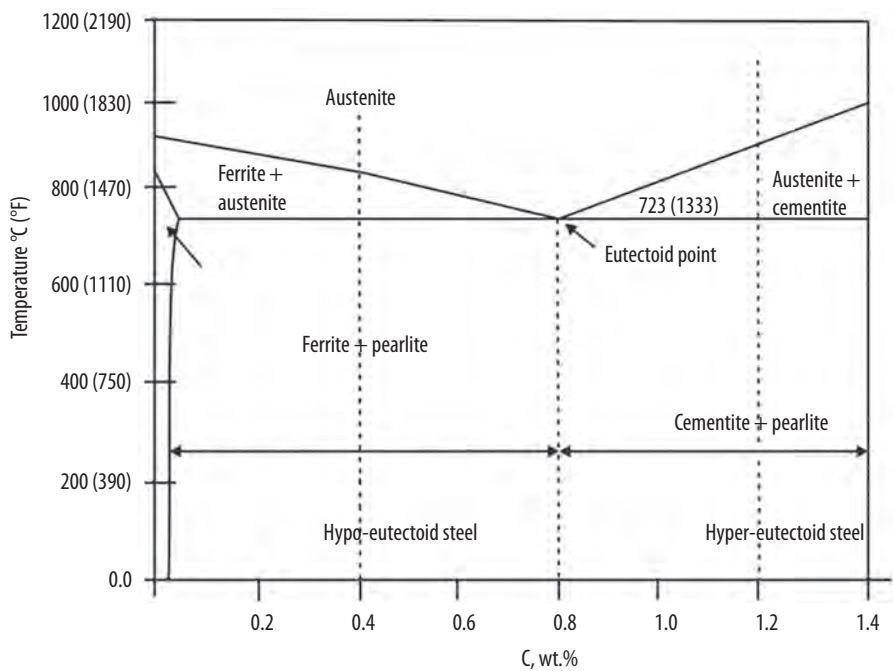


Fig. 3.9 Steel portion of the iron-carbon diagram

nuclei takes place with the absorption of additional ferrite and cementite until each pearlite grain has been transformed to austenite. Thus, between A_1 and A_3 temperatures, the structure is ferrite + austenite. At the A_3 temperature, the transformation to austenite will be complete and thus a single-phase austenite will form. Likewise, in hypereutectoid steel (1.2 wt.% C), the transformation begins at the A_1 temperature by the transformation of pearlite to austenite. Heating above A_1 leads to a solution of cementite in austenite until the A_{cm} temperature is reached. At the A_{cm} temperature, the cementite completely dissolves in austenite. Any steel will be thus completely austenitic under equilibrium conditions when the temperature is above A_3 or A_{cm} .

Now, let us see what happens when steel is subjected to cooling across the critical temperature. For example, when a steel containing 0.8 wt.% carbon is cooled slowly from the austenitic range to below the A_1 temperature, a nuclei of cementite forms at the prior austenite grain boundary. The surrounding austenite gets depleted in carbon and transforms allotropically to ferrite. Finally, a lamellar or layered structure of two phases, namely ferrite and carbide/cementite, develops as a result of redistribution of carbon between these two phases. The resultant structure is known as pearlite because it has the appearance of mother of pearl when viewed under the microscope at low magnifications. In pearlite, the ferrite and cementite are present as alternate bands or lamellae such that under the

microscope, the ferrite appears as light areas and the cementite as dark. The decomposition of austenite to form pearlite occurs by nucleation and growth. The mechanical properties of pearlite are intermediate to that of ferrite and cementite alone. Figure 3.10 shows the microstructures of ferrite, austenite, and pearlite.

If a hypoeutectoid steel (containing <0.8 wt.% C) is slowly cooled from above the A_3 temperature, ferrite begins to precipitate from austenite. The precipitation of ferrite continues until the steel reaches the A_1 temperature (i.e., eutectoid temperature). Ferrite that forms prior to the eutectoid temperature is called proeutectoid ferrite. Because α -iron dissolves very small amounts of carbon (<0.025 wt.% C at 723°C), the concentration of carbon in austenite increases until the eutectoid composition is reached. At the eutectoid temperature, the remaining austenite of the eutectoid composition transforms isothermally to pearlite as per the eutectoid reaction discussed above. Figure 3.11 shows the microstructures of hypoeutectoid and hypereutectoid steel.

Similarly upon slow cooling, a hypereutectoid steel (containing >0.8 wt.% C), cementite begins to precipitate at the A_{cm} temperature and

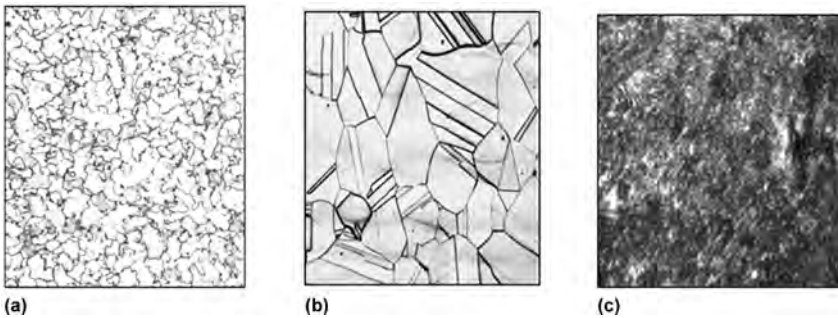


Fig. 3.10 Microstructures of steel, (a) ferrite; 100x; (b) austenite; 200x; and (c) pearlite; 1000x

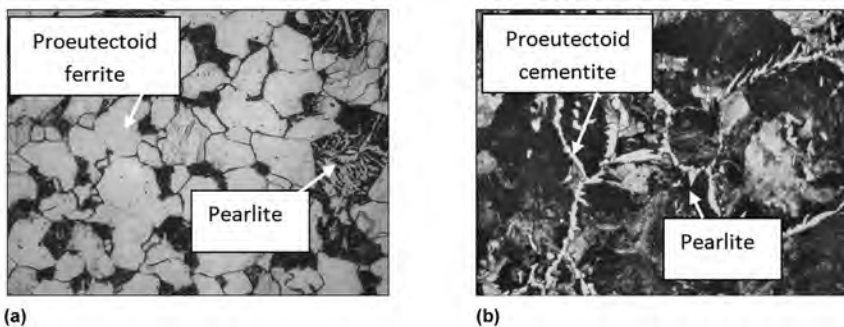


Fig. 3.11 Microstructures of steel, (a) hypoeutectoid, 200x; and (b) hypereutectoid, 200x

continues until the A_1 temperature (i.e., eutectoid temperature), is reached. Cementite that forms prior to the eutectoid temperature is called pro-eutectoid cementite. Precipitated cementite begins to migrate along the grain boundaries of austenite, forming a network. The remaining austenite transforms isothermally to pearlite at the A_1 temperature as per the eutectoid reaction stated above.

3.3 Phase Transformations in Steel

The phase transformation in alloy systems is either diffusion controlled or it is diffusionless. Diffusion-controlled transformation is time dependent and involves change in the composition and/or number of phases, whereas diffusionless transformation is characterized by cooperative movement/displacement of the atoms and is not time dependent. The iron-carbon phase diagram, though it gives information about the nature of the phases present for any given composition and temperature, does not tell us about the kinetics of transformation (i.e., it does not give any idea about the effect of the heating or cooling rate on transformation). Some of the phase transformations in the Fe-C system are governed by time and depend on the rate of heating and cooling, whereas others are not time dependent. From a room temperature microstructure and heat treatment point of view, the most important transformations in iron-carbon alloys are the solid-state transformations that occur when steel is subjected to heating or cooling across the critical temperatures.

3.3.1 Isothermal Transformation and TTT Diagrams

The kinetics of the transformation of supercooled austenite (i.e., when it is cooled below A_1 , the lower critical temperature) at different cooling rates can be best described using isothermal transformation (IT) or time-temperature-transformation (TTT) curves. In view of their shape, TTT curves are also known as “S” curves. The TTT diagrams are plotted by quickly supercooling a steel sample to a certain temperature below A_1 followed by holding it at that temperature until the transformation is complete. This procedure is repeated for a large number of samples by supercooling them to different temperatures and isothermally holding them at the respective temperature until the transformation is complete. The degree of transformation or decomposition in each case is determined by subjecting the samples to metallography or dilatometry.

A typical TTT diagram for eutectoid steel is shown in Fig. 3.12(a) and (b).

The figure is a semi-log plot of temperature versus time with a logarithmic time scale. A horizontal line at the top of the S curve denotes the eutectoid temperature (i.e., critical temperature A_1 below which the supercooled austenite is in a metastable condition). At temperatures above the eutectoid and for all times, only austenite will exist.

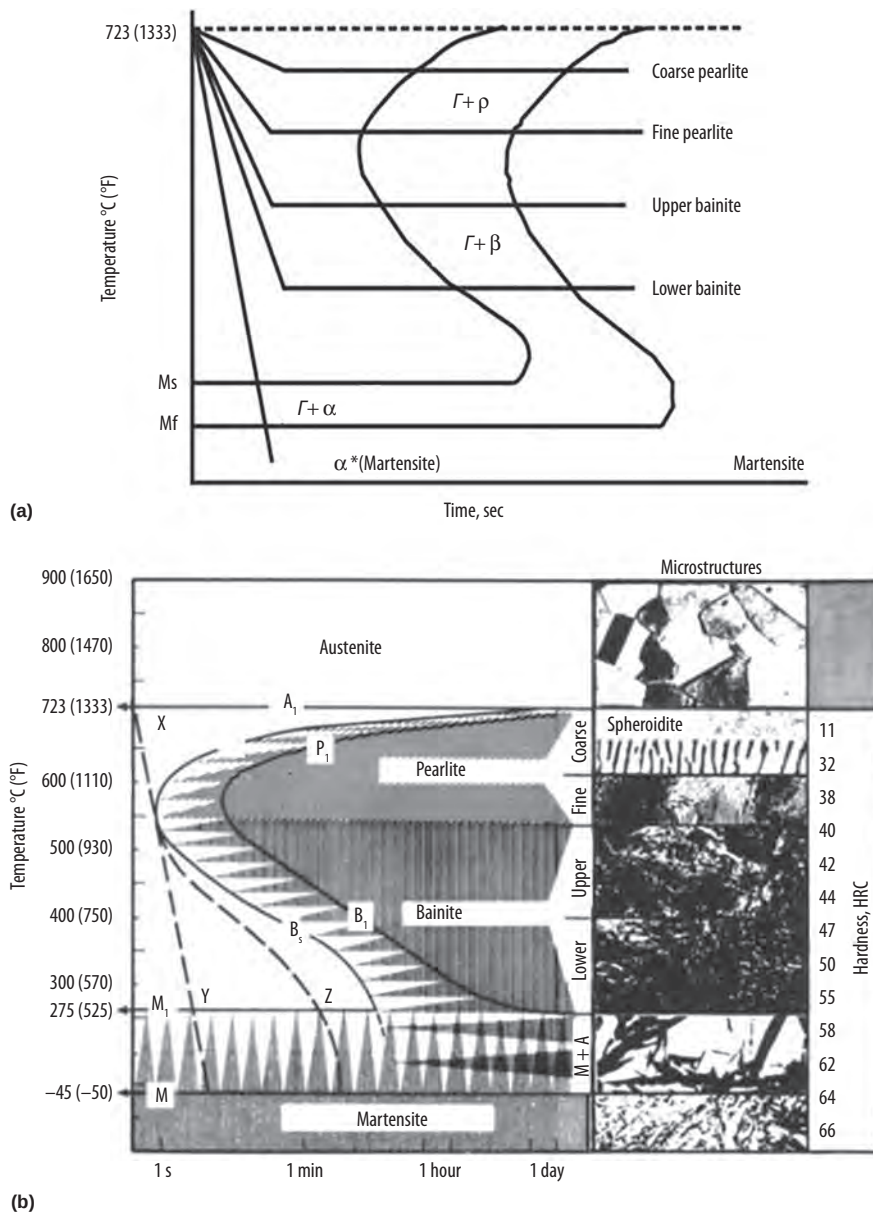


Fig. 3.12 A typical TTT diagram for eutectoid steel (a) with isothermal holding curves superimposed (Source: Ref 3.4) and (b) microstructures superimposed. Source: Ref 3.5

In Fig. 3.12(a), the S-shaped curves as shown by two solid lines represent the time corresponding to the start and end of the transformation. The time to the left of the TTT curve is known as the incubation period and it indicates the metastable nature of the supercooled austenite. The dashed curve in Fig. 3.12(b) corresponds to 50% of transformation completion. To the left of the start curve, only metastable austenite will be present,

whereas to the right of the end curve, products of decomposition such as pearlite will exist. The point corresponding to the minimum incubation period is called the “nose” of the TTT curve. At this temperature, where the austenite stability is minimum, the rate of transformation is very high. (In carbon steels, the length of the incubation period at this temperature does not exceed 1 or 1.5 seconds.) In between two curves, the austenite is in the process of transforming to pearlite, and hence both austenite and pearlite will coexist. The amount of transformed austenite can be determined as a function of time at constant temperature.

The process of phase transformation involves phenomena of nucleation and growth. A small nucleus of the new phase first forms at grain boundaries and other defects, and then grows at the expense of the matrix until the whole structure is transformed. At higher temperatures (i.e., just below the eutectoid temperature where the degree of supercooling is lower), high diffusion rates allow for a higher amount of grain growth at the expense of formation of new nuclei. This results in formation of coarse pearlite with relatively large interlamellar spacing. On the other hand, a slow diffusion rate at low temperatures (corresponding to a high degree of supercooling) leads to a fine-grained microstructure with small interlamellar spacing between ferrite and cementite in pearlite, as shown in Fig. 3.12(b). The isothermal transformation of austenite to pearlite takes place between the eutectoid temperature and 550 °C (1020 °F). For hypo- and hypereutectoid steels, a proeutectoid phase (ferrite or cementite) coexists with pearlite. An additional line for proeutectoid transformation is therefore shown in the TTT diagrams.

The kinetics of decomposition of austenite and the resultant phases formed in plain carbon steel depends on how fast carbon atoms diffuse through it. If the steel is rapidly supercooled to a low temperature such that the rate of diffusion is very low, an altogether different microstructure evolves. The microstructures evolved as a result of fast cooling are termed bainite and martensite.

Martensite is a metastable nonequilibrium phase and hence it does not appear as a phase in the Fe-C phase diagram. Martensite forms only when austenite is supercooled by rapid cooling (i.e., quenching to low temperatures, usually below 200 °C, or 390 °F, at which the diffusion process becomes impossible). Austenite transforms to martensite only on quenching at a rate greater than or equal to the critical cooling rate. This transformation is a diffusionless type; that is, it is not accomplished by a diffusive type of redistribution of carbon atoms in the austenite matrix. Rather, it is accomplished by cooperative movement of atoms by a shear mechanism (i.e., displacement mechanism). Martensite is a supersaturated, interstitial solid solution of carbon in α -iron. It is an extremely hard and brittle phase. The carbon content of martensite can be the same as the carbon content of the initial austenite; that is, it may have 2 wt.% carbon. Martensite has a tetragonal crystal lattice with the ratio $c/a > 1$. The

degree of tetragonality depends on the percentage of carbon in the steel. In a martensitic transformation, the chemical composition remains the same; it is only the crystal structure that changes from fcc to body-centered tetragonal (bct) as shown in Fig. 3.13.

Pearlitic and bainitic transformations are isothermal in nature, whereas martensitic transformations are athermal. On TTT curves, the symbols M_s and M_f are usually indicated on the temperature scale. They indicate the temperature at which austenite will start to transform to martensite (M_s) and the temperature at which transformation will end (M_f). The M_s and M_f lines on TTT diagrams appear as horizontal straight lines and not as the curved lines typical of the pearlitic or bainitic portion of the diagram. This signifies that the martensitic transformation is independent of time; it is a function only of the temperature to which the alloy is quenched or rapidly cooled. For some steels, the M_f temperature may be below room temperature and hence if they are quenched to room temperature during heat treatment there will be retained austenite in the microstructure as a residual phase.

If the transformation temperature is between 550 and 200 °C (1020 and 390 °F), bainite forms. The bainitic transformation of supercooled austenite combines the features of both pearlitic as well as martensitic transformations. Similar to pearlitic transformation, diffusive redistribution of carbon in the austenite and between the products of its decomposition takes place. Additionally, the transformation also proceeds by the shift type mechanism of austenite to ferrite, which is a typical feature of martensitic transformation. Bainitic transformation differs from pearlitic transformation. Pearlite is nucleated from cementite, and formation of cementite is accomplished with formation of ferrite, whereas bainite is nucleated by ferrite. As a result, the surrounding area within an austenite grain is enriched in carbon, leading to formation of a cementite plate. Eventually, alternate regions of ferrite and cementite develop.

Bainite is a nonequilibrium phase and a eutectoid reaction product of nonlamellar nature. Bainite forms on cooling of austenite to temperatures below that for formation of pearlite and above the M_s temperature. Thus,

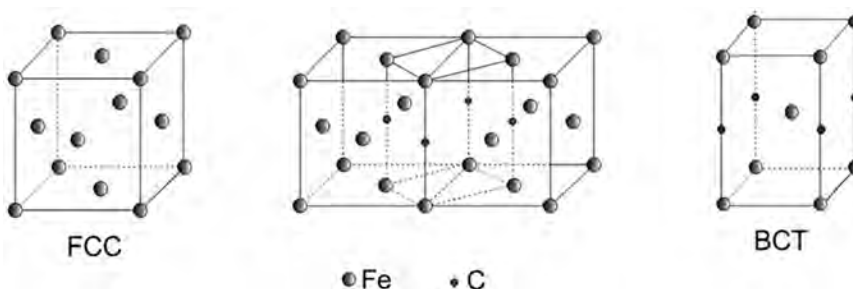


Fig. 3.13 Transformation of fcc austenite to bct martensite, known as the *bain model*

the temperature range for formation of bainite is from below the nose of the TTT curve up to the martensite start temperature (i.e., between 550 and 200 °C). Bainite formed between 550 and 300 °C (1020 and 570 °F) is termed upper bainite. It resembles pearlite and has a feathery appearance. Bainite formed between 300 °C and the M_s temperature (about 200 °C) is termed lower bainite and it resembles martensite on account of its needle-like appearance. Fig. 3.12 shows the temperature range for formation of bainite and its microstructure. At such a low temperature, the distance over which carbon atoms can diffuse is short. As a result, a structure consisting of submicroscopic dispersion of carbides in a matrix of ferrite forms, imparting bainite with more strength than pearlite.

3.3.2 Continuous Cooling Transformation and CCT Diagrams

TTT diagrams are extremely useful to heat treaters as they give information about the hardening response of steels and also the nature of transformed products of austenite at varying degrees of supercooling. However, it is worth noting that during hardening treatment, the steel is not subjected to isothermal holding but rather subjected to continuous cooling by quenching into some medium such as oil or water that rapidly extracts heat from the workpiece. Thus in practice, transformation during heat treatment occurs by continuous cooling, and not isothermally. The rate of cooling depends upon the cooling medium used. This has led to development of continuous cooling transformation (CCT) diagrams. Figure 3.14 shows the CCT curves for different cooling conditions superimposed on the TTT curve for eutectoid steel.

In the diagram, segments of the TTT curves for eutectoid steel indicating the beginning and end of transformation are shown. The different cooling curves corresponding to different cooling rates are superimposed over these curves. Curve-A represents slow cooling as in the case of furnace cooling, resulting in transformation of austenite just below the A_1 temperature and giving rise to coarse lamellar pearlite. This is the practice normally followed in annealing of steels. The cooling curve as indicated by curve-B corresponds to air cooling conditions (adopted during normalizing) and gives rise to finer pearlite than that produced by cooling conditions as represented by curve-A. In the case of curve-C, initial formation of fine pearlite takes place, but insufficient time in the upper range of temperature prevents complete transformation to pearlite, so some of the austenite transforms to martensite at the lower temperatures. Such a transformation is known as a split transformation. With a sufficiently fast rate of cooling such as indicated by curve-D, transformation does not occur until a sufficiently low temperature is reached, and thereafter martensite forms. There is a cooling rate, indicated by curve-E, that will produce a fully hardened structure comprising 100% martensite without any lower products of decomposition such as pearlite or bainite. The

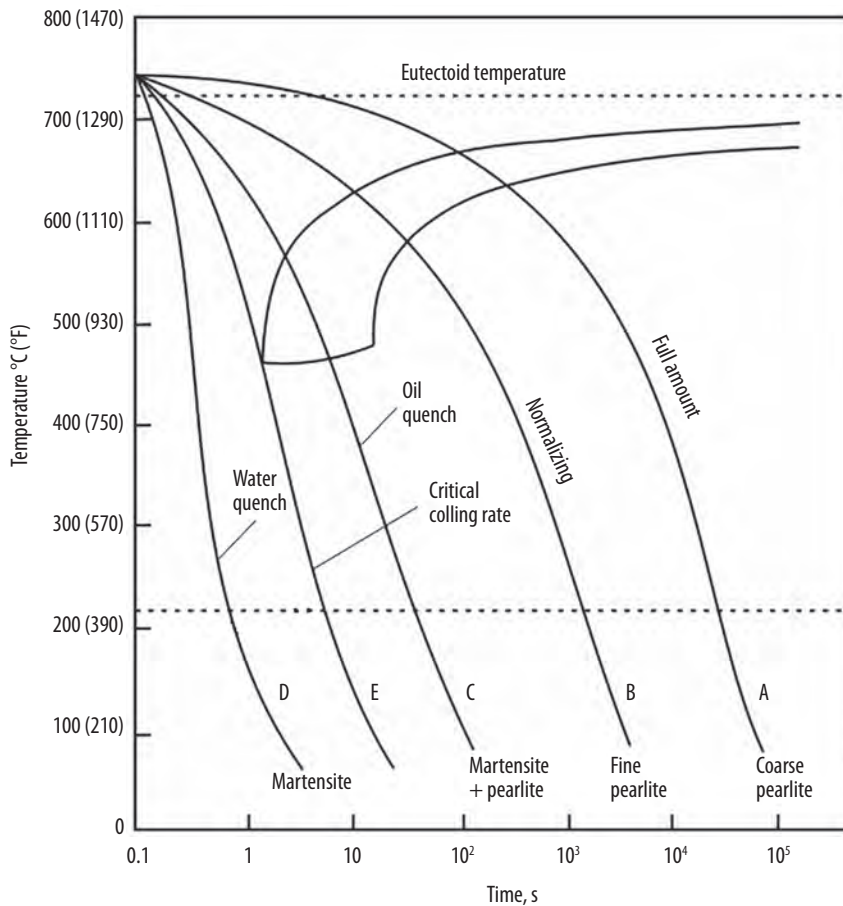


Fig. 3.14 The CCT curves superimposed on the TTT curve for eutectoid steel.
Source: Ref 3.6

cooling rate that accomplishes this is known as the critical cooling rate. A cooling rate slower than critical will allow formation of some pearlite/bainite and therefore will prevent full hardening.

Thus, the minimum cooling rate at which all austenite is supercooled to a temperature below M_s and is transformed into martensite is known as the critical cooling rate. The critical cooling rate is not the same for different kinds of steel and depends upon the austenite stability, which is mainly determined by the composition of the steel. The higher the stability of the austenite, the lower will be the critical cooling rate. Carbon steels have a higher critical cooling rate than alloy steels. Among plain carbon steels, eutectoid steel has the lowest critical cooling rate. Alloying elements that raise austenite stability sharply reduce the critical cooling rate. Cobalt is the only element that reduces austenite stability and raises the critical cooling rate.

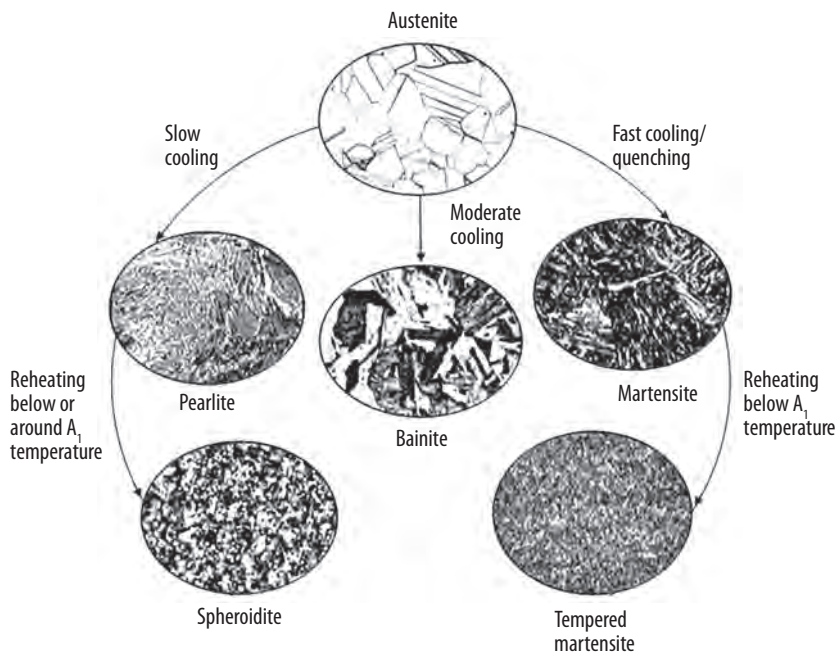


Fig. 3.15 Schematic showing the effect of cooling rate on the transformation of supercooled austenite

The schematic in Fig. 3.15 gives an overall idea about the effect of cooling rate on the transformation of supercooled austenite to different products.

3.4 Classification and Types of Steels

Steels are essentially alloys of iron and carbon with carbon ranging from a few hundredths of a percent to more than 1%. They also contain other elements, known as inherent impurities, such as silicon, manganese, sulfur, and phosphorus, that are always present in any steel in relatively small amounts, as well as traces of oxygen, nitrogen, and hydrogen. These impurities are carried over while processing hot metal to make steel. However, their levels are strictly controlled as they have an adverse effect on the properties of steel if present beyond specified limits. Besides these elements, steels can also have one or more of the alloying elements chromium, manganese, nickel, molybdenum, titanium, niobium, tungsten, vanadium, cobalt, or boron, depending on the end use.

There are approximately 2500 different grades of steel and hence a systematic classification is a must for understanding them better.

Steels can be classified in a number of ways depending on the basis of classification. A brief list of some of the criteria used for classification of steels (Ref 3.7) includes:

- Composition—plain carbon, low-alloy, and high-alloy steels
- Principle alloying element present—Ni steel, Cr steel, Cr-Ni steel, or Cr-Ni-Mo steel
- Structure upon air cooling—pearlitic steels (low alloy content), martensitic steels (more appreciable alloy content), and austenitic steels (high alloy content)
- Method of manufacture—open hearth steel, Bessemer steel, or electric furnace steel
- Deoxidation practice—killed, semikilled, or rimmed steel
- Form—cast steel and wrought steel. Cast steels are obtained by solidification of the molten alloy in ingots or molds. Wrought steels are made by rolling, forging, drawing, or extrusion to obtain a form such as a bar, plate, sheet, strip, tube, or any other structural shape
- Strength level, as specified by the American Society for Testing and Materials (ASTM) standards
- Quality descriptors, such as forging quality and radiographic quality

The most common method of classifying steels is based on the composition as regards the presence or absence of alloying elements. Accordingly, steels can be classified into two broad categories, namely plain carbon steels or carbon steels and alloy steels.

3.4.1 Plain Carbon Steels

The American Iron and Steel Institute (AISI) defines carbon steel as follows (Ref 3.8): “Steel is considered to be carbon steel when no minimum content is specified or required for chromium, cobalt, columbium [niobium], molybdenum, nickel, titanium, tungsten, vanadium or zirconium, or any other element to be added to obtain a desired alloying effect; when the specified minimum for copper does not exceed 0.40 per cent; or when the maximum content specified for any of the following elements does not exceed the percentages noted: manganese 1.65, silicon 0.60, copper 0.60.”

In other words, a steel would qualify as a plain carbon steel or carbon steel if it contains manganese up to 1.65 wt.%, silicon up to 0.60 wt.%, and copper up to 0.60 wt.%, with the exception of deoxidizers and boron when specified, and no other alloying element is intentionally added.

Compositional limits for various elements in plain carbon steel are given in Table 3.1.

All steels invariably contain carbon because the process of steel making is such that it is very difficult to remove carbon completely. In plain carbon steel, carbon is the principal alloying element. The properties of plain carbon steel depend primarily on the amount of carbon it contains. As the amount of carbon increases, the percentage of cementite in steel increases. Because cementite has high strength and hardness, with an

increase in the amount of carbon, the strength and hardness of plain carbon steel increases, as shown in Fig. 3.16. But, because cementite is very brittle, with an increasing amount of cementite in steel (i.e., carbon content), the ductility and toughness of the steel decrease.

Depending on carbon content, unalloyed (i.e., plain) carbon steels are subdivided into three types:

- Low-carbon steels, which contain less than 0.30% carbon;
- Medium-carbon steels, which contain from 0.30% to 0.60% carbon; and
- High-carbon steels, which contain more than 0.60% carbon.

Table 3.1 Compositional limits for various elements in plain carbon steel

Element	Amount in wt.%
Carbon	up to 1.20%
Manganese	up to 1.65%
Silicon	up to 0.60%
Sulfur	up to 0.05%
Phosphorus	up to 0.05%
Iron	balance

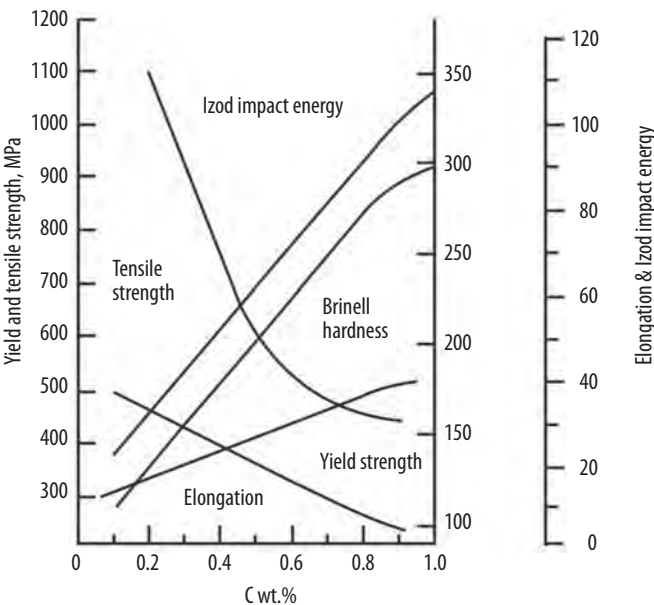


Fig. 3.16 Effect of carbon on mechanical properties of plain carbon steel.
Source: Ref 3.9

3.4.1.1 Low-Carbon Steels. In low-carbon steels, carbon content is less than 0.30 wt.%. They are the most abundant grades of steel and are the least expensive type of steel. Mild steel is low-carbon steel having about 0.2 wt.% carbon. Most steel in this class is used to produce flat-rolled products (i.e., sheet or strip), usually in the cold-rolled and annealed condition. Low-carbon steels have excellent ductility and toughness, along with good weldability as well as machinability. Typical applications of low-carbon steels include industrial products such as bolts, nuts, sheets, strips, and plates. In view of their low carbon level, they do not respond to heat treatment. In other words, they cannot be strengthened by heat treatment as they are not amenable to martensitic transformation and hence cold working is the best option to improve their strength.

3.4.1.2 Medium-Carbon Steels. Medium-carbon steels have carbon in the range of 0.30 to 0.6 wt.%. These steels are heat-treatable steels; that is, they can be subjected to hardening and tempering treatments for improvement of properties. The addition of alloying elements such as chromium, nickel, and molybdenum further improves the heat-treating capacity. For this class of steels, the mechanical and/or service properties can be improved by heat treatment. Typical applications of medium-carbon steels include machinery, automobile and agricultural parts, gears, crankshafts, axles, connecting rods, couplings and forgings, and railway wheels and tracks.

3.4.1.3 High-Carbon Steels. In high-carbon steels, the carbon varies from 0.6 to 1.2 wt.%. These steels are the hardest and strongest of the three types of steels, but at the same time they are brittle. They are invariably used in hardened and tempered condition. They are used in applications demanding high strength and high hardness along with good wear resistance. Typical examples of applications of high-carbon steel are razor blades, cutting tools, high tensile wires and ropes, and musical instrument wires.

Ultra-high-carbon steels contain carbon in the range of 1.20 to 2.0 wt. %.

In summary, plain carbon steels can be successfully used where strength and other requirements are not too severe. They can be used at ambient temperature and in ordinary atmospheres of noncorroding nature. Their main advantage is their low cost and ease of processing. But there are certain limitations of plain carbon steels, which include:

- Increase in strength only at the cost of ductility and toughness
- Low hardenability and hence strength limited to small cross sections
- Major loss of hardness on tempering or stress relieving
- Low corrosion and oxidation resistance
- Low creep strength at elevated temperature
- Risk of distortion and cracking on full hardening during rapid quenching in medium-carbon steels

The above limitations of plain carbon steels have prompted scientists and engineers to develop alloy steels. Alloy steels contain one or more alloying elements besides the elements present in plain carbon steel. The reasons alloying elements are added include:

- To increase hardenability of steel
- To increase resistance to softening on tempering or stress relieving
- To increase resistance to corrosion and oxidation
- To improve high-temperature properties including creep resistance
- To increase resistance to abrasion and wear
- To strengthen steels that cannot be strengthened by quenching

3.5 Effect of Alloying Elements in Steel

About 20 elements are used as alloying elements in various proportions and combinations in the manufacture of alloy steels. Some of the more frequently used alloying elements include chromium, nickel, silicon, manganese, tungsten, molybdenum, vanadium, titanium, niobium, aluminum, copper, sulfur, phosphorus, and boron.

Alloying elements may be classified based on their effect on the iron-carbon system:

- *Elements that form solid solutions with iron:*
C, Cr, Mn, Mo, Si, and Co
- *Elements that tend to stabilize austenite:*
Mn, Ni, Co, Cu, and N
- *Elements that tend to form carbides:*
Cr, W, Ti, Ta, Nb, V, Mo, Zr, and Mn
Generally, carbide formers are also ferrite stabilizers.
- *Elements that tend to stabilize ferrite:*
Cr, W, Mo, V, and Si
- *Elements that tend to graphitize carbides:*
Si, Co, Al, and Ni are graphitizers. Their presence makes carbides unstable.
- *Elements that tend to form nitrides:*
Ti, Al, V, and Zr
- *Elements that remain in a free state:*
Pb and Cu

The alloying behavior of individual elements is discussed in this section.

Carbon. Although it is not generally considered an alloying element, it is present in all steels. Theoretically, the maximum amount of carbon in steel is 2.0 wt.%. Carbon is responsible for an increase in the tensile strength, hardness, resistance to wear, and abrasion of steel. However,

with an increase in the amount of carbon, the ductility, toughness, forgeability, weldability, and machinability of steel decrease.

Manganese is next in importance to carbon as an alloying element. Manganese is usually present in the amount ranging from 0.5 to 2 wt.%, except for certain special steels known as Hadfield manganese steels, which contain 11.0 to 14.0 wt.% manganese. Manganese is normally present in all steels. It acts as a deoxidizer and also imparts strength, hardness, and responsiveness to heat treatment by increasing the hardenability of steel. Manganese increases the strength of ferrite. Steels containing a considerable amount of manganese can be quenched in oil rather than in water, making the steel less susceptible to cracking because of a reduction in thermal stress during quenching. Manganese reacts with sulfur to form manganese sulfide, thereby reducing the risk of hot shortness in steel. By forming manganese sulfide inclusions, manganese improves the machinability of steel.

Silicon, like manganese, is present in all steels irrespective of whether they are a plain carbon steel or alloy steel. However, only steels containing 3.0 to 4.0 wt.% of silicon are called silicon steels, and they are used in electrical transformer stampings. Silicon increases the elastic limit and hence is a useful alloying element in spring steels. It slightly increases the strength of ferrite, and when used in conjunction with other alloying elements can help in increasing the toughness and hardenability of steel. Silicon increases resistance to scaling.

Sulfur is an important element in steel because when present in relatively large quantities, it increases machinability. It increases tool life by reducing friction at the cutting edges of the tool. Therefore, it is used in free-machining steels as an alloying element. The amount generally used for this purpose is from 0.06 to 0.30 wt.%. However, sulfur is detrimental to the hot forming properties of steel. It reacts with iron to form iron sulfide, which produces red or hot shortness. A low-melting eutectic formed weakens the grain boundaries of steel, leading to failure of the steel during hot forming. Sulfur plays a critical role in reducing the weldability, impact toughness, and ductility of steel. Sulfur is a trace element, and has a tendency toward segregation (i.e., to isolate itself in the structure).

Phosphorus is normally regarded as detrimental to steel and every effort is therefore made to keep phosphorus content in steels to a maximum of 0.03 to 0.05 wt.%. It improves the machinability of steels when present in relatively large amounts. Phosphorus is an element that adversely affects the ductility and the toughness of steel. Phosphorus has a tendency to react with iron to form a compound known as iron phosphide (Fe_3P), which being brittle, leads to cold shortness in steel.

Chromium is one of the most important alloying elements in steel. Low-alloy steels have chromium in the range of 0.50 to 1.50 wt.%, whereas high-alloy steels such as stainless steels and heat-resistant steels have

about 12.0 to 25.0 wt.% chromium. Chromium increases response to heat treatment. It increases the hardenability of steel (i.e., it increases the depth to which steel can be hardened). It improves the mechanical properties of steel; both the yield strength and tensile strength of steel increase as a result of chromium addition. Chromium has the ability to increase the hardness of steel and thus increases the resistance to abrasion and wear. In high-alloy steels, its role is to enhance the corrosion and oxidation resistance of steel and to improve creep strength.

Nickel is used as an alloying element both in low- and high-alloy steels. When present between 0.3 and 5.0 wt.%, nickel increases the strength and toughness of steel. Nickel increases the strength of ferrite and thereby increases the strength of steel. In low-alloy steels, nickel is quite often used as an alloying element along with chromium, molybdenum, or vanadium to improve hardenability and toughness. However, in larger concentrations, its main role is to improve the resistance to oxidation and corrosion and to increase the high-temperature stability of steel. It is used in conjunction with chromium in stainless steels and heat-resistant steels on account of its ability to stabilize the passive film of chromium oxide. The amount of nickel in stainless steel varies from 8.0 to 20.0 wt.%. Nickel not only improves the room-temperature toughness of steel but also increases toughness at subzero temperatures and hence is used in steels for cryogenic applications.

Molybdenum is used as an alloying element in comparatively small concentrations (less than 1.0 wt.%, generally between 0.1 and 0.4 wt.%). Molybdenum is a ferrite stabilizer as well as a carbide former. Molybdenum helps to improve the strength and hardness of steel. It increases the hardenability of steel and is usually added as an alloying element in steels having chromium, nickel, and/or vanadium. It increases the resistance of steel to softening during tempering and softening on exposure to high temperature. Its use is therefore recommended in creep-resistant steels. In austenitic stainless steels, when added up to 2.0 wt.%, it improves resistance to pitting corrosion.

Tungsten in steel acts as a solid solution strengthener as well as a carbide former. It is used in some heat- or creep-resistant steels in combination with chromium or other alloying elements where the retention of strength at high temperatures is important. Being a carbide former, it also improves the wear resistance of steel and hence finds applications in tool steels. When present in higher amounts (of the order of 17.0 to 20.0 wt.%), it gives steel a property known as red hardness or hot hardness, which enables a tool steel to retain hardness at high temperature.

Vanadium is used primarily as an alloying element in creep-resistant steels, high-speed steels, and hot forming tool steels. Vanadium is used as a grain refiner in steel. Vanadium, when present in small quantities (~0.1 to 0.3 wt.%), helps control grain growth during heat treatment. By inhibiting grain growth, it also helps to increase the strength and toughness of steel.

Being a strong carbide former, it provides increased wear resistance to steel at room temperature and also effectively promotes strength at high temperatures. Vanadium is also a mild deoxidizer. Vanadium steels have enhanced resistance to fatigue.

Titanium is a strong carbide former. As a stabilizing element, it reacts with carbon in preference to chromium in austenitic stainless steel and resolves the problem of intergranular corrosion due to sensitization. Titanium, when used in conjunction with boron, increases the effectiveness of the boron in increasing the hardenability of steel.

Niobium is also a strong carbide former. Niobium plays a role similar to titanium in making stainless steel immune to chromium carbide precipitation and resultant intergranular corrosion. Niobium is used in carbon steels to develop higher tensile properties.

Copper is added in amounts of the order of 0.20 to 0.50 wt.% to improve resistance to atmospheric corrosion and to increase steel strength with only a slight loss in ductility. Copper-bearing steels are known as weathering steels. Copper is also used as an alloying element in free-machining steels. Because of its limited solubility in steel, copper remains as undissolved particles and improves the machinability of steel by acting as a chip breaker.

Lead, similarly to copper, also improves the machinability of steel. Lead is practically insoluble in steel. It is usually added in amounts of <0.30 wt.%. In finely divided and uniformly distributed form, lead has no known adverse effect on the mechanical properties of steel.

Aluminum is the most powerful deoxidizer. It also acts as a grain refiner. Since aluminum forms very hard nitrides with nitrogen, it is an important alloying element in nitriding steels. Aluminum improves resistance to scaling and hence is often used as an alloying element in ferritic heat-resistant steels.

Boron is added to steel in amounts of 0.0005 to 0.003 wt.% to improve its hardenability without any appreciable loss of ductility. Boron also helps in improving the depth of hardening of steel when present along with certain other elements.

The beneficial effects of different alloying elements on properties of steel are summarized in Table 3.2.

3.6 Alloy Steels

Alloy steels are those steels to which a few specific metallic or nonmetallic elements are added deliberately to improve mechanical, electrical, magnetic, chemical, and environmental or manufacturing properties. There are about 20 different elements, including chromium, nickel, molybdenum, tungsten, vanadium, and cobalt, that are added individually or in a group as alloying elements in order to obtain a special property or set of properties for a particular application. The purpose of adding alloying

Table 3.2 Beneficial effects of different alloying elements on properties of steel

Element	Effect on steel	Element	Effect on steel
Carbon (C)	- Increases strength and hardness - Increases resistance to wear and abrasion	Tungsten (W)	- Increases strength and hardness - Increases hot hardness - Increases wear resistance - Increases creep strength
Manganese (Mn)	- Increases strength, hardness, and wear resistance - Increases response to heat treatment - Acts as deoxidizer	Vanadium (V)	- Acts as grain refiner - Acts as deoxidizer - Increases strength - Increases wear resistance - Improves creep resistance
Silicon (Si)	- Increases elastic limit - Improves resistance to scaling - Improves electrical behavior	Titanium (Ti)	- Increases wear resistance - Takes care of sensitization and intergranular corrosion in stainless steel - Helps in improving high-temperature strength
Sulfur (S)	Improves machinability	Niobium (Nb)	- Takes care of sensitization and intergranular corrosion in stainless steel - Helps in improving high-temperature strength
Phosphorus (P)	Improves machinability	Copper (Cu)	- Improves resistance to atmospheric corrosion - Improves machinability
Chromium (Cr)	- Increases strength and hardness - Increases resistance to wear - Increases response to heat treatment - Increases hardenability - Improves resistance to oxidation and corrosion - Increases creep strength	Lead (Pb)	Improves machinability
Nickel (Ni)	- Increases strength - Increases hardenability - Improves room-temperature and low-temperature toughness - Improves resistance to oxidation and corrosion	Aluminum (Al)	- Acts as deoxidizer - Acts as grain refiner - Improves resistance to scaling - Important element in nitriding steels
Molybdenum (Mo)	- Increases strength and hardness - Increases hardenability - Increases resistance to softening - Improves resistance to pitting corrosion	Boron (B)	Improves depth of hardening

elements is to ensure improvement in strength, hardness, hardenability, toughness, wear resistance, or creep resistance. For example, chromium in stainless steel improves oxidation and corrosion resistance; sulfur or phosphorus in free-machining steels improves machinability; and the presence of cobalt in high-speed steels improves the hot/red hardness of the tool.

3.6.1 Classification of Alloy Steels

There are two main types of alloy steels, low-alloy steels, which contain less than 10 wt.% of the total alloying element(s), and high-alloy steels, with the total amount of all alloying element(s) greater than 10 wt.%.

3.6.1.1 Low-Alloy Steels. Low-alloy steels are steels generally having up to 3 to 4 wt.% of alloying elements such as nickel, chromium, molybdenum, and vanadium. The purpose of adding these elements to low-alloy steels is to increase strength, toughness, and hardenability. These steels exhibit mechanical properties superior to those of plain carbon steels. They have a similar microstructure to plain carbon steels and are subjected to similar heat treatments. Based on the principal alloying element(s) used, low-alloy steels can also be classified as chromium steels, nickel steels, nickel-chromium steels, molybdenum steels, chromium-molybdenum steels, or chromium-molybdenum-vanadium steels.

According to the Society of Automobile Engineers (SAE), low-alloy steels can be classified on the basis of the principal alloying element or elements present. This classification is based on a 4- or 5-digit designation system. Table 3.3 provides the SAE system of classification of low-alloy steels based on chemical composition (Ref 3.10).

The 1%Cr-0.5%Mo, 1%Cr-1%Mo-0.35%V, and 2.25%Cr-1.0%Mo steels are extensively used in power plants for superheater tubes and headers in the heat-treated condition. The heat treatment of these steels consists of austenitization in the temperature range of 900 to 950 °C (1650 to 1740 °F) followed by either air or furnace cooling. Air-cooled steel is tempered in the range of 650 to 730 °C (1200 to 1350 °F). Based on the specific heat treatment, the final microstructures can be of the ferrite-pearlite, ferrite-bainite, or bainite type.

3.6.1.2 High-Alloy Steels. The two most important families of high-alloy steels are stainless and heat-resistant steels, and tool steels; tool steels are used as tool materials at room temperature and high temperature and are not included in the discussion of this book. However, stainless steels are materials of interest for high-temperature application in boiler tubes.

Table 3.3 Classification of steels per SAE system

SAE designation	Type of steel
1xxx	Carbon steels
2xxx	Nickel steels
3xxx	Nickel-chromium steels
4xxx	Molybdenum steels
5xxx	Chromium steels
6xxx	Chromium-vanadium steels
7xxx	Tungsten steels
8xxx	Nickel-chromium-vanadium steels
9xxx	Silicon-manganese steels

Stainless steels are alloys of iron and carbon with a minimum of 12 wt.% chromium. Chromium forms a chromium oxide protective or passive film on the metal surface, offering corrosion resistance to the steel. Austenitic stainless steels of the 18/8 type are used as superheater and reheater tubes in subcritical boilers, whereas 25%Cr-20%Ni-type advanced austenitic heat-resistant grades of steel are preferred for supercritical and advanced supercritical boilers in view of their superior resistance to oxidation and high-temperature creep compared with low-alloy steels. The following discussion pertains to the physical metallurgy of different stainless steels and heat-resistant steels.

3.7 Stainless Steels

Stainless steel is a generic term covering a group of alloys that are commonly known for their oxidation and corrosion resistance. Stainless steels are iron-base alloys that contain a minimum of about 12 wt.% Cr. Stainless steels are primarily known for their corrosion- and heat-resistant properties. In any stainless steel, the chromium reacts with oxygen and moisture present in the environment to form a protective, transparent, and adherent chromium oxide (Cr_2O_3) film of about 20–30 Å thickness over the entire surface of the material.

For a continuous and tenacious passive film to form, a chromium content of at least 11 wt.% is required. Passivity increases fairly rapidly with increasing chromium content up to about 17 wt.% chromium. Figure 3.17 shows the effect of chromium on the corrosion rate of steel.

The passive film so formed is of a self-healing nature such that even if the film is damaged locally, the chromium in the steel reacts rapidly with oxygen and moisture in the environment to reform it. Increasing the chromium content beyond the minimum of 12.0 wt.% further enhances the

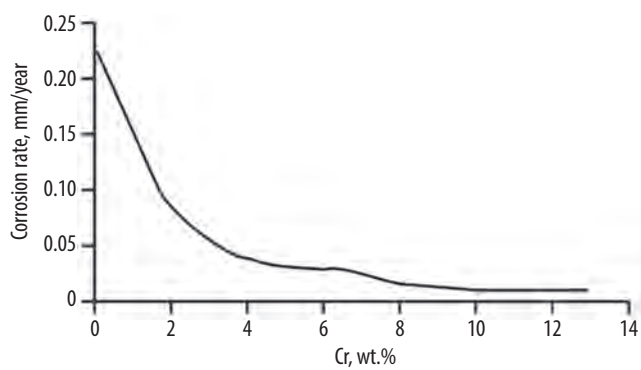


Fig. 3.17 The effect of chromium on the corrosion rate of steel. Source: Ref 3.11

corrosion resistance of stainless steel. Corrosion resistance is increased by the addition of 8% or more nickel.

3.7.1 Classification of Stainless Steels

Stainless steels are classified into five main categories depending on their microstructure at room temperature. Accordingly, different types of stainless steels are:

- Austenitic stainless steels
- Ferritic stainless steels
- Martensitic stainless steels
- Precipitation-hardenable (PH) stainless steels
- Duplex stainless steels

There are several grades of stainless steels within each category that have different compositions.

3.7.1.1 Austenitic Stainless Steels. Austenitic stainless steels are the most widely used stainless steels among all the categories both in terms of the number of available grades and the usage. In order to obtain austenite as the stable phase at room temperature, the austenite/ferrite transformation temperature is suppressed by adding alloying elements such as nickel, manganese, or nitrogen. These alloys exhibit an fcc structure; the γ phase is the stable phase at room temperature and in the entire solidus temperature range. The structure of 18% Cr steel can be made fully austenitic by the addition of a minimum of 8% Ni. Austenitic stainless steels are not heat treatable and hence the only way to increase their strength is by cold work. Austenitic stainless steels are nonmagnetic in nature.

There are two sets of grades of austenitic stainless steels, the first identified as the AISI 2xx series and the other as the AISI 3xx series. The 2xx series contains manganese-substituted stainless steels comprising iron-chromium-manganese-nickel alloys, whereas the 3xx series consists of more conventional iron-chromium-nickel alloys with or without other elements added for specific purposes.

In 2xx alloys, manganese (5 to 10 wt.%) replaces some of the nickel and more is replaced by the addition of nitrogen. The 2xx series stainless steels are cheaper than 3xx alloys.

Austenitic stainless steels contain 16–26 wt.% Cr with 8–22 wt.% Ni, little carbon (0.15% C max.), and small amounts of other alloying elements such as molybdenum, titanium, niobium, and nitrogen. Grade 304 is the most popular grade, containing 18 wt.% Cr and 8 wt.% Ni, and is the base alloy. It is also termed 18/8 steel. Table 3.4 lists the chemical composition of various grades of austenitic stainless steels (Ref 3.12).

Figure 3.18 shows the microstructure of austenitic stainless steel with grains of austenite separated by grain boundaries.

The corrosion resistance of austenitic stainless steels is superior to that of ferritic or martensitic steels. Their corrosion resistance varies from good to excellent depending on the composition. They have good formability as well as weldability. Because of their good impact toughness and low ductile-to-brittle transition temperature, they are also used for cryogenic applications.

Table 3.4 Chemical composition of various grades of austenitic stainless steels

UNS	Grade	C	Si	Mn	Cr	Ni	Mo	S	P	Others
S20100	AISI 201	0.15	1.00	5.5–7.5	16.00–18.00	3.50–5.50	...	0.030	0.060	0.25N
S20200	AISI 202	0.15	1.00	7.5–10.0	17.00–19.00	4.00–6.00	...	0.030	0.060	0.25N
S30200	AISI 302	0.15	1.00	2.00	17.00–19.00	8.00–10.00	...	0.030	0.045	...
S30400	AISI 304	0.08	1.00	2.00	18.00–20.00	8.00–10.50	...	0.030	0.045	...
S30403	AISI 304L	0.03	1.00	2.00	18.00–20.00	8.00–12.00	...	0.030	0.045	...
S30900	AISI 309	0.20	1.00	2.00	22.00–24.00	12.00–15.00	...	0.030	0.045	...
S31000	AISI 310	0.25	1.50	2.00	24.00–26.00	19.00–22.00	...	0.030	0.045	...
S31600	AISI 316	0.08	1.00	2.00	16.00–18.00	10.00–14.00	2.0–3.0	0.030	0.045	...
S31603	AISI 316L	0.03	1.00	2.00	16.00–18.00	10.00–14.00	2.0–3.0	0.030	0.045	...
S31651	AISI 316N	0.08	1.00	2.00	16.00–18.00	10.00–14.00	2.0–3.0	0.030	0.045	0.10–0.16N
S32100	AISI 321	0.08	1.00	2.00	17.00–19.00	9.00–12.00	...	0.030	0.045	5x%C min Ti
S34700	AISI 347	0.08	1.00	2.00	17.00–19.00	9.00–13.00	...	0.030	0.045	10x%C min Nb
S34800	AISI 348	0.08	1.00	2.00	17.00–19.00	9.00–13.00	...	0.030	0.045	0.20Co, 8x%C min Nb, 0.1Ta



Fig. 3.18 Microstructure of austenitic stainless steel

3.7.1.2 Ferritic Stainless Steels. Ferritic stainless steels are alloys of iron and chromium with chromium in the range of 11.0 to 27.0 wt.% along with molybdenum, aluminum, niobium, or titanium in some of the grades, and are essentially considered nickel-free steels. As per the AISI practice of steel designation, they belong to the 4xx series of stainless steels. Type 409 is the base alloy of ferritic stainless steel, having 11 wt.% Cr. Figure 3.19 shows the microstructure of ferritic stainless steel with grains of ferrite separated by grain boundaries. Table 3.5 gives the chemical composition of some of the important grades of ferritic stainless steels (Ref 3.12).

Ferritic stainless steels are composed of ferrite (bcc) as the stable phase at room temperature all the way up to the liquidus temperature. They are ferritic at all temperatures and do not transform to austenite; therefore,



Fig. 3.19 Microstructure of ferritic stainless steel

Table 3.5 Chemical composition of ferritic stainless steels

UNS	Grade	C	Si	Mn	Cr	Ni	Mo	S	P	Others
S40500	AISI 405	0.08	1.00	1.00	11.50–14.50	0.60	...	0.030	0.040	0.10–0.30Al
S40900	AISI 409	0.08	1.00	1.00	10.50–11.75	0.50	...	0.045	0.045	6x%C–0.75 max Ti
S43000	AISI 430	0.12	1.00	1.00	16.00–18.00	0.75	...	0.030	0.040	...
S43600	AISI 436	0.12	1.00	1.00	16.00–18.00	...	0.75–1.25	0.030	0.040	5x%C–0.70 max Nb + Ta
S44200	AISI 442	0.20	1.00	1.00	18.00–23.00	0.60	...	0.030	0.040	...
S44600	AISI 446	0.20	1.50	1.00	23.00–27.00	0.75	...	0.030	0.040	0.25N

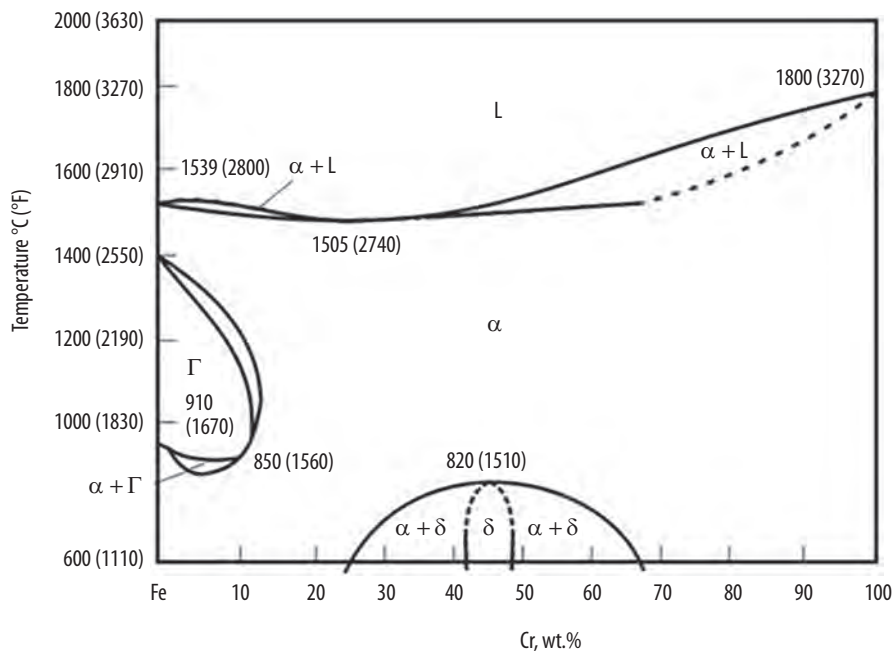


Fig. 3.20 Fe-Cr binary phase diagram. Source: Ref 3.13

they are not hardenable by heat treatment (i.e., their properties cannot be improved by hardening-tempering).

They have very low carbon content. As regards their chromium content, the compositions of ferritic stainless steels fall outside the γ loop, as shown in the binary diagram for the Fe-Cr system (Fig. 3.20).

Ferritic stainless steels are magnetic and possess limited formability. They can be readily welded in thin sections, but suffer from grain growth with consequential loss of properties when welded in thicker sections. They also suffer from microstructure-related problems of 475 °C (890 °F) embrittlement and sigma phase formation. Ferritic stainless steels are known for their superior resistance to high-temperature oxidation and corrosion and hence they are used for furnace and turbine parts.

3.7.1.3 Martensitic Stainless Steels. Martensitic stainless steels are similar in composition to the ferritic group but have higher carbon and lower chromium contents, which makes them hardenable by heat treatment. They have carbon in the range of 0.15 to 1.20 wt.% and chromium from 10.5 to 18 wt.%. They are known as the 4xx series of stainless steel. Grade AISI 410 has 0.15% C, 1.0% Mn, 1.0% Si, and 11.5–13.5% Cr, and is a representative grade of this category of stainless steel. The chemical compositions of different grades of martensitic stainless steel are given in Table 3.6 (Ref 3.12).

Unlike ferritic and austenitic stainless steels, martensitic stainless steels are hardenable steels. These steels will transform to austenite on heating

and, therefore, can be hardened by formation of martensite on cooling. It is possible to improve the strength and hardness of martensitic stainless steels by a hardening-tempering process similar to that of carbon steels. The heat treatment of these steels involves austenitizing in the temperature range of 950 to 1000 °C (1740 to 1830 °F) within the γ loop region, as represented in the Fe-Cr binary diagram of Fig. 3.20, followed by rapid cooling to form martensite. Figure 3.21 shows the typical microstructure of martensitic stainless steel.

Martensitic stainless steels are magnetic. They are stronger than ferritic and austenitic steels on account of a higher carbon content and

Table 3.6 Chemical compositions of different grades of martensitic stainless steel

UNS	Grade	C	Si	Mn	Cr	Ni	Mo	S	P	Others
S40300	AISI 403	0.15	0.50	1.00	11.50–13.00	...	...	0.030	0.040	...
S41000	AISI 410	0.15	1.00	1.00	11.50–13.50	...	...	0.030	0.040	...
S41600	AISI 416	0.15	1.00	1.25	12.00–14.00	...	0.60	0.15 min.	0.060	...
S42000	AISI 420	0.15 min	1.00	1.00	12.00–14.00	...	...	0.030	0.040	...
S42200	AISI 422	0.20–0.25	0.75	1.00	11.50–13.50	0.50–1.00	0.75–1.25	0.030	0.040	0.15–0.30V, 0.75–1.25W
S43100	AISI 431	0.20	1.00	1.00	15.00–17.00	1.25–2.50	...	0.030	0.040	...
S44002	AISI 440A	0.60–0.75	1.00	1.00	16.00–18.00	0.75	...	0.030	0.040	...
S44003	AISI 440B	0.75–0.95	1.00	1.00	16.30–18.00	0.75	...	0.030	0.040	...
S44004	AISI 440C	0.95–1.20	1.00	1.00	16.30–18.00	0.75	...	0.030	0.040	...

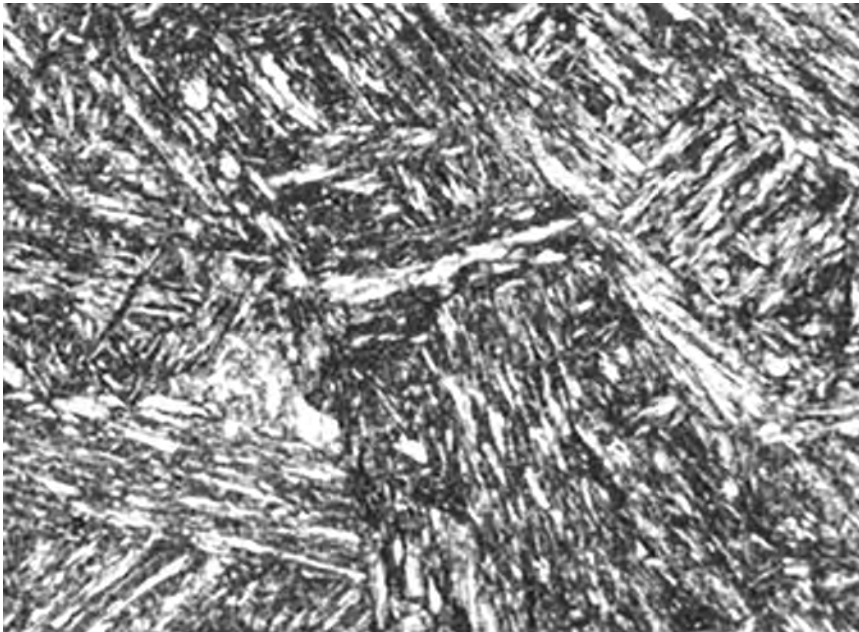


Fig. 3.21 Typical microstructure of martensitic stainless steel

martensitic structure. Because of the higher carbon content, their formability and weldability is poor. They have moderate corrosion resistance (i.e., their corrosion resistance is lower than that of other stainless steels of the same chromium and alloy content). They are susceptible to hydrogen-assisted corrosion, particularly in sulfide environments.

Martensitic stainless steels are used in cutlery, turbine blades, and high-temperature parts.

3.7.1.4 Precipitation-Hardenable Stainless Steels. Precipitation-hardenable stainless steels are iron-nickel-chromium alloys to which other elements such as aluminum, copper, molybdenum, or titanium are added. Under appropriate conditions, it is possible to produce precipitation of intermetallic compounds by solution and aging heat treatment, giving rise to strengthening.

There are three main types of PH stainless steels, namely martensitic, semi-austenitic, and austenitic. Table 3.7 lists the composition of selected grades of PH stainless steels (Ref 3.12).

An example of the martensitic type of PH stainless steels is 13-8Mo steel with 0.90–1.35 wt.% aluminum. Solution treatment produces homogeneous austenite that transforms to martensite on cooling. Precipitation of the intermetallic phase takes place when the martensite is aged at 450 to 650 °C (840 to 1200 °F). In the 17-7PH semi-austenitic type of alloy, the microstructure is austenitic at room temperature. When cold-working the alloy at room temperature or cooling it to subzero temperature, the transformation of austenite to martensite can be ensured so that its aging provides required strengthening. Significant strengthening is obtained from the martensite formed before aging. Because of a relatively high amount of nickel (24–27 wt.%), austenitic types of PH stainless steel such as A-286 cannot be transformed to martensite by refrigeration or cold

Table 3.7 Chemical composition of precipitation-hardenable stainless steels

UNS	Grade	C	Si	Mn	Cr	Ni	Mo	S	P	Others
Martensitic type										
S13800	PH13-8Mo	0.05	0.10	0.10	12.25–13.25	7.5–8.5	2.0–2.5	0.008	0.01	0.90–1.35Al, 0.01N
S15500	15-5 PH	0.07	1.00	1.00	14.00–15.5	3.5–5.5	...	0.03	0.04	2.5–4.5Cu, 0.15–0.45Nb
S17400	17-4 PH	0.07	1.00	1.00	15.0–17.5	3.0–5.0	...	0.03	0.04	3.0–5.0Cu, 0.15–0.45Nb
Semi-austenitic type										
S15700	PH15-7Mo	0.09	1.00	1.00	14.5–16.0	6.5–7.75	2.0–3.0	0.04	0.04	0.75–1.5Al
S17700	17-7 PH	0.09	1.00	1.00	16.0–18.0	6.5–7.75	...	0.04	0.04	0.75–1.5Al
Austenitic type										
S66286	A-286	0.08	1.00	2.00	13.5–16.0	24.0–27.0	1.0–1.5	0.025	0.025	1.90–2.35Ti, 0.35max. Al, 0.10–0.50V, 0.003–0.010B

work. Such alloys are therefore subjected to solution treatment for 1 h at 1000 °C (1830 °F), water quenched, and finally aged at 730 °C (1350 °F).

3.7.1.5 Duplex Stainless Steels. Duplex stainless steels are developed with the intention of combining the beneficial properties of ferritic and austenitic stainless steels. Duplex stainless steels have about 20–25 wt.% Cr, 6–8 wt.% Ni, and 2–4 wt.% Mo, as well as small amounts of copper and nitrogen. Table 3.8 lists the chemical composition of a few representative grades of duplex stainless steels (Ref 3.12).

Their microstructure consists of approximately 50% ferrite and 50% austenite because of the addition of an excess of ferrite-forming elements such as chromium and molybdenum. Figure 3.22 shows the microstructure of

Table 3.8 Chemical composition of duplex stainless steels

UNS	Grade	C	Si	Mn	Cr	Ni	Mo	S	P	Others
S31200	44LN	0.03	1.00	2.00	24.0–26.0	5.50–6.50	1.20–2.00	0.03	0.045	0.14–0.20N
S32304	SAF 2304	0.03	1.00	2.50	21.5–24.0	3.03–5.5	0.05–0.6	0.04	0.04	0.05–0.20N
S31803	2205	0.03	1.00	2.00	21.0–23.0	4.50–6.50	2.5–3.5	0.02	0.03	0.08–0.20N
S32750	2507	0.03	0.80	2.00	24.0–26.0	6.0–8.0	3.0–5.0	0.02	0.03	0.24–0.32N
S32550	Ferrallium 255	0.04	1.00	1.50	24.0–27.0	4.50–6.50	2.0–4.0	0.02	0.03	1.5–2.5Cu, 0.1–0.25N
S31260	DP-3	0.03	0.75	1.00	24.0–26.0	5.50–7.50	2.50–3.50	0.03	0.03	0.2–0.8Cu, 0.10–0.30N, 0.1–0.5W

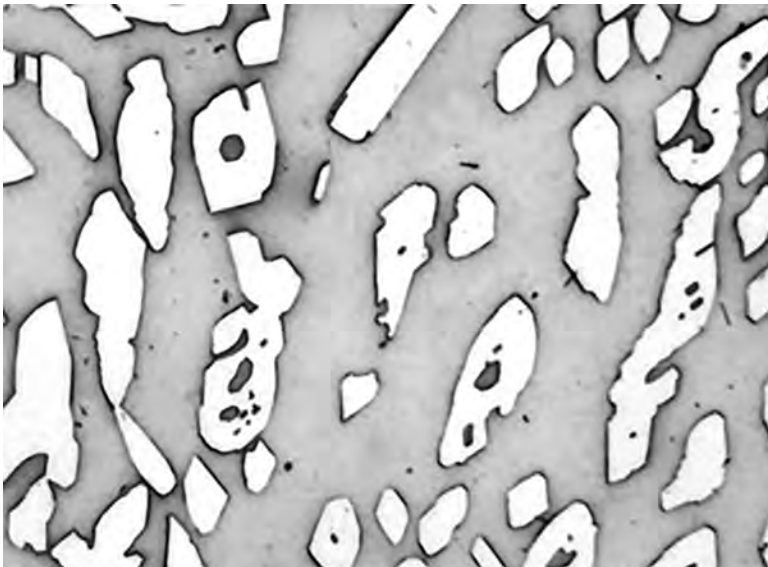


Fig. 3.22 Microstructure of duplex stainless steel

cast duplex stainless steel consisting of grains of austenite (white areas) and ferrite (gray areas).

A duplex microstructure consisting of austenite and ferrite provides an excellent combination of high corrosion resistance with mechanical properties (i.e., strength). The toughness of duplex stainless steels is inferior to that of austenitic steels but superior to that of ferritic stainless steels, while the strength is greater than that of austenitic stainless steels. These steels offer improved resistance to chloride-induced corrosion as well as stress corrosion cracking. They also have good resistance to pitting and crevice corrosion. In view of this, duplex stainless steels are used in refinery, chemical, petroleum, and electric power industries.

3.8 Microstructural Defects in Stainless Steels

Stainless steels are prone to the development of microstructural defects under certain temperature and cooling rate conditions. The following discussion pertains to such defects found in austenitic and ferritic stainless steels.

3.8.1 Chromium Carbide Precipitation/Sensitization

When austenitic stainless steel of an 18-8 composition (18% Cr-8% Ni) is heated or exposed to the temperature range of 425 to 650 °C (795 to 1200 °F) for an appreciable length of time, followed by slow cooling, chromium-rich carbides precipitate along the grain boundaries of the austenite. This phenomenon of carbide precipitation is termed *sensitization* and the concerned steel is said to be sensitized. During sensitization, carbon atoms diffuse from the interior of the grains to the grain boundaries and combine with chromium atoms to form precipitates of chromium carbide along the grain boundaries. As a result of this, the area adjacent to the grain boundaries becomes depleted in chromium. In turn, the chromium-depleted areas become anodic with respect to the bulk of the metal and are preferentially attacked when exposed to corrosive media. This type of failure is known as intergranular corrosion. Thus, intergranular corrosion of stainless steel occurs as a result of sensitization.

One way to avoid carbide precipitation is to use very low carbon steels (i.e., steels having less than 0.03 wt.% carbon). If adequate carbon is not made available to chromium to form Cr_{23}C_6 precipitates, sensitization will not occur. Grades 304L and 316L are developed with this objective. Another approach is to use solution annealing, wherein the sensitized steel is heated to a temperature of about 1050 °C (1920 °F) and then rapidly cooled through the sensitization range. One more way to combat the problem of sensitization is to use stabilizing elements such as niobium, titanium, or tantalum. These are strong carbide formers and therefore they preferentially react with carbon to form their carbides, thus leaving

no carbon for chromium to react with. The grades so developed are known as stabilized grades. Grade 321, 347, and 348 of the austenitic class are known as stabilized stainless steels. Figure 3.23 shows the microstructure of sensitized austenitic stainless steel with a network of chromium carbide precipitates along the grain boundaries.

3.8.2 *Sigma Phase Embrittlement*

The problem of sigma phase formation is noticed in austenitic, ferritic, and duplex stainless steels. The sigma phase is an intermetallic phase with a variable composition; it is represented by the chemical formula FeCr and is observed in Fe-Cr alloys. In highly alloyed stainless steels having more than 20 wt.% chromium, it is difficult to prevent the precipitation of the sigma phase. Once the sigma phase is formed, the steel is embrittled. Precipitation of the sigma phase first occurs at the triple points (i.e., at the junction where the grain boundaries meet) and then it occurs along the grain boundaries. Though there are several factors affecting sigma phase formation, the main factor is the composition. Elements such as Cr, Nb, Si, Ti and Mo (which are strong ferrite stabilizers) are known to promote sigma phase formation in stainless steels. The presence of delta ferrite accelerates sigma precipitation. The formation of the sigma phase in austenite is about 100 times slower than that in ferrite.

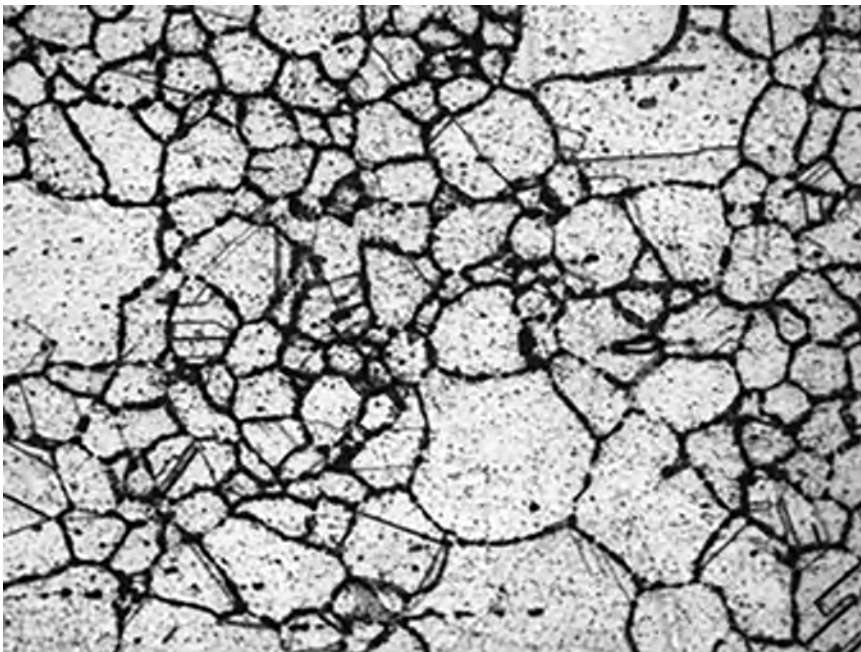


Fig. 3.23 Microstructure of sensitized austenitic stainless steel

When ferritic stainless steels are heated for very long times between 540 and 750 °C (1005–1380 °F), the sigma phase is precipitated. The embrittlement can be removed by reheating the steel above 800 °C (1470 °F) such that the sigma phase is redissolved.

Austenitic stainless steels having a large percentage of ferrite-forming elements, when exposed to the temperature range of 600–900 °C (1110–1650 °F), suffer from sigma phase formation. Steels subjected to formation of the sigma phase in general suffer in terms of substantial loss of ductility.

3.8.3 475 °C or 885 °F Embrittlement

High-chromium ferritic stainless steels such as Grade 446 are susceptible to the so-called *475 °C or 885 °F embrittlement*, which is caused by decomposition of the Fe-Cr solid solution in two phases, Fe- and Cr-rich phases, respectively. The embrittlement occurs due to precipitation of a coherent chromium-rich phase throughout the grains of ferrite. This type of embrittlement develops when a steel is held at temperatures between 370 and 540 °C (700 and 1005 °F) and results in a severe drop in impact toughness along with an increase in hardness. It can be remedied by reheating the steel above 800 °C (1470 °F) and cooling it.

3.9 Creep-Resistant Steels

Previously, 9–12 wt.% chromium steels emerged as one of the most promising high-alloy steels for power plant application. The development of power plant technology toward larger units and higher efficiencies is linked with the development of creep-resistant steels. Steels with 9–12 wt.% chromium belong to the class of creep-resistant steels and have creep rupture strength superior to Cr-Mo type low-alloy steels and stainless steels. These steels are viewed as an extension of conventional ferritic stainless steel. In this sense, they have, besides 9–12 wt.% chromium, alloying elements such as vanadium, niobium, and nitrogen added to increase the creep strength. The specific alloys developed are:

T91/P91 grade: 9Cr-1Mo-V-Nb steel

T92/P92 grade: 9Cr-1.8W-0.5Mo-V-Nb steel

T122/P122 grade: 11Cr-2W-0.5Mo-Cu-V-Nb steel

The most noteworthy feature of these steels is that with more than 7 wt.% chromium, a lath martensitic structure is developed, not the ferritic microstructure as expected. In order to achieve this microstructure, the steel is first normalized by heating in an austenite regime (usually at 1040–1100 °C, or 1900–2010 °F) and then air-cooled to room temperature. The high chromium level (9–12 wt.% Cr) of these grades of steel enables martensitic transformation on air cooling, and a lath martensitic tempered

structure on tempering with high dislocation density. The microstructure also reveals finely distributed carbides, nitrides, or carbonitrides of alloying elements such as chromium, molybdenum, vanadium, and niobium. Figure 3.24 shows the microstructure of T/P 91 steel.

The corrosion resistance of 9–12 wt.% chromium steels can be attributed to higher chromium, whereas the high creep strength of these steels is mainly due to three strengthening mechanisms: solid solution strengthening, precipitation strengthening, and dislocation strengthening. Substitutional solute atoms such as tungsten and molybdenum account for solid solution strengthening. The precipitation of submicroscopic fine particles of chromium carbide (Cr_3C_6), vanadium carbide (V_4C_3), molybdenum carbide (Mo_2C), vanadium carbonitride (VCN), and niobium carbonitride $\text{Nb}(\text{C},\text{N})$ during tempering causes precipitation hardening, depending on the specific composition of the grade. These fine precipitate particles impede the movement of dislocations through the matrix of lath martensite and result in further strengthening of the steel by the mechanism of dislocation strengthening (Ref 3.14).

3.10 Heat Treatment of Steel

Heat treatment is an operation or combination of operations involving heating of a metal or an alloy in the solid state to a certain soaking temperature, holding at that temperature for a predetermined length of time,

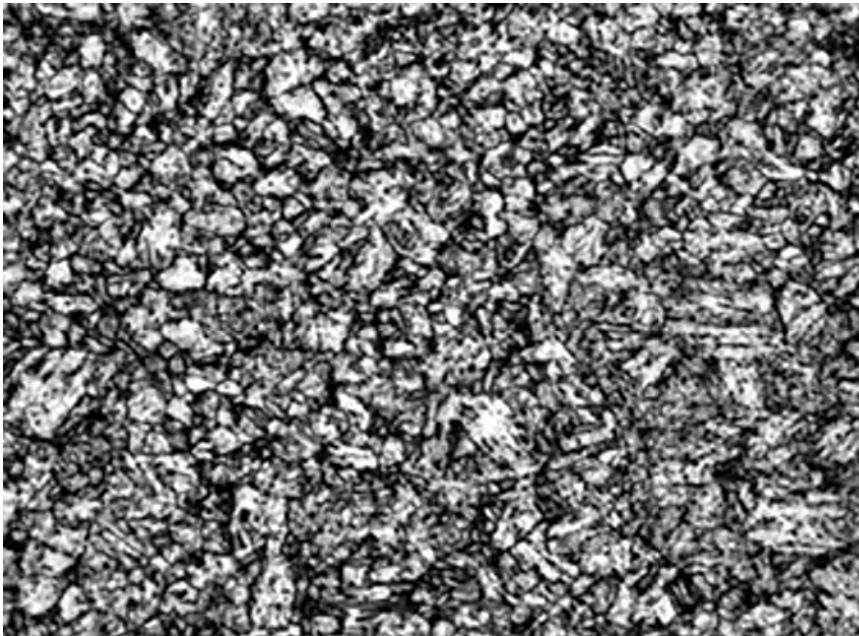


Fig. 3.24 Microstructure of T/P 91 steel

followed by cooling at a specified rate to room temperature or below room temperature for the purpose of obtaining certain intended properties. The purpose of heat treatment is to ensure change in the microstructure of the material so as to achieve desired properties such as physical, mechanical, chemical, electrical, and magnetic. Heat treatment generally involves phase transformation during heating and cooling leading to change in the microstructure in the solid state, but there are exceptions where there is no phase change. Conventional heat treatment involves only thermal processing; however, there are certain heat treatment processes that involve thermal as well as mechanical treatment. Such a process is termed thermo mechanical treatment.

Annealing, normalizing, hardening, and tempering are the four most widely used heat treatment processes for metals and alloys that affect their microstructure and properties. Figure 3.25 shows the CCT curves

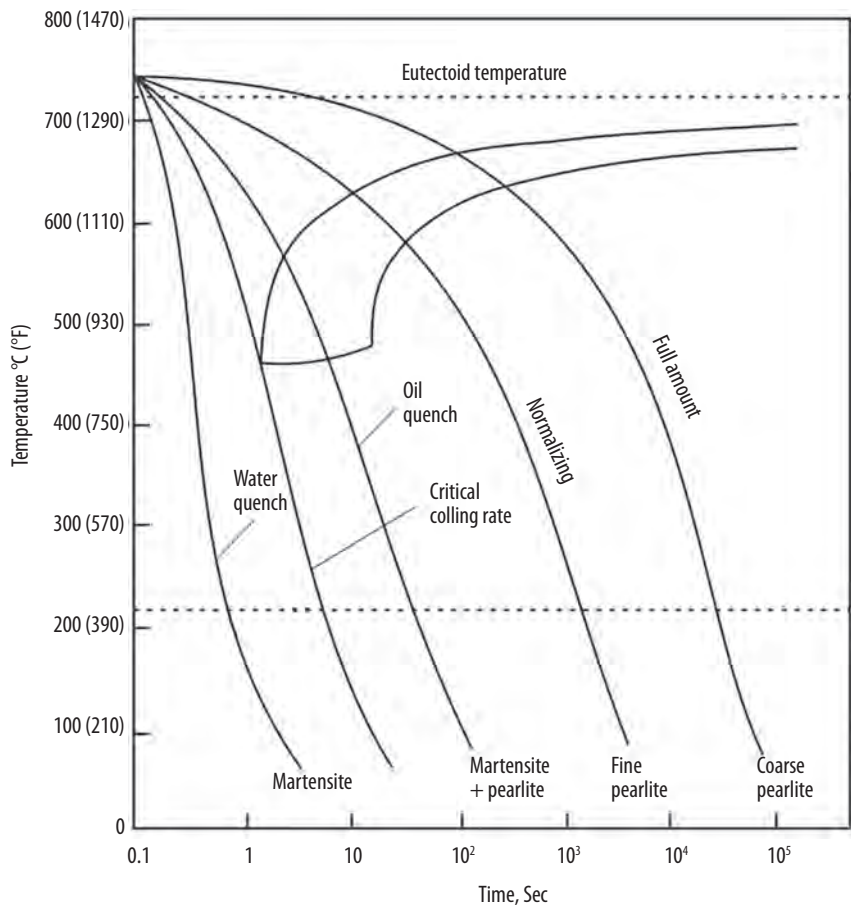


Fig. 3.25 CCT curves for different cooling rates superimposed on the TTT curve for eutectoid steel. Source: Ref 3.6

superimposed on the TTT curve for eutectoid steel (0.8 wt.% C steel) corresponding to different cooling rates and in turn different heat treatments and resultant microstructures.

3.10.1 Annealing

The term annealing refers to a group of thermal treatments where the primary objective is to soften the metal, relieve the residual stresses developed on account of previous cold work or operations such as welding, and homogenize the microstructure. More specifically, the purpose of annealing ensures one or more result :

- reduction of hardness (i.e., softening the metal)
- improvement of ductility and toughness
- relief of internal stresses
- homogenization of the composition and remove micro-segregation
- refinement of the grain structure
- facilitation of cold working or machining
- alteration of various mechanical, electrical, or magnetic properties

During annealing, the steel is heated above the transformation temperature (i.e., the critical temperature) to form austenite, soaked or held at that temperature for a defined time period, and finally subjected to furnace cooling (i.e., very slow cooling) to room temperature. The typical cooling rate during annealing is 1.0 °C (2 °F) per min.

The important variants of the annealing process are full annealing or conventional annealing, process annealing, isothermal annealing, spheroidizing annealing, and stress relieving.

3.10.1.1 Full Annealing. In the full annealing process, the steel is first heated to a temperature above A_3 (i.e., the upper critical temperature for hypoeutectoid steels) and above A_1 (i.e., the lower critical temperature for hypereutectoid steels), by 3050 °C (55–90 °F) (Fig. 3.26). It is then held or soaked at that temperature for a defined time in order to cause uniform temperature across the entire cross section of the component and to achieve a homogeneous austenitic structure. Finally, the component is subjected to slow cooling in the furnace, until it reaches room temperature. The cooling rate must be low to ensure formation of coarse pearlite. A full annealing treatment is done for a variety of purposes, including to reduce its hardness and increase ductility, to relieve internal stresses induced due to prior operations, to refine the grain structure, to make the material homogenous as regards its chemical composition, and to improve machinability.

Full annealing requires higher temperatures, longer soaking times, and slower cooling rates and is more time consuming and expensive than isothermal annealing or normalizing.

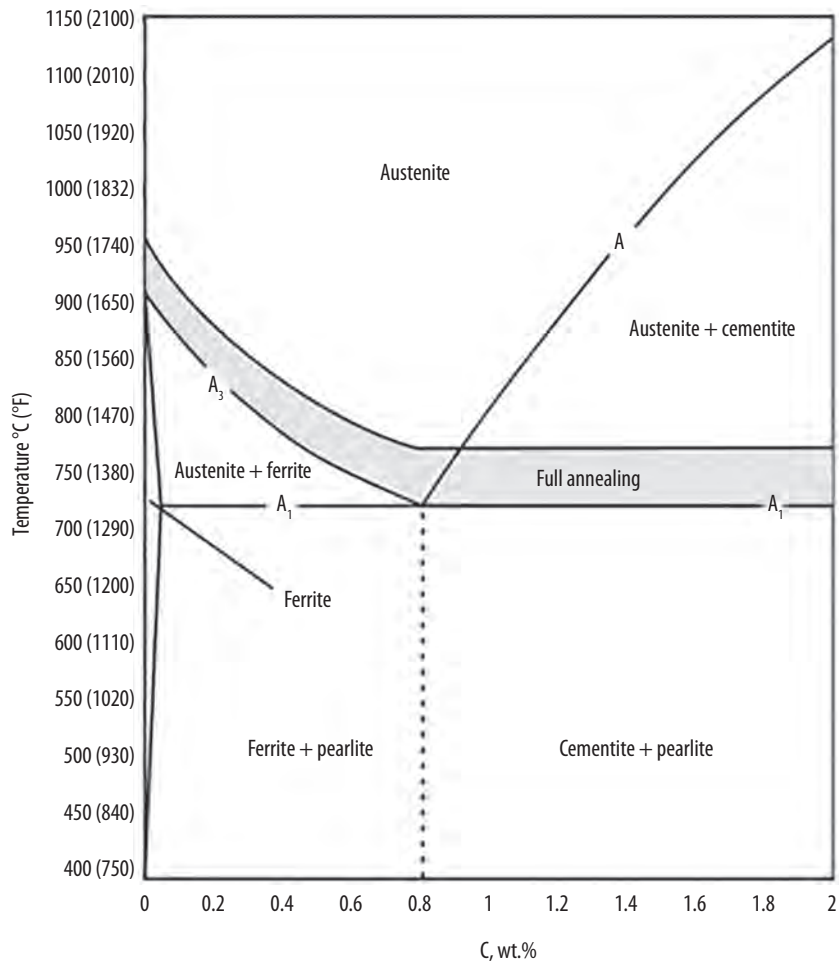


Fig. 3.26 Temperature range for full annealing. Source: Ref 3.15

3.10.1.2 Process Annealing. Process annealing is recommended for wrought cold-worked steel such as sheet, strip, or rolled sections. Because cold working leads to work hardening of the steel, it becomes brittle, and during further cold working it cracks, unless an intermediate annealing pass is given to it to restore its ductility. Process annealing is usually applied to cold-worked low-carbon steels to soften the steel sufficiently to allow further cold working. Such annealing between processing steps is known as *process annealing*, and the overall operation is known as the *cold work-anneal-cold work* cycle.

Process annealing consists of heating the steel to a temperature just below A_1 for a short time and then cooling it in air (Fig. 3.27). Slow cooling is not essential for process annealing, since any cooling rate from temperatures below A_1 results in the same microstructure and hardness as there is no phase change involved.

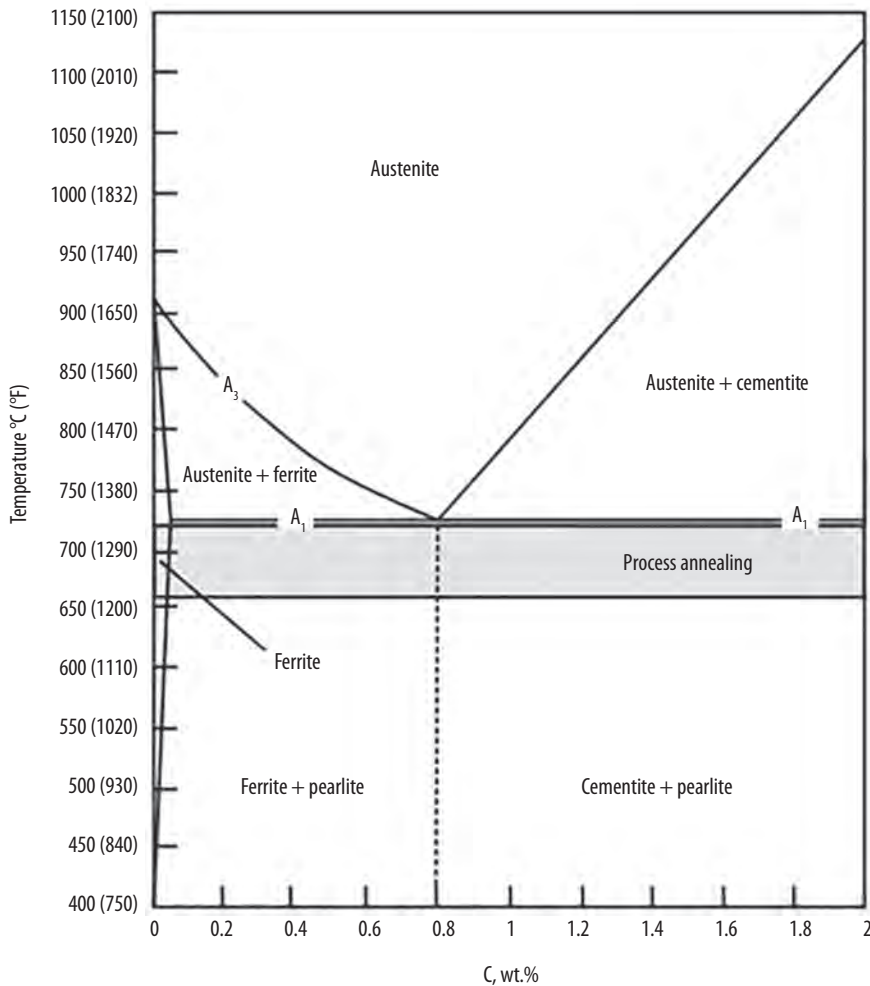


Fig. 3.27 Temperature range for process annealing. Source: Ref 3.15

3.10.1.3 Isothermal Annealing. Because the full annealing cycle takes a long time, an alternative route called *isothermal annealing* is, at times, adopted for small parts. In isothermal annealing, steel is first heated to the austenitization temperature in a manner similar to that for full annealing. Instead of slowly cooling the steel in the furnace, it is subjected to slightly faster cooling from the usual austenitization temperature to a constant temperature just below A_1 . It is then held at this temperature for a sufficient time to ensure the completion of phase transformation (i.e., austenite to pearlite). In practice this is done by transferring the parts to a constant-temperature bath (maintained below the A_1 temperature) containing molten salts. Finally, the steel is cooled to room temperature at the desired rate.

3.10.1.4 Stress Relieving. Stress relieving is also called stress relief annealing. Manufacturing processes such as cold working and welding often result in stresses known as residual stresses. Residual stresses must be completely removed or at least minimized so as to eliminate the risk of brittle fracture of the material. The stress relieving process, which is one type of annealing only, relieves the internal stresses in cold-worked steels without any loss of strength and hardness of the steel. There is no microstructural change involved in stress relieving. The stress relieving treatment is more common in cases of hypoeutectoid steels. Stress relieving is also used to relieve internal stresses developed from rapid cooling and phase transformation.

For stress relief annealing, the cold-worked steel is heated to a temperature between 500 and 550 °C (930 and 1020 °F), (i.e., below its recrystallization temperature), for a required length of time and finally cooled to room temperature in air.

3.10.1.5 Spheroidizing. Spheroidizing is a process to produce a microstructure consisting of the rounded/globular (spheroid) form of cementite or carbides in the soft and ductile matrix of ferrite (Fig. 3.28). Medium- and high-carbon steels as well as high-alloy steels such as tool steels are subjected to spheroidizing treatment in order to soften them for machining or forming operations. Spheroidized structures are softer than

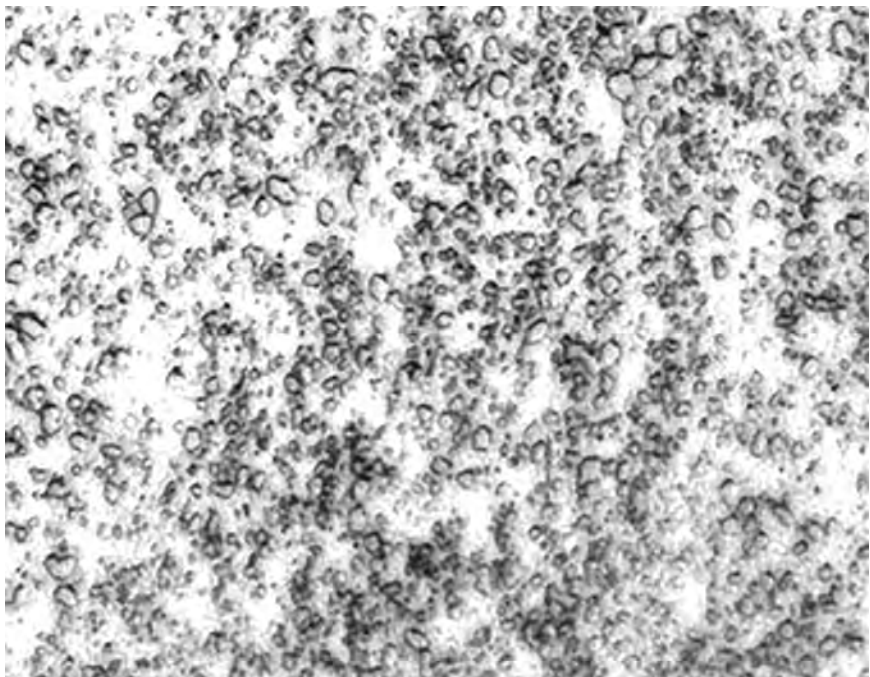


Fig. 3.28 Microstructure of medium-carbon steel with globules of cementite in ferrite matrix

fully annealed structures and have excellent machinability. The spheroidal carbide particles act as chip breakers and thus improve the machinability of steels that are otherwise difficult to machine on account of their higher carbon content and high hardness.

There are two ways to obtain a microstructure with globular carbide particles. In one approach, steel with a pearlitic microstructure at room temperature is heated to a temperature just below the lower transformation point (i.e., below A_1) held at that temperature for a length of time, and then cooled very slowly. Another option is the cyclic heating and cooling of the steel between temperatures that are just above and below the A_1 temperature (Fig.3.29).

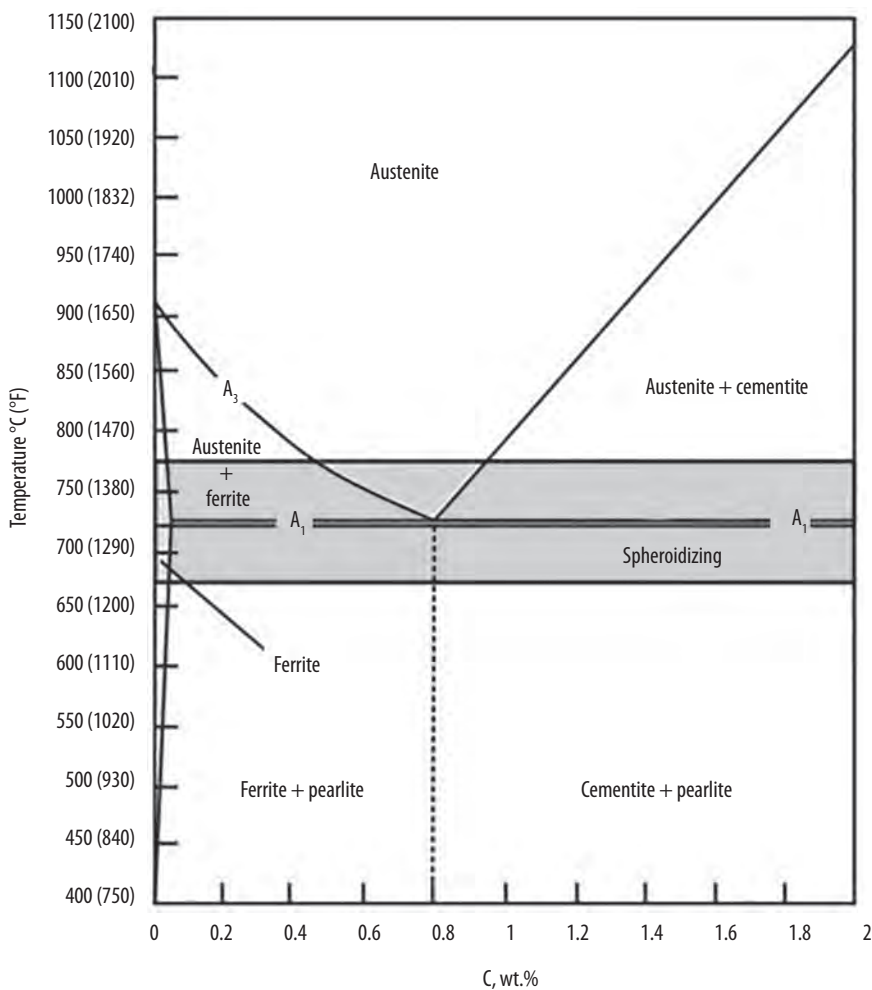


Fig. 3.29 Temperature range for spheroidizing. Source: Ref 3.15

3.10.2 Normalizing

The process of normalizing is similar to annealing except for the cooling rate. The typical cooling rate during annealing is 1.0 °C (2 °F) per minute, whereas that for normalizing is 5 to 10 °C (9 to 18 °F) per minute. The faster rate of cooling is obtained by withdrawing the component from the furnace when soaking is completed, and cooling it in the air.

For normalizing the steel, the steel is heated to a temperature about 50 °C (90 °F) above the upper critical temperature (i.e., above A_{C3} for hypoeutectoid steels and above A_{cm} for hypereutectoid steels), held at that temperature until homogeneous austenization is reached, and then cooled in the air to room temperature (Fig. 3.30). As a rule of thumb, the holding time is 1 hour per inch of thickness.

On account of faster cooling rates, the grain size of pearlite in normalized steel is finer than that in steel subjected to annealing, as displayed in Fig. 3.31.

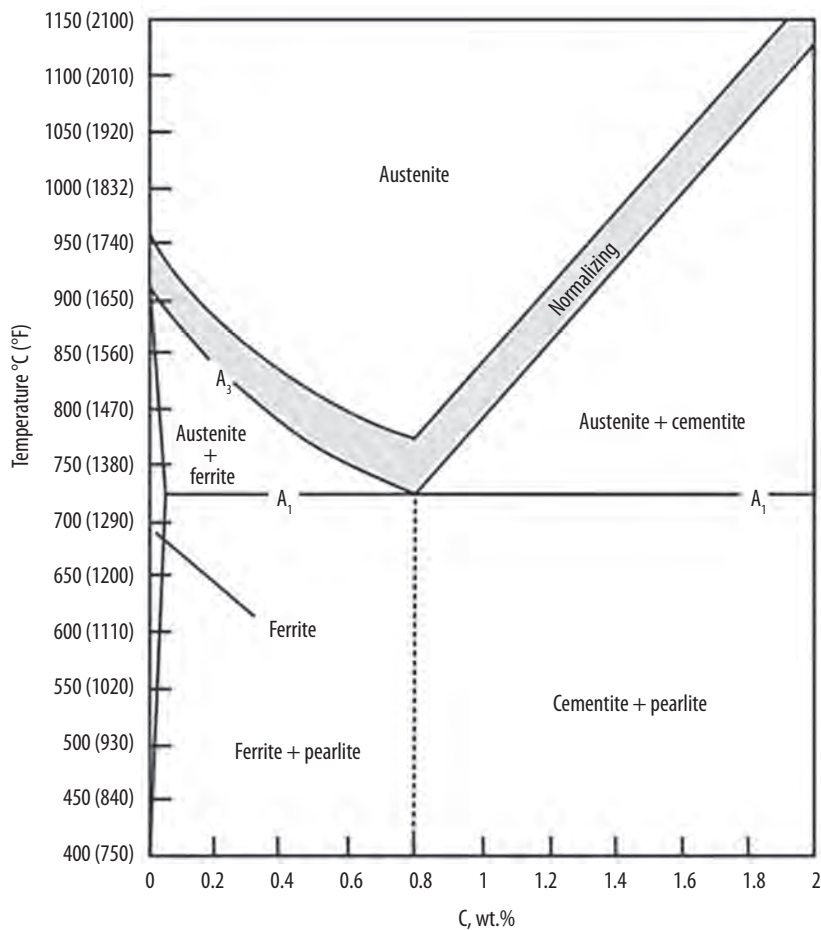


Fig. 3.30 Temperature range for normalizing. Source: Ref 3.15

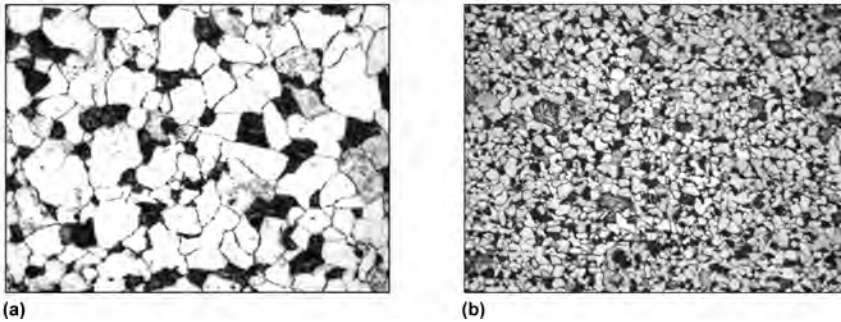


Fig. 3.31 Microstructures of steel at a glance, (a) annealed, 200x; and (b) normalized, 200x

Steel is normalized to refine grain size, make its structure more uniform, or to improve machinability. The fine-grained structure offers improved yield strength and toughness. Normalizing improves the ductility without any appreciable loss of strength and hardness. Normalizing is also used to relieve internal stresses induced by welding, casting, forging, forming, or machining.

3.10.3 Hardening or Quenching

The principal objective of hardening is to improve steel strength and hardness. Conventionally, the hardening process consists of heating a hypoeutectoid steel to above A_3 or hypereutectoid steel above A_1 by about 30 to 50 °C (55 to 90 °F). It is held there for a sufficient length of time to form homogeneous austenite and then cooled rapidly to room temperature or below room temperature at a rate sufficient to exceed the critical cooling rate. Figure 3.32 shows the temperature range for hardening of hypo- and hypereutectoid steels.

As discussed earlier, with a fast cooling rate, the transformation of austenite to pearlite or bainite is suppressed and a new metastable phase, martensite, forms. Martensite has much higher strength and hardness compared with pearlite but is very brittle. A fully martensitic structure is obtained when the rate of cooling is greater than or equal to the critical cooling rate. The critical cooling rate is represented by the curve that just bypasses the nose of the TTT curve for a given steel. The rate of cooling required, and the quenching medium or the quenchant to form a fully martensitic structure for alloy steels, depends upon their composition, whereas that for plain carbon steels depends on the carbon content of the steel. The critical cooling rate required to form martensite in alloy steels is lower; some grades of tool steels are even air-hardenable (e.g., a martensitic structure can be obtained in such steels by air cooling). The critical cooling rate for high-carbon steels is somewhat higher; they are subjected to hardening by quenching in oil. Medium-carbon and low-carbon steels

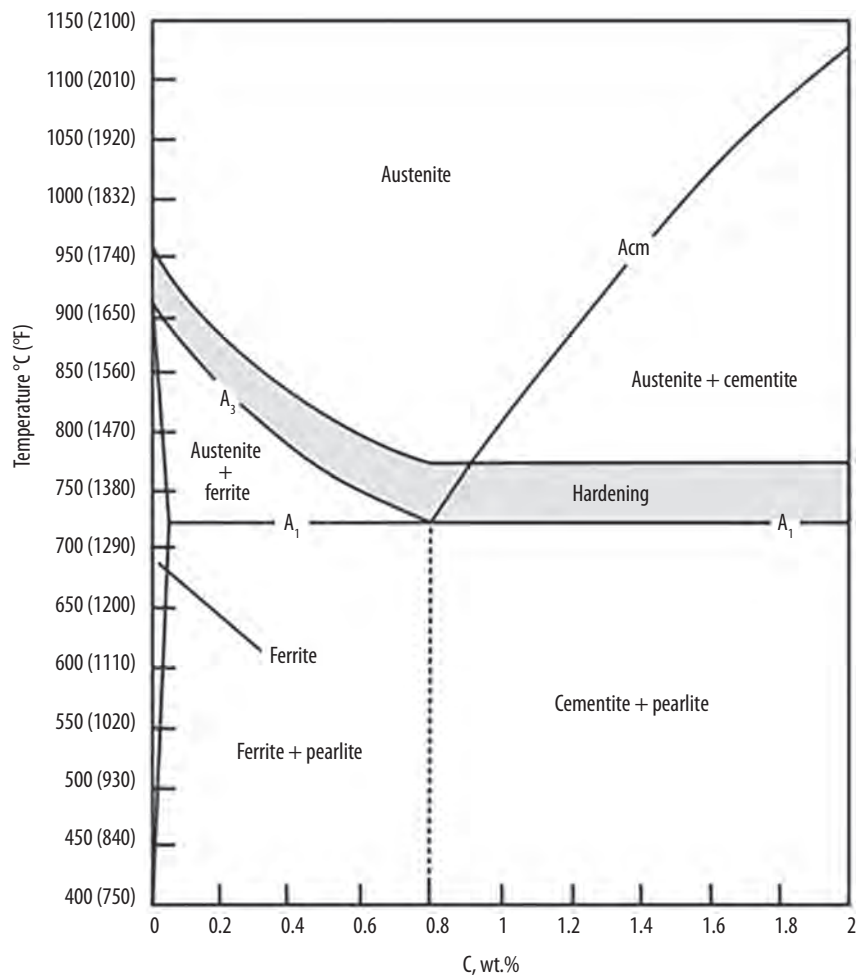


Fig. 3.32 Temperature range for hardening of steel. Source: Ref 3.15

have still higher critical cooling rates; in order to form martensite in these steels, water or brine (salt water) quenching is a must. The term *severity of quench* indicates the ability of a quenching medium to extract heat from a hot-worked piece of steel; accordingly, different quenching media in decreasing order of their severity of quenching are listed as brine → water → oil → air.

3.10.4 Tempering

Steel cannot be subjected to end use in an as-hardened condition because of certain limitations. As-hardened martensite is a supersaturated solid solution of carbon in a bct lattice of iron and has acicular needle-like structures of martensite. This makes the steel brittle. The tetragonal nature of

the crystal lattice of martensite induces high internal stresses. Besides this, the room temperature microstructure of as-hardened steel contains one more phase called *retained austenite*, which appears as white areas under a microscope. Both martensite and retained austenite are meta-stable phases and are prone to transform to a stable form over time. But the transformation to a stable state is associated with volume changes that give rise to internal stresses and cracking. All of these factors do not permit steel to be used in an as-hardened condition, and therefore, hardening treatment is followed by a mandatory step known as *tempering*.

Tempering involves heating as-hardened steel to a temperature below A_1 , holding the component at this temperature for a necessary soaking time, and then cooling it to room temperature. The resultant microstructure is known as *tempered martensite*. Tempered martensite consists of extremely small and uniformly dispersed cementite particles embedded within a continuous ferrite matrix. Because the tempering temperature is below the lower critical point, there is no phase change upon cooling to room temperature and therefore the rate of cooling has no effect upon the microstructure of the alloy. Cooling from the tempering temperature is normally done in air; however, it can also be done in oil or water. Figure 3.33 shows the microstructure of as-hardened and hardened-tempered steel.

The temperature range available for tempering of steel is broad, from 200 to 680 °C (390 to 1260 °F). High-alloy steels such as tool steels are tempered in the range of 500 to 650 °C (930 to 1200 °F), whereas low-alloy steels are tempered above 400 °C (750 °F). With a rise in tempering temperature, the strength and hardness decrease, whereas ductility and toughness increase. Tempering is therefore used to restore the ductility and toughness of the steel. Tempering also relieves internal stresses and reduces the brittleness of the steel.

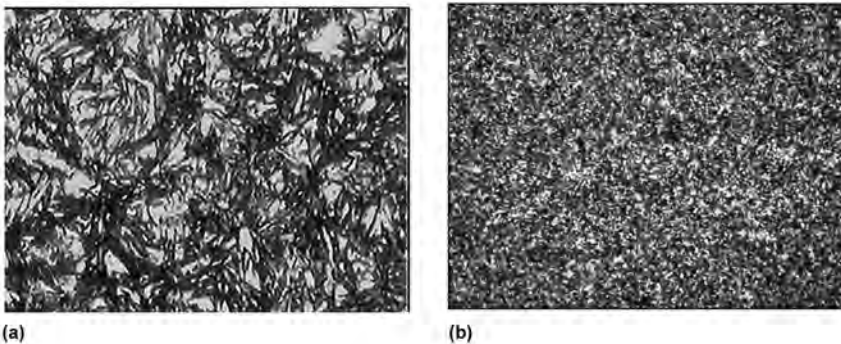


Fig. 3.33 Microstructure of steel in (a) as-hardened condition, 1000x, and (b) after tempering, 400x

3.10.5 Precipitation Hardening

Precipitation hardening, or age hardening, is a heat treatment process where strengthening is achieved by a precipitation of finely dispersed submicroscopic second phase particles within the matrix. The size of the precipitate particles is much smaller than even the size of the grains. Precipitates are of nanometric dimension and cannot be resolved under an optical microscope. The second phase particles give rise to a distortion of the crystal lattice of the matrix phase and produce a localized internal lattice strain as well as offering resistance to movement of dislocations through the matrix, resulting in matrix strengthening.

The precipitation hardening treatment consists of two steps. The first step is known as solution treatment. During solution treatment, the second phase (i.e., solute) is completely dissolved (in solid state) within the matrix by heating the alloy to a solution temperature. From the solution temperature, the alloy is quenched (i.e., cooled rapidly so that the second phase remains in the solid solution). The second step is called *aging*, which is carried out at a relatively lower temperature than the solution temperature. Upon aging, the second phase particles precipitate within the matrix, resulting in strengthening of the alloy. The process of precipitation hardening is schematically shown in Fig. 3.34.

For an alloy to be subjected to precipitation hardening or age hardening, there must not only be an appreciable solubility of the second phase at a high temperature within the matrix (in the order of several percent-age points), but also a limited solubility at lower temperatures; in this way

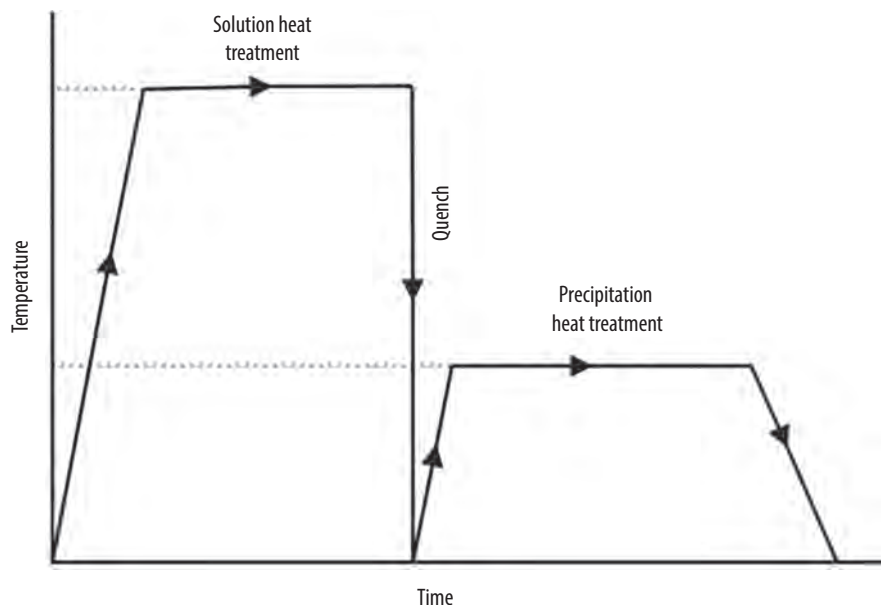


Fig. 3.34 Schematic of precipitation hardening process

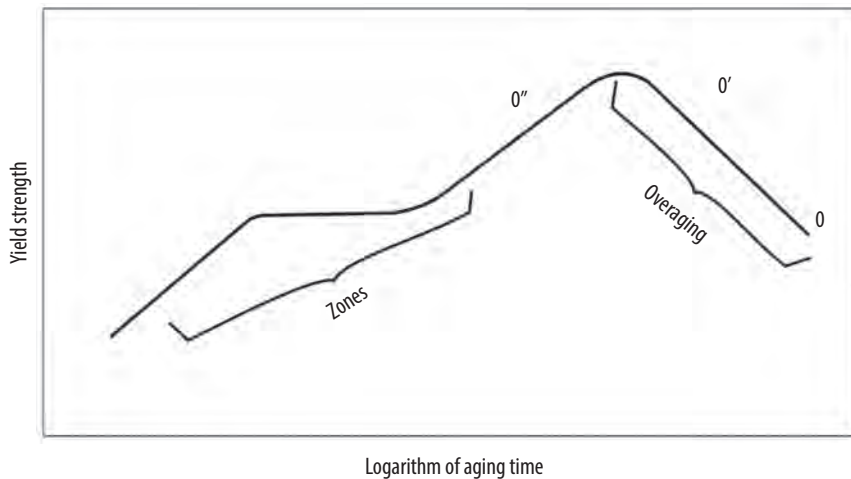


Fig. 3.35 Effect of aging time on strength and hardness in age hardening.
Source: Ref 3.16

the solubility of the second phase should decrease with decreasing temperature. This leads to precipitation of the second phase (θ'' phase) on aging. The precipitates formed are coherent with the matrix and account for an increase in the strength and hardness of the alloy. The coarsening of the precipitates on overaging of the alloy (represented by formation of θ phase) leads to a drop in hardness as shown in Fig. 3.35.

The precipitate particles impede the movement of dislocations through the matrix and give rise to strengthening. The precipitate particles interact with dislocations in two distinct ways. When the particles are small and coherent, they are cut by the dislocation. As a result, new surfaces are created and the particle/matrix interfacial energy increases. On the other hand, in an overaged condition when the particles are coarsened, a dislocation may bow around a particle and leave behind a dislocation loop. Looping or bowing of the dislocations increases the length of the dislocation. Both of these events lead to matrix strengthening.

3.11 Superalloys

Superalloys are a special class of heat-resistant alloys for high-temperature applications such as aircraft, power plant components, marine and industrial gas turbines, space vehicles, rocket engines, nuclear reactors, and submarines. They are a class of precipitation-hardenable alloys that achieve high strength and corrosion resistance above the temperature limits ($>800^\circ\text{C}$, or 1470°F) normally applicable to stainless steels. Superalloys have an exceptional combination of high-temperature strength, toughness, and resistance to degradation in corrosive or oxidizing environments.

There are three types of superalloys based on what the principal element in the alloy is, namely, iron-base, nickel-base, and cobalt-base superalloys. Besides the matrix phase superalloys can have as many as 12 to 13 different microalloying elements, including high-melting-point refractory metals.

Out of the three types of superalloys, nickel-base superalloys are the materials with an exceptional combination of high-temperature strength, toughness, resistance to thermal fatigue, and resistance to degradation in corrosive or oxidizing environments. They are known for their creep resistance at high temperature, good surface stability, and corrosion and oxidation resistance. Their age-hardening property makes them an ideal candidate for power plant application. In a solution-annealed condition, they are soft and ductile and therefore can be formed easily. They are amicable to rolling and drawing to form sheets and tubes. Their high strength is attributed to precipitation of different phases, which occurs only on aging of the alloy after a forming operation.

Wrought nickel-base superalloys typically contain 10 to 20 wt.% chromium, up to about 8 wt.% aluminum and titanium combined, 5 to 15 wt.% cobalt, and small amounts of alloying additions of boron, zirconium, magnesium, rhenium, and ruthenium, in addition to 0.02 to 0.2 wt.% carbon.

The nickel-aluminum binary system, as shown by the phase diagram given in Fig. 3.36, is the basis for development of various nickel-base superalloys. As shown in this diagram, as the amount of aluminum added to nickel increases, an intermetallic compound forms as the precipitate phase. This phase has a nominal composition of Ni_3Al and is designated as the γ' (gamma prime) phase. The presence of a high-volume fraction of the γ' phase is the key to strengthening of superalloys.

The major phases present in nickel-base alloys are summarized as (Ref 3.17):

- A gamma matrix (γ phase), comprising a solid solution of nickel with elements such as cobalt, iron, chromium, molybdenum, and tungsten. All nickel-base alloys contain the γ phase as the matrix.
- A γ' phase, which forms coherent precipitates of an intermetallic compound of a nominal composition Ni_3X , where X is a mixture of Al, Ti, and Nb, which is stable over a relatively narrow range of compositions as shown in Fig. 3.36. The intermetallic compound is Ni_3Al , Ni_3Ti , or Ni_3Nb , or a mixture thereof. This phase is required for high-temperature strength and creep resistance.
- MC-type carbides formed as a result of interaction of carbon with the refractory elements tungsten, molybdenum, vanadium, titanium, tantalum, hafnium, zirconium, and niobium. During heat treatment and service, these MC-type carbides tend to decompose to form other carbides, such as M_{23}C_6 , M_7C_3 , or M_6C , at grain boundaries.

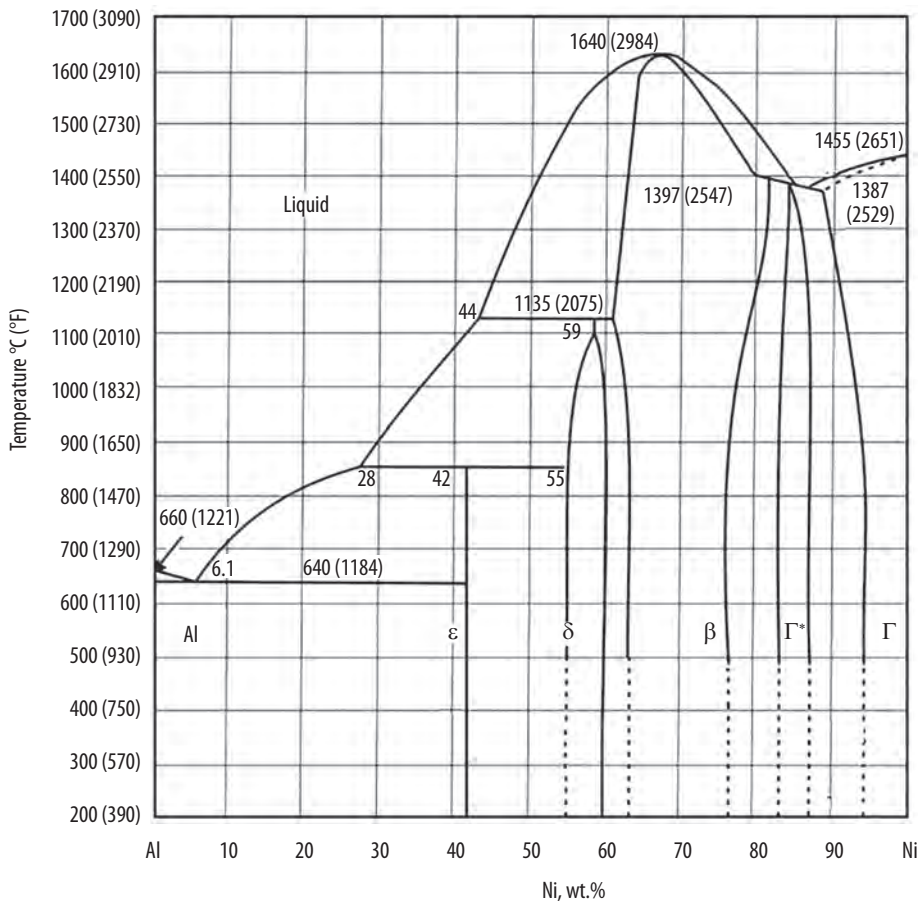


Fig. 3.36 Nickel-aluminum phase diagram. Source: Ref 3.17

- Plate-like or needle-like topologically close-packed (tcp) phases σ and μ . These are undesirable phases because they lower rupture strength and ductility. Alloys containing a high level of chromium, tungsten, tantalum, niobium, and molybdenum are most susceptible to tcp formation.

The properties of nickel-base superalloys are attributed to the alloying additions. For example, elements aluminum, chromium, yttrium, lanthanum, and cerium improve oxidation resistance by forming a protective oxide film. Aluminum and titanium form a γ' phase $[\text{Ni}_3(\text{Al,Ti})]$ that offers creep resistance by impeding the movement of dislocations within the crystal lattice. Refractory metal carbides increase the strength of the alloy by a grain boundary strengthening mechanism.

The heat treatment of nickel-base superalloys consists of three steps: solution annealing, quenching, and aging. Solution treatment in the

temperature range of 1050 to 1200 °C (1920 to 2190 °F) dissolves second phases including the γ' phase and all carbides other than the very stable MC-type carbides. After solution annealing, quenching is done to obtain a supersaturated matrix at room temperature and also to obtain a finer particle size of the γ' phase after the aging process. Finally, the aging treatment strengthens the nickel-base superalloys by precipitation of one or more phases such as the γ' phase ($\text{Ni}_3(\text{Al,Ti})$), the γ'' phase (Ni_3Nb), carbides (M_{23}C_6 , M_7C_3 , M_6C , etc.), and tcp phases from the supersaturated solid solution matrix. Figure 3.37 shows the scanning electron microscopy micrograph of a nickel-base superalloy showing cuboidal precipitates of the γ' phase in the matrix of the γ phase.

3.12 Condenser Tubes

3.12.1 Copper-Base Alloys

Important copper-base alloys are brasses, bronzes, cupronickels, and silver nickels; brasses and cupronickels are used in applications of condenser tubes found in thermal power plants. In the case of brasses, copper and zinc form a solid solution of up to ~39% zinc at 454 °C (849 °F), providing a wide range of properties. Based on the binary phase diagram of the Cu-Zn system (Fig. 3.38a), the elements copper and zinc are completely

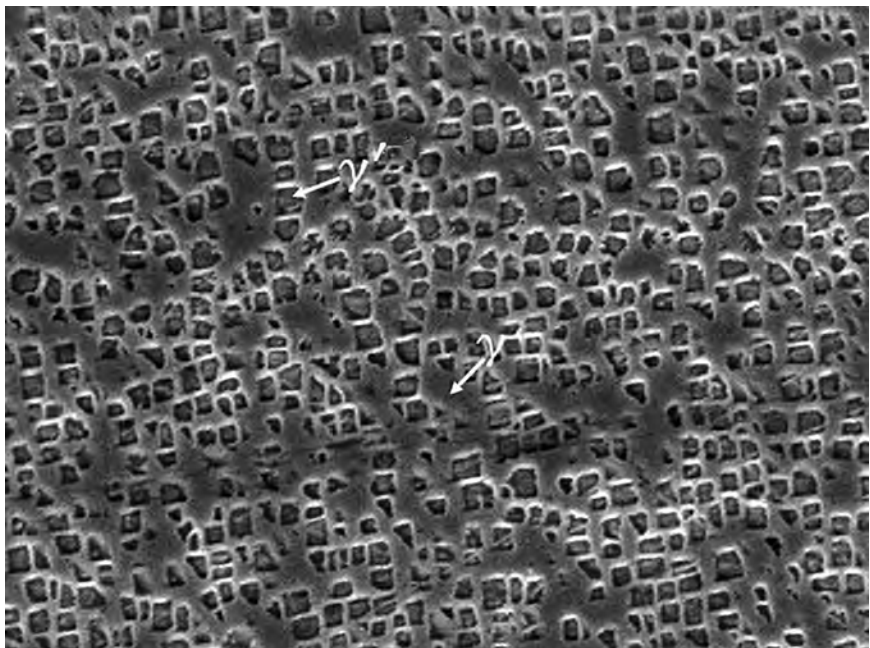


Fig. 3.37 Typical microstructure of nickel-base single-crystal superalloy

soluble in each other in the liquid state. However, they have limited solubility in the solid state, and when cooled, they form a series of intermediary phases such as α , β , γ , δ , ϵ , and η during solidification. A primary α solid solution (i.e., solution of Zn in Cu) has an fcc crystal structure similar to pure copper and dissolves at a maximum of 39% zinc. Figure 3.38(b) shows the microstructure of α brass consisting of grains of the α phase along with annealing twins. The mechanical properties and corrosion resistance of copper may be improved by alloying using elements such as tin, aluminum, silicon, magnesium, nickel, and lead.

The α brasses normally used for condenser tube applications are relatively soft and ductile and can be easily cold-worked. The 70Cu-30Zn alloy has the maximum ductility among all alpha alloys. Alloys with a higher amount of zinc are known as α - β brasses. They contain both α and β phases at room temperature. The β phase has an ordered bcc crystal structure and is harder and stronger than the α phase. As a result, α - β alloys are harder and stronger than α alloys but have poor ductility and therefore cannot be strengthened by cold working.

The addition of 1% tin to α brass gives rise to an alloy with improved corrosion resistance for seawater service known as admiralty brass. Likewise, aluminum brass (an alloy consisting of 76Cu-22Zn-2Al) offers better corrosion resistance by forming a tenacious and self-healing protective film and is suitable for freshwater application.

One of the commonly encountered problems in brasses that leads to failure is dezincification. Dezincification is defined as the selective dissolution or loss of zinc from brass as a result of an electrochemical reaction between zinc and water. Dezincification is a form of dealloying phenomenon and can be noticed by the naked eye because the alloy changes in color from yellow to red. Dezincification occurs: by way of selective

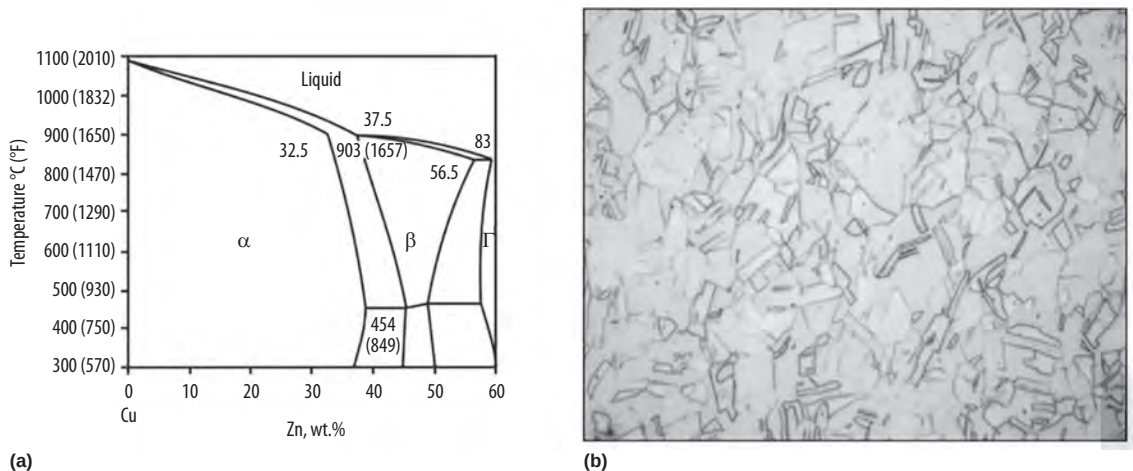


Fig. 3.38 (a) Binary phase diagram of Cu-Zn system (Source: Ref 3.18) and (b) microstructure of alpha brass, 400x

removal or dissolution of zinc from the surface of the brass that is in contact with the corrosive medium, or the entire alloy is dissolved and then the copper is replated or deposited from the solution as a fine copper dust, leaving behind a highly porous mass.

There are two types of dezincification: the layer type and plug type. Conditions favoring the layer type or a uniform attack are slightly acidic water with low pH and low salt content; those leading to the plug type or a localized attack are neutral or alkaline waters and waters with high salt content. Small amounts of tin or antimony minimize dezincification in brasses.

3.12.2 Cupronickels

Copper-nickel alloys are single phased throughout the full range of compositions. The Cu-Ni binary phase diagram in Fig. 3.39 shows complete solubility between the elements copper and nickel; the solubility is not only in the liquid state but also in the solid state.

Copper-nickel alloys, up to 30% nickel, are popularly called cupro nickels. The addition of nickel to copper improves the strength and corrosion resistance of the alloy. Cupronickels fall under the category of non-heat-treatable alloys and therefore their properties can be improved only by cold working. They have high resistance to corrosion, corrosion fatigue, erosion, and cavitation in all natural waters including seawater and brackish, treated, or polluted waters; they also have good formability and show

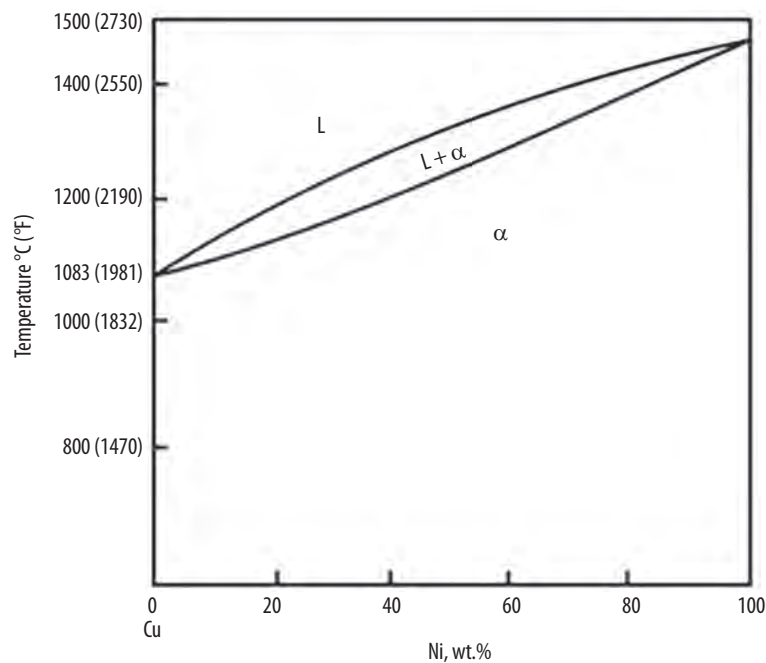


Fig. 3.39 Binary phase diagram of Cu-Ni system. Source: Ref 3.19

excellent resistance to stress-corrosion cracking. The two most popular grades of cupronickel alloys used for condenser tube applications contain 10 or 30% nickel.

3.12.3 Titanium Alloys

Because of their high strength to weight ratio and exceptional corrosion/erosion resistance, titanium and its alloys are preferred for chemical process as well as marine and industrial applications such as heat exchanger and condenser tubing.

Pure titanium exists in two allotropic forms. The low-temperature form, α , exists up to a temperature of 882 °C (1620 °F) and has an hcp structure. Above this temperature, it transforms to the β phase with a bcc crystal structure. Alloying additions result in the increased stability of either the α or β phase, depending on the element added. Depending on the influence of different alloying elements on the β -transus temperature, alloying elements are classified as α stabilizers or β stabilizers. Aluminum, oxygen, carbon, and nitrogen are known as α stabilizers, while molybdenum, vanadium, niobium, tantalum, and tungsten act as β stabilizers. Tin, silicon, and zirconium exhibit neutral behavior; they have practically no effect on the α/β phase boundary (i.e., they stabilize neither the α phase nor the β phase). Figure 3.40 shows the portions of the three types of binary phase diagram for titanium alloys.

In an α -peritectoid type of system, the main alloying elements used are aluminum, carbon, oxygen, and nitrogen. The β -eutectoid type of alloy system is characterized by the presence of alloying additions such as iron, chromium, nickel, manganese, and copper. The β -isomorphous alloys include binary titanium alloys with vanadium, molybdenum, tantalum, and niobium.

Based on the phase diagrams, there are four types of titanium alloys (Ref 3.20):

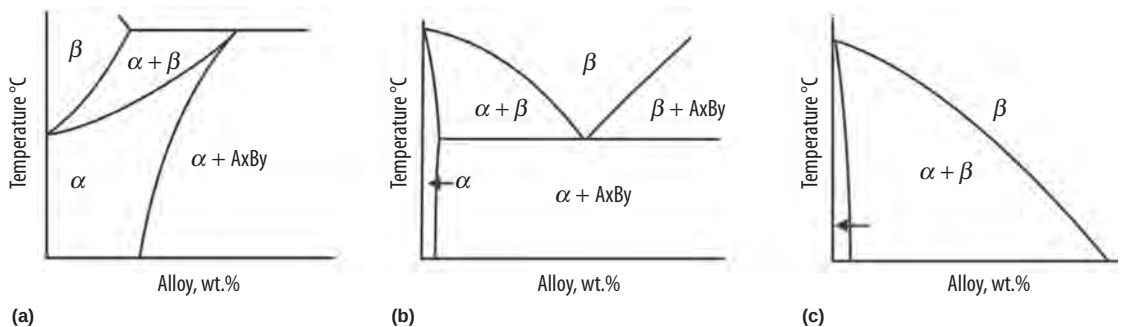


Fig. 3.40 Portions of the three types of binary phase diagram for titanium alloys, (a) alpha peritectoid, (b) beta eutectoid, and (c) beta isomorphous. Source: Ref 3.20

3.12.3.1 Commercially Pure Titanium Alloys. Commercially pure grades of titanium contain well-defined amounts of oxygen besides iron, carbon, nitrogen, and hydrogen. They are non-heat-treatable alloys with moderate strength, weldability, and good corrosion resistance. The strength of commercially pure titanium is attributed to the presence of oxygen, which strengthens the matrix by solid solution strengthening. It is used as condenser tube material. Figure 3.41 shows the typical microstructure of pure titanium having equiaxed, recrystallized grains of the α phase.

3.12.3.2 Alpha Alloys. Alpha alloys contain only a small amount of β stabilizers, resulting in a microstructure consisting of small amounts of the β phase uniformly dispersed in the α matrix. These are heat-treatable alloys.

3.12.3.3 Alpha-Beta Alloys. Alpha-beta titanium alloys contain both α and β stabilizers. They offer higher strength and better formability compared with α -Ti alloys. They can be subjected to thermomechanical treatment to achieve desired microstructures and properties. Based on the morphology of the β phase dispersed in the α matrix, there are three different microstructures of α - β alloys: fully lamellar, bimodal or duplex, and equiaxed or globular. Ti-6Al-4V alloy is a representative grade of this class.

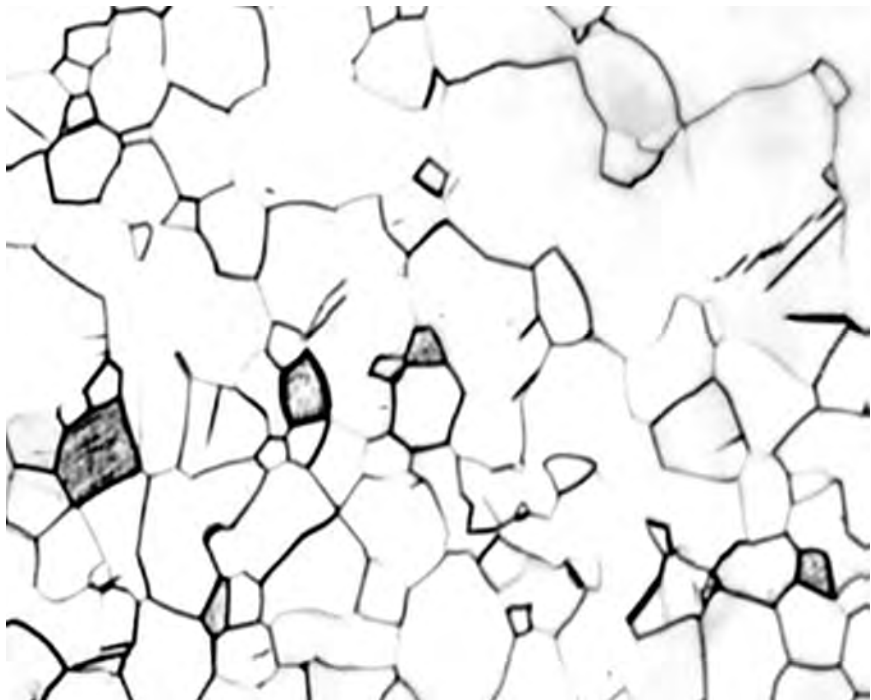


Fig. 3.41 Microstructure of commercially pure (unalloyed) titanium

3.12.3.4 Beta Alloys. Beta alloys have a high percentage of β -stabilizing elements added, which results in a microstructure that is metastable β after solution annealing treatment. On subsequent aging, decomposition of the unstable β phase results in strengthening of the alloy.

REFERENCES

- 3.1 R.E. Smallman and R.J. Bishop, *Modern Physical Metallurgy and Materials Engineering*, 6th ed., Butterworth–Heinmann, 1999
- 3.2 F.C. Campbell, Ed., *Phase Diagrams: Understanding the Basics*, ASM International, 2012
- 3.3 D. Kopeliovich, “Iron-Carbon Phase Diagram,” last modified 2012, http://www.substech.com/dokuwiki/lib/exe/fetch.php?w=&h=&cache=cache&media=iron-carbon_diagram.png
- 3.4 P. Sundaram, Heat Treatment of Steels (slide presentation)
- 3.5 H.N. Oppenheimer, Fundamentals of the Heat Treating of Steel, *Practical Heat Treating*, ASM International, 2006, p 23
- 3.6 H.K. Khaira, “Time-Temperature-Transformation Diagram,” 2013, <https://image.slidesharecdn.com/tttdiagram-131118222243-phpapp01/95/ttt-diagram-63-638.jpg?cb=1384813482>
- 3.7 D. Clark and W.R. Varney, *Physical Metallurgy for Engineers*, Van Nostrand, 1962
- 3.8 L. Jeffus, *Welding Principles and Applications*, 7th ed., Delmar Cengage Learning, 2011
- 3.9 V. Masseria, Ed., Metals Handbook: *Heat Treating*, Vol 4, 9th ed., ASM International, 1981, p 9
- 3.10 R.C. Creese, *Introduction to Manufacturing Processes and Materials*, Marcel Dekker, Inc., 1999
- 3.11 “Corrosion and Corrosion Properties of Stainless Steels: Part One,” Key To Metals AG, 2008, http://www.totalmateria.com/images/Articles/kts/Fig232_1.jpg
- 3.12 P.R. Roberge, *Handbook of Corrosion Engineering*, McGraw-Hill, 1999
- 3.13 “Austenitic Steels—The Iron-Chromium Equilibrium Diagram,” Key To Metals AG, 2003, http://www.totalmateria.com/images/Articles/kts/Fig104_1.gif
- 3.14 K. Maruyama, K. Sawada, and J.I. Koike, Strengthening Mechanisms of Creep Resistant Tempered Martensitic Steel, *ISIJ International*, Vol 41 (No. 6), 2001, p 641–653
- 3.15 ASM Handbook, *Heat Treating*, Vol 4, ASM International, 1991
- 3.16 H.K. Khaira, “Precipitation Hardening,” 2013, <https://image.slidesharecdn.com/f-precipitationhardening-131118222304-phpapp01/95/precipitation-hardening-22-638.jpg?cb=1384813737>
- 3.17 “Superalloys,” NED University, 2010, www.materialrulz.weebly.com/uploads/7/9/5/1/795167/superalloys.pdf

- 3.18 “Binary Phase Diagram of Cu-Zn System,” Key To Metals AG, 2003, http://www.totalmateria.com/ArticleImages/Fig69_1.gif
- 3.19 “Binary Phase Diagram of Cu-Ni System,” accessed October 2016, <http://d2vlcm61l7u1fs.cloudfront.net/media%2F098%2F098c345c-dee9-4cc6-b503-e07a813baaeb%2FphpXMLhpq.png>
- 3.20 “Alloy Effects in Titanium Alloys,” accessed October 2016, http://www.dierk-raabe.com/s/cc_images/teaserbox_2455480112.jpg?t=1427621010

CHAPTER 4

Materials for Boiler Tubes

4.1 Introduction

Boiler technologies developed over time are known as subcritical, supercritical (SC), ultra-supercritical (USC), and advanced ultra-supercritical (A-USC), differing from one another in terms of the maximum operating steam temperature and pressure and the power generation capacity of the plant. As one moves from subcritical to A-USC, materials with enhanced stability at higher and higher temperatures are needed.

The key components of a boiler carrying high-temperature and high-pressure steam can be broadly classified into two categories, thick-walled sections and thin-walled sections. Thick-walled sections generally include headers or steam pipes, while thin-walled sections are grouped as furnace-wall or waterwall tubes, superheater (SH) or reheater (RH) tubes, and economizer tubes (Ref 4.1). A header is a thick-walled pipe penetrated by a number of tubes. These heavy-section components have to handle creep and mechanical fatigue, whereas for tubing applications, thermal fatigue is not a key issue because of the smaller section size. Waterwall tubes are the tubes in a boiler where water is evaporated to steam and are often known as steam generating tubes. These tubes form the walls of the boiler and are therefore named waterwalls or waterwall panels. Superheater and reheater tubes operate at relatively higher temperature in the creep range and they ensure heat transfer between the hot flue gases and the high-pressure steam passing through them. The economizer tubes act as a heat exchanger. They extract heat from the waste gases that exit the last SH or RH and utilize this heat to raise the temperature of the water leaving the highest pressure feed water heater to the saturation temperature.

In general, materials used at elevated temperatures must satisfy requirements such as:

- Adequate strength, not only at room temperature, but also at elevated temperatures, to resist creep and rupture
- Adequate resistance to cyclic loading conditions; in other words, good fatigue strength

- Low coefficient of thermal expansion to resist thermal stresses
- Good thermal conductivity for efficient heat transfer
- Good oxidation and corrosion resistance
- Resistance to microstructural degradation under given operating conditions
- Ease of fabrication at affordable cost

Based on these guidelines, a wide range of materials including carbon and low-alloy steels, high-alloy steels such as stainless steels, and specialty materials such as superalloys and dispersion-strengthened materials have been developed over the past several decades; new materials are also under development. Materials based on nanotechnology principles are being researched (Ref 4.2, 4.3).

Carbon steels are suitable and economical up to an operating temperature of about 510 °C (950 °F), whereas low-alloy steels are employed for metal temperatures up to about 565 to 600 °C (1050 to 1110 °F) (Ref 4.2). Carbon steels suffer from low resistance to oxidation and corrosion at high temperatures, and lack creep strength.

The oxidation resistance of steel depends on the nature of the protective oxide scale formed at the surface. Improved resistance to oxidation for alloy steels as compared with carbon steels is due to the difference in the nature of the scale formed in the two cases during exposure to high temperatures. Based on the oxidation conditions, the scale formed in the case of carbon steels may consist of layers of hematite, magnetite, or wüstite. In alloy steels of the ferritic and martensitic type with up to 9 to 12% Cr, the inner layer of the scale is made up of iron-chromium spinel (FeCr_2O_4); in the case of austenitic stainless steels, the inner layer is made up of chromia (Cr_2O_3), offering enhanced resistance to oxidation (Ref 4.4). This has resulted in the use of alloy steels in place of carbon steels in boilers as operating steam temperatures and pressures increase.

Alloying elements such as chromium, nickel, molybdenum, vanadium, and titanium play a major role in improving corrosion resistance over conventional plain carbon steels and form the basis for development of various types of stainless steels.

Addition of elements from the refractory metals group, namely chromium, tungsten, molybdenum, vanadium, niobium, tantalum, and zirconium, increases the creep strength of steel by matrix strengthening due to solid solution effects, precipitation hardening, and dispersion strengthening.

4.2 Materials for Subcritical Boilers

Some of the most frequently used steels for boiler tubes include low-alloy steels containing alloying elements such as chromium, nickel, molybdenum, and vanadium, 9–12% chromium steels, austenitic stainless steels, austenitic heat-resisting steels, and nickel-base heat-resisting alloys.

Traditionally, plain carbon steels or unalloyed steels were used for handling steam for boiler components exposed to a maximum temperature of 350 °C (660 °F) and pressure of about 15 bar (0.2 ksi) until the 1920s. However, the rise in operating steam temperatures to a level of 450 °C (840 °F) and pressures to 35 bar (0.5 ksi) necessitated the development of low-alloy steels because above this temperature, plain carbon steels undergo microstructural degradation in the form of breakdown of pearlite colonies, resulting in loss of the strength and integrity of the steel.

Eventually, low-alloy steels took over from plain carbon steels for applications in waterwalls, thick-sectioned headers, and pipes and in relatively cooler sections of RH and SH tubes due to the poor resistance of plain carbon steels to creep. The main advantage of low-alloy steels is that they possess adequate creep strength at temperatures up to 550 °C (1020 °F), at which point plain carbon steels undergo severe microstructural degradation resulting in loss of strength and rigidity. In these steels, chromium imparts resistance to oxidation, whereas molybdenum provides strength. In low-alloy steels, carbon, apart from iron, forms undissolved carbides with metallic elements, such as chromium, molybdenum, titanium, and niobium and brings about matrix strengthening not only at room temperature but also at high temperatures. In the presence of nitrogen, some of these elements form nitrides and carbonitrides and give rise to strengthening by precipitation hardening. Some elements form intermetallic compounds called *Laves phases*, resulting in matrix strengthening. Various low-alloy steels used for subcritical boilers for operating temperatures around 470 to 600 °C (880 to 1110 °F) include grades such as T1, T11, T12, T22, T23, and T24. Previously, T11 and T22 steels were used (and are still used) for waterwalls, SHs, and parts with thicker sections in boilers (Ref 4.2). However, increasing operating temperature and pressure in power plants started prohibiting their use in waterwalls. This is because the waterwall panels cannot be subjected to postweld heat treatment (PWHT) due to their large size. The development of T23 and T24 steels has overcome this limitation by not requiring any PWHT. Grade T23 is a modified 2Cr1Mo steel where improvement in properties is ensured by addition of tungsten and boron. Further refinement of the microstructure of T23 steel is ensured in grade T24 steel by modification of vanadium, niobium, titanium, boron, tungsten, and molybdenum levels. Additionally, in T23 and T24 grades, the presence of refractory elements such as vanadium, tungsten, niobium, titanium, and boron provides strengthening by precipitation. More recently, 3Cr–3W(Mo)V steels that have higher creep strength than T23 and T24 grades have been developed with and without addition of tantalum. The creep rupture strength of this new class of steel is higher than T23 and T24 for the entire test temperature range and also higher than T91 steel, up to 615 °C (1140 °F) (Ref 4.2, 4.5).

The selection of a particular grade of steel depends on the maximum allowable temperature at which it can be used. The typical recommended maximum allowable temperature for SA 209 T1A (C-0.5Mo steel) is 525 °C

(975 °F), that of SA 213 T2 (0.5Cr-0.5Mo steel) is 550 °C (1020 °F), that of SA 213 T11 (1.25Cr-0.5Mo steel) is 565 °C (1050 °F), and that of SA 213 T22 (2.25Cr-1Mo steel) is 600 °C (1110 °F) (Ref 4.2).

Table 4.1 lists the nominal chemical composition of some of the more frequently used low-alloy steels for subcritical-boiler-related applications (Ref 4.6, 4.7).

For SC and USC steam conditions with reduced wall thickness of the pressure parts, 9–12% Cr high-alloy ferritic steels are employed in order to ensure that thermal stresses are at a minimum (Ref 4.8–4.10). P/T91 and P/T92 steels modify the 9–12% Cr grade (i.e., P/T9 steel) with additions of vanadium, niobium, and nitrogen, and are the representative grades of this class of steel. Seamless tubes of the SA 213-T91 grade (9Cr-1Mo-V steel) can be used up to a maximum temperature of 650 °C (1200 °F) (Ref 4.2). These steels have high strength not only at room temperature but also at high temperatures, offering improved oxidation resistance, greater resistance to thermal fatigue, improved corrosion resistance, and higher limits of maximum allowable stresses during elevated temperature service. These steels have a higher percentage of chromium along with other alloying elements in order to ensure strengthening by solid solution mode, precipitation hardening, and dispersion strengthening effects. Chromium forms $M_{23}C_6$ carbides, imparting improved creep resistance to this class of steel. Chromium not only strengthens the matrix by forming a solid solution with iron but also improves oxidation and corrosion resistance. Additionally, MX, M_2C , M_3C , M_6C , Laves, and Z-phases are also formed in these steels. The elements vanadium, titanium, niobium, and tungsten with carbon form very fine precipitates of an MX type at the dislocations in the matrix and give rise to improved creep strength of the steel by inhibiting the movement of dislocations by a dislocation pinning effect. Likewise, chromium, vanadium, and niobium form Z-phase with the chemical formula $Cr(V,Nb)N$. However, Z-phase formation has been reported to decrease the long-term creep strength of the steel. Elements such as tungsten and molybdenum increase the strength of the alloy primarily by their solid solution strengthening action. These elements also form

Table 4.1 Nominal chemical composition of low-alloy steels used in subcritical-boiler-related applications

Type	Grade specifications	C	Si	Mn	Cr	Mo	W	Co	V	Nb	B	N	Others
1-1/4 Cr steel	ASME T11/1/2Mo	0.1–0.2	0.1–0.5	0.3–0.8	...	0.44–0.65	...	...	...	...	...	...	...
	ASME T11/13CrMo 4 4	0.15	0.5	0.45	1.25	0.5	...	...	...	...	...	...	...
	ASME T12	0.05–0.15	0.5	0.3–0.61	0.8–1.25	0.44–0.65	...	...	...	...	...	...	...
2-1/4 Cr-1 Mo steel	ASME T22/10CrMo 9 10	0.12	0.3	0.45	2.25	1.0	...	...	...	...	...	...	...
	ASME T24/7CrMoVTiB10-10	0.05–0.1	0.15–0.45	0.3–0.7	2.2–2.6	0.9–1.1	...	...	0.2–0.3	...	...	0.012	0.02 Al, 0.05–0.1Ti

intermetallic phases (Laves phases) represented by the chemical formula $(\text{Fe,Cr})_2(\text{Mo,W})$. Laves phase precipitation increases the creep strength by precipitation hardening but adversely affects it when its size increases. Elements such as vanadium and niobium form fine and coherent precipitation of $\text{M}(\text{C,N})\text{X}$ carbonitrides in the ferrite matrix and give rise to precipitation strengthening. Nickel, when present, improves the toughness of the steel but at the cost of its creep strength. At times this is remedied by partially replacing nickel with copper (as in the case of P/T122 grade). The element boron helps in reducing the coarsening of chromium carbide precipitates and also helps in nucleation of vanadium nitride precipitates. Cobalt is an austenite stabilizer and also promotes nucleation of finer secondary carbides on tempering. Table 4.2 lists the nominal chemical composition of frequently used high-alloy ferritic steels such as 9Cr1MoVNb (SA 213 T91), 9Cr1MoWVNb (SA 213 T92), X20CrMoV 12 1, X20CrMoWV 12 1, and X12CrMoWVNbN 10 11 (E911) for applications above 580 °C (1075 °F) (Ref 4.7, 4.11). These steels not only have higher oxidation resistance compared with conventional carbon steel and low-alloy steel such as T22, but also offer enhanced levels of maximum allowable stress and stress rupture strength at temperatures up to 620 to 650 °C (1150 to 1200 °F) and hence are extensively used as SH and RH tubes.

Above an operating temperature of 580 °C (1080 °F), properties such as oxidation and creep resistance play a predominant role in governing the process of material selection. Low-alloy steels do not have adequate resistance to oxidation and creep above 580 °C, and therefore, austenitic stainless steels were used in power plants designed in the 1950s (Ref 4.4).

Table 4.2 Nominal chemical composition of frequently used high-alloy ferritic steels

Type	Equivalent grade specifications	C	Si	Mn	Cr	Mo	W	Co	V	Nb	B	Others
9 Cr steel	P/T9	0.12	0.6	0.45	9.0	1.0	...	...	...	...	...	...
	P/T91/ X10CrMoVNb9 1	0.08–0.12	0.2–0.5	0.30–0.60	8.0–9.5	0.85–1.05	...	...	0.18–0.25	0.06–0.1	...	< 0.4 Ni, 0.03–0.07 N
	P/T92/ NF616 / X10CrMoWVNb 9 2	0.07–0.13	<0.5	0.30–0.80	8.5–9.5	0.3–0.6	1.5–2.0	...	0.15–0.25	0.04–0.09	0.001–0.006	...
	E911/ X10CrMoWVNb 9 1 1	0.12	0.2	0.51	9.00	0.94	0.9	...	0.20	0.06	...	0.25Ni
	HCM9M	0.07	0.3	0.45	9.0	2.0	...	...	...	...	...	...
12 Cr steel	HT91/X20 CrMoV 12 1	0.20	0.4	0.60	12.0	1.0	...	...	0.25	...	...	0.5Ni
	HT9/X20 CrMoWV121	0.20	0.4	0.60	12.0	1.0	0.5	...	0.25	...	...	0.5Ni
	HCM12	0.10	0.3	0.55	12.0	1.0	1.0	...	0.25	0.05	...	0.03N
	P/T122/HCM12A	0.11	0.1	0.60	12.0	0.4	2.0	...	0.20	0.05	0.003	0.06N, 1.0Cu
	NF12	0.08	0.2	0.50	11.0	0.2	2.6	2.5	0.20	0.07	0.004	...
	SAVE 12	0.10	0.3	0.20	11.0	...	3.0	3.0	0.20	0.07	...	0.07Ta, 0.04Nd, 0.04N

In a coal-fired thermal power plant, austenitic stainless steels are used for SH/RH tubing whose main function is to provide heat transfer between the hot flue gases and the high-pressure steam handled by them. This is that area of the boiler operation where the tubes are likely to be subjected not only to oxidation and creep but also to fire-side and steam-side oxidation as well as thermal fatigue. Austenitic steels have greater oxidation resistance and creep-rupture strength than ferritic/martensitic steels. They possess good room temperature ductility and are easy to fabricate.

AISI 304 steel containing 18%Cr-8%Ni is the base alloy of the class of austenitic stainless steels that is developed by addition of enough nickel to an iron-chromium matrix. The origin of the family of austenitic stainless steels is 18/8 steel with 18% Cr and 8% Ni as the principal alloying elements that impart a certain level of high-temperature creep strength. Modifications in 18/8 steel are essential to enhance its creep strength because this grade of steel is suitable in the highest temperature region of SH and RH sections of boilers with conventional steam parameters only.

There are two ways to increase the creep strength of an 18/8 base alloy. The first is to choose understabilization; the second is to make additions of alloying elements such as niobium and copper. Precipitation strengthening by the understabilization method involves change in the morphology of carbide precipitation. Here, the amount of stabilizing elements such as titanium and niobium is decreased, which hinders chromium carbide formation to the extent where their contents are insufficient for carbon fixation.

Modified grades are developed from a base alloy by the addition of elements such as manganese, molybdenum, tungsten, copper, aluminum, titanium, niobium, and vanadium. AISI 304, 310, 316, 321, and 347 type austenitic stainless steels and their modifications developed this way are recommended for operating temperatures up to about 760 °C (1400 °F) (Ref 4.2). For fossil-fuel plants operating under normal steam parameters, the TP304H, TP321H, TP316H, and TP347H grades are still in use, with the TP347H grade demonstrating the highest allowable stress among this group. The creep strength and oxidation resistance of TP347H steel is further improved by refinement of its grain size in the case of the TP347HFG grade of steel. The Esshete 1250 and Tempaloy A-2 grades fall under the 15Cr-15Ni category of steels and are known for their higher allowable stress at higher temperatures than 18Cr-8Ni steels. The principal strengthening mechanisms in these steels include solid solution strengthening, strengthening due to precipitation of intermetallic compounds, and carbide precipitation.

The chemical compositions of representative grades of austenitic stainless steel for boiler tube application are given in Table 4.3 (Ref 4.7).

Conventional 18/8 stainless steels are used in SH- and RH-related applications for subcritical boilers. However, in the case of SH/RH tubes for SC and USC power plants, the service conditions are more demanding in

Table 4.3 Nominal chemical composition of typical austenitic stainless steels

Type	Equivalent grade specifications	C	Si	Mn	Cr	Ni	Mo	V	Nb	N	Others
18Cr ...	AISI 304	0.08	1.0	2.0	18.0	8.0	...	...	...	...	...
8Ni steel	Super 304H	0.10	0.2	0.8	18.0	9.0	...	...	0.4	0.10N	3.0Cu
	AISI 310	0.25	1.5	2.0	24.0	19.0	...	...	...	...	...
	AISI 316	0.08	1.0	2.0	17.0	12.0	2.5	...	...	...	...
	TP316H	0.08	0.6	1.6	16.0	12.0	2.5	...	...	...	...
	AISI 321	0.09	1.0	2.0	17.0	11.0	...	...	...	...	0.15Ti
	TP321H	0.08	0.6	1.6	18.0	10.0	...	...	...	...	0.5Ti
	TP347H	0.08	0.6	1.6	18.0	10.0	...	...	0.8	...	...
	TP347 HFG	0.08	0.6	1.6	18.0	10.0	...	...	0.8	...	...
	Tempaloy A-1	0.12	0.6	1.6	18.0	10.0	...	...	0.1	...	0.08Ti
15Cr...	Esshete 1250	0.12	0.5	6.0	15.0	10.0	1.0	1.0	...	...	0.2 W, 0.06 Ti
15Ni steel	Tempaloy	0.12	0.6	1.6	18.0	14.0	1.6	...	0.24	...	0.1 Ti
	A-2										

terms of their high temperature performance, so conventional grades of 18/8-type austenitic stainless steel are not the right candidates. Instead, steels with higher chromium and nickel content and additional alloying elements are recommended. For example, instead of 18/8 stainless steels, 25%Cr-20%Ni-type advanced austenitic heat-resisting grades with better high-temperature strength, greater resistance to high-temperature corrosion, and steam oxidation resistance are used. They are recommended for use at a maximum operating temperature of about 815 °C (1500 °F) (Ref 4.2). Further improvement in the high-temperature strength of 25%Cr-20%Ni alloys is ensured by using a different strengthening mechanism such as precipitation hardening or dispersion strengthening and grain boundary strengthening in addition to the more commonly used solid solution strengthening mechanism of adding alloying elements such as titanium, vanadium, niobium, tungsten, molybdenum, copper, and boron. Some of these high-strength creep-resistant stainless steels are TP310, NF 707, NF 709, SAVE 25, and HR3C. Table 4.4 lists the nominal chemical composition of some of the austenitic heat-resisting steels (Ref 4.7).

In general, austenitic stainless steels are more expensive than the corresponding ferritic steels. The cost increases with greater percentages of chromium and nickel in a steel. Major issues with austenitic stainless steels are their susceptibility to steam oxidation and stress corrosion cracking, besides poor weldability. They also have a greater coefficient of thermal expansion and relatively poor thermal conductivity.

Therefore, for the most stringent operating conditions in terms of steam temperature and pressure (with operating steam temperature around 700 °C, or 1290 °F), nickel-base high strength alloys known as superalloys have been developed. They are high-Cr, high-Ni alloys, and elements such as

Table 4.4 Nominal chemical composition of austenitic heat-resisting steels

Type	Equivalent grade specifications	C	Si	Mn	Cr	Ni	Mo	Ti	Nb	Others
25Cr-20Ni steel	TP310	0.08	0.6	1.6	25.0	20.0	...	...	...	...
	TP310NbN	0.06	0.4	1.2	25.0	20.0	...	...	0.45	0.2N
	NF 707	0.08	0.5	1.0	21.0	35.0	1.5	0.1	0.2	...
	NF 709	0.15	0.5	1.0	20.0	25.0	1.5	0.1	0.2	...
	HR3C	0.06	0.4	1.2	25.0	20.0	...	...	0.45	0.2N
	SAVE 25	0.1	0.1	1.0	23.0	18.0	...	...	0.45	1.5 W, 3.0Cu, 0.2N
	Tempaloy A-3	0.05	0.4	1.5	22.0	15.0	...	...	0.7	0.15N, 0.002B
	Incoloy 800H	0.08	0.5	1.2	21.0	32.0	...	0.5	...	0.4Al

molybdenum, tungsten, and cobalt account for solid solution strengthening. The higher amount of chromium compared with that in heat-resisting steels discussed earlier offers enhanced corrosion resistance to nickel-base superalloys. Further strengthening is achieved by precipitation and the aging process using additions of aluminum, titanium, and niobium. The precipitation hardening process involves formation of an intermetallic compound represented by a general chemical formula Ni_3X , where X may be a mixture of aluminum, titanium, and niobium. The precipitates show a typical cubic shape under scanning electron microscopy and are designated as gamma prime (γ') precipitates. A special feature of nickel-base superalloys is that they are relatively soft and formable in the solution-treated condition. In this condition, they can be rolled and drawn to form sheets and tubes, and the tubes can be cold-formed by bending. Subsequent aging treatments impart high strength to these alloys by precipitation hardening.

Inconel 617, Inconel 671, Inconel 740, Inconel 718, and HR6W, listed in Table 4.5, are typical examples of nickel-base superalloys used for SC and USC boiler applications. Haynes 230, Inconel 740, and CCA 617 are selected for heavy sections, high-temperature headers, pipes, and SH/RH tubing. Nickel-base superalloys offer a much higher maximum allowable stress at operating temperatures in the order of 700 °C (1290 °F) compared with stainless steels and austenitic heat-resisting steels. The HR6W, SAVE25, and Sanicro25 nickel-base superalloys permit a maximum allowable stress in the order of 90 MPa (13 ksi) at 100,000 hours at temperatures as high as 700 °C (Ref 4.11–4.13).

At steam temperatures exceeding 700 °C, the strength levels exhibited by nickel-base superalloys are inadequate and other heat-resistant materials are needed. Oxide dispersion strengthened (ODS) alloys that have an iron- or nickel-base matrix with a fine and uniform dispersion of sub-micron and nanoparticles of Y_2O_3 have been developed that offer good creep strength at high temperatures (i.e., >1000 °C, or 1830 °F). They are normally produced by powder metallurgy, a course of pressing-sintering-hot pressing/hot extrusion of mechanically alloyed powders. Table 4.6 lists the typical composition of ODS alloys (Ref 4.14).

Table 4.5 Nominal chemical composition of high-chromium, high-nickel, heat-resisting alloys

Type	Equivalent grade specifications	C	Si	Mn	Cr	Ni	Co	Mo	Nb	Fe	Others
High-Cr High-Ni steels	HR6W	0.08	0.4	1.2	23.0	43.0	...	...	0.18	bal	6.0W, 0.08 Ti, 0.003 B
	CR30A	0.06	0.3	0.2	30.0	50.0	...	2.0	...	bal	0.2 Ti, 0.03 Zr
	Inconel 617	0.07	0.4	0.4	22.0	54.0	12.5	8.5	...	1.5	1.2 Al, 0.3Ti, 0.2Cu
	Inconel 671	0.05	...	...	48.0	51.5	...	...	...	...	Ti 0.35
	Inconel 718	0.04	...	...	18.0	bal	...	3.0	...	18.5	Cb 5.1
	Inconel 740	0.03	0.5	0.3	25.0	bal	20.0	0.5	...	...	0.9Al, 0.7Fe, 2.0Nb/Ta
	Incoloy 800H	0.08	0.5	1.2	21.0	32.0	...	...	0.3	bal	0.5Ti, 0.4Al
	Haynes 230	0.1	0.4	0.5	22.0	bal	5.0	2.0	...	3.0	14.0W, 0.3Al, 0.005B, 0.02La
	Sanicro 25	0.08	0.2	0.5	22.0	25.0	...	...	0.3	bal	3.0W, 3.0Cu, 0.2N
	Nimonic 263	0.06	0.4	0.6	20.0	bal	20.0	5.9	...	7.0	2.2Ti, 2.6Al, 0.005B, 0.2Cu

Table 4.6 Typical composition of ODS alloys

Type	C	Si	Mn	Cr	Mo	W	Ti	Y ₂ O ₃	Fe/Ni
ODS 10CrTiY ₂ O ₃	0.065–0.12	...	...	9–13	...	2	0.12–0.22	0.8–0.35	bal
ODS 12CrTiY ₂ O ₃	<0.05	...	...	12.3	...	0–3	0.0–0.39	0.24–0.25	bal

4.3 Materials for Supercritical, Ultra-Supercritical, and Advanced Ultra-Supercritical Boilers

There has been a gradual increase in boiler operating steam parameters over time in order to enhance plant efficiency. Thermodynamically, the efficiency of a coal-fired power plant is governed by what fraction of the total energy that is fed into the cycle is converted into electrical energy. The greater the amount of electrical energy generated for a given amount of energy input, the higher the plant efficiency. Besides other factors, the plant efficiency depends on operating steam temperature and pressure. The rise in steam temperature and pressure has a direct influence on the plant efficiency. Conventional subcritical boilers of the early 1960s operated at steam temperatures of <540 °C (1005 °F) and pressures of <25 MPa (3.6 ksi). Between the late 1980s and early 2000s, steam temperatures were <593 °C (1100 °F) and pressures were <30 MPa (4.3 ksi); from 2000 to 2010, they were about <620 °C (1150 °F) and <33 MPa (4.8 ksi). With advancements in power plant technology, a steep rise in boiler steam temperatures to 700 °C (1290 °F) and pressures between 35 and 45 MPa (5 to 6.5 ksi) has been observed since 2010.

As discussed earlier, conventional subcritical boilers normally work at about 38% gross plant efficiency at a typical steam pressure of 16.7 MPa

(2.4 ksi), SH operating temperature of 537 °C (998 °F), and RH operating temperature of 537 °C (generally reported as 16.7 MPa/537 °C/537 °C). In the case of SC boilers with steam parameters of 24.7 MPa/565 °C/593 °C, the gross plant efficiency increases to 40 to 41%, representing an improvement of 2 to 3% compared with conventional subcritical boilers. Likewise, it has been possible to achieve a gross plant efficiency of 41 to 42% for USC units with steam parameters of 28 MPa/593 °C/593 °C, which is about 3 to 4% higher than that of subcritical boilers. With further increases in operating steam temperature and pressure, A-USC boilers are able to offer plant efficiency as high as 47 to 49%, where the typical steam temperature corresponds to 700 °C and pressure is 35 MPa and above. Thus, about an 11% improvement in plant efficiency can be achieved with this change. The aim of industry is to achieve power plant efficiencies in the range of 50%. It is worth mentioning that improvements in plant efficiency not only reduce fuel costs, but also reduce CO₂ emission, sulfur oxide (SO_x) and nitrogen oxide (NO_x) emissions, and water use.

The improvement in plant efficiency, which is possible only with a rise in the operating steam temperatures and pressures, is mainly governed by the metallurgy of the materials used for boiler components. In other words, the transition from subcritical to SC, USC, and finally to A-USC boiler technology demands newer and newer materials with higher creep strength, greater corrosion resistance, and ease of fabrication. Figure 4.1 demonstrates the correlation between plant efficiency for a given set of steam conditions and the recommended boiler material.

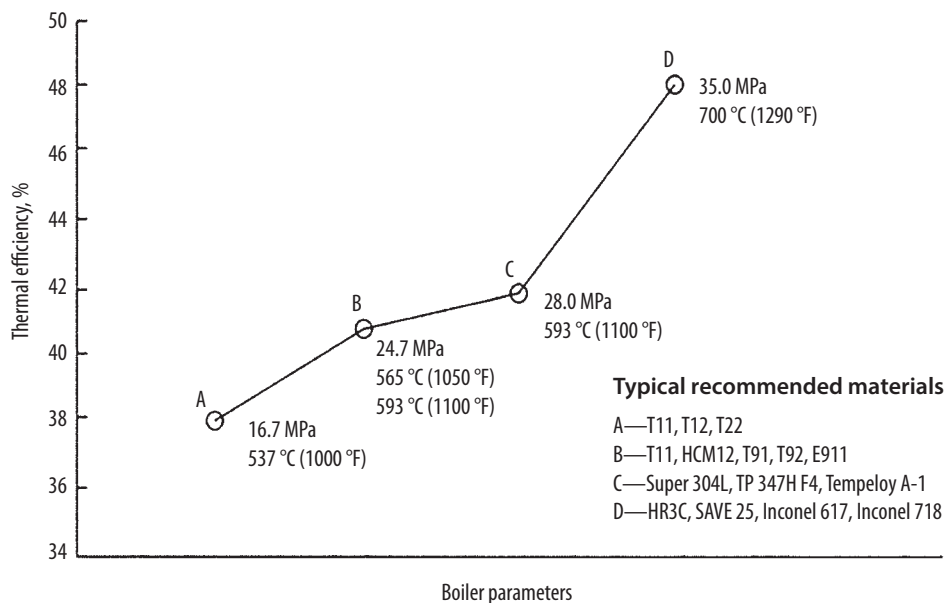


Fig. 4.1 Correlation between the plant efficiency for a given set of steam conditions and the recommended boiler material

A subcritical boiler is one in which the operating live steam pressure is about 22.1 MPa (3.2 ksi) and the temperature is 374.15 °C (705.45 °F). For these steam parameters, there is a nonhomogeneous mixture of water and steam in the evaporator part of the boiler (i.e., waterwalls). In order to separate steam from the water, drum-type boilers are used, and the separated steam is subsequently superheated in the SH and RH before it is fed to the turbine. Contrary to this, in once-through boilers used in SC and USC or A-USC technologies, there is a single-phase fluid (i.e., dry steam) with homogeneous properties that does not require any separation in the drum. An SC boiler does not have a drum and has only one continuous tube through which the water and steam generated in the furnace waterwalls pass through only once.

As in conventional subcritical boilers, there are many different components in SC, USC, and A-USC power plants (herein termed SC power plants for convenience), such as waterwalls, SH/RH tubes, headers, and the main steam pipe. Because the steam parameters for advanced boiler technologies are more demanding, there is a need for materials that can offer enhanced high-temperature creep strength, oxidation and corrosion resistance, and resistance to thermal fatigue. Therefore, it is mandatory to use materials with high strength levels and reduced wall thickness, resulting in low thermal stresses for the high-pressure, high-temperature steam conditions prevailing in SC power plant technologies. The resultant effect is the transition from conventional low-alloy steels to austenitic steels and Inconel-type high-nickel superalloys for tube materials and related components such as pipes and headers (Ref 4.14–4.16).

In a subcritical boiler, the waterwall tubes are generally designed to work as evaporators. However, in SC power plants with higher steam temperatures and pressures, the fraction of evaporator heating surfaces decreases, with the result that part of the waterwall must also function as an SH. In other words, materials with better thermal stability and creep strength are needed. In view of this, for main steam temperatures of 600 °C (1110 °F) and above, the creep strengths of the waterwall tube materials commonly used, such as T11 and T12, are no longer sufficient, and therefore low-alloy steel grades such as T23 and T24 are employed.

At elevated temperatures, high-alloy ferritic steels such as T91, T92, and HCM12 are recommended, due to their better creep strength. However, the major limitation of these steels is their poor oxidation resistance because of a relatively lower chromium content compared with stainless steels. Additionally, the tubes require PWHT before subjecting them to service. This problem is overcome by the use of nickel-base alloys. Nickel-base alloy tubes do not need PWHT and are thus superior for fabrication. However, they are more expensive than ferritic and martensitic steels.

Similarly, ferritic or martensitic steels are used for construction of SH/RH tubes up to an operating steam temperature of 550 °C (1020 °F). At temperatures of 600 to 700 °C (1110 to 1290 °F), austenitic steels such as

Super 304H, TP 347H FG, and Tempaloy A-1 provide adequate levels of creep strength. However, for still higher temperatures, the creep strength of these materials is lower than 100 MPa (14.5 ksi) for 100,000 h and therefore they are not the right choice.

In the case of USC and A-USC power plants operating in the temperature range of 700 °C, the SH tube temperature at the final stage is more than 700 °C, which is too high for conventional austenitic steels to reliably withstand. In view of this, specially developed nickel-base alloys such as NF707, NF709, HR3C, SAVE 25, Incoloy 800, Inconel 617, Haynes 230, CCA 617, high-Cr high-Ni alloy HR6W, Inconel 718, Inconel 740, and Tempaloy A-3 are recommended as SH/RH tubes. The highest creep strength is achieved in Inconel 617. Likewise, for headers and pipes with operating steam temperatures around 700 °C, nickel-base alloys such as Alloy 617 (mod.), Alloy 263, and HR6W are used.

Table 4.7 summarizes the chemical composition of some of the alloys employed for different components of a coal-fired power plant using SC, USC, and A-USC technologies.

Table 4.7 Chemical composition of the alloys used in SC, USC, and A-USC power plants

Grade designation	C	Si	Mn	Cr	Ni	Mo	W	V	Nb	B	N	Fe	Others
E911	0.12	0.2	0.51	9.0	0.25	0.94	0.9	0.2	0.06	...	...	bal	...
SAVE 12	0.1	0.3	0.2	11.0	...	...	3.0	0.2	0.07	...	0.04	bal	3.0Co, 0.07Ta, 0.04Nd
NF 707	0.08	0.5	1.0	21.0	35.0	1.5	...	...	0.2	...	...	bal	0.1Ti
NF709	0.15	0.5	1.0	20.0	25.0	1.5	...	...	0.2	...	...	bal	0.1Ti
HR3C	0.06	0.4	1.2	25.0	20.0	...	...	...	0.45	...	0.2	bal	...
Incoloy 617	0.1	0.5	0.5	22.0	52.0	9.0	...	...	...	...	...		1.5Fe, 12.5Co, 0.3Ti, 1.2 Al, 0.2Cu
Incoloy 800	0.08	0.5	0.8	21.0	32.5	...	...	...	...	...	...	46.0	0.4Al, 0.4Ti, 0.4Cu
Haynes 230	0.1	0.4	0.5	22.0	bal	2.0	14.0	...	...	0.005	...	...	5.0Co, 3.0Fe,0.3Al,0.02La
Inconel 740	0.03	0.5	0.3	25.0	...	0.5	...	...	2.0	...	...	...	0.9Al, 1.8Ti, 0.7Fe, 20.0Co
CCA 617	0.06	0.17	...	22.0	55.0	8.7	0.26	...	0.03	...	...	...	11.6Co, 1.2Al, 0.4Ti
HR6W	0.08	0.4	1.2	23.0	43.0	...	6.0	...	0.18	...	...	bal	0.08Ti, 0.003B
Super 304H	0.1	0.2	0.8	18.0	9.0	...	...	...	0.4	...	0.1	bal	3.0Cu
Esshete 1250	0.12	0.5	6.0	15.0	10.0	1.0	0.2	1.0	...	...	...	bal	0.06Ti
Inconel 718	0.04	...	...	18.0	bal	3.0	...	...	5.1	...	...	...	18.5Fe
Nimonic 263	0.06	0.4	0.6	20.0	bal	5.9	...	...	...	0.005	...	...	20.0Co, 7.0Fe, 2.2Ti, 2.6Al, 0.2Cu
347HFG	0.08	0.6	1.6	18.0	10.0	...	...	...	0.8	...	...	bal	...
Sanicro25	0.08	0.2	0.5	22.0	25.0	...	3.0	...	0.3	...	0.2	bal	3.0Cu
CR30A	0.06	0.3	0.2	30.0	50.0	2.0	...	...	...	...	...	bal	0.2Ti, 0.03Zr
310N	0.2-0.5	<1.3	<1.5	25.0	20.0	...	...	...	1.5	...	...	bal	...
HR120	0.05	...	...	25.0	37.0	2.5	2.5	...	0.7	...	0.2	bal	...

From the end user point of view, the most important properties of a material to be used for boiler tube application are creep strength or creep rupture strength, maximum allowable stress, and maximum safe working temperature. The selection of any material for an intended application is based on these properties. The curves shown in Fig. 4.2 provide overall information about the properties and performance of various materials on a comparative basis (Ref 4.5, 4.7, 4.8, 4.11, 4.17–4.19).

Figure 4.2 shows creep rupture strength of representative boiler tube materials with respect to temperature.

The plots for maximum allowable stress as a function of temperature for representative materials are shown in Fig. 4.3. These plots help in determining the temperature capabilities of various classes of alloys. The nickel-base alloys Inconel 740, Haynes 230, Inconel 625, Inconel 617, and HR 120 have much higher temperature capability compared with austenitic steels, followed by ferritic steels.

Thus, a vast majority of alloys are available for boiler applications in general and more specifically for tubes, pipes, and headers, and therefore the metallurgy and intended service conditions of an application must be considered in appropriate selection of the specific grade.

Table 4.8 summarizes the data for maximum allowable temperature for boiler tubes and pipe materials used in thermal power plants.

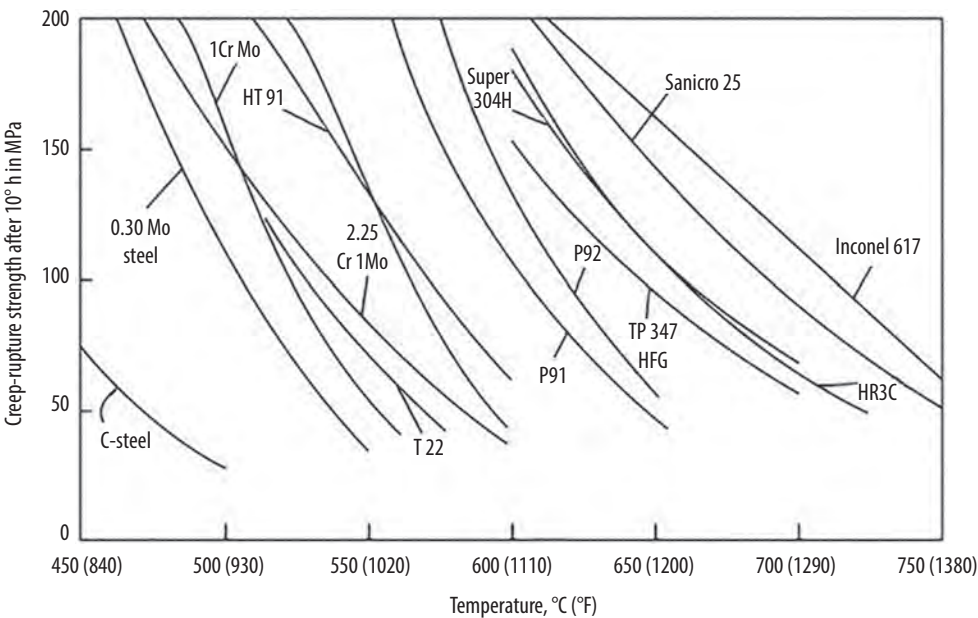


Fig. 4.2 Creep strength of different materials used as boiler tubes and related applications

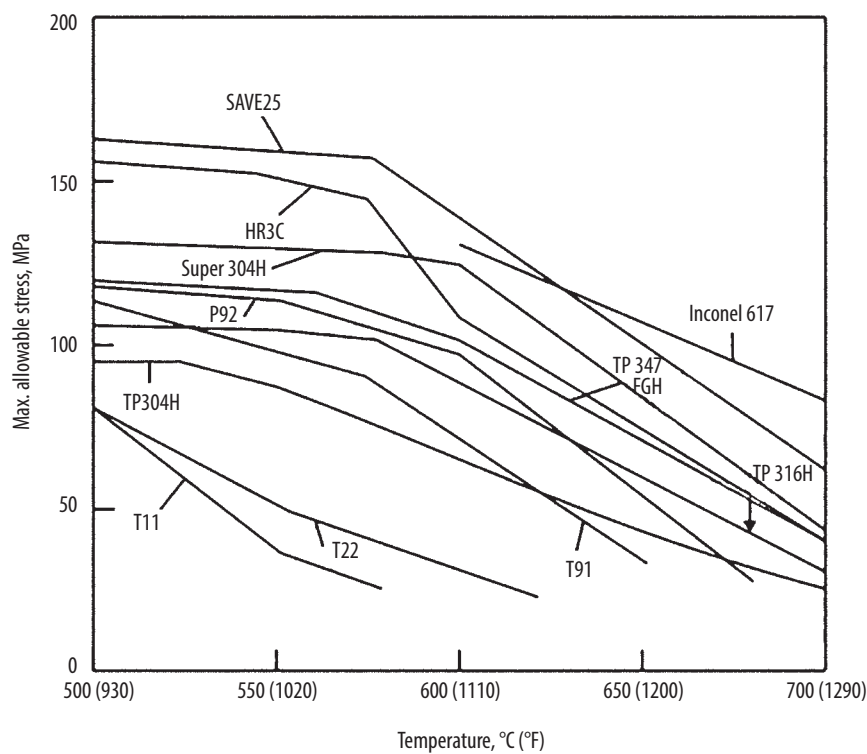


Fig. 4.3 Maximum allowable stresses for various classes of alloys with respect to temperature

4.4 Materials for Condenser Tubes

In thermal power plants, low-pressure steam leaving the steam turbine is condensed back to water to be reused as boiler feedwater. The objective is to improve the thermal efficiency of the process. A surface condenser, which is a water-cooled “shell and tube” type heat exchanger, is normally employed for this purpose. The condenser converts steam from its gaseous to liquid state at a pressure below atmospheric pressure.

The condenser tube material should therefore possess good thermal conductivity, a low coefficient of thermal expansion, resistance to erosion and corrosion, and adequate mechanical properties in terms of tensile, creep, and fatigue strength. Copper-base alloys possess this set of properties and hence are traditionally used for the manufacture of condenser tubes. However, more severe operating conditions in terms of water chemistry, water velocity, and temperature have prompted researchers and tube manufacturers to switch over to other materials.

Various ferrous and nonferrous alloys used as condenser tubes include copper-base alloys such as brass or bronze, cupronickels, stainless steels, and titanium-base alloys, depending on the plant and cooling water

Table 4.8 Maximum allowable temperature for boiler tubes and pipes

Specification	Product form	Nominal composition	Recommended temp	
			°C	°F
SA 178A	ERW tube	Carbon steel	510	950
SA 178C	ERW tube	Carbon steel	510	950
SA 192	Seamless tube	Carbon steel	510	950
SA 210A1	Seamless tube	Carbon steel	510	950
SA 106B	Seamless pipe	Carbon steel	510	950
SA 106C	Seamless pipe	Carbon steel	510	950
SA 210C	Seamless tube	Carbon steel	510	950
SA 250T1A	ERW tube	C-Mo steel	525	975
SA 209T1A	Seamless tube	C-Mo steel	525	975
SA 335P1	Seamless pipe	C-Mo steel	525	975
SA 250T2	ERW tube	0.5Cr-0.5Mo	550	1020
SA 213T2	Seamless tube	0.5Cr-0.5Mo	550	1020
SA 250T11	ERW tube	1.25Cr-0.5Mo-Si	565	1050
SA 213T11	Seamless tube	1.25Cr-0.5Mo-Si	565	1050
SA 335P11	Seamless pipe	1.25Cr-0.5Mo-Si	565	1050
SA 250T12	ERW tube	1Cr-0.5Mo	565	1050
SA 213T12	Seamless tube	1Cr-0.5Mo	565	1050
SA 335P12	Seamless pipe	0.5Cr-0.5Mo	565	1050
SA 250T22	ERW tube	2.25Cr-1Mo	600	1110
SA 213T22	Seamless tube	2.25Cr-1Mo	600	1110
SA 335P122	Seamless pipe	11Cr2WMoVNbCu	620	1150
SA 213T91	Seamless tube	9Cr-1Mo-V	650	1200
SA 335P91	Seamless pipe	9Cr-1Mo-V	650	1200
SA 213T92	Seamless tube	9Cr2WMoVNbN	650	1200
Haynes 230	Seamless tube	57Ni22Cr14W2MoLa	700	1290
Inconel 617	Seamless pipe	52Ni20Cr11Co9MoAl	700	1290
Inconel 740	Seamless tube	50Ni25Cr20Co2Nb1.8TiVAl	750	1380
SA 213TP304H	Seamless tube	18Cr-8Ni	760	1400
SA 213TP347H	Seamless tube	18Cr-10Ni-Cb	760	1400
SA 213TP310H	Seamless tube	25Cr-20Ni	815	1500

Source: Ref 4.2, 4.20

requirements (Ref 4.21–4.23). The cooling water can be freshwater, bore well water, water from reservoirs, seawater, brackish water, treated effluents, or recycled water.

Three important copper-base alloys used for condenser tube applications are admiralty brass, aluminum brass, and cupronickels. Admiralty brass is a cartridge brass (an alloy of 70% Cu and 30% Zn) with 1 to 2% tin added for improved corrosion resistance. Admiralty brass tubes have a small amount of arsenic or antimony, which also makes them resistant to failure due to dezincification. It has good ductility and cold-forming

properties in addition to excellent corrosion resistance in freshwater service. However, admiralty brass is prone to attack by dissolved oxygen and carbon dioxide, leading to pitting corrosion. Admiralty brass is also susceptible to stress corrosion cracking (SCC) in the presence of ammonia.

Another type of brass used as condenser tubes is aluminum brass. It belongs to the family of alpha brasses and has 1.8 to 2.5% Al added to improve resistance to corrosion. Small amounts of arsenic impart resistance to dezincification. It is recommended for applications requiring exposure to freshwater, brackish water, and seawater. Aluminum brass is recommended in preference to admiralty brass for conditions dealing with unpolluted waters having higher chloride.

Table 4.9 lists the nominal chemical composition of admiralty and aluminum brasses used as condenser tube material.

Cupronickels are alloys of copper and nickel. These alloys have lower thermal conductivity than brass but much greater resistance to corrosion in brackish and seawater than brass. They possess good strength and ductility and are resistant to SCC. The 90/10 and 70/30 cupronickels are more popular as condenser tubing. Table 4.10 gives the nominal chemical composition of representative cupro-nickel alloys.

Stainless steels used for condenser tube applications include traditional grades such as 304, 304L, 316, and 316L; duplex stainless steels such as 2205 and 2507; and super ferritic stainless steels. Stainless steels are intended for freshwater conditions. Type 304 stainless steel is one of the best tube materials for freshwater once-through or recirculating cooling water systems. Both 304 and 316 stainless steel offer excellent resistance to all forms of corrosion in freshwater. Stainless steels are resistant to sulfide attack, but the chloride levels must be kept low (below 70 ppm for SS304 and below 300 ppm for SS316). Stainless steels are susceptible to

Table 4.9 Nominal chemical composition of frequently used brasses

Type	Grade	Cu	Sn	Al	As	Zn
Admiralty brass	UNS C44300	70–73	0.9–1.2	...	0.02–0.06	bal
Aluminum brass	UNS C68700	76–79	...	1.8–2.5	0.02–0.06	bal

Table 4.10 Nominal chemical composition of cupro nickel alloys

Type	Grade	Ni	Mn	Fe	Pb	Zn	Cu
CuNi 90/10	UNS C70600	9.0–11.0	<0.1	1.0–1.8	<0.05	<1.0	bal
CuNi 80/20	UNS C71000	19.0–23.0	<0.1	0.5–1.0	<0.05	<1.0	bal
CuNi 70/30	UNS C71500	29.0–33.0	<0.1	0.4–1.0	<0.05	<1.0	bal

biofouling and scaling. For conditions having seawater with a high sulfide concentration, new austenitic and ferritic stainless steels are recommended as they provide resistance to sulfide pitting attack. The nominal chemical compositions of these grades of stainless steel are listed in Tables 3.4 and 3.8 in Chapter 3, *Metallurgy of Steels and Boiler Tube Materials*, in this book. The chemical compositions for typical advanced ferritic and austenitic stainless steels for condenser tubes are shown in Table 4.11.

Titanium has become the most efficient and cost-effective material for condenser tube application. It not only possesses good mechanical properties but also offers unmatched corrosion resistance. Commercially pure titanium is used especially in areas where stainless steels are unable to provide adequate corrosion resistance. Table 4.12 shows the nominal chemical compositions of commercially pure titanium for condenser tubes.

Titanium has a high affinity with oxygen in the presence of moisture and air, giving rise to the formation of TiO_2 protective film. This protective TiO_2 film essentially makes underlying titanium resistant to all oxidizing media. Titanium tubes have excellent resistance to erosion corrosion, impingement, and cavitation attack even when the water velocity is 8 to 10 m s^{-1} . However, the problem with titanium tubes is their high fouling rate when the water velocity is low. Titanium tubes are preferred when the cooling medium is seawater, brackish water, or polluted seawater.

Table 4.11 Nominal chemical compositions of advanced ferritic and austenitic stainless steels used as condenser tubes

Type	Grade	C	Cr	Ni	Mo	Mn	Si	N	S	P	Others
SEA-CURE	S44660	0.06	25.0–28.0	1.0–3.5	3.0–4.0	1.00	1.00	0.04	0.03	0.04	(a)
AL29-4C	S44735	0.03	28.0–30.0	1.00	3.60–4.20	1.00	1.00	0.045	0.03	0.04	(a)
254SMO	S31254	0.02	19.5–20.5	17.5–18.5	6.0–6.5	1.00	0.80	0.18–0.25	0.015	0.03	0.05–1.00 Cu
AL6XN	N08367	0.03	20.0–22.0	23.5–25.5	6.0–7.0	2.00	1.00	0.18–0.25	0.03	0.04	0.75Cu

(a) $(\text{Ti} + \text{Nb}) = 0.20 - 1.00$; $(\text{Ti} + \text{Nb}) = 6(\text{C} + \text{N})$

Table 4.12 Nominal chemical composition of commercially pure titanium

Grade	C	N	O	H	Fe
Commercially pure unalloyed Ti Grade 2 (R50500)	0.08	0.03	0.25	0.015	0.30
Commercially pure unalloyed Ti Grade 3 (R50550)	0.08	0.08	0.35	0.015	0.30
Commercially pure unalloyed Ti Grade 4 (R50700)	0.08	0.08	0.40	0.015	0.50

REFERENCES

- 4.1 V. Viswanathan, R. Purgert, and P. Rawls, Coal-Fired Power Materials, *Adv. Mater. Processes*, Vol 166 (No. 8), August 2008, p 47–49
- 4.2 J.R. Davis, *ASM Specialty Handbook: Heat Resistant Materials*, ASM International, 1997
- 4.3 A. Shirzadi and S. Jackson, Eds., *Structural Alloys for Power Plants—Operational Challenges and High-Temperature Materials*, 1st ed., Woodhead Publishing, July 2014
- 4.4 D. Laverde, T. Gomez-Acebo, and F. Castro, Continuous and Cyclic Oxidation of T91 Ferritic Steel Under Steam, *Corros. Sci.*, Vol 46, 2004, p 613–631
- 4.5 F. Abe, T.-U. Kern, and R. Viswanathan, Eds., *Creep Resistant Steels*, Woodhead Publishing, 2008
- 4.6 A. Fry, S. Osgerby, and M. Wright, “Oxidation of Alloys in Steam Environments—A Review,” NPL Report MATC (A) 90, Sept 2002
- 4.7 R. Viswanathan and W.T. Bakker, “Materials for Ultra Supercritical Fossil Power Plants,” Report TR-114750, EPRI, March 2000
- 4.8 Z.F. Hu, Heat-Resistant Steels, Microstructure Evolution and Life Assessment in Power Plants, *Thermal Power Plants*, M. Rasul, Ed., Intech, 2012
- 4.9 R.L. Klueh, “Elevated Temperature Ferritic and Martensitic Steels and Their Application to Future Nuclear Reactors,” ORNL/TM-2004/176, Nov 2004
- 4.10 K. Maruyama, K. Sawada, and J.-I. Koike, Strengthening Mechanisms of Creep Resistant Tempered Martensitic Steel, *ISIJ Int.*, Vol. 41 (No. 6), 2001, p 641–653
- 4.11 R. Viswanathan, R. Purger, and U. Rao, “Materials Technology for Advanced Coal Power Plants,” 2005, www.msm.cam.ac.uk/phase-trans/2005/LINK/188.pdf
- 4.12 G. Smith and L. Shoemaker, Advanced Nickel Alloys for Coal-Fired Boiler Tubing, *Adv. Mater. Processes*, Vol. 162 (7), July 2004, p 23–26
- 4.13 J.J. de Barbadillo, B.A. Baker, and R.D. Gollihue, Nickel-Base Superalloys for Advanced Power Systems—An Alloy Producer’s Perspective, *The 4th International Symposium, Supercritical CO₂ Power Cycles*, Pittsburgh, Sept 9–10, 2014, p 1–15
- 4.14 A. Nagode, L. Kosec, B. Ule, and G. Kosec, Review of Creep Resistant Alloys for Power Plant Applications, *Metalurgija*, Vol 50 (No. 1), 2011, p 45–48
- 4.15 R. Viswanathan, “Boiler Materials for Ultra-supercritical Coal Power Plants,” Department of Energy, 2006
- 4.16 A. Di Gianfrancesco, Ed., *Materials for Ultra-Supercritical and Advanced Ultra-Supercritical Power Plants*, Woodhead Publishing, 2017
- 4.17 C. Chi, H. Yu, and X. Xie, Advanced Austenitic Heat-Resistant Steels for Ultra-Super-Critical (USC) Fossil Power Plants, *Alloy Steel—Properties and Use*, E. Valencia Morales, Ed., Intech, 2011

- 4.18 K.H. Mayer, et al., New Materials for Improving the Efficiency of Fossil-Fired Thermal Power Stations, *VGB Power Tech*, Jan 1998, p 22–27
- 4.19 R. Viswanathan, *Damage Mechanisms and Life Assessment of High Temperature Components*, ASM International, 1989
- 4.20 D. Zhang, Ed., *Ultra-Supercritical Coal Power Plants: Materials, Technologies and Optimization*, Woodhead Publishing, 2013, p 36
- 4.21 D.S. Janikowski, “Selecting Reliable Heat Exchanger Tube Materials—Factors to Consider,” *API Power Chem 2014*, Queensland, May 27, 2014
- 4.22 D.S. Janikowski, “Selecting Tubing Materials for Power Generation Heat Exchangers,” *Southwest Chemistry Workshop*, Irving, Texas, July 28–31, 2003
- 4.23 P. Rodriguez, “Selection of Materials for Heat Exchangers,” *HEB 97*, Alexandria, Egypt, April 5–6, 1997, p 59–72

CHAPTER 5

Tools and Techniques for Material Characterization of Boiler Tubes

5.1 Introduction

Material characterization is a subject of interest for scientists and engineers because the properties of the material are governed by its composition and structure. Over the last few decades several tools and techniques have been developed to characterize different materials, including metals and alloys. The three broad categories into which different material characterization techniques are grouped are (Ref 5.1):

- Techniques based on microscopy principles such as optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and focused ion beam microscopy.
- Techniques based on spectroscopy principles such as optical emission spectroscopy, energy dispersive spectroscopy (EDS), wavelength dispersive spectroscopy, x-ray fluorescence spectroscopy (XRF), and x-ray photoelectron spectroscopy (XPS).
- Techniques based on diffraction principles such as x-ray diffraction (XRD), electron diffraction, and neutron diffraction.

These techniques provide information on the chemical composition of the material, microstructure and phase analysis, and also the surface characteristics.

From a failure investigation point of view, the characterization of boiler tubes entails the determination of the chemical composition of the tube material; understanding its microstructure with respect to the phases present and studying the effect of temperature on phase transformation

and resultant changes in microstructure; examining the morphology of various defects such as inclusions, second-phase-like carbide precipitates, and the sigma phase; and the evaluation of the effect of the environment on the tube material, leading to issues such as scaling and corrosion.

Some of the more frequently used techniques for characterization of boiler tubes are quantitative metallography (i.e., optical microscopy) using an image analyzer, SEM in conjunction with EDS, XRD, emission spectroscopy, XRF, atomic absorption spectrometry (AAS), and surface analysis techniques such as XPS or electron spectroscopy for chemical analysis. While some of these techniques are qualitative in nature, others provide quantitative information for the property being evaluated. It is possible to conduct bulk analysis as well as elemental or surface analysis of the material using an appropriate technique.

This chapter discusses some of the previously mentioned techniques and provides a brief overview of their fundamentals and the underlying principles on which they are based. The purpose for providing this background information is to ensure that the individual characterization technique is thoroughly understood from a failure investigation point of view.

5.2 Image Analysis

Conventional metallography practice using optical microscopy, SEM, or TEM has one major limitation: the information provided about the microstructural features is highly qualitative in nature. For example, by looking at the microstructure using a traditional microscope, the grain size of a material can be reported as either coarse or fine. However, this description is absolutely qualitative in nature. The problem is partially remedied by using grain size comparison charts (ASTM practice E112-13), whereby the material's grain size is assigned an arbitrary number ranging from 0 to 14 (Ref 5.2). But the fact remains that in any material, all of the grains never have the same size (i.e., diameter), and at times there is a large variation in grain diameter. Therefore, the average grain size as reported by the comparison chart does not give a complete and correct picture about the grain size. In short, ASTM practice E112 is somewhat subjective and the accuracy and reliability of the results obtained is rather poor. Similar difficulties are encountered when estimating and reporting the phase fractions in a multiphase material or the inclusion rating of steel. Thus, there are several limitations in translating microstructural details (which are primarily of qualitative nature) into quantitative information so as to correlate it with the structure-sensitive bulk properties of the material. Recently, these limitations have been improved by use of image analysis techniques for microstructural characterization of the materials (Ref 5.3). Image analysis enables quantification of different microstructural features.

Quantitative image analysis is a fast, reliable, reproducible, and versatile approach for quantification, analysis, and documentation of the microstructure of the material. Commercially developed image analyzers make use of the latest developments in the fields of electronics, computing, and software technology. Commercial image analysis systems transform the analog image of the microstructure into a digital image in order to make it suitable for measurements in a required quantitative format and then actually measure values of interest.

The two main components of an image analysis system are the basic hardware and the image analysis software. The hardware includes a microscope, a high-resolution charge-coupled device (CCD) camera, PC-based image acquisition card (also known as a frame-grabber card), and a computer with a printer. The image of the microstructure captured by the CCD camera is digitized by the frame-grabber card. Before any measurements are taken, the digitized image is subjected to operations such as background illumination correction, image enhancement, thresholding, and image filtration. The image analysis software performs functions including controlling the frame-grabber card, measurement of various features of the image, and analysis of these features. Various feature specifics and global parameters measured by image analysis software are length, area, perimeter, equivalent diameter, Feret diameter, area fraction, volume fraction, roundness, and aspect ratio (Ref 5.4).

Some of the most important applications of image analysis techniques for investigation of boiler tube failures, discussed briefly in subsequent paragraphs (Ref 5.4), are:

- Grain size measurement
- Phase/volume fraction measurement
- Delta ferrite and retained austenite measurement
- Inclusion rating
- Depth of carburization/decarburization
- Scale thickness measurement
- Pearlite banding studies
- Microhardness measurement and hardness profile

5.2.1 Grain Size Measurement

Perhaps the most frequently carried out measurement of any microstructural feature is grain size because it has a direct relevance to the mechanical properties of the material such as its strength, hardness, and ductility. The ASTM grain size number, N , is defined as:

$$n = 2^{N-1}$$

where n is the number of grains per square inch at 100× magnification.

Grain size is expressed as a number of grains per unit area or it can also be reported as the average grain diameter.

Several procedures for measurement of grain size, including the use of comparison charts, are described in ASTM E112. The use of comparison charts per ASTM E112 involves comparison of the grain structure of a sample under investigation with a series of graded images, either in the form of a wall chart or an eyepiece reticle. The grain size of an etched sample is compared with the appropriate comparison chart at the same magnification, and the grain size number corresponding to the matching grains in the chart is assigned to the sample. The repeatability and reproducibility of comparison chart ratings are generally plus or minus 1 grain size number, and are thus poor. Figure 5.1 shows the schematic of a grain size comparison chart. The number adjacent to each frame indicates the grain size number.

Typical results for grain size measurement of a steel sample using image analysis techniques are shown in Fig. 5.2. The results clearly speak to the superiority of this technique over the conventional method of grain size measurement based on a comparison chart. By the image analysis method, it is possible to obtain values for minimum grain size, maximum grain size, and standard deviation. The results are exhibited in the form of a graph or histogram as the number of grains with a certain grain size number or grain diameter; see Fig. 5.2.

5.2.2 Phase/Volume Fraction Measurement

The area/volume percent or area/volume fraction of various phases in a microstructure has an equally great influence on the properties of a material as does its grain size. For instance, in hypoeutectoid steels, an increase in the percentage of ferrite improves ductility and toughness, whereas strength and hardness decrease. Phase analysis can be done by area or volume fraction measurements per ASTM E562-11 (Ref 5.5).

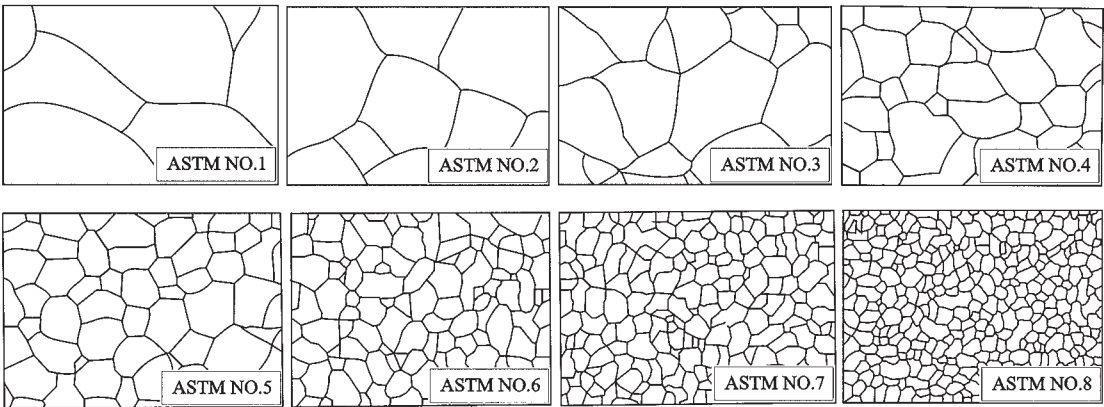


Fig. 5.1 Schematic of grain size comparison charts

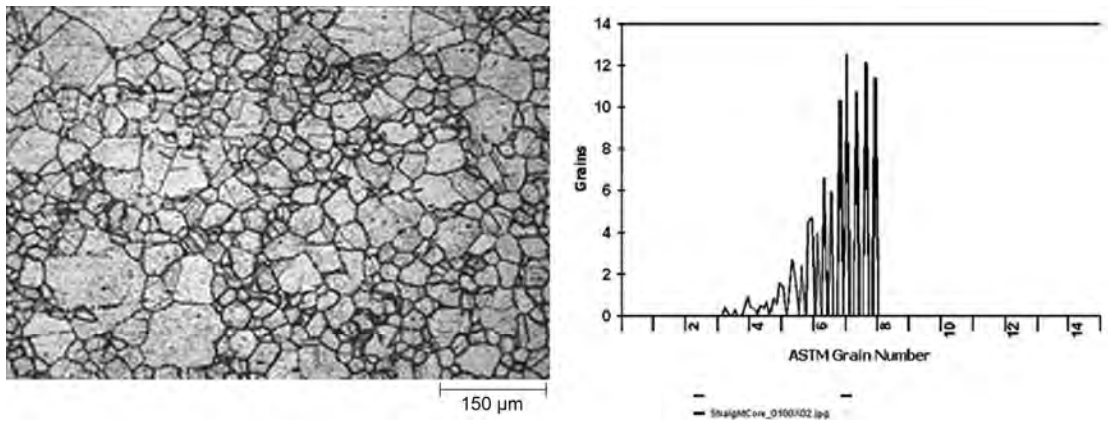


Fig. 5.2 Grain size measurement on final superheater tube sample

Figure 5.3 and the tabulated data give the results of volume fraction measurement in terms of the percentage of bainite and martensite for a superheater tube sample. On similar lines it is also possible to measure the relative proportions of ferrite and pearlite in carbon steel, ferrite and austenite phases in duplex stainless steel, delta ferrite or sigma phases in stainless steel, or retained austenite in steel.

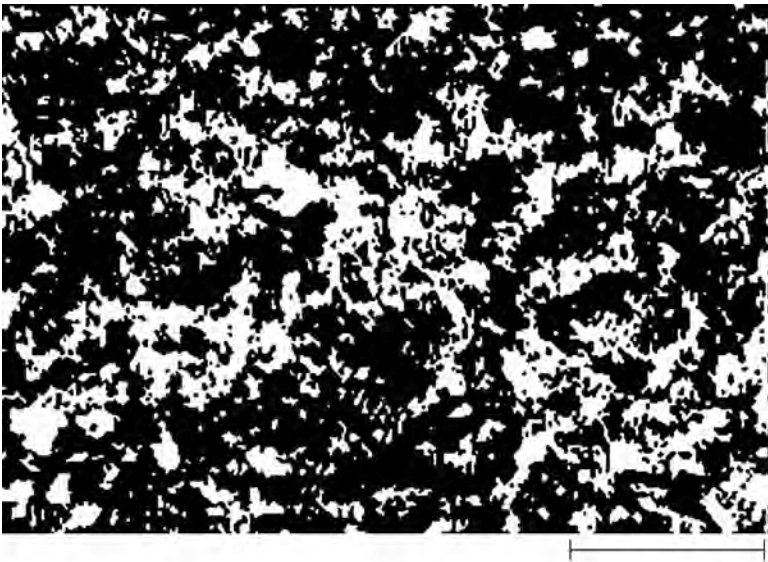
5.2.3 Inclusion Rating

Nonmetallic particles in metals and alloys are termed inclusions. The most commonly found are oxide, sulfide, and silicate inclusions. Inclusions are characterized by their type, shape, size, and distribution. According to ASTM E45-05, *Standard Test Methods for Determining the Inclusion Content of Steel*, the inclusion rating for wrought steels is determined on the basis of similarity in their morphology, and not on the basis of their chemical identity (Ref 5.6). ASTM E45 follows the JK-type inclusion rating system. Accordingly, four types in which the inclusions are classified are:

- Type A, sulfide type
- Type B, alumina type
- Type C, silicate type
- Type D, globular oxide type

Types A and C are very similar in size and shape. Type A sulfide inclusions are light gray in color whereas type C silicate inclusions are black when viewed under a microscope in brightfield illumination mode.

Inclusions are also classified on the basis of their thickness as heavy or thin. Finally, they are characterized on the basis of their severity level based on the number or length of the inclusions present in a 0.50 mm² field of view.



Sr. No.	Bainite (black areas), vol%	Martensite (white areas), vol%
1	43.9	54.3
2	35.9	61.8
3	38.9	59.7
4	39.3	59.1
5	37.1	61.9
Avg	39.02	59.36

Fig. 5.3 Volume fraction measurement on a steel sample

One of the options for determination of the inclusion rating of steel per this standard is to make use of comparison charts, similar to those for grain size estimation. But this method is also subjective in nature and therefore prone to error. Inclusion rating by image analysis provides an idea about the type of inclusion, average size, minimum and maximum size, and density (i.e., number of inclusions per unit area) and features the benefits of reproducibility and reliability.

In order to determine the quality of steel based on nonmetallic inclusion content, the rating is carried out per ASTM E-45 after metallographic polishing of a sample, in an un-etched condition. The results shown in Fig. 5.4 and Table 5.1 indicate the presence of type A sulfide and type D globular oxide inclusions.

5.2.4 Depth of Decarburization

Boiler tubes are often prone to steam-side decarburization due to interaction between carbon from the steel and steam that forms carbon

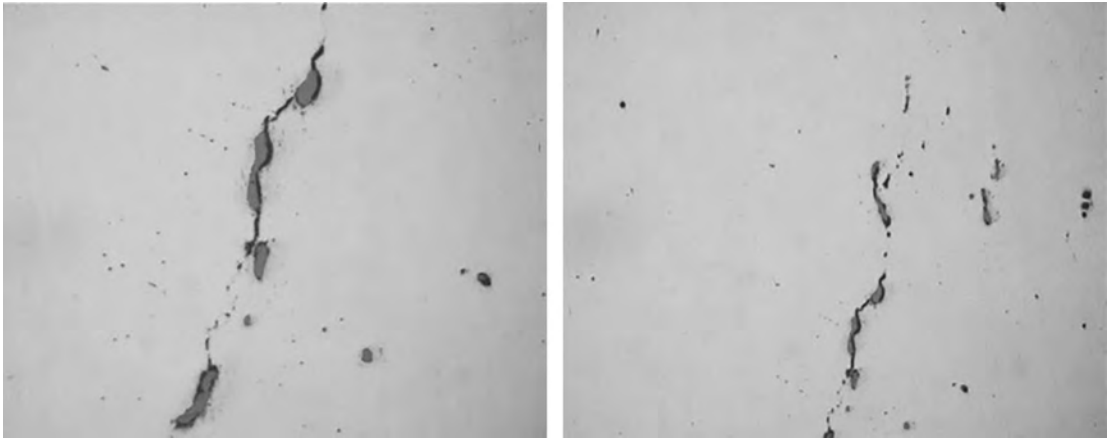


Fig. 5.4 Oxide and sulfide inclusions in a boiler tube sample

Table 5.1 Inclusion rating in a boiler tube sample

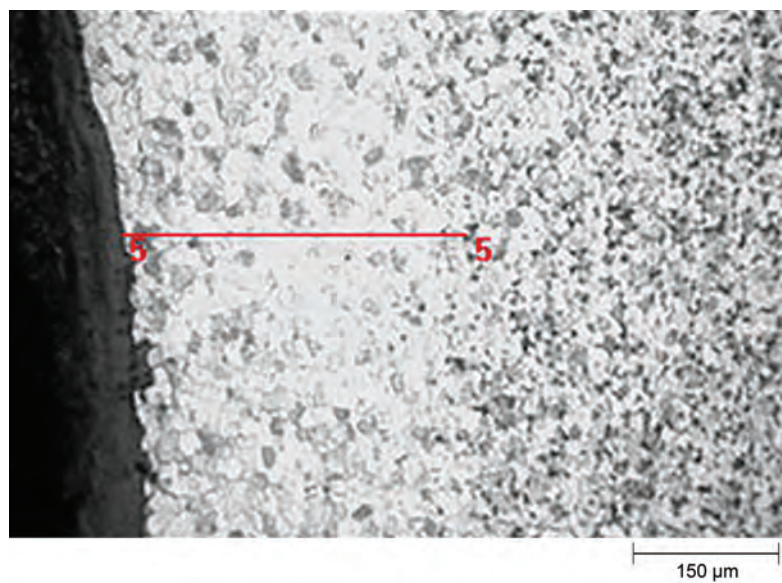
	Type A		Type B		Type C		Type D	
	Thin	Thick/ heavy	Thin	Thick/ heavy	Thin	Thick/ heavy	Thin	Thick/ heavy
Inclusion rating	...	2.5	...	...	...	...	1.5	1.0

monoxide and hydrogen. The decarburization reaction occurs on the inside diameter (ID) surface of the tube such that the carbon from the interior of the tube diffuses to the surface, leading to depletion of carbon in the tube. Decarburization gives rise to carbon-free areas of more or less pure ferrite just beneath the ID surface of the tube. ASTM E1077, *Standard Test Methods for Estimating the Depth of Decarburization of Steel Specimens*, provides guidelines for estimating the depth of decarburization in steel (Ref 5.7). The method estimates the change in the carbon concentration across the cross section of the tube sample using metallography approaches. Figure 5.5 shows the cross section of the outside diameter (OD) side of a superheater tube sample that has undergone decarburization viewed under a microscope.

The results of the measurement can be reported as the average depth of decarburization or minimum and maximum depth of decarburization based on the data shown in tabular form.

5.2.5 Scale Thickness Measurement

Scale formation on the water side is a very common problem for boiler tubes, leading to failure of the tube due to overheating. The deposition of scales occurs when elements such as calcium, magnesium, and silica,



Location	Decarb depth, μm
1	384.7
2	397.5
3	394.9
4	359.3
5	361.8
Avg	379.6

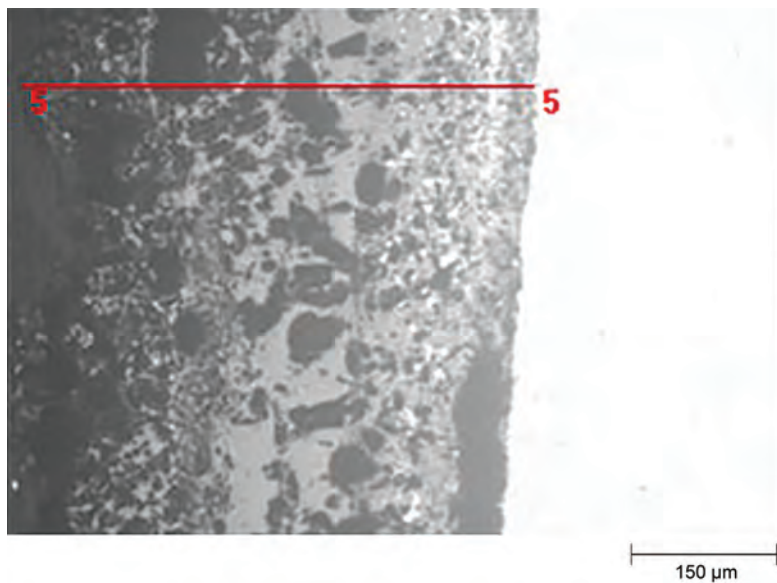
Fig. 5.5 Cross section of superheater tube sample that has undergone decarburization

commonly found in boiler feedwater, react with the tube material to form a continuous layer on the water side of the tube. Scale formation can occur on the OD side of the tube as well, mainly due to flue gases (Fig. 5.6). Because the thermal conductivity of the scale is considerably less than that of the tube material, even thin scale layers serve as an effective insulator and retard heat transfer across the tube wall. The result is overheating of the boiler tube metal, leading to tube failure.

It is possible to estimate the thickness of the scale formed on the surface of the boiler tubes using the image analysis technique (Fig. 5.6 and the tabulated data). The procedure to be followed is similar to that for measuring the depth of decarburization discussed above.

5.2.6 Studies on Pearlite Banding

Boiler tubes sometimes have a structure consisting of banded pearlite, as shown in Fig. 5.7. The microstructure of the steel in such a case shows



Location	Scale thickness, μm
1	583.5
2	575.8
3	524.9
4	675.2
5	537.6
Avg	579.4

Fig. 5.6 Variation in scale thickness on flue gas side of a superheater tube

the colonies of pearlite aligned to form bands having alternate layers of ferrite and pearlite rather than a random orientation of pearlite in the microsection.

The root cause of this problem is the segregation of alloying elements during solidification of the molten alloy in the ingot mold. Areas of higher carbon concentration in austenite are developed as a result of segregation. The rolling of the ingot to form a sheet and the subsequent tube-making operation give rise to elongation of high-carbon areas in the forming direction that develop into pearlite banding. Such a structure is undesirable because a crack once initiated in this high-carbon area easily propagates through ferrite, leading to failure of the tube. Image analysis can be performed to study pearlite banding by using a specially developed software program. The method evolved is based on the measurement of the Feret diameter distributions in two directions, parallel and perpendicular to the rolling direction (Ref 5.8).



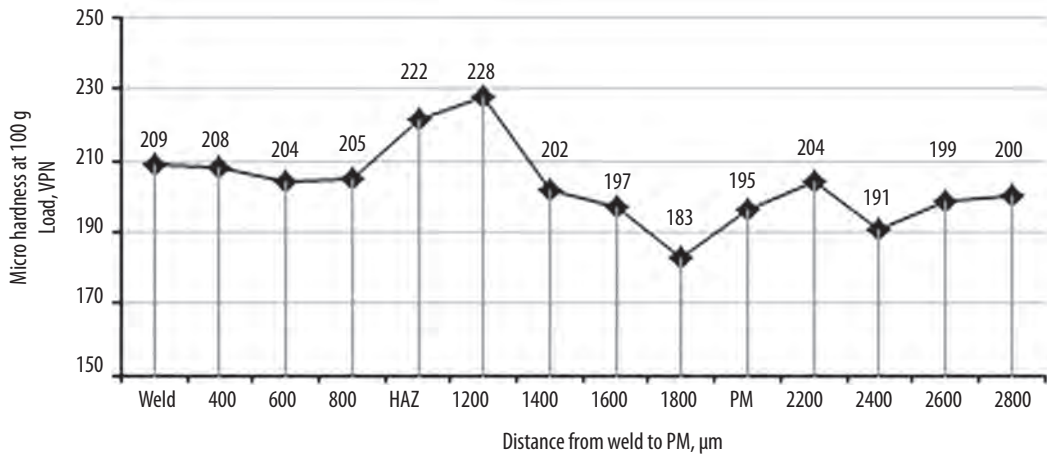
Fig. 5.7 Microstructure of steel showing pearlite banding

5.2.7 Microhardness Measurement and Hardness Profile

During Vickers hardness testing of a sample, measurement of diagonal lengths of the impression using microscope eyepiece rulers becomes difficult, particularly when indentation is made at lower loads of 10 to 200 g. Image analysis software can be used to measure the microhardness of a sample, provided a diamond pyramid impression has already been formed by indenting the test sample and the image of the impression formed has been captured by CCD camera. The software ensures accurate and reliable measurement of the size of the indentation formed. It is also possible to obtain a microhardness profile if several indentations are taken from surface to core of the sample at predefined intervals. A plot of the microhardness value on the y-axis versus the distance along the x-axis (mm/ μm) from the edge of the sample to the location of the indentation gives a microhardness profile as shown in Fig. 5.8 and the tabulated data.

5.3 Scanning Electron Microscopy

General practice for macrostructural examination of metals and alloys involves use of devices such as the hand lens, stereo microscope, and optical microscope. These devices are also used for fractographic studies (i.e., study of the fracture surface of any failed component). Their main advantage is that they are relatively inexpensive and easy to use. However, there are certain serious limitations of these devices with respect to



Distance, μm	Microhardness in VPN at 100 g load	Distance, μm	Microhardness in VPN at 100 g load
Weld	209	1600	197
400	208	1800	183
600	204	PM	196
800	205	2200	204
HAZ	222	2400	191
1200	228	2600	199
1400	202	2800	200

Fig. 5.8 Microhardness profile for an economizer tube sample; PM, parent metal

the maximum attainable magnification, their resolving power, the depth of field or depth of focus that they offer, and the working distance. To overcome these limitations, researchers have developed electron microscopes, namely, the scanning electron microscope and the transmission electron microscope; both use a beam of energetic electrons rather than light to examine the materials on a very fine scale. Table 5.2 gives comparative data for the three microscopic techniques.

Based on the data in Table 5.2, the illumination source used in scanning electron microscopy (SEM) and transmission electron microscopy (TEM) is an electron beam, whereas that used in optical microscopy is a light beam. Because the wavelength of an electron beam is considerably shorter than that of a light beam, electron beams can penetrate into a bulk solid to a greater depth. This permits study of not only the surface details of any material but also its internal details. The resolution (i.e., the ability to discriminate two closely spaced objects) of an electron microscope is much higher than that of an optical microscope. The depth of field (D) of

Table 5.2 Comparative data for different microscopic techniques

Feature	Optical microscope	SEM	TEM
Application	Surface and sectional examination	Surface morphology	Crystal structure studies, phase analysis
Illumination source	Light	Electrons	Electrons
Wavelength	4000–7500 Å	> 0.5 Å	0.02–0.04 Å
Magnification	10–2000x	10–150,000x	10–300,000x
Resolution	250 nm or 2500 Å	5 nm or 50 Å	0.01 nm or 0.1 Å
Depth of field	0.08 μm at 1200x	10 μm at 10,000x	...

a microscope is the height over which the sample can be clearly focused. Because of poor D, an optical microscope can be used to examine only ground and polished samples with smooth surfaces. Contrary to this and because the D of a scanning electron microscope is about 300 times that of an optical microscope, a sample with an uneven surface (as in the case of a fractured surface) can be examined at higher magnification without any deterioration in image quality. The higher D of a scanning electron microscope permits a large amount of the sample area to be in focus and produces an image that is representative of the three-dimensional sample (Ref 5.9). On account of such distinct advantages, the scanning electron microscope has emerged as a very popular tool in failure investigation from a topographic, morphological, and compositional analysis point of view.

Scanning electron microscopy is an important material characterization technique for any investigation relating to the processing, properties, and behavior of materials that involves their surface properties and microstructure. Material characterization using SEM deals with the topography (i.e., the surface features of an object), morphology (i.e., the shape and size of microscopic features such as inclusions or second-phase particles) and the microstructure of the material at higher magnifications with high resolution. From a failure investigation point of view, SEM is used for fractography as well as microstructure evaluation. Fractographic examination using SEM mainly involves assessment of initiation and propagation of cracks, evaluation of the mode of cracking such as intergranular or transgranular, and evaluation of the type of fracture such as ductile, brittle, fatigue, wear, or overload.

Scanning electron microscopy is also used for the study of various types of corrosion-related failures such as pitting, erosion-corrosion, cavitation, and stress corrosion cracking. Scanning electron microscopy is employed to perform measurements such as the coating/plating thickness or thickness of the scale formed as a result of corrosion with greater precision. Typical SEM fractographs are shown in Fig. 5.9.

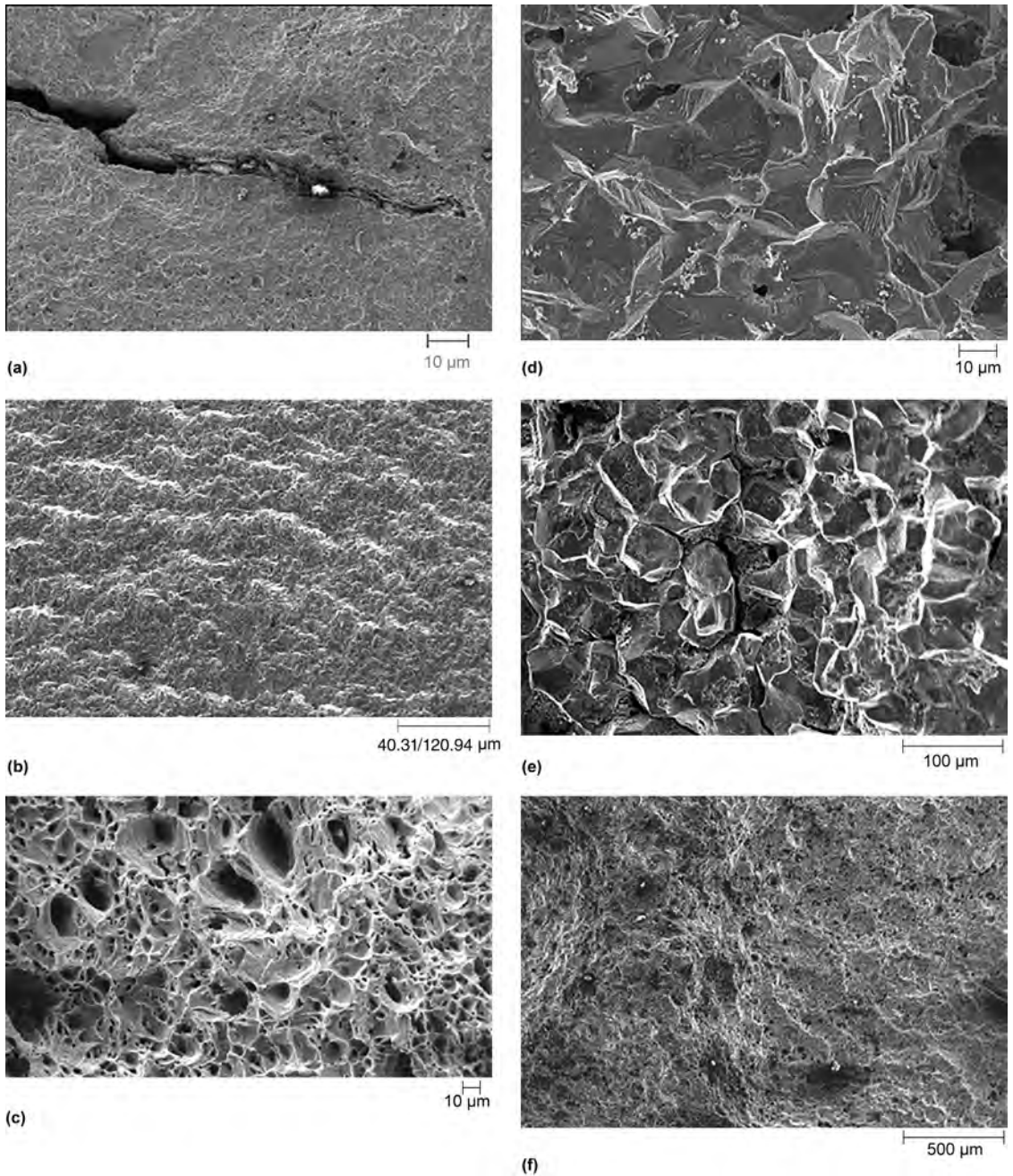


Fig. 5.9 Typical SEM fractographs showing (a) crack filled with corrosion products in a carbon steel tube, 100 $\times$; (b) striations in a fatigue failure, 250 $\times$; (c) dimples in ductile failure, 500 $\times$; (d) cleavage facets in a brittle fracture, 1000 $\times$; (e) brittle fracture with an intergranular mode of cracking, 250 $\times$; (f) corrosion pits, 50 $\times$

Scanning electron microscopy is thus a surface analysis technique developed specifically for high-resolution imaging of sample surfaces. In SEM, a focused beam of electrons with a final probe diameter as small as about 10 Å is produced by heating a filament made up of tungsten or single-crystal lanthanum hexaboride (LaB₆). The beam is accelerated to a potential of 5–50 kV and is focused on the sample surface using a set of electromagnetic lenses. Figure 5.10 shows the expanded view of a typical scanning electron microscope.

The interaction of the primary electron beam with the sample atoms not only produces an SEM image on the cathode ray tube (CRT) screen but also gives various data signals, namely secondary electrons (SEs), back-scattered electrons (BSEs), x-rays, and light photons, as shown by the schematic given in Fig. 5.11. The phenomenon is known as scattering. From an SEM image point of view, SEs and BSEs are of more importance. These signals are analyzed with the help of a set of detectors and analyzers to provide information on the topography and composition of a sample.

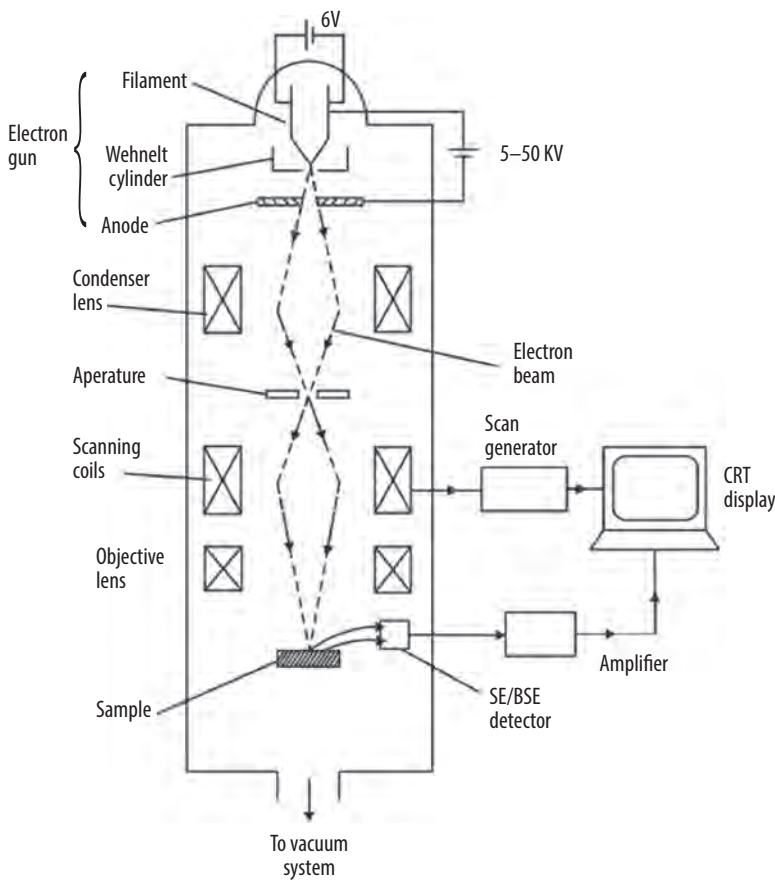


Fig. 5.10 Expanded view of a typical scanning electron microscope

The SE imaging signals are obtained as a result of inelastic collisions (i.e., electron-electron collisions) between the primary beam electrons and the electrons of the sample atoms, as shown in Fig. 5.12. They are low-energy electrons (normally with energy of less than 50 eV) and are emitted from the sample's surface and near surface. They are generally emitted from a

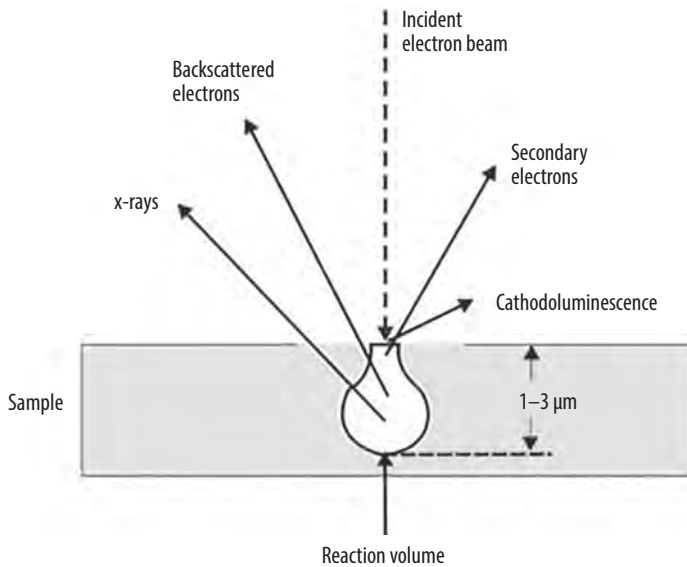


Fig. 5.11 Interaction of primary electron beam with the sample. Source: Ref 5.10

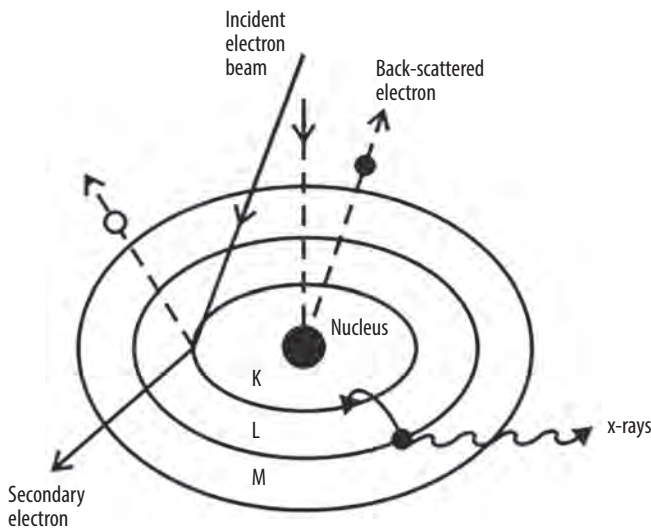


Fig. 5.12 Mechanism of emission of secondary electrons, back-scattered electrons, and x-rays in SEM

5 to 50 nm depth from the surface of the sample, and therefore are used for high-resolution imaging of fine surface morphology.

The elastic interaction between the primary electron beam with the nucleus of the sample produces BSEs, as shown in Fig. 5.12. They have high energy, are comparable with the incident electrons, and are emitted from a greater depth with respect to the surface of the sample in comparison with SEs. The BSE imaging mode gives limited information on the surface topography of the sample but provides image contrast as a function of elemental composition. This makes the BSE mode a powerful compositional analysis tool for the material under investigation. The intensity of the BSE signal is a function of the average atomic number (Z) of the specimen. Heavier elements produce more BSEs. Areas of the sample with a higher atomic number emit more BSEs and appear brighter than areas with a lower atomic number in a BSE image, providing image contrast.

5.3.1 Energy Dispersive Spectroscopy

Energy dispersive x-ray spectroscopy, also known as energy dispersive analysis by x-rays (EDAX), is a chemical and microanalysis technique used in conjunction with SEM. This technique detects x-rays emitted from the sample to determine the elemental composition of the analyzed volume when the sample is bombarded by a beam of electrons. Because the x-rays generated have energy and wavelengths characteristic of the elemental atom from which they originate, the elemental composition of the material can be found by using this method. It is possible to analyze the composition of the features or phases as small as 1 μm with a detection limit of 0.1 wt.% by EDS. Elements with atomic numbers ranging from 4 (beryllium) to 92 (uranium) can be detected.

Applications of SEM in conjunction with EDS also include:

- Rapid material alloy identification
- Surface contaminants analysis
- Identification of inclusions and precipitates
- Corrosion studies
- Elemental diffusion profiling
- Compositional analysis of coatings

As demonstrated in Fig. 5.13, when the sample is bombarded during SEM with a beam of primary electrons, some of the electrons from inner orbits of the sample atoms are knocked off (dislodged) and their position is filled up by an electron from a higher orbit that has greater energy. The energy difference between the two electron orbital states is balanced by the emission of a distinct quantum of energy in the form of x-rays. The energy of the emitted x-rays is characteristic of the element from which

they are emitted. Analysis of these characteristic x-rays is carried out by EDS for qualitative and quantitative estimation of the elements present in the vicinity of the sample surface.

The spectrum of x-ray energy versus counts is evaluated to determine the elemental composition of the sampled volume. Figure 5.14 and

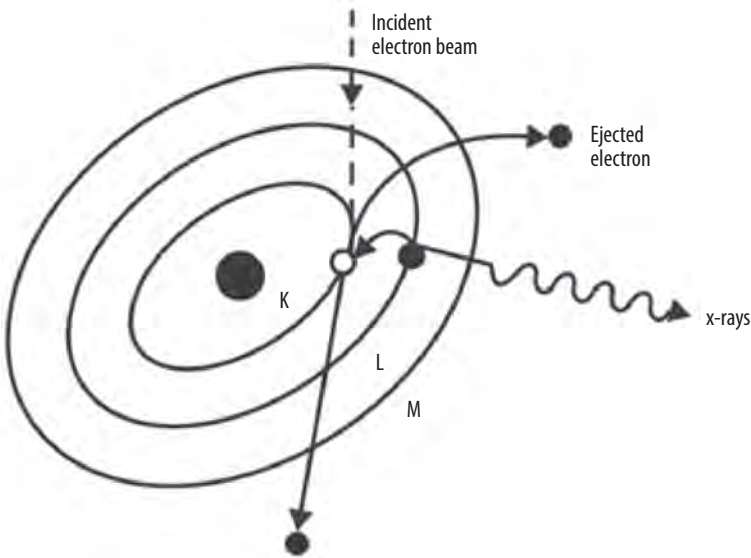


Fig. 5.13 Electron transition and x-ray emission

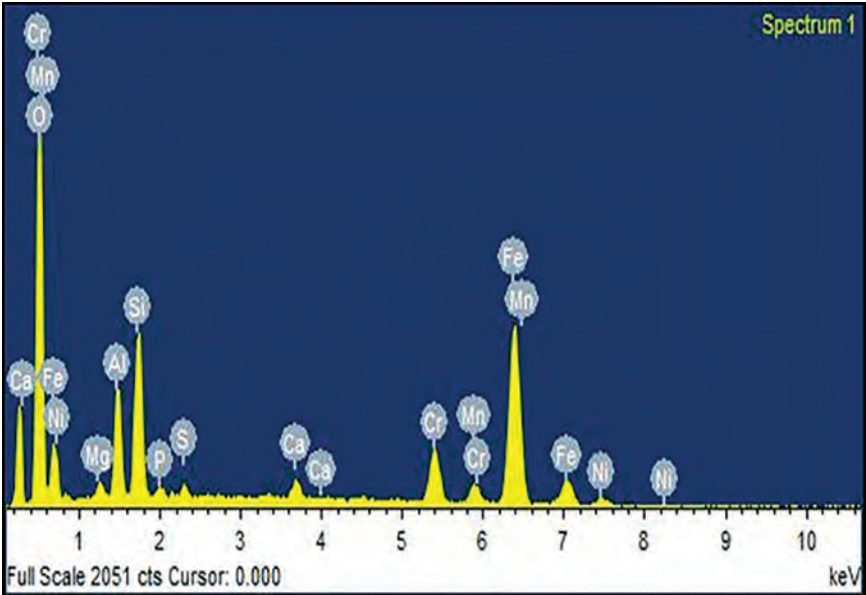


Fig. 5.14 EDS spectrum for outer surface of a superheater tube sample

Table 5.3 Elemental composition of outer surface of superheater tube

Element	Amount, wt%	Element	Amount, wt%
Oxygen	14.28	Calcium	0.76
Magnesium	0.74	Chromium	8.62
Aluminum	6.01	Manganese	3.64
Silicon	8.63	Iron	52.22
Phosphorus	0.77	Nickel	3.75
Sulfur	0.60	...	...

Table 5.3 give a typical EDS spectrum of the surface of a superheater tube sample along with its elemental analysis. The data given in the table clearly shows a greater percentage of aluminum and silicon, pointing toward high ash content in the coal used.

The SEM-EDS method can also be used to obtain the relative elemental concentration for each element at different locations along a preselected line on the sample surface. The method is called *line profile analysis*. Here, the electron beam is scanned along a preselected line across the sample surface while x-rays are detected for discrete positions along the line. Analysis of the x-ray energy spectrum at each position provides plots of the relative elemental concentration for each element versus position along the line. Figure 5.15 shows the line scan EDS spectra for concentrations of carbon, chromium, nickel, and iron in a sensitized stainless steel sample.

Likewise, in the elemental mapping method, the characteristic x-ray intensity is measured relative to the lateral position on the sample. Variations in x-ray intensity at any characteristic energy value indicate the relative concentration for the applicable element across the surface.

5.4 Optical Emission Spectroscopy

Emission spectroscopy is a group of techniques for quantitative chemical analysis of metals and alloys. Optical emission spectroscopy is one of these techniques and can simultaneously determine the concentration of more than 40 elements in a sample. It is further defined as arc emission spectroscopy or spark emission spectroscopy depending on whether the emission of energy radiation is ensured by means of an arc or a spark. Light elements such as nitrogen, hydrogen, oxygen, and noble gases cannot be detected by this technique. The technique is used to analyze various elements present in a sample in the range of a couple of micrograms to several percentage points by weight of sample. It is a fast, accurate, and reliable method offering about 1 to 3% relative precision and a limit of

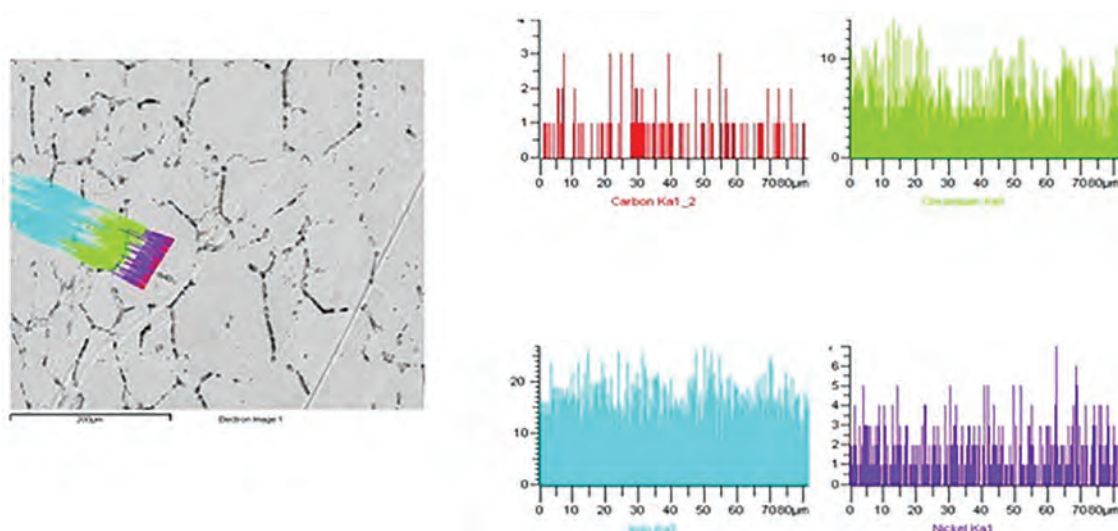


Fig. 5.15 Line scan EDS spectra for concentrations of carbon, chromium, nickel, and iron in a sensitized stainless steel sample

detection for most elements around 10 to 50 ppm. In general, the technique can be used for qualitative as well as quantitative elemental analysis of metals and alloys. The sample must be at least 25 mm (1 in.) in diameter with a ground and polished flat surface.

In spark emission spectroscopy (Fig. 5.16), high voltage is applied across a tungsten electrode and the test sample is maintained in an inert atmosphere. This generates an electric spark at the surface of the sample leading to vaporization and excitation of the sample atoms. When the sample atoms become excited, they jump to higher energy levels. Subsequently, when these atoms return to their original states, they emit light (photons) having characteristic wavelengths. The emitted light is then made to pass through a narrow vertical slit and is dispersed by means of a prism or a diffraction grating into its component wavelengths. Thus, a spectrum of light of different wavelengths is obtained. Within the spectrum, the wavelength of emitted light is characteristic of or specific to an element. For each element, a photomultiplier tube is placed at its characteristic wavelength. Photomultiplier tubes act as detectors and simultaneously measure the light intensity at wavelengths characteristic of each element.

The positions (in terms of the wavelength) and intensities of the lines produced are compared with the lines produced by suitable standard samples of known composition. By proper calibration it is possible to obtain the concentration of different elements in a sample from their observed line intensities. The presence of characteristic lines at certain

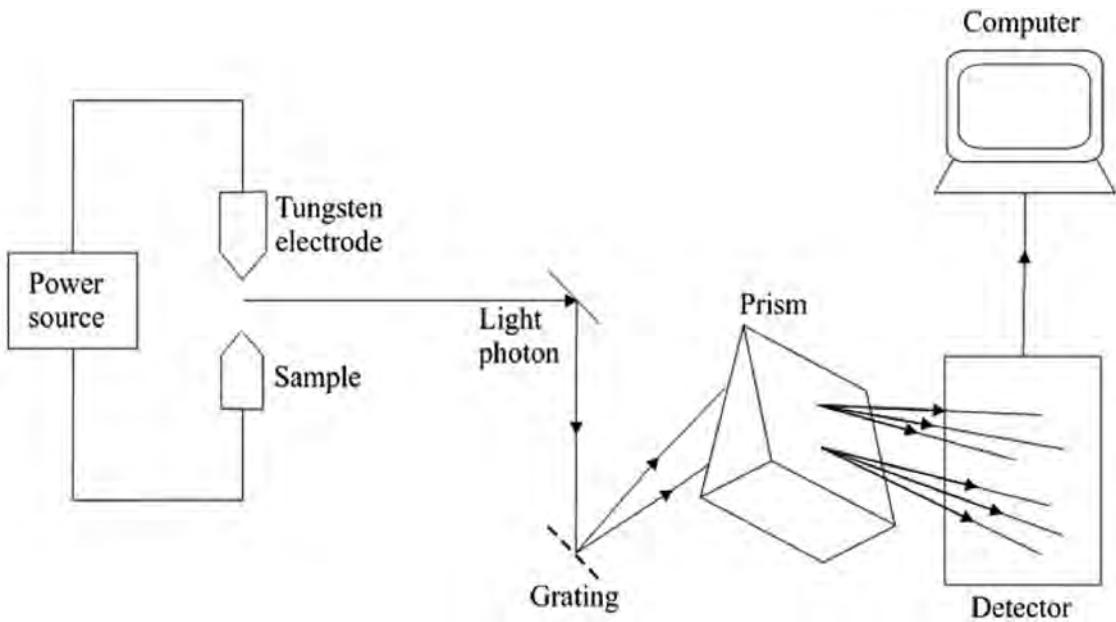


Fig. 5.16 Schematic of a spark emission spectrometer. Source: Ref 5.11

specific wavelengths provides qualitative data, whereas their intensity gives the concentration (i.e., amount) of each element present, enabling quantitative analysis of the sample. Both laboratory-type stationary spectrometers as well as portable spectrometers are available commercially. The emission spectrometer is thus a very useful tool for quick and reliable analysis of metals and alloys not only during production but also for on-site use for failure investigation.

5.5 Atomic Absorption Spectroscopy

Atomic absorption spectroscopy (AAS) is an analytical technique used for trace analysis of about 60 to 70 different elements in a solution using water or organic liquids as the solvent. Atomic absorption spectroscopy, being a highly sensitive technique, is capable of measuring the concentration of an element in a sample present in ppm to ppb levels. By conventional flame atomic absorption spectroscopy/spectrometry, only one element can be analyzed at a time. From a failure investigation point of view, the importance of this technique is in terms of estimation of metals such as sodium, calcium, magnesium, iron, silicon, and aluminum in boiler feed water.

Atomic absorption spectroscopy is one of several optical spectroscopy techniques and involves the measurement of change in the energy of an

atom as a result of absorption of a radiation of a certain wavelength. The electrons present in an atom have definite energy levels. The energy is released or absorbed when electrons in an atom move from one energy level to another. When an electron moves from a higher to a lower energy level, energy is released, whereas when it jumps from a lower to a higher energy level, energy is absorbed by the atom. The amount of energy released or absorbed is element specific.

The AAS technique is used for determining the concentration of an element in the solution of a sample and is governed by the Beer-Lambert law. According to the Beer-Lambert law, “The absorbance of a beam of collimated monochromatic radiation in a homogeneous isotropic medium is proportional to the absorption path length, and to the concentration” (Ref 5.12). Atoms of different elements present in a sample absorb characteristic wavelengths of light. Therefore, analyzing a sample to see whether it contains a particular element or not means using light from that element. This confirms the presence or absence of that element in the sample. The amount of light absorbed is proportional to the number of atoms of that element present (i.e., concentration) in the sample. A calibration curve is therefore developed by running several samples of known concentration of a certain element under the same conditions as the unknown. The amount of light absorbed by the unknown is compared with the calibration curve to calculate its concentration in the sample.

An atomic absorption spectrometer includes a radiation or light source, a nebulizer that acts as a source of atoms, a monochromator to isolate the wavelength of interest, and a detector for measuring the specific light absorbed. Figure 5.17 is a schematic of a flame AAS setup.

A hollow cathode lamp (HCL) is used as a light emission source and produces the line spectrum for the specific element of interest. An AAS instrument has several HCLs (also known as source lamps), each one for a different element or group of elements. The lamps are mounted on a rotating turret, enabling easy selection of a particular lamp per the requirement. When high voltage is applied across the argon-filled lamp housing an anode and cathode (made up of metal as the element to be detected), the argon is ionized. The ionized gas particles in turn eject metal atoms from the cathode to form a vapor. Some of these ejected atoms are in an excited state and emit light (in the form of a spectrum) with the frequency characteristic to the metal.

The light emerging from the HCL then passes through the sample (present as gas atoms in the flame). In order to achieve this, the sample, which is in the form of a solution, is first sprayed into an air-acetylene flame by means of a device called a nebulizer. The fine sample droplets produced by the nebulizer are vaporized and then atomized (i.e., broken down into individual atoms) by the flame. The light coming from the HCL will be absorbed if it meets atoms of the same element in its path. The degree

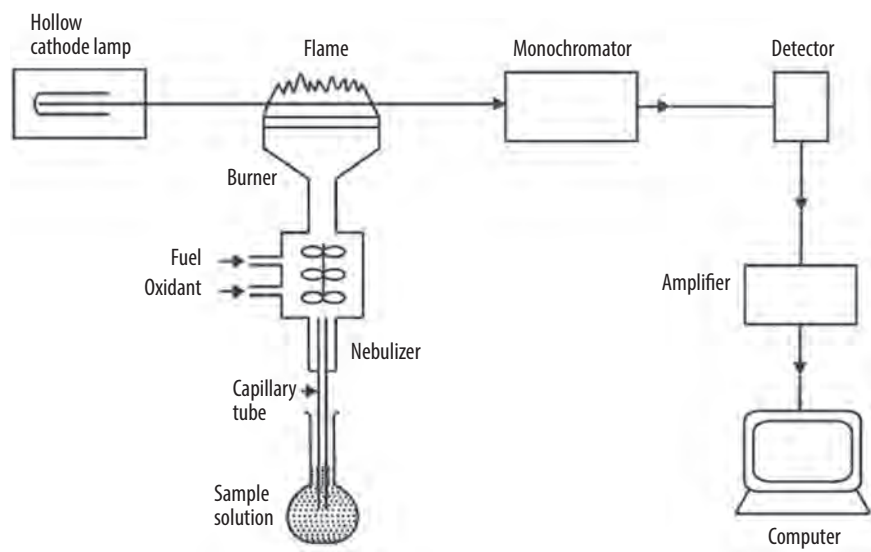


Fig. 5.17 Schematic of flame atomic absorption spectrometer. Source: Ref 5.13

of absorption is proportional to the concentration of the atoms present in the sample.

The light spectrum is then passed through a monochromator. Depending on the element to be detected, a specific wavelength of light is selected by means of a monochromator and all other wavelengths are excluded. This is the wavelength that is absorbed by the sample atoms in the flame. This enables the determination of the selected element in the presence of others. Finally, the light selected by the monochromator is directed onto a detector.

Atomic absorption spectroscopy instruments make use of either a set of photomultiplier tubes or solid-state detectors. The detector converts the light signal into an electrical signal proportional to the light intensity. A correlation is developed between the amount of light absorbed and the concentration of analytes present in the known standard samples. The data generated is used to determine the concentration of analytes in an unknown sample by measuring the amount of light they absorb.

5.6 X-Ray Fluorescence Spectroscopy

X-ray fluorescence spectroscopy (XRF) is a technique used for the determination of elemental composition of materials, qualitatively or quantitatively. The sample for XRF analysis may be in the form of a solid, powder, liquid, or emulsion. The detection range covers all elements from boron to uranium and the concentration can range from 100% down to the ppm level. X-ray fluorescence spectroscopy is used for highly accurate

determination of the major elements present in a given sample and also to obtain a broad elemental survey of the sample composition. The measurement accuracy of this technique is $\sim 0.1\%$ of the major elements present. The main advantage of XRF spectroscopy is that it is a nondestructive, multielemental, fast, and cost-effective method for elemental analysis of various materials including metals and alloys.

There are two main types of XRF instruments available in the market, namely, energy dispersive (EDXRF) and wavelength dispersive types. Energy dispersive spectrometers measure x-ray intensity as a function of energy, whereas wavelength dispersive spectrometers measure x-ray intensity as a function of wavelength. While energy dispersive spectrometers are faster and less expensive, wavelength dispersive spectrometers are more sensitive and have higher resolution. Most of the commercial machines are EDXRF.

An EDXRF system consists of an x-ray excitation source, a sample chamber, a silicon (lithium) detector, amplifiers, and a multichannel pulse height analyzer (Fig. 5.18).

The source of x-ray radiation may be an x-ray tube or a radioisotope such as Fe-55, Co-57, Cd-109, or Am-241. The radioisotopes emit x-rays of definite energy. Therefore, to analyze a broad range of elements, a combination of radioisotope sources is necessary.

For chemical analysis by XRF, the material is exposed to x-rays or gamma rays of high energy, and as the x-rays (or photons) strike an atom (or a molecule) in the sample, energy is absorbed by the atom. If this energy is high enough, a core electron (i.e., an inner shell electron) is ejected out of its atomic orbital. An electron from an outer shell then jumps into the unoccupied inner shell to fill the vacancy left behind, as demonstrated in Fig. 5.19(a). The energy difference between the two shells is given off as an x-ray photon of fixed, characteristic energy that can be detected by a fluorescence detector. As the electron energy levels are characteristic of the atom, in turn the energy of the emitted photon is characteristic of

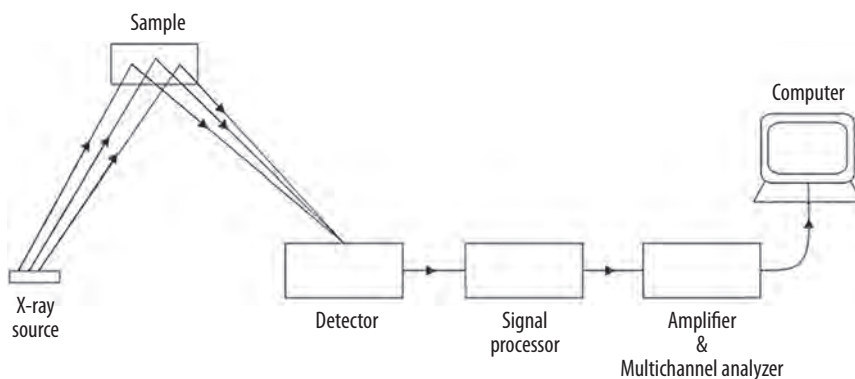


Fig. 5.18 Schematic of typical EDXRF setup. Source: Ref 5.14

the atom of each element. The x-ray spectrum acquired during the above process reveals a number of characteristic peaks. A typical XRF spectrum is given in Fig. 5.19(b).

In this spectrum, the energy of the peaks (i.e., the location of the peak on the x-axis) enables the identification of the elements present in the sample (qualitative analysis), while the intensity of the peaks (as given by

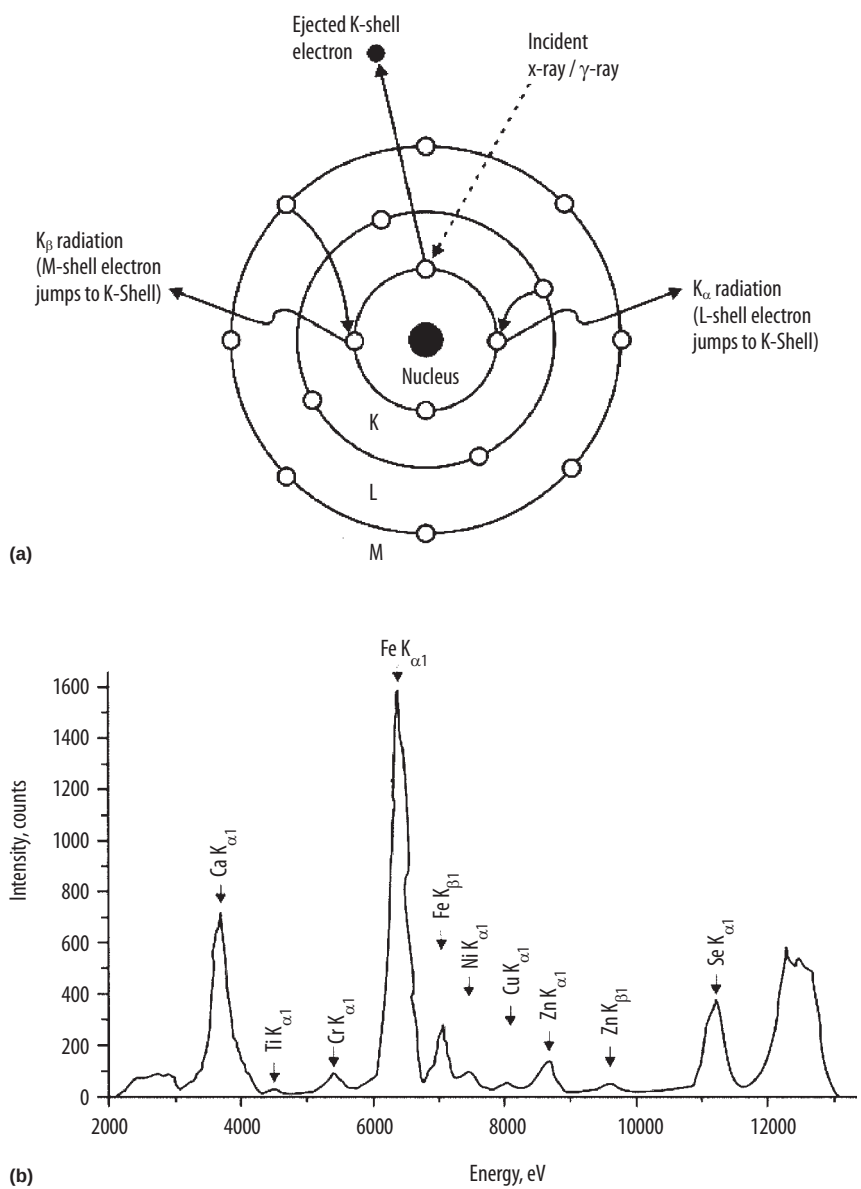


Fig. 5.19 (a) Underlying principle of XRF (Source: Ref 5.15) and (b) typical XRF spectrum of a rock sample. Source: Ref 5.16

the height of the peak/fluorescence count) provides the elemental concentration (semiquantitative or quantitative analysis).

Thus, qualitative analysis involves identifying atoms present in a sample by associating observed characteristic lines with their atoms. Quantitative analysis involves determining the amount of each atom present in the sample from the intensity of measured characteristic x-ray lines.

For failure investigation of boiler tubes, XRF proves to be a useful technique for analyzing boiler water chemistry mainly for elements such as calcium, sodium, potassium, and chlorine.

5.7 X-Ray Diffraction

5.7.1 Basic Fundamentals

One of the ways to classify different solids is based on the manner in which atoms or ions are arranged in the solid. Accordingly, different solids are classified as either crystalline or amorphous. In crystalline solids, there is periodicity in arrangement of atoms such that both short and long range ordering of atoms prevails (i.e., the nearest atoms to a reference atom and the farthest atom both have the same surrounding). Contrary to this, amorphous solids such as glass or asphalt do not have periodicity in atomic arrangement; short range order exists but long range order does not.

When a beam of light falls on an atom, the atom is scattered. During scattering, radiation is first absorbed and then emitted in different directions. Besides scattering, a light beam undergoes diffraction when it meets an obstacle. Diffraction of light is caused by bending of light around the edge of an object, leading to the development of an interference pattern.

X-rays also undergo diffraction in a similar manner to light. In general, particles of media such as light, sound, or electromagnetic radiation, including x-rays and gamma rays, when made to fall on small moving particles such as atoms, neutrons, and electrons, give rise to diffraction. Diffraction is the bending and spreading of waves around the obstacles. Diffraction involves a change in the direction of waves around a barrier in their path. Such a behavior is the result of interference (a phenomenon observed wherein superimposed waves are reinforced, causing constructive interference, or where waves cancel each other out due to destructive interference) and is most pronounced when the wavelength of the radiation is comparable to the linear dimensions of the obstacle.

The wavelength of visible light is in the range of 4000 to 7000 Å (i.e., 400 to 700 nm), whereas x-rays have a wavelength in the range of 0.5 to 2.5 Å (0.05 to 0.25 nm). The distances between the atoms in metals and alloys range from 2.0 to 3.0 Å (0.2 to 0.3 nm). This close match on length scales makes x-rays suitable for the study of crystalline materials using x-ray diffraction (XRD) principles. The scattering of x-rays by atoms in a crystalline

solid produces a diffraction pattern, which contains information about the atomic arrangement within the crystal. An amorphous material such as glass does not have a periodic array and does not produce a diffraction pattern. About 95% of all solid materials are crystalline. Every crystalline substance gives a diffraction pattern. The same substance always gives the same pattern, and in a mixture of substances, each one produces its pattern independent of the others. The XRD pattern of a pure substance is, thus, like a fingerprint of the substance.

X-ray diffraction has therefore emerged as one of the most powerful tools for qualitative and quantitative analysis of phases present in a crystalline solid. It is ideally suited for characterization and identification of polycrystalline phases. The XRD technique is used specifically for phase analysis and not just elemental analysis. For example, conventional methods of analysis for a steel sample will report the amount of elements such as iron, carbon, manganese, chromium, and nickel that it contains. But these methods are unable to determine whether the phases present in this steel are austenite, pearlite (a mixture of ferrite and cementite), bainite, or martensite. Apart from metallography, only XRD can provide this information.

Oxidation and scaling are very common phenomena observed in steels exposed to an oxidizing atmosphere at high temperature. The constituents of the scale formed may comprise phases such as wustite (FeO), hematite (Fe_2O_3), or magnetite (Fe_3O_4) depending on the service conditions. Classical methods of chemical analysis will report only the elements present in the scale (i.e., iron and oxygen), and not their form. It is XRD analysis that defines the composition of the scale from the point of view of phases formed between the elements iron and oxygen. Figure 5.20 gives an XRD pattern for a scale formed on the surface of steel during hot rolling, showing diffraction peaks for Fe_2O_3 and Fe_3O_4 besides Fe (Ref 5.17). Similarly, Fig. 5.21 shows the XRD profile for a low-alloy steel that has undergone corrosion. Various oxide phases, FeO , Fe_3O_4 , and FeCr_2O_4 , form as a result of corrosion, and are marked on the diffraction peaks.

X-ray diffraction has also proven to be a useful tool in the analysis of materials that have the same chemical composition but different crystal structures. For example, titanium dioxide has three allotropic forms namely, anatase, brookite, and rutile. All of these allotropic forms have the same chemical formula, TiO_2 , but different crystal structures. Anatase has a tetragonal crystal structure, whereas brookite has an orthorhombic structure. A close look at the XRD profiles for these two minerals (Fig. 5.22) shows that the position and intensity of diffraction peaks for these two materials are different even though they have the same chemical formula (Ref 5.19). This is because they have different crystal structures, and therefore a different set of planes with different interplanar spacing (d values); hence, they produce different XRD patterns.

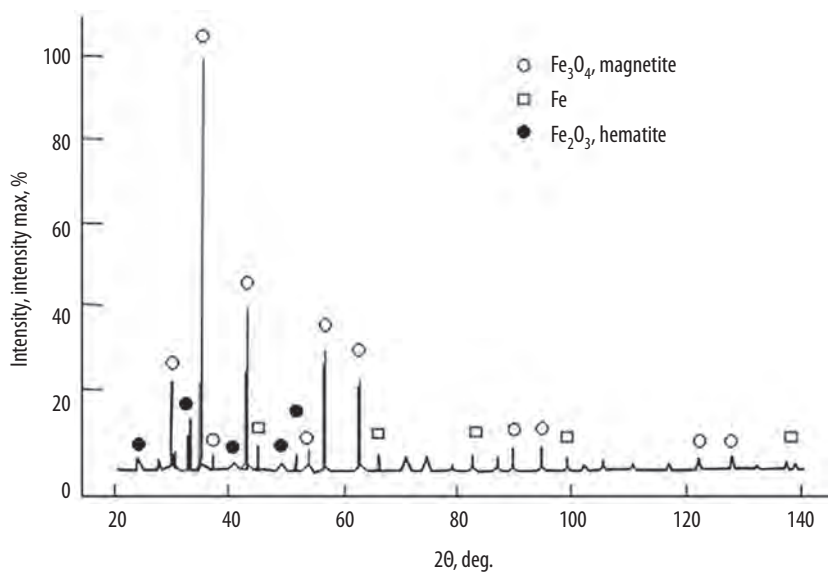


Fig. 5.20 X-ray diffraction pattern of a scale on hot-rolled steel. Source: Ref 5.17

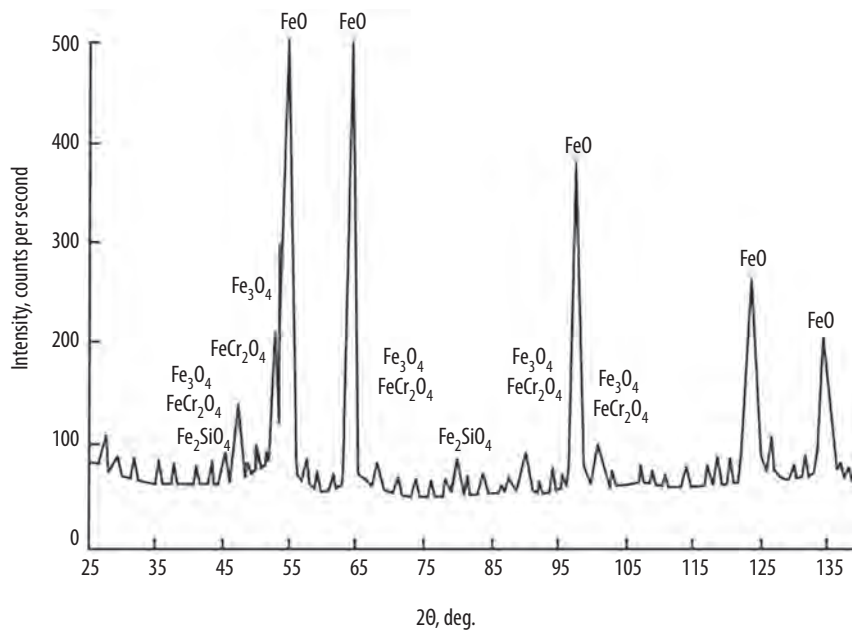


Fig. 5.21 X-ray diffraction profile for corrosion products formed on steel surface. Source: Ref 5.18

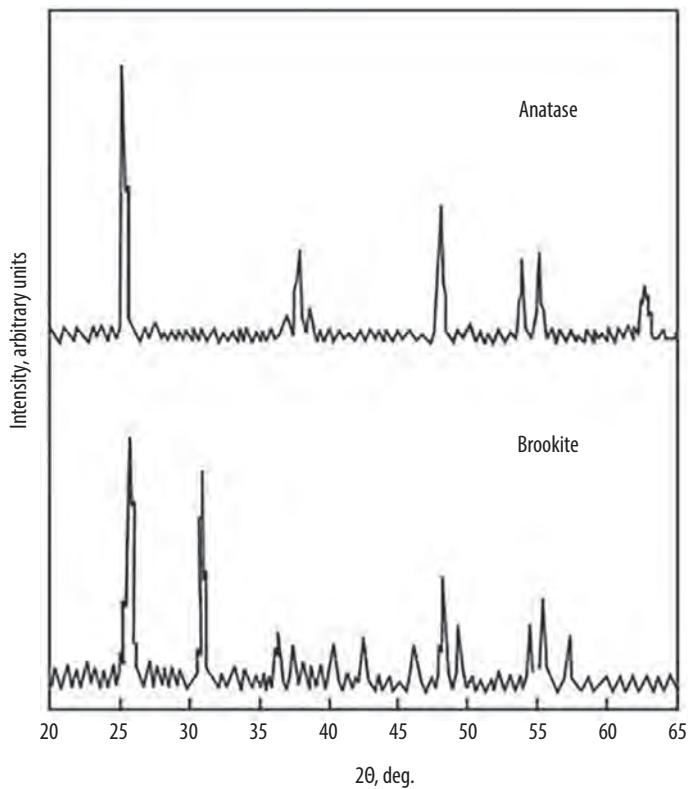


Fig. 5.22 X-ray diffraction pattern of anatase and brookite. Source: Ref 5.19

X-ray diffraction is a unique, nondestructive, fast, and reliable technique for qualitative and quantitative phase analysis of crystalline solids.

5.7.2 Production of X-Rays

X-rays, by virtue of their short wavelength and high depth of penetration, are used in diffraction studies. Generation of x-rays involves emission of an electron beam from a hot filament (such as tungsten) by a process of thermionic emission. These electrons are then bombarded against a water-cooled metal target usually made up of copper (but also at times platinum, tungsten, molybdenum, or chromium) under high vacuum and high accelerating voltage conditions. Figure 5.23 shows the schematic of the Coolidge x-ray tube used for production of x-rays.

The incident electron beam ionizes the target metal atom such that the electrons from its K-shell are knocked off and their positions are filled up by the electrons dropping down from the L- or M-shell, as displayed in Fig. 5.24(a).

Interaction of an incident electron beam with the electrons of the target metal atoms gives two types of radiation, continuous or white radiation (with a variable wavelength) and characteristic radiation (with a fixed wavelength), shown as K_α and K_β in Fig. 5.24(b). For diffraction studies, x-rays with fixed wavelengths are used. The wavelength of characteristic radiation is a function of the target metal, as shown in Table 5.4.

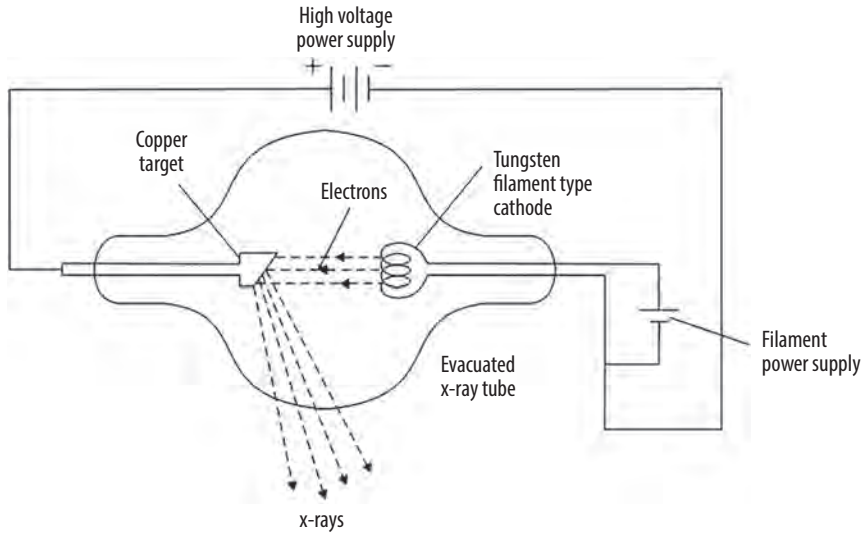


Fig. 5.23 Schematic of Coolidge x-ray tube used for production of x-rays

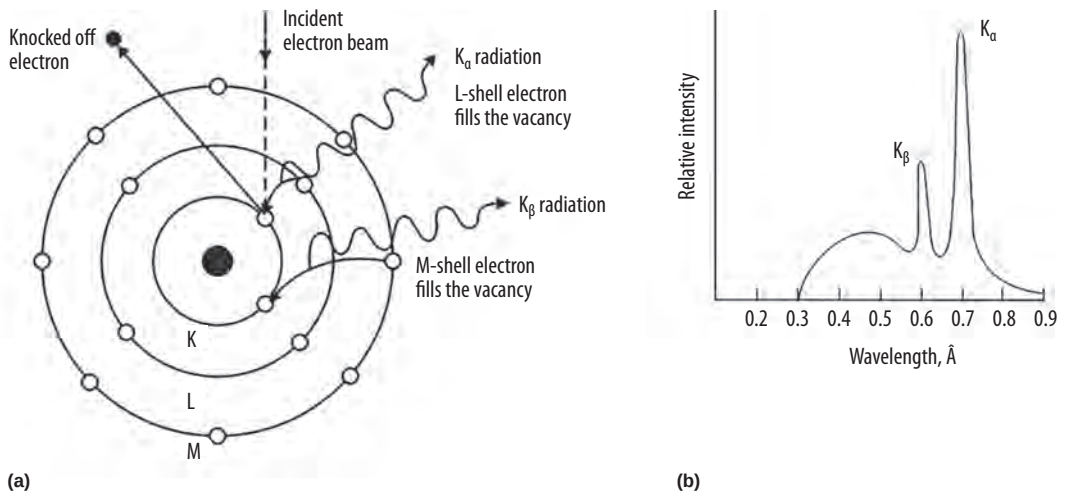


Fig. 5.24 (a) Mechanism of x-ray generation (Source: Ref 5.20) and (b) typical x-ray spectrum from copper target. Source: Ref 5.21

Table 5.4 Typical data on target material and characteristic wavelength

Target metal	K _α wavelength, Å	Target metal	K _α wavelength, Å
Cu	1.5405	W	0.2110
Mo	0.7093	Co	1.7889
Cr	2.2910	...	...

Though the sample for diffraction studies can be in the form of bulk solids, thin films, or coatings, ideally the sample should be in powder or polycrystalline form. The sample should consist of finely ground powder particles with tens of thousands of randomly oriented crystals or grains less than 10 μm in size. The powder sample is pressed over a ground glass sample holder so as to have a smooth flat surface.

5.7.3 *Bragg’s Law and Diffraction of X-Rays*

When a beam of x-rays is focused on a single isolated atom, the electrons around the atom start to oscillate with the same frequency as the incoming beam. In almost all directions there is destructive interference (i.e., the combining waves are out of phase and there is no net energy exiting the atom). However, the atoms in a crystal are arranged in a regular pattern that forms an ordered array. In such an ordered array of atoms, there are planes of high atomic density (i.e., more atoms per unit area of the plane) and in turn planes of high electron density. These electrons scatter the incident monochromatic beam of x-rays in such a way that the scattered beams may add together in a few directions and reinforce each other to give diffraction maxima. This phenomenon is known as constructive interference. The physicist Bragg derived the condition for constructive interference of x-rays scattered from a set of parallel lattice planes. For every set of diffracting planes, there will be one diffraction peak in the XRD pattern of that sample. Bragg’s law is derived as follows:

Two parallel planes of atoms 1–1’ and 2–2’ are shown in Fig. 5.25 with the same *h*, *k*, and *l* Miller indices and separated by the interplanar spacing *d_{hkl}*. A monochromatic beam of x-rays of wavelength **λ** strikes these two planes at an angle **θ**. Two rays in this beam, labeled R₁ and R₂, are scattered by atoms M and N.

Constructive interference between the diffracted rays R₁’ and R₂’ occurs at an angle **θ** to the planes, only when the path difference between the waves R₁–M–R₁’ and R₂–N–R₂’ (i.e., SN + NT) is equal to an integral multiple (*n*), of wavelength **λ**:

$$\text{i.e., } n\lambda = SN + NT$$

$$\text{or } n\lambda = d_{hkl} \sin \theta + d_{hkl} \sin \theta$$

$$\text{i.e., } n\lambda = 2d_{hkl} \sin \theta$$

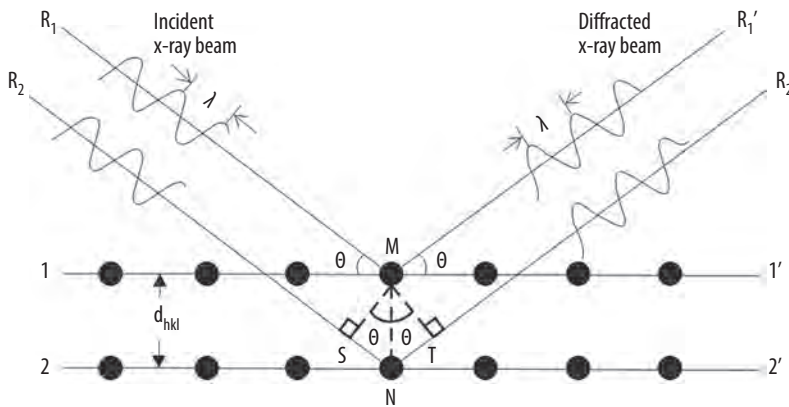


Fig. 5.25 Schematic showing basic principle of x-ray diffraction.

The equation $n\lambda = 2d \sin \theta$ is known as Bragg's law, where

n = an integer

λ = the wavelength of the x-rays

d = the interplanar spacing generating the diffraction

θ = the diffraction angle

The λ and d are measured in the same units, usually angstroms. For parallel planes of atoms, with interplanar spacing d_{hkl} between the planes, constructive interference occurs only when Bragg's law is satisfied.

The instrument employed for phase analysis using XRD is called an x-ray diffractometer. Because the sample used here is in powder form, this method is called the powder diffraction method. In a diffractometer, a monochromatic (single wavelength) beam of x-rays is focused on the surface of a powder sample pressed on a ground glass sample holder, and the diffracted beam is received by a detector that measures its intensity. The angle of incidence of the x-ray beam is continuously changed and a spectrum of diffracted beam intensity versus the angle between incident and diffracted beams is produced. This is how an XRD pattern for any material is obtained.

Fig. 5.26(a) is a schematic diagram of a horizontal-goniometer-type x-ray diffractometer system used for diffraction of powder samples. It consists of an x-ray tube for generation of x-rays. Before the x-rays interact with the sample, they are passed through incident-beam optics that has a set of apertures and filters. There is a goniometer that is a rotating turntable to hold and rotate the sample, optics, detector, or x-ray tube in the horizontal plane as desired. The sample is mounted on a sample holder. The incident x-ray beam strikes the sample at an angle " θ " and interacts with the atoms of the crystals or grains of the sample. It is then diffracted through

twice (i.e., 2θ). The diffracted beam, after passing through the receiving side optics, enters the detector, where the number of x-rays diffracted by the sample is counted. The detector records the values of angle 2θ at which the families of the lattice planes diffract the x-ray beams and in addition, the intensity of the respective diffracted beam is measured and expressed as counts or counts per second. An x-ray diffraction pattern so obtained is a plot of the intensity of diffracted x-rays versus angular position 2θ (Fig. 5.26b). The diffraction pattern is characteristic of and unique to the sample material.

Though normally the XRD patterns are collected as 2θ versus absolute intensity, it is customary to report results of XRD analysis as relative intensity versus interplanar spacing. The position of the diffraction peak in an XRD pattern is determined by the interplanar spacing (i.e., the value of d_{hkl}). Bragg's equation is used to convert the observed value of 2θ corresponding to each peak position, to d_{hkl} . The intensity of the diffraction peak is governed by the arrangement of atoms in the crystal and in turn by the number of electrons. In a given polycrystalline sample, crystallographic planes with high electron density (i.e., those with high atomic density) will reflect strongly and give a more intense peak, whereas those with low electron density will have weak peaks. The relative intensity is obtained by dividing the absolute intensity of every peak by the absolute intensity of the most intense peak, and then expressing a percentage.

5.7.4 Phase Identification Using X-Ray Diffraction

The most important application of the XRD technique from a failure investigation point of view is qualitative and quantitative phase analysis.

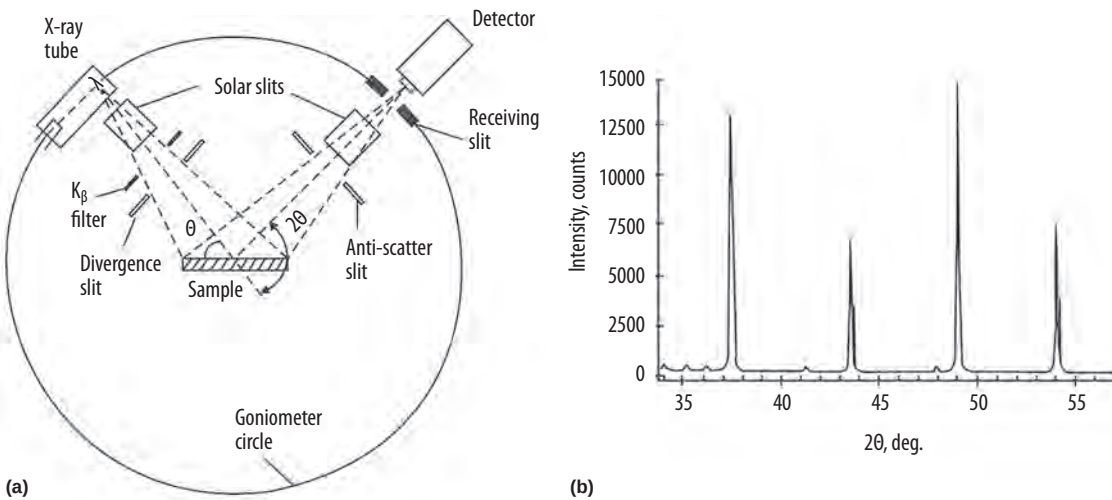


Fig. 5.26 (a) Schematic diagram of a diffractometer system and (b) typical x-ray diffraction pattern

Phase analysis is achieved by comparing the positions and intensities of the observed diffraction peaks in a test sample against a library of diffraction data for known crystalline materials. Once the diffraction pattern for a test sample is procured, phase identification is accomplished by comparing the spectrum (i.e., either 2θ or d values of diffraction peaks and their relative intensities) obtained for a test sample with spectra of known crystalline substances provided by the International Center for Diffraction Data (ICDD) based in Geneva. The ICDD was formerly known as the Joint Committee on Powder Diffraction Standards (JCPDS). These organizations maintain a powder diffraction database for a large number of inorganic and organic samples. Currently, the Powder Diffraction File (PDF) database contains over 300,000 diffraction patterns and has two versions: PDF-I and PDF-II. The PDF-I database comprises information on the d -spacing, chemical formula, and relative intensity for different known compounds; the PDF-II database contains full information on a particular phase, including cell parameters. Modern diffractometers are equipped with search-match programs that can be used to quickly compare the diffraction data of a test sample with the patterns of known compounds included in the database. A typical data card for sodium chloride is shown in Fig. 5.27.

①	5-628	②	③	④							
	d	2.82	1.99	1.63	3.26	NaCl					
	I/I_1	100	55	15	13	Sodium Chloride					
						(Halite) ★					
⑤	Rad. CuK α_1 λ 1.5405 Filter Ni Dia. Cut off I/I_1 Diffractometer I/I cor. Ref. Swanson and Fuyat, NBS Circular 539, Vol. 2, 41 (1953)					d Å	I/I_1	hkl	d Å	I/I_1	hkl
	Sys. Cubic S.G. Fm3m (225) a_0 5.6402 b_0 c_0 A C α β γ Z 4 Dx 2.164 Ref. Ibid.					3.258	13	111			
⑥											
⑦	e α $n\omega/\beta$ 1.542 e γ Si gn 2 ν D mp Color Colorless Ref. Ibid					2.821	100	200			
	An ACS reagent grade sample recrystallized twice from hydrochloric acid. X-ray pattern at 26°C Merck Index, 8th Ed., p. 956 Halite-galena-periclase group.					1.994	55	220			
⑧											
						1.701	2	311			
						1.628	15	222			
						1.410	6	400			
						1.294	1	331			
						1.261	11	420			
						1.1515	7	422			
						1.0855	1	511			
						0.9969	2	440			
						0.9533	1	531			
						0.9401	3	600			
						0.8917	4	620			
						0.8601	1	533			
						0.8503	3	622			
						0.8141	2	444			

The information furnished in the data card may be summarized as:

- File number
- Three strongest diffraction peaks
- Lowest-angle line
- Chemical formula and name of the compound
- Data on diffraction method used
- Crystallographic data
- Optical and other data
- Data on specimen
- Data on diffraction pattern

According to the Hanawalt method for qualitative phase analysis, because more than one material can have the same or nearly the same d value, each material is characterized by its three strongest diffraction peaks (d_1 , d_2 , d_3). The steps to identifying an unknown phase in a material are:

- Identifying the three most intense peaks in the recorded pattern of the test sample
- Designating them as d_1 , d_2 , and d_3
- Locating the d_1 group in the Hanawalt Search Manual
- After finding a close match for d_1 , looking for the closest match for d_2
- Repeating the process for d_3 and also matching the intensities of this peak
- When full agreement is obtained, the unknown test sample is identified

The XRD method is also used for quantitative phase analysis. The quantitative estimation of phases in a test sample involves measurement of the intensity of various diffraction peaks present. The fact remains that the intensity of the diffraction peaks of a particular crystalline phase in a phase mixture depends on the weight fraction of that phase in the mixture. Therefore, it is possible to obtain the weight fraction (i.e., amount) of a phase in a given test sample by measuring the intensities of peaks assigned to that phase. Instead of using values of absolute intensity, the integrated intensity is preferred as it gives greater precision. The integrated peak intensity can be obtained by measuring the area under the peak and is estimated using the diffractometer software. The phases in single and multiphase materials are quantitatively determined using pattern calculation and pattern fitting methods (Rietveld refinement). For further details on quantitative phase analysis, any title on x-ray diffraction or structural metallurgy may be consulted.

5.8 X-Ray Photoelectron Spectroscopy or Electron Spectroscopy for Chemical Analysis

X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis, is a widely used quantitative spectroscopic

surface analysis technique. X-ray photoelectron spectroscopy can determine the elemental composition of the surface of solids. It is the only technique that provides information on chemical bonding within a material surface. With the help of XPS, information can be obtained on chemical states by analyzing the data on variation in binding energies, or chemical shifts of the photoelectron lines. Chemical shift is the change in the binding energy of a core electron of an element due to a change in the chemical bonding of that element. X-ray photoelectron spectroscopy can be employed for the detection of a large number of elements from lithium (having an atomic number of 3) and above. Unlike SEM, very little surface charging occurs during XPS, which makes this technique useful for both electrically conductive and nonconductive samples.

X-ray photoelectron spectroscopy is a surface-sensitive technique and has a typical sampling depth of 30 to 100 Å from the surface of the sample. In XPS, only electrons that are generated near the surface can escape and be detected. They have relatively low kinetic energy. Those electrons originating from a greater depth below the surface cannot escape with sufficient energy to be detected. Detection limits for most of the elements ranges from parts per thousand (ppt, i.e., 0.1%) to parts per million (ppm, i.e., 0.0001%).

X-ray photoelectron spectroscopy is based on the principle of photoelectric effect. Every material is composed of atoms of the respective elements present in it and each atom has a set of electrons revolving around its nucleus in different orbits. Each core electron in an atom has a characteristic binding energy depending on its relative position with respect to the nucleus. If a beam of x-rays having photons with a sufficiently large amount of energy is directed onto the sample atoms, the energy of the x-ray photon is absorbed by the core electron of the atom. In turn, the core electron (called a photoelectron) then escapes from the atom and is emitted out of the surface of the sample. The energy of the emitted photoelectron depends on the energy of the incident x-ray photon and the binding energy of the electron in a given orbit of that atom. The binding energy of the emitted photoelectron is characteristic of the element from which it is emitted. As a result of this, each element has a characteristic set of peaks in the photoelectron spectrum at kinetic energies determined by the energy of the incident x-ray photon and the binding energy of the respective core electron per the following relationship.

Based on the principle of energy conservation, the relationship governing the interaction of a photon with a core level is:

$$KE = h\nu - BE - \Phi$$

$$\text{i.e., } BE = h\nu - KE - \Phi$$

where

KE = the kinetic energy of the ejected photoelectron

$h\nu$ = the characteristic energy of the x-ray photon

BE = the binding energy of the atomic orbital from which the electron is ejected

Φ = the spectrometer work function

The appearance of peaks at particular binding energy values in the spectrum therefore indicate the presence of a specific element, whereas the intensity of the peaks denotes the concentration of the element within the sample. Figure 5.28 shows a typical XPS spectrum for silver coating on a substrate. X-ray photoelectron spectroscopy can thus be used for quantitative analysis of the surface composition.

The sample that is examined is subjected to an ultra-high vacuum (higher than or equal to 10^{-9} torr) and exposed to a low-energy, monochromatic source of radiation (photons of fixed energy). A typical x-ray source used is AlK_{α} with energy of 1486.7 eV, or MgK_{α} radiation with energy of 1253.6 eV. In general, XPS uses soft x-ray (200 to 1500 eV) radiation to examine the core levels of sample atoms. Incident x-rays cause the ejection of core-level electrons from sample atoms. The kinetic energy distribution of the emitted photoelectrons (i.e., the number of emitted photoelectrons as a function of their kinetic energy) is obtained using an electron energy analyzer and reported as a spectrum. Each element

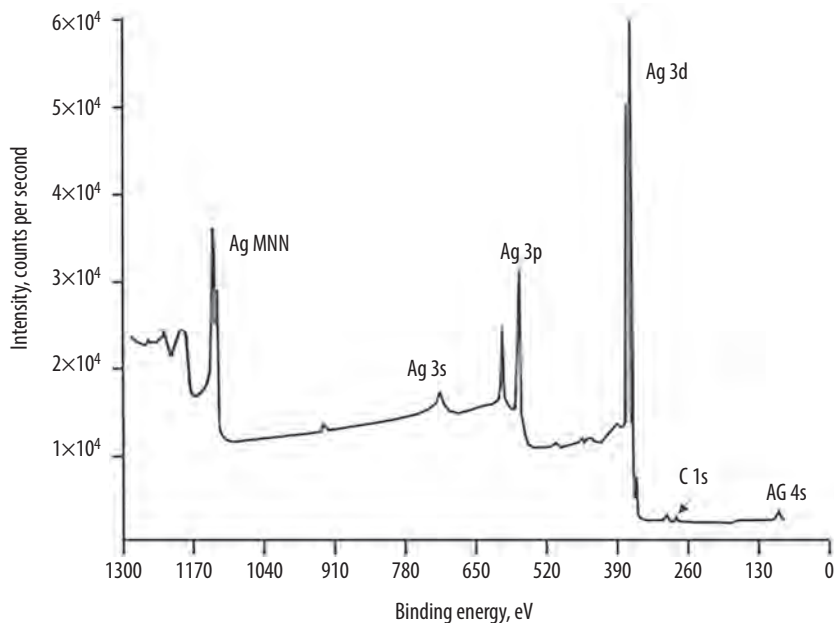


Fig. 5.28 Typical XPS survey scan spectrum of silver coating on a substrate.
Source: Ref 5.23

emits specific photoelectron energies, thus allowing fingerprinting of the material, and thereby making XPS a powerful elemental compositional analysis technique.

X-ray photoelectron spectroscopy is a very useful technique in failure investigation of boiler tubes. The internal surface of a boiler tube exposed to steam consists of a layer of iron oxide. This oxide layer may consist of magnetite (Fe_3O_4), hematite (Fe_2O_3), or wustite (FeO), or a combination thereof, depending on the temperature and the partial pressure of the steam. Through use of XPS, it is possible to ascertain the composition of the oxide layer. In an XPS spectrum for iron oxide, the position of $\text{Fe } 2p_{1/2}$ and $\text{Fe } 2p_{3/2}$ peaks depends on the ionic state (i.e., oxidation state) of Fe. The same is true for positions of their satellite peaks. By analysis of the position of these peaks in the XPS spectrum, it is possible to determine the ionic states of the iron and to determine the proportions of Fe^{3+} and Fe^{2+} ions, and in turn the relative proportion of Fe_3O_4 and Fe_2O_3 . Along similar lines, it is possible to analyze the type of oxide formed as a result of corrosion or scaling. X-ray photoelectron spectroscopy can also be used for investigation of failures of boiler tubes due to pitting and caustic gouging. Figure 5.29 gives XPS spectra for Fe 2p lines for various oxidation states of iron.

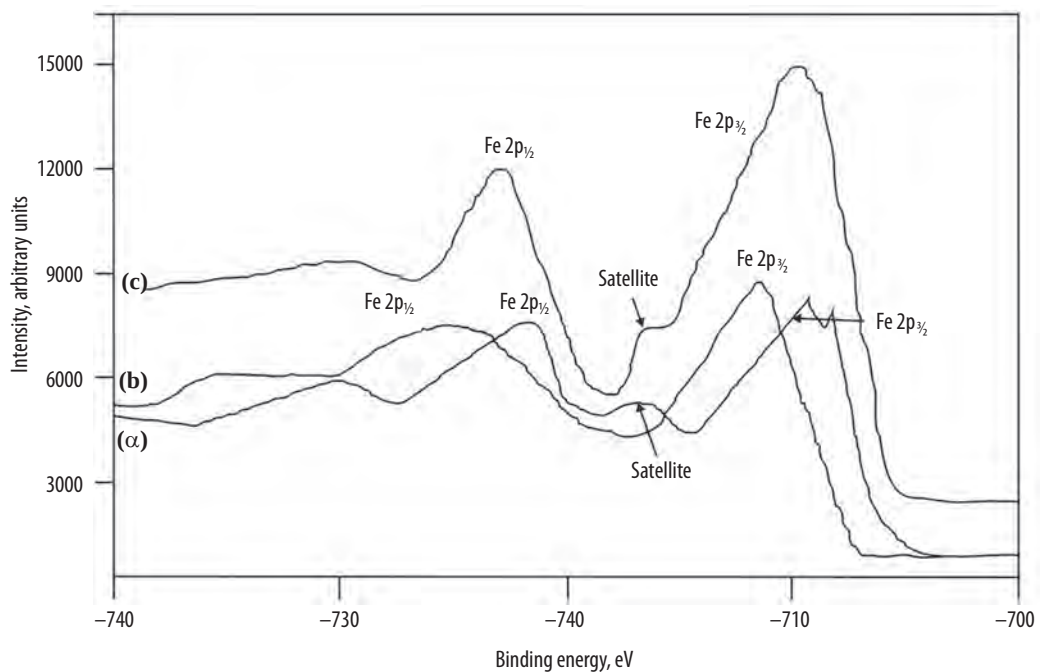


Fig. 5.29 XPS spectra for (a) Fe_2O_3 , (b) Fe_3O_4 , and (c) FeO . Source: Ref 5.24

5.9 Deposit Weight Density Determination

The water- and steam-side surfaces of boiler tubes are prone to scaling and deposition despite stringent control of the feedwater and condensate chemistry. For efficient heat transfer across the tube wall, the internal surfaces of boiler tubes must be kept clean and free of oxide scales and deposits. If the internal scales and deposits are not checked periodically, tube failure can occur by mechanisms such as *under deposit corrosion* and overheating.

How effective the boiler chemical treatment program is and if the boiler tubes need cleaning are judged by the deposit weight density (DWD) measurement. For this, the deposits from areas in the boiler or steam generator where the heaviest and most complex deposits have accumulated are removed and subjected to quantification. Preferably, the location selected for DWD measurement is the highest heat-flux area and/or the low-flow area of the boiler.

There are three widely used methods for determining the specific DWD from the boiler and heat recovery steam generator tube surfaces: (A) a mechanical scraping and vibratory tool cleaning method; (B) a chemical solvent cleaning method; and (C) a glass bead blasting cleaning method. These methods are covered by ASTM D-3483-83 (2005) in *Standard Test Methods for Accumulated Deposition in a Steam Generator Tube* (Ref 5.25). They are based on the determination of the weight per unit area of water-side deposits on heat-transfer surfaces of boiler and steam generator tubes. The change in the weight of the tube divided by the water-affected area from where the deposits were removed gives the DWD in units of grams per square foot (g/ft^2).

Mechanical scraping and vibratory tool cleaning method (Test method A):

A vibrating tool physically removes the water-side deposits from a measured area of the tubing. The scraped deposits are collected and weighed. The weight of the deposits divided by the surface area of the tube gives the DWD.

Chemical solvent cleaning method (Test method B):

An inhibited acid such as hydrochloric acid is used to dissolve the water-side deposits from a selected area of the tube. The weight of the tube with deposits minus the weight of tube after chemical dissolution treatment, divided by the surface area of the tube, gives the DWD.

Glass bead blasting cleaning method (Test method C):

The tube sample is weighed, blasted with non-abrasive glass beads until the surface appears gray, and then reweighed. The weight change divided by the surface area of the tube is reported as the DWD.

Table 5.5 Typical recommendations on action to be taken for a measured deposit or scale density

Scale density mg/cm ² or (g/ft ²)	Recommended action
< 25 (23)	No action required
25–75 (23–70)	Chemically clean within one year
75–100 (70–93)	Chemically clean within three months
> 100 (93)	Chemically clean before further operation

Table 5.5 shows the typical recommendations on action to be taken for a range of scale density (Ref 5.26).

In addition to a measure of deposit loading, the DWD also provides information on the chemical composition of the deposits in the tube.

REFERENCES

- 5.1 Wikibooks, “Material Science/Material Characterization,” last modified May 2017, https://en.wikibooks.org/wiki/Materials_Science/Material_Characterization
- 5.2 “Standard Test Methods for Determining Average Grain Size,” ASTM E112-13, *Annual Book of ASTM Standards*, Vol 3.01, ASTM, 2013
- 5.3 H.E. Exner and H.P. Hougardy, *Quantitative Image Analysis of Microstructures: A Practical Guide to Techniques, Instrumentation and Assessment of Materials*, R Publications Ltd, 1988
- 5.4 Buehler Sum-Met, *The Science Behind Material Preparation—A Guide to Material Preparation and Analysis*, Buehler, 2007
- 5.5 “Standard Test Method for Determining Volume Fraction by Systematic Manual Point Count,” ASTM E562-11, *Annual Book of ASTM Standards*, Vol 3.01, ASTM, 2011
- 5.6 “Standard Test Methods for Determining the Inclusion Content of Steel,” ASTM E45-05, *Annual Book of ASTM Standards*, ASTM, 2005
- 5.7 “Standard Test Methods for Estimating the Depth of Decarburization of Steel Specimens,” ASTM E1077-14, *Annual Book of ASTM Standards*, Vol 3.01, ASTM, 2014
- 5.8 J. Komenda and R. Sandström, Assessment of Pearlite Banding Using Automatic Image Analysis: Application to Hydrogen-induced Cracking, *Materials Characterization*, Vol 31 (No. 3), 1993, p 143–153
- 5.9 B.L. Gabriel, *Scanning Electron Microscopy—A User’s Manual for Material Science*, American Society for Metals, 1985
- 5.10 Core Laboratories, “Electron Beam Sample Interaction,” last modified 2018, <http://www.corelab.com/ps/cms/images/environmental-sem2.jpg>
- 5.11 I.Z. Alzamil, “Arc-Spark Emission Spectrometry,” 2016, <https://i.ytimg.com/vi/LJub7fuBEYQ/maxresdefault.jpg>

- 5.12 IUPAC, *Compendium of Chemical Terminology*, 2nd ed. (the “Gold Book”), A.D. McNaught and A. Wilkinson, Eds., Blackwell Scientific Publications, 1997, <https://goldbook.iupac.org/html/B/B00626.html>
- 5.13 G. Prasanth, “Flame Atomic Absorption Spectrometer,” 2014, <https://image.slidesharecdn.com/prasanth-141007111927-conversion-gate01/95/atomic-absorption-spectrophotometry-15-638.jpg?cb=1412681932>
- 5.14 I. Campbell et al., The Use of EDXRF for Pharmaceutical Material Elemental Analysis,” 2012, <http://www.americanpharmaceuticalreview.com/1504-White-Papers-Application-Notes/124874-The-Use-of-EDXRF-for-Pharmaceutical-Material-Elemental-Analysis/>
- 5.15 Niton, “Principle of XRF,” last accessed 2016, <https://chem.libretexts.org/@api/deki/files/99701/XRF-Excitation-Model.png>
- 5.16 A. Ryser et al., Typical XRF Spectrum of a Rock Sample, *Geochemical Transactions*, Vol 6 (No. 1), American Institute of Physics, 2005, <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC1475786/figure/F5/>
- 5.17 M.J.L. Gines, G.J. Benitez, T. Perez, E. Merli, M.A. Firpo, and W. Eglil, Study of the Picklability of 1.8mm Hot-rolled Steel Strip in Hydrochloric Acid, *Lat. Am. Appl. Res.*, Vol 32, 2002, p 281–288
- 5.18 B.L. Bramfitt and A.O. Benscoter, *Metallographers Guide—Practice and Procedures for Irons and Steels*, ASM International, 2002, p 163
- 5.19 A. Di Paola, M. Bellardita, and L. Palmisano, Brookite, the Least Known TiO₂ Photocatalyst, *Catalysts*, Vol 3 (No. 1), 2013, p 36–73
- 5.20 “Mechanism of X-Ray Generation,” 2015, <http://ars.els-cdn.com/content/image/1-s2.0-S1882761614000258-gr1.jpg>
- 5.21 Brooks/Cole–Thomson, “X-Ray Spectrum From Copper Target,” 2006, http://images.slideplayer.com/25/7919337/slides/slide_26.jpg
- 5.22 Y. Liao, JCPDS Cards for XRD Analysis, *Practical Electron Microscopy and Database*, Figure 2496, Globalsino.com, 2006, <http://www.globalsino.com/EM/image1/2496.jpg>
- 5.23 T.I. Török, É. Kun, and D. Sós, “Nano Scale Characterization of Thin Immersion Silver Coatings on Copper Substrate,” NASF Surface Technology White Papers, Vol 79 (No. 8), 2015, p 1–11
- 5.24 T. Yamashita and P. Hayes, Analysis of XPS Spectra of Fe²⁺ and Fe³⁺ Ions in Oxide Materials, *Applied Surface Science*, Vol 254(8), 2008, p 2441–2449
- 5.25 “Standard Test Methods for Accumulated Deposition in a Steam Generator Tube,” ASTM D-3483-83, *Annual Book of ASTM Standards*, ASTM, 2005
- 5.26 M.D. Majnoui and A.E. Jaffer, Chemical Cleaning of an Industrial Boiler—An Overview, *The Analyst*, Vol 11 (No. 4), 2004

CHAPTER 6

Damage Mechanisms with Case Studies

6.1 Introduction

In coal-fired power plants, boiler tubes run over several kilometers of distance and are an important component of the entire system. These tubes are exposed to highly adverse conditions, including high skin temperatures, exposure to flame, corrosive and erosive conditions on their outer surface, and high-pressure, high-temperature water and steam from the inside. As a result, and despite due care, tubes fail from time to time, leading to forced outages. Most boiler tube failures can be attributed to faulty operating conditions, improper or inadequate maintenance, and improper engineering practices, in addition to improper material selection or faulty design (Ref 6.1). A root cause investigation of tube failures becomes essential to restore the boiler back to normal operation and to eliminate or minimize recurrence of similar failures and resultant plant outages.

There are several mechanisms responsible for failure of boiler tubes and one or more than one can be operative for a particular failure (Ref 6.2). The different damage mechanisms are classified into seven broad categories (Ref 6.3, 6.4).

6.2 Boiler Tube Failure Mechanisms

Seven broad categories of failure mechanisms are:

1. Stress rupture failures:

- Overheating
 - a. Long-term overheating
 - b. Short-term overheating
- High-temperature creep

- Graphitization
- Dissimilar metal welds (DMW)

2. Water-side corrosion:

- General corrosion/oxidation damage
- Under-deposit corrosion
 - a. Hydrogen damage
 - b. Caustic corrosion/caustic gouging
 - c. Phosphate corrosion or phosphate hide out
- Microbially induced corrosion
- Flow-assisted corrosion (FAC)
- Erosion corrosion
- Cavitation damage
- Oxygen attack or oxygen pitting
- Stress-corrosion cracking (SCC)
- Caustic stress-corrosion cracking or caustic embrittlement
- Stress-assisted corrosion (SAC)
- Chelate corrosion

3. Fire-side corrosion:

- Waterwall corrosion or reduced atmosphere corrosion
- Fuel ash corrosion
 - a. Coal-ash corrosion
 - b. Oil-ash corrosion
- Hot corrosion
- Acid dew point corrosion or cold-end corrosion
- SCC
- Polythionic acid stress-corrosion cracking (PASCC)

4. Fire-side erosion:

- Soot blower erosion
- Fly ash erosion
- Coal particle erosion
- Falling slag erosion
- Erosion due to steam cutting

5. Fatigue:

- Mechanical fatigue
- Thermal fatigue
- Corrosion fatigue
- Creep-fatigue interaction

6. Operation failures:

- Failures due to operational problems
 - a. Rapid start-ups
 - b. Excessive load swing

- c. Excessive heat inputs
- Failures due to poor water chemistry control
- Water-treatment-related failures
 - a. Conventional treatment
 - b. All volatile treatment (AVT)

7. Lack of quality control or improper quality control:

- Failures attributed to various defects
 - a. Material defects due to selection of wrong material
 - b. Forming and welding defects
 - c. Design defects
- Failures related to cleaning and maintenance

Each one of these failure mechanisms is discussed in the following sections of this chapter along with relevant case studies.

Stress Rupture Failures

Mechanical components of a boiler can fail due to reasons such as creep, fatigue, erosion, and corrosion. Creep is defined as the time-dependent deformation of a material at elevated temperature under mechanical stresses of constant magnitude. A failure from such a condition is referred to as a creep or stress rupture failure. Stress rupture failures also cover failure due to short-term or long-term overheating (Ref 6.1).

Overheating Failures

The waterwalls, superheater, and reheater tubes carrying water or steam in a boiler are all susceptible to overheating failure (Ref 6.1, 6.5). Fracture due to overheating generally takes place along the longitudinal axis of the tube, but at times it can be accompanied by fracture in the circumferential direction as well. The visual appearance of the fracture is like a *fish mouth*. Based on the degree of plastic deformation and the resultant thinning that the tube undergoes prior to fracture, it is called a *thick-lip* or *thin-lip fish-mouth* fracture. Depending on the time to which the tube has been exposed to high temperature prior to fracture, the failure is called *short-term overheating* (with exposure time as low as a few minutes) or *long-term overheating* (with exposure time of a few months to a few years). Figure 6.1 depicts thick-lip and thin-lip fractures.

Long-Term Overheating (Thick-Lip) Type of Fracture

Thick-lip fractures generally occur after long-term or prolonged overheating at a temperature slightly above the maximum safe working



(a)



(b)

Fig. 6.1 (a) Thick-lip rupture in a boiler tube due to long-term overheating. (b) Thin-lip rupture in a boiler due to short-term overheating

temperature for the tube material. It results in very little or no reduction in the wall thickness with little or moderate bulging of the tube. The failure is accompanied by formation of a scale or corrosion product on the inner side of the tube. The most frequently encountered reasons for long-term overheating failures include partially restricted water or steam flow due to partial blocking of the tubes; buildup of an internal scale/deposits leading to an insulating effect, which thereby reduces heat transfer across the tube wall; more than normal heat input from the burners due to uneven burner adjustment; steam blanketing in horizontal or inclined tubes; and undesired channeling of fire-side gases. Superheater and reheater tubes generally fail after many years of service as a result of creep. Waterwall tubes also can fail from long-term overheating.

Apart from a change in the physical condition of the tube, long-term overheating also leads to microstructural changes. In the case of carbon and low-alloy steels, long-term overheating below Ac_1 results in the decomposition of pearlite into ferrite and globular/spheroidal carbide, finally causing loss of strength. With a very long duration of exposure, it can even lead to degradation of the material by way of void formation along the grain boundaries of the steel followed by grain separation, and finally failure of the tube through the stress-rupture mode. Figure 6.2 shows optical scanning and electronic microscopy (SEM) micrographs of degraded microstructure for a carbon steel tube that has failed in a thick-lip manner due to prolonged overheating.

Case Study 1—Failure Investigation of a Screen Tube

Background Details A 75 mm (3 in.) diameter screen tube failed due to leakage, after about 6 years of service. The failure was noticed when water was observed seeping through the insulation at the bottom of the boiler. It was a fuel-fired boiler using heavy fuel oil as well as refinery and regasified liquefied natural gas as fuel. The material of construction (MOC) of the tube was SA 210 Grade A1, and the tube dimensions were 76.2 mm (3 in.) outside diameter (OD) and 4.06 mm (0.16 in.) thickness.

Investigation and Findings A close-up view of the leakage location on the outer surface indicated a linear rupture in the longitudinal direction with jagged contours and an uneven opening (Fig. 6.3a). At the corresponding location on the inner surface, a similar linear opening was noticed. The leakage was thus through and through. An uneven scale on the inside diameter (ID) surface was seen surrounding the leakage area (Fig. 6.3b).

Wet fluorescent magnetic particle inspection (WFMPI) highlighted discontinuous hairline cracks near the failure location on the outer surface, as shown in Fig. 6.4.

Scanning electron microscopy (SEM) examination revealed the presence of discontinuous fissures filled with scales on the outer surface of the tube and showed creep cavities and cracks on the fracture lip (Fig. 6.5a and b).

Energy dispersive spectroscopy (EDS) analysis on the ID surface showed

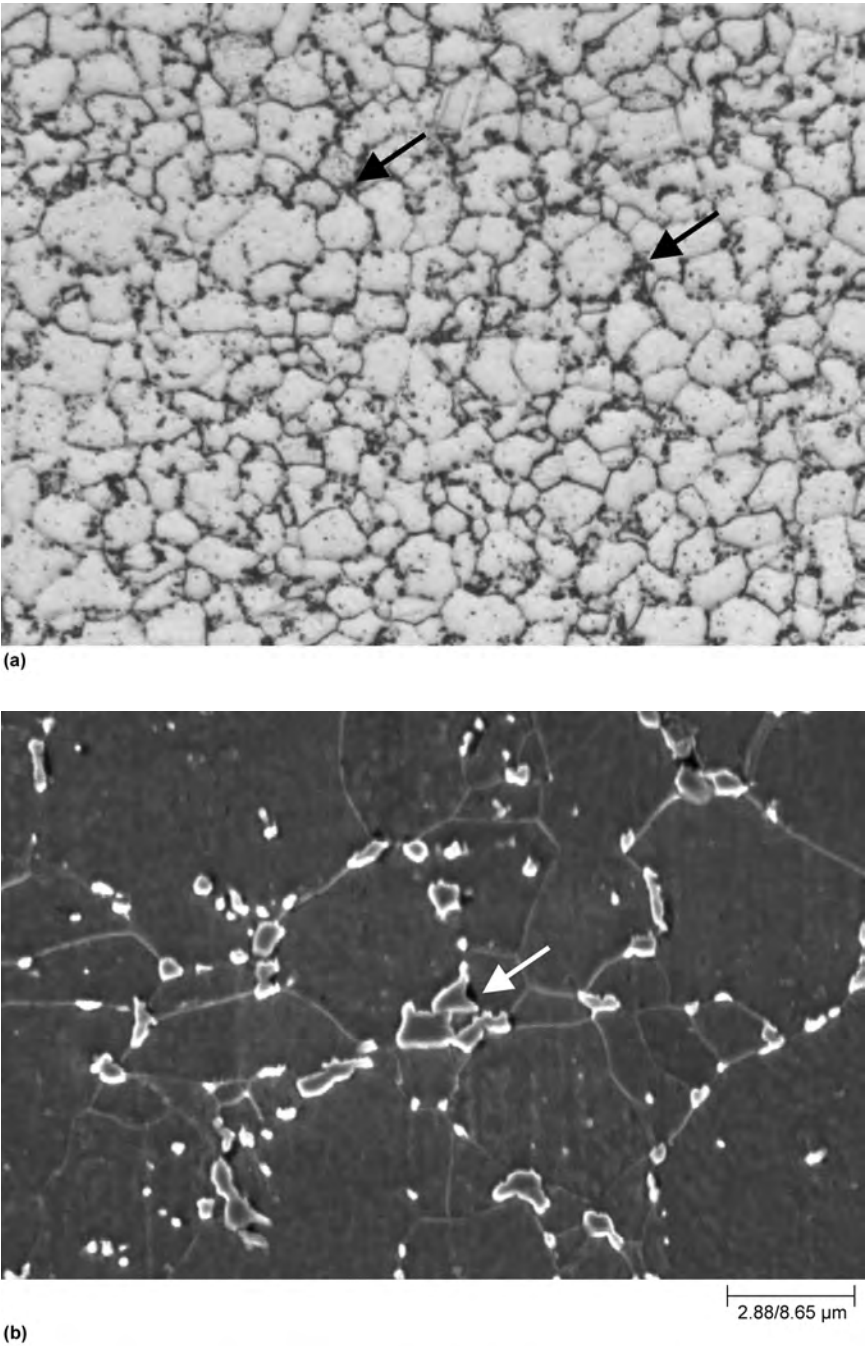
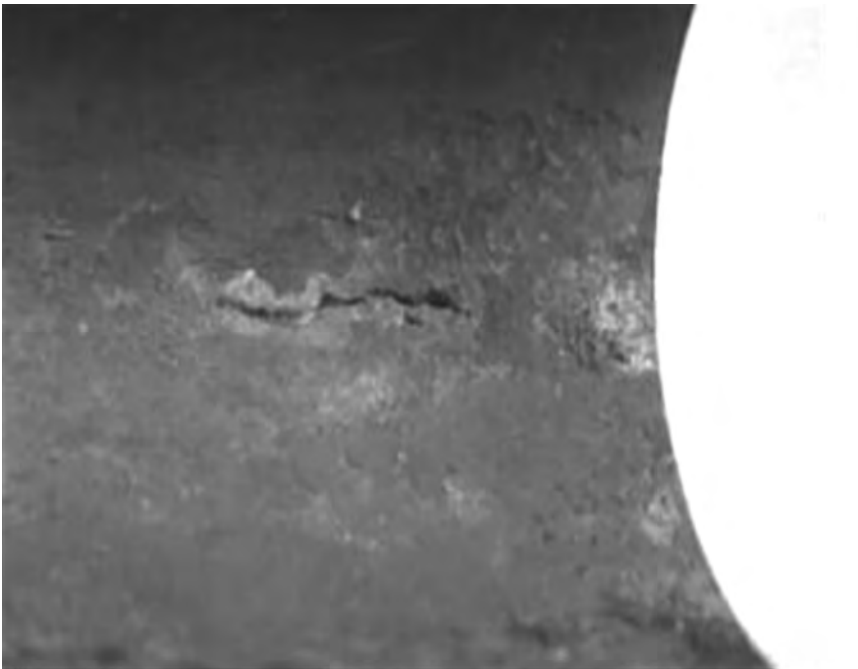


Fig. 6.2 Carbon steel boiler tube sample subjected to prolonged overheating below A_{c1} showing voids (black) along the grain boundaries and spheroidization of carbides, (a) optical micrograph, 200 $\times$; and (b) SEM image, 3500 $\times$



(a)



(b)

Fig. 6.3 (a) Close-up view at the leakage location on outer surface of the sample and (b) corresponding location on inner surface showing similar linear opening

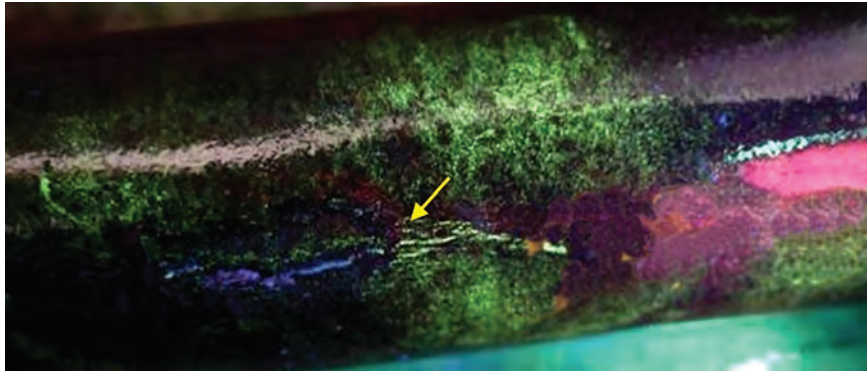


Fig. 6.4 Tube sample in WFMPI tested condition showing cluster of hairline cracks near failure location

the presence of oxygen, magnesium, aluminum, silicon, calcium, phosphorus, and zinc, whereas the OD surface showed the presence of elements such as oxygen, magnesium, aluminum, silicon, sulfur, potassium, calcium, phosphorus, sodium, titanium, vanadium, and nickel.

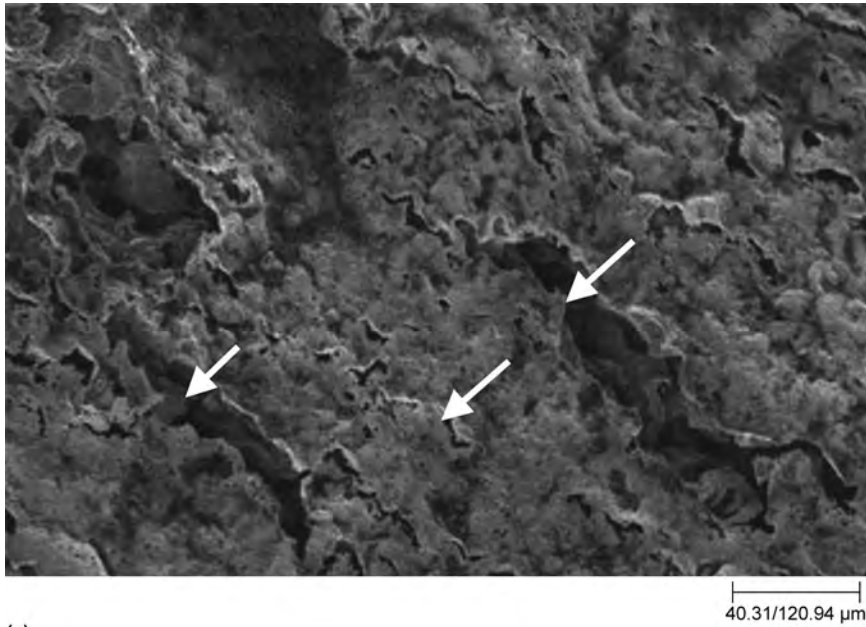
The results of mechanical testing on the failed tube sample indicated that it did not meet the standard requirements. For example, the yield strength was 230 N/mm^2 instead of 250 N/mm^2 , and the ultimate tensile strength was 365 N/mm^2 instead of 450 N/mm^2 . Likewise, the average surface and core hardness values were 100 and 102 BHN, respectively, whereas the recommended value is 140 BHN max.

The microstructure at the outer surface of the tube sample at a different location on the far side (i.e., not facing the flue gases or the failure location) was that of banded ferrite and pearlite (Fig. 6.6a). This is the normal microstructure for the tube material. Near the failure location, the structure comprised spheroidized coagulated carbides in the ferrite grains (Fig. 6.6b). Scaling was found on both the outer and inner surfaces of the tube.

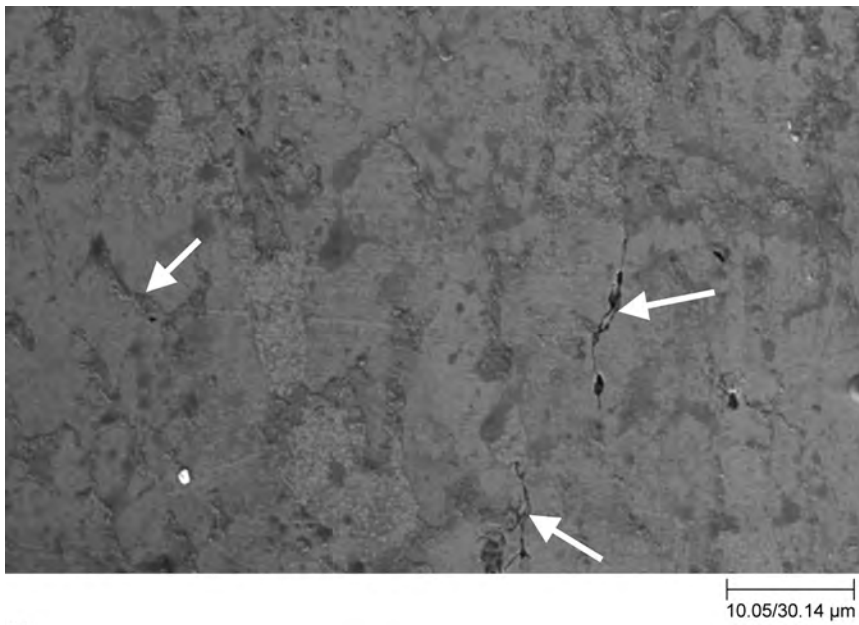
Creep cavities were seen on the rupture lip. The microstructure at the rupture lip was elongated ferrite grains with coagulated carbides both at the grain boundaries and within the grains (Fig. 6.7a). Discontinuous fissures filled with scales were seen on the outer surface (Fig. 6.7b).

Taking into account the approximate working hours, the estimated skin temperature from the calculations based on the Larson-Miller parameter (LMP) was 460°C (860°F). The rise in temperature might be attributed to the greater internal scaling. The scale thickness on the ID surface on the fire side of the failed screen tube was $135 \mu\text{m}$, instead of 30 to $50 \mu\text{m}$, which is normally admissible.

All of the above findings pointed toward a failure of the screen tube due to creep on account of long-term overheating. This is a typical phenomenon observed when a carbon steel surface is exposed to a temperature above 450°C (840°F) for a long period.



(a)



(b)

Fig. 6.5 (a) SEM micrograph of OD surface showing discontinuous fissures filled with oxide scales, 250 $\times$; and (b) SEM after metallography at location near failure showing fissures, 1000 $\times$

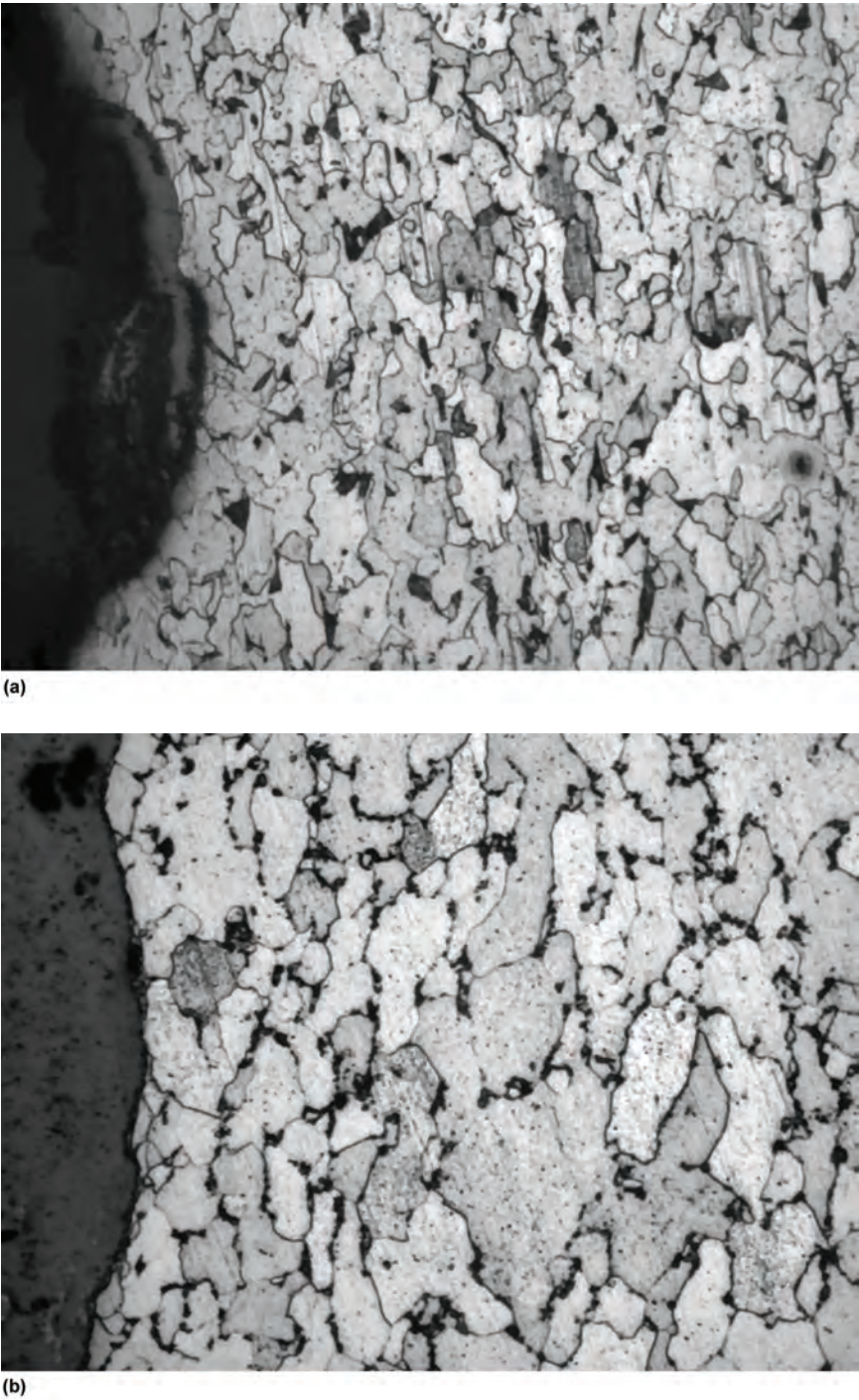
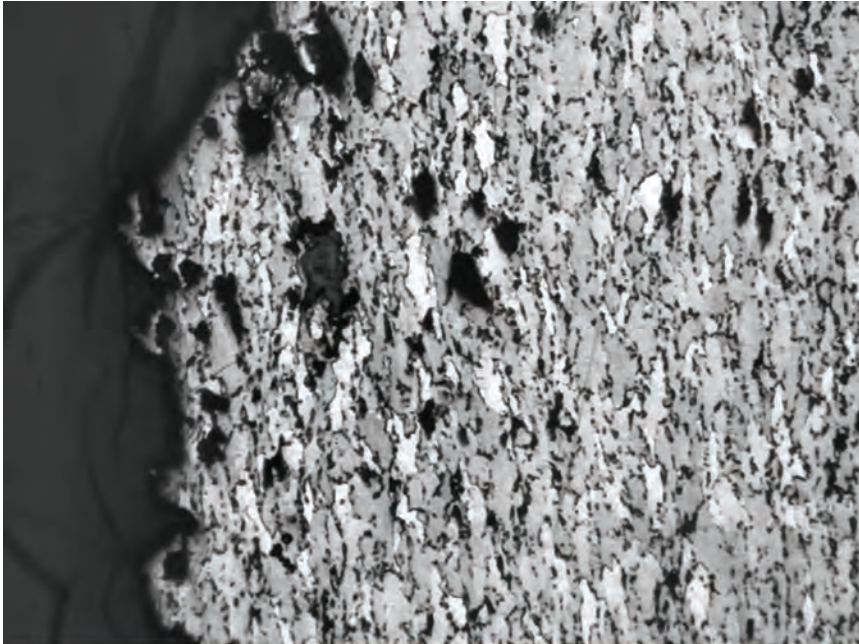
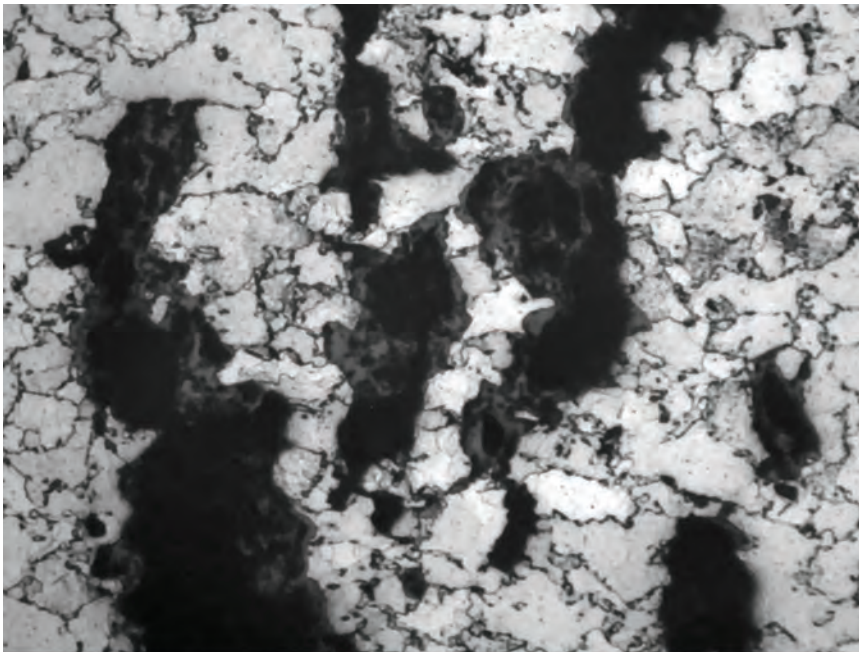


Fig. 6.6 OD microstructures at (a) far-side location of banded ferrite and pearlite, 200 $\times$; and (b) near-side failure location of ferrite grains and degraded pearlite in the form of spheroidization with coagulated carbides, 400 $\times$



(a)



(b)

Fig. 6.7 Microstructures at (a) fracture lip having elongated ferrite grains with coagulated carbides and scattered creep cracks at ferrite grain boundaries, 100 $\times$; and (b) OD surface near fracture lip showing ferrite and coagulated carbides having fissures filled with scales, 400 $\times$

Conclusions The failure of the screen tube was due to long-term high-temperature exposure above the permissible design limits, resulting in creep damage.

Case Study 2—Failure Investigation of Reheater Outlet Tube

Background Details The reheater outlet tube of a coal-fired boiler failed by rupture during operation after about 5 years of service. The MOC of the failed tube was A 213 Grade T22 steel. This tube was one end of a DMW joint, at the other side of which was a tube whose MOC was A 213 Grade T91 steel. The tube dimensions were 54.0 mm (2.12 in.) OD and 4.0 mm (0.15) thickness.

Investigation and Findings Visual examination of the tube displayed a rupture opening with fine lips. Bulging was noticed around the rupture contours. The ID surface had a scale, which was grayish black in color (Fig. 6.8). The measurements across the transverse cross section of the tube at different locations, as well as the thickness measurement survey, did not show significant reduction in wall thickness of the tube, which pointed toward a thick-lip nature of failure.

Scanning electron microscopy was performed at the rupture lip surface to reveal more details about the failure mechanism. Scanning electron microscope examination of the fracture surface revealed an intergranular nature of the fracture with scattered cavities (Fig. 6.9a). Scanning electron microscopy after metallography indicated the onset of creep damage (Fig. 6.9b).

Microstructural examination of an unaffected location revealed grains of ferrite with partially degraded bainite and globular carbides (Fig. 6.10a). The microstructure at the rupture location facing the flue gas side consisted of nonuniform grains of ferrite along with globular carbides both within the grains and at the grain boundaries (Fig. 6.10b). Bainite was almost completely degraded at the rupture location.

Comparative study of the microstructures at a higher magnification confirmed that the structure at the unaffected location on the far side consisted of partially degraded bainite in addition to ferrite grains and globular carbides (Fig. 6.11a). However, the microstructure at the failure location showed enhanced degradation at the rupture location by non-uniform ferrite grains along with globular carbides both within the grains and at the grain boundaries, in addition to the absence of bainite (Fig. 6.11b). The microstructural degradation thus pointed toward a temperature excursion beyond permissible limits.

The tube sample was also subjected to scale thickness measurement. The average scale thickness at a location on the side facing the flue gas was 980 μm . Excessive scale formation is indicative of a temperature rise beyond permissible design limits.

The degradation of the microstructure, particularly the breakdown of bainite into ferrite and globular carbides, along with an excessive tendency



(a)



(b)

Fig. 6.8 (a) Rupture opening with fine tips and (b) inner surface view after cutting the tube into two halves showing presence of grayish black scale

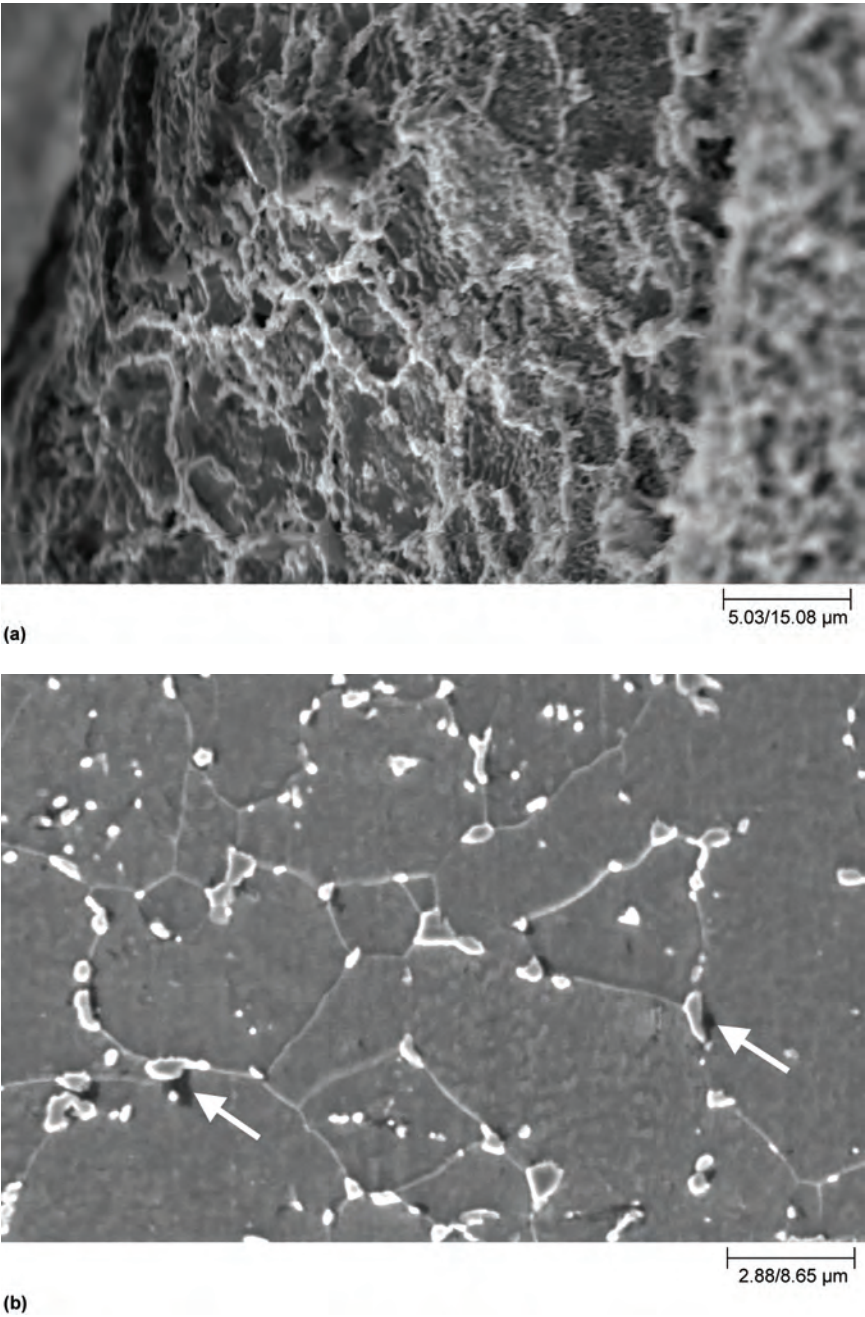
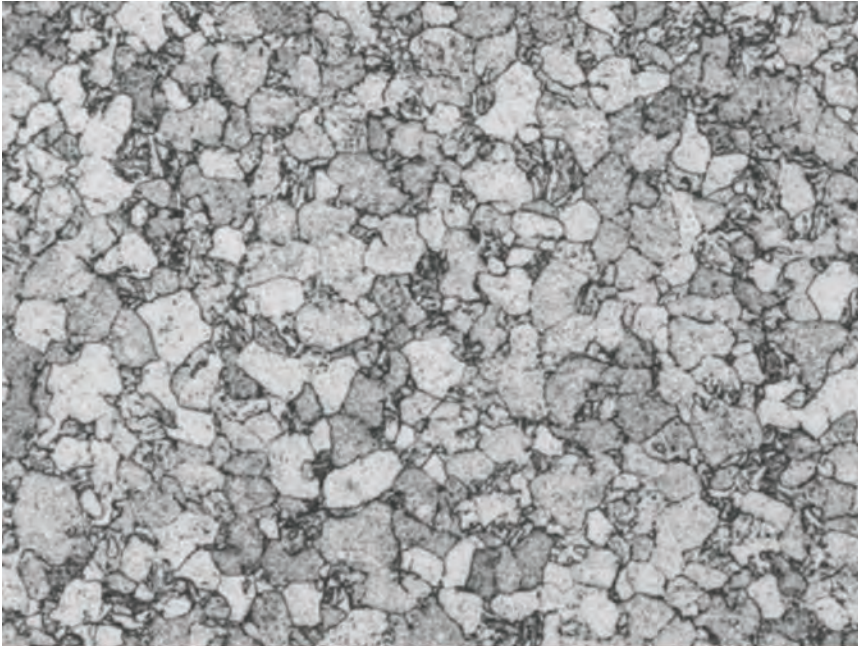
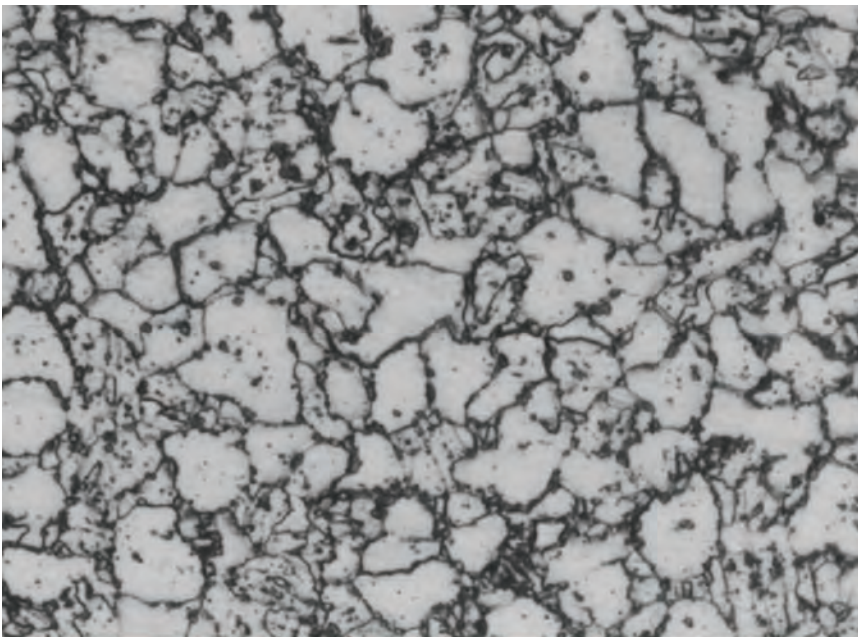


Fig. 6.9 (a) SEM micrograph showing intergranular nature of fracture having cavities, 2000×; and (b) SEM micrograph after metallography indicating scattered creep cavities pointing toward onset of creep damage and carbides along grain boundaries, 3500×



(a)



(b)

Fig. 6.10 Microstructures at (a) unaffected location showing grains of ferrite with partially degraded bainite and globular carbides, 200 $\times$; and (b) at rupture location having nonuniform grains of ferrite along with globular carbides both within the grains and at grain boundaries, 400 $\times$. Bainite is almost completely degraded at rupture location.

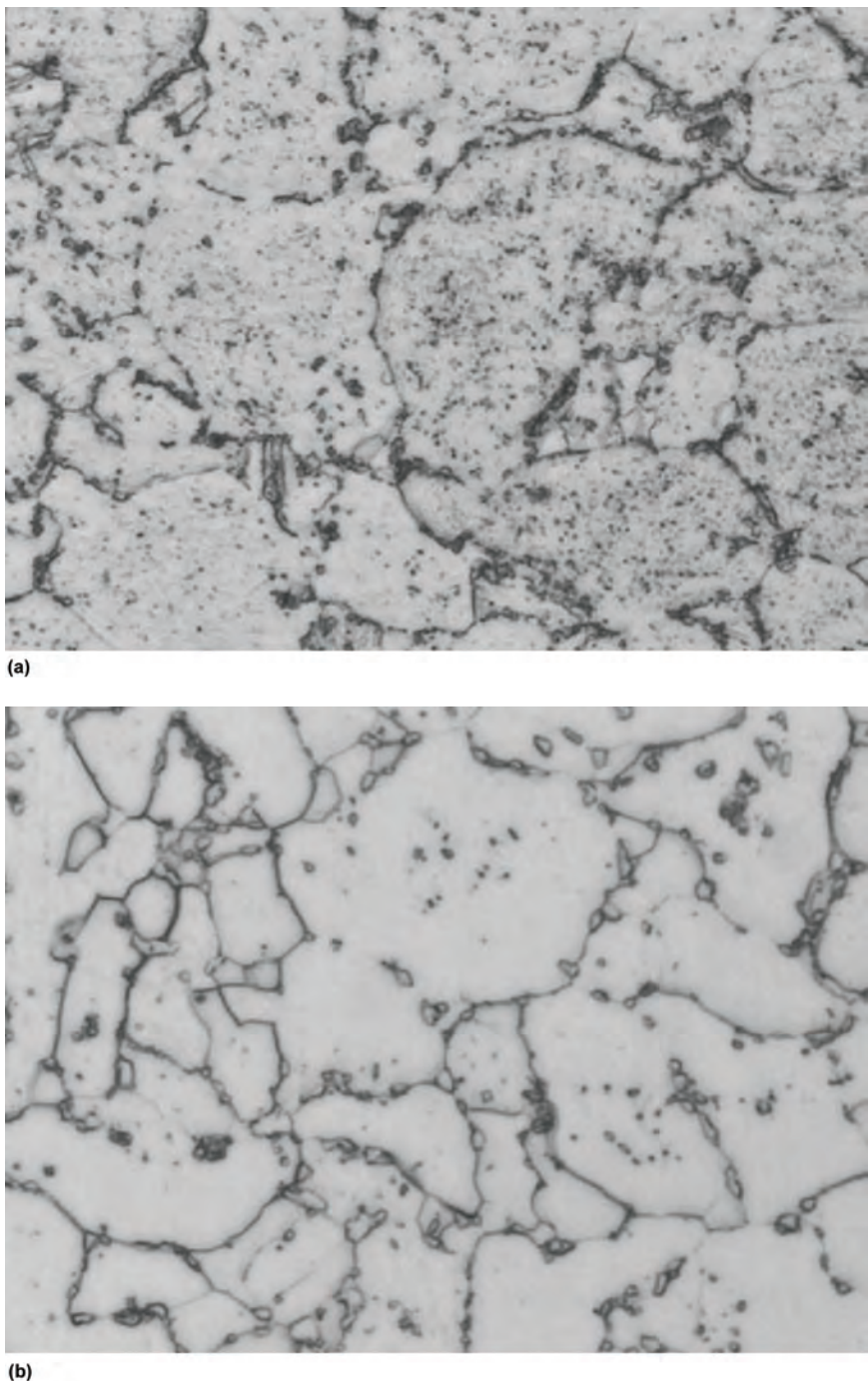


Fig. 6.11 Comparative microstructures at (a) unaffected location, 1000× and (b) failure location, 1000×

to scale formation, is indicative of long-term overheating beyond permissible design limits. The calculated temperature rise based on the scale thickness measurement and the service life of the tube was 640 °C (1185 °F) instead of the normal operating temperature of 540 °C (1005 °F).

Conclusions The failure of the tube can be attributed to the onset of creep damage due to long-term overheating of the tube, above the allowable design temperature.

Case Study 3—Failure Investigation of a Reheater Tube of a Supercritical Boiler

Background Details Failure was noticed in the reheater tube of a coal-based supercritical boiler. It was indicated by an increase in make-up water consumption as well as a warning alarm and sound from the subject region. The MOC of the tube was SA 213 T91 steel, and the tube dimensions were 60.0 mm (2.35 in.) diameter and 4.5 mm (0.15 in.) wall thickness.

Investigation and Findings Visual examination was carried out on a tube sample received for investigation. This showed a rupture opening in the longitudinal direction, with fine lips at the failure location (Fig. 6.12). Dimensional measurements highlighted tube bulging across the failure location, and also showed bending of the tube near the failure location. A visual examination showed a thick-lip fish-mouth fracture. The thickness measurement survey indicated a minimum tube thickness equal to 4.0 mm (0.15 in.). The tube's outer surface had a thin adherent scale, grayish black in color. The inner surface of the tube, after it was cut into two halves, revealed patches of uneven but adherent scaling, grayish black in color (Fig. 6.13a). Figure 6.13(b) is an SEM image of the cross section of



Fig. 6.12 Reheater tube sample showing bulging and bending at failure location with thick-lip fish-mouth rupture

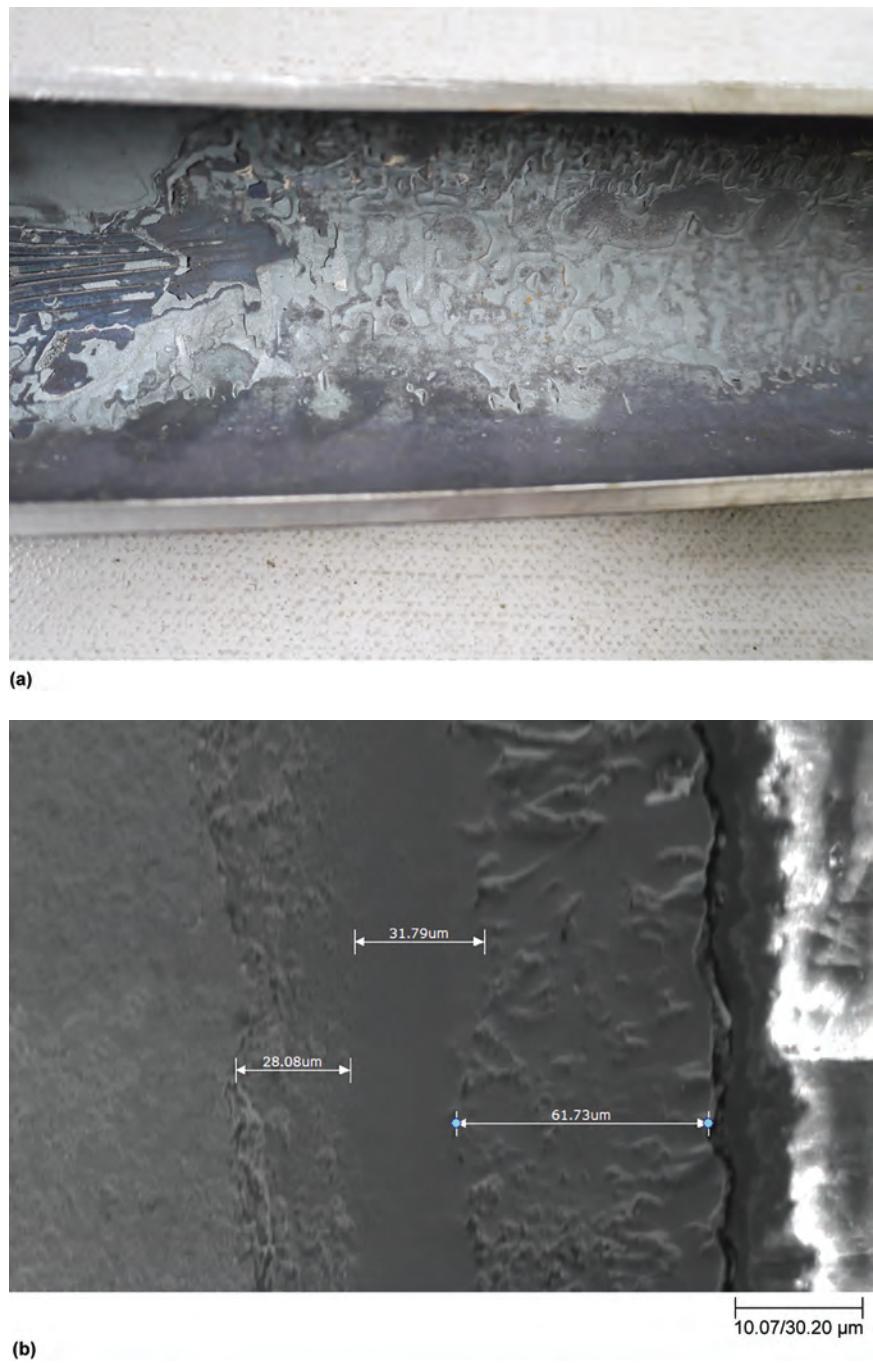


Fig. 6.13 (a) Close-up view of the inner surface of the tube indicating patches of uneven but adherent scaling. (b) SEM image of cross section of the tube showing multilayered nature of scale, 300×

the tube showing the multilayered nature of the scale typical of a supercritical boiler.

Microstructural examination of an unaffected location showed a tempered martensitic structure, which is the normal structure for the T91 steel of the tube material (Fig. 6.14a). The microstructure at the fracture edge was also tempered martensite. However, the fracture edge was covered with a scale. Additionally, scattered fissures surrounded the fracture edge (Fig. 6.14b).

Scanning electron microscopy was performed at the rupture lip surface. Scanning electron microscope examination of the fracture surface revealed the presence of creep voids on the fractured surface (Fig. 6.15a). Scanning electron microscopy after metallography of the unpolished sample indicated the onset of creep damage in the form of formation of creep voids (Fig. 6.15b).

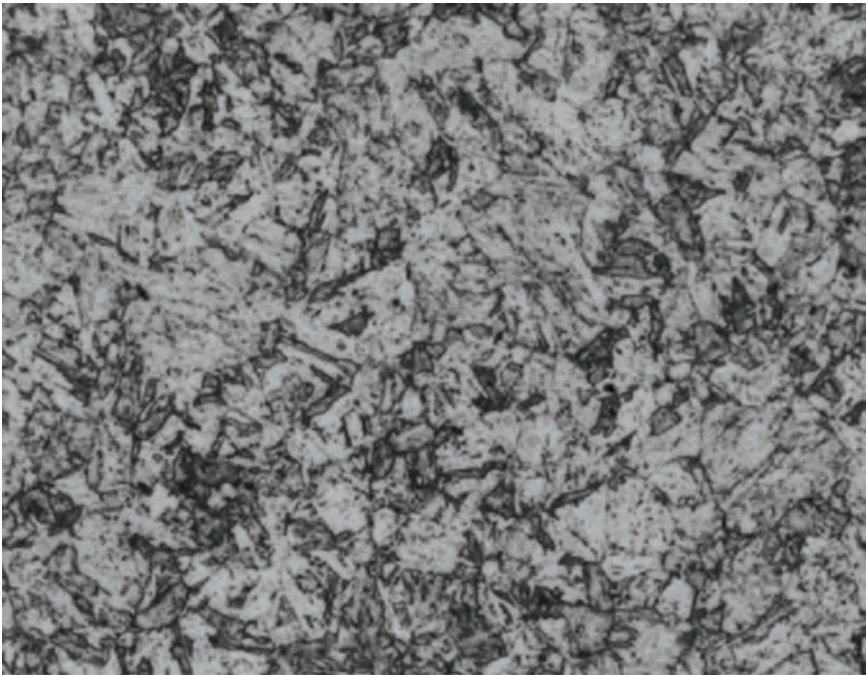
The OD and ID surfaces of the tube were subjected to EDS analysis to characterize the nature of the scale formed. Energy dispersive spectroscopy analysis on the ID surface showed the presence of oxygen, sodium, magnesium, aluminum, silicon, sulfur, chlorine (as chloride), and calcium. Energy dispersive spectroscopy on the OD surface showed the presence of oxygen, magnesium, aluminum, silicon, sulfur, potassium, calcium, and titanium.

The average scale thickness at the near side on the ID and OD surfaces was 160 μm and 70 μm , respectively. At the far side at the ID and OD surfaces, it was 162 μm and 136 μm , respectively.

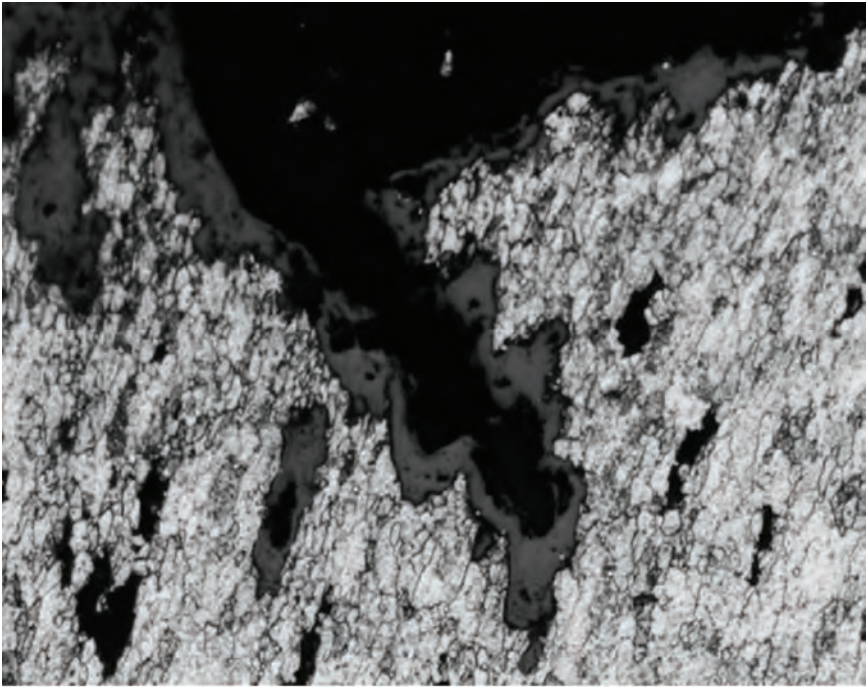
As shown in Fig. 6.13(b), SEM on the ID edge showed the layered nature of the scale formed. The innermost layer was a spinel crystal structure followed by hematite and magnetite layers.

Chemical analysis confirmed the MOC of the tube as SA 213 T91 steel. The microstructure was tempered martensite, with normal tensile and hardness values. However, the thickness of the internal scale, which was in the range of 160 μm , was a real concern because internal scaling can lead to a rise in the crown temperature of the tube.

Based on the metallurgical investigation, the failure showed a thick-lip fracture with creep damage. This indicated long-term overheating. The microstructure at the failure region showed creep voids. The tube had seen a service life of approximately 22,000 hours. The creep fissures seen in the microstructure and creep voids in SEM substantiated the supposition that the creep mode was the damage mechanism. The steam temperature inside the reheater tube as reported was about 570 °C (1060 °F). Hence, the tube skin temperature was likely to be about 620 °C (1150 °F) under a steady-state condition. The degraded microstructure seen at the localized region of failure indicated a consistent long-term temperature rise, promoting the creep mode of failure. This long-term temperature exposure was highly localized; no microstructural degradation was seen at the unaffected location. The estimated temperature based on the

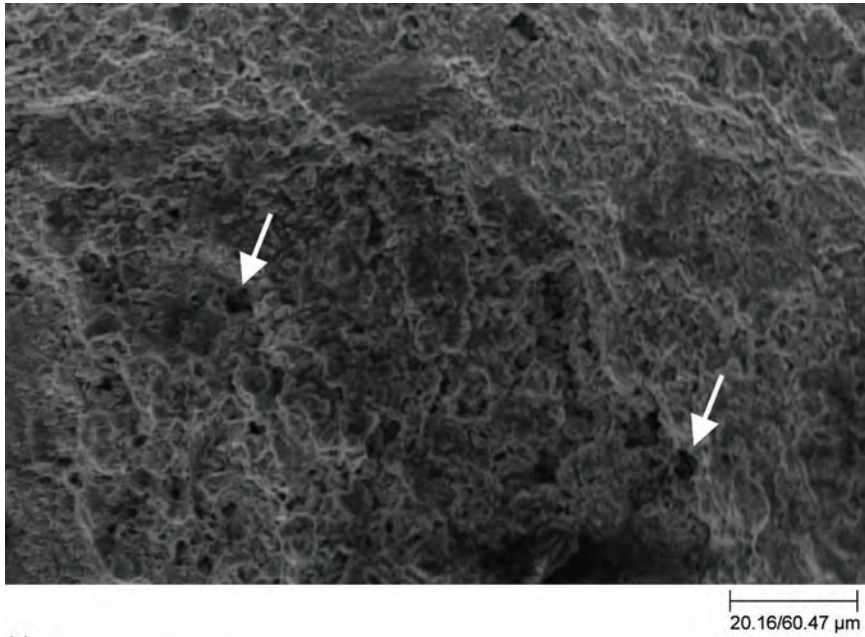


(a)



(b)

Fig. 6.14 Tempered martensite, (a) at unaffected location, 400×; and (b) at fracture edge with scattered fissures in the matrix. The fracture edge is covered with a scale, 200×.



(a)



(b)

Fig. 6.15 (a) SEM fractograph showing presence of creep voids on fracture lip surface, 500 $\times$; and (b) SEM image of as-polished sample after metallography showing scattered creep voids, 1000 $\times$

Larson-Miller Parameter (LMP) was about 682 °C (1260 °F), which resulted in long-term overheating.

Conclusions The tube failure can be attributed to long-term overheating of the tube to a temperature of about 680 °C, leading to a thick-lip rupture of the tube.

Short-Term Overheating (Thin-Lip) Type of Fracture

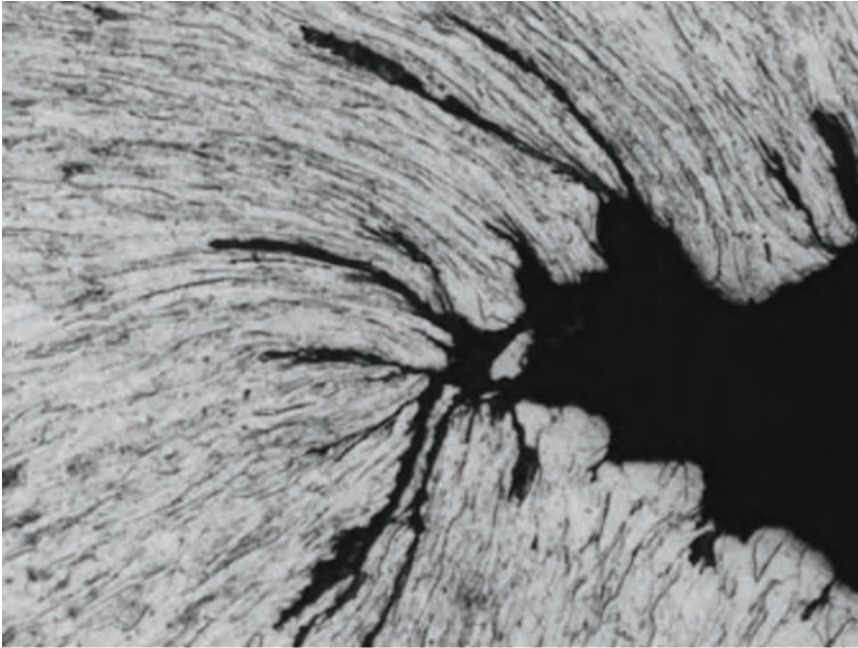
Short-term or rapid overheating of carbon and low-alloy steel tubes above the Ac_1 temperature (i.e., typically 723 °C, or 1333 °F) leads to a thin-lip fracture. This is a high-temperature tensile fracture of the tube material because of the decrease in its yield strength. A tube will fracture in the thin-lip mode with a fish-mouth appearance when it is subjected to rapid overheating above the safe working temperature for the tube material. There is considerable reduction in the wall thickness of the tube and the rupture location is often like a knife-edge. A thin-lip fracture is also characterized by a considerable swelling or bulging of the tube surrounding the rupture area. Lateral bending of the tube is noticed when high-velocity steam passing through the tube tries to escape from the ruptured area. Some frequently encountered factors accounting for thin-lip failure of boiler tubes are blockage of the tube, particularly for superheaters and reheaters; tube leakage, mainly in the case of waterwall tubes, and the resultant starvation and overheating due to flame impingement; low water levels in the boiler drum; rapid start-ups; and excessive load swings.

Microstructural changes in a thin-lip fracture are governed by the temperature to which the tube is heated with respect to its recrystallization temperature. Rapid heating below the recrystallization temperature produces severely elongated grains. On the other hand, rapid heating to a temperature between Ac_1 and Ac_3 (above the recrystallization temperature) produces a pearlitic or bainitic structure. Figure 6.16 shows representative microstructures in each case. However, the microstructure depends on the alloy content of the tube MOC.

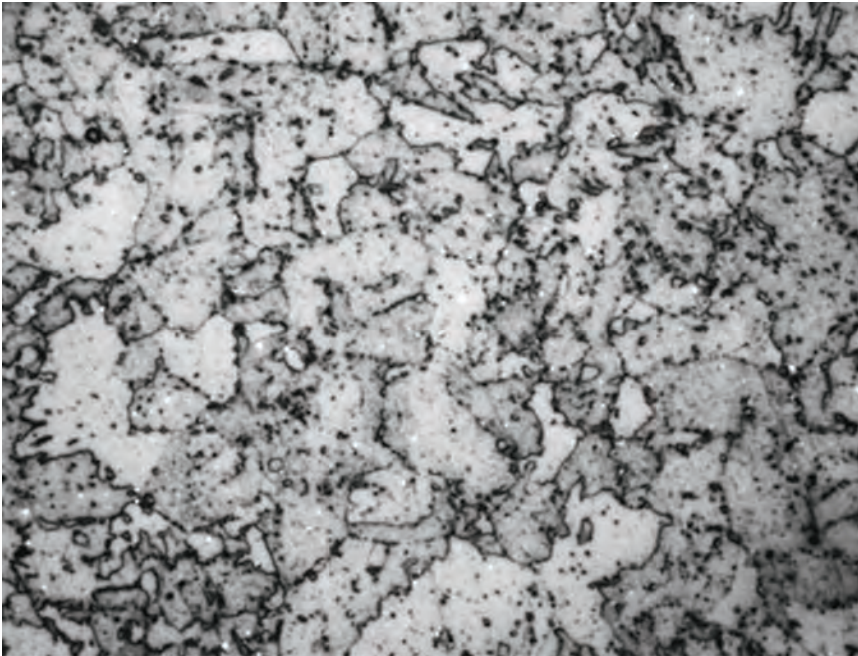
Case Study 4—Failure Investigation of Back Pass Front Wall Screen Tube of a Supercritical Boiler

Background Details The back pass front wall screen tube in a coal-fired supercritical boiler failed in the form of a rupture after about 1½ years of service. The MOC of the tube was SA 213 Grade T12 steel, and the tube dimensions were 51.0 mm (2 in.) OD and 8.0 mm (0.3 in.) wall thickness. The failure was noticed due to abnormal sounds heard from the subject's location.

Investigation and Findings Visual examination highlighted a fish-mouth opening with thinned contours and fine tips. Bulging was noticed surrounding the rupture location, and the tube was slightly bent (Fig. 6.17). Dimensional measurements at various locations on the tube confirmed bulging of the tube at the rupture location. Thickness measurements



(a)



(b)

Fig. 6.16 Typical microstructures of low-carbon steel boiler tube samples showing (a) elongated grains near tensile rupture resulting from rapid overheating below the recrystallization temperature, 200 $\times$; and (b) mixed structure near rupture resulting from rapid overheating between A_{c1} and A_{c3} and subsequent quenching by escaping water or steam, 400 $\times$



Fig. 6.17 Close-up views of the failed screen tube showing (a) thin-lip fish-mouth fracture and (b) bulging and bending of the tube

highlighted progressive thickness reduction toward the rupture location as well as on the rupture contours. Chemical analysis confirmed the MOC of the tube to be SA 213 T12.

The failed tube sample was subjected to optical microscopy and SEM in order to assess the microstructural degradation of the tube, if any. Figure 6.18(a) shows the as-polished view of the fracture lip with tapered contours. Figure 6.18(b) shows the deformed grains adjacent to the fracture lip. The microconstituents cannot be resolved.

Figure 6.18(c) and (d) shows a comparison of the microstructures at the far side and on the failure side of the tube. The far-side core microstructure per Fig. 6.18(c) consists of uniformly distributed grains of ferrite and pearlite. Here, the phase morphology is not altered; i.e., the ferrite grains are equiaxed. Contrary to this, the core microstructure near the failure location consists of fine and elongated grains of ferrite. Also, pearlite colonies have a tendency to orient toward ferrite grain boundaries.

An SEM image of the fracture lip shown in Fig. 6.18(e) highlights the elongated dimpled nature of the fracture surface, which is covered with a scale.

The tube MOC conforms to SA 213 T12 steel. The microstructure at a location away from the fracture included uniformly distributed grains of ferrite and pearlite, and the mechanical properties were satisfactory. The

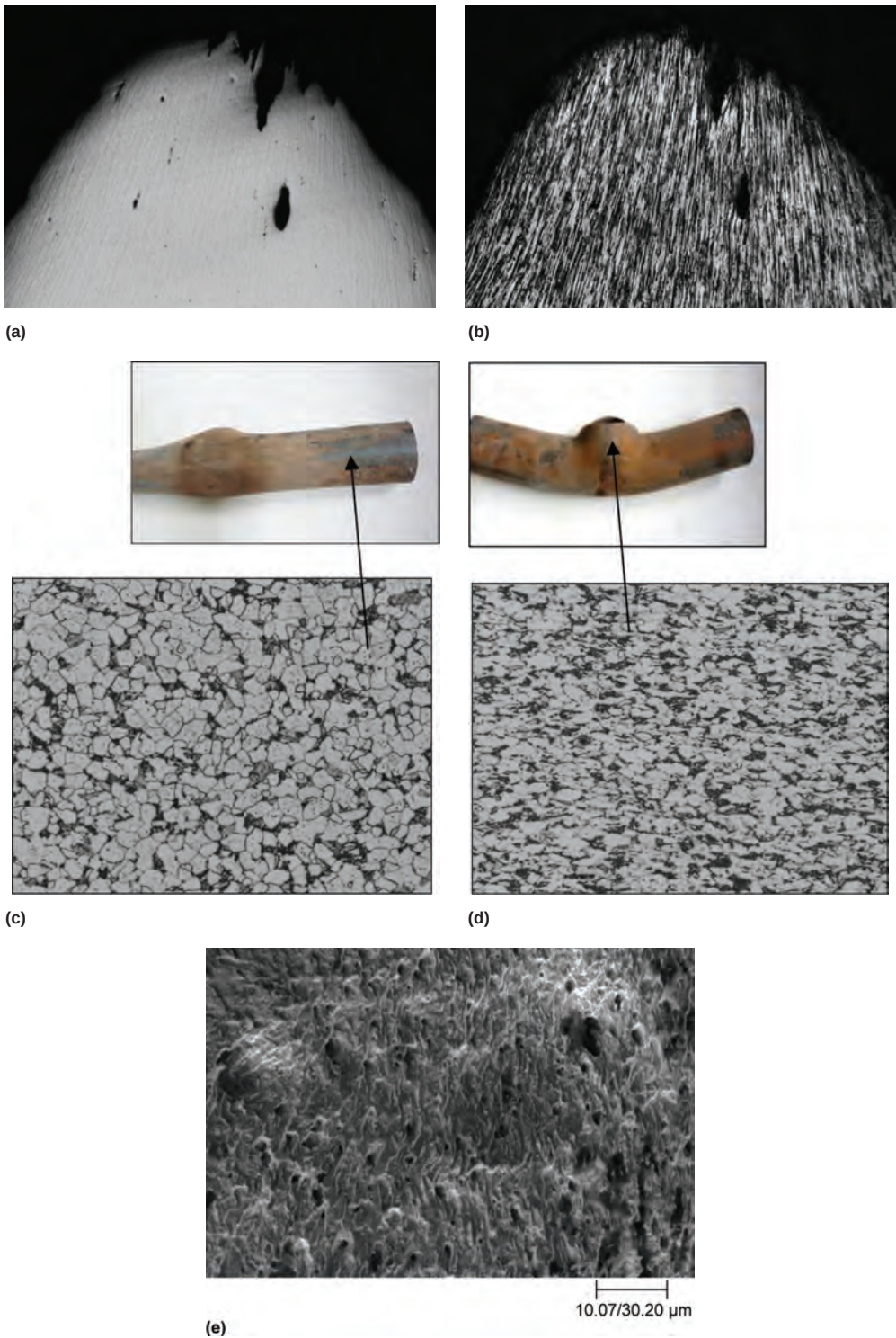


Fig. 6.18 Optical micrographs of a failed tube at different locations: (a) unetched view at fracture lip, 100 $\times$; (b) etched view at fracture lip, 100 $\times$; (c) at back side unaffected location, 200 $\times$; (d) at failure location, 200 $\times$; and (e) SEM fractograph of fracture lip, 1000 $\times$

fish-mouth opening, concomitant with tube bulging and thinning at the rupture contours, was indicative of failure under short-term overheating conditions. The ductile mode of failure coupled with tapered contours evidenced failure under localized overheating. Elongated but fine-grained ferrite morphology with pearlite orientation at the grain boundaries was indicative of a temperature excursion to a value below AC_1 .

The tube could no longer sustain the internal pressure conditions, which resulted in bulging with a reduction in tube thickness. When a critical level of thinning was reached, the tube could not withstand the internal pressure, and failure took place in the form of a thin-lip fish-mouth rupture through the ductile mode.

Conclusions The tube failure in the form of a thin-lip fish-mouth opening was because of short-term overheating taking place at the subject location.

Case Study 5—Failure Investigation of Waterwall Tube of Supercritical Boiler

Background Details Failure in the form of a rupture was noticed on the vertical water wall tube of a boiler after only 5 days of service from the first synchronization. Similar failures had taken place earlier in the vertical waterwall section at the left and right side walls and the rear wall. The material of the waterwall tubes was SA 213 T12 steel, and the tube dimensions were 31.8 mm (1.25 in.) diameter and 6.2 mm (0.24 in.) wall thickness.

Investigation and Findings Figure 6.19 shows a photograph of the failed waterwall tube sample received for investigation. The failure was in the form of a fish-mouth opening. On the outer surface, brownish black colored scaling was observed, whereas on the inner surface, there was an adherent black scale. At one of the tips of the fish-mouth opening, there was a hairline crack. The fracture surface was relatively flat with scattered

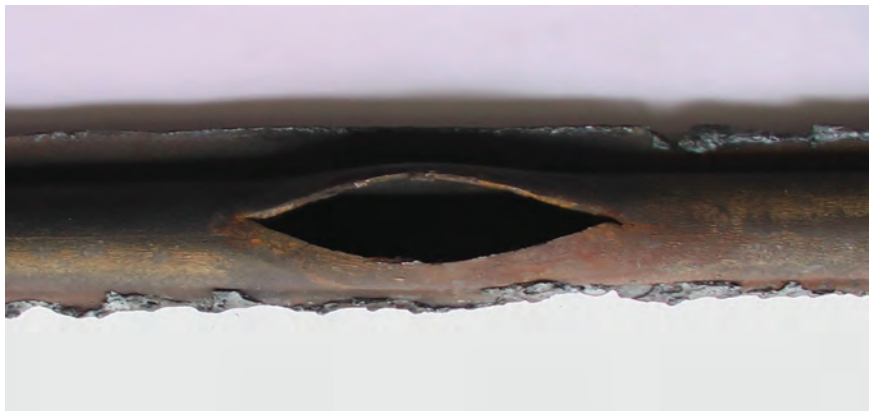


Fig. 6.19 Failed waterwall tube showing thin-lip fish-mouth fracture

corrosion scales. The surrounding area showed a serration-like pattern, presumably due to its high-temperature exposure.

Both visual (Fig. 6.19) and low magnification (Fig. 6.20a) views confirmed slight bulging at the failure location. A thickness measurement survey indicated reduction in wall thickness toward the failure location with a minimum wall thickness equal to 2.9 mm (0.1 in.). Wall thinning was observed on the fire side.

Scanning electron microscopy of the fractured lip indicated features resembling a typical short-term heated ruptured surface because cavities were joined to form the crack (Fig. 6.20b).

The microstructural examination of the failed waterwall tube sample showed a deformed grain structure at the fracture edge (Fig. 6.21a). At the lip of the fracture, the structure was a recrystallized dual-phase structure composed of ferrite and bainite on the OD and ID surfaces at the fire side, more prominently visible at the failure location (Fig. 6.21b). Bainite was formed due to the quenching effect of steam subsequent to the high-temperature exposure during failure. The core microstructure was acceptable banded ferrite and pearlite. The microstructure on the opposite side to the failure location did not indicate any effects of high-temperature exposure and showed a normal ferrite and pearlite structure. Away from the failure location, the microstructure displayed high-temperature exposure toward the flue gas-facing side on either side of the failure, whereas on the opposite side it showed a normal ferrite and pearlite structure. Figure 6.22 shows a comparison of the microstructures at different locations on the failed tube sample.

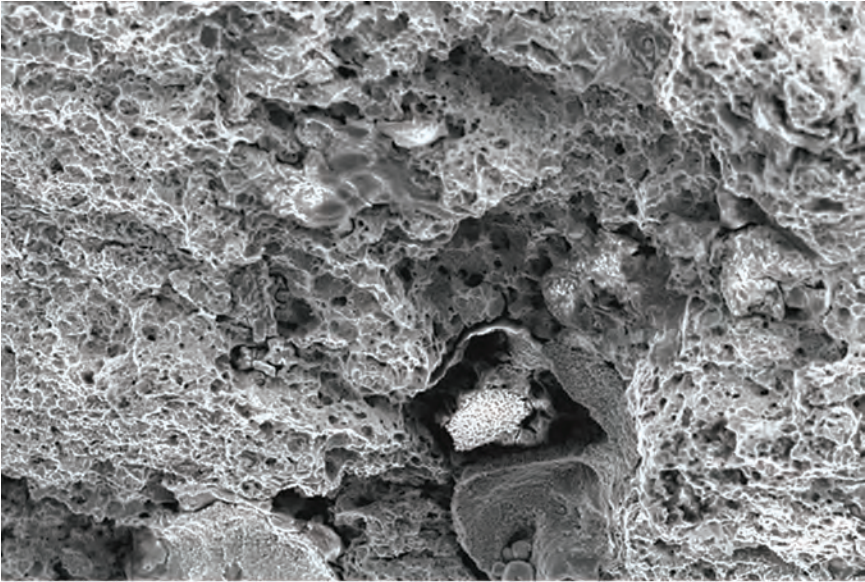
Hardness values at the location where maximum thinning had taken place as well as at the fracture lip were higher due to the formation of a low-temperature transformation product (i.e., bainite), as a result of high-temperature exposure and subsequent quenching.

In low-alloy steel, bainite can form only when the steel is heated well above 723 °C (1333 °F) in the range of 750 to 850 °C (1380 to 1560 °F) and rapidly quenched. Quenching was caused by steam leakage that took place after the failure. In this case, such a structure would develop only if the boiler tube was heated too rapidly to an excessively high temperature in the initial stages or if there had been a process upset that promoted momentary starving inside the tube. Retarded heat transfer from the tube to water inside the tube would have increased the surface temperature. In either case, the reduced strength of the tube across the section at high temperature resulted in bulging and wall thinning, making the cross section oblong as heating was taking place from one surface and internally the tube was pressurized.

Because the tube had been exposed to a temperature well above the design values, its strength was reduced. The prevailing pressure inside could not be withstood, resulting in failure of the tube in the form of a rupture.



(a)

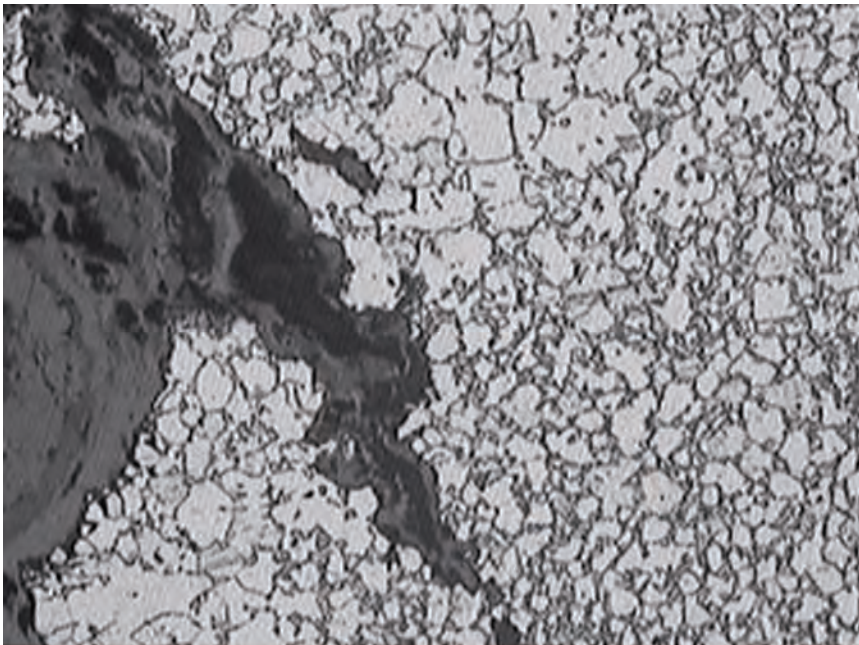


(b)

Fig. 6.20 (a) Low-magnification view at the tip of the fish-mouth rupture, 250×; and (b) SEM micrograph showing typical short-term heat ruptured surface, 250×



(a)



(b)

Fig. 6.21 (a) Deformed grain structure at the fracture edge, 400×. (b) Recrystallized dual phase structure composed of ferrite and bainite on OD and ID surfaces at fire side, 200×

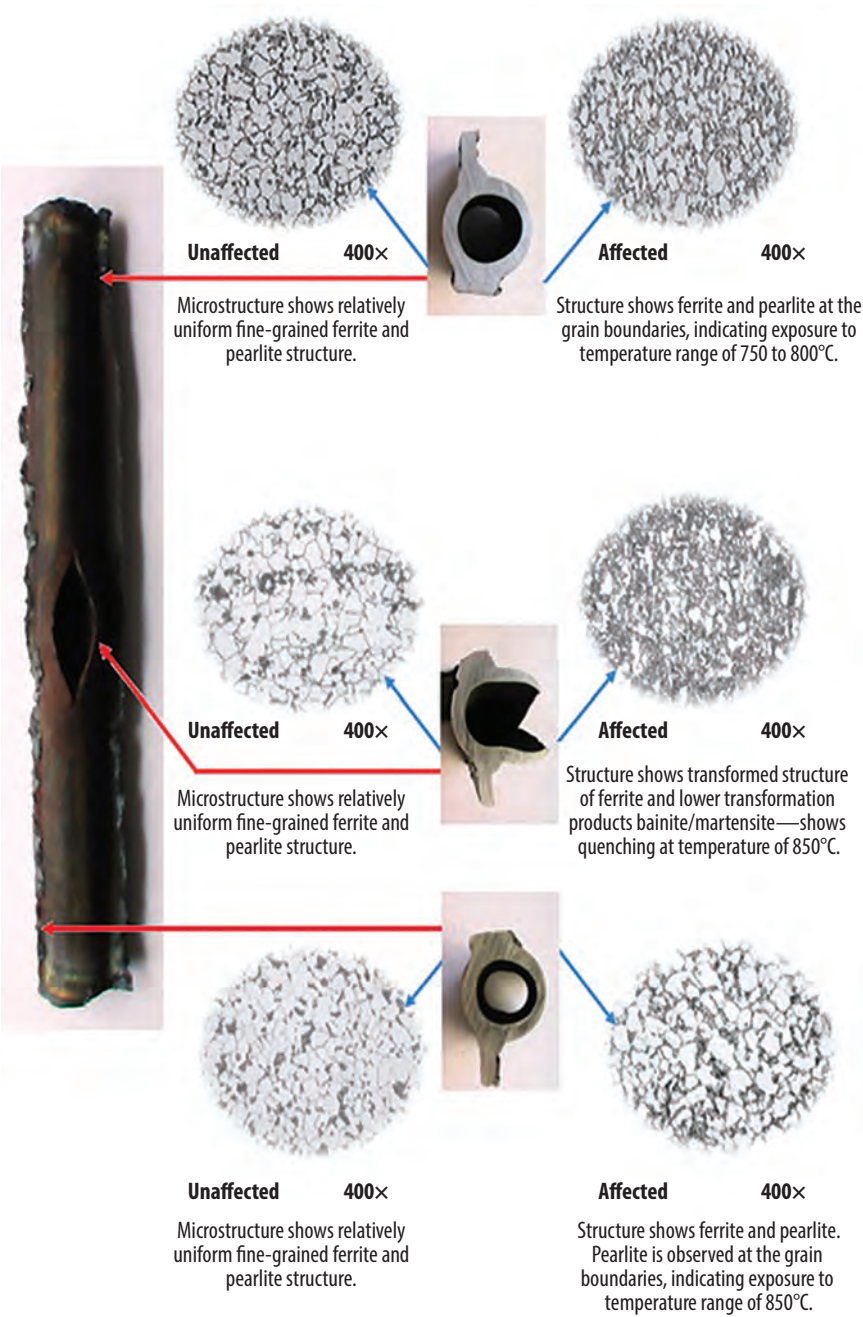


Fig. 6.22 Microstructures at different locations on failed tube sample

Conclusions Short-term overheating of the waterwall tube surface from the fire side that had resulted either from process upset causing poor circulation of the fluid, or from rapid heating to an excessively high temperature, led to rupture.

Case Study 6—Failure Investigation of Superheater Tube of Final Inlet Coil

Background Details The superheater final inlet header coil of a coal-fired supercritical boiler failed in the form of a burst opening. The failure occurred in two tubes of the final superheater inlet coil. The MOC of the superheater tube was in conformance with ASTM A213 T91. The tube dimensions were 42.2 mm (1.66 in.) OD and 6.45 mm (0.25 in.) thickness. The flue gas temperature remained around 700 to 800 °C (1290 to 1470 °F).

Investigation and Findings Visual examination showed that the superheater tubes, which were otherwise straight tubes, had completely bent by 180° after a violent burst (Fig. 6.23). Wall thinning was noticed at the rupture contours. Uneven wall thinning had not only caused buckling of the contours but also a wide variation in wall thickness at the failure. The ID surface was smooth with a thin adherent grayish black scale. Tube bulging was noticed toward the failure. A thickness measurement survey indicated a reduction in wall thickness at the failure location. The minimum thickness near the failure location was 5.6 mm (0.22 in.).

Microstructural examination highlighted scattered recesses formed on the rupture lips due to extensive plastic deformation (Fig. 6.24a). This was indicative of prevailing stress, exceeding the yield stress. The grains at the puncture lips were heavily deformed, which is indicative of plastic deformation (Fig. 6.24b).

The microstructure was tempered martensite (Fig. 6.25a). Scanning electron microscopy after metallography indicated an absence of creep voids, confirming that there was no creep damage (Fig. 6.25b).

The evidence obtained in visual and microstructural examination confirmed that the tube had undergone an extensive degree of plastic deformation. It was quite evident that the failure had occurred due to localized overstressing, possibly due to local overheating. The nature of the failure was violent and indicated starvation that could have resulted in an increase in tube temperature under pressurized conditions.

The general microstructure did not undergo any phase transformation since the A_{c1} temperature for this material specification is about 800 °C (1470 °F). Calculations based on basic principles indicated that the temperature necessary to cause plastic deformation and resultant burst opening of the tube was 678 °C (1252 °F). This temperature limit could have been reached if steam starvation occurred.

Conclusions The failure of the superheater tube took place due to an instantaneous and localized temperature rise, which eventually led to burst failure due to steam starvation.

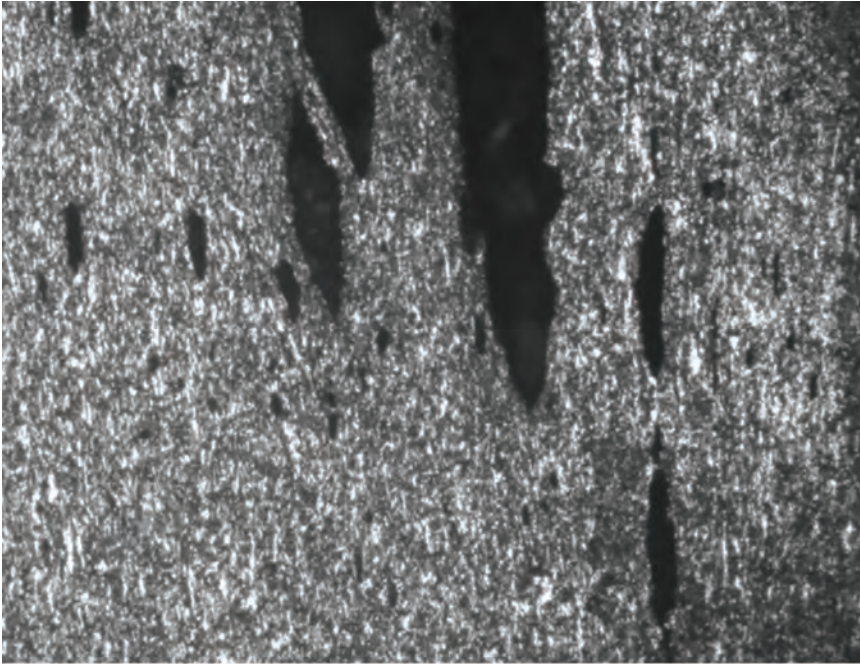


(a)

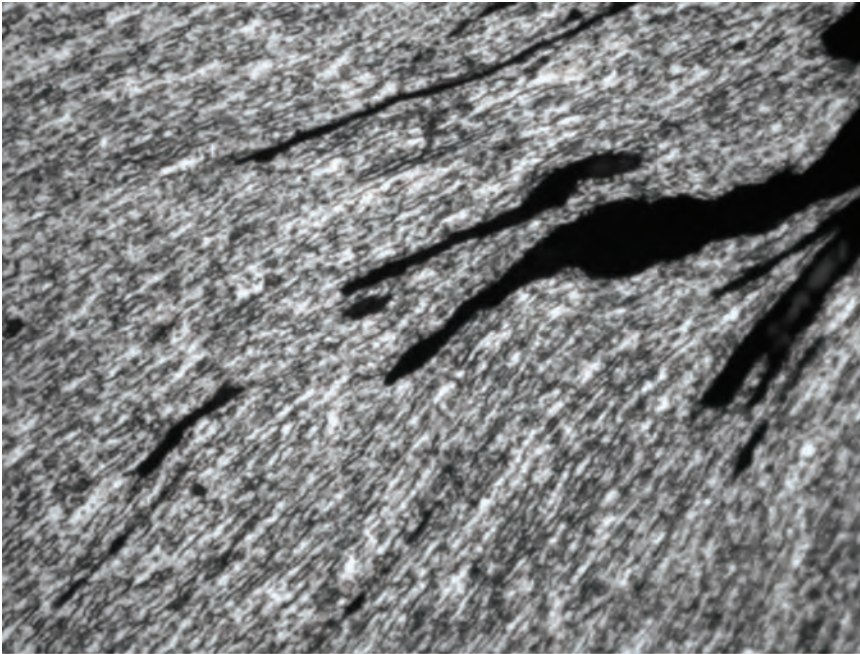


(b)

Fig. 6.23 Failed superheater tube (a) showing 180° bending and (b) opposite end view showing a burst opening with disordered contours



(a)



(b)

Fig. 6.24 (a) Scattered recesses at rupture lips, 200 $\times$. (b) Heavily deformed grain structure at rupture lip indicative of plastic deformation, 400 $\times$

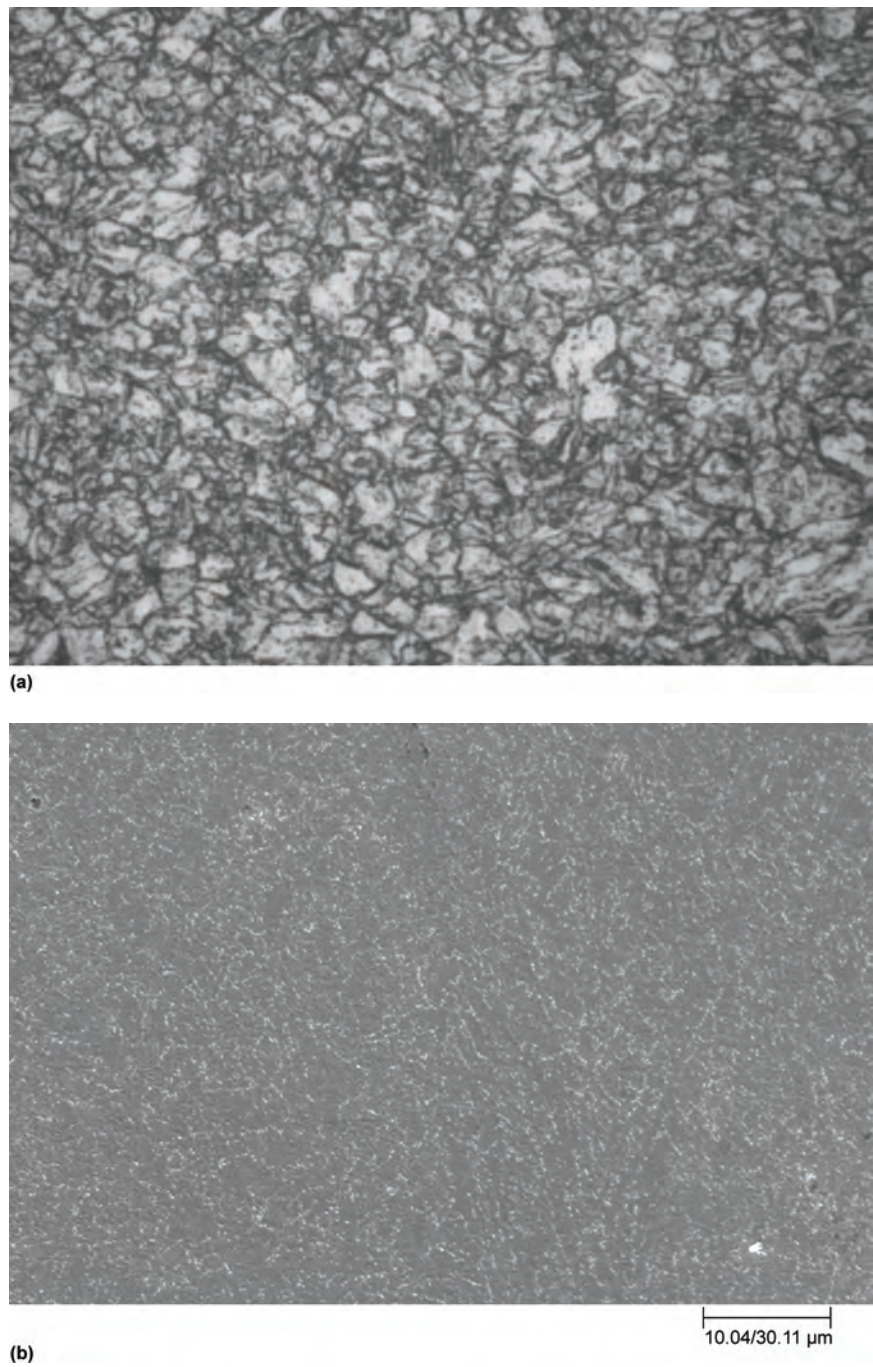


Fig. 6.25 (a) Optical micrograph showing tempered martensitic structure of the tube, 400×. (b) SEM micrograph indicating absence of creep voids, 1000×

High-Temperature Creep

One of the types of failure of boiler tubes under the stress rupture category is high-temperature creep. Creep is defined as the plastic deformation of a material at high temperature under a constant stress. The stress required to cause a material to creep is less than the yield strength of the material. Failure of superheater or reheater and waterwall tubes takes place due to creep when they are subjected to long-term overheating, quite often for a period of several years. The creep rate depends upon the strength of the material, the stress imposed, and the temperature. If the creep process continues unabated, it leads to final rupture of the tube. Creep damage is characterized by very little or no reduction in the wall thickness of the tube.

Some of the reasons for overheating of boiler tubes leading to their high-temperature creep damage are formation of internal (steam-side) surface oxide scales or chemical deposits resulting in reduced heat transfer across the tube; restricted flow of the tube coolant or gas flow because of debris/scaling or condensates; overfiring or uneven firing of fuel burners; and use of the tubes at temperatures greater than the maximum allowable temperature (Ref 6.6).

The optimal approach to assess the extent of any damage due to creep is to periodically subject the tubes to microstructural examination. In the case of plain carbon and low-alloy steel tubes, the initial microstructure is ferrite and pearlite. Prolonged exposure of the tube to elevated temperatures under stress leads to a gradual deterioration in the microstructure of the tube, from the lamellar nature of platelets of ferrite and cementite in pearlite to a degraded structure with ferrite plus carbide, as shown in Fig. 6.26.

This microstructural change is a gradual one. The initial microstructure of the tube is a typical ferrite-pearlite structure. The gradual decomposition of pearlite first leads to an in situ decomposition of lamellar pearlite to a globular one and then to a structure consisting of dispersed carbides in the ferritic matrix, which finally turns into an accumulation of carbides at the grain boundaries. With further exposure of the tube to elevated temperatures, the grain boundary carbides undergo spheroidization, and finally there may be formation of voids along the grain boundaries. Creep voids at the grain boundaries have a tendency to coalesce with time and form intergranular microcracks, leading to the final failure of the tube through the stress rupture mode.

Case Study 7—Failure Investigation of Reheater Outlet Tube

Background Details Failure in the form of leakage from a crack in the reheater outlet coil of a coal-fired supercritical boiler took place after about 5 months of operation. The tube was made of SA 213 Grade T91 steel and had dimensions of 63.5 mm (2.5 in.) OD and 6.1 mm (0.24 in.)

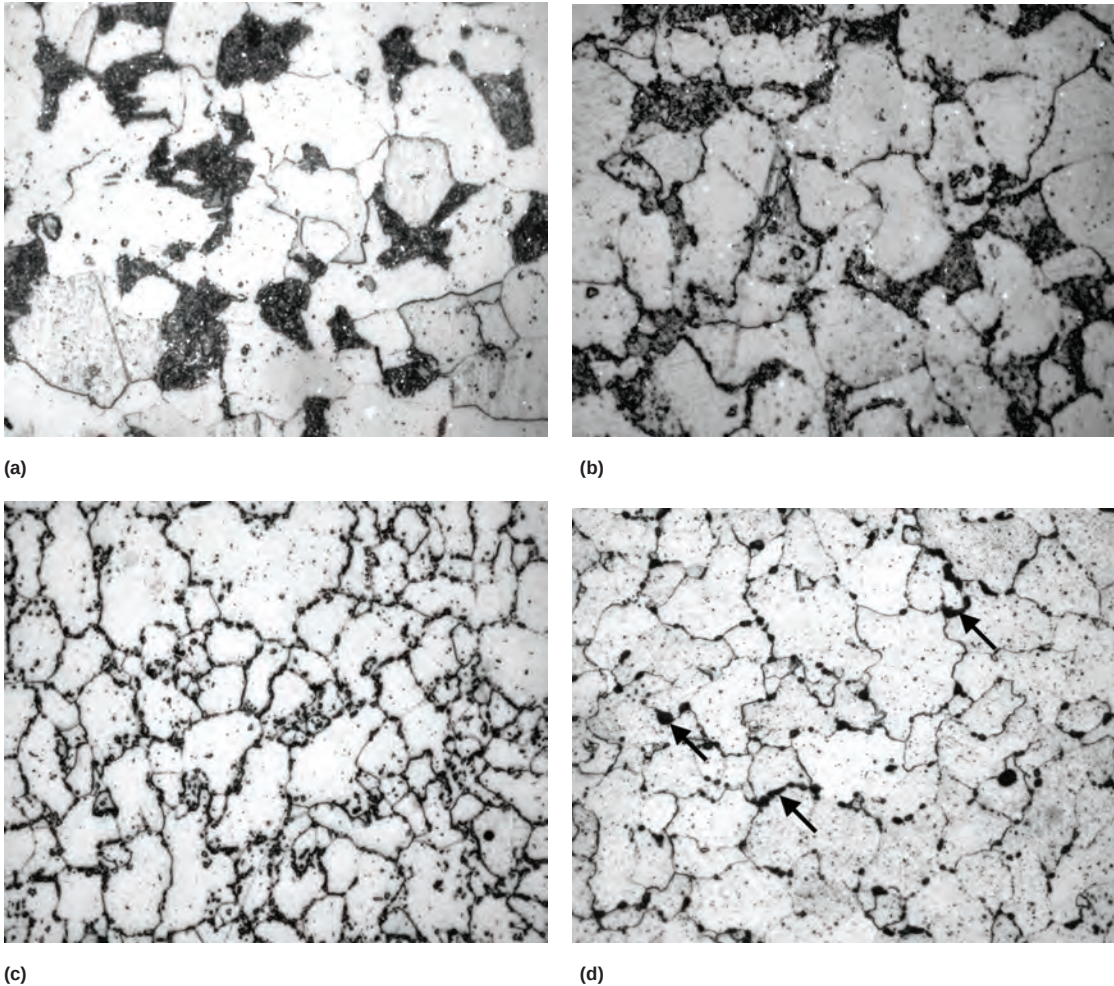


Fig. 6.26 Microstructural evolution during high-temperature creep damage: (a) initial ferrite plus pearlite, (b) in situ spheroidized carbide, (c) grain boundary carbides, (d) creep voids

thickness. The operating pressure and the temperature in the reheater section were 60 bar and 600 °C (1110 °F), respectively.

Investigation and Findings Per the photograph in Fig. 6.27, there was a longitudinal crack in the tube at the leakage location. The area surrounding the leakage location had bulged.

The tube sample received for investigation showed oxide scales on both the OD and ID surfaces. Half of the OD surface had a thin scale, dark brown in color, whereas the ID surface of the tube appeared brownish black, as shown in Fig. 6.28.

Dimensional measurements indicated bulging of the tube diameter toward the failure/crack side. In contrast to the nominal diameter of 63.5 mm (2.5 in.), the maximum diameter at the bulge was 68.0 mm (2.7 in.),



Fig. 6.27 Longitudinal crack in a tube



Fig. 6.28 (a) Dark brown scale on OD surface. (b) Brownish black scale on the ID surface of a tube

giving rise to an about 7% increase in diameter. Thickness measurements at different locations indicated an about 0.6 mm reduction in wall thickness on the crack side.

The scale thickness on the OD surface was 160 to 190 μm , and on the ID surface, it was 165 to 180 μm . The ID-side scale was subjected to deposit weight density measurement, and the results obtained are shown in Table 6.1.

Table 6.1 Deposit weight density measurement for ID-side scale

Parameter	Value
ID of tube, cm	5.13
Length of tube, cm	15.0
Area, cm ²	241.63
Deposit weight, mg	5936.84
Deposit weight density, mg/cm ²	24.57

The chemical composition of the tube material matched the specifications. Energy-dispersive x-ray spectrometry analysis on the OD surface showed the major constituent to be iron, with oxygen, magnesium, aluminum, silicon, sulfur, potassium, and calcium present as impurities. These impurities were expected to be from the flue gases because this was a coal-fired boiler.

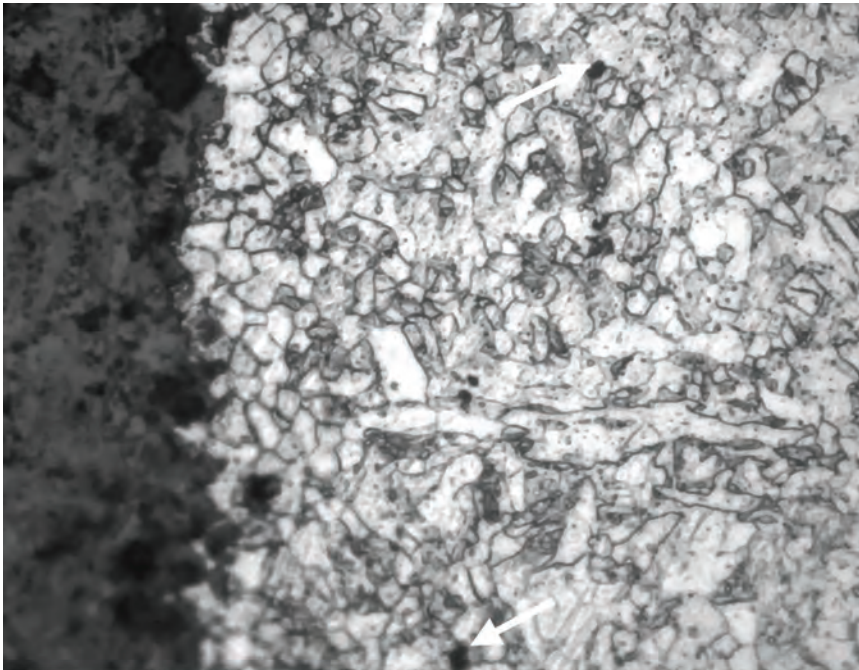
Metallographic examination of the ground and polished tube sample after etching revealed a structure consisting of tempered martensite. Scattered creep cavities were seen at the grain boundaries. Agglomeration and coarsening of carbides was observed in the OD- and ID-side microstructures (Fig. 6.29a and b). Even the core microstructure clearly indicated coarsening of carbides at the grain boundaries in the tempered martensitic matrix (Fig. 6.30).

Scanning electron microscope examination after metallography on the OD side of the failed sample revealed the presence of scattered creep cavities and grain boundary cracking both near the crack and at a location away from the crack (Fig. 6.31). Agglomerated and coarsened carbide particles were seen at the grain boundaries. Grain boundary carbide coarsening and creep cavities at a location away from the crack indicate loss of creep life of the tube.

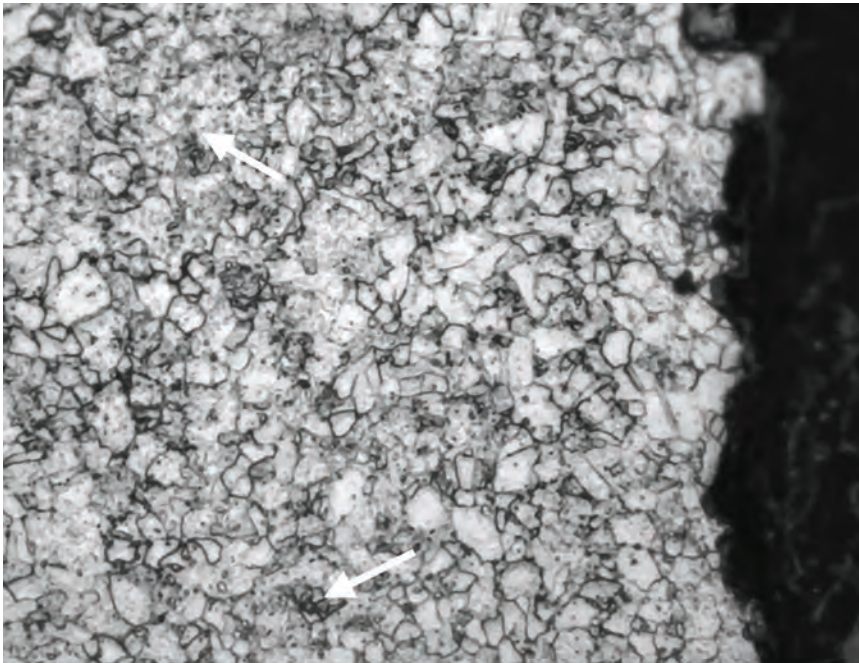
A hardness value of approximately 170 BHN was on the low side, which further confirmed thermal degradation of the microstructure. The normal required level of hardness to enable good creep life is between 190 and 210 BHN.

Scale formation on both the OD and ID surfaces was indicative of a temperature excursion on the entire tube. Thickness measurements and macrostructural examination indicated thinning on the crack side surface, which may be attributed to the loss of wall thickness from the flue gas side. The presence of scattered creep cavities seen under optical microscopy indicated the onset of tertiary creep damage. This onset was also evident in SEM micrographs, also in the form of scattered creep cavities, grain boundary cracking, and heavy grain boundary carbide coarsening.

The creep resistance of 9Cr steel is derived from the solid solution strengthening and fine precipitation of carbides/nitrides at the laths of the martensite. During operation, if the temperature is excessively high, these precipitates are coarsened and reduce creep resistance by forming alloy



(a)



(b)

Fig. 6.29 Microstructure of (a) OD side, 400 $\times$; and (b) ID side showing tempered martensitic structure with agglomerated and coarsened carbides in addition to scattered creep cavities at the grain boundaries, 400 $\times$

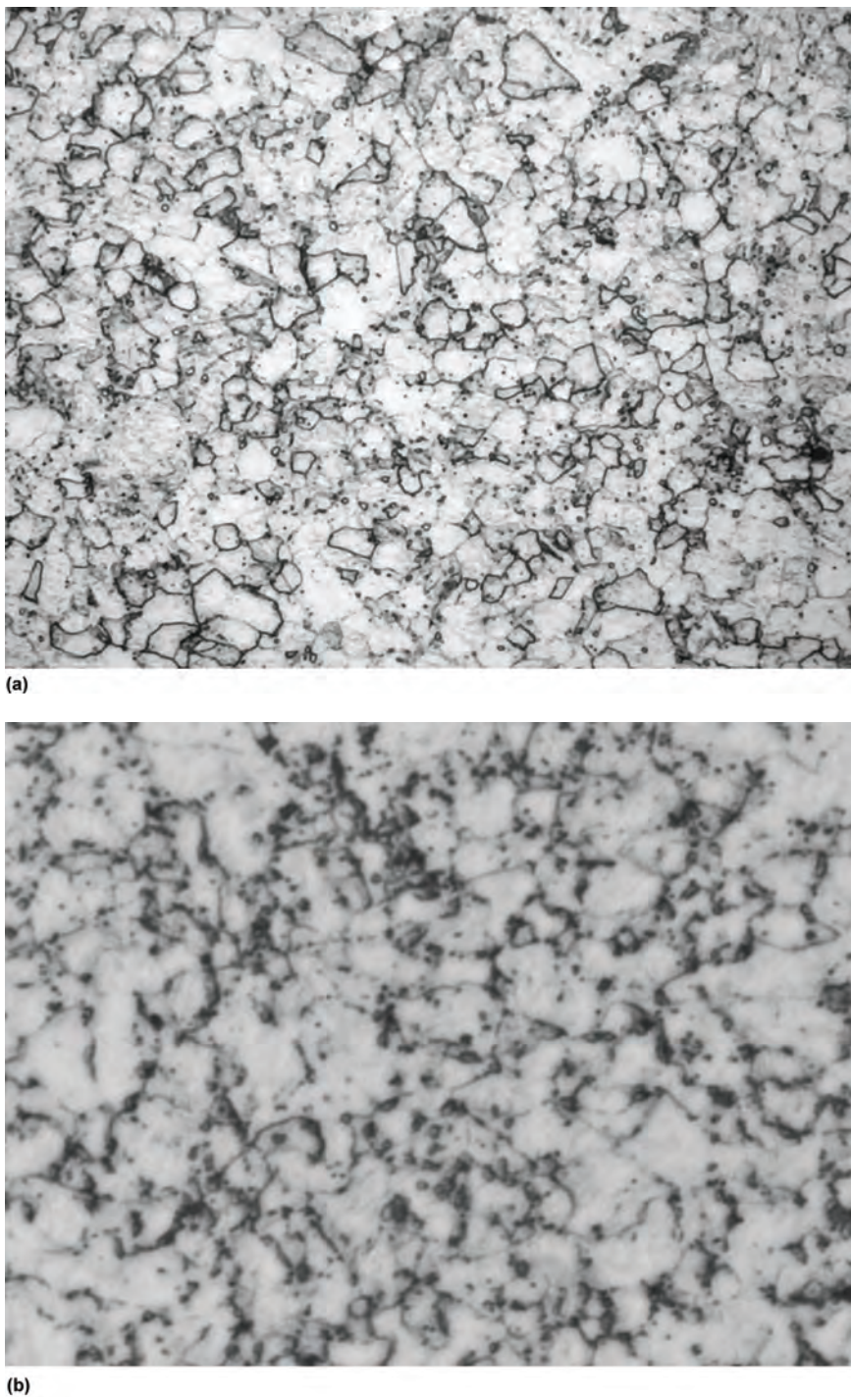


Fig. 6.30 Core microstructure indicating coarsening of carbides at the grain boundaries in the tempered martensitic matrix, (a) 400×, (b) 1000×

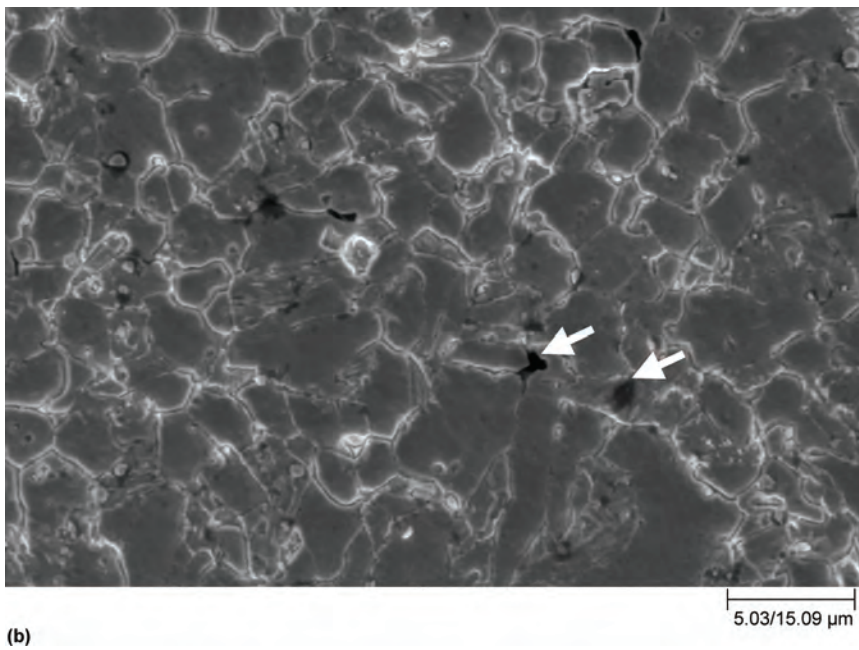
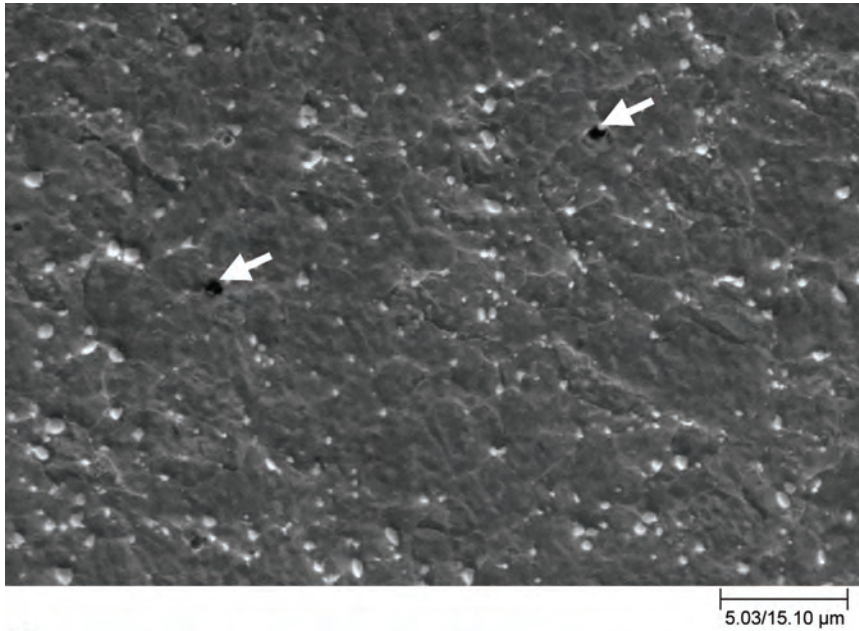


Fig. 6.31 SEM micrograph (a) at OD near crack, 2000 $\times$; and (b) at OD but away from crack, showing scattered creep cavities and grain boundary cracking, 2000 $\times$

carbides, mostly chromium carbides. The formation of carbides reduces chromium from the surrounding matrix and leads to loss of creep strength.

Based on the LMP curve for a tube diameter of 68.0 mm (2.67 in.) with a thickness of 6.4 mm (0.25 in.) at 60 bar pressure, the estimated skin temperature resolves to 690 °C (1295 °F). This is far above the permissible safe working temperature for T91 steel. Normally, the service temperature should not exceed 595 °C (1100 °F), with the temperature only occasionally reaching 640 °C (1185 °F).

Conclusions Based on an analysis of the investigation findings, the reason for failure of the reheater tube was creep damage due to an excessive operating temperature.

Case Study 8—Failure Investigation of Primary Superheater Tube of Coal-fired Boiler

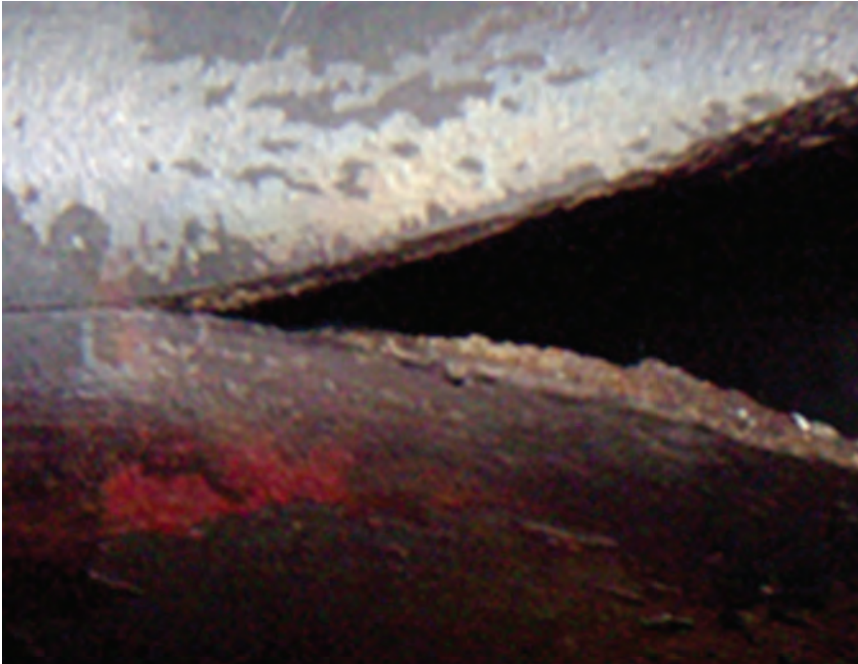
Background Details The primary superheater (PSH) tube of a boiler failed after a short service span of 2 months. The portion of the tube facing the flue gas side failed in the longitudinal direction during operation. It was the third tube in a coil of PSH tubes where no possibility of direct impingement of flue gases was envisaged. The exact location of the failure was 200 mm (7.85 in.) away from the weld joint toward the U-bend. The specifications of the tube material were in accordance with ASTM A213 T2, and the tube dimensions were 63.5 mm (2.5 in.) OD and 10.0 mm (0.4 in.) thickness. The steam inlet temperature was 350 °C (660 °F), and the steam exited the tubes at 430 °C (805 °F). Tubes were placed horizontally, although the flue gases passed vertically at 520 to 550 °C (970 to 1020 °F) from the top to the bottom.

Investigation and Findings Visual examination performed on an as-received cut piece of the PSH sample showed a fish-mouth opening at the ruptured region with no significant thickness reduction (Fig. 6.32a). The total thickness loss toward the fire side was 2.6 mm (0.1 in.), whereas on the opposite side, it was 3.6 mm (0.14 in.). Bulging was noticed at the other end of the failure (Fig. 6.32b). The inner surface of the tube had a tightly adherent black colored scale.

Low-magnification examination of the fracture surface revealed the brittle nature of the failure, as indicated in Fig. 6.33(a) and (b).

Chemical analysis of the tube material by optical emission spectroscopy revealed that it did not meet the requirements of ASTM A213 T2, especially with respect to the amounts of important alloying elements such as chromium and molybdenum. The amount of these two elements in the failed tube sample was found to be less than that specified by the standard. The chemical analysis indicated that the tube material conformed to plain carbon steel, as shown in Table 6.2.

Microstructural examination provided important evidence with regard to the failure mechanism. The microstructure at the fracture region displayed ferritic grains with a few carbide particles, but on the opposite side, it showed a ferrite-pearlite structure, which indicates that the temperature

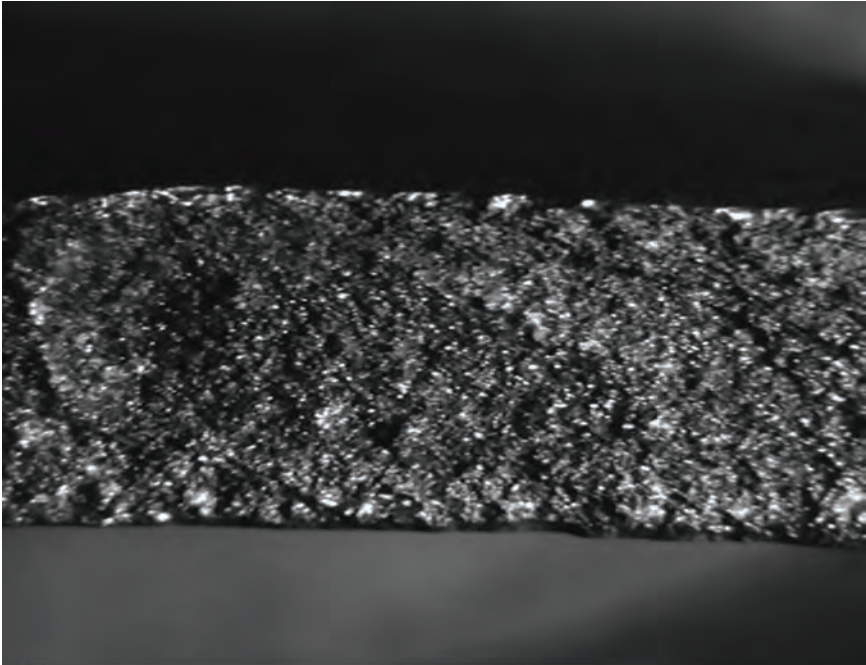


(a)

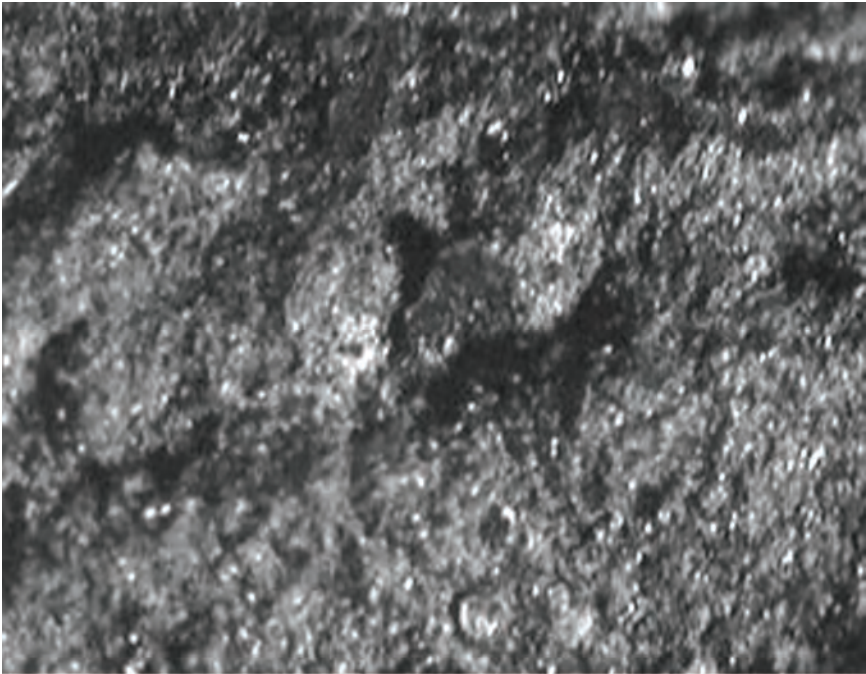


(b)

Fig. 6.32 (a) Fish-mouth thick-lip failure of a PSH tube; (b) bulging on outer surface of the tube



(a)



(b)

Fig. 6.33 Enlarged views of the fracture surface indicating brittle nature of failure, (a) 8 $\times$, and (b) 13 $\times$

Table 6.2 Chemical analysis of tube material

Element	Actual, wt.%	Required, wt.%	Element	Actual, wt.%	Required, wt.%
Carbon	0.110	0.06–0.2	Chromium	0.130	0.3–0.75
Sulphur	0.010	0.035 max	Nickel	0.104	0.3 max
Phosphorus	0.008	0.035 max	Molybdenum	0.033	0.41–0.64
Manganese	0.710	0.4–1.0	Copper	0.175	0.25 max
Silicon	0.200	0.05–0.4	Tin	0.019	0.03 max

was higher at the fracture location than at the far side of the tube. Creep cracks and oriented creep cavities indicated enhanced degradation of the tube facing the flue gas side (Fig. 6.34a and b). Cracks that originated from the OD were filled with oxides. The presence of orientated creep voids was quite evident in the microstructure.

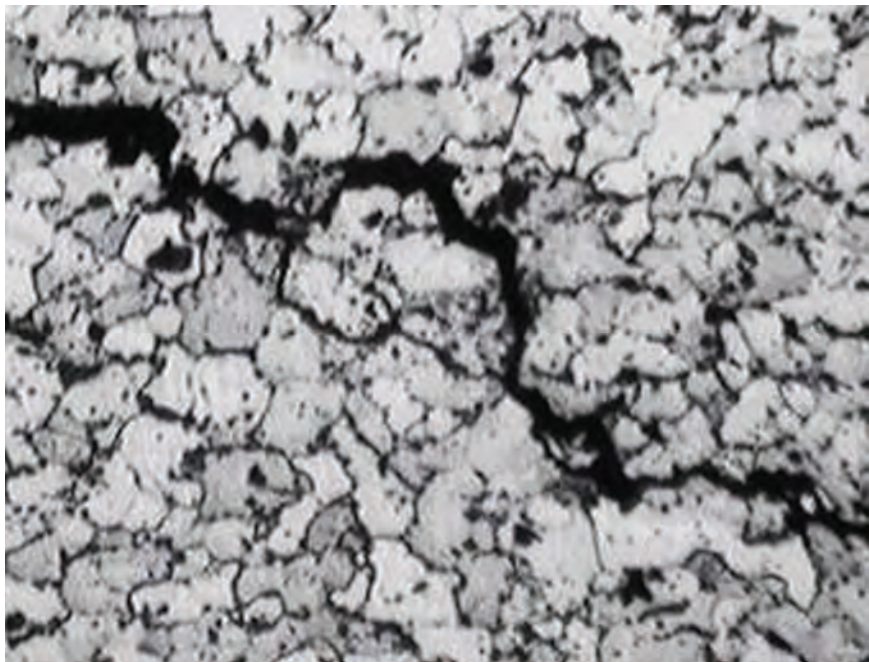
Scanning electron microscopy indicated the presence of creep cavities and cracks toward the fire-side region, whereas at the far side, the extent of the creep damage was lower. Scanning electron microscopy also showed oriented creep cavities along the grain boundaries (Fig. 6.35a). The OD cracks were found to be filled with oxide scales because the material was exposed to flue gases (Fig. 6.35b). This confirmed that the tube metal had undergone creep damage and the openings of creep cracks on the outer surface were oxidized during operation.

A hardness traverse across the transverse section of the tube revealed lower hardness values at the fire side than those at the far side. This lower hardness value at the fire side was because of deterioration in the microstructure due to the higher operating temperature of the tube facing fire side. Additionally, tensile testing of the tube sample further confirmed the poor mechanical properties of the tube material in regard to its 0.2% proof strength, and the ultimate tensile strength. Both values are lower than that recommended by the standard.

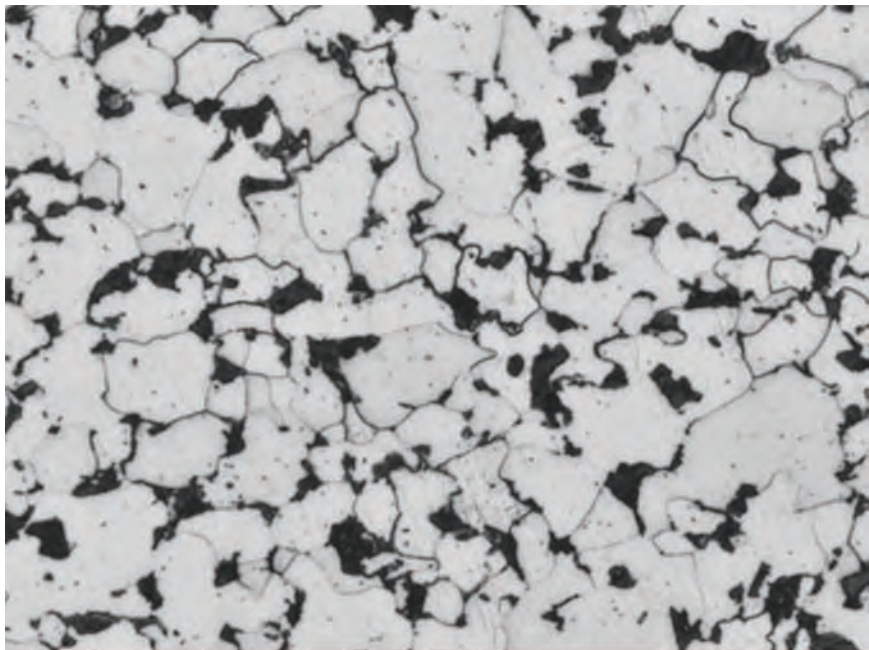
Conclusions The PSH tube failed in the creep mode due to use of improper material (i.e., carbon steel in place of low-alloy steel). The carbon steel tubes could not withstand such high operating pressure and temperature. The operating conditions were not conducive for carbon steel as the tube material, which resulted in failure within a short service span of 2 months through the creep mode.

Case Study 9—Failure of Final Superheater Tube in a Thermal Power Plant

Background Details The final superheater tube in a thermal power plant failed after 16,000 hours of service. The failure was noticed by the operators due to a loud noise. The MOC of the superheater tube was SA 213



(a)



(b)

Fig. 6.34 (a) Microstructure of fracture edge with grains of ferrite and creep crack along with oriented creep cavities, 400 $\times$; (b) normal ferrite-pearlite structure away from failure location, 400 $\times$

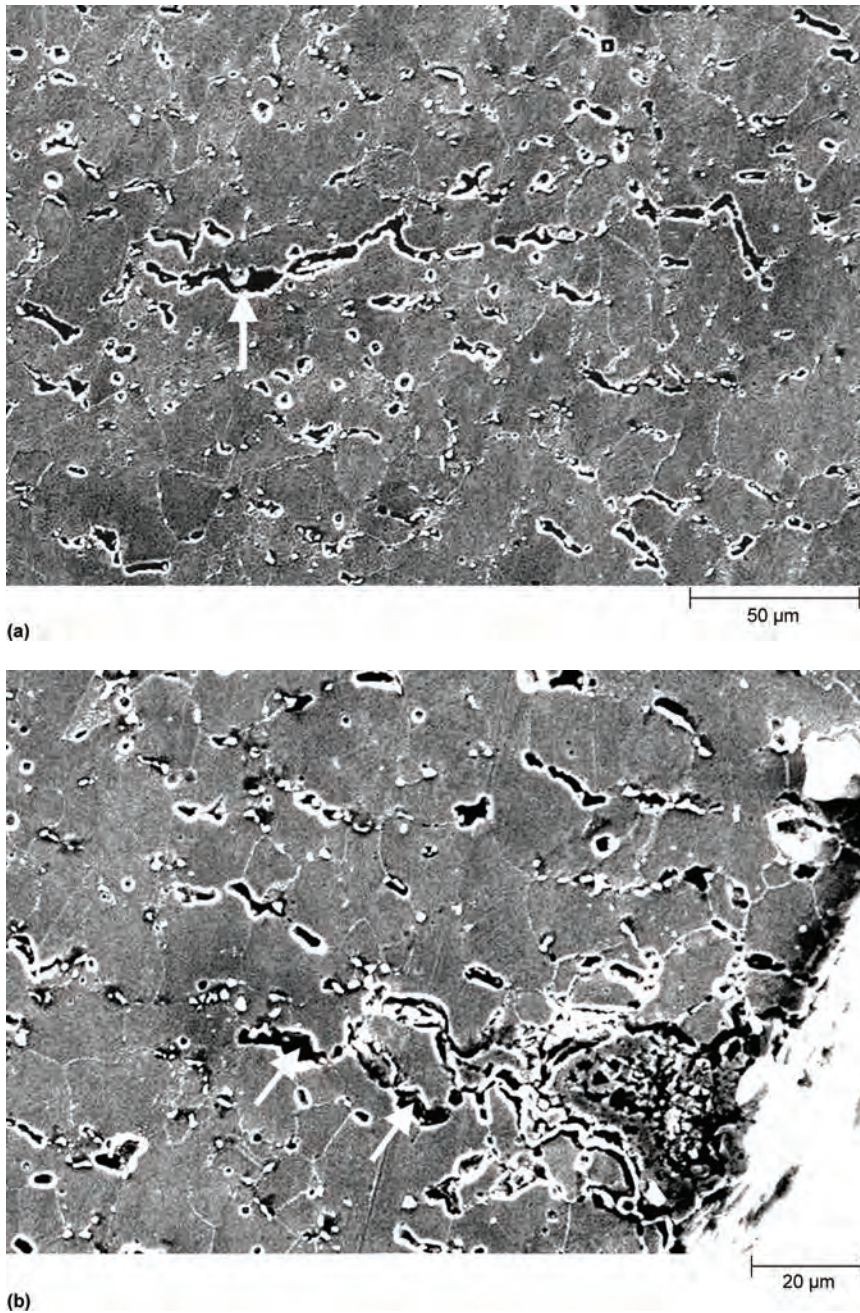


Fig. 6.35 SEM micrographs showing (a) ferritic structure with orientated creep cavities and microcracks, 500 $\times$; and (b) creep cracks originating from OD filled with oxides, 750 $\times$

Grade T91 steel, and the tube dimensions were 51.0 mm (2 in.) OD and 11.0 mm (0.43 in.) thickness. The operating steam temperature and pressure were 575 °C (1067 °F) and 25.4 MPa, respectively, whereas the superheated steam flow rate was 2120 tons/hour. An attemperation system was available in the superheater area.

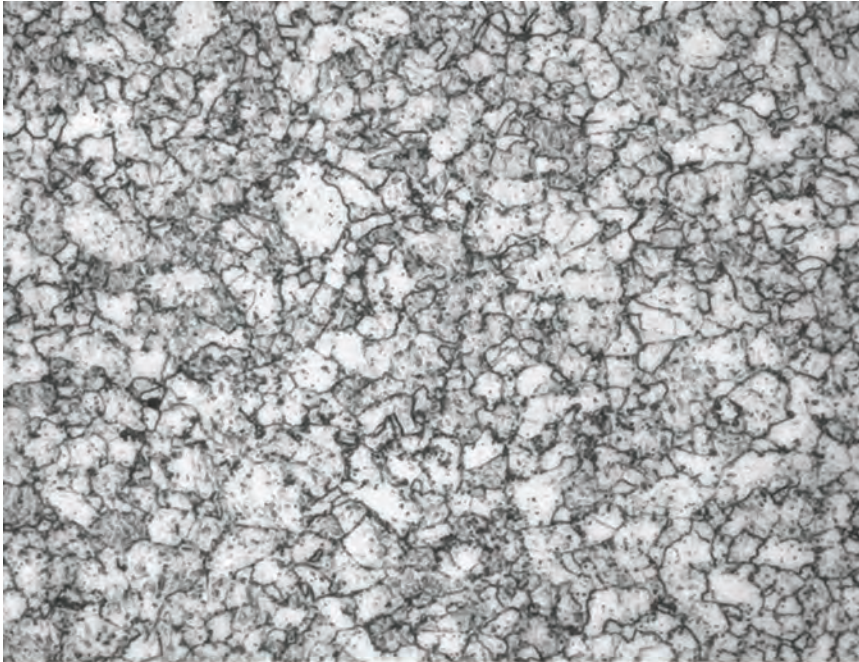
Investigation and Findings Figure 6.36 shows close-up views of the failed tube. Bulging of the tube was noticed surrounding the ruptured area. The rupture was in the form of a thick-lip fish-mouth opening. The rupture occurred at a distance of 40 to 50 mm (1.5 to 2 in.) from the welded joint. A craze pattern was observed on the outer surface near the burst.

The failed tube was subjected to tests such as dimensional measurements, thickness measurements, wet fluorescent magnetic particle inspection (WFMPI), chemical composition analysis, tensile and hardness testing, macro- and microfractography using SEM, and microstructural examination. Dimensional checking and the thickness measurement survey showed wall thinning at the rupture contours. The lowest thickness found was 5.2 mm (0.2 in.), compared with the nominal thickness of 11.0 mm (0.4 in.) per specifications. The WFMPI highlighted two hairline cracks at the rupture tips. The results of chemical analysis confirmed that the material corresponds to the requirement of SA 213 Grade T91. An EDS analysis on the inner surface showed presence of oxygen, magnesium, and silicon. Energy dispersive spectroscopy performed on the outer surface and scale collected from the outer surface showed elements such as oxygen, sodium, magnesium, aluminum, silicon, phosphorus, sulfur, potassium, calcium, titanium, and zinc.

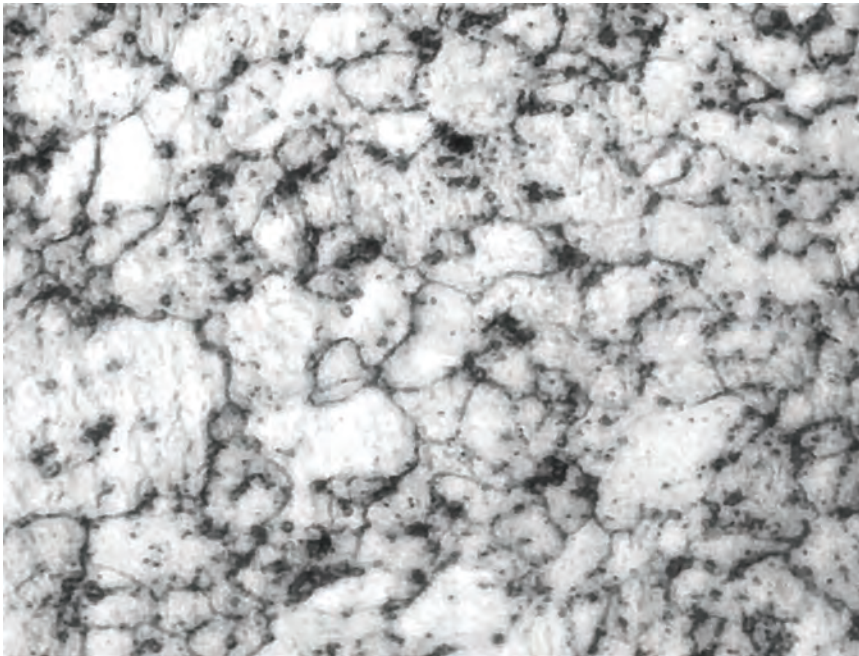
Microstructural examination of the tube indicated the presence of ferrite and tempered martensite phases rather than a fully tempered martensitic structure, thus revealing a manufacturing deficiency at the time of heat treatment of the tube (Fig. 6.37). T91 steel derives its creep resistance from



Fig. 6.36 Close-up views of a superheater tube at the failure location



(a)



(b)

Fig. 6.37 Core microstructure of a tube showing ferrite and tempered martensite, (a) 400 $\times$, (b) 1000 $\times$

a microstructure of 100% tempered martensite, which was not found in this case. Scanning electron microscopy after metallography showed the presence of coalesced creep voids (Fig. 6.38).

The presence of ferrite in the microstructure was reflected in tensile test results; this resulted in low strength compared with the recommended value (measured proof strength was 270 N/mm², compared with the standard 415 N/mm²). The hardness value on the parent metal was on the lower side, at 170 HV, whereas at the heat-affected zone (HAZ) and weld, hardness appeared to be normal at 200 and 240 HV, respectively.

Because the tube material had inherently poor metallurgical structure leading to inadequate mechanical properties, when the tube was exposed to high pressure and temperature, it degraded at an accelerated rate due to creep.

Conclusions Failure of the tube was attributed to inadequate metallurgical integrity of the tube material, which had poor microstructure and therefore poor mechanical properties. The tube eventually failed due to creep in the stress rupture mode when the tube cross section could not sustain the operating conditions.

Case Study 10—Failure Investigation of a Superheater Tube in a Supercritical Boiler

Background Details A failure was noticed in the final superheater tube of a supercritical boiler after 5 years of service. The MOC of the superheater tube was in conformance with SA 213 Grade TP-347 HFG, and the tube

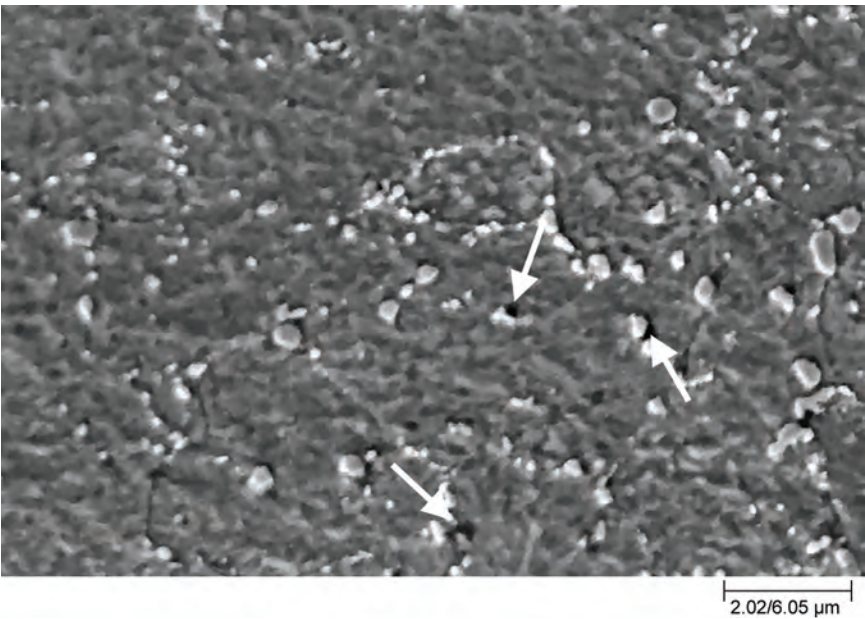


Fig. 6.38 SEM micrograph showing coalescence of creep cavities along the grain boundaries, 5000×

dimensions were 50.0 mm (2 in.) OD and 8.0 mm (0.3 in.) thickness. The operating steam temperature and pressure were 570 °C (1060 °F) and 25.4 MPa, respectively.

Investigation and Findings Visual examination of the failed tube sample revealed a rupture in the form of a fish-mouth opening. A crack extended in the longitudinal direction from one end of the rupture up to the weld region. Bulging of the tube was noticed surrounding the ruptured area. Figure 6.39 shows a close-up view of the failed tube.

The failed tube was subjected to tests such as chemical composition analysis, tensile and hardness testing, fractography using SEM, EDS analysis, and microstructural examination. The results of chemical analysis confirmed that the material corresponds to the requirements of SA 213 Grade TP-347 HFG. Tensile and hardness values were normal. The SEM examination showed scattered creep voids and cracks along the austenite grain boundaries (Fig. 6.40).

Microstructural examination of the tube indicated the presence of the sigma phase in the matrix of worked austenite (Fig. 6.41).



Fig. 6.39 Close-up view at the failure location. The rupture is in the form of a fish-mouth opening. A crack extends in the longitudinal direction from one end of the rupture.

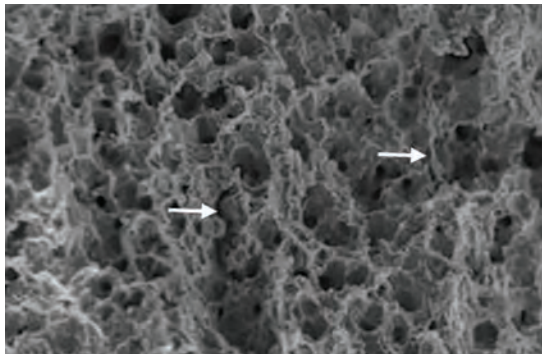


Fig. 6.40 SEM fractograph of the rupture surface showing scattered creep voids and cracks

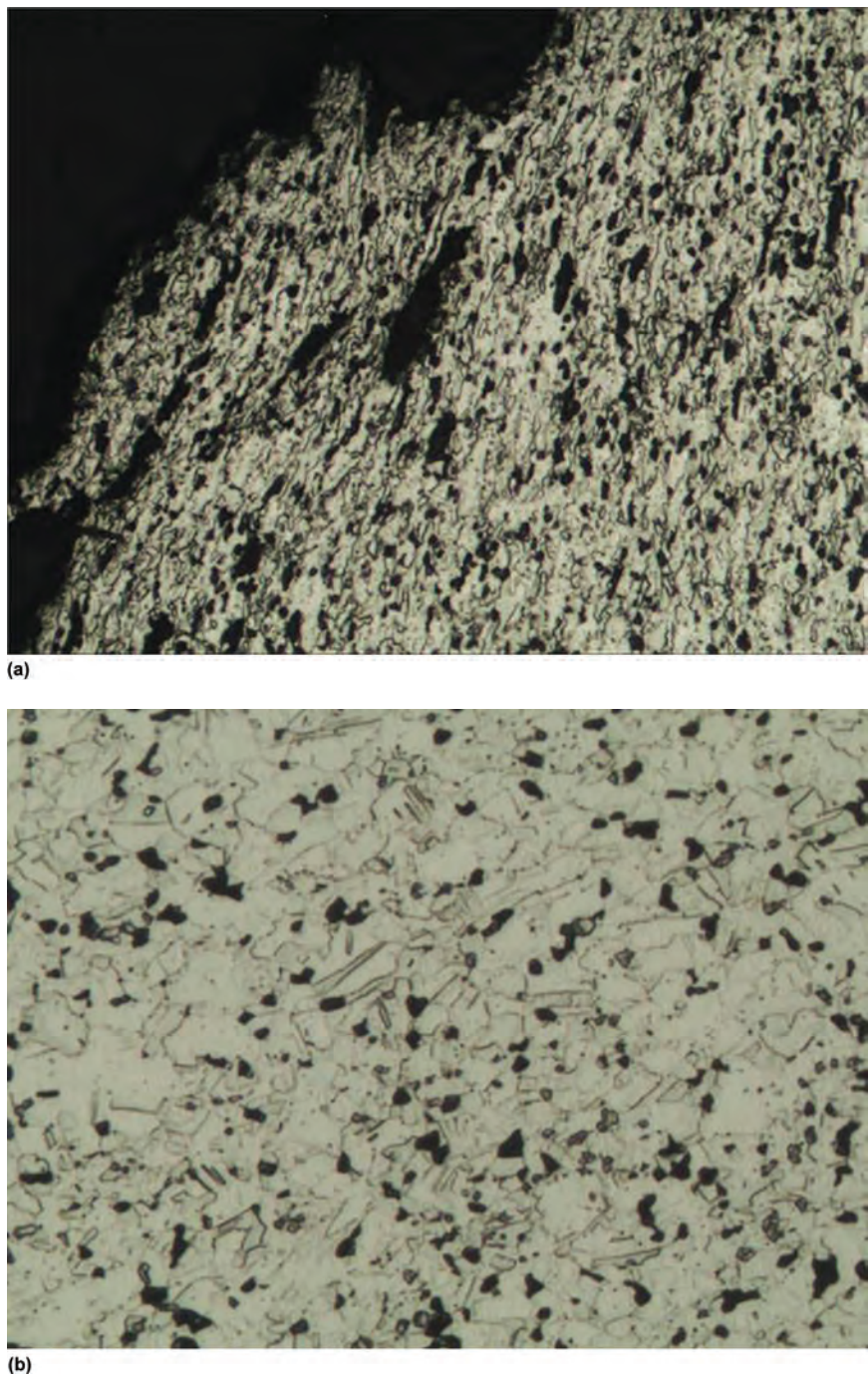


Fig. 6.41 Microstructure of a tube comprising sigma phase in the worked austenite matrix at (a) OD surface, 200 $\times$; and (b) within the core of the tube, 400 $\times$

Energy dispersive spectroscopy analysis after metallography on the dispersed phase within the austenite matrix showed the presence of elements such as carbon, silicon, chromium, manganese, nickel, and iron (Table 6.3).

The average amount of sigma phase calculated per image analysis was 8.3% at the failure location, and on the opposite side, it was 2.9%. This indicated that the flue gas side was exposed to higher temperature.

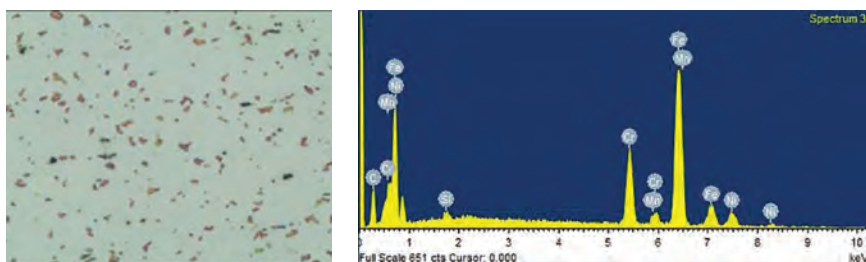
The steam temperature inside the superheater tubes was 570 °C (1060 °F), and in turn the skin temperature of the tubes should be around 620 °C (1150 °F). This is the temperature at which the sigma phase develops in austenitic stainless steels. Austenitic stainless steels are prone to sigma phase formation when exposed to a temperature range of 600 to 900 °C (1110 to 1650 °F) for a prolonged duration. In addition to the sigma phase, the exposure of the tube to temperatures beyond the design temperature for a long time resulted in formation of creep voids.

Conclusions The failure of the tube was attributed to sigma phase formation and creep due to its long-term elevated-temperature exposure.

Graphitization

Carbon and low-alloy steels in annealed and normalized conditions, at and near ambient temperatures, have a ferrite-pearlite structure with alternate platelets of ferrite and cementite in the grains of pearlite. Such steels are called pearlitic steels. The mechanical properties of pearlitic steels are due to their lamellar structure, offering high intermediate-term low-stress creep resistance. However, when these steels are exposed to elevated temperatures for a long time, their microstructure changes.

Table 6.3 EDS analysis of dispersed sigma phase in austenite matrix



Element	Amount by wt. %	Element	Amount by wt. %
Carbon	2.74	Manganese	1.30
Silicon	0.80	Iron	63.57
Chromium	18.43	Nickel	13.16

Prolonged exposure of carbon and low-alloy steel boiler tubes (such as C-Si and C-0.5Mo steels) above 450 °C (840 °F) results in decomposition of pearlite. This involves the transformation of metastable or unstable cementite having a lamellar structure to its equilibrium or stable state with a different morphology of carbon. The transformation process is called *spheroidization* when the carbon in the cementite has a spherical or spheroidal morphology. When the graphite particles have a nodular shape, the process is termed *graphitization*. Graphitization is defined as the process of formation of free carbon, or graphite, in steel.

In the case of graphitization, pearlite decomposes when the steel is subjected to long-term use in a temperature interval of about 450 to 550 °C (840 to 1020 °F). The long-term microstructural degradation of carbon steel results in the formation of graphite with a chain or plane of nodules. This weakens the steel by severely embrittling it and ultimately leads to failure of the tube. Graphitization causes a loss in strength, ductility, and/or creep resistance of the steel.

Whether spheroidization or graphitization occurs when the tubes are exposed to elevated temperatures depends on the composition and microstructure of the steel, and the service temperature. For plain-carbon steels, the transition point in the competing processes of spheroidization and graphitization is approximately 500 °C (930 °F). Above this temperature, spheroidization occurs before graphitization, and below this temperature, graphitization occurs before complete spheroidization (Ref 6.7). Figure 6.42 shows a normal pearlitic structure, and spheroidized and graphitized microstructures at a glance. The addition of chromium and molybdenum to a steel improves the high-temperature strength, resistance to spheroidization and graphitization, and resistance to oxidation.

Case Study 11—Failure Investigation of a Low Temperature Superheater Tube

Background Details The low temperature superheater (LTSH) tube of a 110 MW boiler failed with a burst opening. This failure occurred after 6 years of service. The specified MOC of the tube was SA 213 Grade T11. The tube dimensions were 45.0 mm (1.5 in.) OD and 5.1 mm (0.20 in.) thickness. The operating steam pressure in the superheater section was 138 kg/cm². The steam inlet temperature was 425 °C (795 °F), and the steam exited the tubes at 540 °C (1005 °F).

Investigation and Findings Per Fig. 6.43(a) the tube ruptured in the longitudinal direction. The surrounding area of the rupture location bulged. The scale on the external surface of the tube showed serrations due to the tube expansion. The ID surface of the tube also showed the presence of scaling with serrations (Fig. 6.43b).

Chemical analysis of the tube material carried out by optical emission

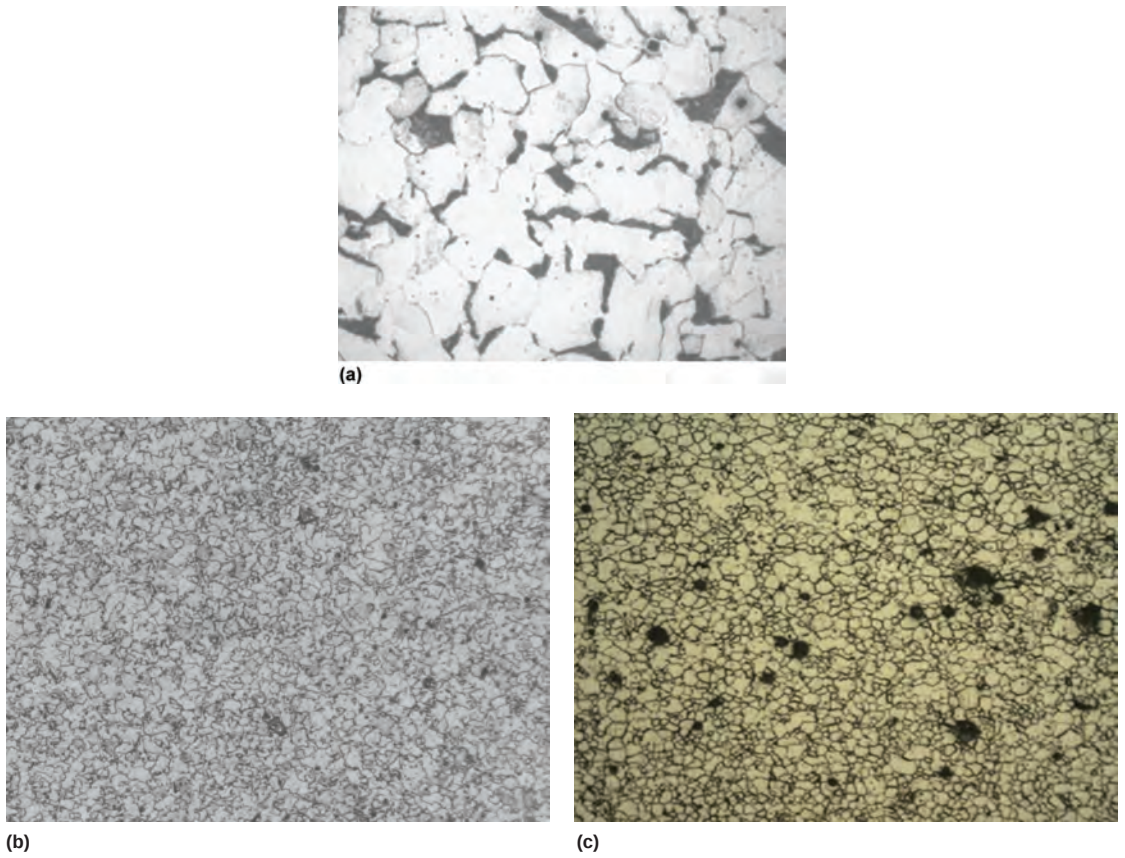


Fig. 6.42 Structures at a glance: (a) normal pearlitic, 200 $\times$; (b) spheroidized, 100 $\times$; (c) graphitized, 100 $\times$

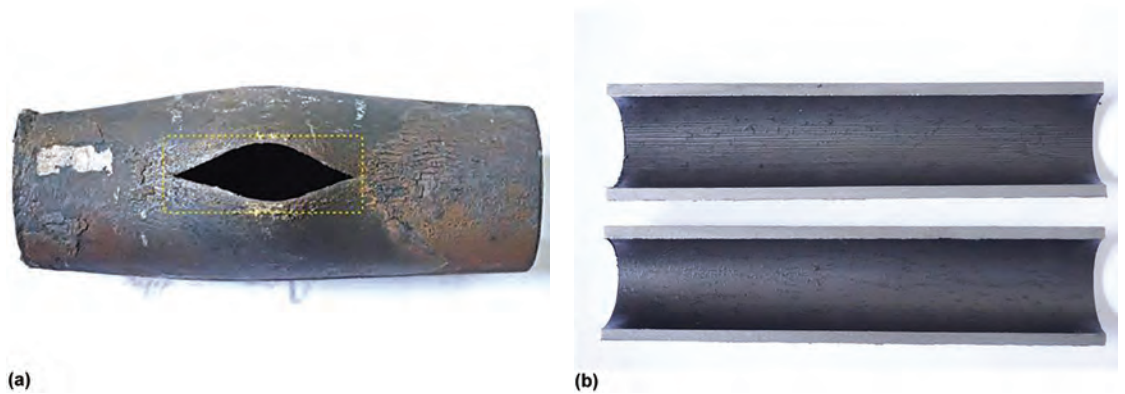


Fig. 6.43 Failed tube showing (a) rupture in the longitudinal direction and (b) presence of scaling with serrations on ID surface

Table 6.4 Chemical analysis of tube material

Elements	Measured value, wt.%	Required value per SA 213 Grade T11, wt.%	Elements	Measured value, wt.%	Required value per SA 213 Grade T11, wt.%
Carbon	0.274	0.050–0.15	Silicon	0.284	0.50–1.00
Sulfur	0.013	0.025 max	Chromium	0.028	1.00–1.50
Phosphorus	0.024	0.025 max	Molybdenum	0.012	0.44–0.65
Manganese	0.870	0.30–0.60			

spectroscopy revealed that it did not meet the requirements of SA 213 Grade T11, especially with respect to the amounts of important alloying elements such as chromium and molybdenum. The amount of these two elements in the failed tube sample was found to be less than that specified by the standard. A chemical analysis of the tube material conformed to plain carbon steel, as shown in Table 6.4.

The overall microstructure of the tube was of the banded ferrite and pearlite type. However, it showed the presence of graphite nodules (Fig. 6.44a and b). The microstructure at the failure edge showed a structure consisting of spheroidized pearlite with graphite nodules (Fig. 6.44c). An SEM examination after metallography revealed the presence of scattered creep voids and grain boundary cracking (Fig. 6.44d).

Tensile testing of the tube sample pointed toward the poor mechanical properties of the tube material in regard to its ultimate tensile strength. The tensile strength was less than that recommended by the standard. Hardness values were also on the lower side.

Per data provided, the LTSH tube temperature varied from 425 °C (795 °F) at the inlet to 540 °C (1005 °F) at the outlet end. The skin temperature of the tube is usually 40 to 50 °C (70 to 90 °F) higher than the steam temperature. This is the temperature range in which plain carbon steel degrades by a process of graphitization and also undergoes degradation of its pearlite colonies. The poor metallurgical structure developed due to use of the wrong tube material (i.e., use of carbon steel tube in place of alloy steel) resulted in inadequate mechanical properties. The loss of mechanical properties due to graphitization and pearlite degradation resulted in tube rupture.

Conclusions The failure of the tube was attributed to inadequate metallurgical integrity of the tube material as a result of the synergistic effect of graphitization and pearlite degradation and therefore poor mechanical properties. The tube eventually failed due to creep in the stress rupture mode.

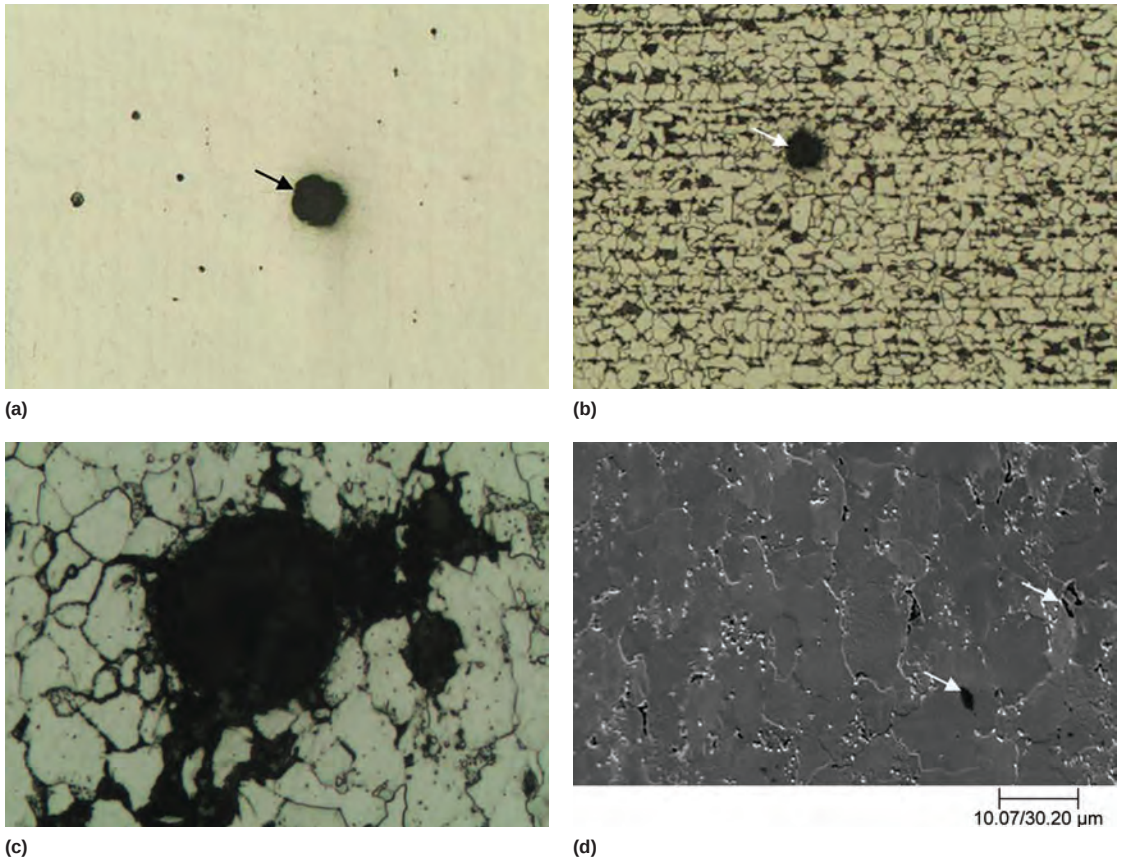


Fig. 6.44 (a) Graphite nodules in as-polished (unetched) sample, 100 ×; (b) fine, banded ferrite-pearlite structure of the core with graphite nodules, 400×; (c) microstructure at the edge consisting of completely spheroidized structure with intergranular cracks and graphite nodules, 400×; and (d) SEM after metallography highlighting presence of creep voids, 1000×

Dissimilar Metal Welds Failures

For techno-economic reasons, fabrication of coal-fired boilers involves a combination of ferritic steels for relatively low-temperature components and austenitic stainless steels for the superheater and reheater sections, which operate at higher temperatures. Such combinations can lead to the production of dissimilar metal welds (DMW).

Dissimilar metal welds account for some stress rupture failures of boiler tubes. For example, a butt joint between an austenitic stainless steel (SS 347) and a ferritic steel tube of SA 213 grade T91 material resulted in a circumferential rupture on the ferritic side of the joint along the weld fusion line (Fig. 6.45). Such failures were found in cases of dissimilar weld joints of tubes belonging to superheaters and reheaters. Figure 6.45 displays a typical case of failure due to dissimilar weld joints.



Fig. 6.45 Typical dissimilar metal weld joint

One reason for DMW-type failures is diffusion of carbon from the HAZ of the ferritic side to the austenite side of the weld metal. This forms a band of carbon-depleted low-alloy steel immediately adjacent to the weld interface. Such a band has much lower resistance to creep than average and gives rise to creep failure. Other reasons are the difference between the thermal expansion coefficients of the two grades of steel, resulting in a significant temperature-induced stress at the austenitic to ferritic weld interface; and the difference between the oxidation/corrosion resistance of the two grades, which leads to the formation of an oxide wedge on the ID and OD sides of the tube (Ref 6.8). Finally, the reduction in effective tube thickness reduces its load bearing capacity and causes failure through the stress rupture mode.

Dissimilar metal weld failures are usually catastrophic in nature with little or no prior indication of the damage.

Water-Side Corrosion Failures

Role of the Oxide Layer in Corrosion of Boiler Tubes

Corrosion is defined as the deterioration and loss of material due to chemical attack. There are two basic modes of corrosion in boiler tubes:

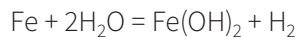
- *Internal corrosion or water-side corrosion:* For example, hydrogen damage, acid phosphate corrosion, caustic gouging, and pitting
- *External corrosion or fire-side corrosion:* For example, waterwall fireside corrosion, superheater/reheater fireside corrosion, and acid dew point corrosion

The process of oxidation of iron is known as *rusting* or *corrosion*. The interaction of steam and water at the internal surface of the tube usually gives rise to the formation of a scale. The scale comprises different oxides of varying thickness. Three important oxides of iron that normally constitute the scale are FeO (i.e., wustite), Fe₂O₃ (i.e., hematite), and Fe₃O₄ (i.e., magnetite). There can also be formation of a compound Fe(OH)₂ (i.e., ferrous hydroxide) in the presence of moisture.

The composition of an oxide layer varies considerably for carbon and low-alloy steel pipes and tubes with less than 3% Cr, depending on the temperature. For example, below 570 °C (1060 °F), the main constituent of the scale formed is magnetite (Fe_3O_4), whereas above 570 °C, it is wustite (FeO). In either case there is a thin layer of hematite (Fe_2O_3) as the outermost layer, as shown in Fig. 6.46. Below 570 °C, the magnetite layer is the major constituent of the scale, and hematite and wustite are the minor constituents. Contrary to this, above 570 °C, wustite is in the form of a thick layer, whereas magnetite and hematite are thin layers (Ref 6.9). For steels with greater amounts of alloying elements, such as T91 steel with 9% Cr and 1% Mo, there is an additional innermost layer of spinel oxide such as $(\text{Fe}, \text{Cr})_3\text{O}_4$ or $(\text{Fe}, \text{Cr}, \text{Mo})_3\text{O}_4$.

A detailed discussion on the process of oxidation of iron is given below for the purpose of understanding the effect of the oxide layer on the performance of boiler tubes.

Exposure of iron to water in the form of condensate leads to formation of ferrous hydroxide:



Ferrous hydroxide in the presence of oxygen further gives rise to the formation of ferric oxide (i.e., Fe_2O_3) or hematite (also known as red rust because of its reddish brown color). Formation of a layer of hematite on the inner walls of the boiler tubes is generally not desired for two reasons. Firstly, this layer has poor thermal conductivity and therefore it contributes to overheating of the bottom area of the tube. The overheating of the tube results in failure of the tube by stress rupture. Secondly, the hematite layer is not densely adherent to the tube surface, but it is in the form of porous loose/fluffy deposits that become detached or exfoliated easily

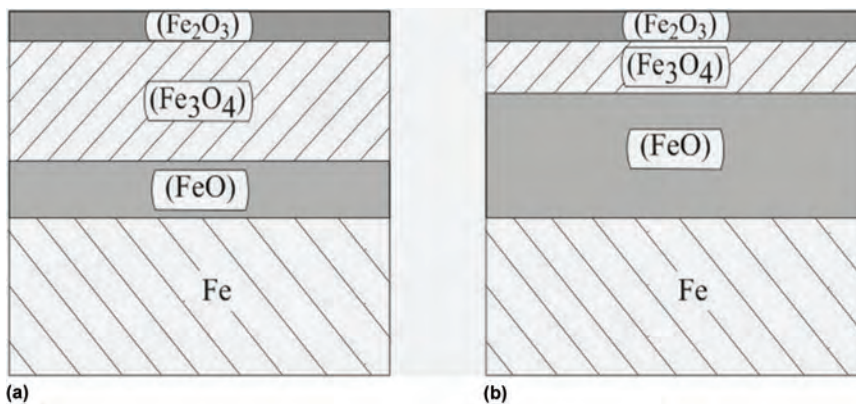


Fig. 6.46 Schematics showing formation of oxide layers on steel surface at (a) temperature <570 °C (1060 °F) and (b) temperature >570 °C

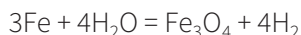
and can lead to deposition and choking in the downstream of the boiler. In turn, it leads to overheating of the tube. The breakage of the scale into small pieces due to exfoliation can cause problems in the turbine as well. The broken pieces are carried over to the turbine, resulting in serious problems due to erosion.

At relatively high temperatures, ferrous hydroxide dissociates to form ferrous oxide (i.e., Fe_3O_4) or magnetite:



Unlike hematite, the magnetite forms a thin, black, and firmly adherent layer on the tube surface that helps to improve the heat transfer across the tube wall due to its excellent thermal conductivity. It is worth noting that hematite forms under oxidizing conditions, whereas magnetite forms under reducing conditions. The main advantage of the magnetite layer is that, once formed, it protects the tube from subsequent corrosion. In other words, it acts as a passive layer and therefore is desired for longer life of the tube. Treatment of boiler feedwater (BFW) with water treatment chemicals such as hydrazine helps to promote the formation of a protective oxide film of magnetite on the water side of boiler tubes. The amount of dissolved oxygen in the BFW has a direct influence on the magnetite layer. The magnetite layer remains intact as long as the dissolved oxygen level of the BFW is low.

Magnetite can also form directly by interaction of iron from the steel with water vapor or steam:



Per this equation, at temperatures above 100 °C (210 °F) under reducing conditions, an electrochemical reaction between water and steel results in formation of a layer of magnetite. Ideally, the water-side surface of the boiler tubes should be coated with a thin layer of magnetite. A scale with thickness of up to about 0.3 mm (i.e., 300 μm) is considered to have a positive influence on the tube life, but beyond this it has an adverse effect. Ideally it should be maintained below 50 μm . The magnetite layer must be dense and compact, almost free of porosity, and tightly adherent to the metal surface.

The formation of a magnetite layer is favored when the boiler is in operation, whereas hematite forms when the boiler is out of service or in a shut-down phase.

T91 steel has a special significance as a boiler tube material for supercritical boilers and therefore it is worth knowing the composition of the scale formed for this steel. When T91 steel undergoes oxidation on exposure to high-temperature steam, three well-defined layers are formed with differences in their composition and microstructure. An innermost

layer immediately next to the tube surface is $(\text{Fe,Cr})_3\text{O}_4$ with a spinel structure, followed by an intermediate, somewhat porous layer of magnetite (Fe_3O_4), and an outermost compact and thin layer of hematite (Fe_2O_3). The thickness of the $(\text{Fe,Cr})_3\text{O}_4$ layer is greater than that of the other two. The intermediate magnetite (Fe_3O_4) layer is porous and less thick than the innermost layer, whereas the outer hematite (Fe_2O_3) is thinner and more compact in nature. Fig. 6.47 shows the oxidation process in T91 steel schematically.

The composition and thickness of the scale formed govern the heat transfer behavior across the tube wall and the possibility of damage due to overheating.

General Corrosion/Oxidation Damage

Corrosion is the destructive attack of metal by chemical or electrochemical reactions. Boiler tubes are subjected to general or uniform corrosion. This results in a uniform loss of material rather than a localized attack. The tube surface may or may not be covered with the corrosion product.

Waterwall tubes suffer from general corrosion, according to the following reaction, giving rise to the formation of a protective layer of magnetite (Fe_3O_4), which, in fact, protects it from further damage. The thickness of the magnetite layer is a few microns.

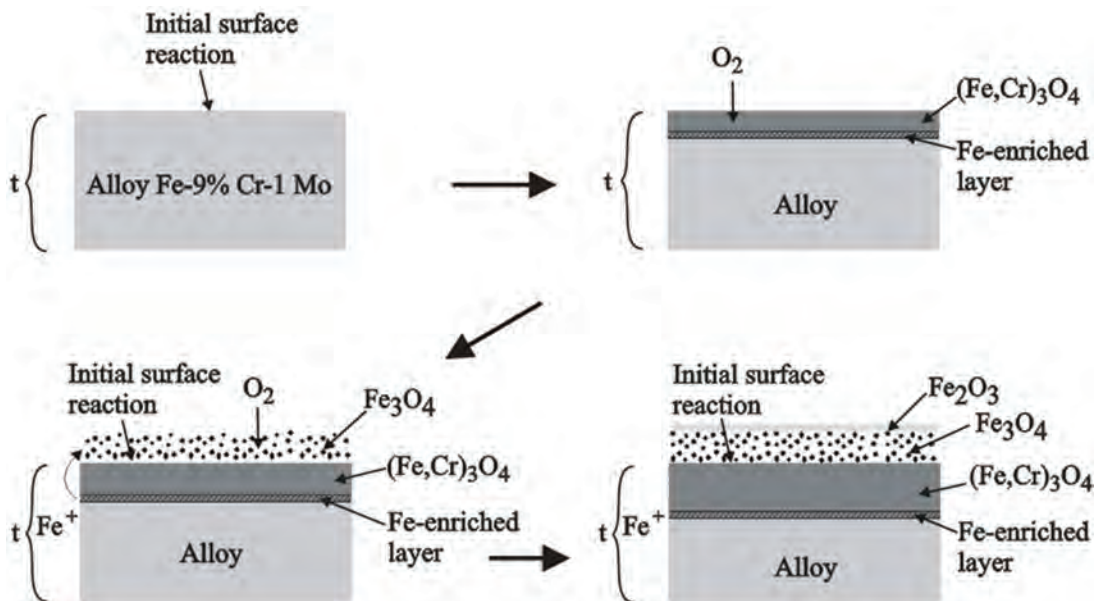
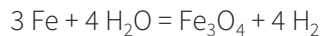


Fig. 6.47 Schematic showing oxidation of T91 steel in steam environment. Source: Ref 6.10

Corrosion in waterwall tubes occurs through the action of chloride or sulfate salts and occurs at relatively low temperatures. The salts react with the protective magnetite layer and make it porous to the extent that it hardly remains protective.

From the point of view of the pH of the water, the development of either alkaline or acidic conditions at the metal surface leads to corrosion. In other words, the corrosion of boiler tubes can take place under low pH (i.e., acidic) or high pH (i.e., alkaline) conditions. Hence, this form of corrosion can be controlled by reducing the activity of both hydroxyl ions and hydrogen ions (i.e., by maintaining a neutral pH). Boiler tubes also fail due to corrosion in the presence of dissolved oxygen or carbon dioxide, and therefore it is also necessary to control the amount of dissolved oxygen in BFW.

Overall low pH conditions are generated when BFW is contaminated with acidic contaminants such as sea or river water that is low in alkali salts. Localized low pH conditions can also develop when acidic conditions are generated in a small region such as the pit because of the high amount of dissolved oxygen or chloride ions. Places where boiling is taking place are prone to acidic corrosion.

Corrosion under high pH conditions entails a high degree of local concentration of alkalis, such as NaOH. Corrosion due to high pH occurs typically in areas where steam blanketing occurs and is known as caustic corrosion or caustic gouging. The damage mechanism of boiler tubes by caustic corrosion or caustic gouging is discussed separately in this book.

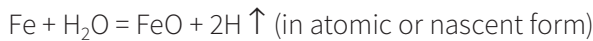
Under-Deposit Corrosion

Under-deposit corrosion is a consequence of deposition that occurs on the preboiler and boiler sides of the heat recovery system generator (HRSG). It is a result of carryover of material from one location and its subsequent deposition at a certain strategic site. The major sources for deposits in boiler tubes are: corrosion products developed at some location and their subsequent carryover to the deposition site, deposition from water borne chemicals, deposition from treatment chemicals such as caustic treatment chemicals, phosphate treatment or all-volatile treatment (AVT), and deposition of various unwanted contaminants. The deposits may consist of metal oxides such as silica and oxides of zinc and nickel, silicates, carbonates and bicarbonates, phosphates, sulfates of metals such as calcium or magnesium in the form of complex compounds, and elemental copper. There can also be other organic and inorganic types of impurities that are carried over to the deposition site from the upstream areas.

Under-deposit corrosion affects the flow characteristics of the medium being handled or the heat transfer across the tube wall. Under-deposit corrosion may be grouped into three categories: hydrogen damage, caustic corrosion, and phosphate attack.

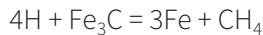
Hydrogen Damage

Hydrogen damage or hydrogen attack is a type of boiler tube failure wherein the electrochemical corrosion reaction between iron and water or steam under high-pressure (>1000–1500 psig) and high-temperature (normally above 500 °C, or 930 °F) conditions leads to liberation of atomic or nascent hydrogen under heavy deposits per the following reaction (Ref 6.11):



The liberated atomic hydrogen migrates into the steel and accumulates at preferred locations, for example, voids or inclusions, as diatomic hydrogen molecules (i.e., H_2). The molecules of hydrogen in turn exert tremendous pressure leading to intergranular fissuring or microcracking, or formation of *fish eyes* (Fig. 6.48).

The nascent or atomic hydrogen can diffuse into the steel and react with cementite, Fe_3C , to form methane per the following reaction (Ref 6.12):



The methane molecule, in view of its larger size, is unable to effuse out of the steel. Instead, it accumulates and is trapped at the grain boundaries between ferrite and pearlite in steel. The steel loses its strength because of decarburization due to methane formation. In addition, there is high aerostatic pressure exerted by the methane gas bubbles. All of this results in discontinuous intergranular fissuring or microcracking, as shown in Fig. 6.48. Hydrogen damage is accompanied by decarburization.

A boiler tube is subjected to hydrogen attack only when a hard, dense scale is present on the tube surface. This facilitates the concentration of hydrogen under the deposit, where it can diffuse into the metal.

Whether it is due to accumulated hydrogen at the voids or trapped methane gas, as more and more microcracks are formed there is a marked reduction in the strength of the tube. A stage is reached when the pressure exerted by the internal fluid exceeds the strength of the tube, and the tube fails in a brittle catastrophic manner in the form of a thick-walled, longitudinal burst. A large, rectangular section of the wall is blown out, producing a rectangular *window-like* appearance (Ref 6.1), as shown in Fig. 6.49. Thus, it is a fracture that occurs violently and without any prior warning.

Hydrogen damage can occur under low as well as high pH conditions. The leakage of condenser cooling water (i.e., brackish or seawater used for cooling), or even acidic excursions of boiler water chemistry for short times can develop low pH (i.e., acidic conditions within the boiler tubes), causing hydrogen damage. The damage preferentially takes place in the under-deposit areas of the tube. In other words, clean tubes are less susceptible to hydrogen damage. Under-deposit corrosion due to excessive

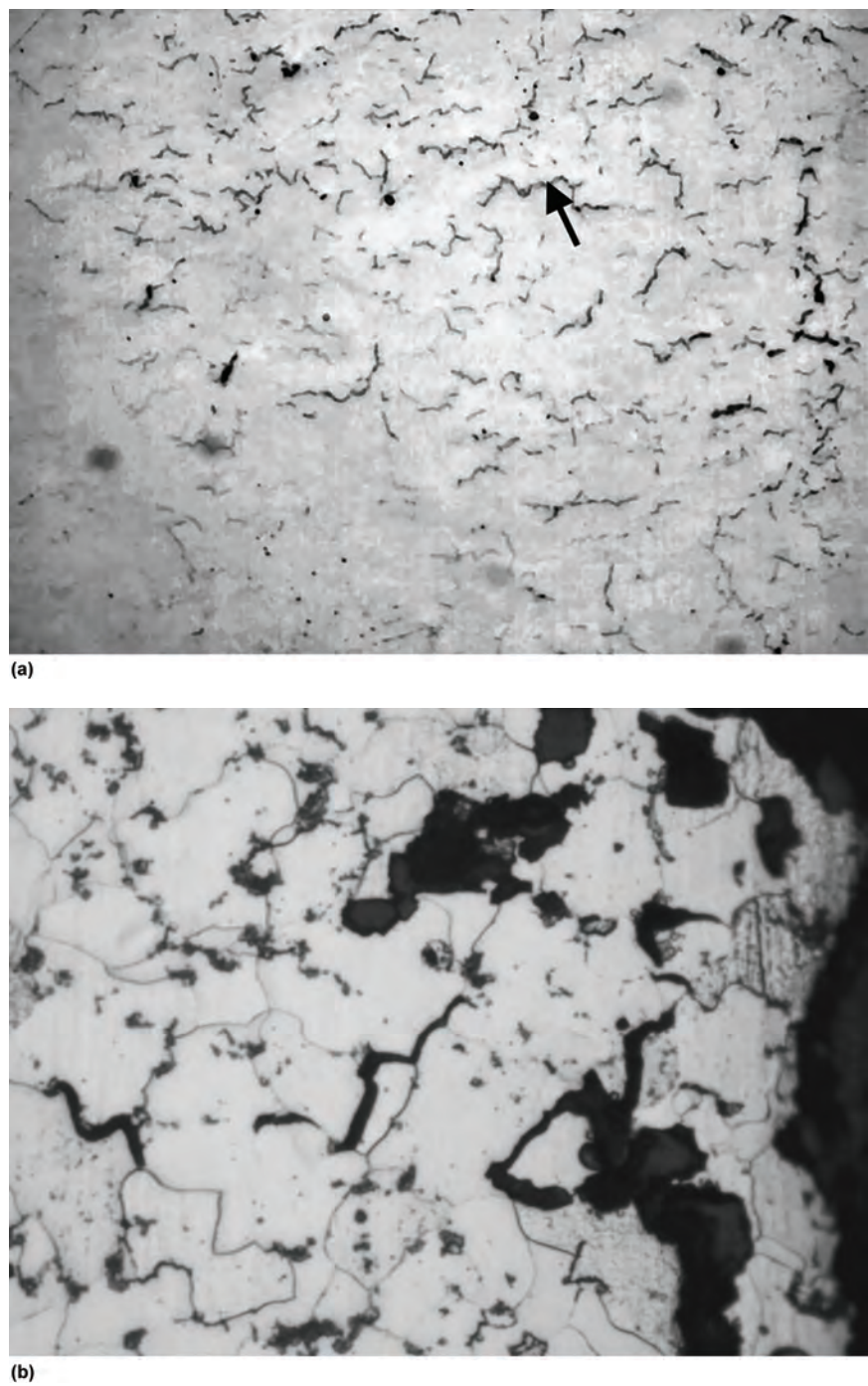


Fig. 6.48 Decarburization and discontinuous intergranular cracking in a carbon steel boiler tube resulting from hydrogen damage, (a) unetched view, 200× and (b) etched view, 200×



Fig. 6.49 Window-type fracture in waterwall tube due to hydrogen damage

deposition on ID tube surfaces as a result of poor chemical cleaning practices further contributes to hydrogen damage. The damage occurring under high pH conditions of alkaline water is occasionally called *caustic corrosion* and is discussed separately in this chapter. In both instances, it is a result of the formation of atomic hydrogen as a product of a chemical reaction between iron and an acidic or alkaline environment on the ID side of the tube. Hydrogen damage is almost always associated with metal gouging. The gouging is evident as an irregular wastage of metal beneath the porous deposits. In general, the high-heat-flux zones in the upper burner area, horizontal or slanted tubes, and the heat-transfer regions at or adjacent to the welds are prone to hydrogen damage.

Hydrogen attack or hydrogen damage is different from hydrogen embrittlement. Hydrogen attack is a high-pressure, high-temperature service-related failure, whereas hydrogen embrittlement occurs near or at room temperature.

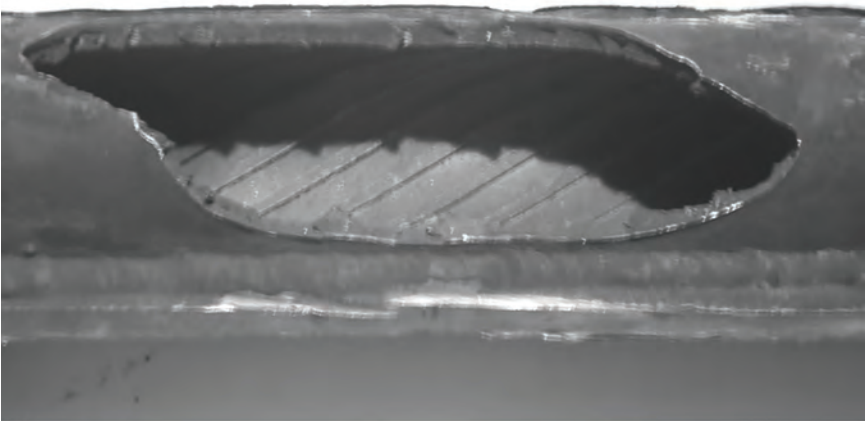
Case Study 12—Failure Investigation of a Waterwall Tube

Background Details A rupture from a high-temperature region of a waterwall tube of a 310 MW capacity boiler was reported. Details regarding the material of construction (MOC), service life rendered, and extent and location of the failure were not available. However, from the sample provided for failure investigation, it was clear that rifflled tubes with an OD of 75.0 mm (2.95 in.) were used for construction of the waterwalls of the boiler and that the failure had occurred from the tube facing the fire side.

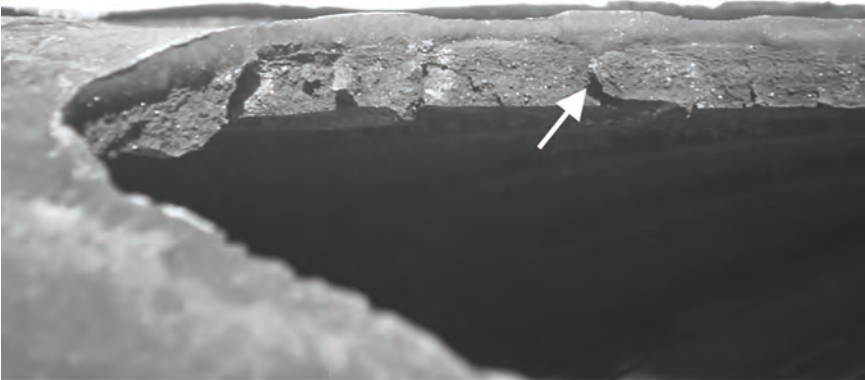
Investigation and Findings Visual examination of the failed tube indicated a window-type fracture with complete detachment of a tube piece in the form of a window. On visual and low-magnification examination, the fracture surface appeared to be brittle in nature and indicated initiation of the fracture from the ID side. The fracture surface showed uniform ridges corresponding to the spacing of spiral internal fins (Fig. 6.50b). The fracture edge did not indicate any apparent reduction in wall thickness or

any bulging. Chemical analysis of the tube sample revealed that the tube was made of plain carbon steel with 0.2 wt% nominal carbon.

Scanning electron microscopy examination of the fracture surface showed the presence of fissures and a discontinuous network of microcracks with an intergranular mode of fracture (Fig. 6.51a). Scanning electron microscopy after metallography revealed the presence of microvoids and fissures that had formed preferentially on the pearlite phase. Progressive coagulation of fissures led to formation of microcracks along ferrite grains (Fig. 6.51b). This clearly indicated the possibility of failure due to hydrogen damage.



(a)



(b)

Fig. 6.50 Failed waterwall tube (a) with window-type fracture and (b) ridges on the fracture surface

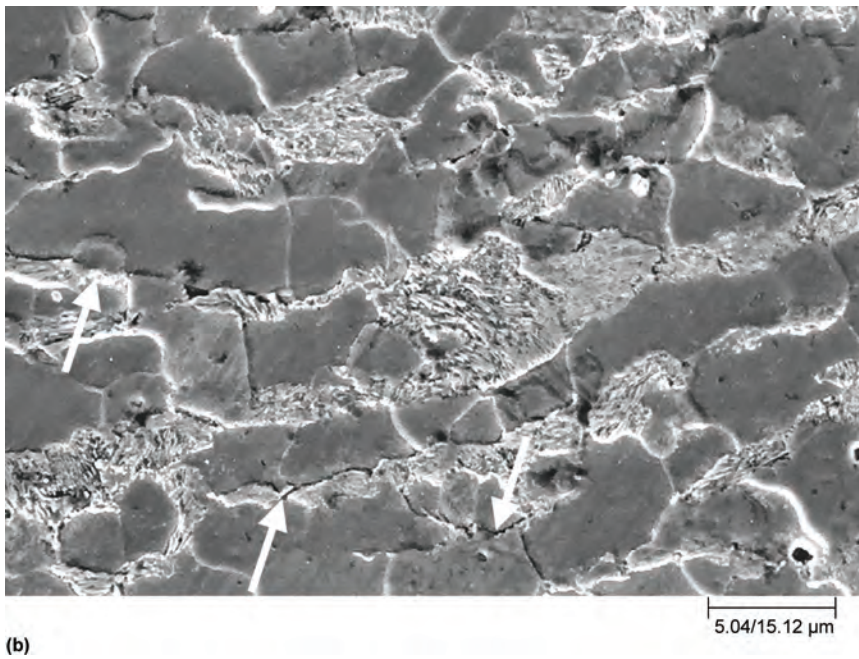
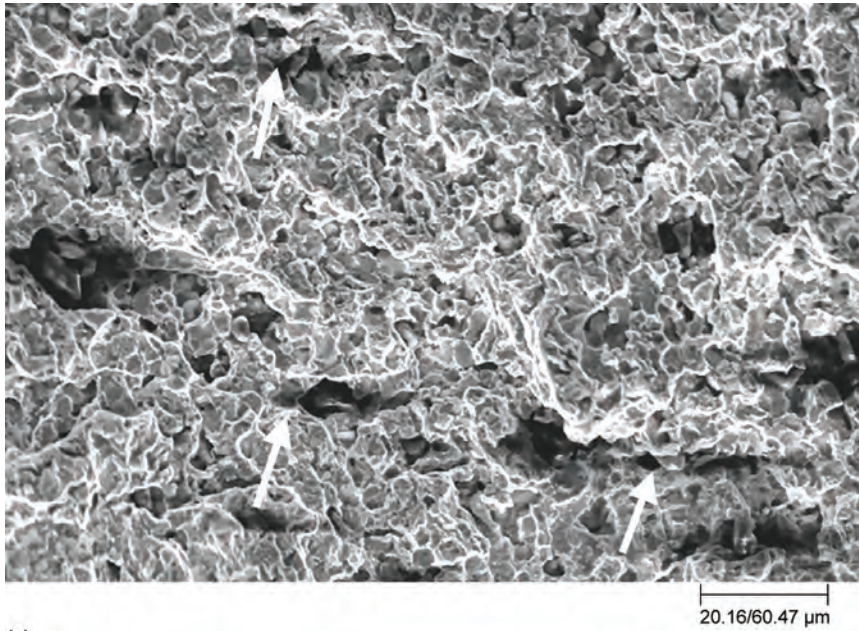


Fig. 6.51 SEM micrographs showing (a) fracture surface having fissures and discontinuous network of microcracks, 500 $\times$; and (b) coagulated fissures leading to formation of microcracks along ferrite grains, 2000 $\times$

Energy dispersive spectroscopy analysis on the scale at the ID surface indicated the presence of oxygen, sulfur, potassium, sodium, magnesium, and calcium along with the base metal element (i.e., iron).

Measurement of the scale thickness was carried out on both the ID and OD sides of the tube. An average oxide layer thickness of 350 μm was observed on the ID surface of the fire-facing side, while nearly 50 μm was observed on the opposite side. The average scale thickness on the OD side was 325 μm and 15 μm at the fire-facing and opposite sides, respectively. The oxide layer was porous with numerous cracks.

Optical microscopy highlighted the presence of fissures and a discontinuous network of microcracks near the fracture edge (Fig. 6.52a). The microstructure was of the banded ferrite-pearlite type. The structure consisted of slightly deformed grains at the failure edge (Fig. 6.52b). The fissures were predominantly observed on the fire side. Their intensity was higher on the ID at the failure location on the fire side.

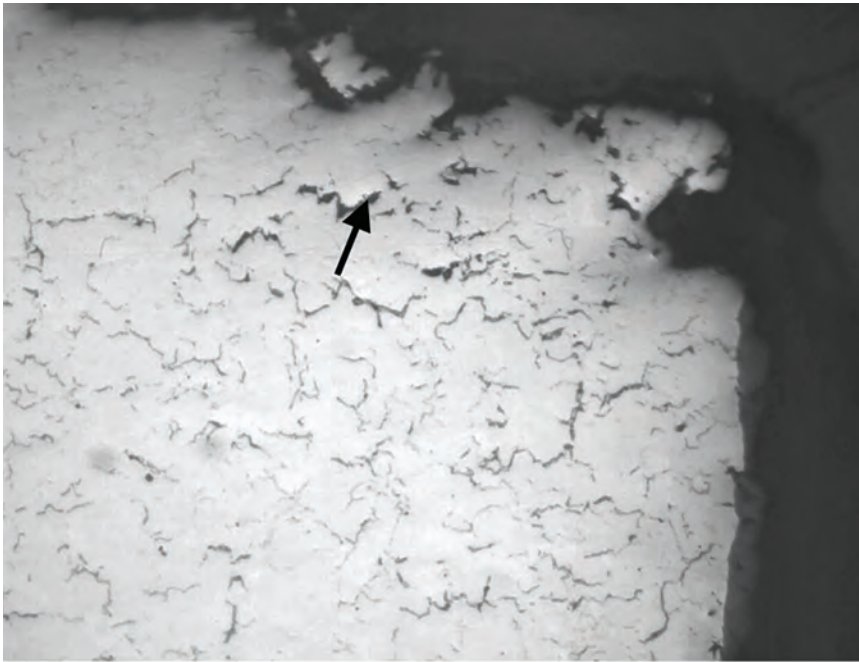
The investigation revealed that there was considerable degradation of pearlite per SEM and microstructural analysis. This pearlite degradation was due to depletion of carbon from the material, which could possibly be a result of a preferential chemical reaction that would have occurred in the presence of atomic hydrogen. The evolution of atomic hydrogen is possible when a localized acidic or alkaline environment exists for a prolonged period during service at the ID side of the tube. The porous oxide scaling on the ID side clearly indicated that corrosion of the material had occurred. Liberated atomic hydrogen diffused into the steel, either reacting with iron carbides (i.e., cementite), forming methane gas, or accumulating at grain boundaries to produce molecular hydrogen. This in turn created voids and fissures at the pearlite interface.

Once having formed a network of microcracks at the ID, the tube would have sustained the internal pressure only as long as the effective cross-sectional thickness could resist the applied stresses. The final fracture in a rapid brittle mode occurred after critical growth of microcracks.

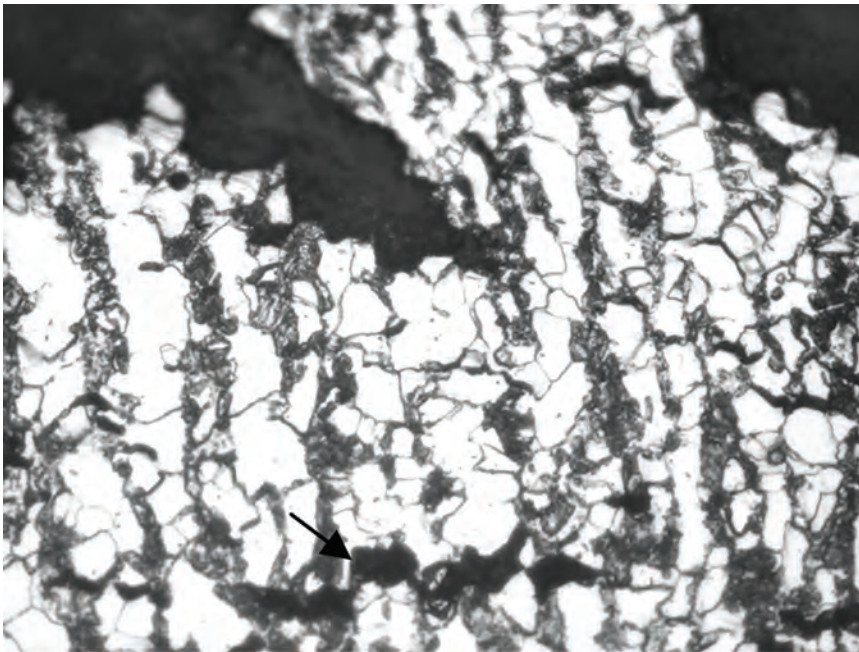
Conclusions The failure of the waterwall tube occurred due to hydrogen damage by the formation of fissures and microcracks at the ID side that led to window failure.

Case Study 13—Failure Investigation of Riffled Waterwall Tube

Background Details The failure of a riffled waterwall tube occurred in a 525 MW capacity boiler after about 2 years of operation. Earlier, failures had been taking place at weld joints, and this was the first time that a failure occurred in the parent metal of the tube. A window-type rupture occurred as the primary failure in the parent metal, whereas a secondary erosion failure took place in the adjacent tube. The tube was made per SA 210 Grade C specifications and had dimensions of 51.0 mm (2.0 in.) OD and 5.6 mm (0.2 in.) thickness.



(a)



(b)

Fig. 6.52 (a) Unetched view of ID fracture edge showing microfissures, 400 $\times$; and (b) etched view at ID fracture edge showing ferrite-pearlite structure with microfissures preferentially on pearlite colonies, 200 $\times$

Investigation and Findings Visual examination highlighted a window-type rupture of the tube, elliptical in shape. The rupture contours were sharp but uneven and not deformed. Apparently, there was no reduction in wall thickness. The failure was away from the weld joint. The outer surface showed a thin adherent scale, brick red in color, while the inner surface showed a thin adherent magnetite scale, which was grayish black in color. Figure 6.53(a) shows the failed waterwall tube samples, and Fig. 6.53(b) shows a close-up view at the primary failure location.



(a)



(b)

Fig. 6.53 (a) Window-type fracture in riffler waterwall tube; and (b) close-up view at primary failure location

Scanning electron microscope examination of the fracture surface highlighted the intergranular nature of the brittle fracture. The rupture lip surface at the fracture also showed discontinuous fissures and grain boundary cracking (Fig. 6.54).

The polished and etched metallographic sample, when subjected to optical microscopy, revealed that the inner edge of the tube had undergone surface decarburization. Severe decarburization was noticed on the inner surface, leading to grain boundary scale penetration that had also attacked pearlite colonies. The inner surface was corroded and covered with a porous scale. This scale was more pronounced toward the failure location. The intensity of the scale decreased further away from the failure location Fig. 6.55(a). Also, there were grain boundary fissures filled with scales. The core microstructure as seen in Fig. 6.55(b) was of a normal banded ferrite and pearlite type. The outer edge of the tube also had scale formation, but it was thinner.

Energy dispersive spectroscopy on the fracture surface showed the presence of oxygen, aluminum, silicon, sulfur, chlorine (as chloride), and calcium. Energy dispersive spectroscopy on the red-colored corrosion product that had formed on the outer surface of the tube showed carbon, oxygen, magnesium, silicon, potassium, and calcium. The contamination was essentially due to moisture, unburnt fuel, and ash content from the flue gases. Energy dispersive spectroscopy on the inner surface indicated the presence of oxygen, sodium, and calcium.

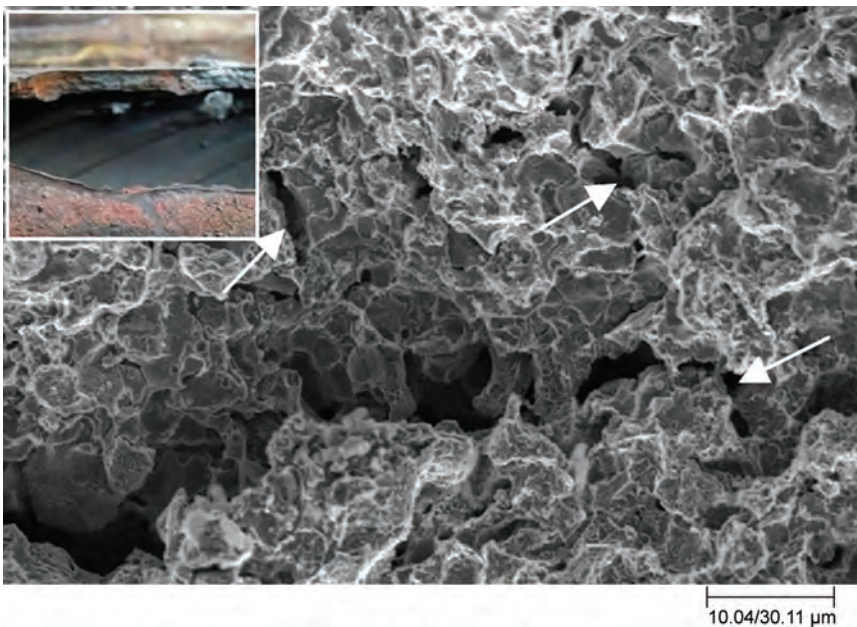


Fig. 6.54 SEM micrograph of waterwall tube showing intergranular nature of brittle fracture with discontinuous fissures and grain boundary cracking, 1000×

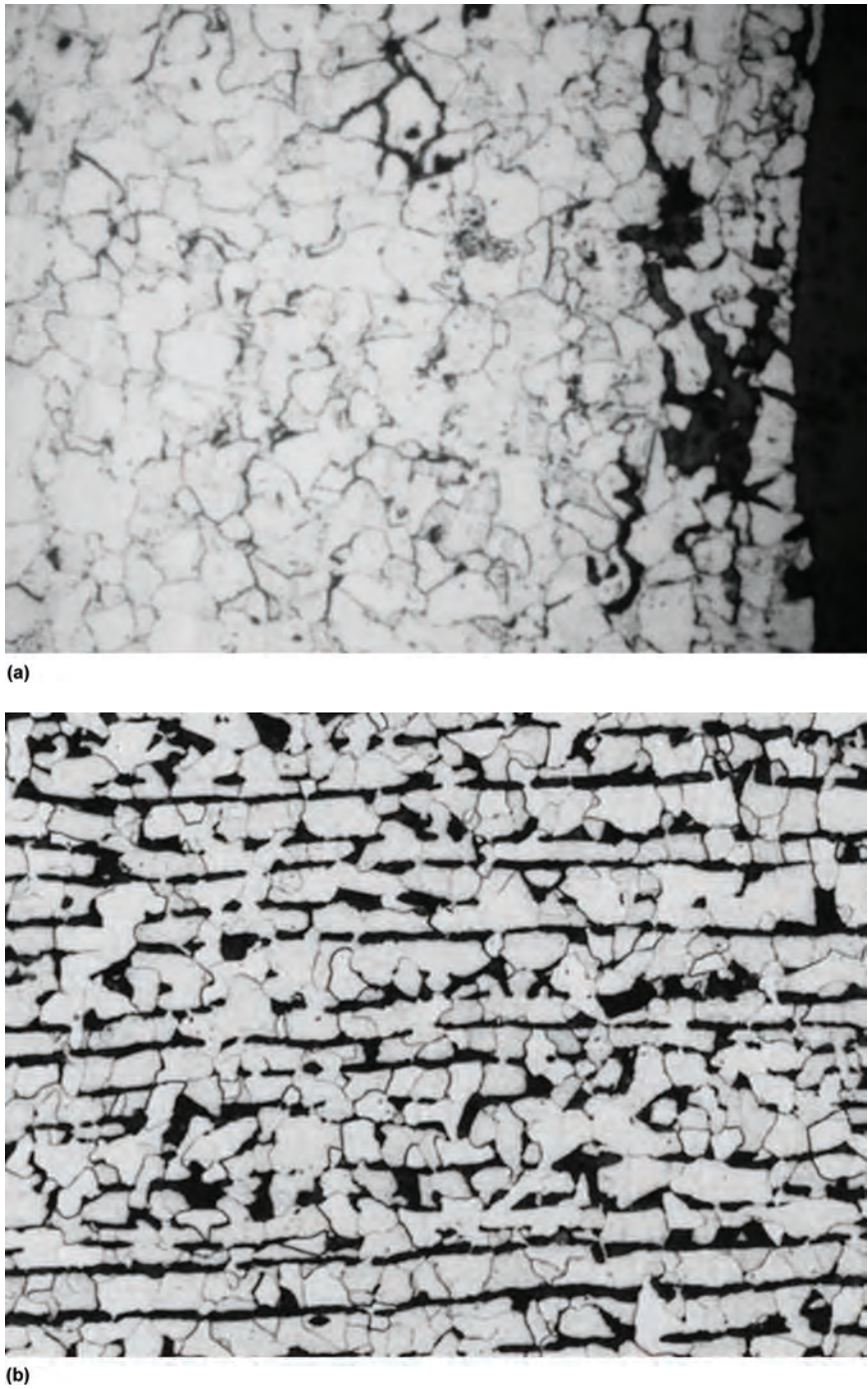


Fig. 6.55 Microstructure of (a) inner edge of the tube showing scale formation, decarburization and grain boundary fissure, 400×; and (b) normal ferrite-pearlite structure of core having pearlite banding, 400×

Earlier findings clearly indicated that the damage was essentially on the inner surface of the tube facing the fire side, which occurred subsequent to intense surface decarburization. Pearlite degradation was due to depletion of carbon from the material that had occurred on account of a chemical reaction taking place in the presence of hydrogen. The presence of sulfur, alkali, and rare earth ions in the scale and on the inner surface, as reported by the EDS analysis, facilitated localized under-deposit corrosion at the failure location and thereby hydrogen evolution. The diffused atomic hydrogen in turn reacted with cementite in pearlite colonies, forming methane gas, which left pockets and voids due to volumetric expansion as confirmed by SEM.

Once having formed a network of microcracks toward the inner surface, the tube could sustain the internal pressure only up to a threshold limit. The load bearing capacity of the tube dropped further, and the final rupture took place in the form of window opening in a brittle mode.

Conclusions The failure of the waterwall tube was essentially due to hydrogen damage leading to the formation of fissures and microcracks that weakened the tube matrix at the failure location. The hydrogen damage occurred due to under-deposit corrosion at a localized region.

Case Study 14—Failure Investigation of Heat Recovery Steam Generator Waterwall Tube

Background Details The waterwall tube of an HRSG boiler failed during operation. The boiler tripped on *furnace pressure high* protection. It was noticed that one waterwall riser tube (goose neck) of the furnace east wall had a window opening at a 200 mm (8 in.) radius bend location (Fig. 6.56).



Fig. 6.56 Failed waterwall tube with window opening at tube bend

The opening was approximately 120 mm (4.5 in.) in length and 55 mm (2 in.) in width. The window opening was from the longer radius of the bend facing the burners.

No reduction in thickness was found through measurement at different locations of the tube adjacent to the failure location. Also, no bulging was noticed on the failed tube or on other nearby tubes.

The MOC of the waterwall tube was ST 45.8 III (carbon steel), and the tube dimensions were 57.0 mm (2.2 in.) OD and 5.0 mm (0.2 in.) thickness. The tube temperature was 250 °C (480 °F) and pressure was 100 bar.

Investigation and Findings Visual examination indicated a burst pipe failure where a portion of the tube metal had buckled out, and the puncture contours were also buckled (Fig. 6.57a). The inner surface was dark brown in color with scattered scale asperities. The protective grayish black magnetite layer was damaged in the vicinity of the failure region. Figure 6.57(b) shows the longitudinal cut section of the tube. The internal surface appeared reddish brown in color with a thin adherent scale. Scale asperities were seen scattered over the internal surface.

Low-magnification examination indicated the brittle nature of the puncture lip with a crack initiating from the inner surface of the tube. The puncture lips were puckered in nature with discontinuous cracks as shown in Fig. 6.58. Dimensional measurements revealed thinning of the tube mainly confined to the ruptured lips at a few locations.

The failed sample was subjected to SEM, which showed a brittle and intergranular mode of failure at the inner-edge fracture surface. Discontinuous grain boundary fissures were also visible on the fracture surface, as shown in Fig. 6.59a. Scanning electron microscopy after metallography showed grain boundary cracks, discontinuous in nature, that had formed due to the coalescence of fissures (Fig. 6.59b).

Energy dispersive spectroscopy analysis of the scale formed on the inner surface of the tube near the failure location revealed the presence of copper and sulfur apart from other elements. According to the plant data, no condensate water was used for recycling; therefore the copper contamination must have been either from the boiler feedwater (BFW) or from the dosing chemicals. Copper is cathodic to iron and therefore promoted corrosion, causing anodic dissolution of iron beneath the deposits.

Microstructural examination at the fracture edge showed scattered grain boundary fissures with a tendency to form discontinuous cracks (Fig. 6.60a). Their intensity was higher toward the ID, and they were more or less absent nearer the OD. With fissure formation at the grain boundary, pearlite degradation and decarburization were also noticed. Pearlite was fully degraded, forming fissures and grain boundary cracking toward the inner surface. The degradation became partial toward the core (Fig. 6.60b), and its intensity was receding toward the outer surface.

There was a thick adherent scale formed on the inner surface, which was partially porous. Scale formation was found to a lesser extent on the



(a)



(b)

Fig. 6.57 (a) Close-up view of the puncture portion of the failed waterwall tube.
(b) Longitudinal cut section showing ID surface

outer surface. The nature of the deposits, with a scale on the ID surface of the tube, pointed toward a disturbance in the water chemistry. Besides this, thinning of the tube had occurred in the high-heat-flux region (i.e., facing the flue gas side). As a result, localized rupture of the magnetite layer and the deposits must have occurred, promoting wick boiling conditions

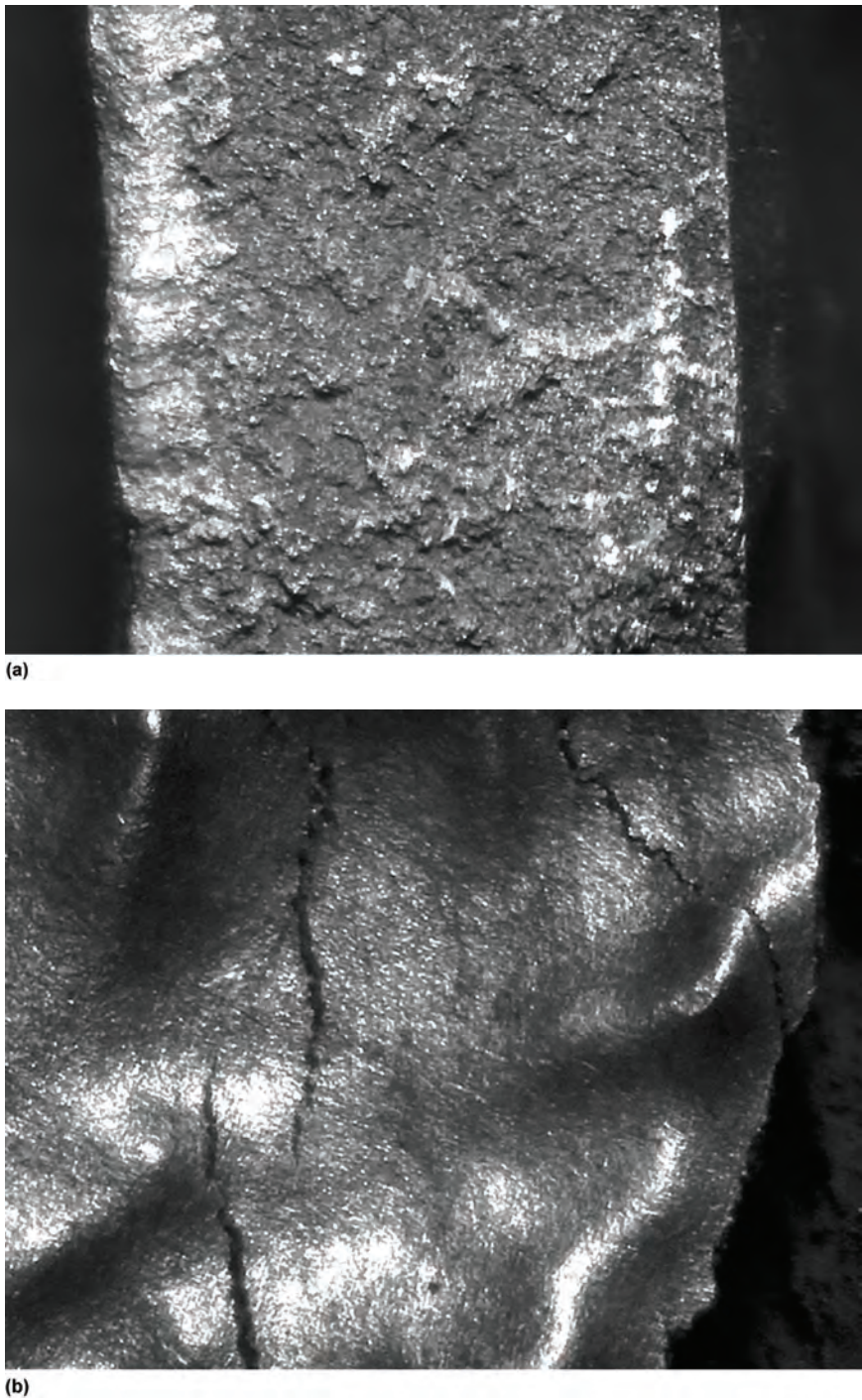


Fig. 6.58 Low-magnification views showing (a) brittle nature of failure, 11 $\times$; and (b) inner surface of the tube at rupture location showing cracks, 11 $\times$

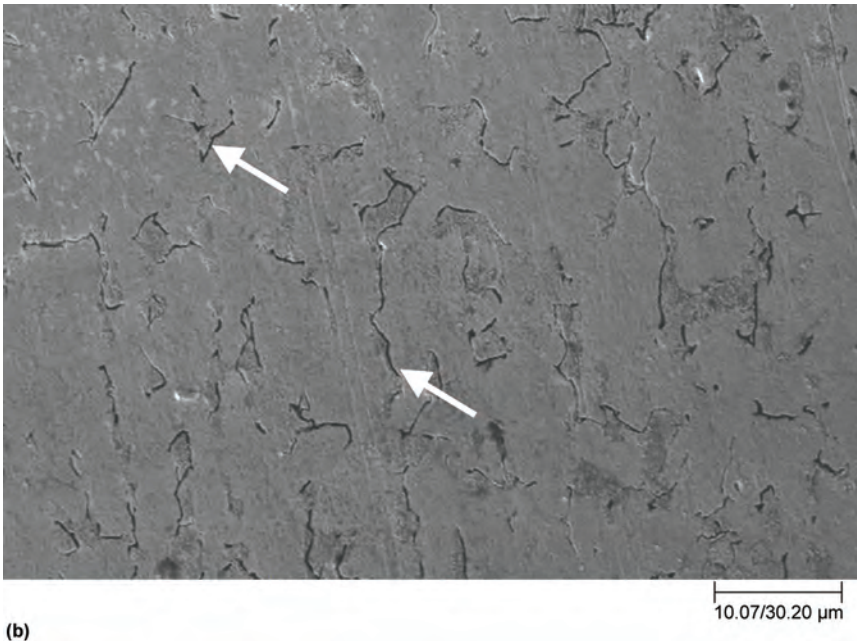
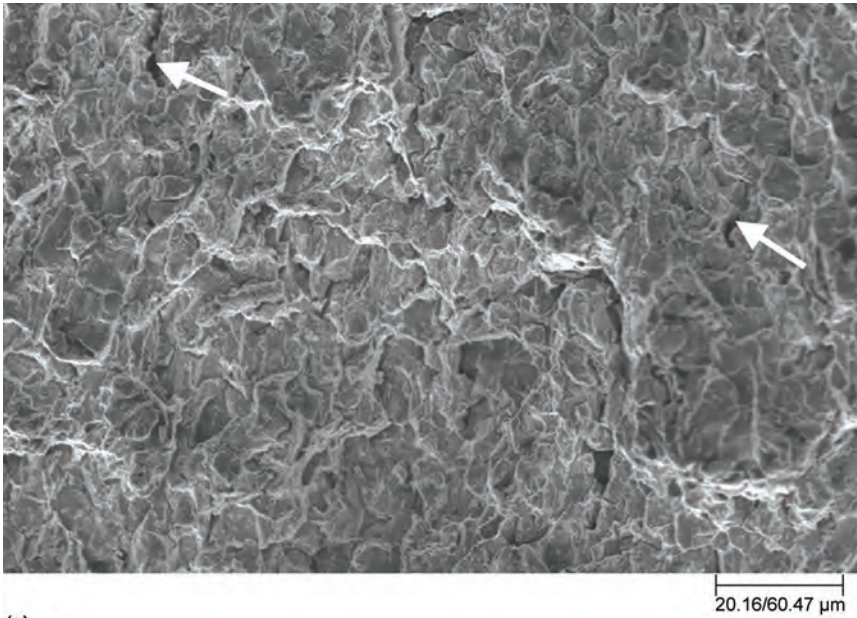


Fig. 6.59 SEM micrographs for (a) inner-edge fracture surface showing grain boundary fissures, 500 $\times$; and (b) post-metallography sample showing discontinuous grain boundary cracks, 1000 $\times$

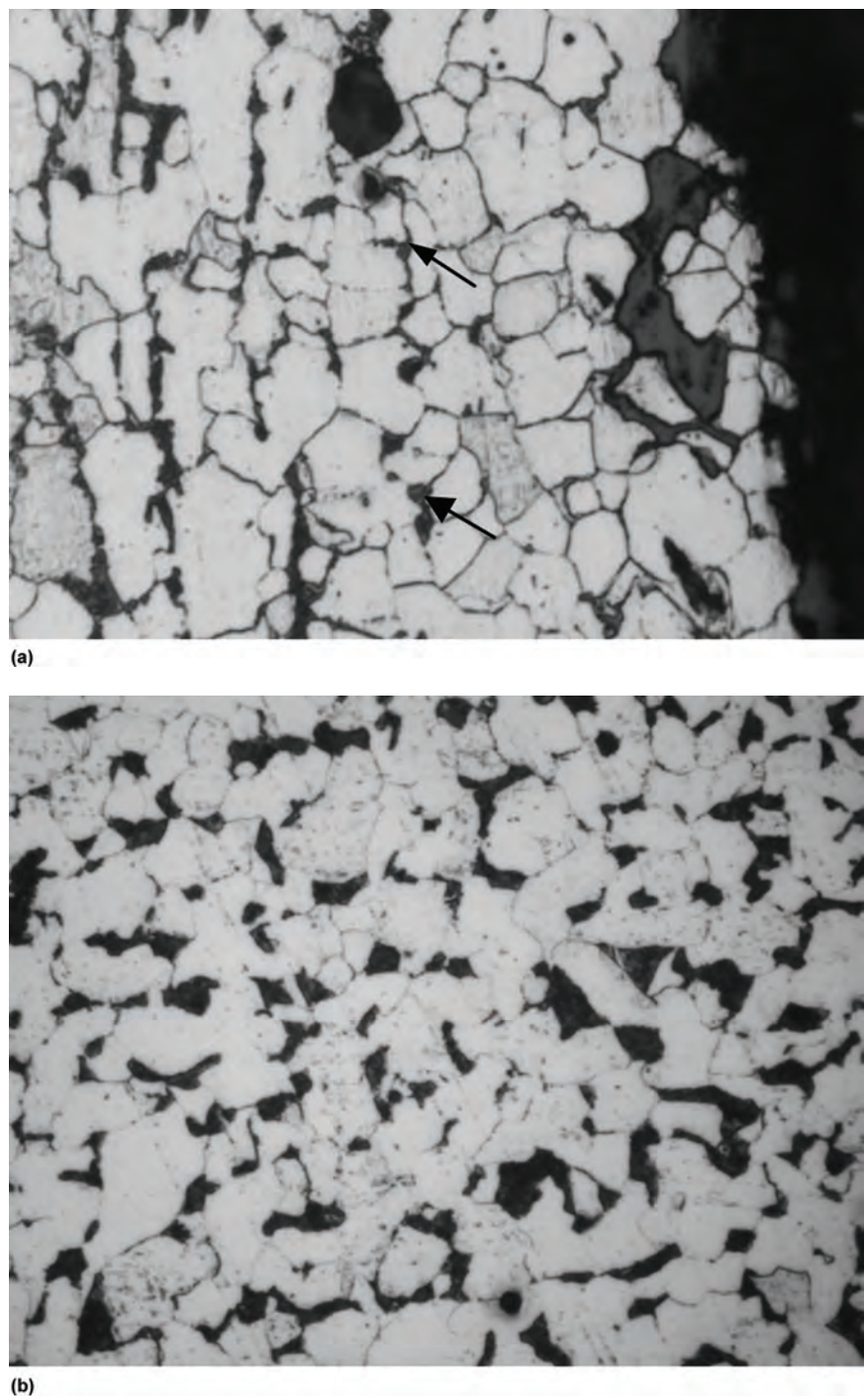


Fig. 6.60 (a) Inner-edge microstructure with grain boundary fissures and degraded pearlite, 400×. Structure shows mostly ferrite grains only.
(b) Core microstructure of tube showing partial degradation of pearlite, 200×

and further scale formation. The resultant under-deposit corrosion of iron beneath the copper deposits gave rise to the evolution of monoatomic hydrogen.

Analysis of these findings indicated the nature of failure typically to be hydrogen attack.

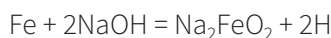
Conclusion The failure of the waterwall tube was under the combined influence of under-deposit corrosion caused by the presence of copper, leading to thinning as well as hydrogen attack.

Caustic Corrosion or Caustic Gouging

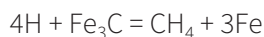
Caustic corrosion or caustic gouging is mainly observed in phosphate-treated boilers where tube deposits form, particularly at areas of high heat input or poor circulation (Ref 6.13). Failure occurs in the form of distinct hemispherical or elliptical depressions or gouges on the ID side of the tube. These depressions are sometimes filled with corrosion products in addition to sparkling crystals of magnetite. The damage occurs especially in the presence of heavy scale deposits on the water side and in high-heat-flux areas as well as on the ID surfaces of slanted or horizontal tubes. Below the scale deposits, the local concentration of sodium hydroxide is high enough to remove the protective magnetite film per the following reaction (Ref 6.14):



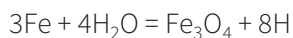
Once the protective magnetite film is damaged, the concentrated sodium hydroxide directly reacts with the underlying metal per the following reaction, to liberate nascent or atomic hydrogen.



The liberated nascent hydrogen diffuses into the steel and recombines at grain boundaries or inclusions to form molecular hydrogen. Alternatively, it can react with cementite in the steel to form methane.



Once the protective magnetite film is destroyed, there is also a possibility of a direct reaction between iron and water per the following reaction, leading to the evolution of hydrogen in atomic form.



Molecular hydrogen or methane accumulated at the grain boundaries generates pressure and finally gives rise to the development of micro-cracks along the grain boundaries of the steel, leading to final fracture.

Figure 6.61 shows a photograph of deep caustic gouging below the insulating deposits on the ID side of a tube.

There are several factors responsible for the buildup in concentration of a caustic solution underneath the deposits. Steam blanketing is one of them, in which a layer of steam forms between the water flowing through the boiler tube and the tube wall. As a result of steam blanketing, insufficient water reaches the tube surface. Whatever water that does reach the tube wall is rapidly evaporated, leaving behind a concentrated caustic solution of corrosive nature as a residue. Likewise, localized boiling underneath the porous deposits on the ID side of the tube is another possible cause of local high concentrations of caustic solutions.

Sometimes a caustic addition is made intentionally. For instance, some programs for boiler water treatment choose an addition of caustic elements in controlled concentrations for pH maintenance. pH maintenance is essential for maintaining the protective magnetite film on the ID side of the tube. However, if the concentration of the caustic or alkaline salt exceeds its threshold limit, it leads to corrosion (Ref 6.15).

Case Study 15—Failure Investigation of Screen Tube

Background Details Multiple failures were noticed in screen tubes after 19 years of service in a single-drum natural circulation boiler used for captive power generation. The type of fuel used normally was low-sulfur



Fig. 6.61 Deep caustic gouging below the insulating deposits on ID side of an economizer tube

heavy stock with an air to fuel ratio of 14:1. Phosphate dosing was done at the boiler steam drum, and hydrazine was fed into the BFW.

The screen tubes were made of SA 210 Grade A1 steel and had dimensions of 63.5 mm (2.5 in.) OD and 4.9 mm (0.19 in.) thickness. Leakage was noticed in one of the screen tubes upon a sudden drop in boiler drum level and high furnace pressure. The failed part of the screen tube subjected to failure investigation was from the slanted portion of the 30° bend.

Investigation and Findings Visual examination of the outer surface of the sample showed two leakage spots. The major one was a linear opening, whereas the minor one was a pinhole puncture. Figure 6.62(a) shows a close-up view of the outer surface of the failed screen tube sample, indicating a crack-like opening. Visual examination of the inner surface revealed corrosion damage. The entire inner surface of the tube sample had corroded with a nonuniform, fairly adherent scale, which was grayish black in color (Fig. 6.62b). It had spalled out at several places. Thinning and scale formation were more prominent on one half of the tube, which had brownish scale patches. The area surrounding the puncture on the inner surface showed heavy metal wastage.

Figure 6.63(a) shows a transverse cut section view of the failed tube near the leakage area. Localized metal wastage from the ID side was noticed; the band is clearly defined by the region marked by an arrow.

Low-magnification examination of the ID surface revealed aggravated metal wastage surrounding the puncture, indicating gouging of the tube on the inner surface (Fig. 6.63b).

Scanning electron microscopy indicated corrosion damage at the ID surface and at rupture lips along with the presence of fatigue striations, which point toward final cracking from the already thinned region under the influence of fluctuating stresses (Fig. 6.64).

Energy dispersive spectroscopy on the ID scale revealed the presence of oxygen, sulfur, calcium, chloride, and copper in relatively larger quantities, besides sodium, phosphorus, and potassium (Table 6.5). The presence of copper indicated contamination of the feedwater, possibly due to condensate leakage or from treatment chemicals. Corrosion on account of carryover of copper and phosphorus ions and water-based contaminants in the scale deposits was thus clearly evident.

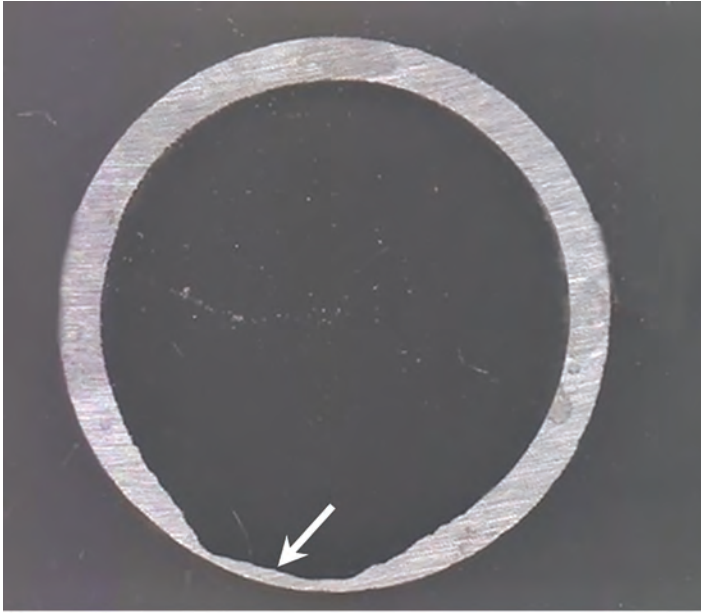
The ID scale was subjected to x-ray diffraction (XRD) to identify the various phases present, and the results of the analysis are shown in Fig. 6.65 and Table 6.6.

The data for measured and standard d values for the phase sodium ferrous sulfate (NaFeO_2) per Table 6.6 show a close match.

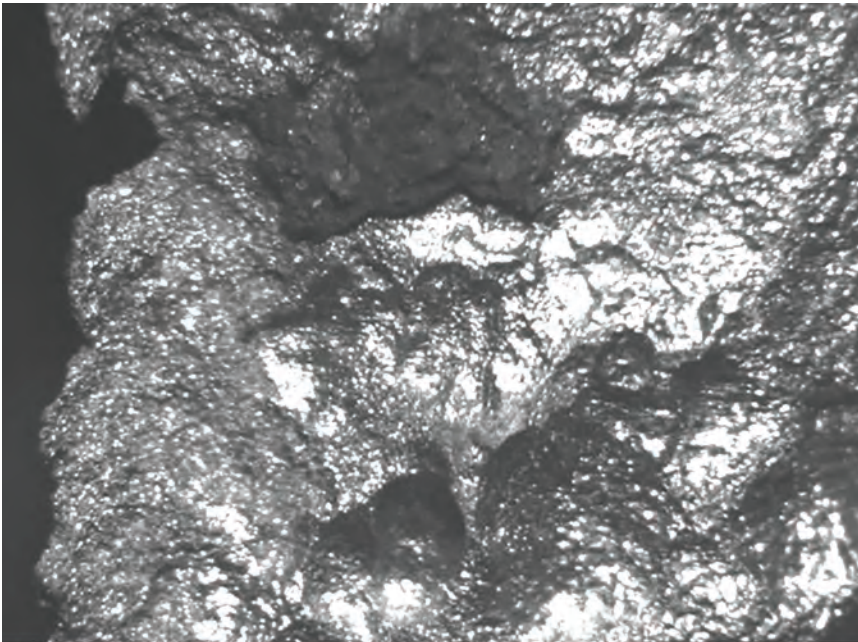
Microstructural examination highlighted thinning at the leakage location essentially from the inside, where metal wastage had occurred, due to gouging. A through and through crack-like opening at the leakage location with wide, thin, and uneven contours filled with scales rich in copper



Fig. 6.62 (a) Outer surface of a failed tube sample showing a linear crack. (b) Inner portion of the tube with grayish black scale



(a)



(b)

Fig. 6.63 (a) Transverse cut section view of the failed tube near leakage area indicating localized metal wastage. (b) Inner surface low-magnification view near leakage showing metal wastage in the form of gouging, 12×

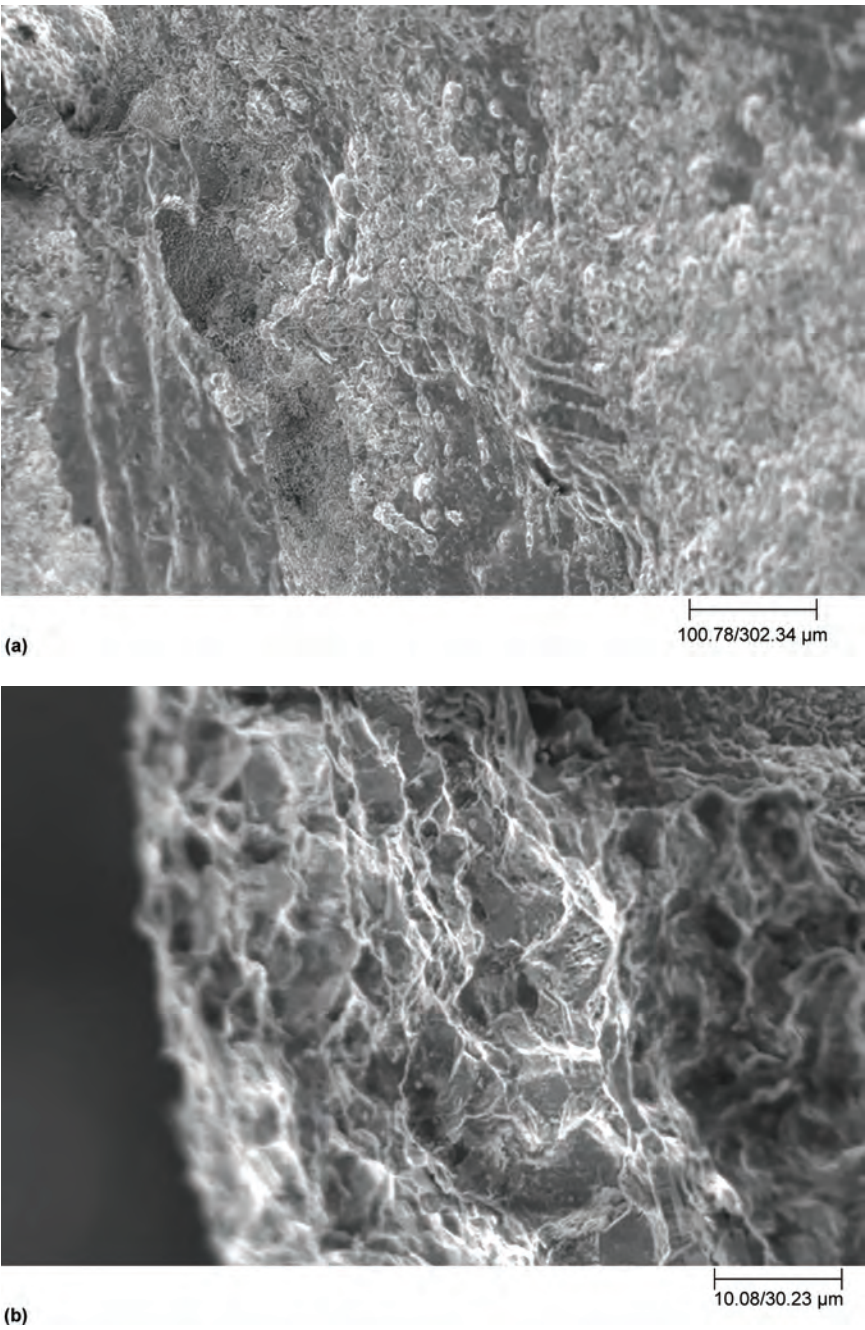
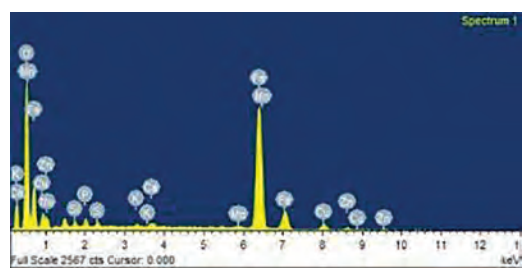


Fig. 6.64 SEM micrographs showing (a) corrosion damage and metal wastage, 100 $\times$; and (b) rupture surface with fatigue striations at the edges, 1000 $\times$

Table 6.5 EDS analysis of ID scale



Element	Amount by wt. %	Element	Amount by wt. %
Oxygen	9.94	Manganese	0.88
Silicon	0.68	Iron	72.78
Phosphorus	1.14	Copper	9.23
Sulfur	0.47	Sodium	1.54
Calcium	0.31	Potassium	0.44

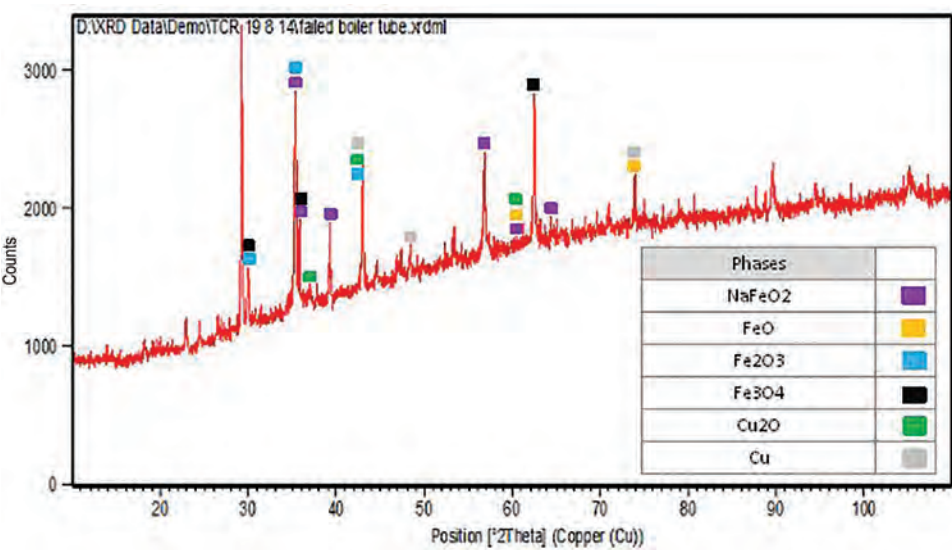


Fig.6.65 X-ray diffraction profile of scale sample showing different diffraction peaks

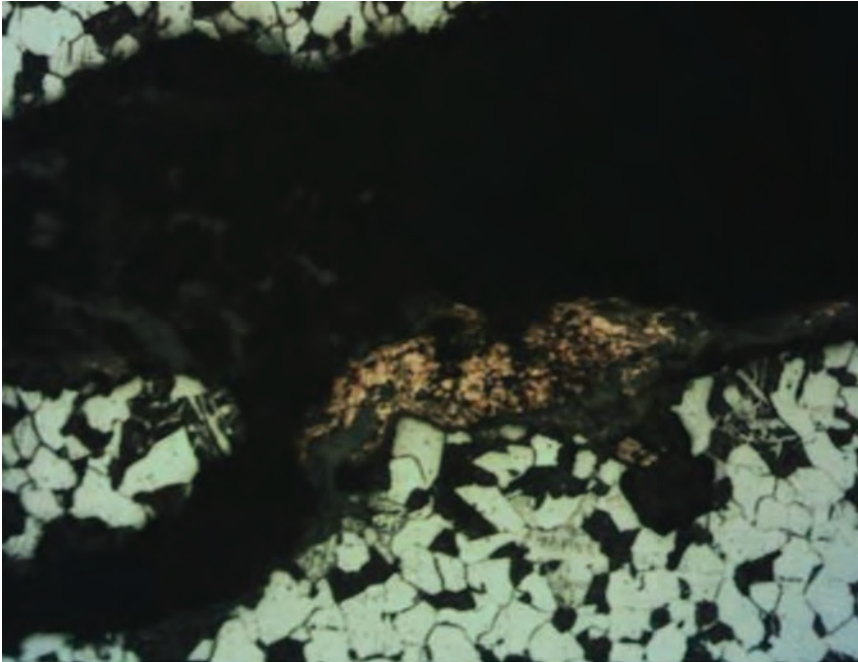
Table 6.6 XRD analysis of scale sample

Name of the compound	NaFeO ₂	FeO	Fe ₂ O ₃	Fe ₃ O ₄	Cu ₂ O	Cu
JCPDS card number	20-115	6-711	15-615	19-629	5-667	4-836
Measured <i>d</i> values	Standard <i>d</i> values per JCPDS cards					
2.98	...	...	2.95	2.97	...	...
2.53	2.59	...	2.52	2.53	...	...
2.51	2.49, 2.51	...	...	...	...	...
2.42	...	...	...	...	2.47	...
2.29	2.20	...	...	...	...	...
2.10	...	...	2.09	...	2.14	2.09
1.88	...	...	...	...	...	1.81
1.61	1.6	...	...	...	...	...
1.52	1.51	1.52, 1.51	...	...	1.51	...
1.48	...	...	...	1.49	...	...
1.44	1.46	...	...	...	...	...
1.28	...	1.29	...	...	...	1.28

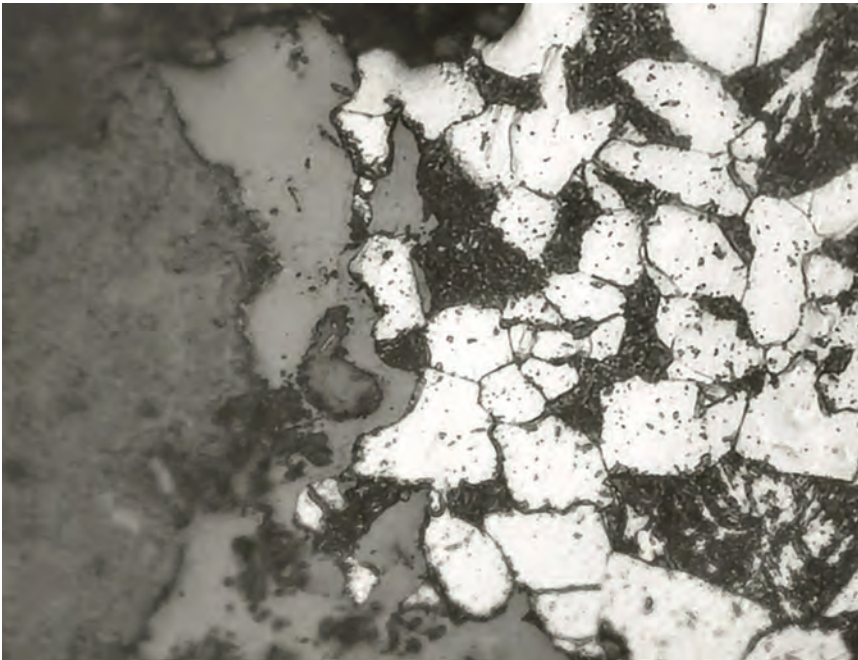
and oxide scales was also observed. The microstructure at all locations comprised ferrite and pearlite with no significant pearlite degradation (Fig. 6.66).

An analysis of the above findings indicated that metal wastage by way of corrosion had occurred due to sodium ion contamination along with other contaminants carried over in the BFW. In conjunction with the metal gouging found during low-magnification examination, the investigation pointed toward caustic gouging as the damage mechanism. The presence of sodium in the ID scale per EDS and the peaks for sodium ferroate (NaFeO₂) per the XRD profile confirm that the failure was due to caustic gouging. The failed part of the screen tube was from the slanted portion of the 30° bend. This circumstantial evidence pointed toward deposits accumulating due to disturbances in water chemistry and *waterline* formation due to load fluctuations. Horizontal or slanted tubes are more susceptible to steam or water stratification. With unfavorable conditions of heat flux relative to boiler water flow rate, steam or water stratification may occur. In addition, boiler operation at excessively low water levels, or excessive blowdown rates, may create waterlines. Waterlines may also be created by excessive load reduction when pressure remains constant. In this situation, water velocity in the boiler tubes is reduced to a fraction of its full-load value. If the velocity becomes low enough in vertical, horizontal, or slanted tubing, steam or water stratification occurs, creating stable or metastable waterlines.

Conclusions The screen tube failure may be attributed to caustic gouging leading to metal wastage from water chemistry disturbances and load fluctuations that formed waterlines.



(a)



(b)

Fig. 6.66 Optical micrographs of (a) crack tip filled with oxide scale and copper deposits, 200 $\times$; and (b) inner surface showing penetration of oxide scale within the matrix of ferrite and pearlite, 400 $\times$

Phosphate Corrosion or Phosphate Hideout

Acid phosphate corrosion or phosphate hideout is one form of *under-deposit corrosion* and is a localized type of attack (Ref 6.16, 6.17). It occurs underneath the deposits or scale on the ID of the tube and appears as gouges, grooves, or depressions similar to those found in cases of caustic corrosion, and therefore may be frequently confused with caustic attack (Fig. 6.67). Phosphate hideout has been a matter of growing concern, as boiler drum operating pressures have been gradually increasing with time. However, it also occurs under lower-pressure conditions where high-purity make-up water is used.

In thermal power plants, as a part of the boiler water treatment program, sodium phosphate is used to buffer boiler water pH to control corrosion. A temperature-dependent interaction occurs between sodium phosphate and iron oxide (i.e., magnetite layer of the tube) to form a compound, maricite (NaFePO_4), which is sodium iron phosphate. Due to its low solubility, maricite precipitates in high-heat-flux areas of the boiler, particularly under high load conditions. The precipitated phosphates hide out at locations where deposits or scales already exist. Thus, phosphate hideout damage usually occurs in boiler tubes in areas with high heat flux and low mass flow, or where there is wick boiling or departure



Fig. 6.67 Rounded pit formed due to phosphate corrosion

from nucleate boiling. Because the deposits are by and large insulating in nature, they lead to localized temperature excursions on the water-side surface. In turn, as the temperature within the deposits increases, the solubility of phosphates decreases and they start precipitating out, leading to phosphate corrosion.

Though caustic corrosion, hydrogen damage, and phosphate hideout are failures covered under an umbrella of *under-deposit corrosion*, there are specific differences between their exact modes of failure (Ref 6.18). For instance, in phosphate corrosion, the scale contains maricite, NaFePO_4 , whereas in a caustic attack, sodium ferroate, NaFeO_2 , is formed and no phosphate-containing corrosion products are formed. Additionally, there is a difference in the ratio of sodium to phosphate (Na/PO_4) ions in the two cases. If the ratio is more than 3:1, then caustic corrosion may occur. However, if the ratio is less than 2.3 at 315 °C (600 °F) or 2.7 at 360 °C (680 °F), then acid phosphate corrosion may result. Thus, it is noteworthy that the ratio shifts the equilibrium from one type of corrosion to another, accompanied by a pH shift. Likewise, acid phosphate corrosion differs from hydrogen damage, because the hydrogen damage is typically a thick-edged failure.

Phosphate hideout depends on load conditions and is observed mainly during load swings or start-ups. During load reduction, there is an increase in PO_4 concentration and a decrease of pH. However, when the load increases, an increase in pH and a reduction in PO_4 concentration is observed.

Microbially Induced Corrosion

Microbially induced corrosion (MIC) is the deterioration of metal as a result of the metabolic activity of microorganisms. It is also known as microbiologically influenced corrosion, biologically induced corrosion, or microbe-induced corrosion. Various types of microorganisms causing MIC are sulfur-sulfide oxidizing, sulfate reducing, iron oxidizing, acid producing, manganese fixing, and ammonia and acetate producing bacteria and fungi. Normally, MIC is not observed in a boiler when in operation because MIC-related bacteria generally grow in the temperature range 4 to 80 °C (40 to 175 °F). However, MIC can occur when the boiler is idle or out of service and during transportation due to improper handling. In addition, the condenser tubes are susceptible to MIC. Microbially induced corrosion is often associated with the presence of tubercles or slimy organic substances. Microbially induced corrosion occurs both as general corrosion and in a localized form such as pitting, although localized pitting is more frequent.

Microbially induced corrosion is caused by microorganisms, such as bacteria, algae, or fungi, in water under low-flow or stagnant conditions. The bacteria form a biofilm or slime with which they adhere to their host

surface and create a microenvironment conducive to corrosion. Alternatively, the bacteria cause corrosion through direct chemical attack by metabolizing a by-product that is highly corrosive. The presence of potentially corrosive bacteria or other organisms alone is not proof of MIC because the microbial growth leading to MIC occurs only when the metal (i.e., the host location), nutrients, water, and oxygen are simultaneously present.

There are two types of bacteria: those that grow in oxygen containing environments are called *aerobic* bacteria and those that grow in oxygen-deficient environments are known as *anaerobic* bacteria. Aerobic bacteria act by creating differential aeration and concentration cells through their biofilms. In seawater-cooled systems, aerobic bacteria such as *Pseudomonas* proliferate and can cause extensive damage to carbon steel and stainless steels. Anaerobic bacteria do not use oxygen in their metabolic processes. *Desulfovibrio* and *Thiobacillus* are anaerobic sulfur reducing bacteria because their metabolism involves the consumption of the sulfate ions in deaerated water, especially under deposits, and they produce hydrogen sulfide and sulfuric acid, respectively. The by-products formed cause corrosion. There is one more important variety of bacteria commonly found in cooling water systems called iron-related bacteria (*Gallionella ferruginea* and *Ferrobacillus* sp.). They cause corrosion of iron and steel by direct metabolism of iron, by consuming iron in their metabolic process and then depositing it in the form of hydrated ferric hydroxide. Likewise, nitrifying bacteria such as *Nitrobacter* oxidize ammonia (NH_3) to nitrate (NO_3) and form nitric acid, responsible for corrosion.

The different microorganisms thrive on varied nutrients including inorganic substances such as sulfur, ammonia, and H_2S , and organic substances such as hydrocarbons or organic acids. In addition, they need water and a source of energy such as light or organic or inorganic substances for cell renewal and growth.

There are two forms of MIC: active corrosion and passive corrosion. Active corrosion is the direct chemical interaction of microorganisms with materials, in which contact produces new corrosion chemistries and/or the marked acceleration of preexisting corrosion processes. This is a localized form of corrosion and is the more commonly found type. In passive corrosion, the biological material acts as a chemically inert substance and is present as deposits over underlying corroding surfaces. This promotes under-deposit corrosion over large areas.

Most metal alloys including aluminum alloys, the 300 series of stainless steels, copper alloys such as brasses, and carbon steels are vulnerable to MIC. Microbially induced corrosion is most common in stainless steel, but less common in copper alloy tubing. Titanium alloys have a much higher resistance to MIC than steels or copper alloys. The factors that contribute to MIC are pH, the presence of nutrients, temperature, lack of flow, and oxygen concentration.

Case Study 16—Failure of Waterwall Tube in a Utility Boiler

Background Details The waterwall tube of a utility boiler failed at a site during a hydro test prior to the commissioning of the boiler. The boiler was fabricated at the manufacturer's unit and transported to the site. It was lying in idle conditions in a tropical environment for about a year before its erection. The failed waterwall tube was made up of SA 210 Grade A1 steel. The dimensions of the tube were 38.1 mm (1.5 in.) diameter and 2.6 mm (0.1 in.) thickness.

Investigation and Findings Visual and low-magnification examination of the failed tube sample revealed clusters of shallow pits scattered all over the outer surface of the tube. Some of the pits were covered with scales (Fig. 6.68).

The failed tube sample received for investigation was subjected to tests such as chemical composition analysis, hardness testing, SEM studies, EDS analysis, and microstructural examination. The results of chemical analysis and hardness measurement confirmed that the material was per SA 210 Grade A1. An SEM examination on the OD surface showed numerous pits. The morphology of the pit contours was indicative of a tunneling effect (Fig. 6.69).

Energy dispersive spectroscopy analysis on the outer surface of the tube showed the presence of elements such as carbon, oxygen, aluminum, silicon, sulfur, potassium, chlorine (as chloride), calcium, and iron (Table 6.7).

The microstructure of the OD surface of the tube showed fine grains of ferrite and pearlite having pits filled with scales (Fig. 6.70). The pit contours showed a tunneling tendency.

Based on the prior history and the findings of this investigation, the failure of the waterwall tube of the utility boiler was attributed to MIC. The boiler was kept in idle condition in a tropical environment at the site for

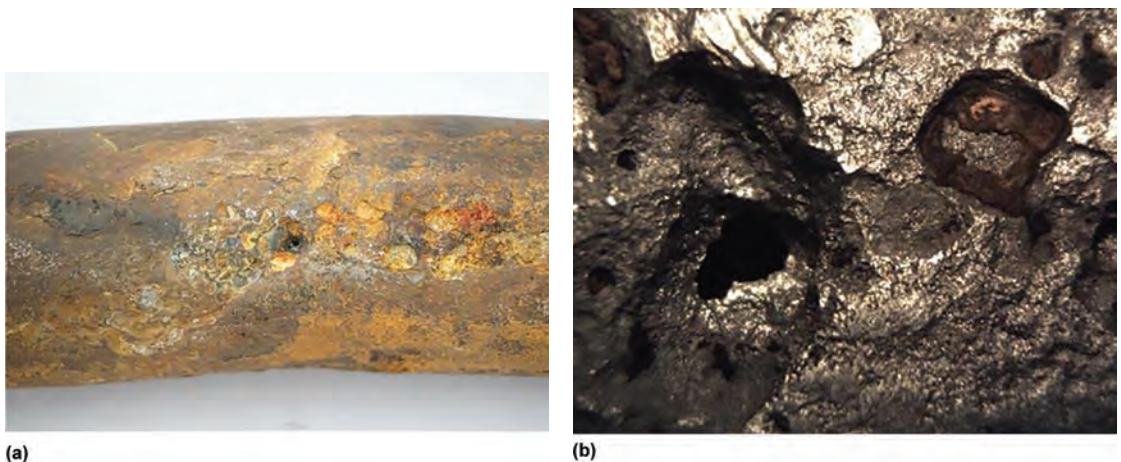


Fig. 6.68 (a) Cluster of shallow pits on tube surface. (b) Low-magnification view indicating presence of scaling over the pits, 6×

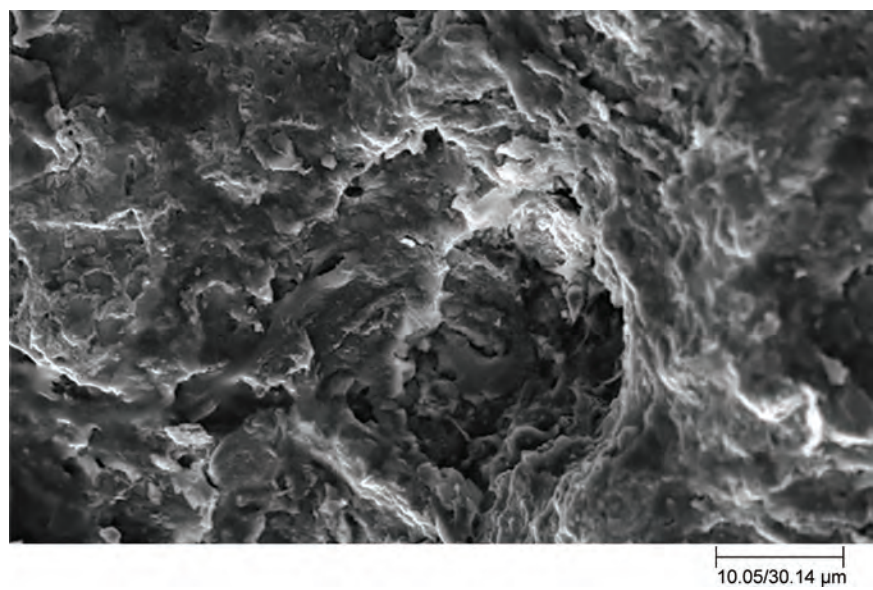
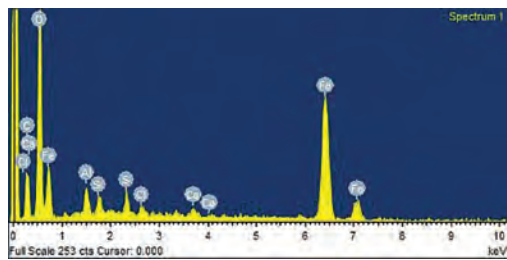


Fig. 6.69 SEM image of the OD surface showing scattered pits with tunneling effect, 1000×

Table 6.7 EDS analysis on outer surface of the tube



Element	Amount by wt. %	Element	Amount by wt. %
Carbon	8.12	Sulfur	1.80
Oxygen	16.59	Chlorine (chloride)	0.88
Aluminum	2.68	Calcium	0.42
Silicon	2.00	Iron	67.51

about a year before its erection and commissioning. In such a situation, any system with free water in contact with it can host microbial activity, provided there is a source of nutrients. When microbes settle on a surface, they set up a protective organic layer called a biofilm. Between the biofilm and the underlying metal surface, waste products from bacterial

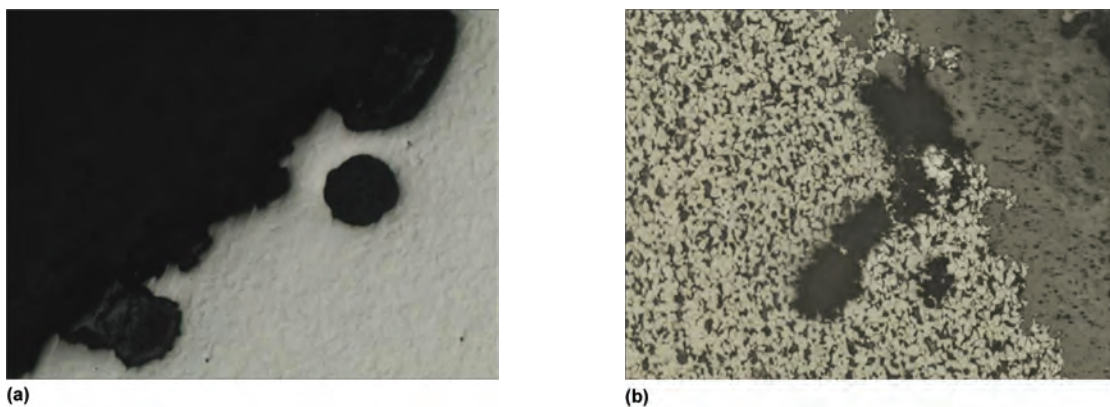


Fig. 6.70 (a) As-polished sample showing the pit contours, 100 $\times$. (b) Microstructure of OD surface comprising fine grains of ferrite and pearlite having pits filled with scales, 100 $\times$. Both micrographs clearly display the tunneling effect.

respiration accumulate, which are typically acidic in nature. This in turn results in pitting damage on the tube surface. The presence of sulfur and chlorine (chloride) ions per EDS on the outer surface of the tube indicated localized acidic conditions, causing a cluster of pits on the tube surface. The tunneling seen on the pit contours during microstructural examination, especially in the failure region, further confirmed MIC damage.

Conclusions The failure of the tube was attributed to MIC.

Flow-Accelerated Corrosion

Flow-accelerated corrosion (FAC) is also known as *flow-assisted corrosion* or *flow-induced corrosion*. It is a damage to boiler tubes where thinning of the tube occurs due to complete or partial dissolution of the protective magnetite (Fe_3O_4) layer (Ref 6.19, 6.20). If the protective film dissolves in a stream of flowing water, it is called single-phase FAC, whereas when the dissolution occurs in the presence of two fluids, namely water and steam (i.e., wet steam), the process is called two-phase FAC. Risk of failure due to FAC increases in a cycling operation involving frequent start-ups and low-load operations. Such conditions account for substantial transients in the chemistry of the BFW contributing to FAC. The most vulnerable areas prone to FAC are the auxiliary feedwater system, economizer tubes, condensers, moisture separation drains, reheater drains, bends in evaporators, and risers. In general, components such as elbows, bends, tees, reducers, and pipe entries are more susceptible to FAC. The eroded surface has, by and large, a shiny appearance without any corrosion products and has a structure like sand dunes, as shown in Fig. 6.71.

The exact appearance of the damaged surface is a function of the type of flow. Flow-accelerated corrosion due to single-phase fluid gives rise to an orange-peel surface with a magnetite layer of less than 1 μm , along with

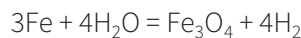
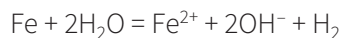


Fig. 6.71 ID surface of a tube showing shiny metal surface with sand-dune-like appearance in the direction of flow due to FAC

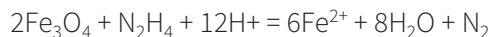
small cavities. Compared with this, damaged surfaces caused by two-phase FAC have a tiger-striped black shiny appearance, as shown in Fig. 6.72.

The mechanism of FAC is described by four reactions:

- Oxidation of iron to soluble ferrous ions and magnetite at the internal interface between the steel and the oxide.

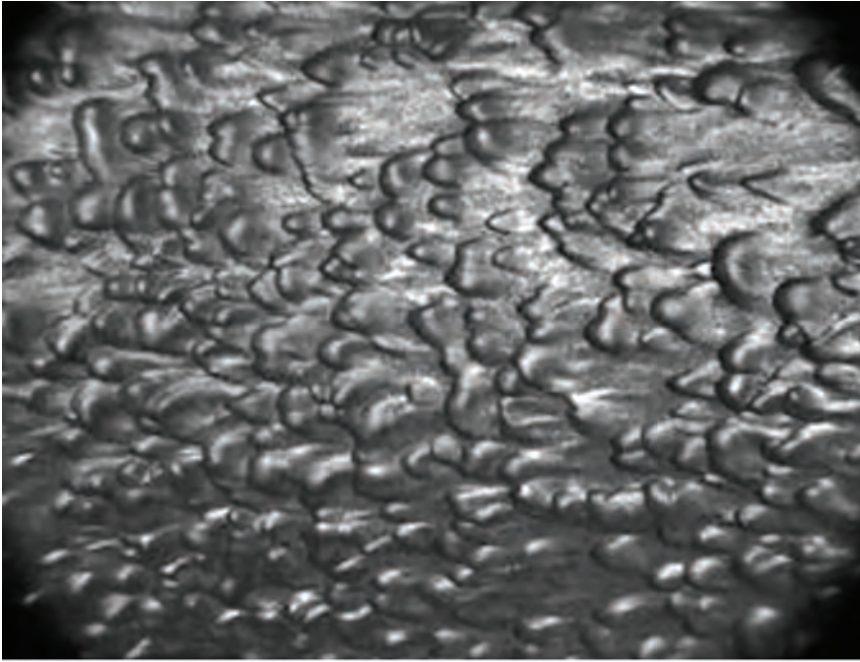


- Diffusion of soluble species (iron and hydrogen) across the porous oxide and diffusion of hydrogen through the carbon steel.
- Dissolution and reduction of magnetite at the external interface between the oxide and the water.

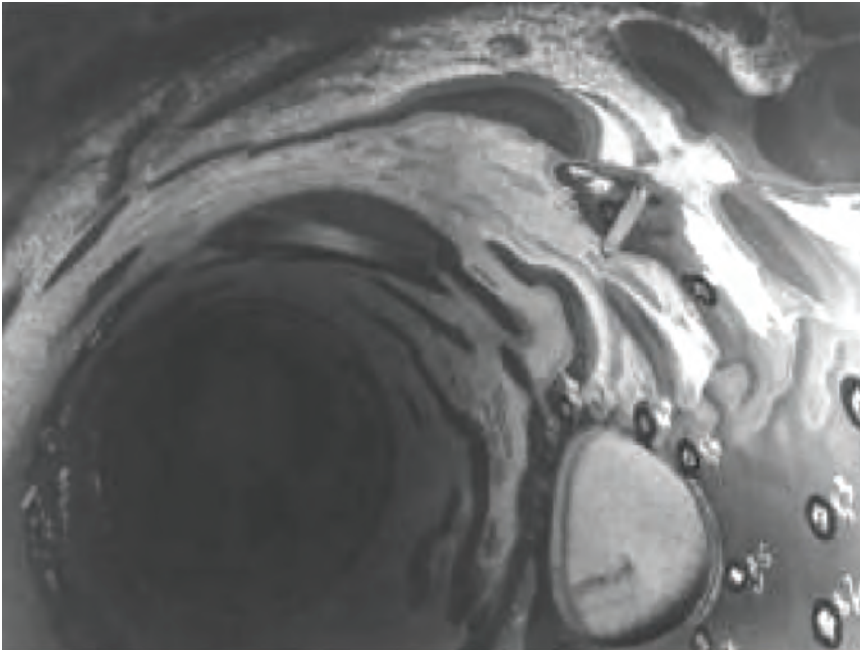


- Transfer of soluble iron species toward the flowing water and transfer of hydrogen toward the air after diffusion through the steel.

The extent of any damage due to FAC depends on several factors, such as the type of fluid (i.e., single-phase or two-phase FAC), fluid velocity, geometry of the component, temperature, pH, dissolved oxygen concentration, and MOC of the component.



(a)



(b)

Fig. 6.72 (a) Orange-peel surface of single-phase FAC, 11 $\times$. (b) Tiger-striped surface of two-phase FAC, 11 $\times$

Single-phase FAC is less aggressive than two-phase FAC due to the less turbulent nature of single-phase water streams compared with wet steams.

The extent of damage due to FAC is mainly governed by local fluid velocity rather than nominal or bulk fluid velocity. At low velocity, two events, dissolution of the protective magnetite film on account of FAC and the growth of Fe_3O_4 at the oxide or steel interface on the ID surface of a tube, counterbalance each other. However, when the fluid velocity is high (typically $>8\text{--}10\text{ m/s}$), the growth of Fe_3O_4 cannot match the flow-accelerated dissolution, resulting in exfoliation and spallation of the protective oxide film. Finally, the protective oxide film thickness decreases to such an extent that it becomes less protective or totally nonprotective.

Straight pipes or tubes are less prone to FAC, but areas of hydrodynamic disturbance such as elbows, bends, and locations downstream of flow control orifices and valves are preferred locations for FAC. Such locations give rise to changes in local velocity, leading to turbulence, and thus promote conditions conducive to FAC.

Flow-accelerated corrosion mainly occurs in the mid-temperature interval (i.e., between 120°C and 200°C , 250 and 390°F) with maximum potential at around 150°C (300°F). This is the temperature normally found in the BFW area.

Acidic (i.e., low pH conditions) promote FAC. Ammonia is used to control the pH of high-purity water, such as condensate and feedwater. A low ammonia concentration (typically around 0.1 ppm) in high-purity feedwater results in lower pH. Feedwater with low pH ($\text{pH} < 8.5\text{--}9$) offers conditions favorable for magnetite dissolution and thus leads to FAC.

Flow-disturbed areas such as elbows, reducers, and tees are affected by FAC when the dissolved oxygen concentration in the feedwater is high. Above 30 ppb of dissolved oxygen in water, corrosion in the form of FAC will be greater. However, in a completely oxygen-free environment, the chances of failure due to FAC are higher. Traces of oxygen are therefore recommended in feedwater (1 to 2 ppb) to minimize FAC damage. This helps in maintaining the protective magnetite layer on the ID surface of the pipes and tubes.

Compared with plain carbon steels, low-alloy steels offer greater resistance to FAC. Steels containing small amounts of chromium, copper, and molybdenum (such as $1.25\text{Cr-}0.5\text{ Mo}$ or $2.25\text{Cr-}1.0\text{Mo}$ steel) significantly reduce the solubility of magnetite and thus offer greater protection against FAC.

Case Study 17—Failure Investigation of Low-Pressure Evaporator of a Boiler in Heat Recovery Steam Generator

Background Details The top bend on a low-pressure evaporator tube belonging to the last row from the flue-gas side started leaking after $16,000$ hours of operation. Initially, an attempt was made to arrest the leakage by repair welding, but it was not successful and hence the tube bend was replaced.

The MOC of the tube was SA 210 Grade A1 steel, and the tube dimensions were 50.8 mm (2 in.) OD and wall thickness 2.67 mm (0.10 in.), with serrated fins.

Plant reports indicated that frequent load variations took place in the HRSG due to variation in power demands, resulting in temperature variations in the gas turbine exhaust. In turn, this disturbed the complete HRSG system's operating parameters and operating steam characteristics.

Investigation and Findings Figure 6.73 depicts the tube bend received for failure investigation, showing the repair weld.

Visual examination of the outer surface of the sample revealed a puncture at the extrados portion of the bend in the repair welded area, as shown in the close-up view in Fig. 6.74(a). A corresponding close-up view of the ID side of the tube is shown in Fig. 6.74(b). The repair welding was done sideways. The internal surface of the tube showed a brownish black appearance. Thinning was apparent on one side of the bend.

Upon close examination of the ID surface of the tube, horseshoe-shaped, scalloping corrosion marks were seen, especially on the outer curvature. Figure 6.75 shows a close-up view of the internal surface of the tube at the extrados portion at the low magnification of 11x.

A thickness survey indicated maximum reduction in thickness at the puncture location at the extrados portion, but marginal reduction in section thickness.

Chemical analysis of the tube material conformed to SA 210 Grade A1 steel. Energy dispersive spectroscopy analysis revealed the presence of carbon, oxygen, sodium, magnesium, calcium, sulfur, and potassium in a yellowish orange scale on the ID side and oxygen, calcium, and magnesium in addition to iron on the overall ID surface.

Metallographic studies on the ID surface showed a banded ferrite-pearlite structure. The relatively smooth ID surface at lower magnification indicated the effect of corrosion under flow marks (Fig. 6.76). The parent

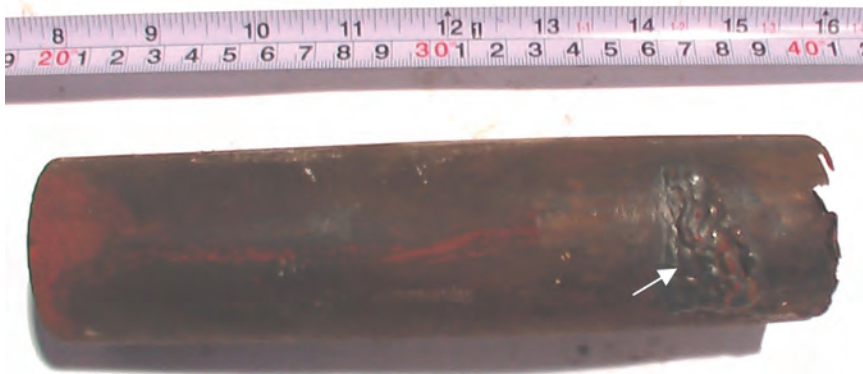


Fig. 6.73 Tube bend in as-received condition



Fig. 6.74 Close-up views of (a) OD side and (b) ID side of the tube bend showing puncture and repair weld area

metal microstructure away from the failure location was also ferrite and pearlite, corresponding to typical normalized conditions.

Plant data revealed that a two-phase mixture of steam and water was flowing through the bend. Moreover, the boiler was subjected to frequent load variations in view of fluctuating power demands that led to variations in the operating steam characteristics and operating parameters.



Fig. 6.75 Internal surface of a tube at extrados portion displaying scalloping marks at low magnification, 11×



Fig. 6.76 Microstructure of an ID-side bend sample, 200×

In view of this, a wide fluctuation in the rate of flow was possible. These process conditions led to corrosion on the ID surface of the tube, with a scattered scalloped and horseshoe corrosion pattern. Both visual and low-magnification examination indicated such features that are typically found in case of an FAC failure. The signature of FAC was also seen in optical metallography. Thinning was noticed at the extrados portion of the tube. To rectify the situation, repair welding was attempted, but it had not proved successful.

Conclusions The puncture on the outer radius of the bend tube was due to FAC damage.

Case Study 18—Failure Investigation of Evaporator Riser Tube Bend of Heat Recovery Steam Generator

Background Details Thinning from the inside surface was found in the case of HRSG evaporator riser tube bends connected to the top header after about 4 years of operation. Thinning of the tubes resulted in an eventual puncture and loss of availability of the HRSG. The MOC of the tube was SA 210 Grade A1 steel, and the dimensions were 38.1 mm (1.5 in.) OD and 2.6 mm (0.10 in.) thickness.

Investigation and Findings It was noticed during visual examination of the tube bend that there was thinning from inside into the bend portion of the sample. There was no apparent damage on the external surface. The ID surface showed scalloping marks and depressions scattered over the bend region (Fig. 6.77).

The tube sample was subjected to thickness measurement, and the results obtained are in Table 6.8. An abnormal reduction in thickness at localized spots over the bend portion was noticed.

Low-magnification and SEM examination on the ID surface of the tube bend exhibited clusters of scalloping depressions with a typical horseshoe pattern (Fig. 6.78a and b).

Energy dispersive spectroscopy analysis on the inner surface edge of the tube revealed the presence of elements including oxygen, magnesium, aluminum, silicon, and sulfur. Table 6.9 gives the results of EDS analysis conducted on the ID edge.

Figure 6.79(a) and (b) shows the microstructure on the ID side at the thinning location, which consisted of fine-grained banded ferrite and pearlite. The microstructure also shows a wave-like corrosion pattern with scale spots on the ID surface at the bend portion of the sample.

There were a number of start-ups and shutdowns and a wide fluctuation in the steam generation due to load fluctuations based on the demand for power. The tube geometry at the failure location consisted of a bend, and the two-phase flow and the fluctuations in the steam generation pointed toward the prevalence of a turbulent flow inside the bend. The nature of the damage observed was such that there was a typical pattern of scalloping and thinning from the extrados region of the bend from inside. The

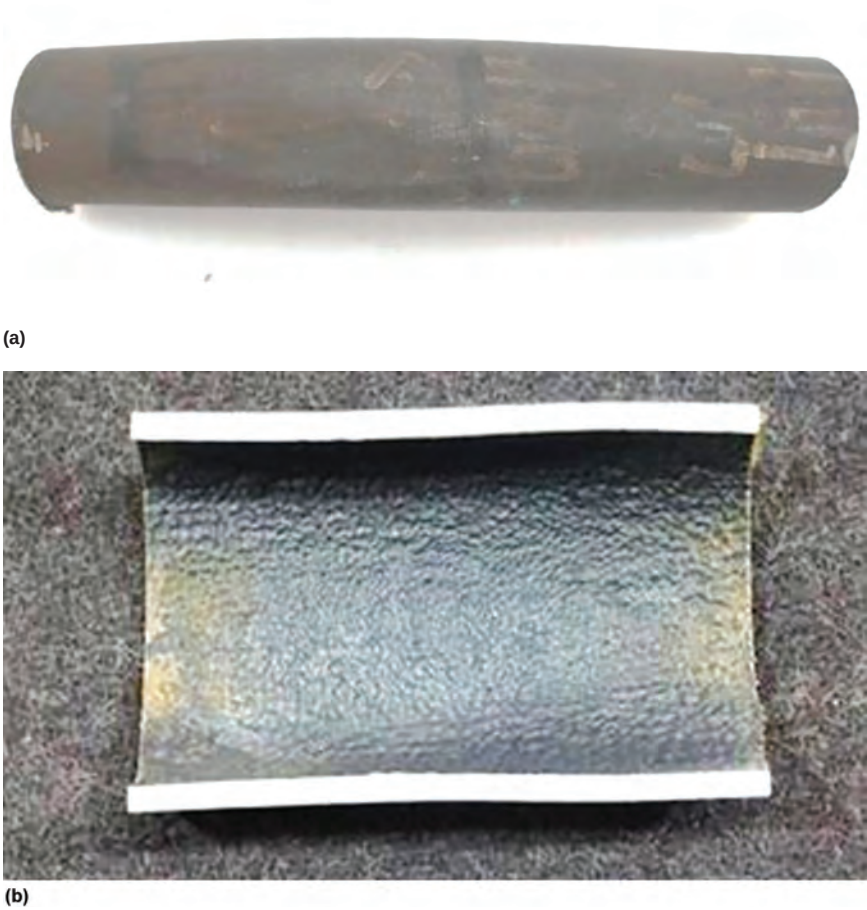


Fig. 6.77 (a) External surface of a tube without any apparent damage except for insignificant deformation. (b) Opened tube showing scalloping pattern with metal wastage marks exhibiting directionality

Table 6.8 Thickness measurement on tube sample

			
	1	2	3
Location	Tube thickness, mm		
0°	2.4	2.4	2.5
90° (Extrados)	1.6	2.3	2.5
180°	2.5	2.4	2.6
270° (Intrados)	2.5	2.8	2.7

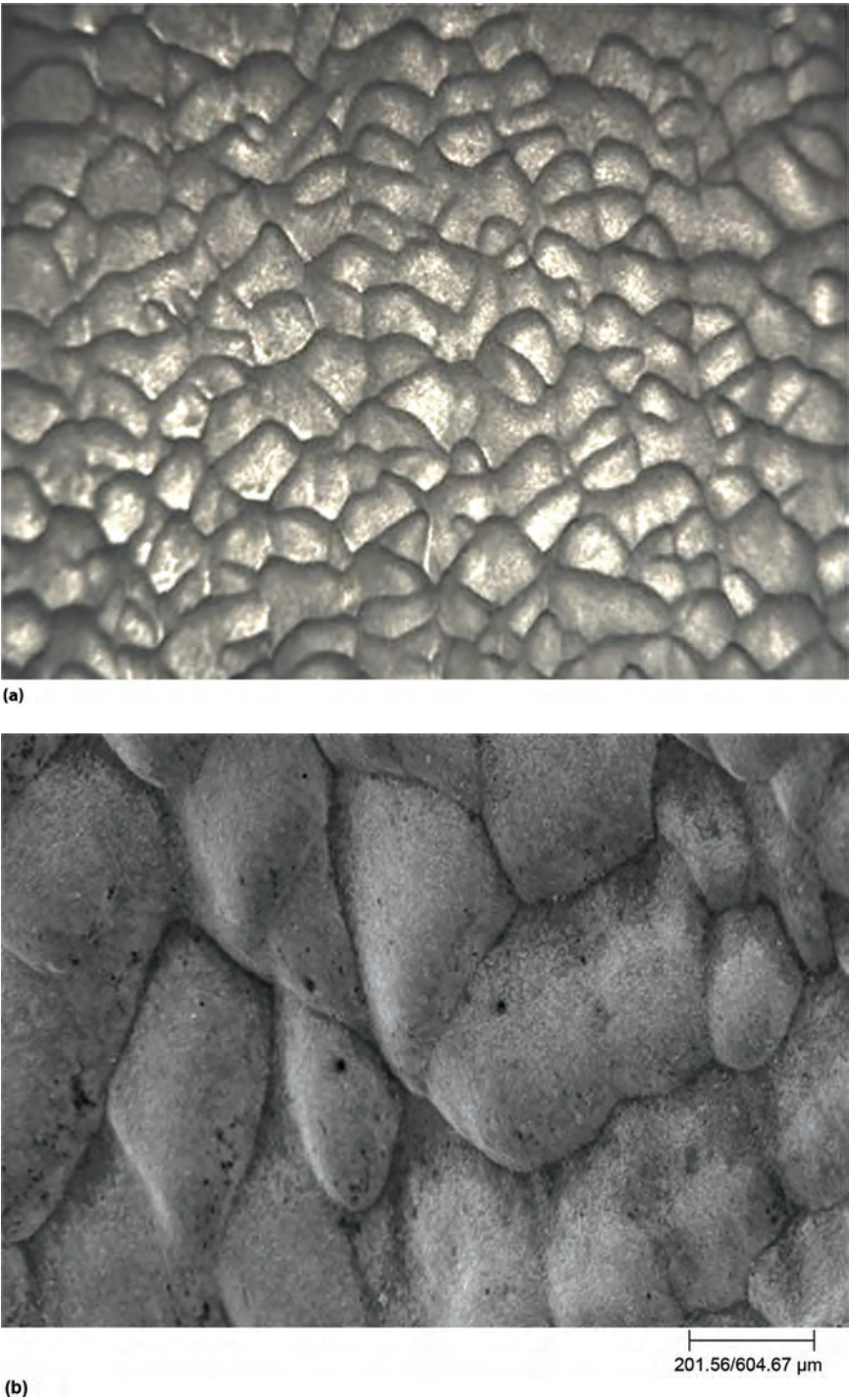
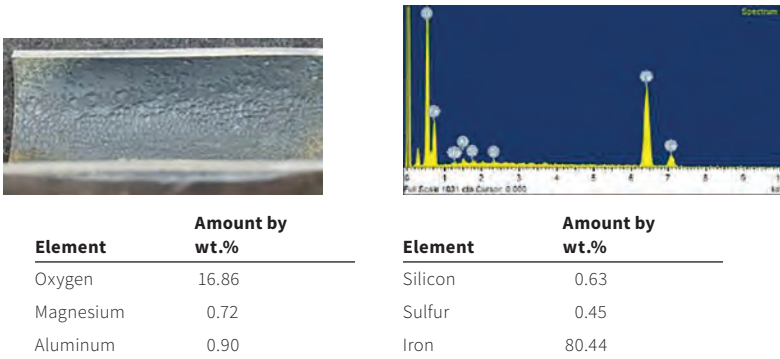


Fig. 6.78 Low-magnification view of the inner surface indicating cluster of scalloping depressions having smooth surface, (a) 6×, (b) 50×

Table 6.9 EDS analysis on ID edge

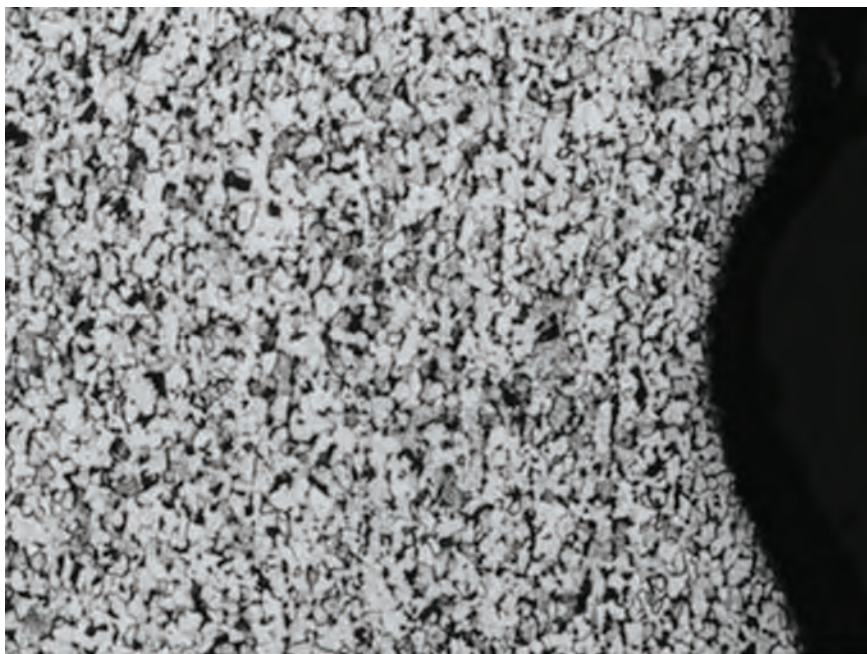
damage area had a very thin layer of magnetite along with general metal wastage. All these features led to failure of the tube bend due to FAC.

Conclusions The thinning observed on the evaporator riser tube bend was due to FAC.

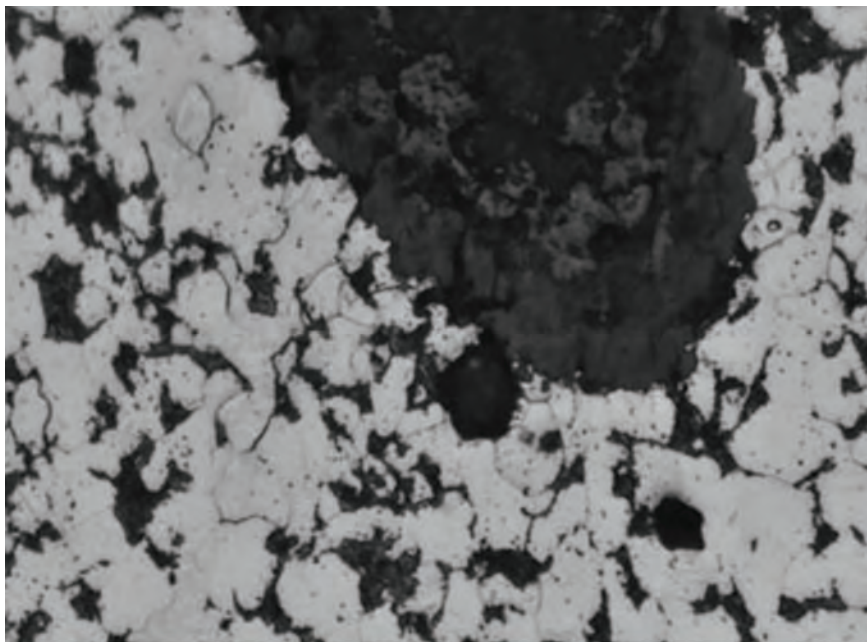
Erosion-Corrosion

Adherent surface films and deposits on the ID side of tube are often disrupted by rapidly flowing fluids. Thinning or removal of these surface films due to erosion by flowing streams results in accelerated corrosion, called erosion-corrosion (EC). Erosion-corrosion is defined as the degradation of the material due to both mechanical and chemical processes. In the case of pipes and tubes, EC is mainly found at locations such as bends, elbows, and joints. Erosion-corrosion takes the form of grooves, waves, gullies, teardrop-shaped pits, and horseshoe-shaped undercuttings in the surface (Fig. 6.80) (Ref 6.21, 6.22).

The term EC covers several erosion and corrosion mechanisms including FAC. The term FAC is used for a very specific set of conditions, but FAC and EC are quite often used interchangeably. Destruction of the protective surface layer or film of magnetite is common to both types of damage mechanism, and also involves removal of the damaged oxide layer or film from the substrate over which it forms. However, the difference between the two is in the manner in which the damaged film is removed. In EC, the oxide film is mechanically removed, whereas in FAC, the protective oxide film is dissolved or prevented from forming further. In either case, corrosion of the unprotected underlying surface takes place. Thus, FAC is based on a chemical dissolution and mass transfer processes, whereas EC relies on mechanical damage and the subsequent removal of the protective oxide layer by turbulence created by high-velocity fluid.



(a)



(b)

Fig. 6.79 (a) Microstructure at ID edge of a tube with wave-like metal wastage, 100×. (b) ID edge comprising fine-grained ferrite and pearlite with scale patches, 400×



Fig. 6.80 Erosion-corrosion damage of economizer tube bend

Case Study 19—Failure Investigation of Atmospheric Fluidized Bed Combuster Boiler Bed Coil

Background Details Recurring failures at an interval of about a year of service were reported in an atmospheric fluidized bed combustor (AFBC) boiler bed coil. Normally, the failure was noticed by a drop in bed temperature, which was indicative of tube leakage. The MOC of the bed coil tube was SA 210 Grade 1 steel. The bed coil was immersed in a fluidized bed of refractory sand in an AFBC boiler.

Investigation and Findings Visual examination of the failed sample revealed damage to the majority of studs on the outer surface, which were either completely or partly missing (Fig. 6.81a). Erosion marks in the form of smooth depressions were seen on the outer surface wherever the studs were completely missing. Leakage had taken place from a puncture that was in the form of a pinhole, and no studs were seen in the area surrounding the puncture. The number of studs on the outer surface at the bent location looked better. They were covered with a corrosion scale (Fig. 6.81b). The inner surface of the tube was smooth and brick red in color (Fig. 6.81c).

A low-magnification view revealed two punctures at the leakage location (Fig. 6.82). Erosion-corrosion damage was seen on the outer surface



(a)

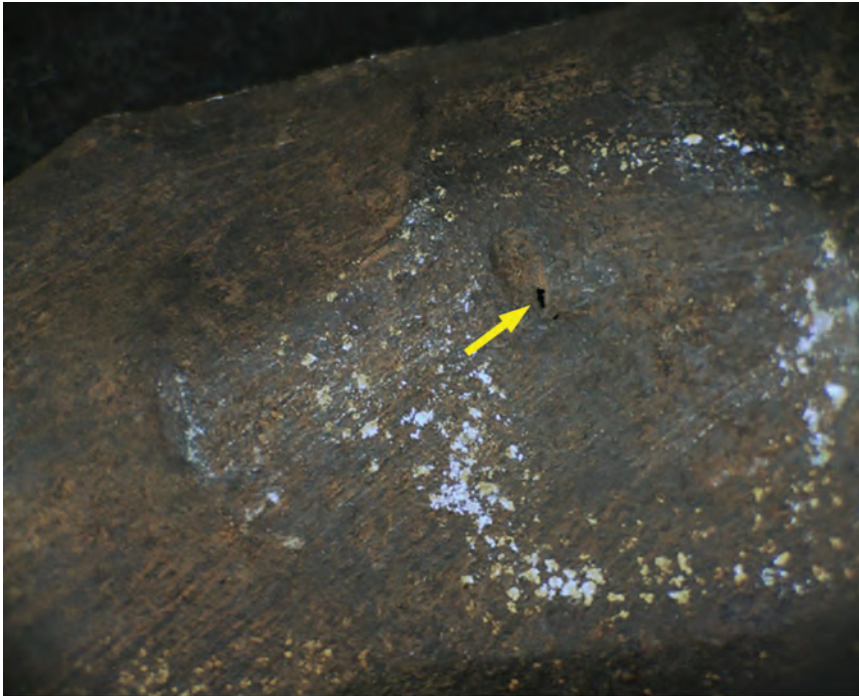


(b)



(c)

Fig. 6.81 (a) Close-up view at leakage location with leakage in the form of tiny pinholes and smooth outer surface with erosion marks where the studs had worn out. (b) Bent location showing scale deposits. (c) Inner surface view brick red in color indicating absence of protective magnetite scale



(a)

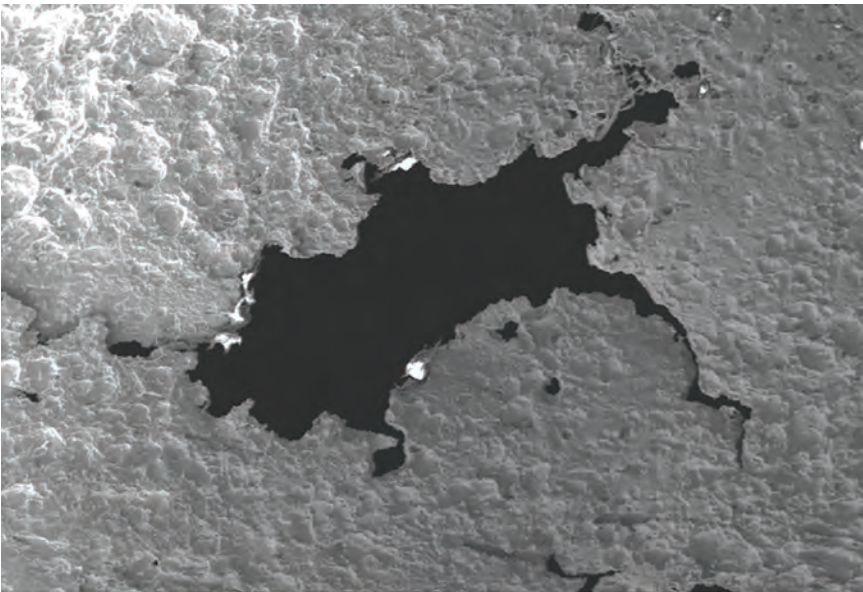


(b)

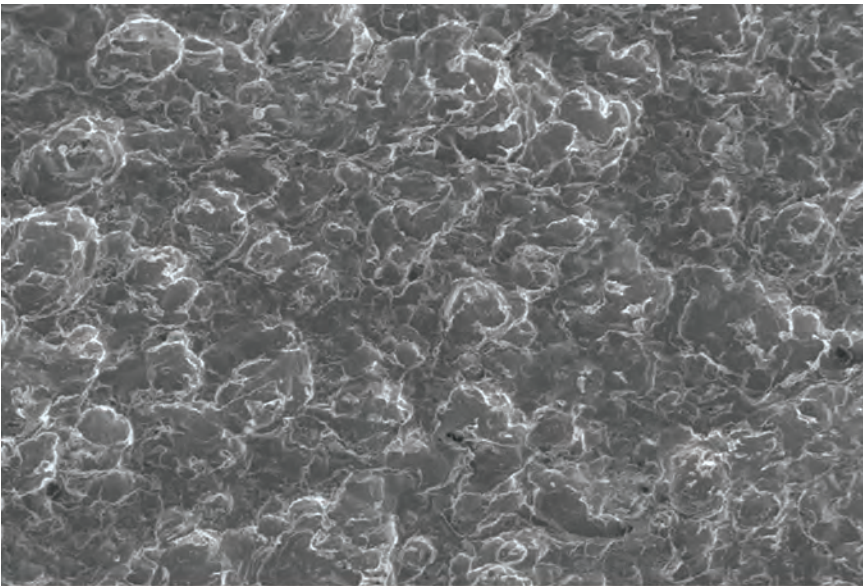
Fig. 6.82 Low-magnification views at outer surface showing erosion-corrosion damage surrounding two punctures, (a) 2 $\times$, (b) 6 $\times$

surrounding the puncture. The contours of the area surrounding the puncture had thinned down.

Scanning electron microscope studies at the puncture location highlighted extensive wall thinning at the puncture contours, which was surrounded by aggravated erosion damage (Fig. 6.83).



(a)



(b)

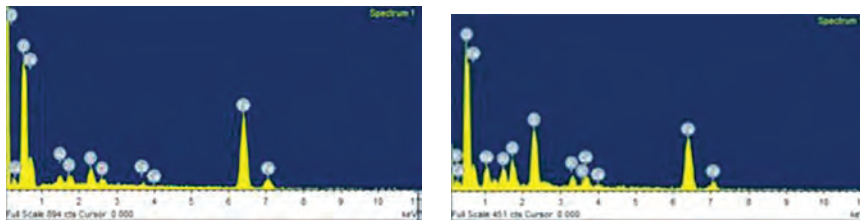
Fig. 6.83 SEM micrographs showing extensive wall thinning at puncture contours surrounded by aggravated erosion damage, (a) 100×, (b) 250×

Energy dispersive spectroscopy analysis of the scale that formed on the outer surface of the tube revealed the presence of oxygen, aluminum, silicon, sulfur, chlorine (as chloride), sodium, potassium, and calcium (Table 6.10).

Microstructural examination indicated EC damage on the outer surface, which was more aggressive near the puncture location. The microstructure was ferrite and pearlite with no signs of overheating (Fig. 6.84).

The metallurgical integrity of the bend appeared to be acceptable and had not undergone any kind of degradation. Tensile and hardness values were acceptable. Visual examination highlighted the absence of studs on the tube surface, barring the bent portion, in most of the locations. Those present on the surface had also lost their shape. Erosion marks in the form of smooth depressions were seen on the outer surface wherever the studs had been shaved off. On the bent portion, though the stud density was better, scaling was noticed. The inner surface looked brick red in color, confirming the absence of any protective magnetite scale. Both low-magnification views and SEM studies indicated aggressive EC damage on the outer surface that had caused wall thinning at the puncture contours. Energy dispersive spectroscopy analysis confirmed EC damage from the outer surface. While erosion was due to the refractory compounds of elements including aluminum and silicon, whose source was the fluidized bed material, corrosion must have been induced by sodium and potassium in the form of sulfates and pyrosulfates whose source was the coal used as fuel. All these findings were further supported by the microstructural examination.

Table 6.10 EDS analysis of scales formed on OD surface



(a) Black scale

(b) Brown scale

Element	Surface scales, wt.%		Element	Surface scales, wt.%	
	Black	Brown		Black	Brown
Oxygen	24.18	26.36	Potassium	...	2.56
Sodium	...	6.52	Chlorine (Chloride)	1.35	...
Aluminum	2.07	3.18	Calcium	0.41	1.27
Silicon	1.92	4.30	Iron	66.43	44.56
Sulfur	3.64	11.25			

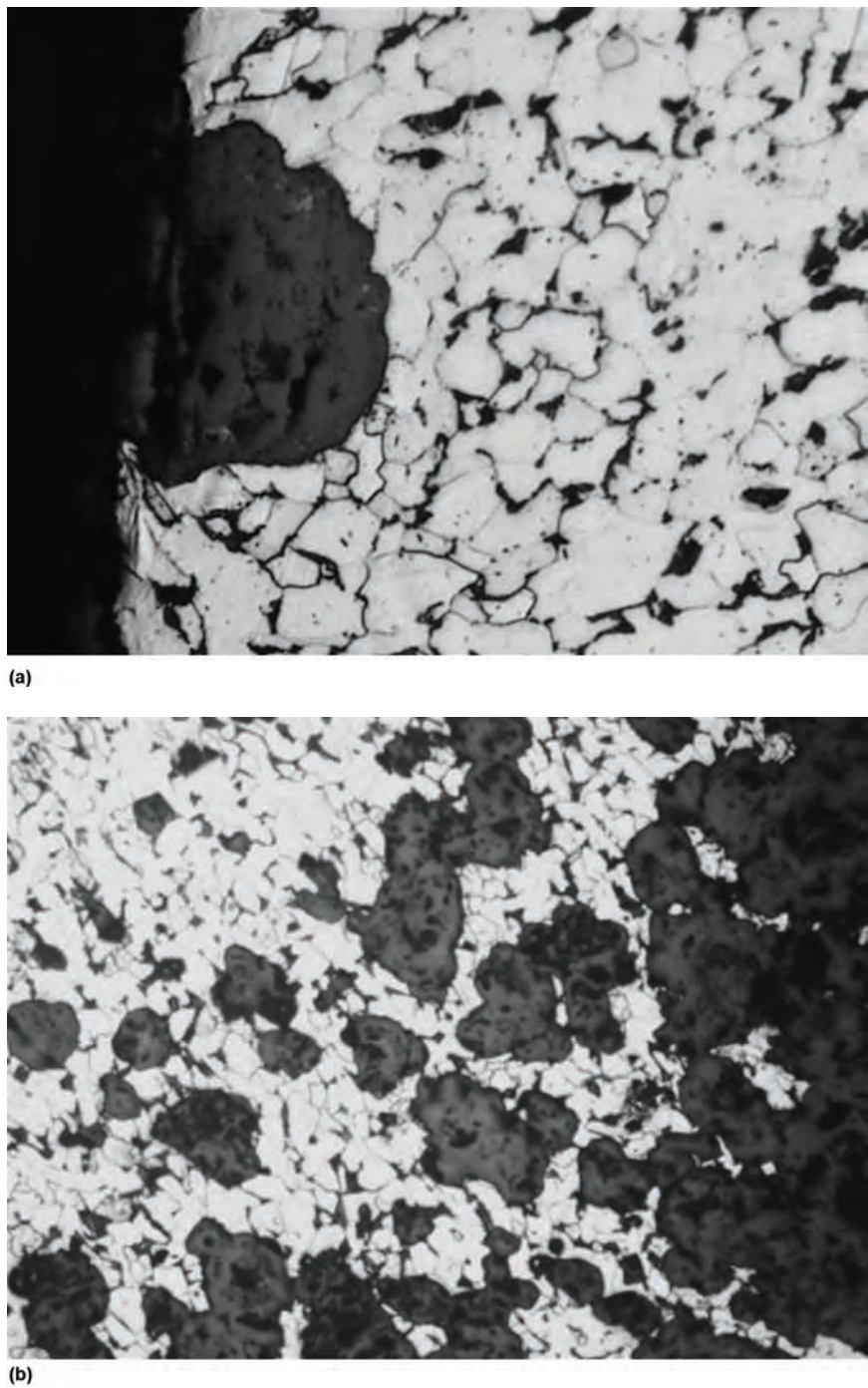


Fig. 6.84 (a) Outer-edge microstructure of ferrite-pearlite with erosion marks on outer surface covered with scale, 400×. (b) Scale patches on outer surface, 100×

Thus, the recurring nature of failure was primarily because of EC damage promoted from the outer surface. The reason for this appeared to be due to design considerations with regard to factors such as the fluidized bed particle size, size of the fluidized bed with respect to steam generated, placement of tubes inside the fluidized bed, location of air burners, wear and tear on the burner nozzles, nonuniform flow of gases into the fluidized bed either due to improper firing or leakage, and formation of clinkers.

Conclusions The recurring nature of premature failure of bed coil tubes in the AFBC boiler was primarily attributed to EC from the outer surface.

Cavitation Damage

Cavitation is a type of failure of boiler tubes wherein the rapidly formed small bubbles in a fluid near the tube surface collapse or implode so as to impact the metal surface, resulting in removal of material from the ID side of the tube. The energy with which the bubbles implode may be just sufficient to rupture the protective magnetite layer or may damage the underlying metal as well. Bubbles form when the pressure of the fluid drops below the vapor pressure (i.e., the pressure at which a liquid becomes a gas). A sudden drop in the pressure and the turbulent flow of fluid accentuate cavitation phenomena. In other words, low pressure generates a high degree of turbulence within the fluid, favoring cavitation (Ref 6.23).

Pits formed due to cavitation exhibit a rough and jagged appearance (Fig. 6.85). The damaged surface exhibits a spongy and honeycomb appearance. Cavitation is a localized form of damage in the sense that the pits formed are generally confined to a specific area and are not on the entire ID surface of the tube.

The extent of damage due to cavitation cannot be controlled simply by proper material selection because it is a result of the system, which includes the tube material, the fluid flowing, and its properties (density, viscosity, surface tension, and flow rate), as well as the temperature and pressure of the fluid. However, it is possible to minimize the extent of damage due to cavitation by using a material with higher fatigue strength or by using overlays; but it cannot be totally stopped.

Case Study 20—Failure Investigation of HCl Reboiler Tubes

Background Details Repetitive tube leakages were reported in an HCl reboiler. Corrosive acidic gases and liquid containing HCl had contaminated an entire steam circuit, resulting in secondary damage and corrosion of pipes and fittings. The tubes carried process gas; the shell side was steam.

The reboiler had undergone as many as 15 instances of tube leakage in the past 4 to 5 years. Initially, the MOC for the tubes was carbon steel,



Fig. 6.85 Cavitation damage in a boiler tube

which failed within a few months of service. Thereafter, Inconel 600 and duplex stainless steel tubes were tried. However, they were also unable to withstand the process conditions. In an attempt to stop failures, the inlet of the shell-side steam was reversed from the original equipment manufacturer design. However, that attempt also proved to be unsuccessful. Essentially, all the leaks were located at the bottom portion of the tube bundle and were not due to the MOC used. In all cases, the leaks initiated from the ID side, which pointed toward leakage failure because of the process environment. The MOC of the failed tube received for failure investigation was SA 210 Grade A1 steel.

Investigation and Findings Visual examination showed that the tubes were straight with a light reddish brown appearance. No significant thinning or effect of corrosion was observed from the OD surface (Fig. 6.86a). The ID surface showed deep pits and grooving-type damage at the puncture, and the cavities were filled with corrosion products (Fig. 6.86b). The adjacent areas to the cavities were found free of any significant corrosion. More importantly, the opposite half of the ID surface with the cavities was found to be free from any such damage.

The ID surface after pickling showed deep pits and groove formation scattered on the surface (Fig. 6.87).



(a)



(b)

Fig. 6.86 Close-up views of (a) OD surface at the puncture location; and (b) ID surface with deep cavities filled with orangish brown corrosion product

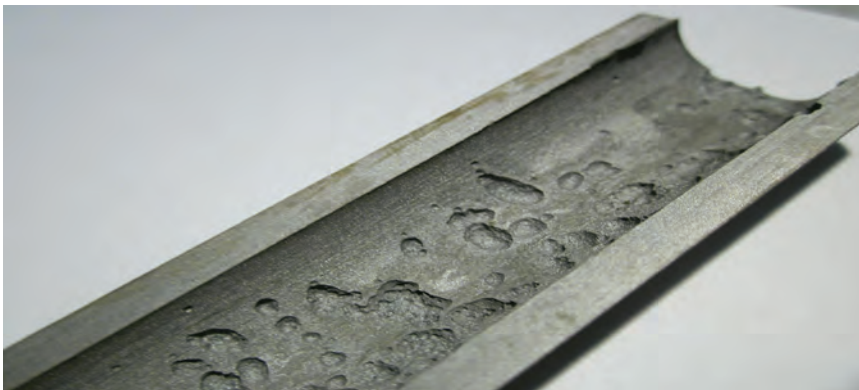


Fig. 6.87 Close-up view of ID surface after pickling showing deep pits and groove formation scattered on the surface

In order to detect the presence of punctures, erosion, or pitting damage, acoustic pulse reflectometry was carried out on the punctured tube. Defects such as holes and erosion marks were observed on the ID surface.

A low-magnification examination was carried out on the punctured tube as well as on one nonleaking tube from the inner side to reveal more details about the failure mechanism or corrosion pattern. It revealed the formation of cavities at the ID surface with a layered effect (Fig. 6.88).

Scanning electron microscopy of the puncture location revealed features typical of cavitation damage (Fig. 6.89). Similar features were also noticed at other locations on the ID surface.

Energy dispersive spectroscopy analysis on the ID surface showed the presence of iron, manganese, silicon, and oxygen, ruling out the possibility of corrosion because of tube-side fluid. The EDS analysis on the OD surface showed the presence of chlorine (as chloride) and sulfur along with oxygen, sodium, magnesium, aluminum, silicon, phosphorus, potassium, calcium, chromium, and iron (Table 6.11). These elements were sourced from the steam-side contamination and were responsible for the external general corrosion of tubes.

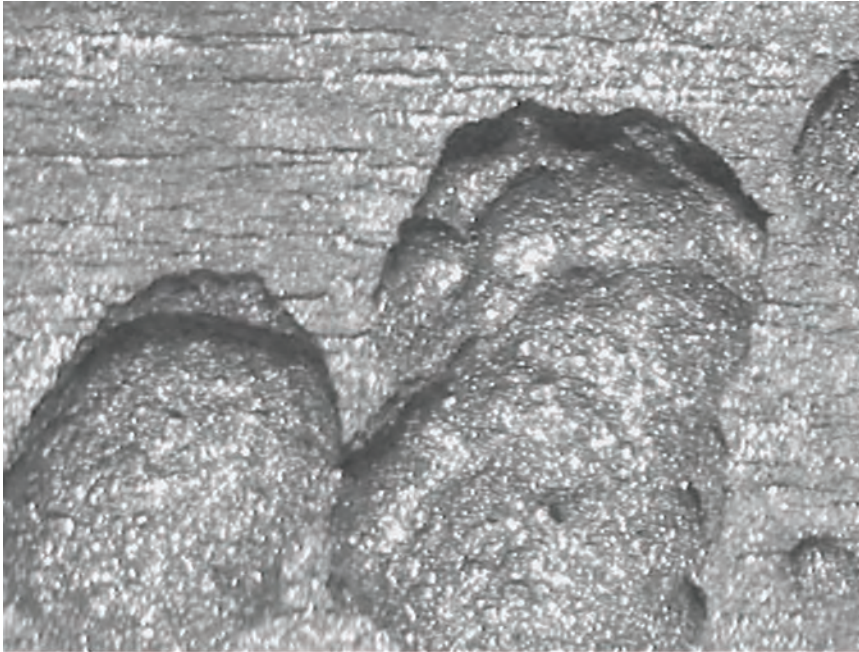
The general microstructure at the core was of ferrite and pearlite, as shown in Fig. 6.90(a). Per the microstructure in Fig. 6.90(b), the primary damage was observed from the ID side and was due to cavitation corrosion.

It had been discovered earlier that when steam was fed from the top, tube failures were taking place from the top end of the heat exchanger. When the steam inlet was changed to the bottom side, tube failures started taking place from the bottom end. Despite having tried tubes made from different schedules of carbon steel, Inconel 600, and duplex stainless steel, failures persisted irrespective of the material specification. Thus, it was obvious that the tube failures were related to the steam inlet orientation, which was causing localized process variations. Both visual examination and low-magnification views evidenced a process of random cavitation on the ID surface. Scanning electron microscopy and microstructural examination confirmed cavitation on the ID surface, which was specific to the tube facing the inlet-side fluid. At different locations or at opposite sides to a failure, no such cavitation was noticed. The failure of the tube pointed to damage due to cavitation corrosion.

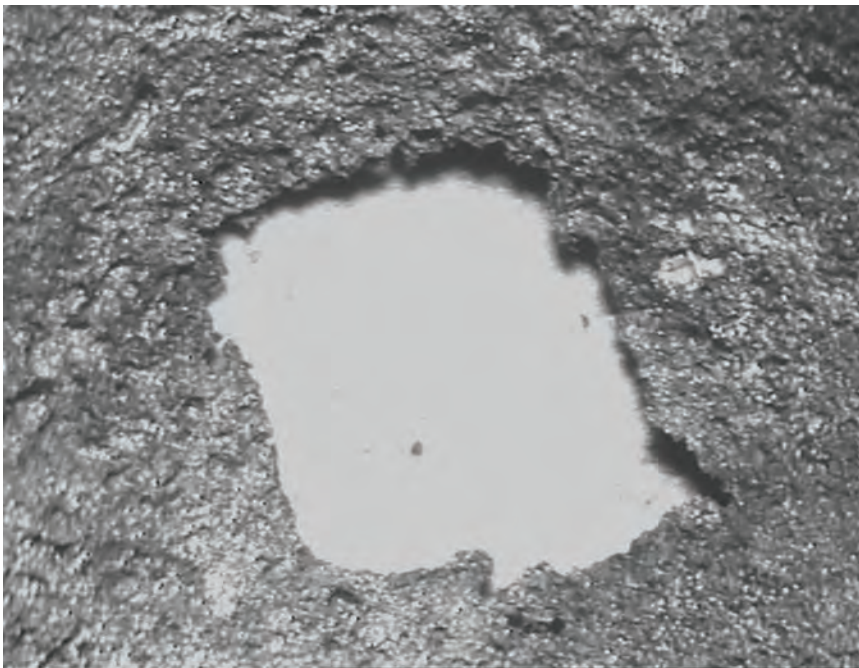
Conclusions The repeated failures in the reboiler tube heat exchanger were due to cavitation corrosion damage at locations where the tubes were facing the shell inlet steam directly.

Oxygen Attack or Oxygen Pitting

Corrosion due to oxygen attack or oxygen pitting is one of the most frequently encountered failures of boiler tubes, occurring due to exposure of the tubes to excessive amounts of dissolved oxygen in water (Ref 6.24,



(a)



(b)

Fig. 6.88 Low-magnification views of ID surface, indicating (a) groove formation and erosion marks on ID surface, 15 $\times$; and (b) thinning surrounding puncture, 15 $\times$

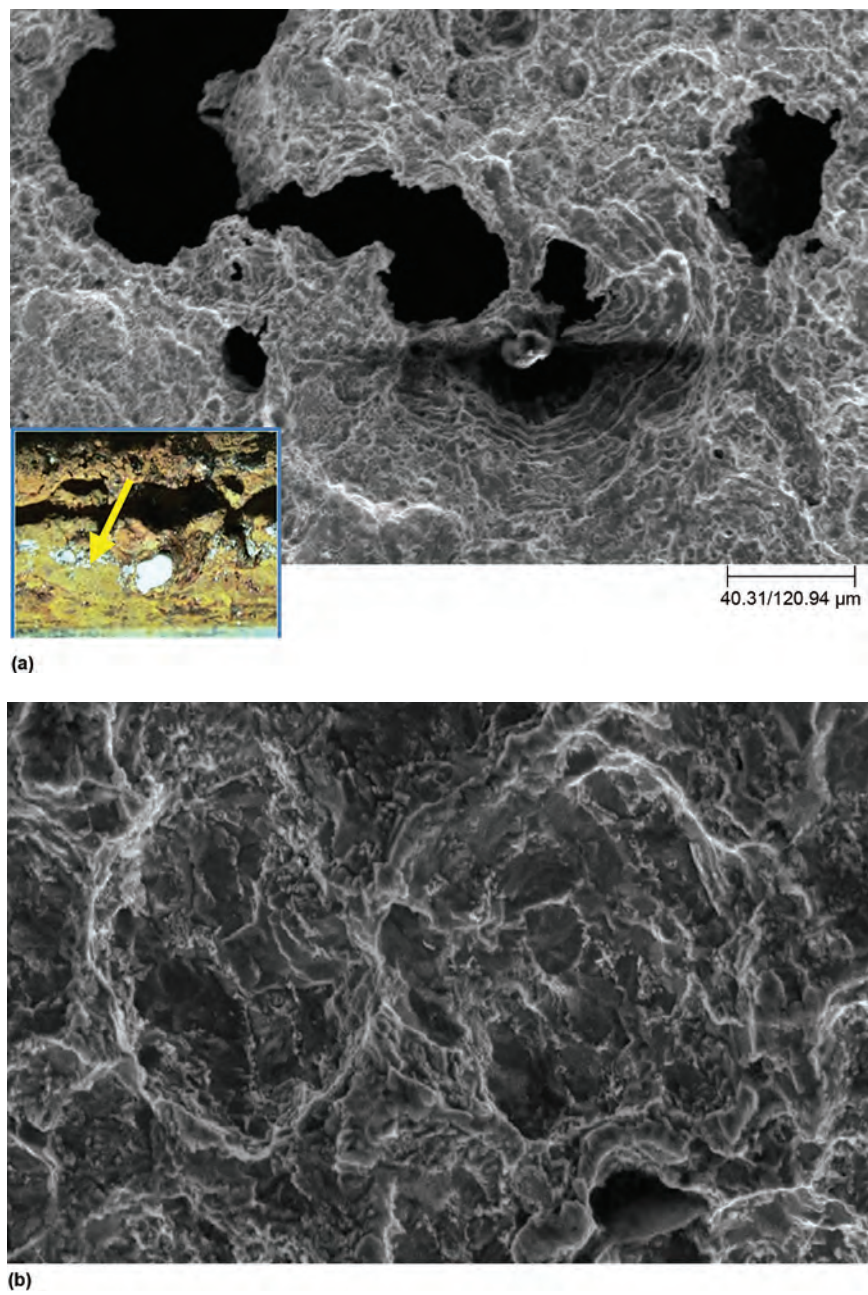
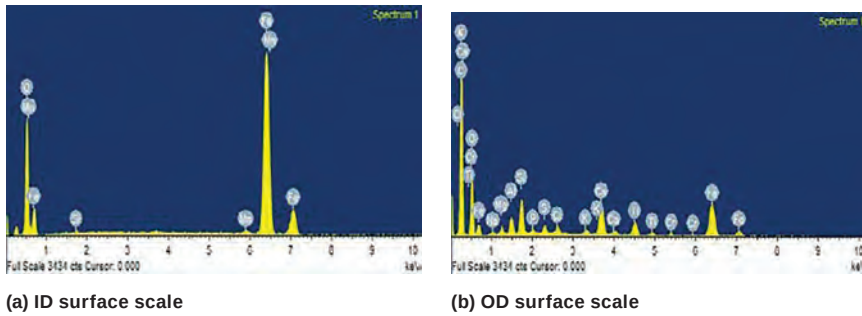


Fig. 6.89 SEM micrograph of (a) the puncture location, 250×; (b) ID surface indicating cavitation-type damage surrounding the puncture contours, 1000×

Table 6.11 EDS analysis on ID and OD surface of the tube

Element	Surface scales, wt.%		Element	Surface scales, wt.%	
	ID	OD		ID	OD
Carbon	...	19.54	Sulfur	...	1.04
Oxygen	35.89	49.57	Chlorine	...	1.02
Sodium	...	0.58	Potassium	...	0.59
Magnesium	0.85	1.24	Calcium	...	4.67
Aluminum	...	2.57	Titanium	...	2.61
Silicon	0.40	4.66	Chromium	...	0.23
Phosphorus	...	0.52	Iron	62.86	11.15

6.25). Air-in leakages at pipe flanges and through other parts under vacuum can also lead to the ingress of oxygen in the system besides what is already present in boiler feedwater (BFW). This type of failure is reported more in cases of idle boilers rather than for boilers in operation. During idle periods, such as outages and storage, if proper procedures are not followed, failures of this nature occur. For boilers that are in operation, oxygen pitting occurs as a result of the malfunctioning of the deaerator or improper oxygen scavenging treatment. The superheater and reheater tubes, feedwater heater, economizer, and condensate lines are the most vulnerable sites for oxygen attack or pitting to take place. Pitting frequently occurs during shutdown, mainly at non-drainable locations such as bends and sags, where the water is not easily drained off.

It is well known that the corrosiveness of water increases as temperature and pH decrease. However, aggressiveness of water generally increases with an increase in oxygen.

The dissolved oxygen in water leads to pitting on the inner surface of the tube. The pitting may be localized, or it may cover a larger area in the form of a pockmarked surface. The pits may vary in shape but are characterized by sharp edges at the surface. The pits are pinhole-size craters that are hemispherical in their morphology (Fig. 6.91). Often the pit tubercles

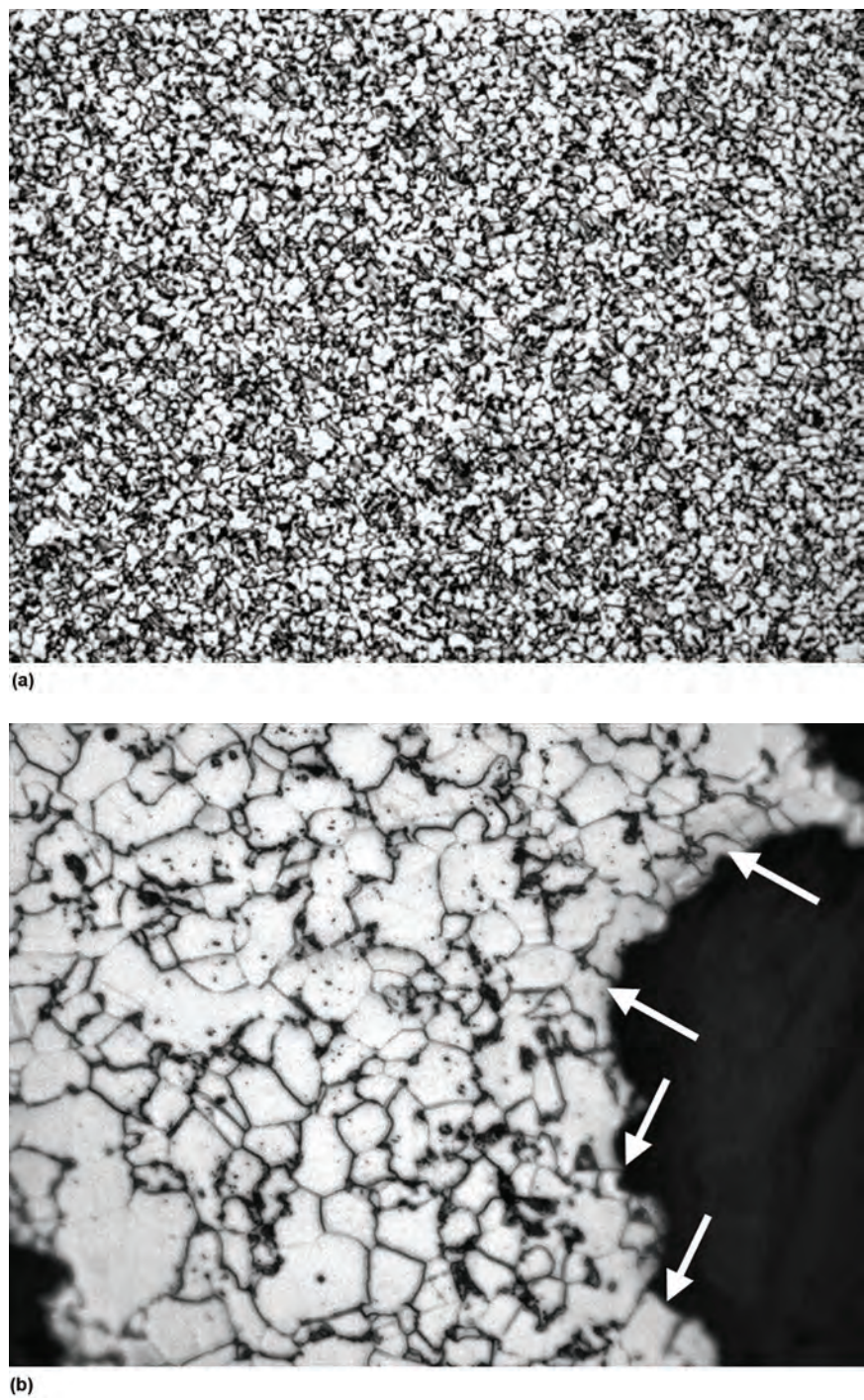
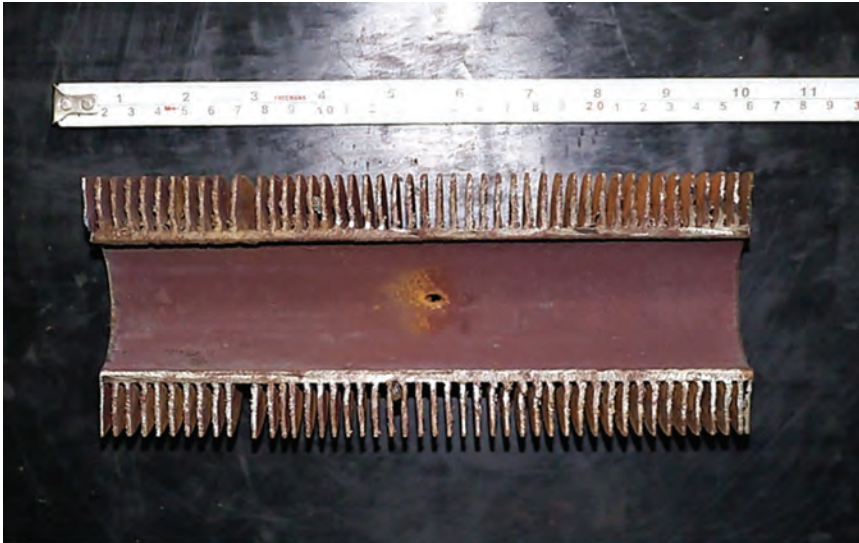


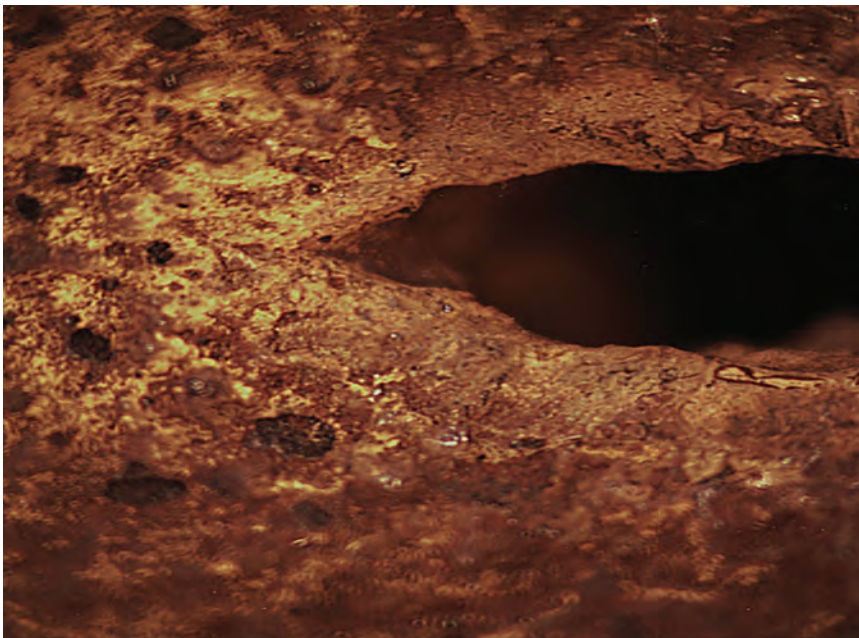
Fig. 6.90 Microstructures, (a) at core of ferrite and pearlite, 100×; and (b) at puncture location showing cavitation damage, 400×

are covered with caps of a corrosion product (i.e., iron oxide), rendering a reddish appearance as shown in the figures. Black iron oxide is observed within the pit when the cap is removed.

The oxygen pits can act as stress raisers, leading to subsequent failure of the tube under corrosion fatigue mode.



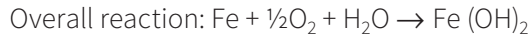
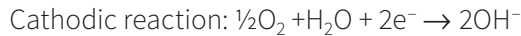
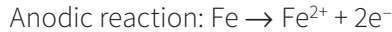
(a)



(b)

Fig. 6. 91 Oxygen pits (a) photograph; (b) 6×

The mechanism of oxygen attack (Ref 6.26) is explained on the basis of three reactions and Fig. 6.92:



According to Fig. 6.92, when an oxygen-containing bubble attaches itself to the tube surface, a potential difference is created between the oxygen-rich area under the bubble and the surrounding areas in contact with relatively oxygen-deficient water. The oxygen-rich area acts as a cathode, whereas the surrounding area, which is low in oxygen, acts as the anode, leading to the formation of a concentration type of galvanic cell. A ring of corrosion product is formed at the anodic areas over the bubble by capillary action, isolating it from the surrounding water. Gradually, as the cap of the corrosion product thickens, oxygen inside the bubble is consumed, leaving inert nitrogen inside the pit. Consequently, the polarity of the cell is reversed, and the area surrounding the bubble becomes cathodic and that beneath the bubble, anodic. Attack proceeds beneath the cap as long as the bubble remains intact. The cap of the corrosion products has to be sufficiently porous to allow the passage of ions, but oxygen depletion persists underneath because whatever oxygen diffuses inward is consumed

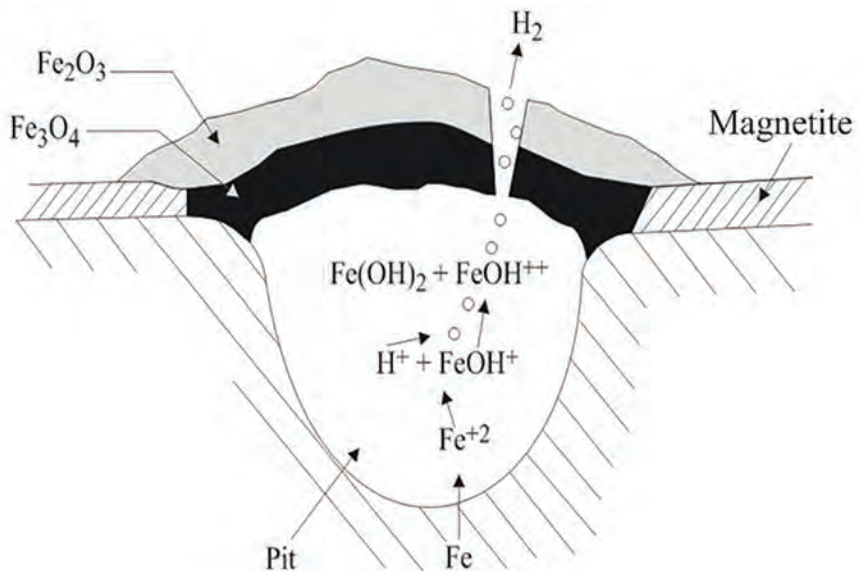


Fig. 6.92 Schematic showing mechanism of oxygen pitting

in the oxidation of corrosion products. Thus, once an oxygen bubble has attached itself to the metal surface, corrosion proceeds by the differential corrosion mechanism.

The three essential conditions responsible for oxygen pitting are: (i) presence of moisture or water, (ii) presence of dissolved oxygen, and (iii) an unprotected metal surface. Unprotected metal surfaces may include acid-cleaned surfaces, surfaces covered with a marginally protective or nonprotective layer of hematite (i.e., Fe_2O_3), and surfaces that are covered with a protective layer of magnetite (i.e., Fe_3O_4), but with cracks.

Severe corrosion occurs when oxygen is present in hot water. Even small concentrations of a few parts per million can cause serious problems. The maximum permissible limit for dissolved oxygen generally varies with the system pressure and temperature of a particular boiler. The dissolved oxygen level of water typically should be less than 0.1 ppm but not more than 2 ppm. The dissolved oxygen level is about 9 ppm in cold boiler makeup water at atmospheric pressure. In a feedwater heater, the dissolved oxygen content is brought down to about 2 ppm by heating the water to 90 °C (195 °F). This can be further reduced to 5–7 ppb by mechanical stripping or deaeration and by using chemical oxygen scavengers such as sodium sulfite, hydrazines, or hydroquinones.

Case Study 21—Failure Investigation of Economizer Tube of Heat Recovery Steam Generator

Background Details Leakage in the form of a puncture (hole) was observed in the finned tube of an economizer HRSG after 20 years of operation. Its location was approximately 3 m from the top header on the side facing the flue gases. In the past, tube leakages had been observed in the same module of the economizer. The MOC of the tube was SA 210 Grade A1 steel, and the tube dimensions were 51.0 mm (2 in.) OD and 3.2 mm (0.12 in.) thickness.

Investigation and Findings Visual examination indicated a puncture in the form of a pinhole on the tube surface in between the fins (Fig. 6.93). There was no apparent damage seen in the tube profile. Crust-like deposits were seen on the tube OD in the gaps between the fins.

The tube ID surface was rough with dark brown coloration (Fig. 6.94a and b). A low-magnification view highlighted the elongated nature of the puncture on the ID surface (Fig. 6.95a). The entire ID surface was covered with shallow pits. The surface was dark brown in color. The punctured surface was quite smooth in nature, which characterizes erosion that appears as an aftermath to leakage. Scanning electron microscopy analysis highlighted shallow pitting corrosion in the ID surface (Fig. 6.95b). Energy dispersive spectroscopy analysis of the ID surface showed oxygen and iron; a scale on the ID surface showed the presence of oxygen, silicon, and manganese.

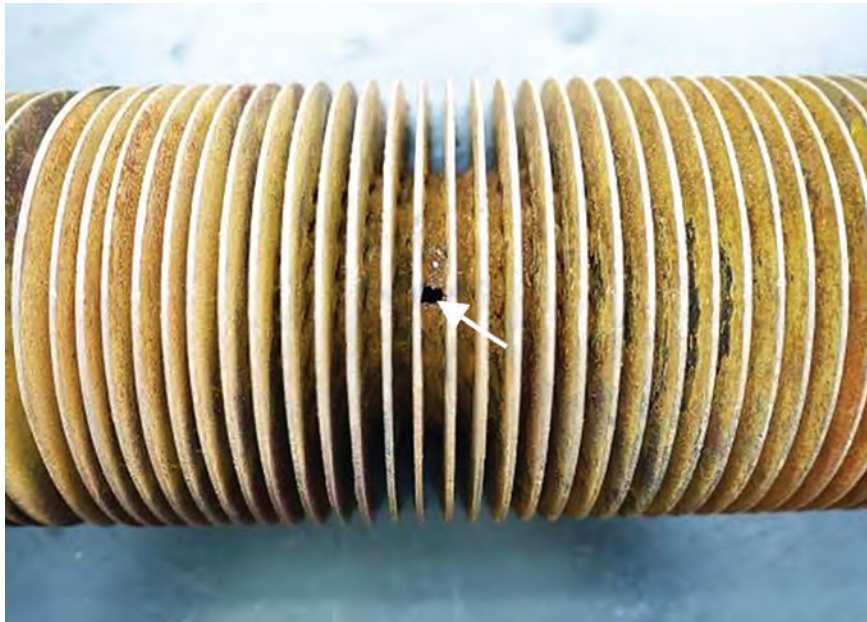
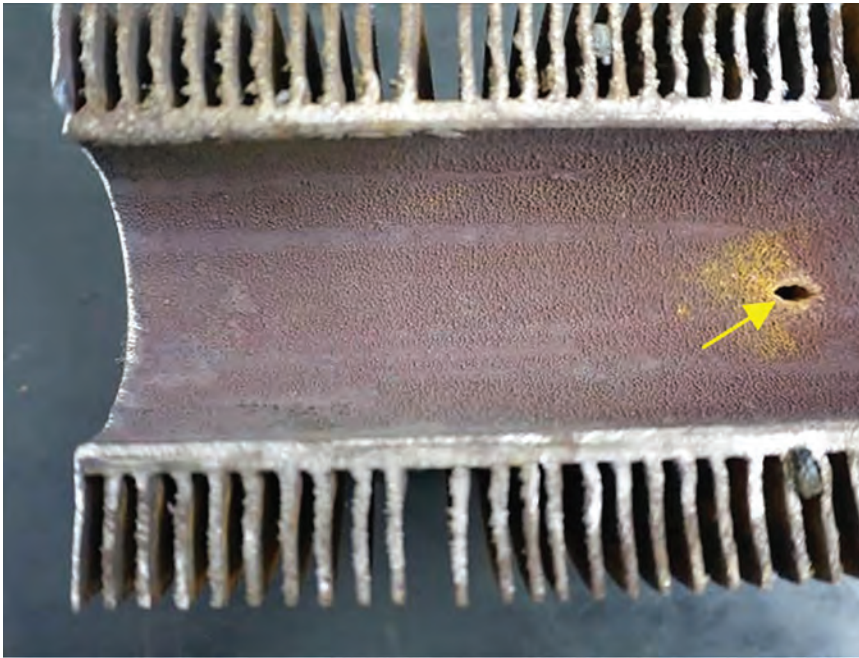


Fig. 6.93 Failed economizer tube showing puncture in the form of pinhole in between the fins

The general microstructure at all locations was ferrite and pearlite (Fig. 6.96a). The ID edge also revealed the presence of a thick scale, as shown in Fig. 6.96(b). The results of tensile and hardness testing were acceptable.

Metallurgical investigation did not reveal any indication of external corrosion. Careful examination at the finned region showed an intact metal surface, and the fins were without any thinning. The dark brown coloration seen on the ID surface along with the rough scale surrounding the pitting indicated the absence of a properly formed magnetite layer. The profile of the puncture contours showing a larger opening from the ID and smaller one at the OD indicated that initiation of the failure had taken place from the ID surface only. Scattered shallow pits were seen on the portion of the ID surface facing the flue-gas side in general, whereas a cluster of pits was surrounding the puncture. The results of SEM as well as EDS analysis indicated the mechanism of damage to be oxygen pitting. Occasional disturbances in water chemistry must have resulted in the ingress of oxygen. The oxygen could also have taken entry at the time of start-up and shut-down during boiler maintenance, with chances of oxygen ingress being higher during start-up.

Oxygen pitting damage occurred at the ID surface of the economizer tube facing the flue gas-side. Its propagation continued during normal operation of the boiler in the form of gradual penetration. Over a long



(a)



(b)

Fig. 6.94 (a) ID surface view of a tube with pinhole-type puncture. (b) Close-up view at puncture location with ID surface showing dark brown adherent scale, 6×

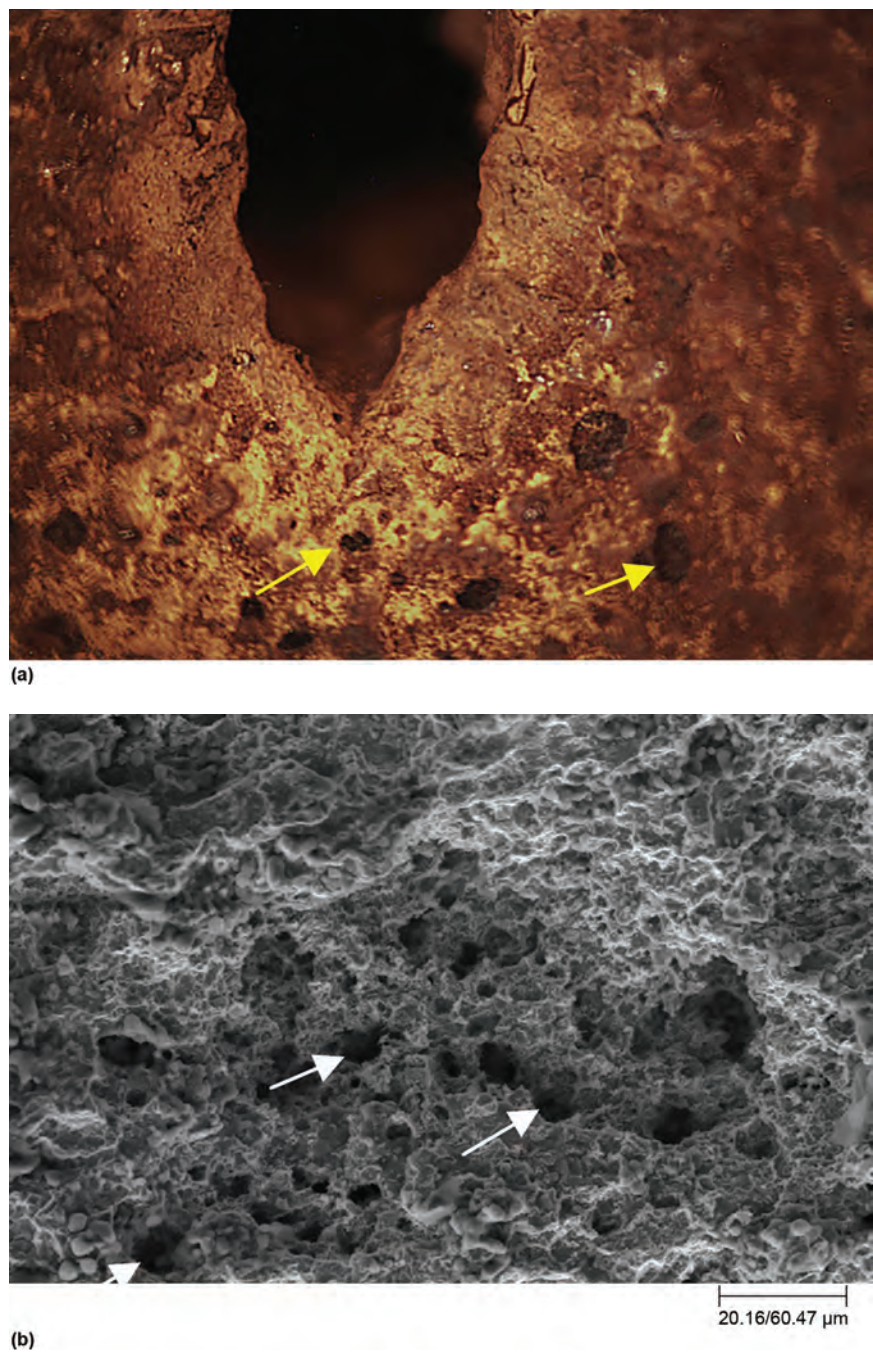
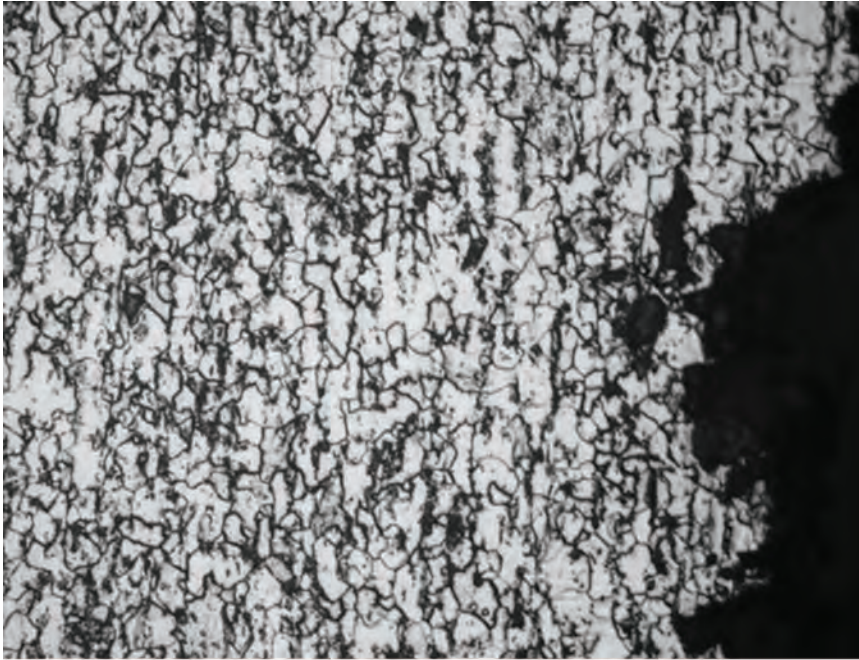
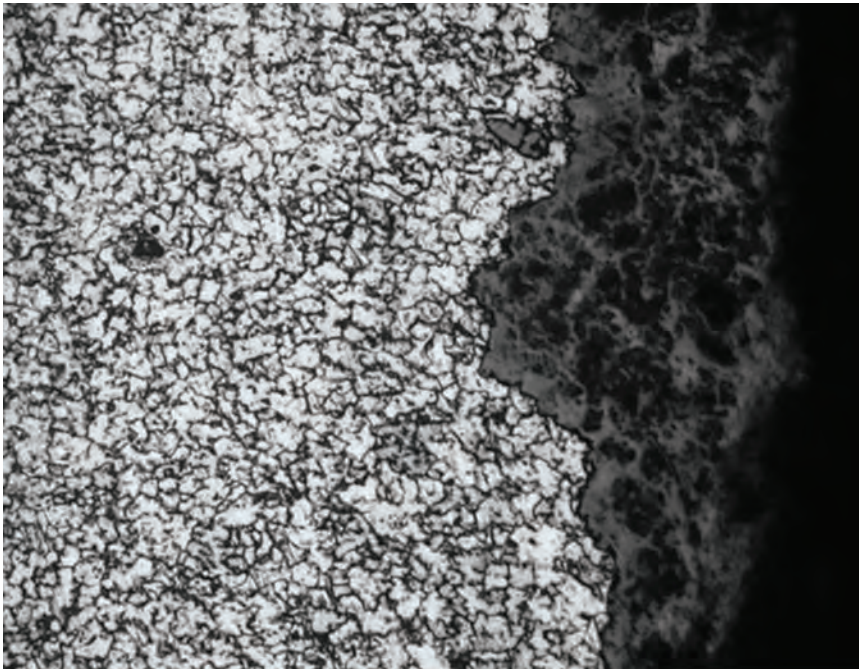


Fig. 6.95 (a) Low-magnification view of ID surface at puncture location with shallow pits in surrounding area, 6 $\times$. (b) SEM image showing shallow pits, 500 $\times$



(a)



(b)

Fig. 6.96 (a) ID surface showing banded ferrite-pearlite and shallow pitting, 200 $\times$. (b) Microstructure of ferrite and pearlite with scale at the ID edge, 200 $\times$

period of service at susceptible locations, one of the pits progressed through the entire cross section of the tube, causing the puncture.

Conclusions The failure of the economizer tube was due to oxygen pitting, which was initiated because of a disturbance in water chemistry during start-ups, which propagated as a deepened corrosion pit at one location, causing through and through puncture.

Case Study 22—Failure Investigation of Waterwall Tube in Captive Power Plant

Background Details The waterwall tube in a captive power plant failed by leakage after about 15 years of service. The tube was a part of the riser section and was embedded in a refractory near the burner. The MOC of the tube was per DIN 17175-79 Grade 15Mo3, and the tube dimensions were 57.0 mm (2.2 in.) OD and 4.5 mm (0.18 in.) thickness.

Investigation and Findings Visual examination highlighted a pinhole puncture on the outer surface, which was surrounded by erosion damage (Fig. 6.97a). The outer surface was reddish brown in color. The inner surface had thin adherent scale that was grayish black in color. Rough spots in the form of shallow grooves were noticed on the inner surface at the leakage location. There were scattered shallow pits on the inner surface (Fig. 6.97b).

Low-magnification examination using a zoom stereo microscope on the ID surface revealed a groove that had formed with distorted contours in the longitudinal direction, crossing over the pinhole puncture. Scattered shallow pits were also found on the ID surface (Fig. 6.98).

Energy dispersive spectroscopy analysis on the outer surface revealed the presence of oxygen, sodium, aluminum, silicon, sulfur, calcium, potassium, and phosphorus. Because the outer surface was covered with refractory, the contaminants appeared to be from water that had leaked subsequent to the failure. Energy dispersive spectroscopy analysis on the inner surface showed the presence of oxygen, potassium, calcium, phosphorus, and zinc, which indicated occasional disturbances in the water chemistry. Energy dispersive spectroscopy analysis at the pit on the ID indicated the presence of oxygen, sodium, aluminum, silicon, sulfur, potassium, calcium, and iron. Energy dispersive spectroscopy analysis after metallography on the scale around the ID showed the presence of oxygen, silicon, and manganese, which pointed toward oxygen pitting damage with a concentration of alkali salts within the pits.

Microstructural examination revealed scattered scale patches and shallow pitting corrosion on the ID (Fig. 6.99a). The pits were filled with scales (Fig. 6.99b). The tendency for the pits on the ID was to grow deeper into the metal. The OD side and core microstructure were ferrite and pearlite. No significant degradation was observed in the microstructure.



(a)



(b)

Fig. 6.97 (a) Close-up view at the leakage location on OD surface with leakage in the form of a pinhole. (b) ID surface indicating fine pits as well as groove-like metal wastage

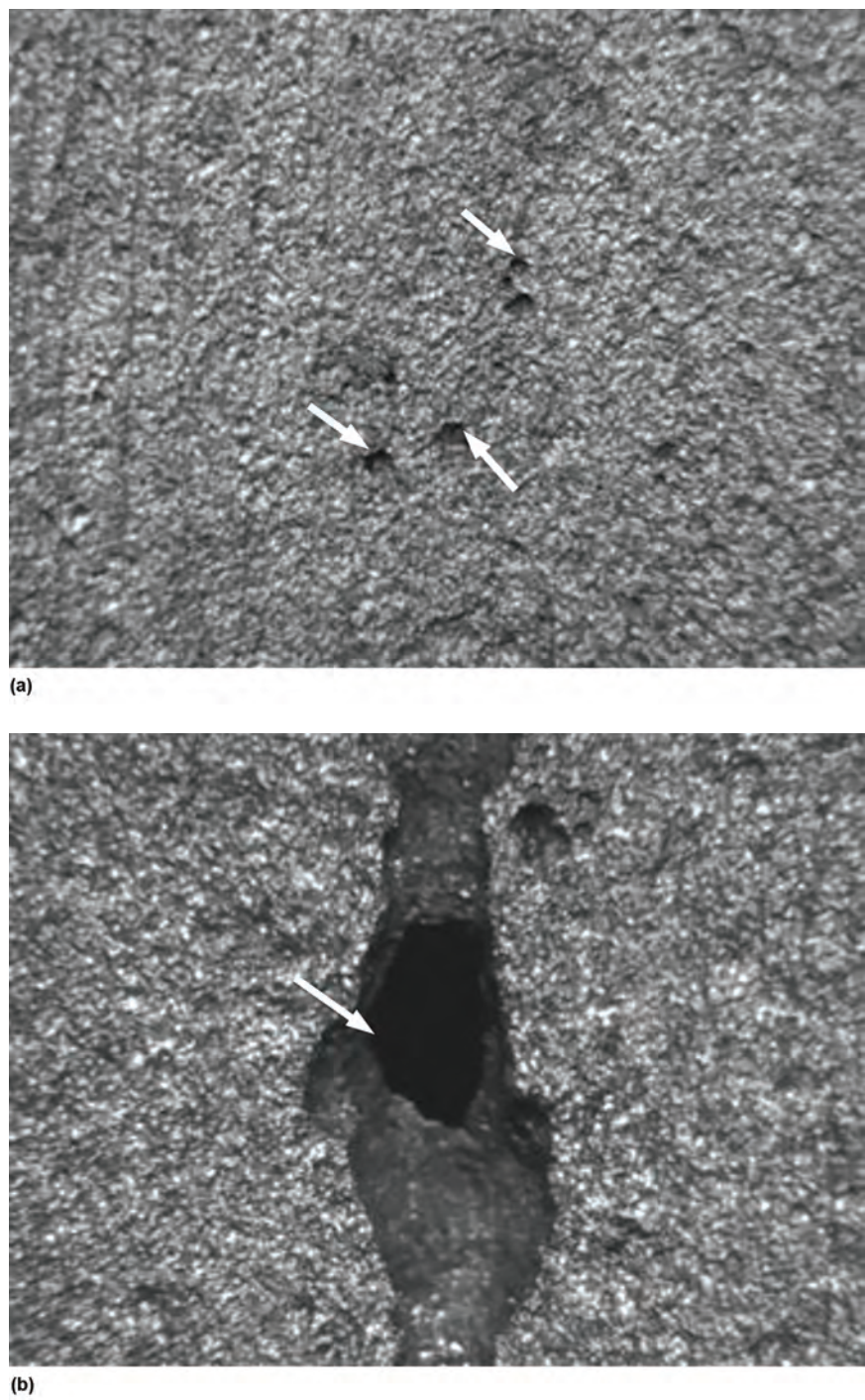
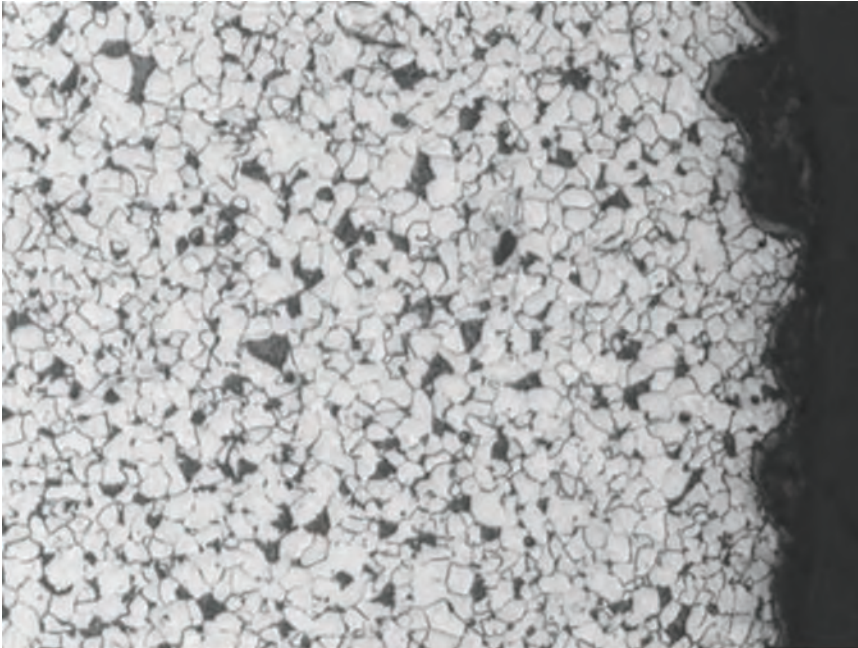
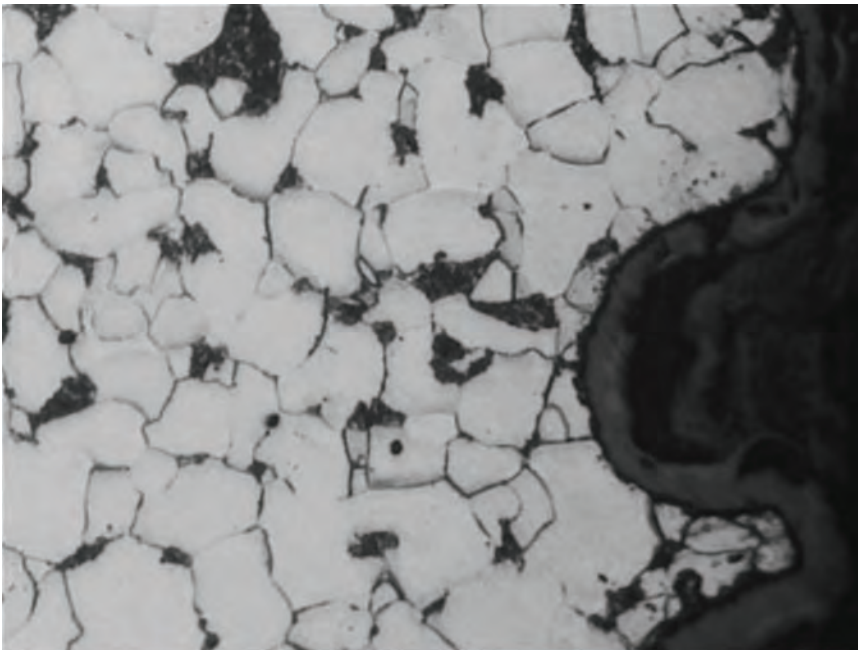


Fig. 6.98 Low-magnification views of ID surface showing (a) scattered shallow pits on the ID surface, 8×; (b) leakage location in the form of a pin-hole with a groove in longitudinal direction with distorted contours surrounding the pin-hole, 16×



(a)



(b)

Fig. 6.99 ID side of a failed waterwall tube showing pits and scale formation, (a) 100 $\times$, (b) 400 $\times$

The results of tensile testing and hardness measurement on the test sample appeared to be satisfactory.

Thus, the metallurgical characteristics of the waterwall tube in terms of the MOC, microstructure, and mechanical properties met the requirements of specification DIN 17175-79 Grade 15Mo3. The scattered pitting corrosion damage seen on the inner surface with a tendency for some of the pits to grow deeper appeared to be the origin of the failure. This type of damage was likely to initiate during idling periods when the boiler remained filled with stagnant water. This stagnant water condition must have initiated shallow pits due to the presence of dissolved oxygen. Since the BFW was subjected to coordinated phosphate treatment, the alkali ions would have entered into the pits during subsequent running of the boiler. Under prevailing pressure and temperature conditions within the tube, the shallow pits proved to be a conducive place for alkali salts to concentrate. There would have been a localized rise in pH levels within the pit, resulting in growth of the pit due to corrosion and in turn leakage of the tube.

Conclusions The failure of the waterwall tube due to leakage in the form of a pinhole puncture was attributed to growth of a pit at one particular location because of an alkali salt concentration that led to corrosion and metal wastage.

Stress-Corrosion Cracking

Stress-corrosion cracking (SCC) is defined as a process involving conjoint corrosion and straining of a metal due to residual or applied stresses. Boiler system waterwall tubes, superheater tubes, reheater tubes, and steam drums are prone to failure by SCC. Failure normally occurs where feedwater or condensate accumulates. The carbon steel and low-alloy steel tubes in a boiler generally fail by attack due to concentrated sodium hydroxide; this mechanism of damage is termed *caustic embrittlement*. Failure of stainless steel tubes is attributed to concentrated sodium hydroxide or chloride ions. Failure due to chloride ions is known as *chloride SCC*. Stress corrosion cracking is an insidious type of failure (i.e., the damage is not detectable on casual or routine inspection and often leads to a catastrophic failure, mainly to austenitic stainless steels).

Stress corrosion cracking is viewed as the result of a synergistic interaction between static tensile stress and a corrosive medium to which a metal is exposed (Ref 6.26). The tensile stress leading to SCC is either acting (i.e., applied stress, arising out of pressure exerted by the internal fluid) or residual stress developed as a result of manufacturing processes such as machining, deformation, heat treatment, internal precipitation, and welding.

Failure due to SCC occurs when the material is susceptible to SCC, and when an aggressive environment and sufficient tensile stress (either acting or residual) are present simultaneously. Not all environments cause SCC cracking of any particular alloy, but a specific alloy-environment combination leads to SCC.

Stress-corrosion cracks may be transgranular (i.e., the cracks pass or cut through the grains) or intergranular (i.e., the cracks propagate along the grain boundaries), depending on the alloy and the environment (Ref 6.27), but are usually extensively branched, leading to the development of secondary cracks as the cracking progresses, as shown in Fig. 6.100. In the case of carbon steel tubes, stress corrosion may result in either intercrystalline or transgranular cracking. Tubes that have failed through SCC exhibit a thick-walled fracture irrespective of the inherent ductility of the material and are characterized by the presence of tight cracks (Ref 6.28). Sometimes both intergranular and transgranular cracks are simultaneously observed, and such cases are known as a mixed mode of cracking.

The tendency toward SCC can be minimized by reducing residual stresses using appropriate heat treatments, or by reducing the severity of the corrosiveness of the environment. Avoiding the formation of internal deposits and high-heat-flux areas, avoiding departure from nucleate boiling, preventing chloride or caustic contamination of attemperation water, and the use of inhibitors are some of the ways and means to protect materials from failure due to SCC.

Case Study 23—Failure Investigation of Superheater Tubes of Incinerator Boilers

Background Details Superheater tubes connecting to a train of incinerator boilers failed after about 2 years of operation. During shutdown, while water filling was taking place, some finned tubes in the top and bottom row were found to be leaking. The MOC of the tube was SA 312 TP304 steel.

Investigation and Findings Visual examination indicated a through and through transverse crack with a wide opening on the OD surface in between the fins (Fig. 6.101a). Scales and deposits were spread on the OD surface, as well as between the fins. The inner surface was covered with black adherent scale and showed branched-type cracking on the ID surface (Fig. 6.101b).

Low-magnification examination of the crack surface indicated that the fracture surface had a relatively brittle nature with a coarse texture (Fig. 6.102).

Macrofractography was conducted using SEM on the crack surface to understand more details about the underlying failure mechanism (Fig. 6.103).

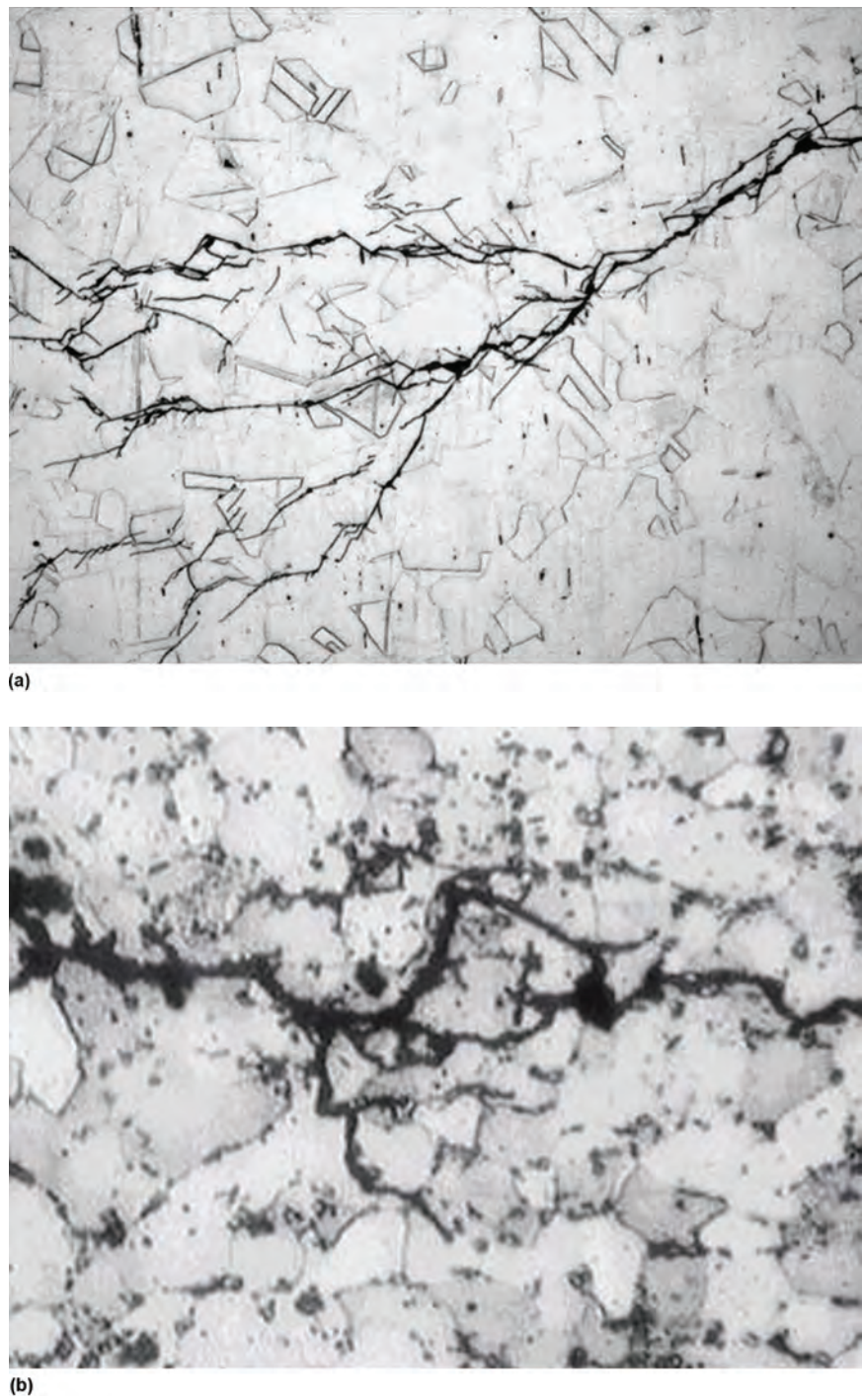
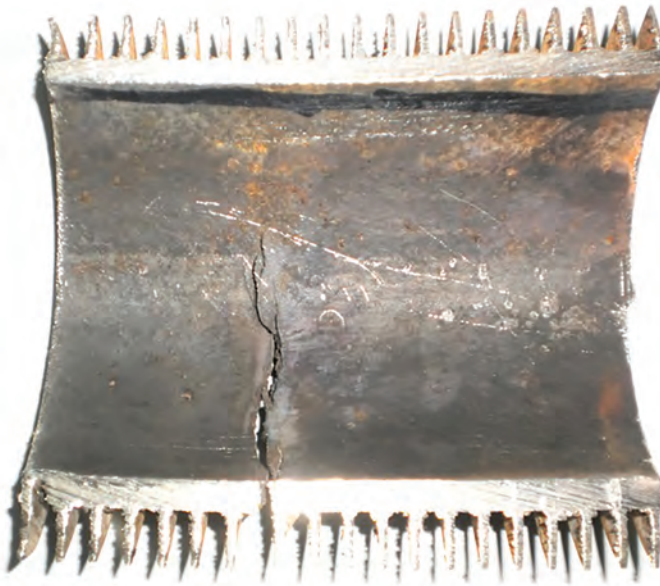


Fig. 6.100 Cracking due to SCC, (a) transgranular, 200×; (b) intergranular, 300×



(a)



(b)

Fig. 6.101 (a) Close-up view of OD surface of the tube at the failure location revealing a transverse crack with wide opening seen between the fins. Corrosion asperities were seen on tube surface and in between the fins. (b) Close-up view at the crack tip on ID surface with a branched-type crack

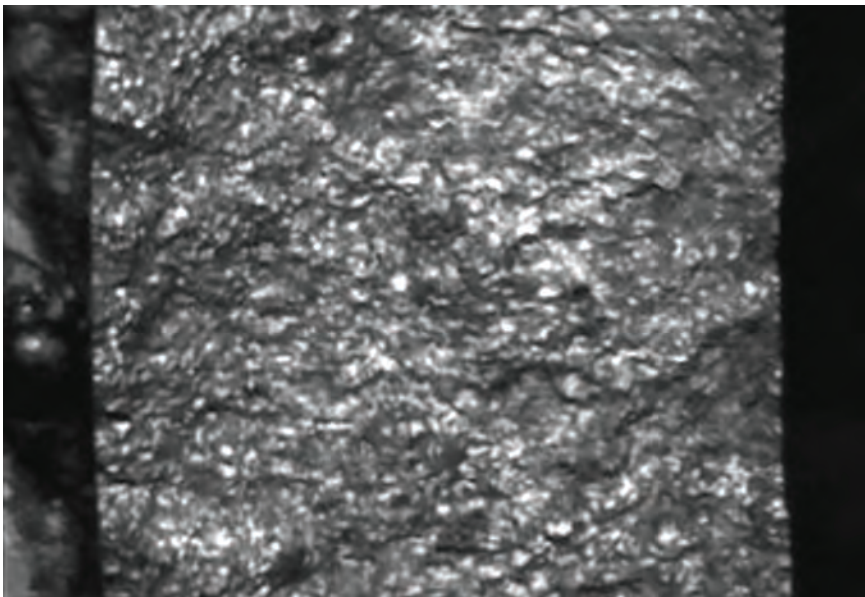


Fig. 6.102 Low-magnification view of fracture surface showing brittle and coarse texture, 16×

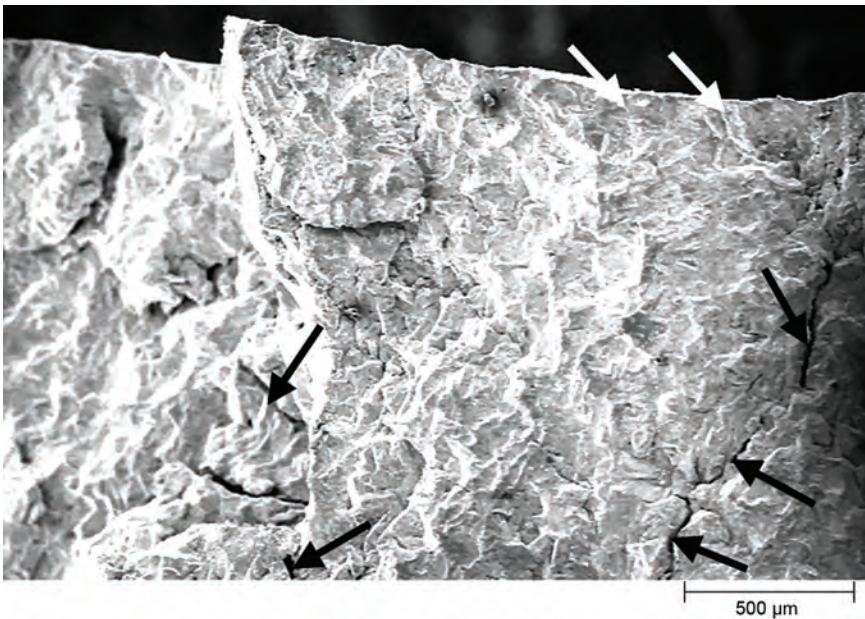


Fig. 6.103 SEM macrograph at ID edge showing multiple crack initiation points (white arrows) and auxiliary cracking on crack fracture surface (black arrows). The overall fracture surface was relatively brittle and covered with corrosion products/scales, 50×

Table 6.12 EDS analysis at different locations of tube sample

Elements	Surface amount, wt.%			Elements	Surface amount, wt.%		
	Crack	ID	Fin		Crack	ID	Fin
Oxygen	31.56	30.81	35.34	Chlorine (Chloride)	0.44	0.61	1.39
Sodium	1.99	0.86	1.55	Potassium	0.57	0.29	1.43
Magnesium	1.85	0.68	0.55	Calcium	0.57	0.41	1.19
Aluminum	1.42	0.54	1.10	Chromium	10.13	4.10	12.37
Silicon	1.81	0.91	0.52	Manganese	1.61	4.07	1.16
Phosphorus	0.38	0.30	1.84	Iron	42.66	53.32	36.08
Sulfur	0.88	0.70	2.57	Nickel	4.13	2.40	2.90

In order to assess the nature of the corrosion damage, EDS analysis was carried out at various locations on the failed tube sample (Table 6.12). The EDS analyses showed the presence of elements including oxygen, sodium, magnesium, sulfur, chlorine (as chloride), potassium, and calcium on the crack surface, the ID surface, and the black portion of the fin.

Optical microscopic examination of the failed sample indicated that the general microstructure of the tube comprised fine-grained slightly worked austenite with the presence of strain-induced martensite (SIM) (Fig. 6.104a). The presence of SIM, especially at the surface layers, confirmed the effect of work hardening and the presence of internal stresses of tensile nature. Severe transgranular stress corrosion cracking (TGSCC) was noticed on the ID surface (Fig. 6.104b). The fin microstructure was fine-grained slightly worked austenite with twins.

Microhardness measurements showed higher values at the OD and ID edges due to work hardening and the formation of SIM.

Critical analysis of the findings of this investigation led to the conclusion that all the amenable conditions that are conducive to promote TGSCC were prevalent here, including:

- Corrosive atmosphere with moisture and chloride ions
- Presence of internal tensile stresses confirmed by SIM in the microstructure
- Operating stresses
- Susceptible material, SS 304

Possible contamination from the BFW allowed wet steam and chloride into the superheater section and allowed TGSCC to occur.

Conclusions The failure of superheater tubes was due to chloride-induced TGSCC.

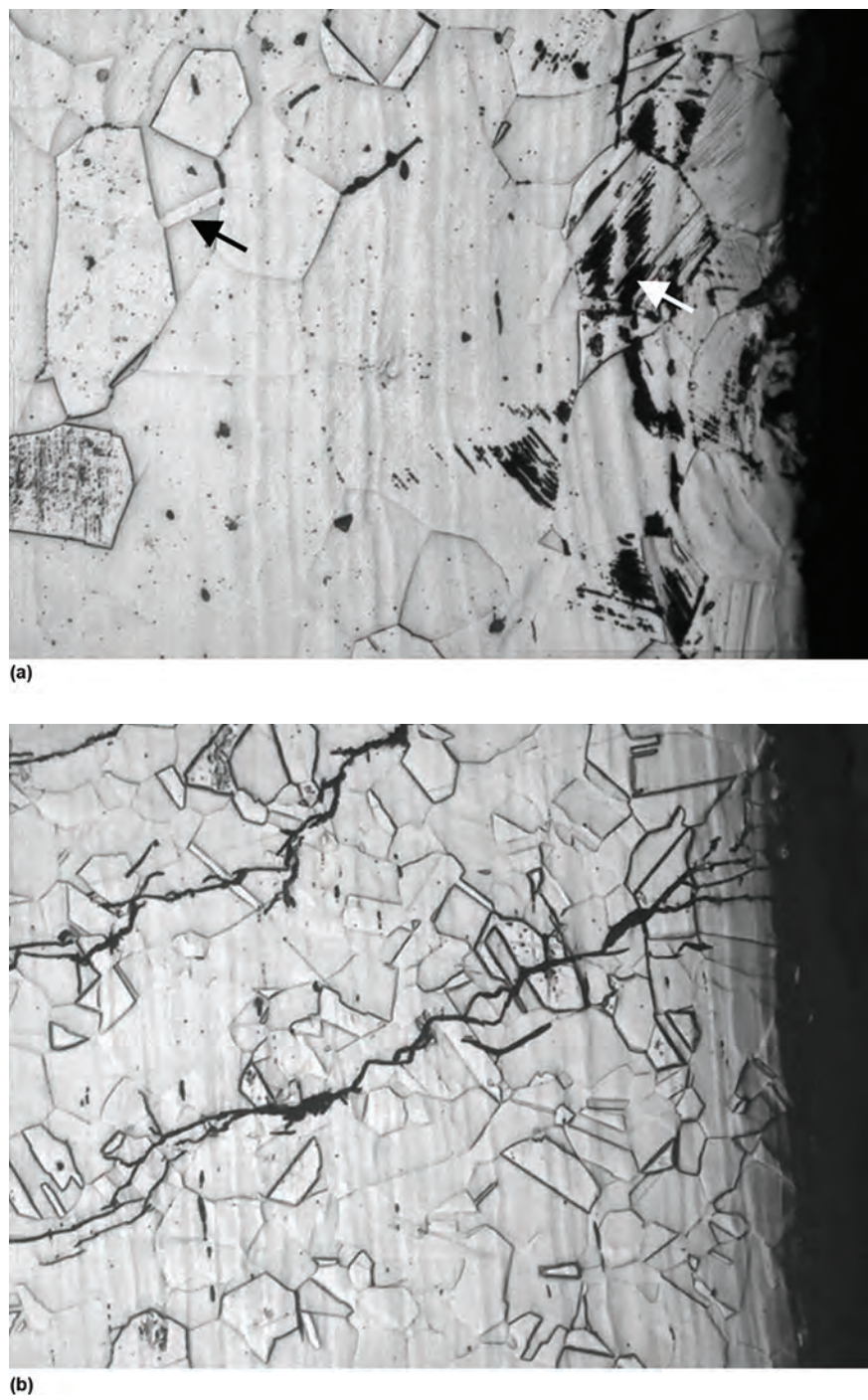


Fig. 6.104 (a) Tube microstructure of worked austenite grains with twins and stain-induced martensite, 200 $\times$. (b) ID etched view having network of transgranular stress-corrosion cracks in the microstructure of slightly worked austenite grains with twins, 100 $\times$

Caustic Stress-Corrosion Cracking or Caustic Embrittlement

Caustic embrittlement is a specific form of SCC. Different areas of boilers such as bends, rivets, and joints, including the boiler tubes, are susceptible to caustic embrittlement. The caustic embrittlement of boiler tubes is observed at locations where tubes are rolled into sheets, drums, or headers (Ref 6.29). It is also known as caustic cracking (Fig. 6.105).

Caustic embrittlement occurs in boilers where caustic substances such as sodium and potassium hydroxide accumulate, making those parts of the boiler brittle to the extent that, ultimately, cracking takes place. This cracking is of an intercrystalline nature and often occurs quite fast and is undetectable, leading to sudden failure. Caustic embrittlement occurs in stressed areas of the boiler. Carbon steel tubes are vulnerable to caustic embrittlement above 65 °C (150 °F) and in stainless steels above 120 °C (250 °F).

Alkali is added to the BFW to maintain its pH, protecting the piping and equipment from corrosion. This is ensured by adding a sodium carbonate softening treatment to BFW. At times, some sodium carbonate is left behind in the water as residual sodium carbonate. When the water evaporates, the local concentration of sodium carbonate in the boiler increases. This is revealed in the form of white caustic deposits. These caustic deposits on hydrolysis give rise to the formation of sodium hydroxide per the following reaction:

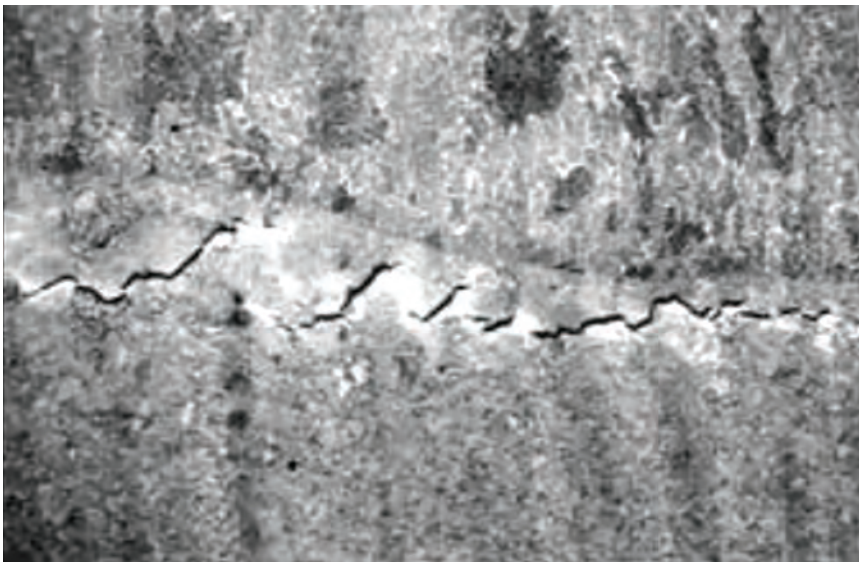
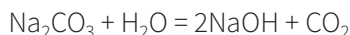


Fig. 6.105 Boiler tube showing cracking due to caustic embrittlement



The sodium hydroxide so formed raises the pH of the water and makes the water alkaline. The alkaline water in turn enters the fine hairline cracks present on the inner walls of the boiler tubes and reacts with the surrounding metal to dissolve the iron to form sodium ferroate per the following reactions:



The excess alkali dissolves the protective magnetite layer, forming sodium hypoferroate and sodium ferroate, both of which are soluble in hot concentrated caustic soda and thus give rise to damage due to caustic embrittlement (Ref 6.19).

Treatment of BFW with sodium phosphate instead of sodium carbonate helps in overcoming the caustic embrittlement problem. Another way is to block hairline cracks in order to prevent the infiltration of sodium hydroxide into the tube. The use of lignin, tannin, or sodium sulfate that block and seal the hairline cracks is advocated for this purpose.

Stress-Assisted Corrosion

Stress-assisted corrosion (SAC), also known as stress-enhanced corrosion or stress-influenced corrosion, is a type of corrosion that occurs due to high static tensile stresses. This type of failure is normally found in those areas of waterwall tubes where the stress levels are high, for example at locations where tubes have been rolled into the drum walls or regions of the tubes with externally welded attachments. Stress-assisted corrosion can take place in all areas of a boiler including economizers, superheaters, and reheaters. The cracks, once initiated, are more likely to propagate during periods of high stress such as start-up or shutdown, rather than during normal operation. Figure 6.106(a) and (b) shows unetched and etched views of the blunt and bulbous nature of the crack in an SAC failure of a flue gas cooler evaporator tube, while Fig. 6.106(c) shows the macroetched view of the transverse section of the tube indicating SAC cracks. Important factors governing SAC are the metallurgy of the material, its stress condition, and the chemistry of the boiler water.

The SAC penetrations were located within about 1.0 cm (0.40 in.) of an attachment weld location. Besides this, there was a decarburized layer of approximately 200–300 μm depth on the ID side of the tube, in which ferrite grains grew significantly larger than the nominal size.

A close resemblance prevails between SAC and corrosion fatigue in terms of their underlying mechanism and causes of failure. Yet there are

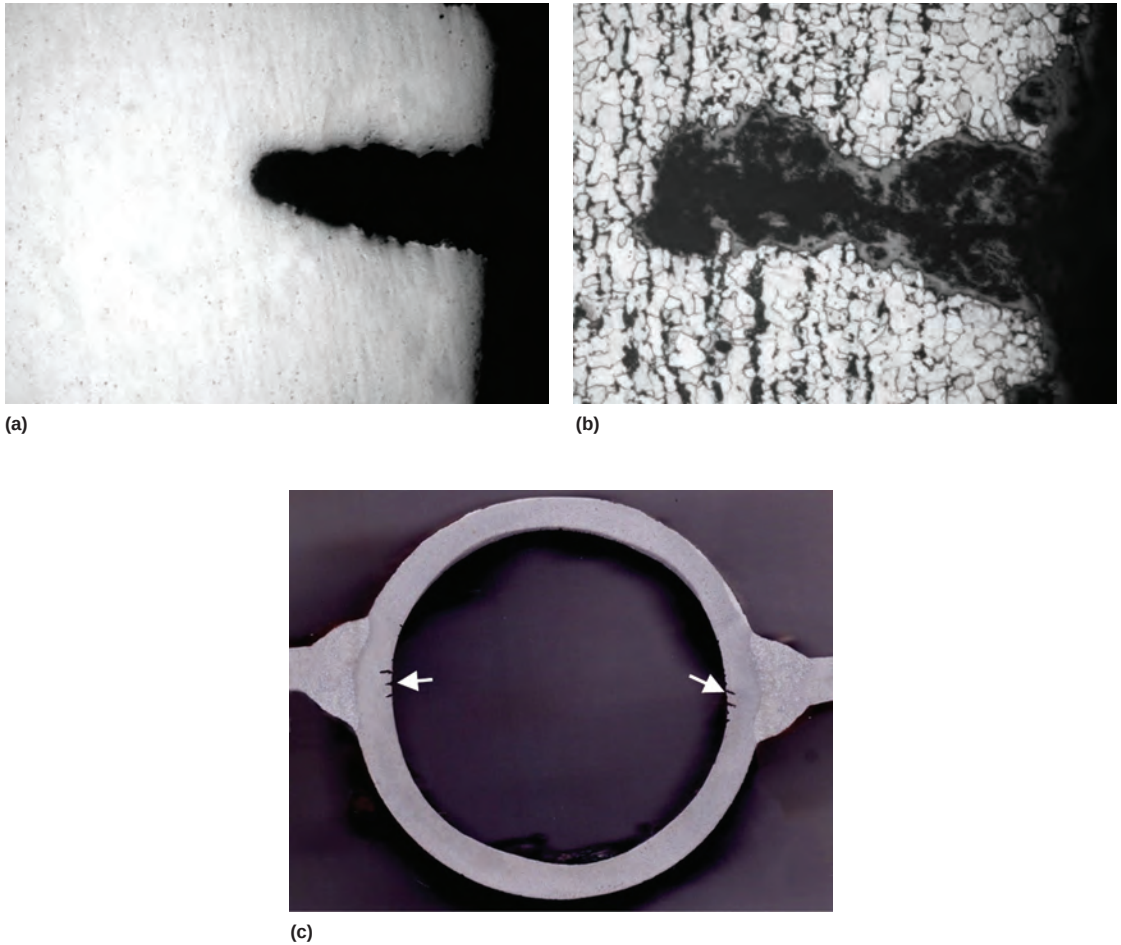


Fig. 6.106 Blunt and bulbous nature of a crack in SAC, (a) unetched, 100 $\times$; (b) etched, 200 $\times$. (c) Macroetched view of a tube cross section showing cracks

certain differences as well. For instance, SAC cracks are blunt cracks with rounded tips, whereas corrosion fatigue cracks have sharp tips (Ref 6.30).

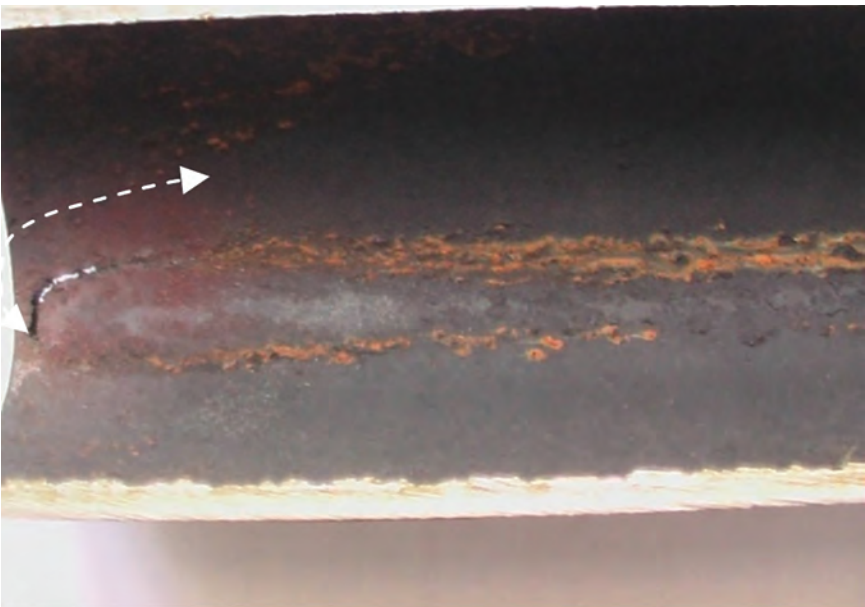
Case Study 24—Failure Investigation of a Waterwall Tube

Background Details Failure in the form of a through and through leak at the fin weld was reported in the waterwall tube of a boiler after 20 years of service. The MOC of the tube was per ASTM A 178 Grade A. The tube dimensions were 60.0 mm (2.4 in.) OD and 4.0 mm (0.16 in.) wall thickness.

Investigation and Findings The weld area of the outer surface was surrounded by a thick brownish porous scale with scattered white scale patches (Fig. 6.107a). The inner surface of the tube showed corrosion with a brownish scale in the form of longitudinal parallel lines. A distinct crack was noticed at the fin plate weld toe and fillet weld end (Fig. 6.107b).



(a)

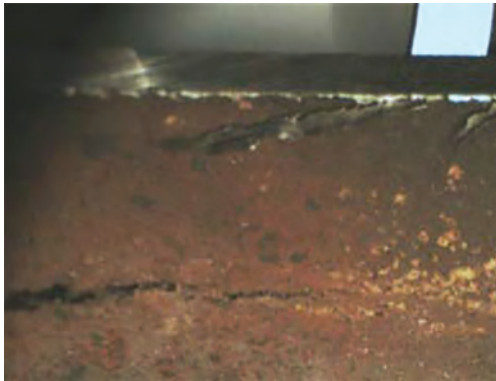


(b)

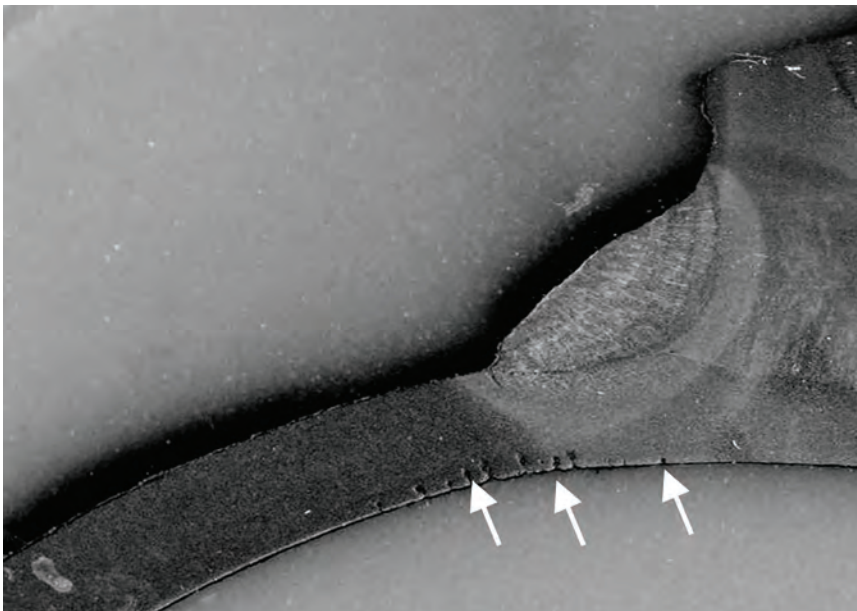
Fig. 6.107 (a) Outer surface of a tube showing weld joint. (b) Close-up view at the leakage location on inner surface indicating a distinct crack

Energy dispersive spectroscopy analysis at the crack tip on the inner surface showed the presence of elements including chlorine (as chloride), in addition to iron and oxygen as major constituents, along with traces of other elements (Table 6.13).

Macrostructural examination at the weld joint revealed the presence of multiple pits and probable crack initiation locations on the inner surface, underneath the fillet weld (Fig. 6.108). Besides this, the inner edge

Table 6.13 EDS analysis on inner surface at crack tip

Element	Surface amount, wt.%	Element	Surface amount, wt.%
Iron	65.65	Chlorine (Chloride)	0.95
Oxygen	30.13	Magnesium	0.35
Nickel	0.79	Cobalt	0.12
Calcium	0.75	Sulfur	0.74
Aluminum	0.52		

**Fig. 6.108** Macrostructure showing a number of pit-like locations on inner surface of a tube

between two fillet welds showed a heavily heat-affected area in comparison with the parent metal.

The tube was subjected to microstructural examination at the weld and at a different location. The parent metal microstructure at the different location comprised ferrite and pearlite. Figure 6.109(a) shows the inner-edge microstructure near the weld location, which comprised ferrite and pearlite with pitting damage and cracks. Microstructural examination also revealed that the major crack that caused the leakage had initiated from the ID surface of the tube. A transgranular crack initiating from a corrosion pit on the ID surface was seen in the microstructure (Fig. 6.109a). The weld microstructure was that of carbides in ferrite dendrites, whereas the heat-affected zone microstructure comprised ferrite and pearlite surrounded by proeutectoid ferrite (Fig. 6.109b).

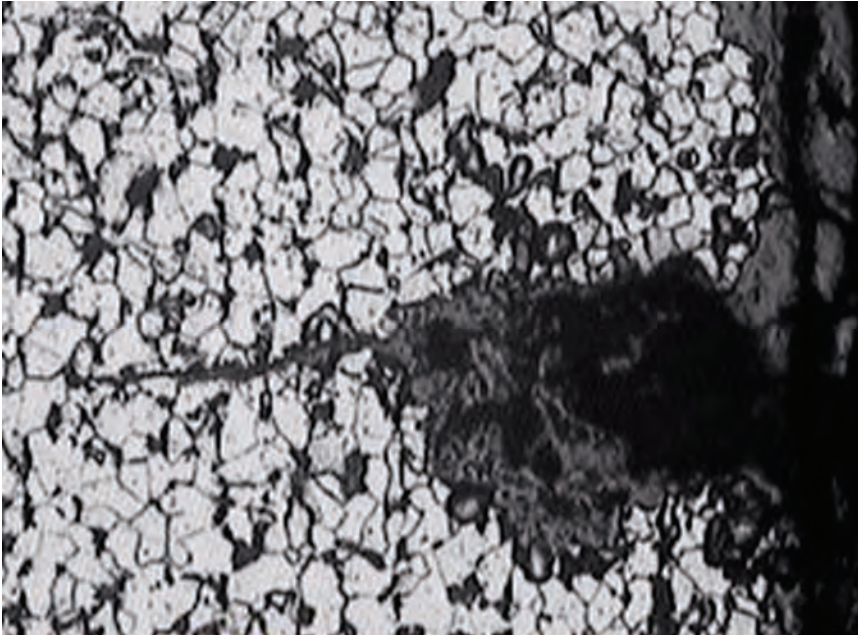
The failure initiated from scattered shallow pits and corrosion cavities initiated on the ID surface. Such pits develop when the oxygen levels in water are higher (as indicated by the results of EDS analysis) either because of poor water treatment or normal water becoming contaminated with treated water. Based on the evidence of the failed sample and EDS analysis, water contamination leading to corrosion was confirmed. Corrosion can also occur due to intermediate water chemistry disturbances. A weld region is an area of high static tensile stresses. Residual stresses on account of welding coupled with corrosion by way of pitting on the ID surface resulted in through and through propagation of one such crack, finally leading to leakage and failure through the SAC mode.

Conclusions The failure of the waterwall tube, especially at welded joints, was attributed to SAC.

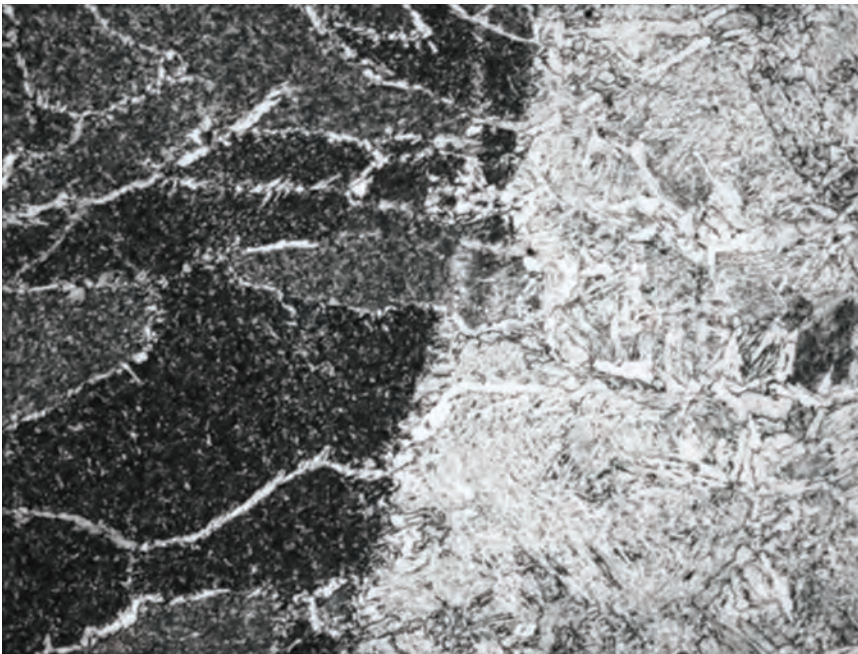
Corrosion by Chelating Agents

Chemical treatment of water inside the boiler is essential whether or not the water has been pretreated. Chelant programs have been found to offer superior cleanliness over phosphate programs; however, there is a potential risk of chelant corrosion, if the feedwater is overfed with the chelating agent. Chelating agents or complexing agents such as nitrilo-triacetic acid (NTA) and ethylene diamine tetra-acetic acid (EDTA) have been used in chemical treatment programs for BFW. These chemicals are added to form complexes with calcium, magnesium, or other metal ions that enter the boiler as a constituent of BFW. Under normal circumstances, such complexing agents do not pose any problem by way of corrosion; however, in concentrated amounts they do attack the protective magnetite layer, leading to corrosion. Once the protective magnetite layer is damaged, direct contact of the feedwater (containing such complexing agents) with the underlying tube gives rise to corrosion.

Though the steam drum is the area most vulnerable to corrosion due to chelating complexes, other locations, such as regions of high-heat-flux



(a)



(b)

Fig. 6.109 (a) Transgranular crack initiating from a pit on ID surface, 200×.
(b) Heat-affected zone comprising fine dendritic structure of ferrite and carbides surrounded by grain boundary primary ferrite, 200×

areas in water-cooled tubes, feed-water distribution lines, and economizer tubes, are also prone to attack.

Conditions favoring chelant corrosion of boiler tubes include high concentrations or overdosing of chelating agent, high fluid velocity and turbulence, departure from nucleate boiling, and high levels of dissolved oxygen.

The general appearance of surface damage due to chelant corrosion is similar to FAC and ID side erosion due to high-velocity steam or water.

Fire-Side Corrosion

The structural integrity of boiler tubes is governed by a protective magnetite (oxide) layer, and any damage to this layer due to conditions leading to corrosion or erosion ultimately results in tube failure. The principal types of fire-side corrosion in boiler tubes are: (i) waterwall corrosion, (ii) fuel ash corrosion such as corrosion due to coal ash and oil ash, (iii) hot corrosion, (iv) acid dew point corrosion, (v) stress corrosion cracking, and (vi) polythionic acid corrosion (Ref 6.1, 6.28).

Waterwall Corrosion or Reduced Atmosphere Corrosion

Fire-side corrosion of waterwall tubes takes place because of incomplete combustion of fuel under reducing conditions and hence it is also known as *reduced atmosphere corrosion*. It leads to substantial loss of wall thickness of the tubes. The main cause of fire-side waterwall corrosion is an inadequate amount of oxygen in the burner zone. Under such circumstances, volatile compounds of sulfur, namely sodium and potassium pyrosulfates ($\text{Na}_2\text{S}_2\text{O}_7$ and $\text{K}_2\text{S}_2\text{O}_7$), with a low melting point (450°C , or 840°F), form. These compounds volatilize at high temperature and condense as a liquid on the relatively cooler surface of the waterwall tubes (Ref 6.31). The reaction between pyrosulfate compounds and the protective magnetite layer damages the protective layer and finally results in a loss of underlying metal.

Typical characteristics of fire-side waterwall corrosion include loss of metal due to corrosion along the crown of the tube; the damage extends along several adjacent tubes. The corroded area is normally covered with a thick layer of corrosion products consisting of iron oxide and iron sulfide. The damage is in the form of circumferential grooving.

Fuel Ash Corrosion

In a thermal power plant, the residue arising out of the combustion of solid or liquid fuel is normally termed *ash*. Ash formed through combustion of

coal, named *coal ash*, contains elements including iron, aluminum, silicon, and calcium along with magnesium, sodium, and potassium. On the other hand, the typical ingredients of *oil ash* formed in oil-fired boilers include elements such as sulfur, sodium, and vanadium.

During fire-side corrosion, a low-melting liquid eutectic phase forms in the ash deposits, which attack the tube surface, leading to local dissolution of the protective oxide (magnetite) layer from the tube surface and subsequent corrosion of the underlying metal (Ref 6.1). The exact constitution of the eutectic liquid phase formed depends on the nature of the fuel used. For example, the liquid phase in the case of coal-fired boilers comprises a mixture of volatile sulfur compounds such as sodium and potassium iron trisulfate, $\text{Na}_3\text{Fe}(\text{SO}_4)_3$ and $\text{K}_3\text{Fe}(\text{SO}_4)_3$, whereas that for oil-fired boilers is a mixture of vanadium pentoxide (V_2O_5), along with sodium oxide (Na_2O) or sodium sulfate (Na_2SO_4). In either case, the liquid phase formed has a low melting point, typically below 500 °C (930 °F). Fire-side corrosion due to a low-melting phase formed in coal ash is termed *coal-ash corrosion*, and that in an oil-fired boiler is *oil-ash corrosion*.

Coal-Ash Corrosion

The high-temperature parts of a boiler such as the superheater and reheater tubes are susceptible to corrosion due to coal ash or oil ash depending on the fuel used. Under high-temperature conditions, a reaction between the low-melting eutectic compounds of sulfur and the tube surface leads to corrosion of superheater and reheater tubes.

During the combustion of coal, minerals in the coal are exposed to high temperatures, which causes the release of volatile alkali compounds and sulfur oxides. In coal-ash corrosion, the deposition of fly ash occurs on the hot surfaces (with operating temperatures ranging from 540 to 700 °C, or 1005 to 1290 °F) of the superheater and reheater tubes. The deposited fly ash may be loose powder or it can be in the form of a sintered or slag-type mass. In turn, the volatile alkali and sulfur compounds condense on these fly ash particles, or sintered mass, and react with it to form complex alkali sulfates, such as $\text{KAl}(\text{SO}_4)_2$, $\text{Na}_3\text{Fe}(\text{SO}_4)_3$, and $\text{K}_3\text{Fe}(\text{SO}_4)_3$, at the interface between the metal and the deposit (Ref 6.1). The interaction of these compounds with the protective magnetite layer under reducing conditions dissolves the magnetite layer and results in corrosion of the tube surface. Eventually, tube wall thickness is reduced to such an extent that under high-metal-temperature conditions, it can no longer withstand the pressure within the tube, and the tube ruptures.

Coal-ash corrosion is promoted in the case of coals that produce aggressive ash. The appearance of damage on account of coal-ash corrosion in coal-fired boilers is a series of grooves, popularly known as *alligator hide*.

Oil-Ash Corrosion

Oil-ash corrosion is the high-temperature liquid-phase corrosion phenomenon that takes place in the temperature range of 590 to 810 °C (1095 to 1490 °F), and hence it is restricted to the superheater and reheater sections of the boiler. The sulfur necessary for corrosion to occur is present in sufficient concentrations in fuel oils. The fuel oil used in oil-fired boilers contains vanadium and sodium, which oxidize as vanadium pentoxide (V_2O_5) and sodium oxide (Na_2O) and interact to form low-melting eutectic compounds called sodium vanadates. The resulting volatile oxides, namely vanadates ($nNa_2O \cdot V_2O_5$) and vanadyl vanadates ($nNa_2O \cdot V_2O_4 \cdot mV_2O_5$), are carried along with the flue gases and condense over the tube surface as liquid slag. These compounds have low melting temperatures (as low as 250 °C, or 480 °F) and they dissolve the protective magnetite layer, resulting in corrosion of the tube surfaces (Ref 6.1). Scale formation and wall thinning of low-alloy steel tubes due to oil-ash corrosion is displayed in Fig. 6.110. Oil-ash corrosion can be combated by addition of MgO , which forms a compound with V_2O_5 , magnesium vanadate ($3MgO \cdot V_2O_5$), which has a high melting point.

Case Study 25—Failure Investigation of Secondary Superheater Tube

Background Details A secondary superheater tube of a utility and off-site crude oil boiler had ruptured in a longitudinal direction after 5 years of service. The MOC of the tube was per SA 213 Grade T11, and the tube dimensions were 44.5 mm (1.75 in.) OD and 4.0 mm (0.15 in.) wall thickness.

Investigation and Findings Visual examination revealed a burst opening at the failure location. The opening contours had extended as longitudinal cracks with a wide opening and had subsequently propagated in the transverse direction (Fig. 6.111a). The outer surface had a thick adherent scale that had peeled off surrounding the failure contours. The inner surface also had a thick adherent scale that was black in color. Transverse cross sections of the tube at different locations indicated wall thinning on the outer surface, which was significant at the failure location. Figure 6.111(b) shows a black adherent scale on the inner surface.

The failed sample was subjected to SEM to study the mechanism of failure. The rupture lip surface exhibited a ductile mode fracture (Fig. 6.112).

Energy dispersive spectroscopy analysis on the outer surface showed the presence of oxygen, sodium, magnesium, aluminum, silicon, sulfur, chlorine, potassium, calcium, and iron, whereas the inner surface showed oxygen, magnesium, aluminum, silicon, phosphorus, sulfur, calcium, iron, and copper (in a relatively small quantity). Significant amounts of sulfur and calcium were present on the OD surface. Table 6.14 gives the results of the EDS analysis on the OD and ID surfaces.



(a)

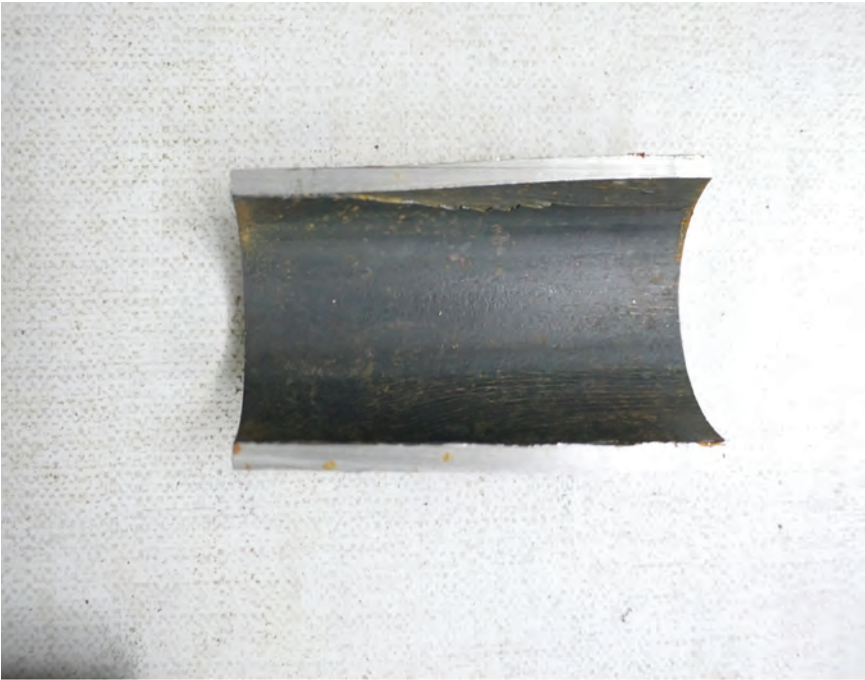


(b)

Fig. 6.110 Oil-ash corrosion in low-alloy steel tube: (a) scale formation, (b) wall thinning



(a)



(b)

Fig. 6.111 (a) Failed tube sample in as-received condition showing presence of yellowish green deposit on external surface. The failure had occurred with rupture and extended on both sides. (b) ID surface view showing black adherent scale

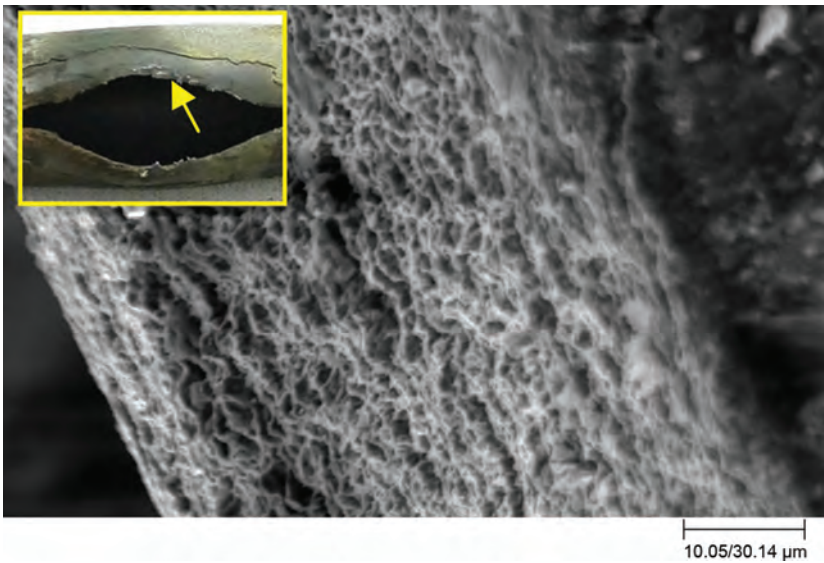
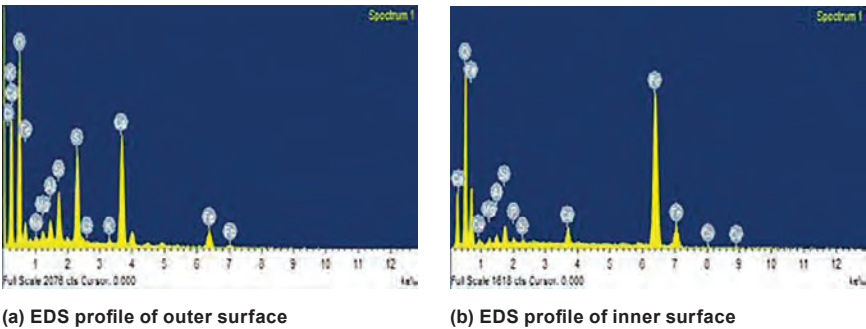


Fig. 6.112 SEM image of rupture lip surface, 1000×

Table 6.14 EDS analysis of scale on outer and inner surface of the tube



Element	Surface amount, wt. %	
	Outer	Inner
Oxygen	25.39	16.46
Sodium	0.59	0.97
Magnesium	0.37	0.56
Aluminum	0.72	0.82
Silicon	0.60	0.97
Phosphorus	0.77	...
Sulfur	11.11	0.49

Element	Surface amount, wt. %	
	Outer	Inner
Chlorine	0.60	...
Potassium	0.64	...
Calcium	0.35	0.19
Vanadium	29.78	0.73
Manganese	...	0.68
Iron	29.09	78.13

Microstructural examination at different locations revealed that the structure comprised ferrite with globular carbides. Pearlite was degraded and almost absent (Fig. 6.113a). The outer surface facing the fire side had corrosion damage, forming shallow pits followed by intergranular corrosion (Fig. 6.113b). The outer surface was covered with a thick crust of scaling (350 μm thick), whereas the inner surface had adherent scaling with a scale thickness of 275 μm .

During the course of service, thick scales formed on both the inner and outer surfaces. The resultant effect of scale formation retarded heat transfer across the tube section. Strong evidence obtained in EDS analysis revealed the presence of sulfur and vanadium in large quantities on the outer surface, whose source was flue gases. The flue gases containing SO_x and V_2O_5 formed low-melting eutectic compounds called sodium vanadates at higher temperatures. When the tube skin temperature exceeded the melting point of these compounds, they became fluxed with the oxide film, leading to its removal by dissolution. With persistent removal of the scale from the outer surface on account of fluxing due to the presence of low-melting alkali compounds, there was gradual thinning of the tube. With increased temperature, the microstructure also started degrading where the pearlite had transformed to ferrite and globular carbides. This was evident in the microstructures of the outer surface and the core that indicated skin to temperature excursions in the range of 600 °C (1110 °F). The microstructural degradation of the material led to a reduction in the strength of the tube. With internal pressure, the reduced wall thickness could no longer sustain the prevailing hoop stresses and eventually ruptured the superheater tube in a ductile manner with localized bulging.

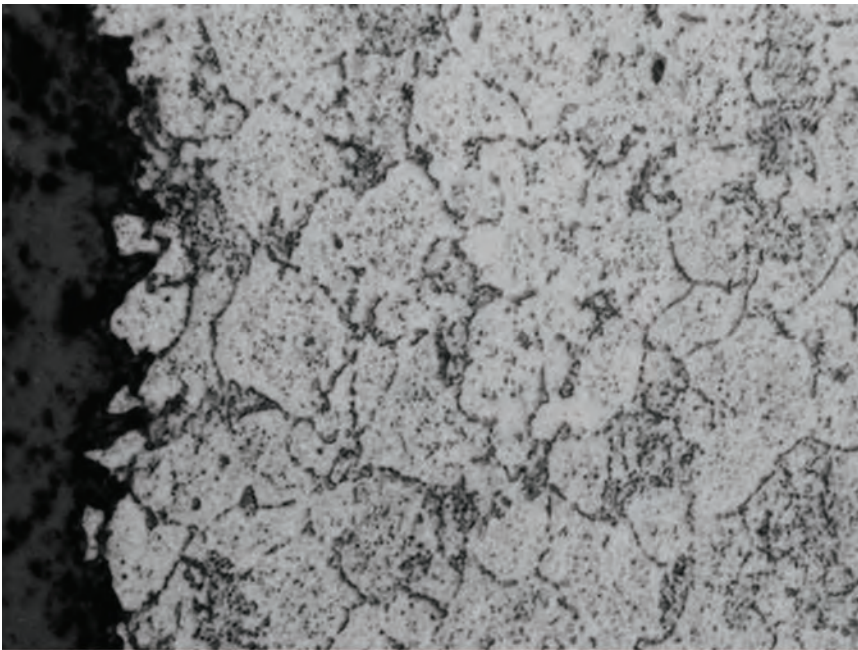
Conclusions The failure of the secondary superheater tube was due to sulfur and vanadium contamination in the flue gases, conjoined with increased scale thickness that promoted a gradual rise in skin temperature. The tube ruptured when the remaining section thickness could no longer hold the internal pressure. Thus, the tube failed on account of oil-ash corrosion.

Hot Corrosion

The coal used in coal-based thermal power plants contains varying amounts of sulfur and phosphorus as impurities in addition to noncombustible constituents such as ash. When coal is burned, sulfur released from the coal forms SO_2 with a small amount of SO_3 . Additionally, sodium and potassium from the mineral matter present in the coal are volatilized in the flame to form Na_2O and K_2O vapors. The gas phase reaction between Na_2O and SO_3 leads to the formation of Na_2SO_4 vapors, which then condense together with fly-ash particles on the pendant superheater and reheater tubes (i.e., in the hot section of the boiler). Similarly, in the case of oil-fired boilers, the combustion products of fuel oil contain sulfur,



(a)



(b)

Fig. 6.113 Optical micrographs showing (a) overall microstructure of a tube comprising of ferrite with globular carbides, 400 $\times$; and (b) outer edge microstructure of ferrite and globular carbides at grain boundaries with almost complete absence of pearlite, 400 $\times$. Intergranular corrosion at outer edge is also visible.

typically as Na_2SO_4 . Sulfate salts concentrate at the deposit or scale interface and become partially fused because they contain alkali metals such as sodium and potassium. The deposited salt forms a film on the surface of the tube, which destroys the protective magnetite layer of the tube surface by fluxing with it, leading to corrosion. This type of failure of boiler tubes, is called *hot corrosion* (Ref 6.32). Hot corrosion is thus a mode of damage in which metals and alloys experience accelerated oxidation or corrosion when their surfaces are coated by a thin film of fused salts (such as Na_2SO_4) in an oxidizing gas. Hot corrosion is generally initiated by sulfur.

Case Study 26—Failure Investigation of Waterwall Tube of a Waste Heat Boiler

Background Details Failure was noticed in the waterwall tube in a waste heat boiler of a fluidized catalytic cracker unit after about 8 years of service. The MOC of the tube was SA 210 Grade A1 HFS, and the tube dimensions were 50.8 mm (2 in.) OD and 4.06 mm (0.16 in.) thickness.

Investigation and Findings Visual examination of the failed sample indicated a fish-mouth opening at the failure location with thinned down contours and fine tips (Fig. 6.114a). Metal wastage surrounding the failure location was essentially from the outer surface, as shown in Fig. 6.114(b). The outer surface was dark brown in color. The inner surface of the tube had a thin adherent scale that was grayish black in color.

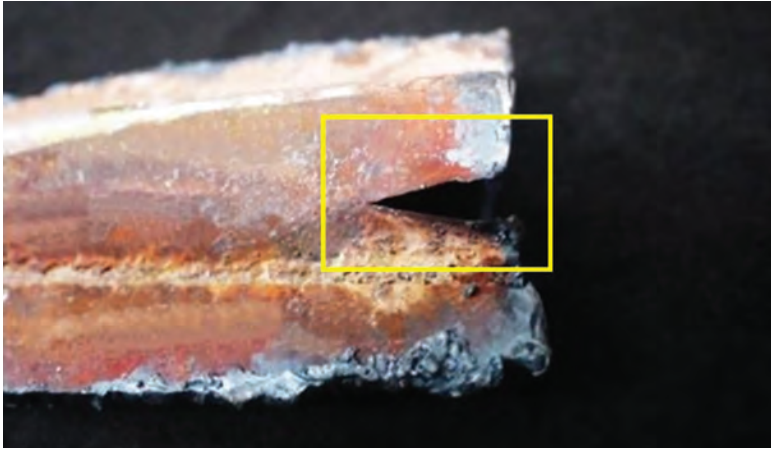
In order to determine the seamless nature of the tube, a sample was cut in a transverse direction followed by etching with 10% ammonium persulfate solution. Macrostructural examination confirmed the seamless nature of the tube, as shown in Fig. 6.115. It also showed metal wastage due to corrosion on the outer surface.

Scanning electron microscopy was conducted on the outer surface of the tube to examine the mode of failure at a micro level. Figure 6.116 shows the SEM image of the outer surface highlighting the onset of damage due to intergranular corrosion.

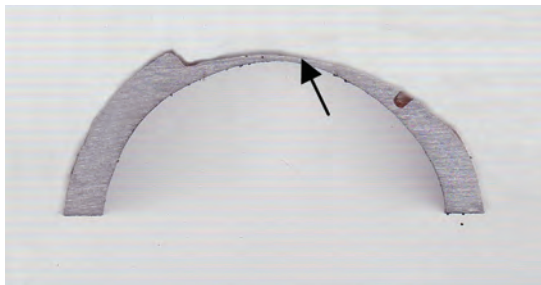
Energy dispersive spectroscopy analysis on the outer surface and the scale formed on the outer surface showed the presence of elements including oxygen, aluminum, silicon, sulfur, calcium, magnesium, phosphorus, and potassium. Energy dispersive spectroscopy analysis after metallography on the scale at the OD contours confirmed the presence of sulfur and phosphorus in the scale. Table 6.15 gives the results of the EDS analysis carried out on the outer surface of the tube and the outer surface scale.

The tube sample was subjected to microstructural examination at various locations. The overall microstructure of the tube was banded ferrite and pearlite. The onset of hot corrosion damage in the form of a grain boundary attack on the outer surface was seen, as displayed in Fig. 6.117.

Severe corrosion damage in the form of a grain boundary attack on the outer surface was also noticed during optical microscopy and SEM.



(a)



(b)

Fig. 6.114 (a) Close-up view at the failure location displaying fish-mouth-type rupture opening with fine tips and thinned rupture contours. (b) Transverse sectional view near failure location showing thinning because of metal wastage essentially from outer surface



Fig. 6.115 Transverse cross section of a tube in macroetched condition. It shows the seamless nature of the tube with metal wastage due to corrosion on outer surface.

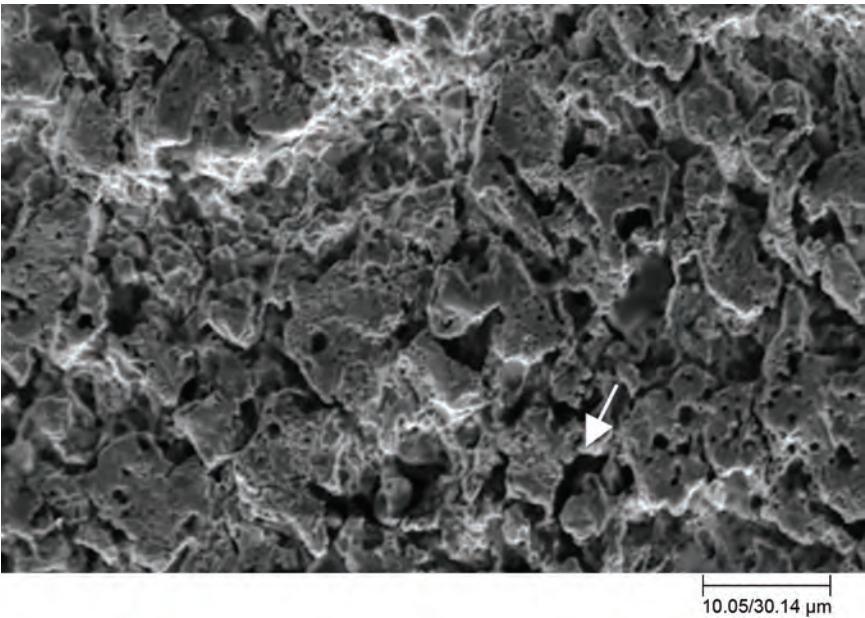
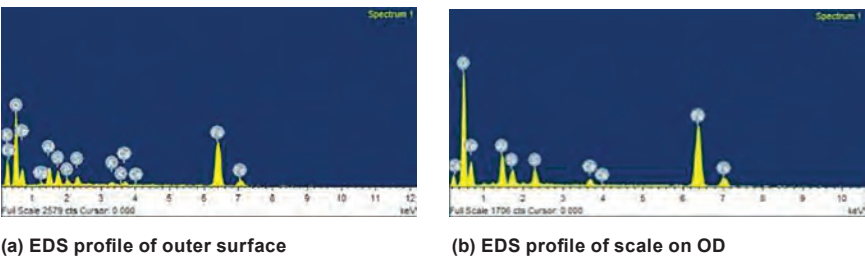
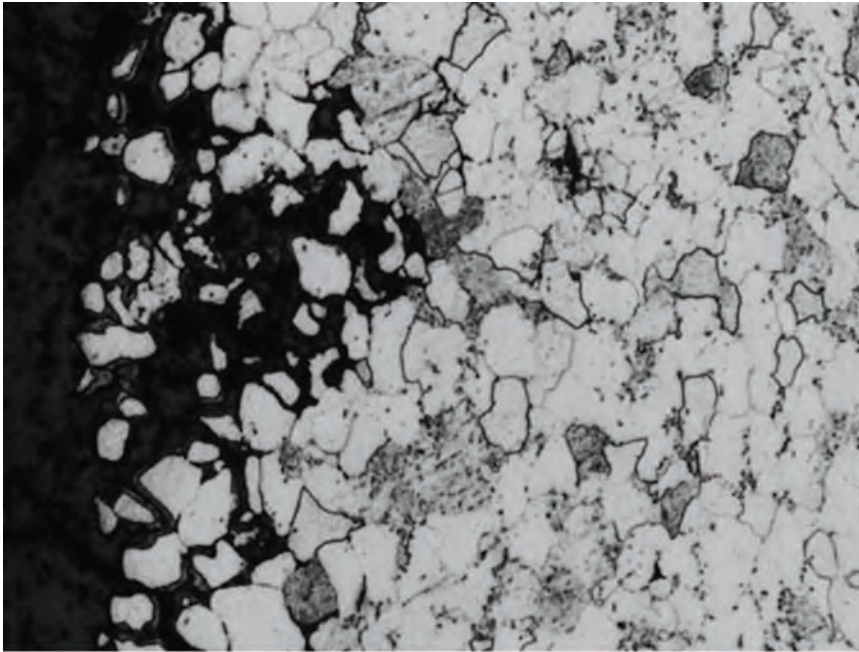


Fig. 6.116 SEM micrograph of outer surface of a tube sample showing onset of intergranular corrosion damage, 1000×

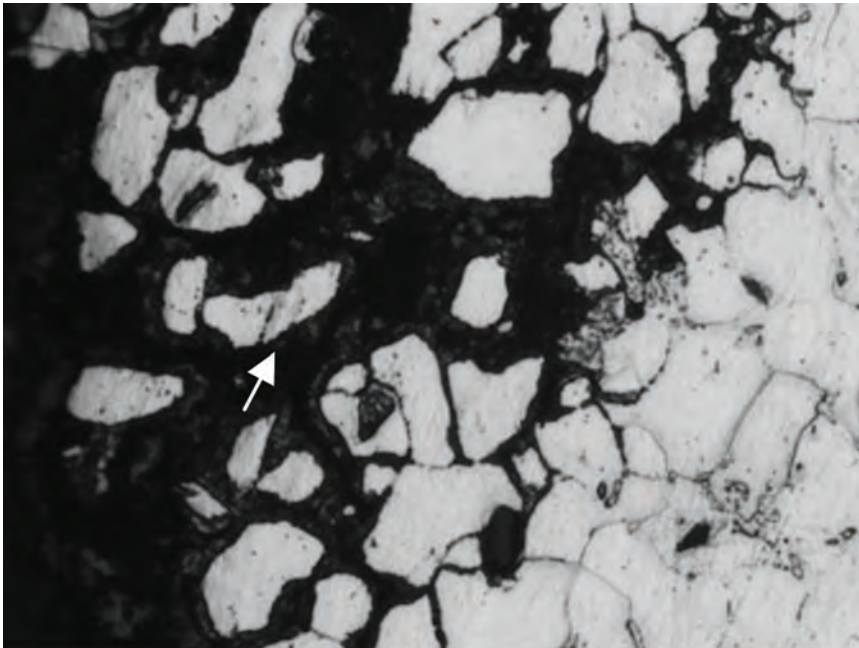
Table 6.15 EDS analysis of outer surface and scale on outer surface of the tube



Element	Surface amount, wt.%		Element	Surface amount, wt.%	
	Outer	Loose scale on OD		Outer	Loose scale on OD
Oxygen	15.30	17.89	Iron	69.01	67.65
Aluminum	5.24	6.62	Magnesium	0.76	...
Silicon	3.93	3.26	Phosphorus	1.61	...
Sulfur	2.55	3.66	Potassium	1.00	...
Calcium	0.61	0.93			



(a)



(b)

Fig. 6.117 Optical micrographs of outer surface showing hot corrosion in the form of grain boundary attack. Microstructure is essentially ferrite-pearlite with some surface decarburization, (a) and (b), 400×

The metal wastage was from the outer surface of the tube. Energy dispersive spectroscopy analysis indicated the presence of potassium and sulfur ions along with moisture-based contaminants. Thus, the metal wastage could be attributed to the formation of volatile sulfur compounds in the form of potassium pyrosulfate ($K_2S_2O_7$). Potassium pyrosulfate has a melting point as low as 427 °C (801 °F) along with high chemical activity. This formed molten slag over the tube surface that fluxed the protective magnetite scale promoting accelerated metal deterioration. The metal wastage resulted in a reduced cross section of the tube at the rupture location to the extent that it could not sustain the prevailing pressure conditions inside the tube, leading to failure.

Conclusions The failure of the waterwall tube was due to localized metal loss from the outer surface due to hot corrosion that had resulted in thinning. Subsequently, the tube failed in the form of rupture due to overstress.

Acid Dew-Point or Cold-End Corrosion

Acid dew-point corrosion or cold-end corrosion is quite common in boilers using fossil fuels for steam generation. It is one type of low-temperature corrosion. When sulfur-bearing fuel (all fossil fuels except natural gas) is burned, the sulfur oxidizes to form sulfur dioxide (SO_2). A small fraction of the total SO_2 formed (about 1 to 3%) further oxidizes to form sulfur trioxide (SO_3) in the presence of excess air. Vanadium pentoxide (V_2O_5) and ferric oxide (Fe_2O_3), commonly found in oil-fired boilers, act as catalysts for the oxidation of sulfur dioxide to sulfur trioxide. The sulfur trioxide so formed reacts with moisture or water vapors present in the flue gases to produce sulfuric acid (H_2SO_4) vapors per following reaction.



The interaction of sulfur dioxide with moisture forms sulfurous acid (H_2SO_3) as well, but as it is a much weaker acid, it does not pose any corrosion problems.

At certain temperatures, these vapors condense as a concentrated solution of sulfurous and sulfuric acid on cooler surfaces of the tubes, and hence this process is termed *cold-end corrosion*. Cold-end corrosion occurs in the form of a localized attack on the fire side of the tube.

The temperature at which the vapors of H_2SO_4 begin to condense is commonly known as the *acid dew point*. By definition, the acid dew point of a flue gas is the temperature, at a given pressure, at which any acid present in gaseous form in the flue gas will start to condense into its liquid form. The condensed form (i.e., liquid form) of sulfuric acid leads to corrosion and destruction of the surfaces over which it forms, which is known as *acid dew-point corrosion* or *cold-end corrosion* (Ref 6.28, 6.33).

The appearance of a surface that has undergone acid dew-point corrosion is usually smooth and uniform, and the metal loss that occurs is featureless to the extent that the overall appearance of the attacked surface is similar to that before the attack. However, the corroded surface is reddish brown in color, resembling that of rust (Fig. 6.118).

The dew point of sulfuric acid depends on the exact concentration of sulfur trioxide in the flue gases and decreases with an increasing concentration of sulfur trioxide, but is normally below 150 °C (between 120 and 150 °C, or 250 and 300 °F). The factors governing acid dew-point corrosion are the amount of sulfur and moisture in the flue gases, amount of excess air present, gas residence time, presence or absence of a catalyst, and surface temperature of the tube. The condensation of acid vapors occurs in areas where the surface temperature of the metal is lower than the dew point.

In thermal power plants, the economizer section and air preheater are the areas where such condensation occurs because the metal surface temperature in these areas is lower than the dew point of sulfuric acid. Additionally, for coal-fired boilers, condensation of sulfuric acid and water vapor can occur on fly ash particles if the flue gas temperature is below the acid dew point. In such a situation, the fly ash particles act as preferred sites for the condensation of both moisture and acid, especially during shutdown cycles.

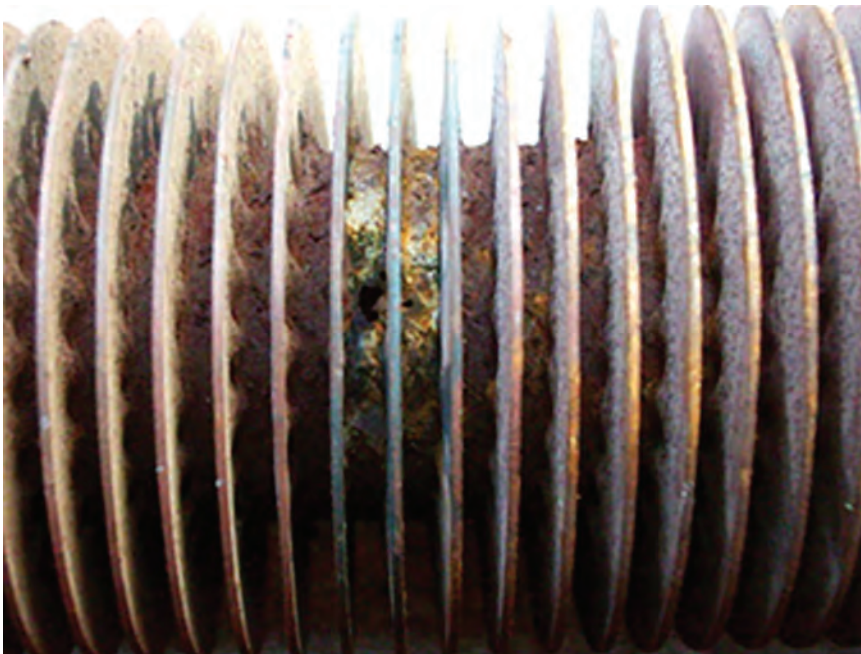


Fig. 6.118 Acid dew-point corrosion on external surface of an evaporator tube

Case Study 27—Failure Investigation of Economizer Tube of Heat Recovery Steam Generator

Background Details Leakage was noticed in the economizer tube of a boiler during a hydro test. The MOC of the tube was SA 210 Grade A1 steel with dimensions of 38.1 mm (1.5 in.) OD and 3.25 mm (0.13 in.) wall thickness. The boiler had been in operation for 12 years, and external deposits were observed at every outage. The flue gas temperature was reported to be about 220 °C (430 °F). The temperature of the boiler feedwater (BFW) at the economizer inlet end was 130–150 °C (265–300 °F) with pressure of 150 Kg/cm². The surface temperature of the tube metal was about 170–180 °C (340–355 °F).

Investigation and Findings Visual examination indicated a puncture that appeared to have burst open, developing thin zigzag contours, which were covered with a blackish scale (Fig. 6.119). The surrounding fins were badly damaged and were eaten away due to corrosion. Fins in the area surrounding the puncture and on the opposite side were fully filled with spongy adherent corrosion products having white- and yellow-colored scales. The tube was slightly bent at the puncture point.

Table 6.16 shows an EDS analysis of white deposits on the OD surface as well as on the ID surface scale. The EDS analysis on the OD surface indicated the presence of iron, sulfur, and oxygen both on the white and the yellow brown scales. The relative amount of sulfur present on the ID surface scale was less than that on the OD surface.

Microstructural examination was carried out at various locations on the failed sample. The general microstructure of the tube was of fine-grained ferrite and pearlite. Heavy scale deposition was noticed on the OD, appearing to penetrate the metal from the gap between the fins and the external surface of the tube (Fig. 6.120a). The microstructure at the OD showed a general form of corrosion in terms of metal dissolution and scale formation on external surfaces of the tube (Fig. 6.120b).

Investigation established that the failure was largely due to acidic corrosion. Energy dispersive spectroscopy analysis of the scale formed on the outer surface indicated a significant amount of sulfur as well as oxygen and iron. The flue gases produced on combustion of gaseous and liquid fuels proved to contain large amounts of moisture. An interaction between sulfur trioxide and moisture or water vapor present in the flue gases produced sulfuric acid in vapor form. When the prevalent surface temperatures of the tube metal decreased below the condensation temperature of the flue gases, the sulfuric acid vapor condensed as a white deposit on the tube surface. At certain locations, the sulfuric acid had eaten away the steel surface to such an extent that subsequent thinning of the tube resulted in failure of the tube in the form of a burst opening.

Conclusions The failure of the economizer tube in the form of a puncture was due to acid dew-point or cold-end corrosion. Moderate corrosion damage at the ID surface had assisted in the failure process. After a threshold



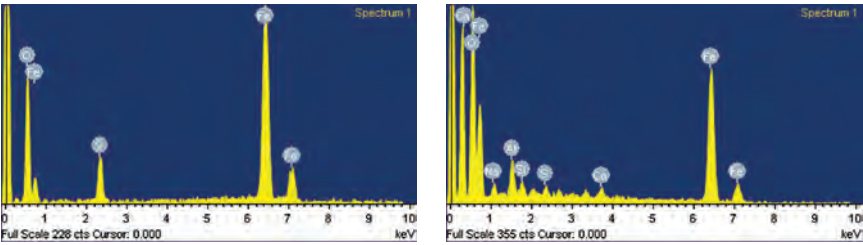
(a)



(b)

Fig. 6.119 Failed tube showing (a) puncture location and surrounding area with damaged fins and (b) close-up view at puncture having thinned contours. Fins and area between the fins show scale deposits.

Table 6.16 EDS analysis of outer and inner surfaces of the tube



Element	Surface amount, wt.%	
	Outer scale	Inner scale
Oxygen	14.99	25.90
Sulfur	3.76	0.93
Sodium	...	2.40
Aluminum	...	3.30

Element	Surface amount, wt.%	
	Outer scale	Inner scale
Silicon	...	1.26
Calcium	...	1.11
Iron	81.25	65.10

thinning, the tube at a particular location could no longer withstand the hoop stresses and it burst open at the puncture location.

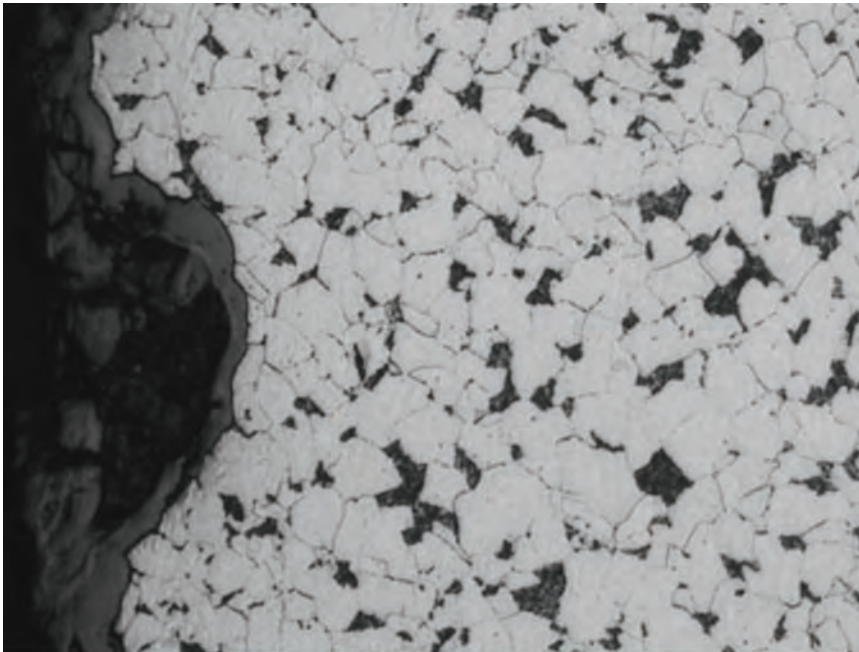
Stress-Corrosion Cracking

Metals and alloys fail by SCC when subjected to the combined action of static tensile stress and a specific corrosive environment to which the metal is sensitive (Ref 6.1, 6.34, 6.35). The tensile stresses are either acting or applied, due to internal pressure of the fluid being handled or residual fluid during various manufacturing processes including welding, heat treating, and forming. Cracking due to SCC may be intergranular or transgranular, depending on the corrodent and stress conditions. Macroscopic features of SCC failures, even of inherently ductile metals and alloys, are brittle. Failure due to SCC is highly environment specific (i.e., the environment that causes SCC for one metal may be only mildly corrosive for another). If the environment is conducive, SCC can occur even on the fire side. Both carbon steel and austenitic stainless steel tubes in a boiler are susceptible to fire-side SCC failure.

For SCC to occur, deposition of corrosive species or corrodents in the presence of moisture is necessary. Since the presence of moisture is a must, SCC can occur only if metal temperatures are below the dew point of water. Superheater and reheater tube surface temperatures are high enough not to permit the existence of water over the tube surface when the boiler is in operation. Fire-side failure of boiler tubes due to stress



(a)



(b)

Fig. 6.120 Optical micrographs showing (a) heavy scale deposition on OD, trying to penetrate the metal from the gap between fins and external surface of the tube, 200 $\times$; (b) microstructure at the OD indicating general form of corrosion as metal dissolution and scale formation on external surface, 200 $\times$

corrosion cracking therefore occurs during idle periods. Figure 6.121 shows a microstructure displaying fire-side stress corrosion cracking in a superheater tube. The microstructure indicates intergranular stress corrosion cracking and grain dropping in the matrix of slightly worked austenite initiating from the fire side of the superheater tube.

Fire-side corrosion can also occur at locations where condensation of moisture take place (such as the economizers and low-pressure sections of the boiler) or where water from leaks or external ingress can contact the fire-side surfaces.

Potential corrodents for fire-side corrosion due to SCC are combustion products such as sulfates and nitrates, or chlorides present in the air, particularly in coastal areas. Fire-side SCC of austenitic stainless steel tubes is attributed to the presence of chlorides and sulfur-containing compounds, whereas that of carbon and low-alloy steels is normally due to concentrated sodium hydroxide.

Polythionic Acid Stress-Corrosion Cracking

Polythionic acids ($\text{H}_2\text{S}_x\text{O}_6$, where $x = 3, 4$, or 5) are known to attack chromium-depleted regions in sensitized austenitic stainless steels.

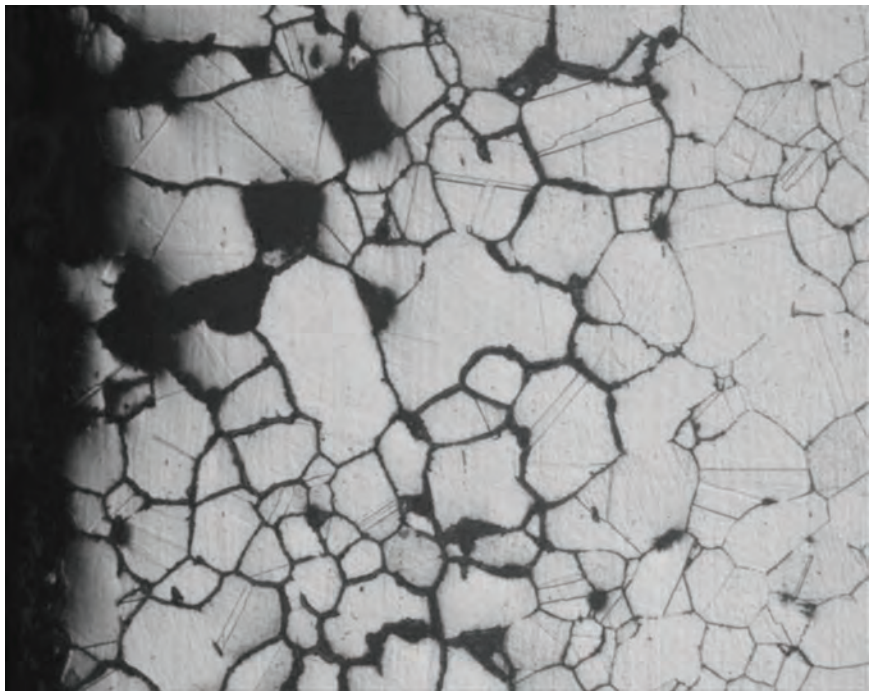


Fig. 6.121 Optical micrograph indicating fire-side intergranular stress corrosion cracking and grain dropping in superheater tube, 400×

Polythionic acid forms when a sulfur-carrying scale interacts with the moisture and oxygen present in the environment. Cracking due to polythionic acid is a specific form of SCC that occurs in sensitized stainless steel (Ref 6.36). Polythionic acid stress corrosion cracking (PASCC) normally occurs during shutdowns, start-ups, or during operation when the tubes are exposed to air and moisture.

In solution-annealed austenitic stainless steel, chromium is uniformly distributed within the austenite microstructure. However, stainless steels undergo sensitization due to chromium carbide precipitation along the grain boundaries of the steel when subjected to temperature intervals of 550 to 850 °C (1020 to 1560 °F) during manufacturing or service. As a result, the areas in the vicinity of the grain boundary are depleted of chromium and undergo corrosion (Ref 6.37). Figure 6.122 shows PASCC of an intergranular nature in an austenitic stainless steel pipe.

Polythionic acid stress corrosion cracking normally occurs in standard (0.08% carbon max.) and high-carbon (0.10% max.) grades of austenitic stainless steels (such as Grade 304 SS) that have become sensitized either by weld fabrication or by operation in the sensitizing range. Low-carbon (0.03% max.) grades such as 304L and 316L and chemically stabilized grades (e.g., with titanium or columbium alloying additions) such as Grade 321 and 347 are more resistant to sensitization, but even these materials

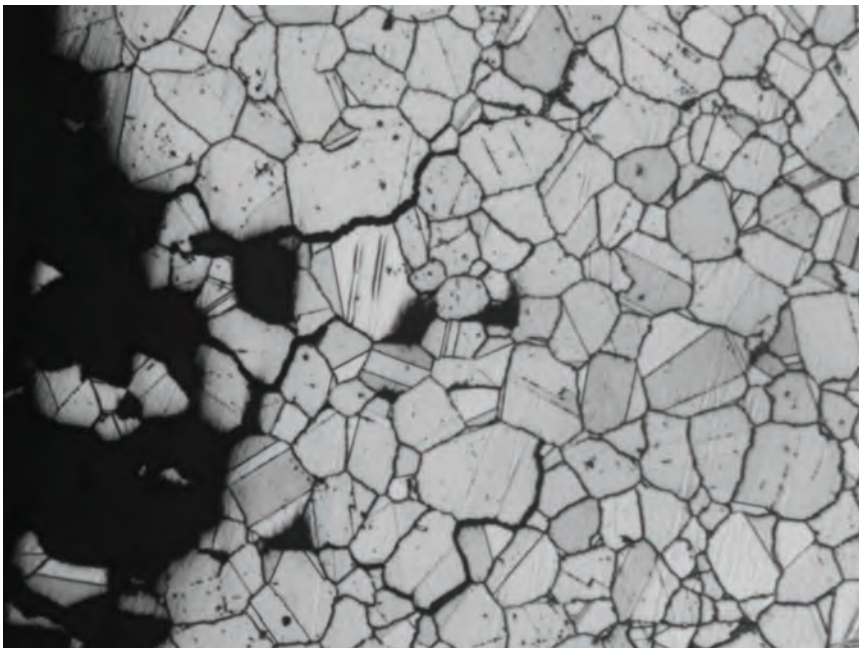


Fig. 6.122 Optical micrograph showing PASCC in an austenitic stainless steel pipe, 100×

can become sensitized after a longer exposure to slightly higher temperatures or with an improper solution annealing heat treatment.

The three boundary conditions that are necessary for PASCC to take place are:

- Susceptible material such as an austenitic stainless steel that has undergone sensitization with grain boundary carbide precipitation
- Corrosive conditions with sulfur ions along with moisture-based contaminants that can produce polythionic acid
- Availability of tensile stresses. Stress is necessary to open up intergranular corroded regions so that fresh chromium-depleted regions at grain boundaries are exposed. These freshly exposed regions further give rise to intergranular corrosion by polythionic acid.

Preventing tubes from being exposed to oxygen and moisture, along with sulfur-based impurities, stops the formation of polythionic acid. Purging with an inert gas such as nitrogen ensures this. Maintaining the tube temperature above the dew point prevents exposure to moisture and thus helps in preventing acid formation. Likewise, a wash with a soda ash solution neutralizes acids and helps in maintaining a basic pH.

Case Study 28—Failure Investigation of a Reheater Tube

Background Details Several reheater tubes of an imported boiler started leaking from the welded joints during a precommissioning hydro test. The reheater tubes were shipped to India by sea. The MOC of the reheater tubes was SA 213 TP304H grade stainless steel, and the tube dimensions were 63.0 mm (2.5 in.) diameter and 4.0 mm (0.16 in.) thickness.

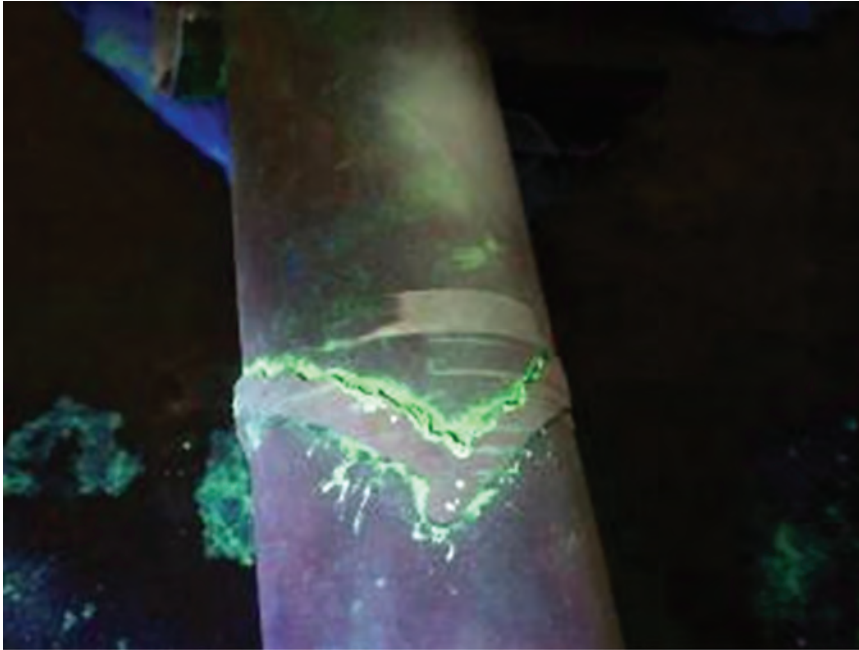
Investigation and Findings Visual examination did not reveal any apparent surface defects. The tube OD surface was painted red, and the paint had peeled off at several places. A tube had been welded over this tube. The ID surface of the tube had a thin uniform scale, black in color.

The failed tube was subjected to a dye penetrant test in order to confirm the presence of any surface defects. Figure 6.123 shows the indications corresponding to defects on the OD and ID surfaces of the tube at weld locations.

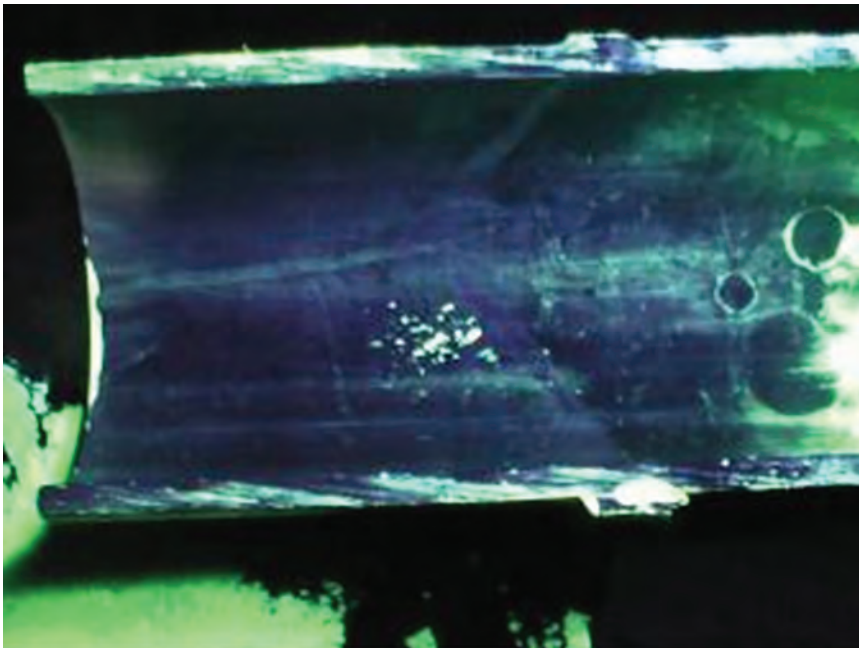
Scanning electron microscopy analysis revealed a deep crack at the HAZ and a network of intergranular cracks of a brittle nature throughout the section (Fig. 6.124).

Besides the other usual contaminants, an EDS analysis indicated the presence of sulfur, chlorine (as chloride), and sodium along with moisture at the crack (Table 6.17) and on the OD surface of the tube.

Optical microscopy indicated intergranular cracking throughout the section on the crack/fracture surface, as well as grain dislodgement (Fig. 6.125a). The general microstructure was fine-grained austenite with traces of SIM and twins (Fig. 6.125b). The weld microstructure comprised



(a)



(b)

Fig. 6.123 DP tested view (a) of OD at weld location after removal of outer cover showing network of fine hairline cracks at heat-affected zone region. (b) ID surface showing fine rounded and linear indications

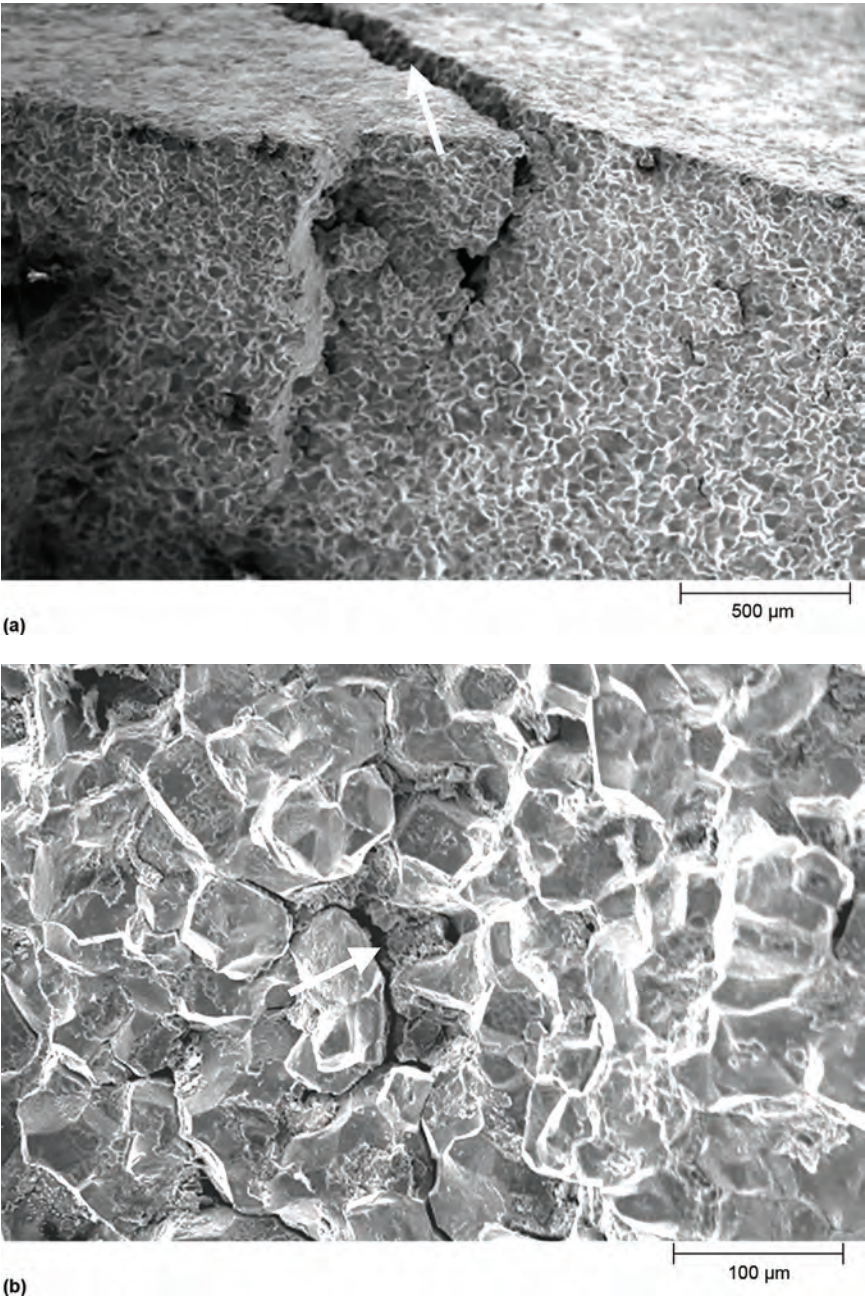
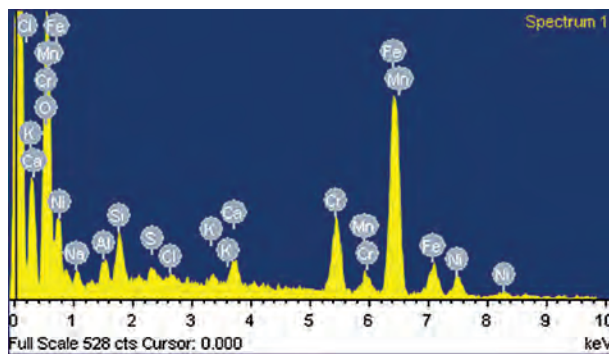


Fig. 6.124 SEM micrographs. (a) OD edge with a deep crack at heat-affected zone, 50×. (b) Intergranular cracking network on brittle fracture surface, 250×

Table 6.17 EDS analysis on OD surface of the tube

Element	Amount by wt.%	Element	Amount by wt.%
Oxygen	25.58	Chlorine (as chloride)	1.13
Sodium	1.53	Calcium	1.47
Aluminum	5.35	Chromium	7.17
Silicon	2.78	Iron	51.48
Sulfur	0.36	Nickel	3.14

a dendritic structure of ferrite pools in an austenite matrix (Fig. 6.125c). There was also continuous precipitation of carbides along the grain boundaries. The oxalic acid etch test exhibited a ditched structure at the OD, ID, and weld locations along with heavy carbide precipitation at the austenite grain boundaries (Fig. 6.125d).

The results of a tensile test were satisfactory. The hardness at the parent metal region was within normal limits, but at the weld heat-affected zone it was quite high.

An analysis of the results of all of these investigations and the plant data indicated that the underlying mechanism for failure of the reheater tube was PASCC. It is well known that a PASCC failure occurs in stainless steels when sulfur-bearing deposits react with oxygen and moisture to form $H_xS_xO_x$ types of acid. In this case, the presence of moisture and sulfur-bearing compounds on the OD as well as the ID surfaces of the tube formed polythionic acid during shipment. The EDS analysis clearly supports this hypothesis. The polythionic acid in turn attacked the sensitized austenite grain boundaries to initiate either intergranular corrosion or intergranular stress corrosion cracking in the presence of high internal stresses.

Conclusions The failure of the reheater tube was attributed to PASCC.

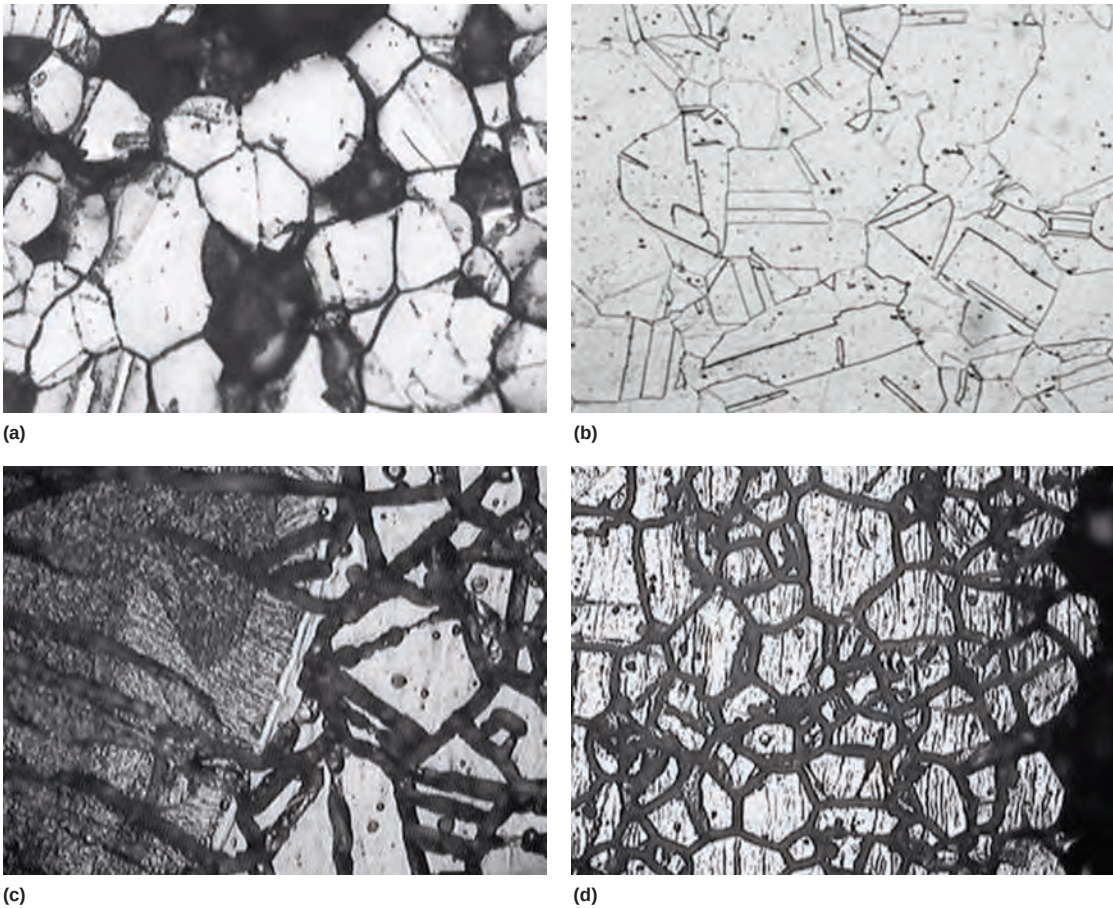


Fig. 6.125 (a) Microstructure at fracture surface, 400 $\times$. (b) General microstructure of a tube, 400 $\times$. (c) Microstructure of a weld and heat-affected zone, 400 $\times$. (d) Microstructure after etching with oxalic acid, 400 $\times$

Fire-Side Erosion

Erosion is defined as the process where metal wastage on the impacting surface occurs mainly because of an abrasive or impact action of solids or liquids. Such an impact can be due to high-velocity turbulent fluid, sudden or abrupt change in the direction of the flowing fluid, sudden changes in the fluid pressure resulting in a jetting effect, the presence of hard abrasive particles in the flowing fluid, or direct impingement of hard particles on a metal surface. The extent of metal loss is governed by the type of erodent (solid or liquid), its velocity and impingement angle, the nature of the impacted surface in terms of its hardness, and abrasion or wear resistance.

Erosion failure of boiler tubes can occur from the water or steam side, or from the fire side. The principal types of fire-side erosion mechanism are erosion due to soot blowing, fly ash attack, coal-particle impingement,

falling slag, and steam cutting action (Ref 6.38, 6.39). Each of these mechanisms is discussed here.

Soot Blower Erosion

The function of the soot blower in a boiler is to blow off soot from the tube surface using a high-velocity jet of steam. However, the steam from soot blowers often leads to erosion of the waterwall tubes when the alignment of the soot blower and tubes is not correct. If the orientation of the soot blower is such that the soot blower lance is blowing directly on the tubes and not blowing between the tubes, erosion of the tube surface occurs. Damage due to soot blower erosion is compounded when wet steam is used.

Erosion due to soot blowers occurs in the direct path of a wall blower or retractable blower discharge and also at the furnace corners. The first tubes adjacent to the soot blower opening are the most affected hit areas. Soot blower erosion can also occur around the economizers, superheaters, and reheaters on account of the carryover of wet steam or fly ash in these areas.

Typical reasons for soot blower erosion are:

- Improper location of the soot blower
- Operation of the soot blower with entrapped condensed water in the steam or air
- Blower causing a high-velocity stream of condensed water droplets
- Excessive blowing pressure injecting a large amount of ash at high velocity
- Misalignment of blower nozzle
- Overall malfunction of the soot blowing system

As a result, there is metal loss due to thinning of the tube from the OD side. Figure 6.126 depicts damage that took place due to malfunctioning of a soot blower.

Soot blower erosion not only leads to a shining and polished surface but can also result in thinning and final rupture of the tube in the longitudinal direction, as shown in Fig. 6.126(b). The portion of the tube on either side of the rupture is usually flattened.

Fly Ash Erosion

Fly ash erosion and erosion due to unburned coal particles are two modes of erosion failure that belong to the category of solid particle erosion. Erosion due to solid particles is a serious issue for thermal power plants because it results in forced outages, loss of efficiency, and additional expenditure due to unwarranted repairs. Solid particle erosion results



Fig. 6.126 Erosion and longitudinal rupture of boiler tube due to misaligned soot blower

in localized or general loss of material from the tube surface due to the mechanical impact of fly ash or coal particles.

Fly ash erosion is a matter of concern especially when dealing with low-grade coal with high ash content. Fly ash erosion is mainly observed in primary superheater and low-temperature superheater bends and tubes, screen tubes, the inlet section of steam reheater tubes, and areas of economizer bends and tubes. The extent of damage due to fly ash erosion multiplies if there is a nonuniform flow of flue gases in such areas. The impact by particles of fly ash in the flue gases causes abrasive erosion of screen tubes or superheater tubes.

Typical features of fly ash erosion include polishing of the impacted surface, formation of flat spots, tube wall thinning, and tube rupture. Occasionally irregular flow marks and grooving are also observed, as shown in Fig. 6.127.

Coal used in coal-based thermal power plants mostly comprises combustible and noncombustible mineral constituents, normally known as ash. For example, the coal used in Indian power plants contains a substantially large amount of ash, as much as 45–50%. Indian coal ash contains about 15% hard abrasive species in the form of hard quartz (SiO_2) besides alumina (Al_2O_3), alkali feldspars, $(\text{K},\text{Na})\text{AlSi}_3\text{O}_8$, and traces of a garnet mineral. All of these constituents of ash contribute to erosion of the boiler tubes when the fly ash particles present in the flue gases impact the tube surface. The extent of damage due to fly ash erosion depends on variables including the velocity of flue gas or fly ash particles, their angle of impact with respect to the tube surface, the shape and size of the particles, the hardness and abrasion resistance of the tube surface, and the flue gas temperature. Of all the variables, fly ash particle velocity is the most important. There is an exponential relation between the rate of erosion and the particle velocity. It is worth noting here that the particle velocity is governed by the local flow velocity of the flue gases at any particular location and not by the bulk velocity of the flue gases. The other two most important variables are the temperature of the flue gas and the mineral content of the coal.

When high ash coals are used, it is not possible to combat fly ash erosion completely; rather, it can only be minimized.

Case Study 29—Failure Investigation of Low-Temperature Reheater Tube of Middle Bank Coil

Background Details The low-temperature reheater (LTRH) tube of a middle bank coil of a coal-fired boiler failed by way of a longitudinal opening after 10 months of service. The MOC of the tube was SA 213 Grade T12 steel. The tube dimensions were 63.5 mm (2.5 in.) OD and 4.0 mm (0.16 in.) thickness. The coal in the as-received condition contained approximately 12.0% moisture, 32.0% ash, 26.0% volatile matter, and 30.0% fixed carbon.

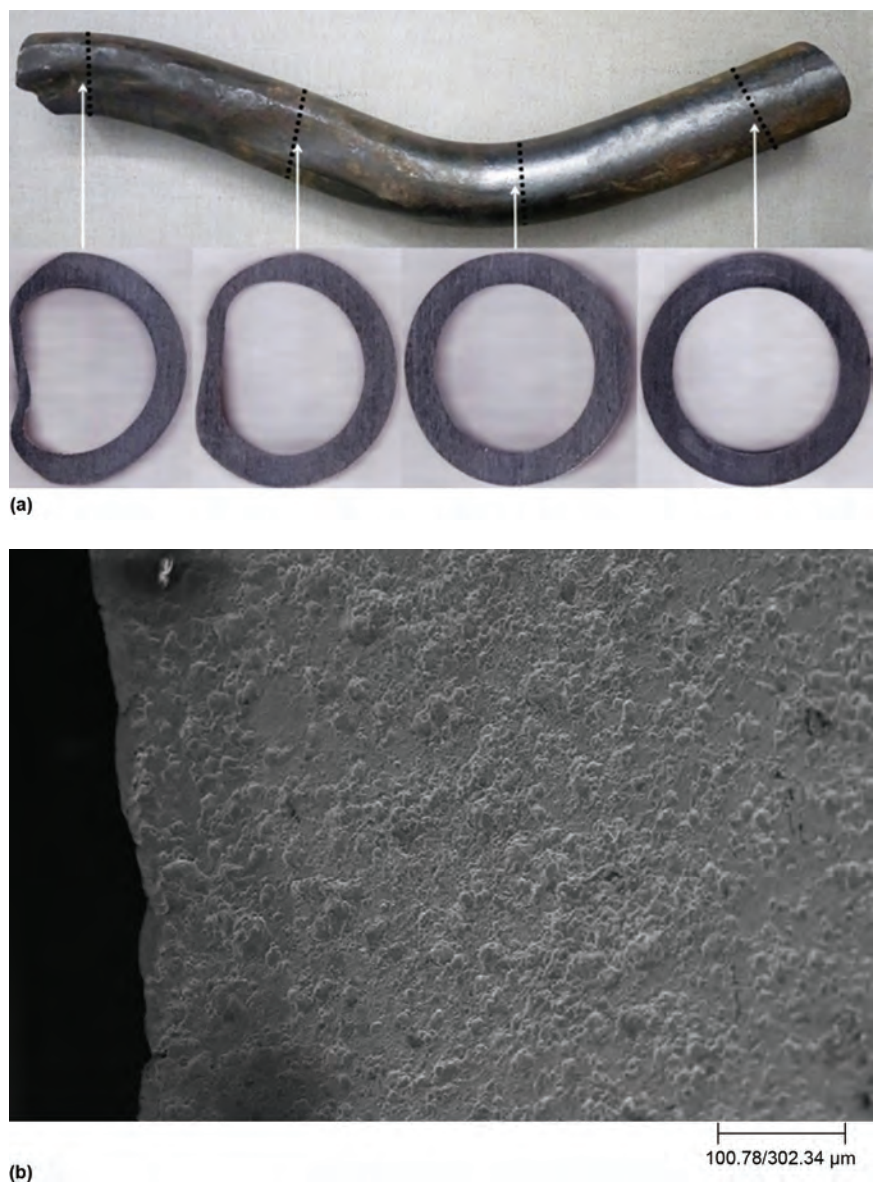


Fig. 6.127 (a) Eroded surface of a screen tube near bend. (b) SEM image of area eroded due to furnace gases containing fly ash, 100×

Investigation and Findings Visual examination showed a fish-mouth opening with sharp tips slightly away from the bend location (Fig. 6.128). The contours of the rupture lip were deformed outward. The area surrounding the contours on the outer surface was yellowish brown in color. The tube bulged slightly at the eroded area. The inner surface was partly

dark brown in color, indicating destruction of the protective magnetite scale in some places. The lip contours at the inner surface were dark brown in color.

Scanning electron microscopy on the outer surface of the tube near the failure location indicated the erosive nature of the damage surrounding the rupture contours, typically due to particle impingement (Fig. 6.129).



Fig. 6.128 Low-temperature reheater tube showing longitudinal rupture opening

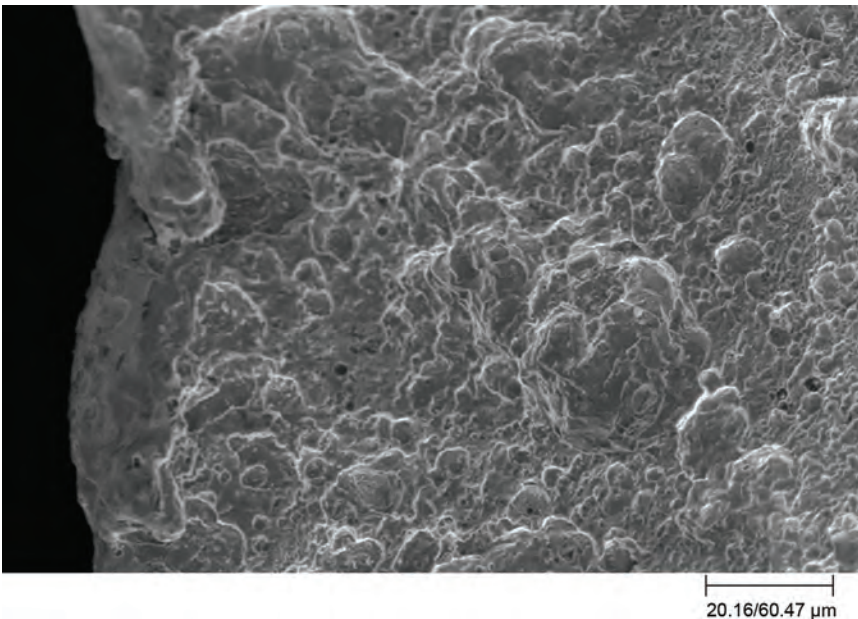


Fig. 6.129 SEM image of outer surface adjacent to rupture lip showing erosion damage, 500×

Energy dispersive spectroscopy on the outer surface showed the presence of oxygen, magnesium, aluminum, silicon, sulfur, calcium, and potassium, and on the inner surface, elements including oxygen, magnesium, aluminum, silicon, sulfur, chlorine (as chloride), and calcium were found.

The overall microstructure of the tube was that of ferrite and pearlite grains. Figure 6.130(a) shows the microstructure at a longitudinal cross section on the outer surface near the failure. The most noteworthy feature is that the structure shows a *crater* formed on the outer surface due to the impact of fly ash particles. The impact caused the underlying metal to deform to a certain depth. Figure 6.130(b) shows the twins (Neumann bands) formed in ferrite grains across the section. The presence of twins in the ferrite grains indicates that the tubes had undergone significant impact or vibrations.

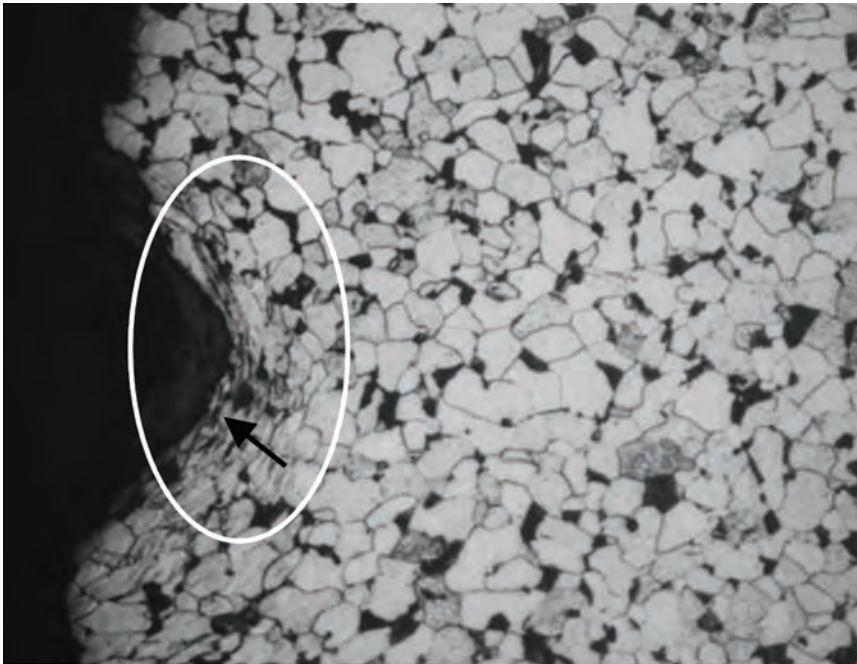
Microstructural studies also showed marginal corrosion damage on the inner and outer surfaces of the tube with a thin adherent scale. The average scale thickness on the flue-gas-facing side of the OD was 40.0 μm , and that on the ID side was 47.0 μm .

Samples drawn from the tube failed both tensile and hardness tests. Tensile test results indicated lower elongation values, whereas the hardness values at different locations were on the higher side. Wall thinning was noticed at the rupture contours. The area surrounding the rupture was dark brown in color, with a rough surface indicating the erosive nature of the damage. The results of optical microscopy and SEM also pointed toward the erosive nature of the damage. The microstructure of the sample indicated the presence of Neumann bands in ferrite grains. Neumann bands are formed when a material is subjected to mechanical deformation by way of sudden impact and are most often observed along the $\{112\}$ plane of body-centered-cubic ferrite. In coal-fired boilers, the rate of wear is influenced by the ash content of the coal, in particular, the content of abrasive particles of minerals such as quartz and mulite. In the present investigation, the presence of such abrasive particles was further confirmed by elements such as silicon, aluminum, and oxygen per the results of an EDS analysis on the outer surface.

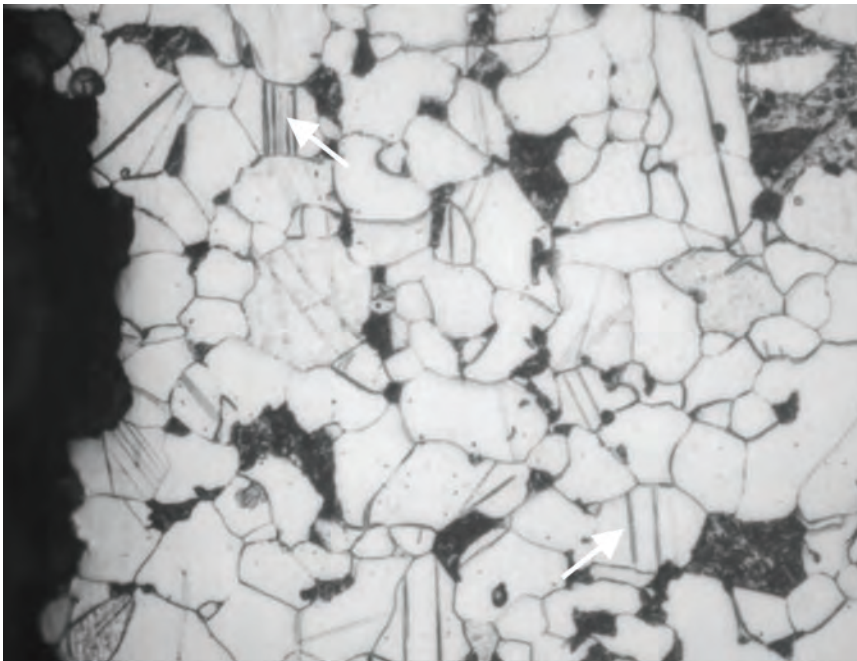
Conclusions The failure of the LTRH tube was attributed to excessive wear caused by high-velocity or large solid and erosive fly ash particles.

Coal Particle Erosion

Erosion of the tube surface due to the impact of incompletely or unburned coal particles is termed *coal particle erosion*, which closely resembles fly ash erosion. Coal particle erosion is more frequently found in utility boilers rather than power boilers. Two locations where coal particle erosion is more pronounced are in cyclone burners, and in areas where the wear resistant refractory lining of the tubes has been damaged or worn out.



(a)



(b)

Fig. 6.130 Optical micrographs showing (a) crater formed on the outer surface by the impact of fly ash particles, 110 $\times$; and (b) twins (Neumann bands) formed in ferrite grains across the section, 400 $\times$

Falling Slag Erosion

Slag particles falling from a height give rise to erosion of the tubes that are located at the bottom end of the boiler. The damage is more pronounced at the side walls or the slanted tubes near the ash hopper located at the bottom. The exact nature of the damage depends on the size of the slag particles and the manner in which they fall. Small slag particles usually give rise to formation of flat spots on the surface of the slanted tubes, whereas a large chunk falling from a substantial height can cause denting on the tube surface and deformation and bending of the tube.

Erosion Due to Steam Cutting

Failure of a boiler tube by a steam cutting action, which causes the failure of an adjacent tube, can occur in any part of the boiler. The severity of the damage due to steam cutting is increased when the internal steam pressure and temperature within the tube are high, such as in the case of superheaters and reheaters. This type of failure is usually localized and follows the *line of sight* principle. It is termed a secondary failure because such failure can occur only when the adjacent tube has failed and punctured on account of a primary reason, resulting in the ejection of water or steam at high pressure. If the original failure is not detected in time, it can result in a chain reaction of failures involving multiple damages. Figure 6.131 shows the failure of a superheater tube due to steam impingement.

Case Study 30—Failure Investigation of Final Superheater Tube

Background Details The final superheater tube of a 600 MW boiler failed during service in the form of a puncture after about 5 years of service. The MOC of the superheater tube was SA 213 T23 steel, and the dimensions



Fig. 6.131 Superheater tube cut by steam leaking from an adjacent tube



Fig. 6.132 Failed tube showing brownish black scale and two punctures side by side, radially approximately 90° apart

were 51.0 mm (2.0 in.) OD and 8.0 mm (0.3 in.) thickness. Leakage was noticed in the adjoining tube prior to failure.

Investigation and Findings Visual examination of the tube sample showed two punctures side by side, radially approximately 90° apart. The area surrounding the puncture had deformed inward and showed a smooth texture. The puncture contours were thinned down and projected outward (Fig. 6.132).

Low-magnification examination of the outer surface showed yellowish brown spots of corrosion surrounding the contour and erosion marks slightly away from the puncture location. The inner surface displayed a craze pattern surrounding the puncture. Thinning was noticed at the contours, which protruded outward (Fig. 6.133).

Scanning electron microscopy on the outer surface of the tube near the failure location indicated the erosive nature of the damage surrounding the rupture contours, typically due to impingement (Fig. 6.134).

The outer-edge microstructure comprised ferrite, bainite, and carbides (Fig. 6.135b).

The extraneous nature of erosion on the outer surface was due to steam jet injections at the failure location, from the adjacent leaking superheater tube. This jetting promoted severe erosion, reducing the wall thickness at a localized spot on the outer surface of the failed tube. With reduced wall thickness, the tube could no longer sustain the internal prevailing pressure and burst open with its contours projecting outward.

Conclusions The failure of the superheater tube was of a secondary nature. It was caused by the external impingement of a steam jet that eroded the tube and also resulted in punctures at two locations.



Fig. 6.133 Low-magnification view of (a) outer surface indicating corrosion and erosion marks, 6×; and (b) inner surface surrounding the puncture with scale, 6×

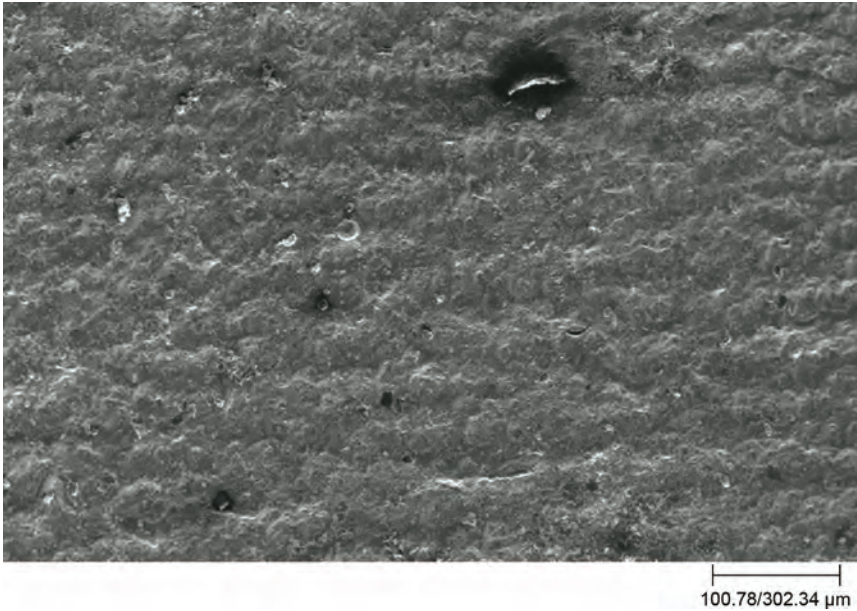


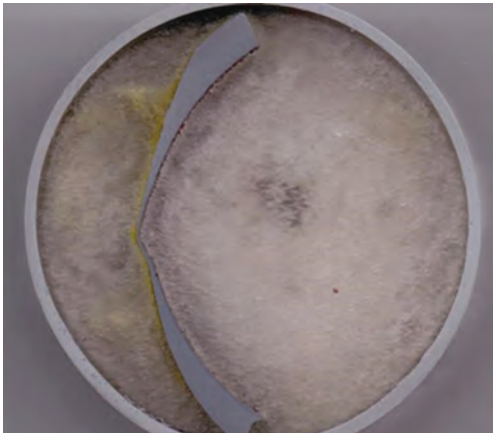
Fig. 6.134 SEM image of outer surface adjacent to rupture lip showing erosion damage, 100×

Fatigue

Failure of boiler tubes under repeated cyclic or fluctuating loading conditions is known as fatigue. Almost 80% of tube failures in firetube boilers are attributed to fatigue. Fatigue can occur at stresses much lower than the yield strength of the material. There are four types of boiler tube fatigue failure that are caused by mechanical loads, thermal cycling, or flow-induced vibrations: mechanical or vibrational fatigue, corrosion fatigue, thermal fatigue, and failure due to creep-fatigue interaction (Ref 6.1). Areas of constraint such as tube penetrations into headers or pipes, welds, and attachments or supports are prone to fatigue failure, normally showing crack initiation at the OD of the tube.

Mechanical Fatigue

Mechanical fatigue is defined as fracture under fluctuating mechanical stresses having a maximum value of stress lower than the ultimate tensile strength of the material. Damage due to mechanical fatigue is mainly associated with externally applied stresses. High-frequency low-amplitude stresses are developed on account of vibrations due to irregular flow of flue gases or soot blowers, whereas low-frequency high-amplitude stresses are attributed to boiler cycling. Defective tube-to-tube welds or



(a)



(b)

Fig. 6.135 (a) Sample in as-mounted condition. (b) Outer edge microstructure of ferrite, bainite and carbides, 100×

tube-to-manifold welds that are subjected to vibrations on account of inadequate supports are areas where failure due to mechanical fatigue is most common.

Thermal Fatigue

Thermal fatigue is defined as a failure resulting from cyclic stresses developed in the material due to temperature (Ref 6.40, 6.41). In boiler tubes, thermal fatigue takes place when the tubes are subjected to a number of

rapid heating and cooling cycles that lead to large differences in thermal expansion or contraction between the tube and the surrounding structural members. The high degree of restraint in the affected areas of the boiler tubes induces biaxial or triaxial stresses. The stress produces micro-cracks on the surface of the tube that continue to propagate with each cycle, giving rise to thick-walled fractures. Cracking of the tube ends is a characteristic feature of thermal fatigue. Thermal fatigue damage typically exhibits numerous cracks and crazing.

Damage due to thermal fatigue can be of the low-cycle or high-cycle type (Ref 6.1). Drastic change in temperature causing thermal shock or a large difference in thermal expansion behavior between two structural members can induce plastic strain, giving rise to low-cycle thermal fatigue. In firetube boilers, the most common cause of thermal fatigue is the internal scale. Thermal fatigue cracking occurs due to reasons including over-firing or incorrect burner settings.

On the other hand, in watertube boilers, failure due to high-cycle thermal fatigue occurs when a liquid (such as water) with a lower temperature comes in contact with the hot surface of a tube. For example, water dripping from a defective valve that falls over a pipeline carrying hot steam leads to high-cycle thermal fatigue. Here, the portion of the tube that has been dampened undergoes contraction, whereas the metal below it does not. This situation generates a large amount of tensile stress in the wetted portion of the tube. When the water evaporates on account of heat being absorbed from the surrounding metal, the surface temperature increases and the stresses developed are relaxed. When this happens repeatedly over a period of time, a crazed pattern of cracks develops. Figure 6.136 shows an SEM image with fatigue striations on the fracture surface, and an optical micrograph showing blunt crack tips. Propagation of some of these cracks through the thickness of the tube gives rise to final fracture.

Thermal fatigue damage is identified as the presence of wedge-shaped cracks and crazing. Once a crack is initiated, freshly exposed metal within the crack undergoes oxidation, creating a wedge effect at the crack tip.

Failure due to thermal fatigue is found in waterwall tubes or such other areas of the boiler that are subjected to departure from nucleate boiling or rapidly fluctuating flow conditions. It is also observed in superheaters subjected to vibrations of low amplitude.

Case Study 31—Failure Investigation of Final Superheater Tube

Background Details The final superheater tube of a 620 MW boiler failed after 4 years of service. The tube was made of SA 213 Grade T23 steel and had the dimensions of 51.0 mm (2 in.) OD and 8.0 mm (0.3 in.) thickness.

Investigation and Findings The superheater tube sample showed failure in the form of a rupture in the transverse direction with respect to the tube axis (Fig. 6.137). No wall thinning was noticed and there was no deformation in the contours. The rupture surface looked brittle in nature.

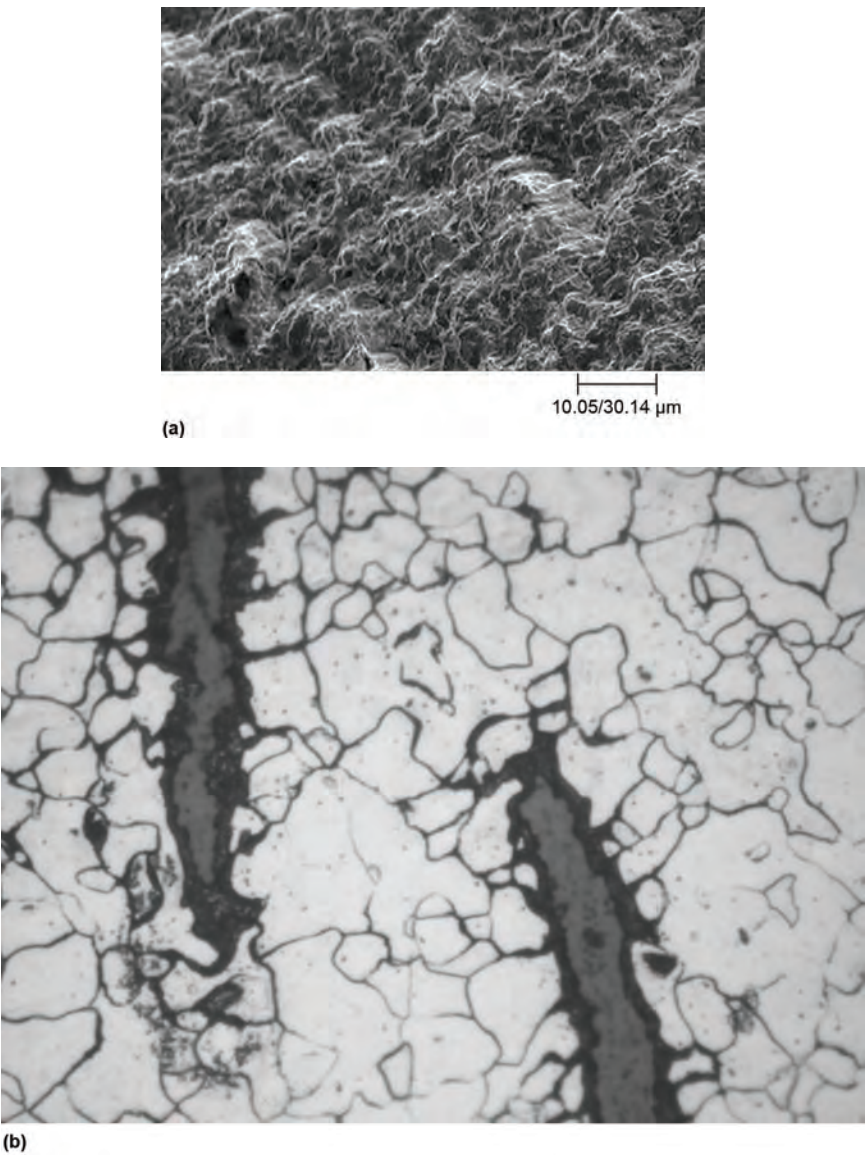


Fig. 6.136 (a) SEM image with fatigue striations on the fracture surface of a stainless steel tube, 1000×. (b) Microstructure indicating transgranular cracks with blunt tip and filled with oxide, 400×

Bulging was noticed at the rupture location. The inner surface of the tube was smooth with a thin adherent magnetite scale that was grayish black in color.

Wet fluorescent magnetic particle inspection studies indicated hairline cracks emanating from the corner of the rupture contours (Fig. 6.138a). A hairline crack was also noticed on the inner surface near the rupture location.



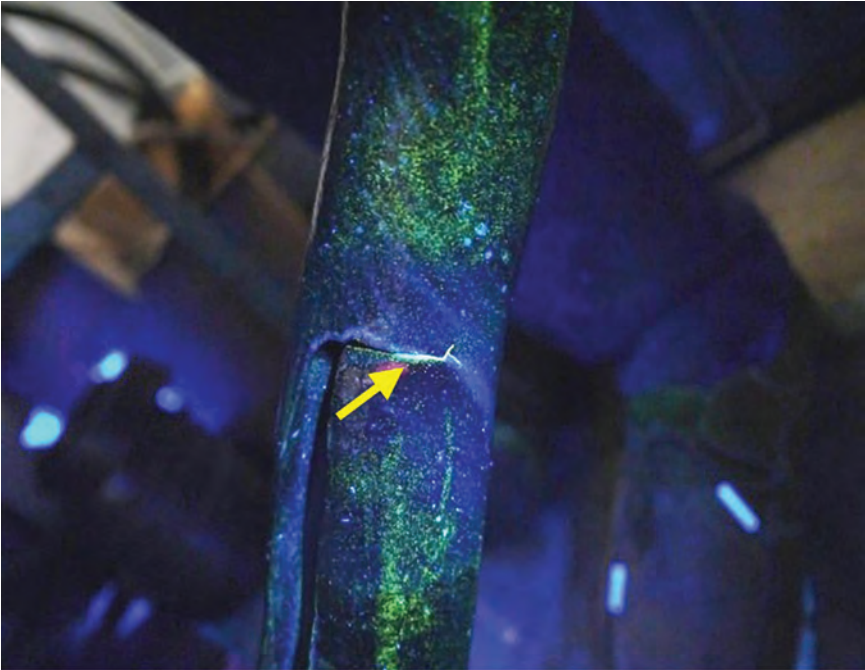
Fig. 6.137 Portion of a failed superheater tube showing failure location

Low-magnification examination of the fracture surface highlighted the presence of chevron marks and the brittle nature of the rupture contours on the coarse fracture surface, with crack initiation from the inner surface (Fig. 6.138b).

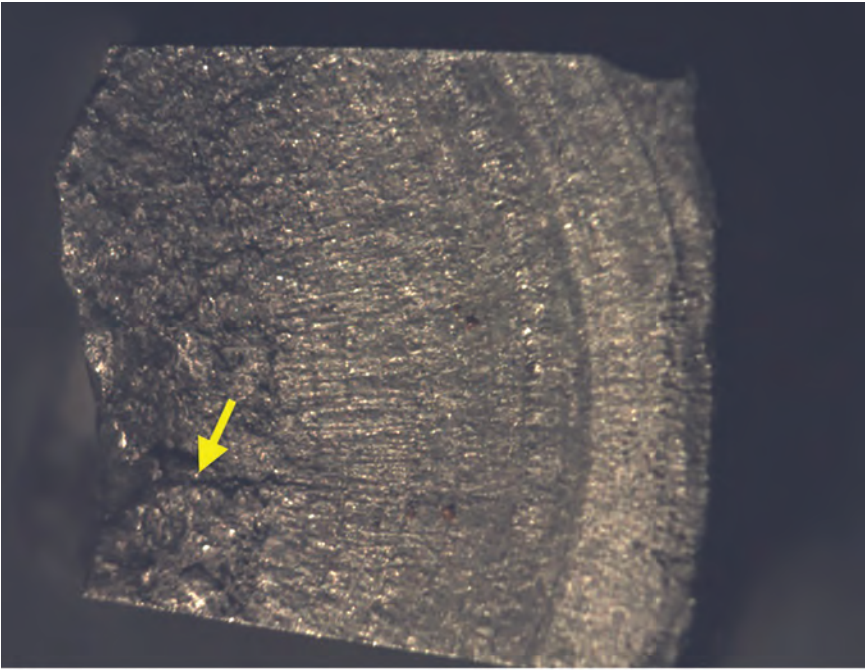
Scanning electron microscopy analysis of the fracture surface revealed fatigue striations on the rupture surface, whereas elsewhere the surface was covered with a scale. The inner surface adjacent to the rupture contours was also covered with an adherent scale (Fig. 6.139a).

Microstructural examination indicated that the microstructure of the tube consisted of grains of ferrite and bainite (Fig. 6.139b).

The results of hardness and microhardness measurements as well as a tensile test were satisfactory. The metallurgical integrity of the superheater tube appeared to be sound. Fatigue as the cause of crack initiation was revealed in the SEM studies, and this was further confirmed during a microstructural examination of the transverse section. The microstructural examination confirmed adherent scaling on the inner surface, which may have been due to contaminants present in water, because sodium and phosphorus were found in substantial quantities on the inner surface of the tube during EDS analysis. Normally such contamination is not observed on the steam-side scale. In the superheater steam coils, the source of water must be attemperation. The majority of the evidence was obtained through SEM as well as microstructural examination, wherein the blunt nature of transgranular cracks filled with scales were seen. These are typical characteristics of failure due to thermal fatigue. Such cracking can be possible only when there is a quenching effect on the inner surface. The possible source of temperature fluctuation from the inner surface at the



(a)



(b)

Fig. 6.138 (a) Outer surface view at rupture location indicating hairline cracks emanating from the corners of the rupture contour. (b) Low-magnification view of the rupture surface indicating crack initiation from inner surface as well as beach marks, 6×

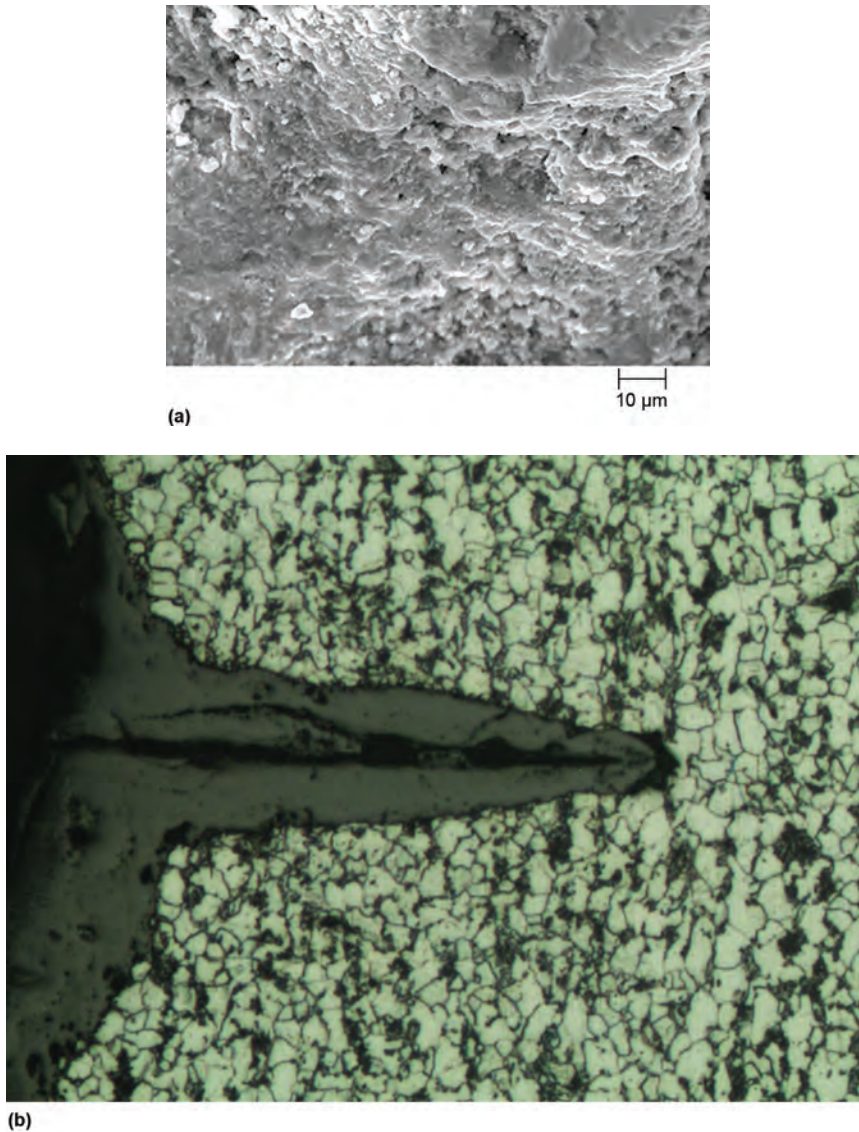


Fig. 6.139 (a) SEM image of fracture surface indicating fatigue striations with oxidized nature of rupture surface, 1000×. (b) Microstructure of a tube with ferrite and bainite as the phases with typical thermal fatigue crack having blunt tip, 100×

superheater coil was carryover of the attemperation water. Fluctuations in the temperature of the skin could promote the typical thermal fatigue cracks that were observed on the inner surface.

Conclusions The failure of the superheater tube was attributed to thermal fatigue cracking. The temperature fluctuation was due to carryover of water or wet steam from the attemperation performed in the final superheater region.

Case Study 32—Failure Investigation of Final Superheater Tube in a Thermal Power Plant

Background Details The superheater coil of a boiler failed after a service life of about 7 years. The failure had occurred in the form of a crack in the transverse direction, and leakage was noticed from this crack during a hydro test. There were white residues and deposits at the superheater tube surface. The MOC of the tube was SA 213 Grade T11 steel, and the tube dimensions were 47.6 mm (1.87 in.) OD and 4.6 mm (0.18 in.) thickness.

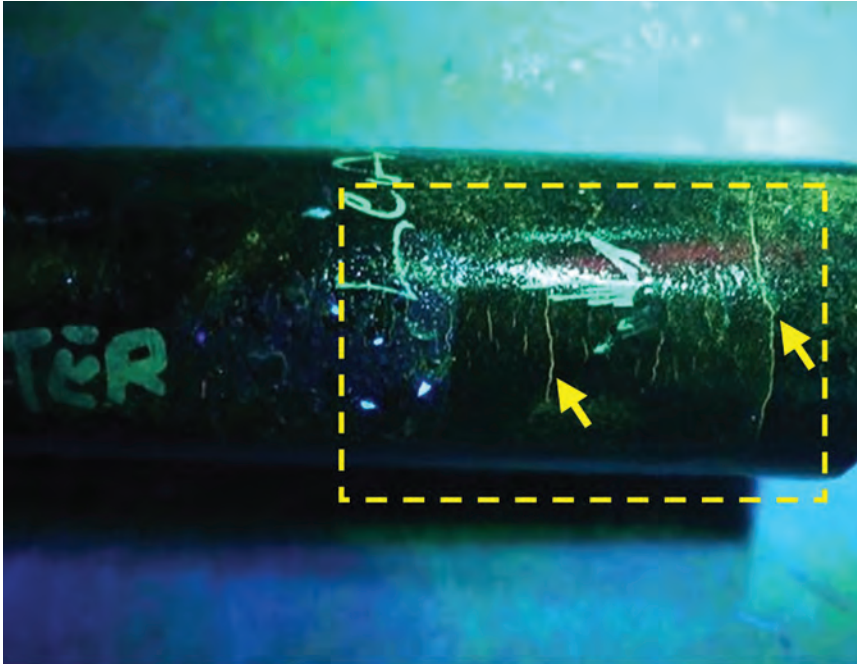
Investigation and Findings Visual examination of the failed tube sample revealed fine multiple and parallel cracks in the transverse (circumferential) direction. The outer surface of the tube was dark brown in color. Overall, the piece appeared straight and free from any visual abnormality with respect to distortion or bulging (Fig. 6.140).

In order to find any surface defects or auxiliary cracking, a wet fluorescent magnetic particle inspection (WFMPI) test was carried out on the sample. Multiple transverse indications were observed on the outer surface of the tube, as shown in Fig. 6.141(a). One such crack was found through and through and was also detected on the ID surface (Fig. 6.141b).

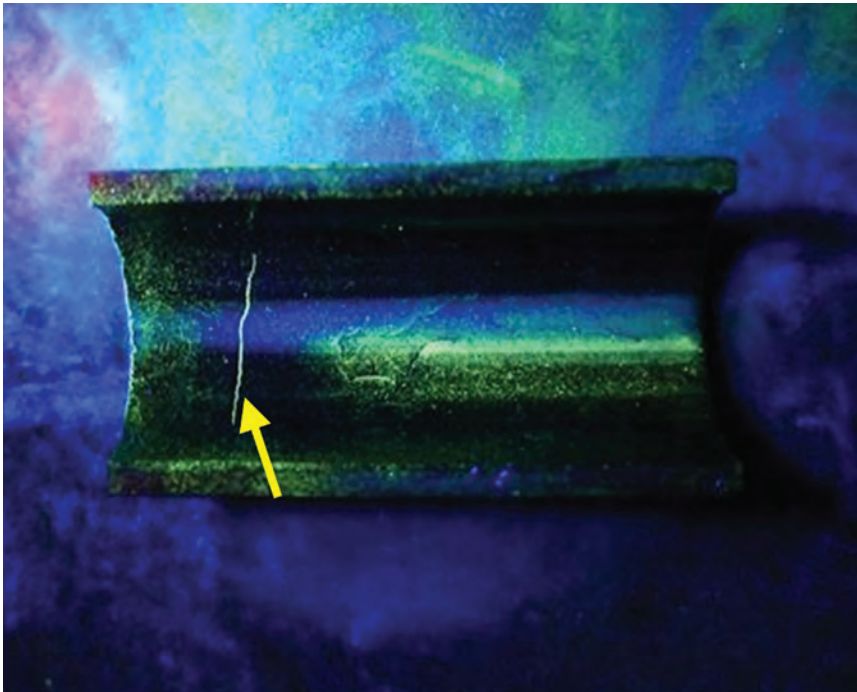
Low-magnification examination on the crack surface of the failed tube sample revealed the presence of coarse ratchet marks and an oxidized layer on the crack surface. It also pointed toward crack initiation from the OD side (Fig. 6.142). The crack features were camouflaged by erosion marks, presumably caused by a water jet after the failure.



Fig. 6.140 Close-up view of a tube at leakage location revealing fine multiple and parallel cracks in transverse (circumferential) direction



(a)



(b)

Fig. 6.141 (a) Multiple transverse indications on OD side. (b) Linear indication in transverse direction on ID surface of a tube in wet fluorescent magnetic particle inspection tested condition

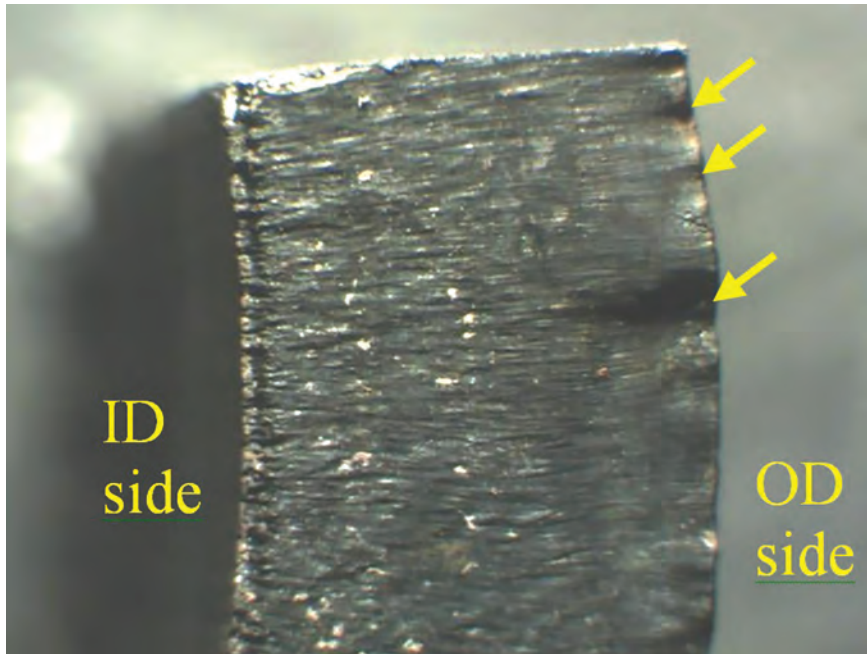


Fig. 6.142 Low-magnification view of a crack surface with ratchet marks pointing toward crack initiation from OD surface of the tube, 8×

Scanning electron microscopy examination was conducted at the crack surface to reveal more details about the failure mechanism (Fig. 6.143). Scanning electron microscopy accentuated the fatigue mode of the crack initiation from the OD edge. The SEM image also showed the presence of an oxide scale on the crack surface. Energy dispersive spectroscopy on the crack surface showed the presence of oxygen, calcium, and phosphorus.

Figure 6.144(a) and (b) shows as-polished and etched views of the OD edge. The crack initiating from the OD edge with a wide opening was filled with scales and was propagating; a blunt tip can be seen. The microstructure at all locations was ferrite and degraded bainite along with globular carbides that had a propensity to move toward the ferrite grain boundaries (Fig. 6.144c). All the cracks had wide openings and blunt tips.

Thermal stresses are generated in the superheater section of a boiler when there are fluctuations in the temperature besides normal operating internal pressure. This happens only when there is a possibility of water or wet steam ingress into the superheater tube. The ingress of water or wet steam causes a sudden chilling of the ID surface and can introduce sharp temperature gradients across the tube section. This, in turn, generates differential stresses along the section of the tube and lead to the initiation of a crack. As the fluctuations or number of cycles increase, the crack

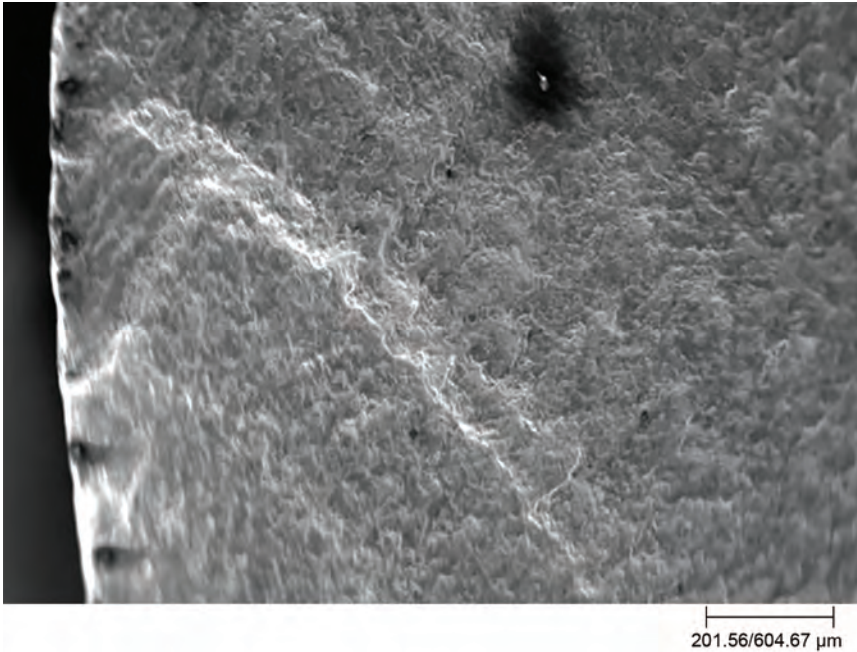


Fig. 6.143 SEM fractograph showing crack surface view that indicates presence of ratchet marks and beach marks initiating from OD, 50×

tends to propagate further and becomes filled with oxide scales. Thus, cracks with a blunted tip that are filled with scales propagate through the cross section. In the present investigation, both the SEM fractograph and the microstructure of the crack surface clearly pointed toward the failure being on account of thermal fatigue.

Conclusions The superheater tube leakage was essentially due to a thermal fatigue mode of cracking resulting from unanticipated thermal fluctuations in a local area on account of possible wet steam or water ingress in the superheater section.

Corrosion Fatigue

Waterwall tubes in pulverized coal power boilers often show circumferential cracking in the form of horizontal banding. This is attributed to the combined action of corrosive conditions and cyclic stress or cyclic loading of the boiler tube that results in corrosion fatigue failure.

Corrosion fatigue is a type of failure that takes place under the combined action of cyclic or fluctuating stress and a corrosive environment at stresses lower than would be required if there had been no corrosive environment. Two factors are necessary for failure of boiler tubes by corrosion

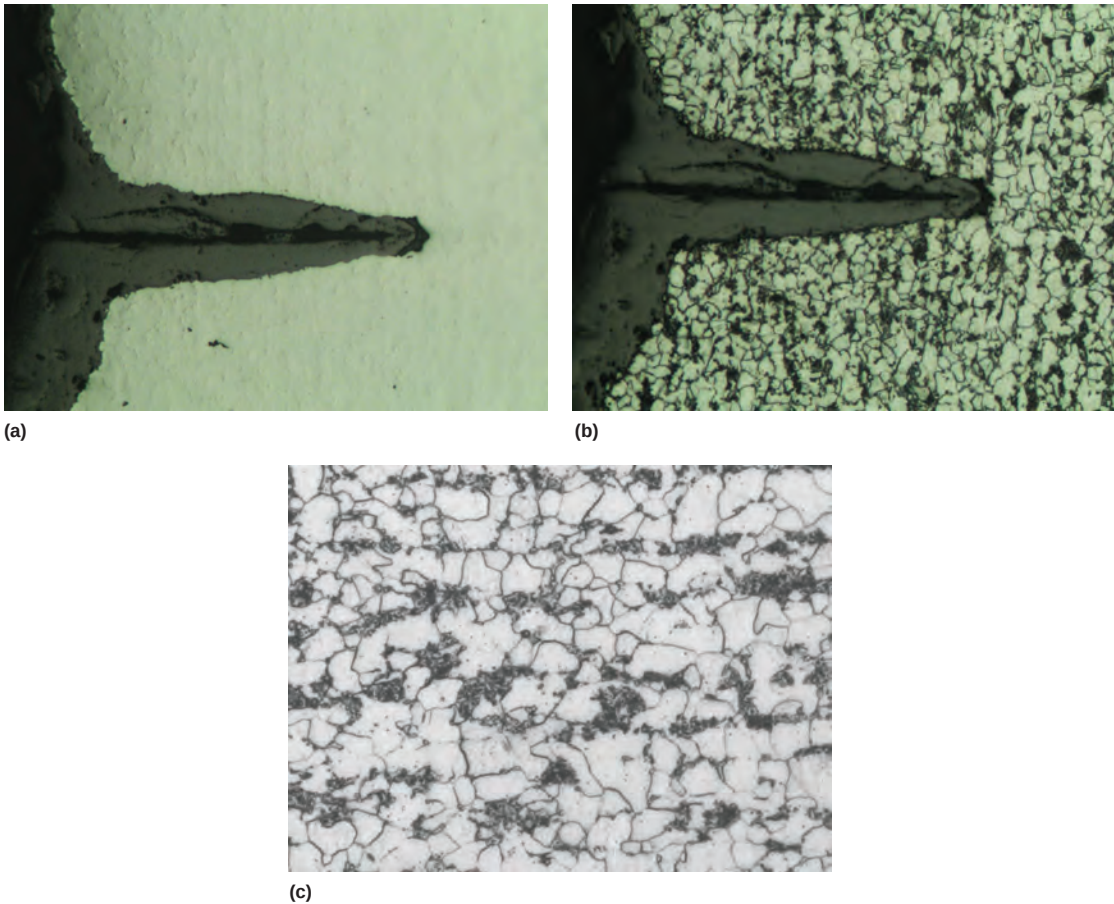


Fig. 6.144 OD edge indicating crack with wide opening and blunt tip filled with scale, (a) as-polished, 200 $\times$; (b) etched, 400 $\times$; (c) Core microstructure of ferrite, degraded bainite, and globular carbides, 200 $\times$

fatigue, namely, a cyclic loading condition and a corrosive environment (Ref 6.42). Cyclic tensile stresses may be developed as a result of cyclically fluctuating internal pressure or constrained thermal expansion and contraction. For corrosion fatigue to occur, the stress must be high enough to crack or break the protective magnetite scale. Additionally, the boiler water has to be corrosive in nature. In other words, the boiler water chemistry is such that either the oxygen concentration of the water is high or there is deviation in pH of the water from the recommended level.

Corrosion fatigue starts with the initiation of a crack in an otherwise protective magnetite scale due to thermal stresses during the first phase of cyclic loading. These thermal stresses result in expansion of the tube, whereupon the magnetite, insulated and brittle in nature, undergoes cracking. Once a crack is formed, further damage occurs as a result of a fresh attack by the corrosive medium such that the exposed metal at the

root of the crack is oxidized. The oxide layer so formed at the crack root breaks in the next cycle. This cyclic process of formation and breakage of the oxide layer continues until a wedge-shaped crack propagates through the entire thickness of the tube wall and the final rupture occurs or the tube wall is penetrated.

Corrosion fatigue cracks are typically parallel and wedge shaped, relatively wide and blunt. They are typically straight and branched. These cracks are transgranular in nature and usually filled with scales. Cracking due to corrosion fatigue is often found close to regions of physical restraint such as connections to inlet or outlet headers, the toe of the weld, a weld undercut, corrosion pits, notches, or similar other sites. Cracks may initiate from the OD or ID side of the tube. Tubes that have failed by corrosion fatigue normally exhibit a thick-walled fracture. Corrosion fatigue from the ID side is quite often from areas close to attachments such as the tube to header or near external welds. Corrosion fatigue from the OD side is in the form of numerous circumferential cracks. Figure 6.145 gives unetched and SEM views of damage due to corrosion fatigue on the OD side of a tube showing crack initiation and fatigue striations.

Though corrosion fatigue can occur at several locations in a boiler including waterwall tubes, reheater tubes, economizer tubes, or deaerators, the failure takes place where there are cyclic stresses of sufficient magnitude. Areas that are prone to departure from nucleate boiling suffer from corrosion fatigue. Boilers that are operated cyclically or discontinuously (i.e., with a break in operation) have a high probability of corrosion fatigue.

Case Study 33—Failure Investigation of Superheater Tube of a Heat Recovery Steam Generator Unit

Background Details Repetitive failure in the form of leakage was observed in low-pressure superheater bottom header tubes. It was observed that water was leaking from a weld joint of the tube. Minor seepage at a couple of other places had also been reported in the past, and those tubes were already plugged. The tubes were made of ASTM A 192 steel.

Investigation and Findings Visual examination of the tube showed the OD surface exhibiting a loosely adherent reddish brown scale. A crack of discontinuous nature in the transverse direction was seen at the weld joint between the tubes of two different wall thicknesses (Fig. 6.146). The ID side of the tube had a smooth black scale tightly adherent to the surface.

Low-magnification examination using a zoom stereo microscope indicated cracks on the outer surface of the tube in a transverse direction with a stepped nature, which were filled with scales (Fig. 6.147a). The surface surrounding the crack had grayish deposits scattered on the scale (Fig. 6.147b).

A microstructure study was carried out at different locations on both the thin and thick tubes as well as at the weld joint of the sample. Figure

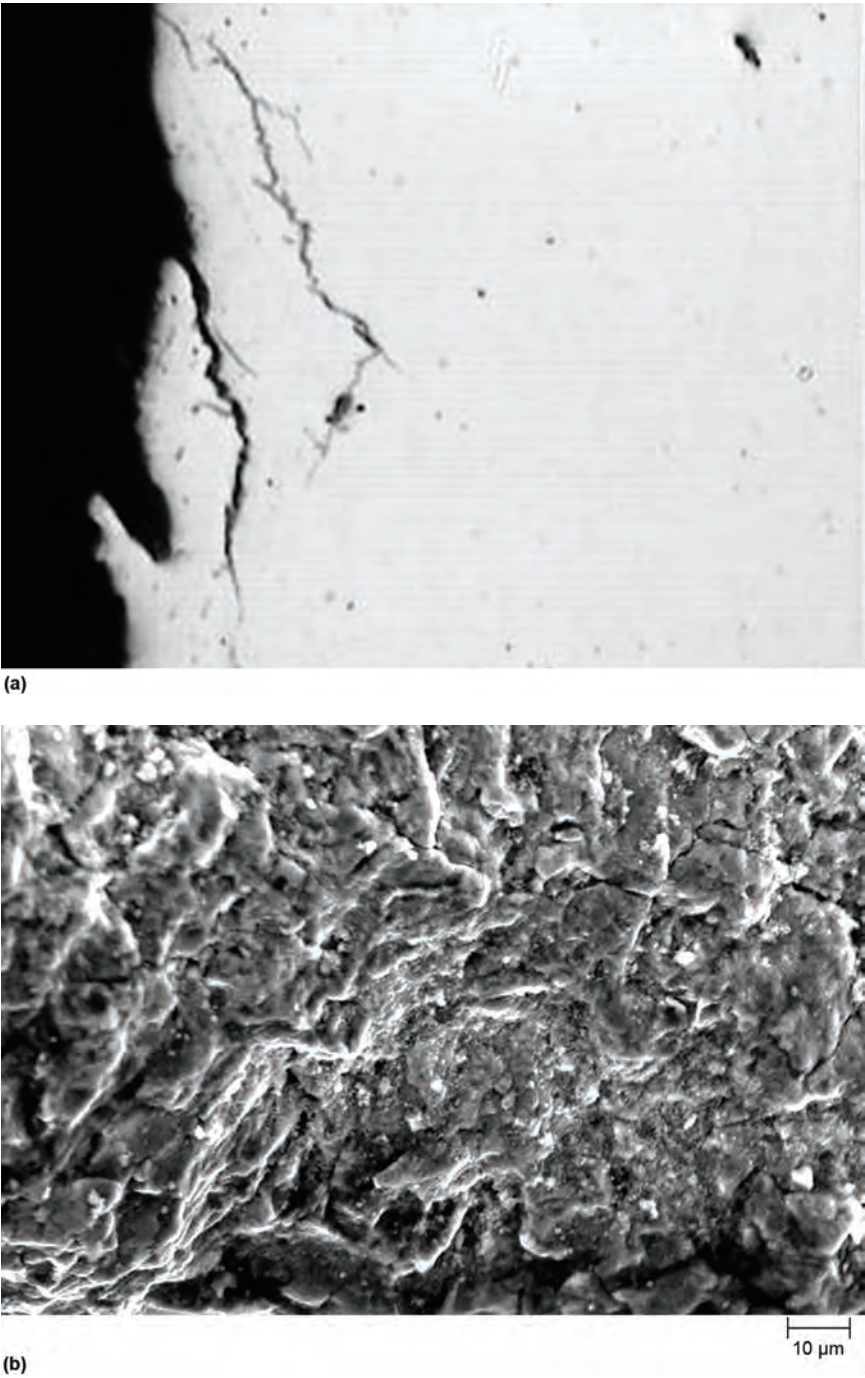


Fig. 6.145 (a) Unetched micrograph indicating wedge-shaped fine hairline cracks emanating from the surface, 100×. (b) SEM image showing fatigue striations for corrosion fatigue failure, 1000×



(a)



(b)

Fig. 6.146 (a) Weld joint with a hairline crack on weldment. (b) ID surface view showing tightly adherent smooth black scale

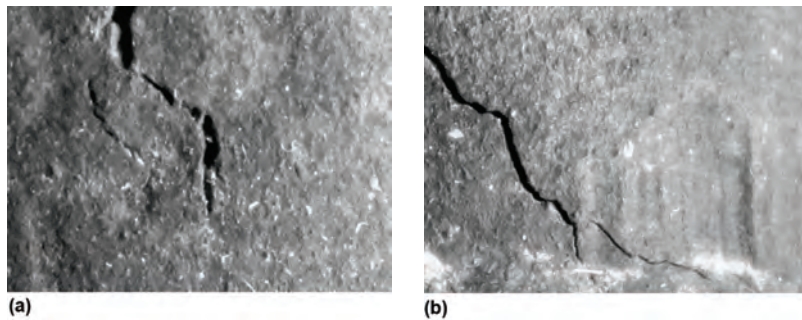


Fig. 6.147 Low-magnification views of outer surface showing (a) transverse cracks, 50 $\times$; and (b) surface surrounding the crack, 13 $\times$

6.148(a) and (b) shows the microstructure of the fracture surface of the thin and thick tubes at the ID, indicating branched hairline cracks filled with oxide scales originating from the damaged ID surface. Figure 6.148(c) and (d) shows the etched view of the weld and heat-affected zone, respectively, revealing a network of hairline-type branched cracks filled with oxide scales within the matrix exhibiting a dendritic pattern of ferrite and carbides.

A scanning electron microscopy analysis was conducted around the crack region to identify the mechanism of failure. The fracture surface at the OD edge showed multiple ratchet marks pointing toward a multiorigin type of failure under cyclic loading (Fig. 6.149a). The fracture surface also exhibited the presence of deposits or scales due to corrosion. The fracture surface at a higher magnification under SEM showed fatigue striations with corrosion deposits or scales (Fig. 6.149b).

Energy dispersive spectroscopy analysis on the ID surface showed the presence of oxygen, magnesium, silicon, sulfur, chlorine (as chloride), potassium, calcium, iron, and copper on the ID (Table 6.18). Energy dispersive spectroscopy analysis on the OD surface showed the presence of oxygen, magnesium, silicon, chromium, and iron. The EDS analysis indicated the influence of flue gases and water chemistry in causing the corrosion damage.

Scanning electron microscopy confirmed the initiation of failure from the OD surface with multiple ratchet marks. The fatigue striations confirmed the movement of the crack under the influence of fluctuating stresses. Indications of scales were seen on both the OD and the ID surfaces of the tube. Furthermore, the secondary cracks were filled with scales, indicating that the cracks had not formed under a single start-up and shutdown. The repetitive nature of the failure at the same region was indicative of a restriction in thermal expansion that generated stresses during start-up and shutdown. The location of the failure was at a local higher hardness zone (i.e., near a weld) with a change in cross section, as tubes of two

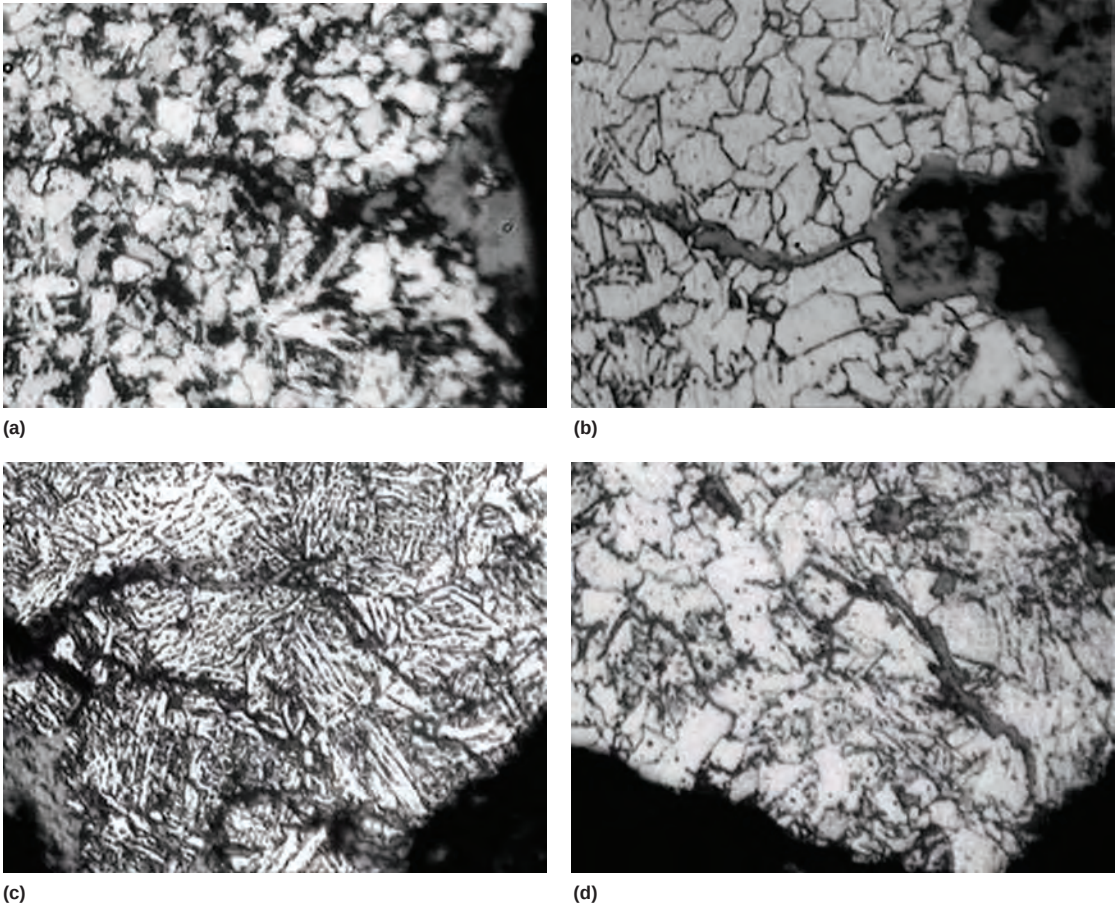


Fig. 6.148 ID side of the fracture surface of thin and thick tubes having network of cracks filled with oxide scales, (a) 400×, (b) 400×. Weld and heat-affected zone microstructure having network of cracks filled with oxide scales (c) 400×, (d) 400×

different thicknesses had been welded. The failure had occurred from the heat-affected zone of the weld toward the lower-thickness tube.

Conclusions The leakage of the superheater tube was due to corrosion fatigue. The failure had initiated from the OD surface at the location of the weld joint due to prevailing operational stresses emanating from restriction in free movement in that region.

Creep-Fatigue Interaction

Creep-fatigue interaction is a complex process of damage involving creep deformation and cyclic stresses, and the predominant damage mode can range from fatigue crack growth at higher frequencies and lower temperatures to creep damage where exposure times are long and the temperature is at the high end of the scale.

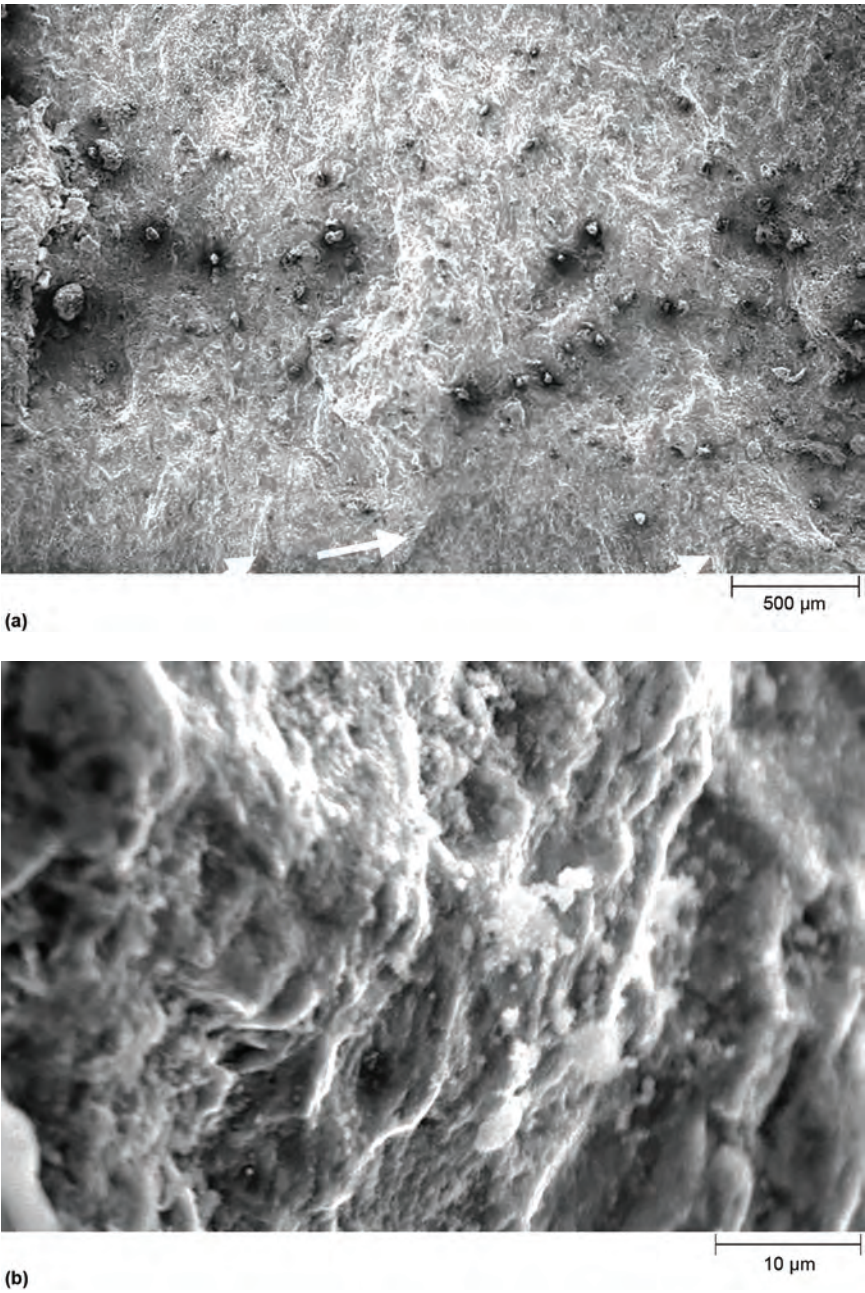
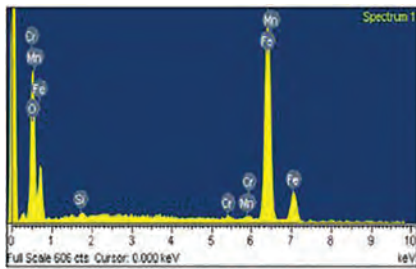
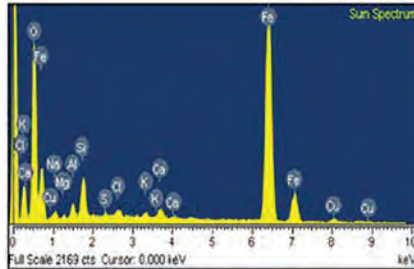


Fig. 6.149 SEM fractographs showing (a) fracture surface at OD edge with multiple ratchet marks, 35 $\times$. (b) Fatigue striations with corrosion deposits/scales, 2000 $\times$

Table 6.18 EDS analysis of OD and ID surfaces of the tube**(a) EDS profile of OD surface****(b) EDS profile of ID surface**

Element	Surface amount, wt.%		Element	Surface amount, wt.%	
	OD	ID		OD	ID
Oxygen	29.25	32.67	Sulfur	...	0.29
Sodium	...	1.88	Chlorine (as chloride)	...	0.61
Magnesium	0.66	0.39	Potassium	...	0.38
Aluminum	...	1.44	Calcium	...	0.82
Silicon	0.60	3.66	Iron	69.00	56.12
Chromium	0.49	...	Copper	...	1.74

Operation-Related Failures

This section briefly discusses three operation-related failures of boiler tubes.

- Failures due to operational problems:
 - a. Rapid start-ups
 - b. Excessive load swing
 - c. Excessive heat inputs
- Failures due to poor water chemistry control
- Water-treatment-related failures:
 - a. Conventional treatment
 - b. All volatile treatment (AVT)

Failures Due to Operational Problems

Apart from the reasons already discussed, boiler tubes also fail because of maloperation of the boiler. Maloperation of the boiler normally includes activities such as rapid start-ups, improper warm-up procedures, excessive load swings, and excessive heat inputs, which in turn lead to short-term overheating, resulting in failure of a tube.

It is necessary to follow the protocol for start-up, operation, and shut-down as recommended by the manufacturer for a steam boiler. The

start-up and the shutdown procedures should be carried out in such a way that the stresses developed at the points of stress concentration do not exceed the maximum allowable values.

Improper warm-up procedures can develop high stresses of a different magnitude in various areas of boilers such as drums and tubes. Because materials with different metallurgy are involved in the manufacture of different components of the boiler, their thermal behavior in terms of thermal expansion and contraction differs significantly, resulting in unequal stresses. The problem is magnified when a particular single material or component is exposed to different temperatures at the same time. Rapid warm-up can result in damage of the refractory as well.

Over-firing of the boiler is another issue that can lead to tube failures. Boilers are quite often run beyond their maximum continuous rated (MCR) capacity. They may be subjected to continuous operation for several hours at 110% of their MCR. Attention may not be paid to the safe working of the auxiliary equipment and other components of the boiler. Without giving due importance to the self-limiting capability of auxiliary equipment, power plant management may insist on running the plant at 110% of the MCR or beyond in order to maximize production. This often results in continuous and sometimes severe over-firing of the equipment, leading to tube failure.

Failures Due to Poor Water Chemistry Control

Boiler feedwater comprises make-up water and condensate returns. The contamination of boiler feedwater (BFW) can be a slow, degenerative process or an instantaneous, catastrophic event.

Boiler water chemistry control has a major role to play in averting boiler tube failure. Boiler water chemistry control is a very vast subject by itself, but essentially covers control of parameters such as dissolved oxygen level, total iron and copper content of water, pH and hardness of water, oils and resins, and other chemicals used in boiler water treatment. Failure to control these parameters can result in tube failure by these mechanisms. For example, the presence of dissolved oxygen in BFW beyond a maximum permissible limit is the cause of tube failure due to oxygen pitting in the form of a localized attack. The buildup of material in the form of deposits because of the ingress of contaminants in feedwater over a period of time results in poor heat transfer across the tube wall and finally gives rise to tube failure due to overheating. Similarly, carryover of caustic salts causes under-deposit corrosion of the boiler tubes.

When a chelant-based boiler water treatment program is exercised to control the BFW quality, it has to be carried out precisely. An excess of chelating chemicals with large amounts of sodium salts can result in problems by way of chelant corrosion. The resultant attack is in the form of dissolution or thinning of metal from the contacting tube surface, and takes place preferentially at areas of high stress.

Likewise, inadvertent use of acids and caustic chemicals can cause damage to the boiler. The presence of either of these chemicals can cause corrosion of the boiler tubes.

The failure of any process equipment such as heat exchangers and pumps is normally a source for ingress of oils and process chemicals into the condensate system. Once the condensate system is contaminated, there is a risk of catastrophic failure of such process equipment. This in turn leads to the introduction of undesirable chemicals or compounds into the boiler.

Boiler feedwater is subjected to ion exchange treatment for softening purposes. A failure of the ion exchange system can contaminate the BFW with ion exchange resin. Eventually, a layer of such resin is formed over the tube surfaces. Based on the nature of the resin used, it can give rise to either acidic or basic conditions leading to corrosion of the boiler tubes.

Water-Treatment-Related Failures

Boiler feedwater consists of returns from condensate, known as condensate water, and make-up water. Feedwater, before being fed to the boiler, is subjected to chemical treatment for two reasons. The first is to prevent the buildup of solid deposits (i.e., scaling over the ID surface of the tubes); and the second is to protect them from corrosion. An absence of adequate external and internal treatment of the BFW leads to operational upsets or unscheduled outages.

Normally the source of make-up water is raw water received through city lakes, reservoirs, or wells, which contain several impurities, including carbon dioxide. As the condensate cools, carbon dioxide dissolves in the water to form carbonic acid, with a range of pH from 6.9 to as low as 4.5. Additionally, raw water contains impurities such as dissolved solids comprising compounds of calcium, magnesium, and silica, which precipitate at high temperatures, forming a coating, popularly termed a *scale*, on the ID side of the boiler tubes. Sources of impurities include condenser cooling water, process condensate, pretreatment or make-up water, chemical feed impurities, and leakages from utility equipment such as pump seals. In view of their insulating nature, scales raise the tube wall temperature and eventually lead to failure of the tube by overheating. Therefore, optimizing BFW purity is the first step toward minimizing corrosion and deposition in the boiler. Treatment of feedwater brings down the level of total dissolved solids to within acceptable limits. The feedwater for industrial boilers operating at low pressures is treated simply using water softeners. However, when a boiler is operated at high pressure or ultra-high pressure and temperature, matters are not as simple. As the operating pressure and temperature of the boiler increase, the conditions for feedwater treatment become more stringent. In such circumstances, a more complex feedwater treatment involving the use of processes such as reverse osmosis and

the use of demineralizers is required. Additionally, a suitable blowdown system must be installed to remove solids from the feedwater.

The second objective of feedwater treatment is to protect the boiler from damage due to corrosion. One of the reasons for corrosion of boiler tubes is dissolved gases such as oxygen, carbon dioxide, and ammonia in BFW, of which oxygen is the most important from a corrosion point of view. Make-up water contains considerable amounts of dissolved oxygen. The higher the amount of makeup water in the feedwater, the higher the amount of impurities and dissolved oxygen. Dissolved oxygen is the main cause of corrosion by oxygen pitting. It is a constant threat to the feedwater heater, economizer, and boiler tube integrity. Once dissolved oxygen is removed from the feedwater by using deaerators, the potential for corrosion drastically decreases. Additional protection against corrosion can be ensured by injecting chemicals such as hydrazine, known as oxygen scavengers, into the deaerator.

A chemical treatment program for low- and medium-pressure boilers follows a conventional phosphate treatment approach, whereas in the case of conventional fossil-fuel fired boilers, AVT or oxygation treatment is preferred.

In phosphate treatment, phosphate is added in the form of disodium phosphate (DSP) to precipitate calcium entering from the feedwater. Because the solubility of calcium phosphate is less than that of calcium carbonate, DSP when added precipitates calcium as calcium phosphate and thus helps in preventing the formation of calcium carbonate deposits as a scale on the water side of the boiler tube. Organic polymers used in conjunction with the phosphate condition disperse the suspended solids and allow them to be removed through blowdown without depositing them on the boiler tubes.

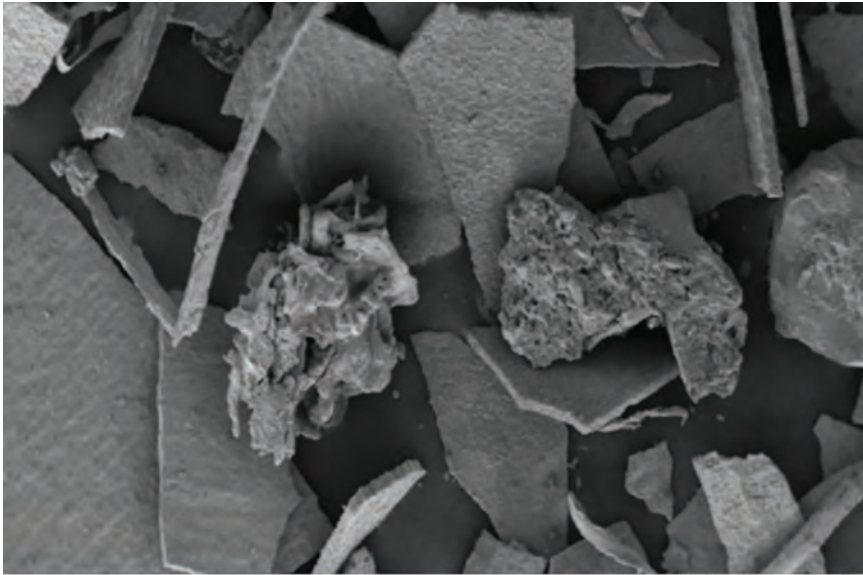
The AVT program is used for very-high-pressure boilers operating above 16.0 MPa (2.3 ksi) pressure. High-purity feedwater should be used, and the condensate water must be subjected to polishing before use to restrict the ingress of any impurities such as salts, silica, chloride, sulfate, and sodium contaminating condensate water as a result of condenser leaks. Oxygen scavengers such as hydrazine are used along with volatile amines including hydroquinones, hydroxylamines, and ketones to keep dissolved oxygen typically below 5 ppb in an AVT program. No nonvolatile solids are permitted when AVT is implemented.

Case Study 34—Characterization of the Scale Formed in Superheater Tubes and Investigation of Its Exfoliation Behavior

Background Details Frequent and recurring failures were taking place in the superheater tubes of a once-through boiler. A preliminary investigation revealed that debris in the form of a scale had accumulated in different portions of the superheater tubes, resulting in choking of the tubes and subsequent starvation. The SA 213 Grade 347H steel constituting one part



(a)



(b)

134.37/403.12 μm

Fig. 6.150 (a) Close-up view of the scale with grayish black color. (b) SEM image revealing plate-like and spongy morphology of particles, 75 $\times$

of the tube was welded to a SA 213 Grade T91 steel tube as the other part, forming a dissimilar weld joint. The tube dimensions were 42.0 mm (1.6 in.) OD and 7.5 mm (0.3 in.) thickness.

Investigation and Findings Visual examination of the sample revealed that the scale was grayish black in color with mostly subangular and flake-type particles. The average particle size of the scale was 160.2 μm with 7.9 and 417.3 μm as the minimum and maximum sizes, respectively. The morphology of the scale particles was further examined using SEM. The scale particles exhibited a mixed morphology, plate-like and spongy. Figure 6.150(a) and (b) displays the morphological characteristics of the scale. It was also found to be magnetic in nature.

The plate-like particles of the scale were subjected to higher-magnification studies of their thickness to examine the multilayered nature of the scale and also to measure the thickness of different layers. Figure 6.151 shows the thickness measurements performed using SEM.

The scale sample was subjected to chemical analysis using x-ray fluorescence spectrometry and EDS to determine its composition. Tables 6.19 and 6.20 list the results of these studies.

For the purpose of phase identification, the scale sample was subjected to x-ray diffraction (XRD) analysis using a powder x-ray diffractometer, and the results of analysis are shown in Fig. 6.152 and Table 6.21.

Discussion Energy dispersive spectroscopy and XRD analysis of the scale confirmed that the scale formed in the superheater tubes comprised oxides of different metallic elements where iron oxides in the form of Fe_3O_4 (magnetite) and Fe_2O_3 (hematite) were predominant. Chromium oxide was

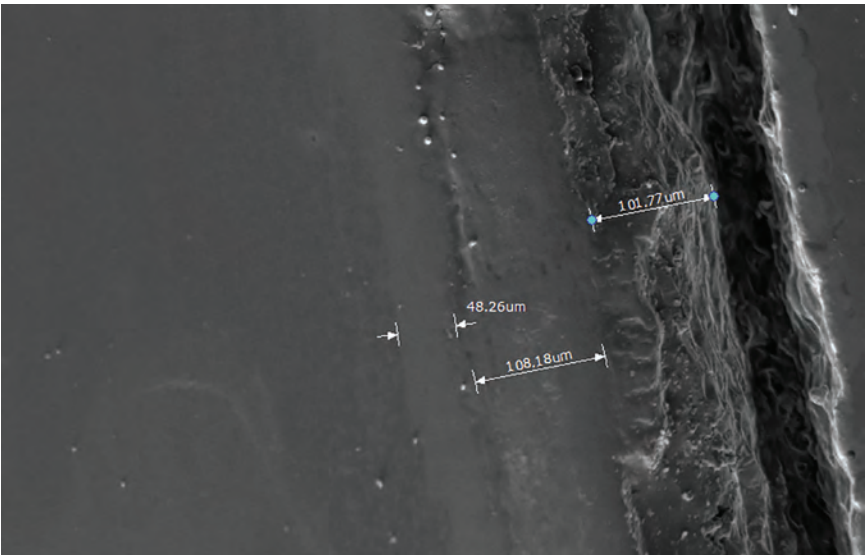


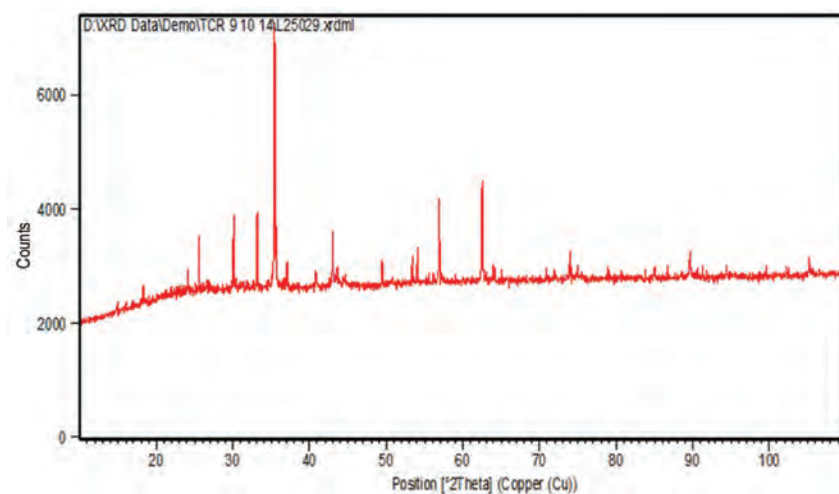
Fig. 6.151 SEM image showing thicknesses of multiple layers of plate-like particles

Table 6.19 X-ray fluorescence spectrometry analysis of scale sample

Element/Compound	Amount by wt.%	Element/Compound	Amount by wt.%
SiO ₂	0.68	ZnO	0.025
SO ₃	0.25	Al ₂ O ₃	0.21
CaO	0.011	MgO	0.16
MnO	0.43	K ₂ O	0.035
Na ₂ O	0.74	FeO	11.26
P ₂ O ₅	0.25	Metallic Fe	7.95
Cr ₂ O ₃	2.62	Total Fe	64.60
NiO	1.74	LOI	4.98
CuO	0.034		

Table 6.20 EDS analysis of scale sample

Element	Amount by wt.%	Element	Amount by wt.%
Oxygen	15.79	Chromium	1.38
Aluminum	0.76	Iron	79.13
Silicon	0.75	Nickel	0.19

**Fig. 6.152** X-ray diffraction profile of scale sample showing different diffraction peaks

also present. Traces of alkali and alkaline earth element oxides were due to impurities carried with the steam. The presence of copper, zinc, and nickel oxides in the form of deposits was due to carryover.

The presence of hematite, magnetite, and chromium oxide in the scale was in line with the oxidation behavior of alloy steels at elevated

Table 6.21 X-ray diffraction analysis of scale sample

Position (2θ)	Relative intensity	d-spacing	Phase(s)
18.2849	9.27	4.84802	Magnetite
24.1257	12.75	3.68591	Hematite
25.5403	22.25	3.48488	Unidentifiable peak
30.0444	31.23	2.97191	Magnetite
33.1204	28.25	2.70259	Hematite
35.3849	100.00	2.53465	Magnetite
37.0185	9.98	2.42646	Magnetite
40.8108	6.22	2.20931	Hematite
43.0092	20.07	2.10133	Magnetite
43.5767	7.89	2.07528	Hematite
44.5318	3.56	2.03296	...
49.3934	9.07	1.84364	Hematite
50.6756	2.97	1.79996	...
53.3610	9.98	1.71553	Magnetite
54.0249	12.89	1.69601	Hematite
56.9319	28.78	1.61611	Magnetite
62.5170	36.02	1.48448	Magnetite/hematite
63.9587	6.40	1.45445	Hematite
73.9615	6.96	1.28053	Magnetite
89.5953	9.40	1.09324	Magnetite
105.2101	5.61	0.96958	...

temperature. Some salient features are described here to establish the mechanism of scale formation in the subject boiler.

The scale formed consisted primarily of three different layers. The innermost layer next to the metal was (Fe,Cr)₃O₄, the next layer was magnetite (Fe₃O₄) of a relatively porous nature, and the dense outermost layer was hematite (Fe₂O₃); sometimes wustite (FeO) was the dense outermost layer, depending on the oxidizing conditions. The chromium oxide had a strong propensity to form a spinel type of structure with iron oxide adjacent to the substrate.

The thickness of the scale formed on internal surface of the tubes was temperature dependent; the higher the temperature, the higher the rate of scale formation. It had a parabolic relationship with the time of exposure at elevated temperatures. The higher the temperature and the longer the soaking time, the more the outer layer, which consisted of magnetite and hematite, became porous and susceptible to spalling. The normal steam velocity was sufficient to knock out the scale. Slight fluctuation in the steam velocity and turbulence aggravated the scale spallation further.

The main cause of exfoliation of the scale formed on the inner surface of the superheater tubes was differential stresses and strains developed on different layers of the scale. The strain developed for two reasons: i) the increase in volume as a result of conversion of metal to oxide and

the constraint imposed by the tube dimensions, and ii) differences in the coefficients of thermal expansion among the oxides present in the scale and the substrate material. Under routine boiler load cycling conditions, the outer scale undergoes thermal expansion with a rise in temperature, and has a tendency to develop *compressive strains* in the magnetite layer. However, during shut-down events, *tensile strains* are generated in the magnetite layer that are sufficient to exceed the criterion for through-scale cracking. As a result of the change in the strain pattern from compressive to tensile with respect to temperature, scale delamination takes place. This phenomenon is more pronounced during start-ups and shutdowns. Also, at ambient temperatures, the residual tensile strain in the magnetite layer was significantly higher than that in the spinel layer. Furthermore, any temperature variations or fluctuations can lead to a similar situation. Mechanical stresses such as tube vibration in the event of cleat failures can also provide mechanical force to exfoliate the scale.

Lack of Quality Control or Improper Quality Control

Failures Attributed to Various Defects

The main reasons for the presence of material defects in boiler tubes are a lack of quality control, or improper quality control checks at one or more stages including the manufacturing stage, during on-site fabrication, storage and handling, and installation of tubes. A variety of failures can occur due to material defects, including stress rupture, fatigue, and corrosion. Selection of the wrong material is one of the reasons for failure of boiler tubes. Three major categories of steels—plain carbon steels, chromium-molybdenum-type low-alloy steels, and high-alloy steels including stainless steels—are used as boiler tube material in different areas of the boiler. The choice of steel from a particular category is mainly governed by the service conditions, such as the required creep strength, resistance to thermal degradation, and the scaling temperature. Alloy steels are superior to plain carbon steels in this respect. Inadvertent use of plain carbon steel in superheater and reheater sections instead of alloy steels is a classic case of wrong material selection.

Forming defects very rarely cause tube failures because of inspections of incoming raw material used for tube making, on-line inspections during manufacture, and quality control and testing of the final product. However, forming defects still remain in the tubes if the tube manufacturer has not strictly adhered to the specified fabrication practices or quality control procedures. Forming defects may be in seamless tubes as well as in the welded tube. The most common forming defects in seamless tubes

are laps and seams, inclusions or laminations, and deep tool marks from tube manufacturing operations such as rolling, piercing, and extrusion. Lack of fusion or incomplete fusion of the weldment during manufacture can be the cause of failure of electric resistance welded tubes for boiler-related applications.

Flaws or negligence in the basic design of the tubes can also lead to tube failure. For example, use of an *elbow* instead of a *bend with a generous radius* can be a cause of erosion or erosion-corrosion damage of a boiler tube. Improper boiler water chemistry further aggravates the problem.

Case Study 35—Failure Investigation of Low-Temperature Reheater Tubes

Background Details Low-temperature reheater (LTRH) tubes of a power boiler were damaged while at the workshop. Five tubes were found damaged while bending. All of them were brand-new tubes. The MOC of the tubes was SA 213 Grade T12 steel, and the tube dimensions were 63.5 mm (2.5 in.) diameter and 4.0 mm (0.16 in) thickness. The LTRH had three banks of coils, each bank consisting of 140 coils.

Investigation and Findings Visual examination revealed a smooth outer surface, with a few rubbing marks. No other defects were visible to the naked eye on the outer surface of the bend (Fig. 6.153a). The inner surface had a smooth texture with a thin adherent general form of corrosion. There was a small depression seen on the inner surface, marked by an arrow in Fig. 6.153(b).

Chemical profiling on the tube sample across the cross section revealed slight variations in carbon content (Table 6.22). The carbon content on the ID side was lower than the nominal carbon. This lower carbon content on the inner surface was due to surface decarburization. The MOC of the tube conformed to SA 213 Grade T12.

Energy dispersive spectroscopy analysis on the inner surface showed the presence of oxygen, aluminum, silicon, chlorine (as chloride), calcium and potassium, whereas EDS on the outer surface revealed carbon, oxygen, magnesium, aluminum, silicon, sulfur, calcium, and potassium. These contaminants were due to exposure of the tube to open atmosphere and to the lubricant used during the manufacturing/tube bending operation.

The overall microstructure of the tube sample showed subangular grains of ferrite with a large variation in grain size, and massive and unevenly distributed pearlite colonies (Fig. 6.154a). The matrix near the outer surface was deformed on account of the forming operation and had a fine-grained ferrite and pearlite structure. The elongation of the grains was in the longitudinal direction of the tube. Ferrite grain size was finer toward the outer edge. At alternative test sites, they were not equiaxed, but subangular in nature. Pearlite colonies were massive and uneven (Fig. 6.154b). The microstructure on the inner surface of the tube showed slight surface decarburization (Fig. 6.154c). Here, also, the microstructure consisted of



(a)

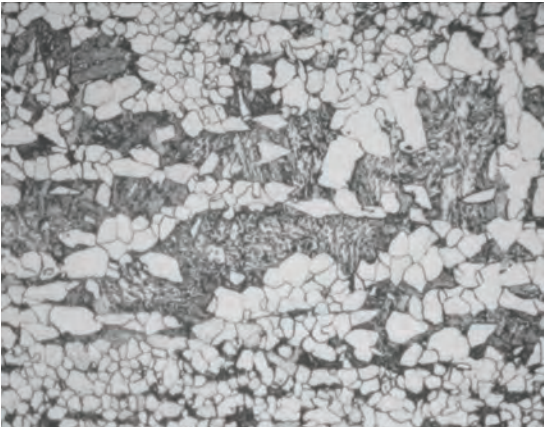


(b)

Fig. 6.153 Close-up views of the (a) outer surface of a tube bend and (b) inner surface with a small depression

Table 6.22 Chemical profiling across the tube section

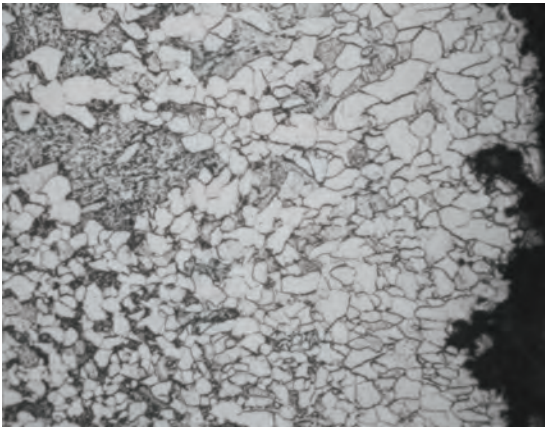
Profiling distance	Amount by wt% of element		
	Carbon	Chromium	Molybdenum
At OD	0.125	0.940	0.474
Distance from OD in mm			
0.5	0.134	0.91	0.473
1.0	0.137	0.91	0.477
1.5	0.144	0.92	0.485
2.0	0.141	0.91	0.475
2.5	0.138	0.92	0.473
3.0	0.140	0.91	0.473
3.5	0.141	0.93	0.473
4.0	0.10	0.91	0.463
At ID	0.0620	0.930	0.463



(a)



(b)



(c)

Fig. 6.154 (a) Overall microstructure of a tube with subangular grains of ferrite and massive and unevenly distributed pearlite colonies, 200×. (b) Deformed fine grains of ferrite and pearlite at outer surface, 200×. (c) Signs of corrosion and surface decarburization on inner surface of the tube, 200×

a nonuniform distribution of massive pearlite and subangular grains of ferrite.

The macro-level metallurgical properties of the reheater tube were satisfactory. The MOC and tensile and hardness values were also acceptable. The tube sample successfully passed the flattening test. The subject problem of tubes damaged during bending was related to heterogeneity observed in the microstructure of the tube material. A small variation in carbon content from point to point was noticed. Coupled with a faulty melting practice and pouring technique, improper heat treatment had resulted in a heterogeneous microstructure in regard to the micro-constituents, ferrite and pearlite. More specifically, the ferrite grain size was grossly uneven; pearlite colonies were massive and did not have a lamellar nature. Moreover, on account of cold bending, the grains were elongated in the bent portion of the tube, signifying a buildup of higher levels of internal stress. With this result, the tube developed a tendency toward microfissures at the time of bending, ultimately leading to failure.

Conclusions The failure of the LTRH tubes was attributed to improper cold working practice and post-cold working normalizing heat treatment that resulted in a heterogeneous microstructure with subangular ferrite grains and massive ferrite colonies. Thus, it was a case of tube failure attributed to faulty manufacturing practice.

Case Study 36—Failure Investigation of Economizer Coil Tube

Background Details A tube from an economizer coil failed due to leakage. The failure was noticed during the first hydro test after erection. The tube was never subjected to operation. As per the specifications, the MOC of the tube was SA 210M Grade A1 steel, and the tube dimensions were 38.1 mm (1.5 in.) OD and 4.06 mm (0.16 in.) wall thickness.

Investigation and Findings Visual examination indicated discontinuity on both the ID and OD surfaces. A linear opening in the longitudinal direction was noticed on the outer surface of the tube (Fig. 6.155a). The inner surface exhibited a crack-like discontinuity with a wide opening at the ID in comparison with the OD, and the area surrounding the opening revealed scattered asperities indicating the presence of a scale (Fig. 6.155b). Overall, the inner surface had a yellowish brown scale.

A wet fluorescent magnetic particle inspection on the outer and inner surfaces confirmed the presence of a linear opening in the longitudinal direction of the tube, which was otherwise also noticeable during visual examination.

Scanning electron microscopy analysis of the crack surface showed the presence of scaling and microcracks (Fig. 6.156).

As shown in Table 6.23, an EDS analysis on the crack surface indicated the presence of oxygen, aluminum, silicon, sulfur, chlorine (as chloride), calcium, chromium, and iron. However, they do not seem to have played any significant role in the damage. Energy dispersive spectroscopy after

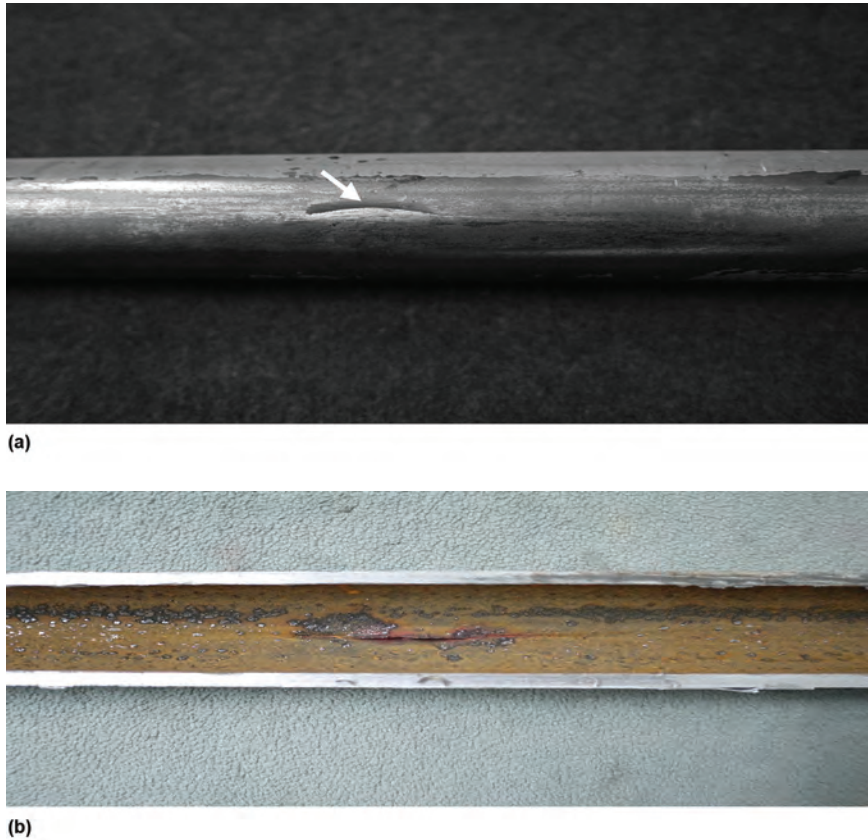


Fig. 6.155 (a) Outer surface of a tube with linear opening in longitudinal direction. (b) Crack-like discontinuity with wide opening on inner surface

metallography into the crack revealed the presence of oxygen, besides silicon and calcium, confirming the nature of the scale to be an essentially oxide scale.

Microstructural examination in the as-polished condition showed the presence of scale entrapment in the form of microcracks filled with scales initiating from the ID surface (Fig. 6.157a). The overall microstructure of the tube was that of ferrite and pearlite. However, the grain size varied toward the ID edge, especially surrounding the scale entrapment (Fig. 6.157b). It was attributed to entrapped scale movement into the tube metal during hot working. No scale entrapment was seen at the OD, except for slight surface decarburization.

The tube metallurgy in terms of the MOC and mechanical properties was satisfactory. Microstructural examination revealed slight variation in grain size near the entrapped scale from the ID surface, pointing toward its genesis from the manufacturing stage. The entrapped scale on the ID surface was due to a deficiency in manufacturing that had a profound influence on the damage. The scale entrapment was due to either lack of

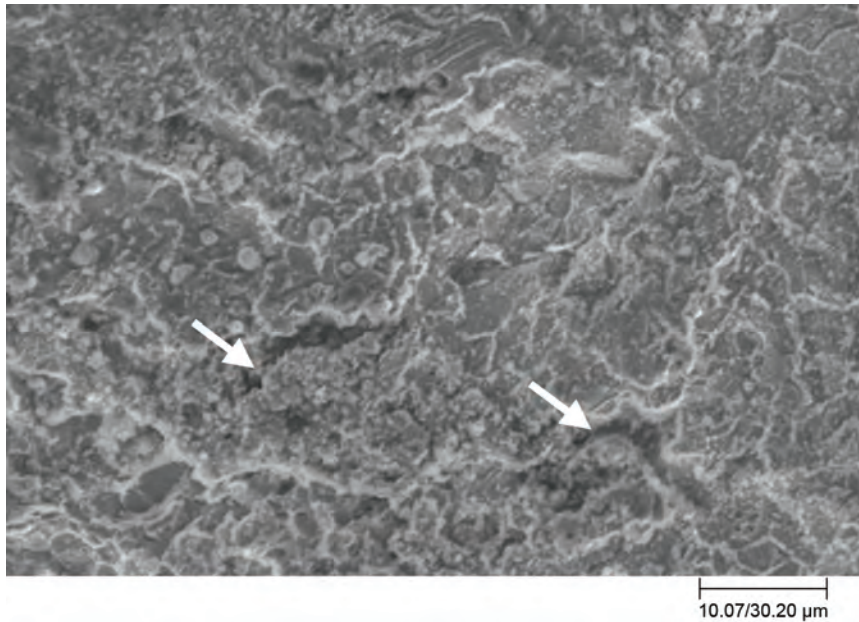
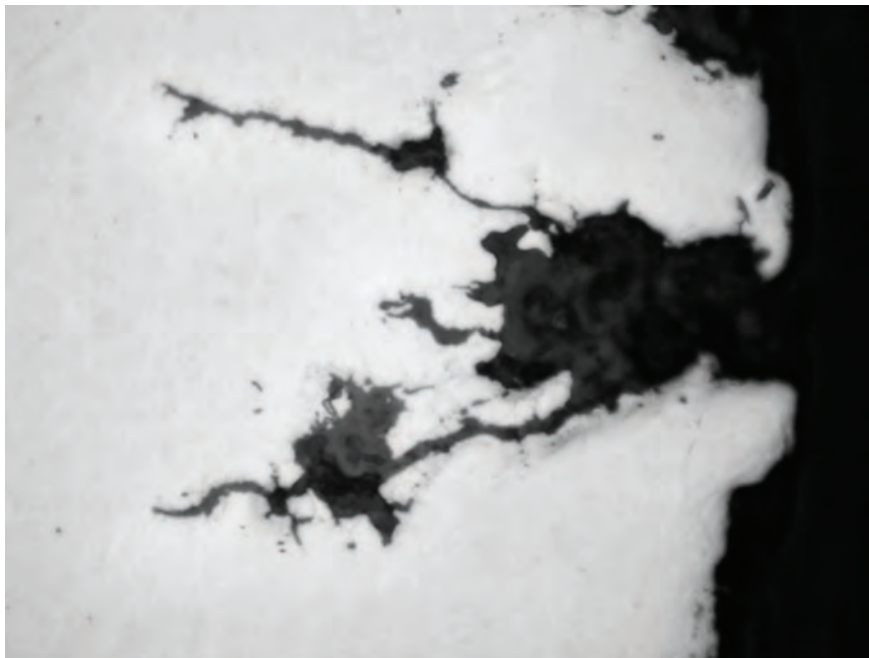


Fig. 6.156 SEM micrograph of the crack surface showing presence of scaling and microcracks, 1000×

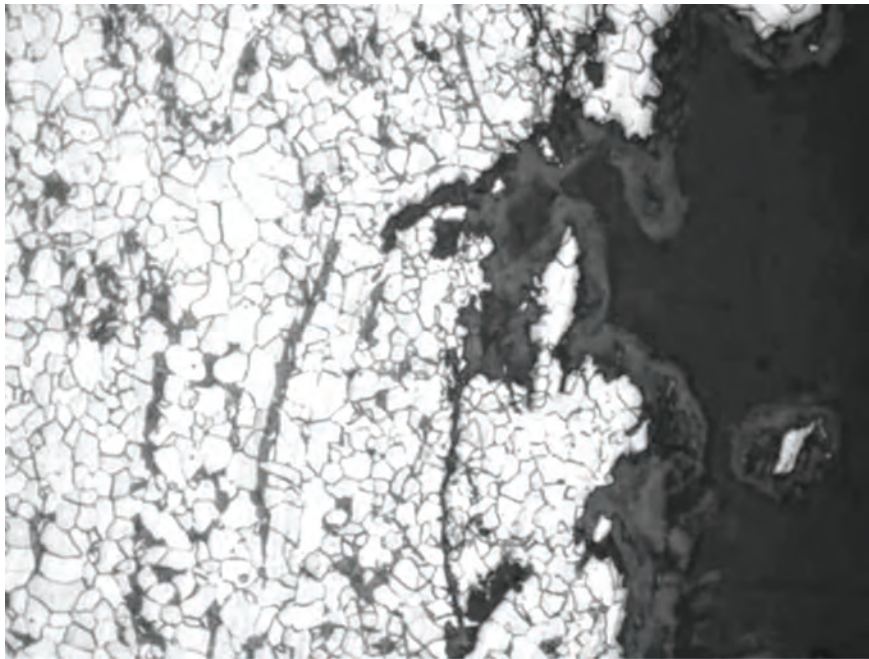
Table 6.23 EDS analysis on crack before and after metallography

Element	Amount, wt.%	
	Crack surface	Inside crack after metallography
Oxygen	13.88	19.91
Magnesium	...	0.52
Aluminum	0.45	...
Silicon	0.61	0.71
Sulfur	...	...
Chlorine (as chloride)	...	...
Calcium	0.33	0.35
Chromium	...	...
Iron	74.41	78.51
Carbon	9.52	...
Titanium	0.80	...

lubrication during hot extrusion or lower temperature during hot working. Subsequently during pilgering, the entrapped scale had a chance to move into the tube matrix to assume the shape of the cracks noticed as branching, filled with scales and uneven contours. The variation in grain size surrounding the crack also corroborated this contention. When a hydro test was carried out, the internal pressure applied permitted unstable crack growth at preexisting defect locations, resulting in leakage.



(a)



(b)

Fig. 6.157 Microstructure on ID surface of a tube: (a) unetched condition showing microcracks filled with scales, 100 $\times$; and (b) etched view toward ID edge showing scale entrapment, 200 $\times$

Conclusions The failure of the economizer tube by way of leakage during a hydro test was on account of scale entrapment resulting in a through and through crack within the tube. Thus, it was a case of failure attributed to a preexisting manufacturing defect.

Case Study 37—Failure Investigation of Site Weld Joint of Superheater Economizer Coil Support Tube

Background Details The site weld joint of a superheater economizer coil support tube of a boiler failed by leakage after a service life of about 5 years. The MOC of the tube was A210 Grade C steel, and the tube dimensions were 38.1 mm (1.5 in.) OD and 4.5 mm (0.18 in.) thickness.

Investigation and Findings Visual examination revealed leakage in the form of multiple punctures precisely at the weld joint, whose quality appeared to be very poor (Fig. 6.158a). The weld crown had an uneven curvature with sharp ripples and deep undercuts. Excessive and nonuniform weld penetration with deep undercuts was noticed on the inner surface (Fig. 6.158b). The inner surface of the tube was rough in texture with a grayish black scale.

The tube sample was subjected to a low-magnification examination using a zoom stereo microscope. Leakage in the form of multiple punctures precisely from the weld location was clearly visible on the outer surface (Fig. 6.159a). The inner surface of the tube showed sharp ripples and deep undercuts, indicating the poor quality of the weld (Fig. 6.159b). The puncture contours on the outer surface were surrounded by erosion damage, which was due to water leakage after the failure.

Macrostructural examination also confirmed the very poor quality of the welding; gross weld porosities and deep undercuts on either side were evident. A through and through crack joining the undercuts was seen, as marked by the arrow in Fig. 6.160. Uneven weld crown curvature as well as excessive weld penetration on the ID side was also visible.

The parent metal microstructure was of a normal banded ferrite-pearlite type. The disturbed banding pointed toward prevailing tube vibrations (Fig. 6.161a). The weld microstructure was acicular ferrite with finely distributed carbides (Fig. 6.161b). The weld exhibited porosity as well. Figure 6.161(c) and (d) shows the ID side view, indicating crack initiation from the ID and corrosion damage, respectively.

Scanning electron microscopy studies indicated initiation of the crack from the ID side and its subsequent propagation in fatigue mode, as confirmed by the presence of fatigue striations on the crack surface (Fig. 6.162). The SEM micrograph also indicated damage due to corrosion by way of localized deposition. Energy dispersive spectroscopy analysis indicated the presence of the usual contaminants attributed to deviation in water chemistry and water carryover.

While the tube metallurgy met the requirements of SA 210 Grade C, the weld joint was of poor quality. It had excessive weld porosity and shrinkage.

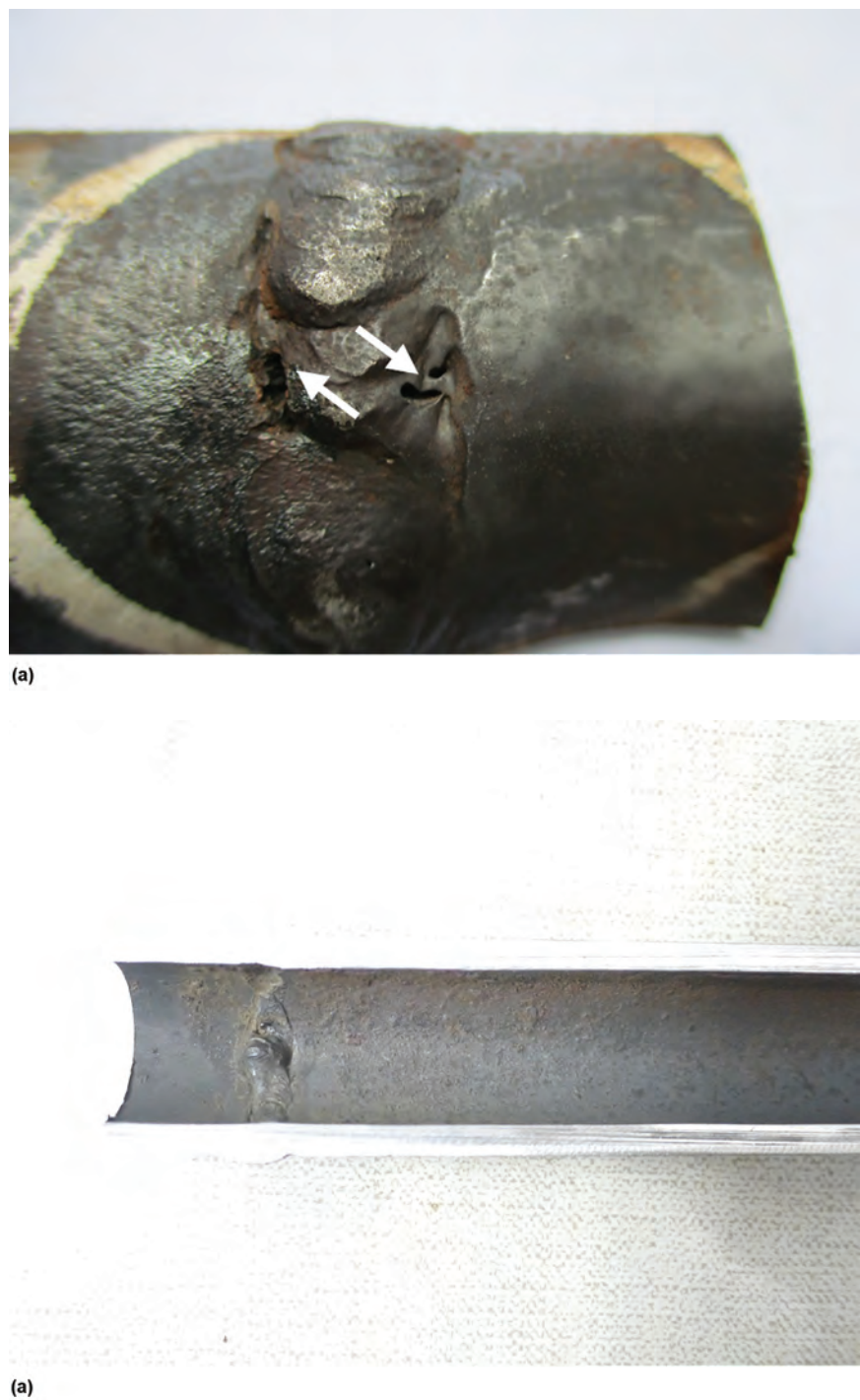
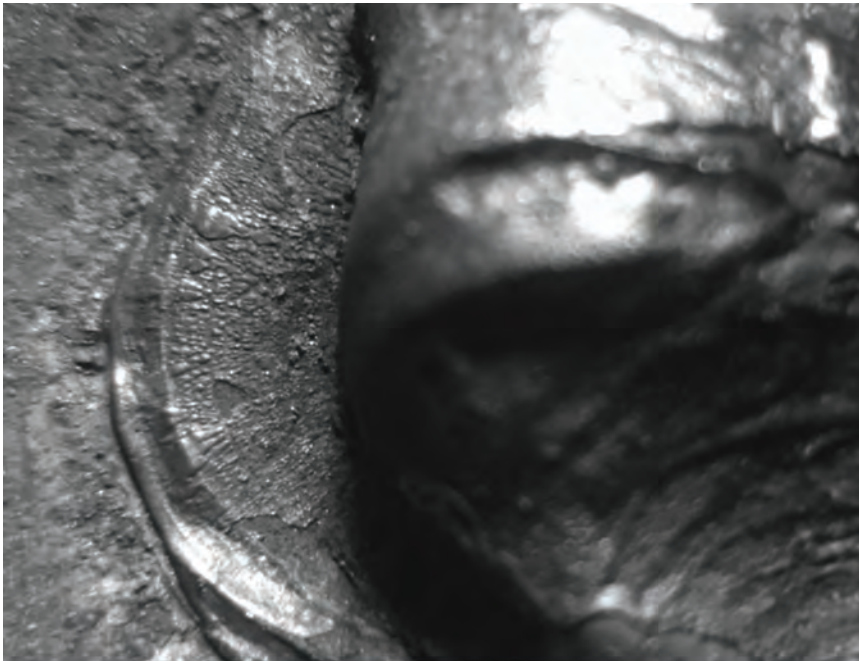


Fig. 6.158 (a) Close-up view of outer surface at failure location showing leakage from the weld joint. (b) Inner surface view at weld location exhibiting excessive and nonuniform weld penetration with deep undercuts



(a)

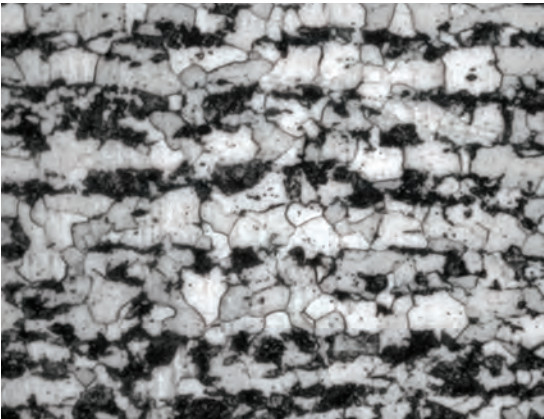


(b)

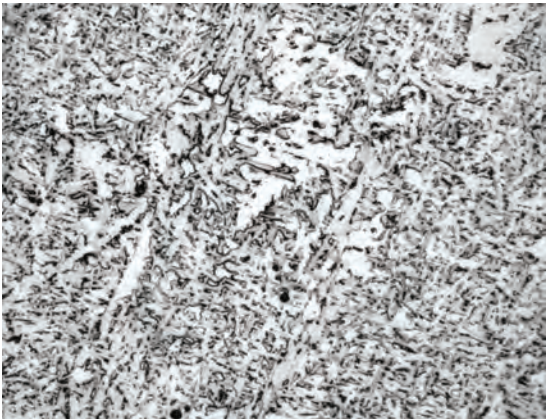
Fig. 6.159 Low-magnification views of the (a) outer surface of a tube with multiple punctures from where leakage had taken place and showing weld crown with nonuniform curvature, 8 $\times$; and (b) inner surface with sharp ripples and deep undercuts indicating poor quality of weld, 8 $\times$



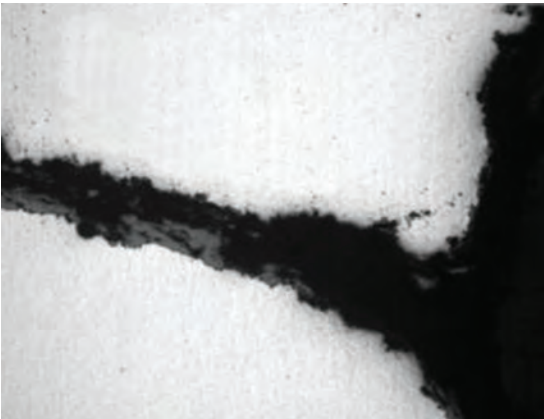
Fig. 6.160 Macrostructure showing longitudinal section view across the weld. The weld shows numerous porosities and through and through crack joining the undercuts from both sides.



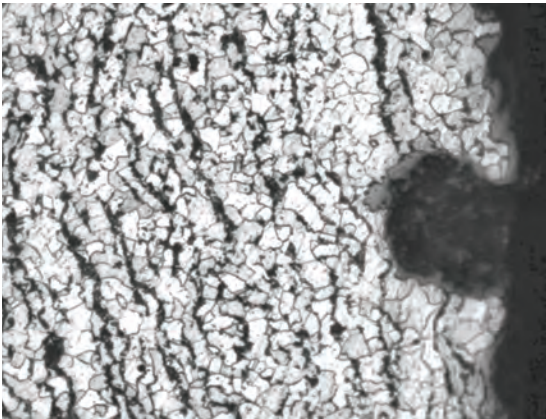
(a)



(b)



(c)



(d)

Fig. 6.161 (a) Parent metal structure of banded ferrite and pearlite, 400 $\times$. (b) Weld microstructure of acicular ferrite with finely distributed carbides, 400 $\times$. (c) Unetched view of ID having crack with wide opening and filled with corrosion product, 100 $\times$. (d) Corrosion on ID surface, 200 $\times$

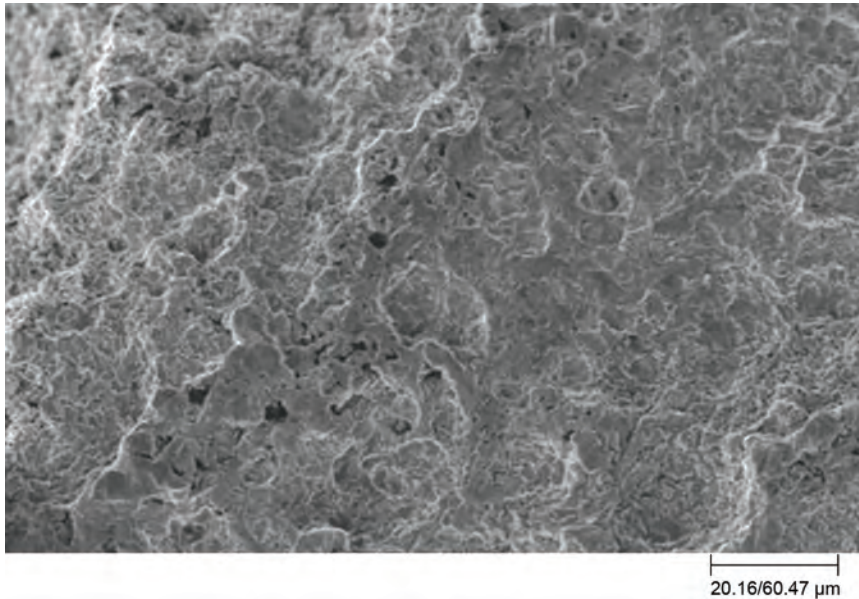


Fig. 6.162 SEM micrograph giving crack surface view. Fatigue striations along with scattered corrosion deposits are shown.

The crown curvature was uneven. There was excessive and nonuniform weld penetration on the inner surface. There were deep sharp undercuts on either side along the entire fusion line, which acted as stress concentration points. The situation was further exacerbated by disturbances in the water chemistry coupled with fluctuating stresses on account of tube vibrations, as well as built-in stresses inside the poor-quality weld joint.

All of this resulted in leakage in the form of punctures because of a through and through crack formed by joining weld undercuts, as well as porosity inside. Finally, the failure took place because of cracking in a corrosion fatigue mode.

Conclusions The superheater economizer coil support tube joint failed due to poor weld quality. Disturbances in water chemistry, stress concentration due to porosity and deep sharp undercuts in the weld, and fluctuating stresses on account of tube vibrations facilitated the failure in the corrosion fatigue mode.

Case Study 38—Failure Investigation of Waterwall Tube

Background Details The waterwall tube of a 620 MW boiler leaked in the form of a pinhole near the junction of a weld between the tube and a fin and a butt weld between the tube and tube attachments. The failure took place after about 6 years of service and was noticed during inspection. The MOC of the tube was per SA 210 Grade C, and the tube dimensions were 66.7 mm (2.62 in.) OD and 9.0 mm (0.35 in.) thickness.



Fig. 6.163 Close-up view of ID surfaces showing puncture located at fusion zone of the butt weld. Uneven weld penetration forming nonuniform ridges at the weld line are shown. The weld metal had excess penetration (as shown by arrow).

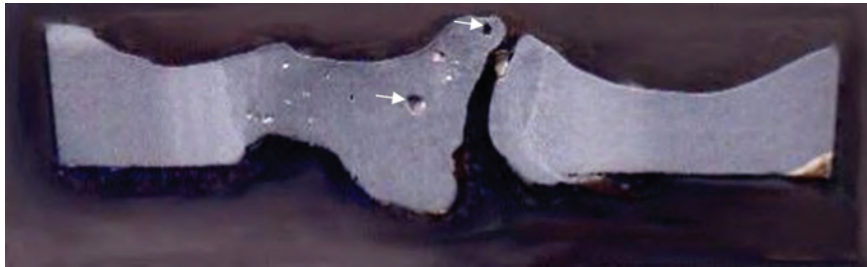


Fig. 6.164 Longitudinal cut section of the tube near puncture, in macro-etched condition showing weld pool having porosities and uneven bead indicating lack of penetration

Investigation and Findings Upon visual examination of the ID surface of the tube, a puncture was seen at the fusion zone of the butt weld (Fig. 6.163). The weld metal had spilled out in the longitudinal direction of the tube, as shown by an arrow in Fig. 6.163. Dimensional measurements did not reveal any tube bulging.

Macrostructural examination revealed the seamless nature of the tube. The cut section at the weld showed the presence of large weld porosities and metal wastage from the OD (Fig. 6.164).

Low-magnification studies on the ID surface of the failed sample clearly indicated that the location of the puncture on the inner surface was almost in the weld region. A portion of the excessive weld that had projected out had been eaten away, forming uneven cavities most likely due to corrosion damage (Fig. 6.165a). A low-magnification view on the outer surface at the puncture location also illustrated that most of the metal in the weld region had been eaten away, exposing the internal porosity (Fig. 6.165b). One such porosity had eventually transformed into a puncture. There was

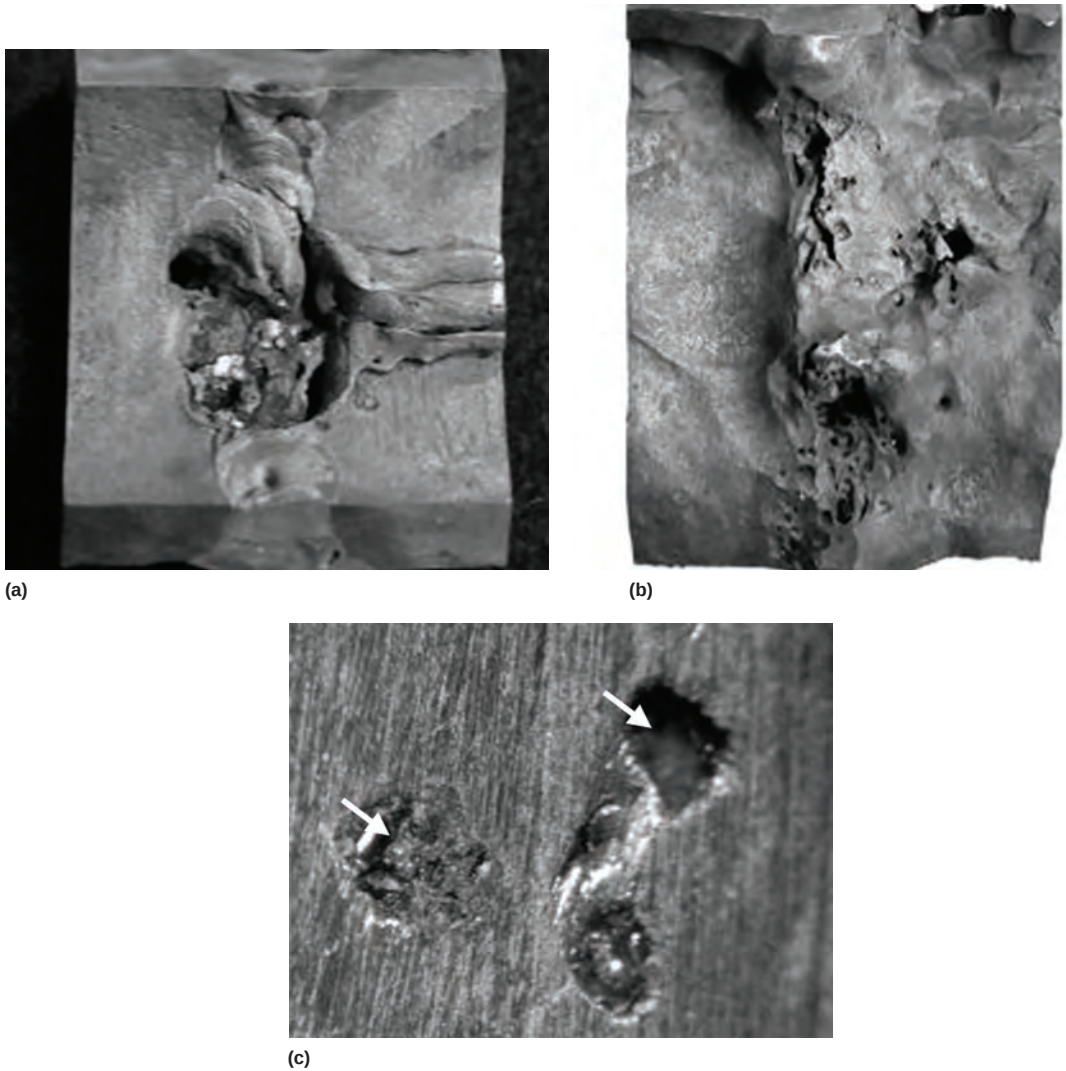


Fig. 6.165 Low-magnification views of inner and outer surface at puncture location indicating nature of damage, (a) 2 $\times$, (b) 2 $\times$, (c) 32 $\times$

corrosion damage in the surrounding area. Fig. 6.165(c) shows a cross section of the weld, highlighting prominent weld porosities.

The failed sample was subjected to microstructural examination at various locations. The parent metal microstructure was banded ferrite-pearlite, a normal microstructure for the tube. The weld microstructure consisted of dendritic ferrite and fine carbides. The weld region showed multiple types of defect such as porosity, undercut, and lack of fusion at the weld interpass (Fig. 6.166a to c). The heat-affected zone (HAZ) microstructure had ferrite and fine pearlite in large amounts, indicating excessive heat input at the time of welding (Fig. 6.166d). Microstructure

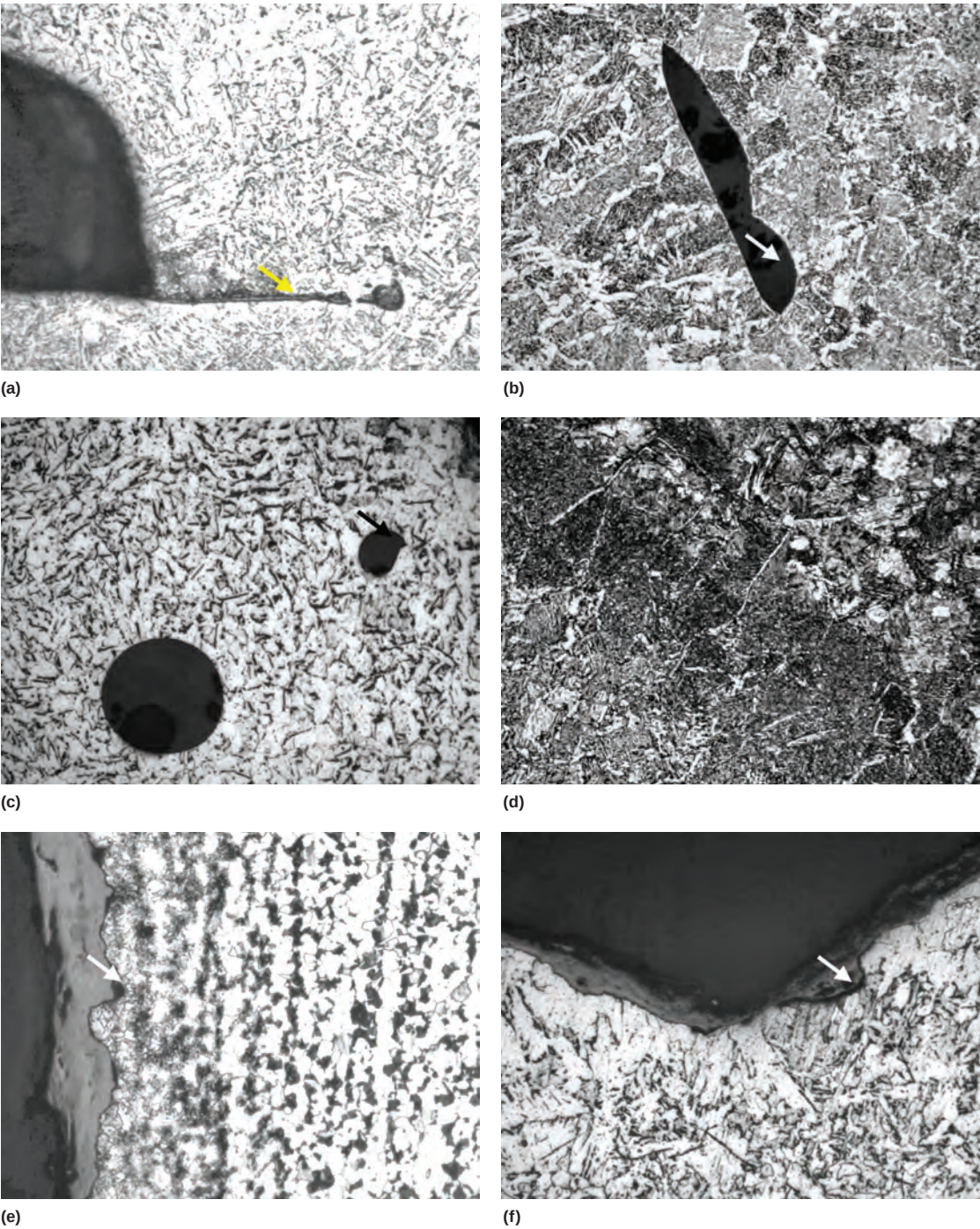


Fig. 6.166 Microstructural defects in weld, (a) 200×, (b) 100×, (c) 200×. (d) Microstructure of the weld, 100×. (e) Microstructure of outer surface near weld, 200×. (f) Puncture contours showing corrosion damage, 200×

studies on the outer surface exhibited fairly aggressive corrosion damage, especially in areas surrounding the puncture (Fig. 6.166e). Puncture contours showed corrosion damage that evidenced the joining of internal weld defects to promote a through-wall leak (puncture) (Fig. 6.166f).

Thus, the butt welding between the tubes reflected poor quality with multiple weld flaws (such as undercuts), lack of fusion, and large porosity. In addition, the weld bead was uneven; it had exceeded the penetration in two locations and the weld pool showed spillage on the ID surface. The improper weld quality forming undercuts and excessive weld projection caused an accumulation of corrosive agents by the formation of a localized stagnant zone—both at the OD and ID surfaces. The alkali and sulfur ion contaminants from flue gases caused fire-side corrosion on the OD surface by forming low-melting alkali pyrosulfate compounds. The corrosion was more aggravated at the weld location due to accumulation of alkali pyrosulfate that eventually exposed the internal porosity. Moreover, during operation, flow-induced vibrations as well as start-up and shutdown cycles linked the defects to form the through-wall leakage. This ultimately resulted in the joining of internal weld porosities and defects, leading to a through-wall puncture and subsequent leakage.

Conclusions The failure of the waterwall tube was due to the poor quality of the welding; the joining of internal defects on account of flue gas (hot) corrosion on the OD surface and operational and start-up–shutdown cyclic stresses finally led to leakage.

Failures Related to Cleaning

Buildup of scales on the water side of a boiler is an inevitable process that takes place progressively over a period of time. Deposition and scale formation occur even if the best possible measures are taken to control the chemistry of the BFW and the condensate. The scale so formed raises the tube wall temperature because the thermal conductivity of the scale (being ceramic in nature) is lower than that of the tube material. Eventually the boiler efficiency decreases. Poor heat transfer across the tube wall due to scale formation leads to a rise in the tube wall temperature beyond its design temperature, finally leading to damage of the tube by creep rupture.

Therefore, scale removal is mandatory in order to ensure efficient heat transfer across the tube walls and for overall protection of the boiler per original equipment manufacturer guidelines.

The basic steps in cleaning a boiler for scale removal consist of mechanical cleaning, water flushing, alkaline treatment, solvent cleaning, and neutralization and passivation. Loosely adherent scales and debris are normally removed by mechanical cleaning and water flushing, whereas oils and hydrocarbons are removed by alkaline treatment. For removal of the scale, inhibited acids are employed as solvent cleaners. At the end

of the solvent cleaning stage, the scale and traces of copper are removed and the fresh metallic surface is exposed. The last step is neutralization and passivation, which removes the traces of the scale and replaces the active metal surface with a passive layer of magnetite.

Chemical cleaning is the most important step from a tube failure point of view. If carried out properly, chemical cleaning helps to improve the boiler heat rate and stabilize the boiler chemistry, which in turn reduces the number of tube failures. However, if the chemical cleaning is not performed properly, it can cause severe damage to the boiler tubes. All types of boiler tube materials are vulnerable to damage due to chemical cleaning. The most frequent reason for damage is lack of neutralization of acidic chemicals utilized during the chemical cleaning process. The acidic solutions used in chemical cleaning, if not completely removed during the neutralization stage, can result in corrosion of the tubes. For example, if there is inadequate flushing, a chemical cleaning agent such as ammoniated ethylene diamine tetra-acetic acid evaporates and reaches the superheaters; this results in failure of the superheater by corrosion. In short, any residual chemical cleaning agent acts as a corrodent and plays a critical role in tube failure.

Failures Related to Maintenance

Case Study 39—Failure Investigation of a Spiraled Waterwall Tube

Background Details Repeated leakage failures at weld locations in the waterwall tubes of a power plant boiler were reported during the commissioning stage. A cut sample of one of the tubes from a leakage location was subjected to detailed investigation to determine the root cause of failure. The MOC of the tube was per SA 213 Grade T12, and the tube dimensions were 35.0 mm (1.38 in.) OD and 6.0 mm (0.24 in.) wall thickness.

Investigation and Findings Visual examination of the failed sample highlighted a pinhole-type puncture at the tube-to-tube butt weld joint, as shown in Fig. 6.167(a). The area surrounding the puncture showed erosion damage on the outer surface due to water leakage. The inner surface of the tube showed a weld region with defects including lack of weld penetration and excessive weld penetration and porosity (Fig. 6.167b). The inner surface showed a rough texture, indicating metal wastage near the weld area.

A transverse cross section of the tube at a few millimeters distance from the leak showed metal wastage on the outer surface projected over a large area (Fig. 6.168a). A low-magnification examination of the inner surface at the weld location indicated poor quality of welding with porosities and deep ripples, as shown in Fig. 6.168(b). Reddish brown localized scale patches were also seen in the low-magnification view.

Macrostructural examination of the longitudinal section at the weld location near the failure confirmed excessive weld penetration on the ID



(a)



(b)

Fig. 6.167 (a) Close-up view of the tube indicating a pinhole-size puncture surrounded by the erosion damage. (b) Inner surface view of tube-to-tube butt weld joint with weld defects and surrounding area with shallow pits

side. There were weld porosities and metal wastage on the outer surface surrounding the weld region (Fig. 6.169).

Scanning electron microscopy studies confirmed that metal wastage was due to erosion on the outer surface. Energy dispersive spectroscopy analysis at the ID near the puncture showed the presence of oxygen, magnesium, and calcium.

Microstructural examination of the tube sample showed that the ID microstructure away from the puncture location consisted of fine grains



Fig. 6.168 (a) Transverse cross section of a tube at a few millimeters distance from the leak indicating metal wastage on outer surface. (b) Poor quality of welding with porosities and deep ripples, 6×

of ferrite and pearlite along with shallow pits formed on the ID surface as a result of oxygen pitting (Fig. 6.170a). The microstructure at the weld location consisted of acicular ferrite and fine carbides, as shown in Fig. 6.170(b). The microstructure also exhibited interconnected porosities and pitting.

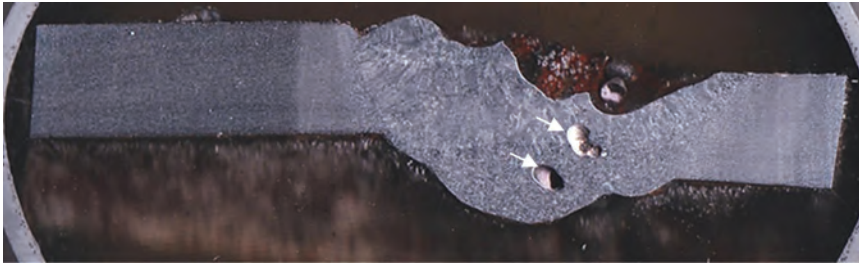


Fig. 6.169 Macrostructure having excessive weld penetration with porosities

The investigation highlighted the poor quality of the tube-to-tube butt weld. It was found to have flaws including weld porosity and uneven welds with both excessive penetration and lack of penetration on the inner surface. There were also uneven weld ripples. The shallow pits observed on the inner surface were a result of corrosion due to oxygen pitting. Oxygen-induced pitting corrosion was also confirmed by the results of the EDS analysis on the inner surface. A microstructure study revealed that the pits formed continued to merge with the weld porosities once initiated from the inner surface as a result of corrosion. Eventually the scattered weld porosity became joined, which led to leakage.

Conclusions The waterwall tube leakage was attributed to the poor quality of welding having uneven weld contours from the inner surface. Merging of the pits formed on the inner surface of the tube with weld porosity on account of corrosion ultimately led to leakage.

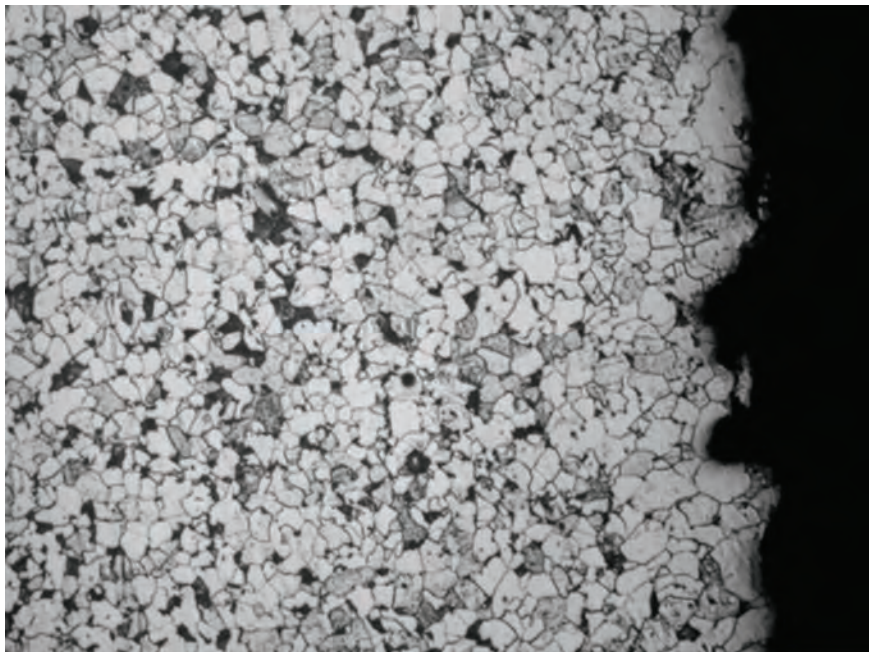
Case Study 40—Failure Investigation of a Final Superheater Tube

Background Details Failure was noticed at the weld joint in a final superheater tube connecting to the inlet header of a boiler during the initial stages of commissioning. The MOC of the tube was SA 213 Grade T91 steel, and the tube dimensions were 42.0 mm (1.6 in.) OD and 6.5 mm (0.25 in.) thickness.

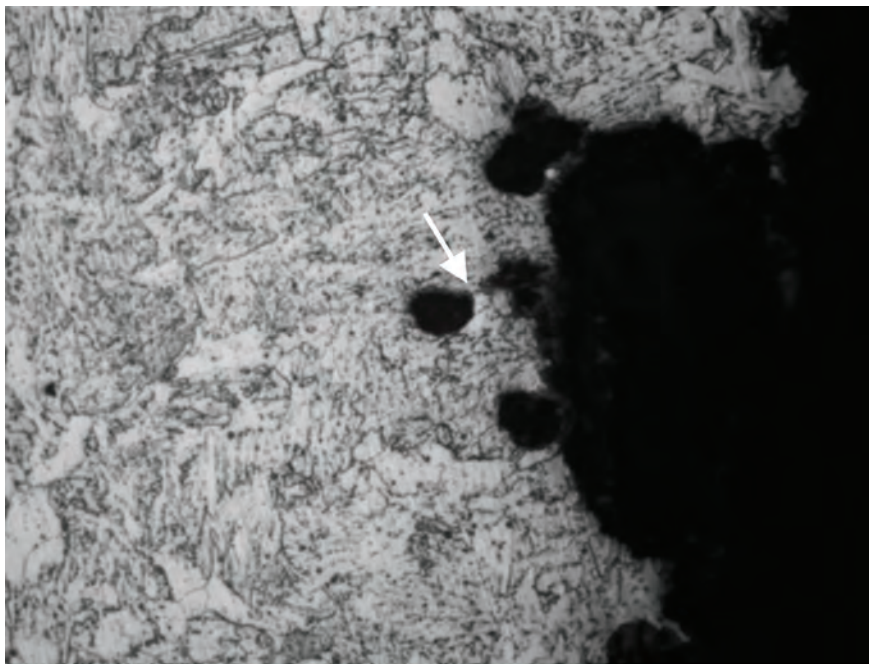
Investigation and Findings Visual examination of the outer surface of the tube revealed a crack in the transverse direction in the HAZ of the weld. The outer surface of the tube showed a brownish scale. Figure 6.171(a) gives the close-up view of the failed tube, showing a transverse crack with irregular contours in the HAZ. A similar crack was also seen on the inner surface in the weld HAZ.

Low-magnification examination on the crack surface revealed the presence of chevron marks emanating from the OD edge, indicating that crack initiation was from the outer surface of the tube (Fig. 6.171b).

Dimensional measurements and an ultrasonic thickness survey on the failed sample did not indicate any significant bulging or reduction in thickness of the tube.



(a)

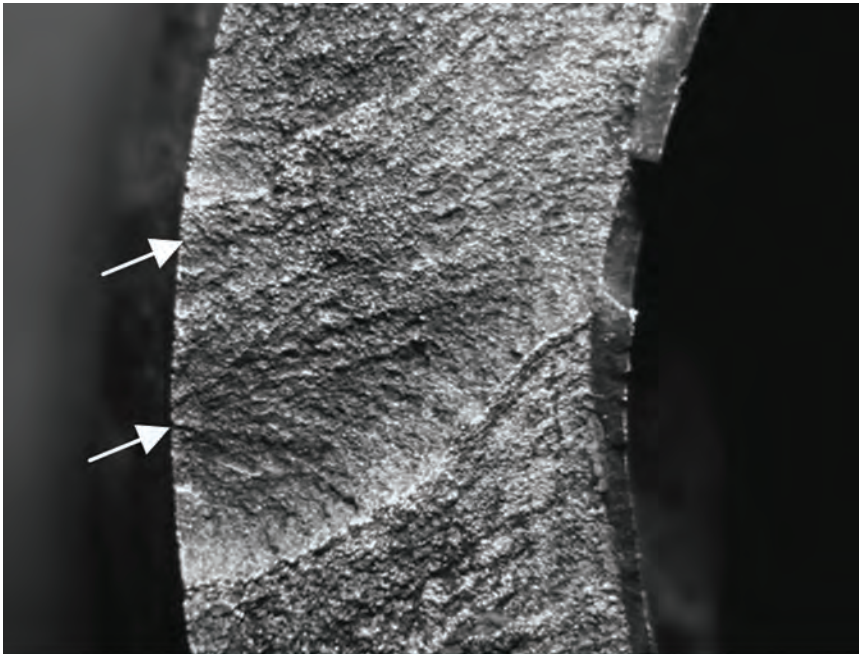


(b)

Fig. 6.170 (a) ID microstructure away from puncture location consisting of fine-grained ferrite and pearlite with shallow pits, 100×. (b) Inner-edge microstructure (acicular ferrite and fine carbides) at weld region indicating merging of pit formed on surface with the weld porosity.



(a)



(b)

Fig. 6.171 (a) Close-up view of the tube indicating a transverse crack with irregular contours in the HAZ of the weld. (b) Crack surface view showing chevron marks emanating from the outer surface

The failed tube sample was subjected to microstructural examination at various locations across the weld. The parent metal microstructure was tempered martensite, which is the normal microstructure for T91 steel in the hardened-tempered condition (Fig. 6.172a). However, the microstructure of the outer edge from where the intergranular cracking occurred, and the HAZ of the weld, comprised martensite that retained an acicular nature (Fig. 6.172b and c).

The tube sample was subjected to microhardness profiling across the weld region. Figure 6.173 and Table 6.24 give the microhardness profile from the weld to the parent metal region of the tube.

The findings of this investigation pointed toward the fact that the metallurgical properties of the weld and HAZ were not up to par. Though the parent metal showed a tempered martensitic structure with normal

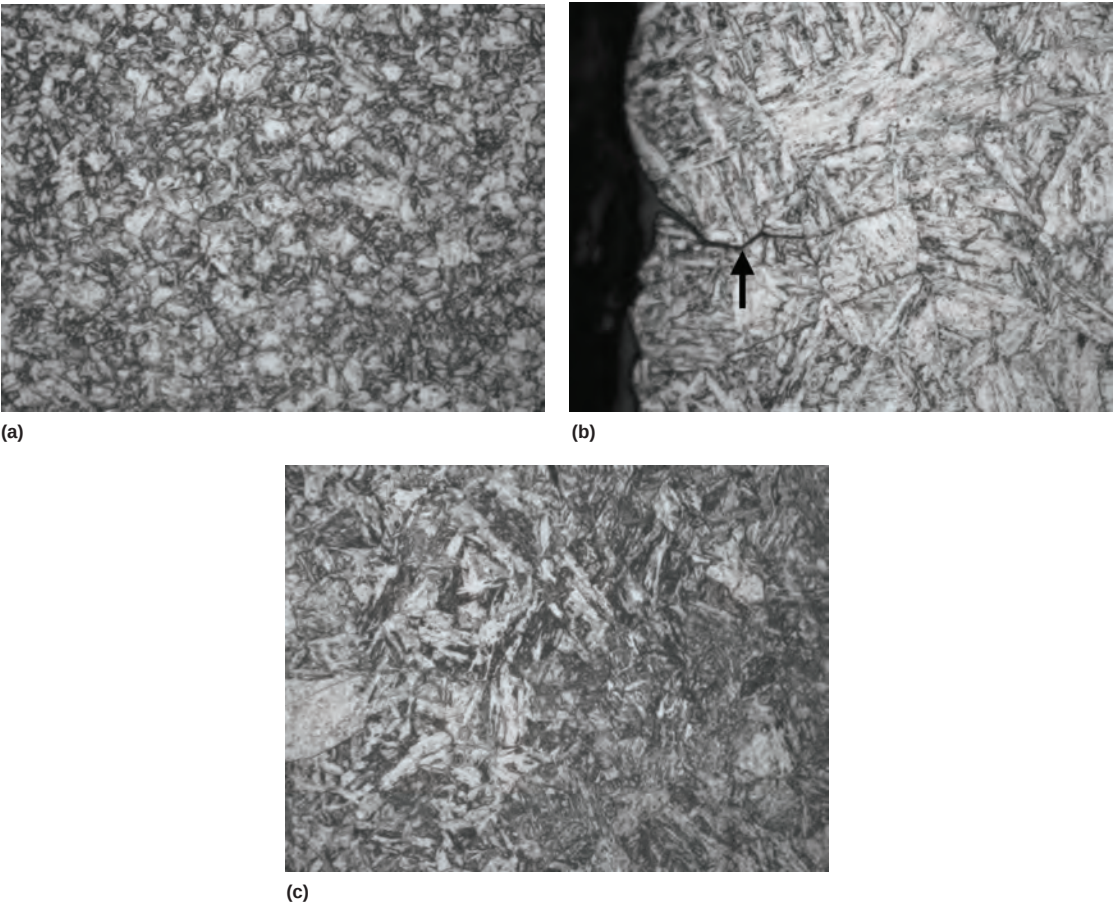


Fig. 6.172 (a) Parent metal microstructure of tempered martensite, 200×; microstructures (b) 400× and (c) 200× are of the outer edge and HAZ consisting of martensite with acicular needles

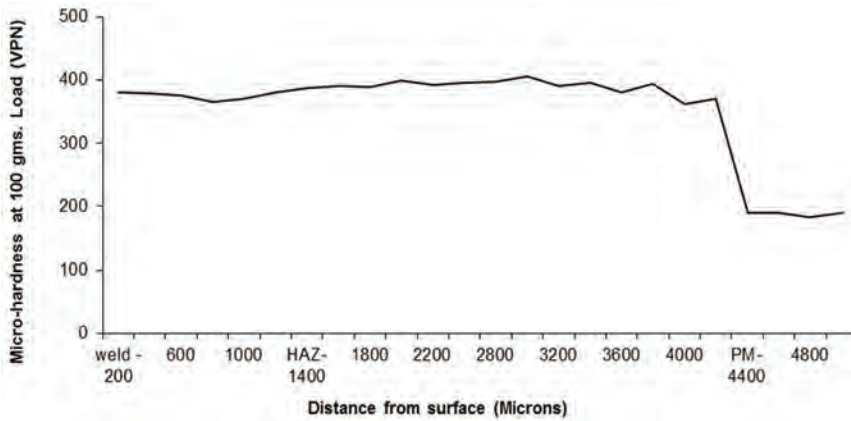


Fig. 6.173 Microhardness profile across the weld region; HAZ, heat-affected zone; PM, parent metal

Table 6.24 Microhardness profile across the weld region

Distance, μm	Microhardness, VPN, 100 g load	Distance, μm	Microhardness, VPN, 100 g load
weld-200	380	3200	390
600	375	3600	381
1000	371	4000	362
HAZ-1400	387	PM-4400	190
1800	389	4800	182
2200	392	5000	190
2800	398		

hardness values, the weld and HAZ exhibited a martensitic structure that had retained the acicular nature of its martensite needles. In both these regions, hardness was found to be very high. This meant that both the weld and HAZ had not undergone proper postweld heat treatment (PWHT) or there was no PWHT applied. Thus, this region became brittle and hence susceptible to cracking. The microhardness profile indicated higher hardness at the weld and HAZ with a sudden drop in hardness at the junction between the HAZ and the parent metal.

Conclusions The failure of the final superheater tube in the HAZ of the weld was due to lack of PWHT or improper PWHT that rendered the HAZ susceptible to cracking.

REFERENCES

- 6.1 D.N. French, Failures of Boilers and Related Equipment, *Failure Analysis and Prevention*, Vol 11, *ASM Handbook*, ASM International, 2002, p 1709–1738
- 6.2 D. French, *Metallurgical Failures in Fossil Fired Boilers*, John Wiley & Sons, January 1993
- 6.3 V. Šijački-Žeravčić, G. Bakic, M. Djukic, and B. Andjelic, Failures at Elevated Temperatures, *The Challenge of Materials and Weldments, Structural Integrity & Life Assessment*, S. Sedmak and Z. Radakovic, Eds., 9th Int. Frac. Mech. School (Bulgaria), Gosa, 2008, p 183–202
- 6.4 V.T. Sathyanathan, “Understanding Tube Failures in High Pressure Boilers,” L. Stonecypher Ed., Bright Hub, Inc., Nov 2010, <https://www.brighthubengineering.com/power-plants/>
- 6.5 B. Dooley and W. McNaughton, *Boiler Tube Failures Theory and Practice*, Vol 2 & 3, Electric Power Research Institute, Inc., 1996
- 6.6 R. Viswanathan, *Damage Mechanisms and Life Assessment of High Temperature Components*, ASM International, 1989, p 191
- 6.7 D.N. French, “Penthouse,” Vol VII (No. 4), Winter 1991. davidnfrench.com/custdocs/Penthouse%20Winter%201991.pdf
- 6.8 P. Hamblin-Smoske, Improved Boiler Reliability with Unit Specific Strategic Planning, *Proceedings of the ASME 2014 Power Conference POWER2014*, 28–31 July 2014 (Baltimore), p 1–7
- 6.9 L. Hoehenberger, “Waterside Scaling, Deposition and Corrosion in Steam Generators,” TÜV SÜD Industry Services (Germany), IMS-Sem, Nov 2005, p 1–19
- 6.10 D. Laverde, T. Gomez-Acebo, and F. Castro, Continuous and Cyclic Oxidation of T91 Ferritic Steel under Steam, *Corrosion Science*, Vol 46, 2004, p 613–631
- 6.11 R.K. Dayal and N. Parvathavarthini, Hydrogen Embrittlement in Power Plant Steels, *S^{adha}n^a* Vol 28, Parts 3 & 4, June/Aug 2003, p 431–451
- 6.12 R.B. Dooley and A. Bursik, Hydrogen Damage, *Power Point Chemistry*, Vol 12 (No. 2), 2010, p 122–127
- 6.13 D. Bain and D. Christophersen, Some Common Mechanisms Leading to Failures in Heat Recovery Steam Generators, *Corrosion 2003*, NACE International, March 2003, p 185–213
- 6.14 R.B. Dooley and A. Bursik, Caustic Gouging, *Power Point Chemistry*, Vol 12 (No. 3), 2010, p 188–192
- 6.15 F. Daneshvar-Fatah, A. Mostafaei, R. Hosseinzadeh-Taghani, and F. Nasirpour, Caustic Corrosion in a Boiler Waterside Tube: Root Cause and Mechanism, *Engineering Failure Analysis*, Vol 28, 2013, p 69–77
- 6.16 H.M. Herro and A. Banweg, Phosphate Corrosion in High Pressure Boilers, *Materials Performance*, Dec 1995, p 49–53

- 6.17 D.N. French, Phosphate Corrosion, *View From The Penthouse*, 14th Annual All Users Conference, Jan 6–8, 2009
- 6.18 B. Dooley, Don't Let Those Boiler Tubes Fail Again, *Power Engineering*, January 1997
- 6.19 J. Estilles and M. Soria, "Reducing Corrosion and Potential Boiler Failure with Superior Iron Transport Technology," GE Infrastructure Water and Process Technologies, 2009, p 1–37
- 6.20 R.B. Dooley, Flow Accelerated Corrosion in Fossil and Combined Cycle/HRSO Plants, *Power Plant Chemistry*, Vol 10 (No. 2), 2008, p 68–89
- 6.21 G.Y. Lai, *High Temperature Corrosion and Materials Applications*, ASM International, 2007, p 235
- 6.22 J. Fan, J. Mazur, N. Melicharek, and M. Schmittiel, "Erosion, Cavitation and Fretting." Last modified 2014, http://www.lettsvankirk.com/index.php?option=com_docman&task=doc_download&gid=35&Itemid=
- 6.23 Y. M. Chen, Cavitation Erosion, *Failure Analysis and Prevention*, Vol 11, *ASM Handbook*, ASM International, 2002
- 6.24 R. Kumar, *Operation and Maintenance of Steam Power Boilers*, Allied Publishers Pvt. Ltd., New Delhi, 2008, p 233
- 6.25 Babcock & Wilcox Power Generation Group, "Boiler Tube Analysis: Reduce Future Boiler Tube Failures," last modified Dec 2014, www.steamforum.com/pictures/e1013153.pdf
- 6.26 D.A. Carter, "Corrosion in Boiler Water Systems," A.I.Ch.E. Meeting, Clearwater, FL, 1989, p 1–18, www.aisce-cf.org/Clearwater/1989/Paper2/89.2.5.pdf
- 6.27 V.S. Raja and T. Shoji, Eds., *Stress Corrosion Cracking—Theory and Practice*, Woodhead Publishing, 2011
- 6.28 J. Colannino, Prevent Boiler Tube Failures Part 1: Fire Side Mechanisms, *Chemical Engineering Progress*, Oct 1993, p 33–36
- 6.29 G.E. Gale, "Corrosion in Boilers and Water Circulation Systems with Special Reference to Marine Installations," p 166–172, last modified 2011, eprints.nmlindia.org/3429/1/166-172.PDF
- 6.30 D. Yang, P.M. Singh, and R.W. Neu, Initiation and Propagation of Stress-Assisted Corrosion (SAC) Cracks in Carbon Steel Boiler Tubes, *Journal of Engineering Materials and Technology*, Vol 129 (No. 4), July 2005, p 559–566
- 6.31 B. Dooley and P.S. Chang, The Current State of Boiler Tube Failures in Fossil Plants, *Power Plant Chemistry*, Vol 2 (No. 4), 2000, p 197–203
- 6.32 I. Andijani and A.U. Malik, "Sulfur and Vanadium Induced Hot Corrosion of Boiler Tubes," presented at Chemistry & Industry Conference, 11–15 Dec 2004 (Riyadh)
- 6.33 M. Beychok, "Chemical Engineering—Acid Dew Point," last modified Aug 2011, <https://chemengineering.wikispaces.com/Acid+dewpoint>
- 6.34 National Physical Laboratory, England, "Basics of Corrosion—Stress

- Corrosion Cracking (SCC),” last modified Dec 2007, www.npl.co.uk/upload/pdf/stress_corrosion_cracking_basics.pdf
- 6.35 O.F. Aly and M. Mattar Neto, “Stress Corrosion Cracking,” Energy and Nuclear Research Institute, São Paulo, Brazil, last modified Feb 2014, <http://cdn.intechopen.com/pdfs/46240.pdf>
 - 6.36 J.R. Davis, Ed., *Stainless Steels*, *ASM Specialty Handbook*, ASM International, 1994, p 195
 - 6.37 G.R. Lobley, Stress Corrosion Cracking: Case Studies in Refinery Equipment, *6th Saudi Engineering Conference*, Vol 5, Dec 2002 (Dhahran), p 17–26
 - 6.38 C. Wagner, Defending Boiler Components Against Corrosive and Erosive Attack, *The Fabricator*, Sept 2013, <https://www.thefabricator.com/article/metalsmaterials/defending-boiler-components-against-corrosive-and-erosive-attack>
 - 6.39 A.S. Khanna, *High Temperature Corrosion*, World Scientific Publishing Co. Pte. Ltd., 2016, p 112
 - 6.40 I. Virkkunen, “Thermal Fatigue of Austenitic and Duplex Stainless Steels,” Ph.D. dissertation, Acta Polytechnica Scandinavica, Finnish Academies of Technology, 2001
 - 6.41 R.A. Chaplin, Ed., *Thermal Power Plants*, Vol 1, EOLSS Publishers Co. Ltd., 2009
 - 6.42 R.B. Dooley and A. Bursik, Corrosion Fatigue, *Power Point Chemistry*, Vol 11 (No. 10), 2009, p 586–591

CHAPTER 7

Role of Water Chemistry in Boiler Tube Failure

7.1 Introduction

Water is used as a raw material in boilers for process applications, as a barrier to heat energy, to cool after-turbine steam, and for plant wash down. In thermal power plants it is used as *boiler water* and demineralized (DM) water for steam generation; water is also required for the cooling tower, the ash handling plant, coal handling, and dust suppression.

Water is available as surface water from ponds or lakes, rivers, reservoirs, rainwater, and the ocean or sea. It is also available as groundwater from bore wells and tube wells. Surface water contains a high amount of insoluble impurities and a lesser amount of soluble impurities, whereas ground water contains less insoluble impurities but more soluble impurities. As rainwater percolates into the soil, the water becomes loaded with dissolved impurities leached from the surface and subsurface. The level of dissolved salts determines the quality of water and its subsequent use.

Whether the quality of water to be used for steam generation in a thermal power plant is adequate or not is determined by two main factors: the boiler operating pressure and its design. The higher the boiler operating pressure, the more critical becomes the removal of impurities from the water. The purity of potable water available for domestic use is far below that required for use in boilers as boiler feedwater (BFW). It is therefore essential to reduce the level of contaminants present in raw water and to add certain chemicals or additives to make it a boiler-quality feedwater.

The main reasons behind many boiler tube failures include the accumulation of scales, corrosion, and pitting on the inner surface of the tubes as a result of contaminated water entering the boiler, and carryover of impurities. Impurities in water also lead to the fouling of heat transfer surfaces and eventually lead to failure of the tubes by overheating (Ref 7.1). Therefore, quality control of the boiler water is of utmost importance and

can be ensured through control of the chemistry of the water entering the boiler. The purposes of controlling the water chemistry through water treatment programs are:

- To generate high-purity steam
- To minimize corrosion and scale formation
- To increase boiler efficiency and reduce plant downtime
- To save fuel, water, chemicals, and additives
- To increase the life of plant equipment
- To reduce the cost of maintenance and repairs

Important terms used in connection with water used for boilers include *make-up water*, *condensate water*, *feedwater*, *boiler water*, and *blowdown water* (Ref 7.2).

7.1.1 Make-up Water

Because of a constant loss of cycle water, it is essential to have a continual source of incoming water. This incoming water is termed make-up water. It is raw water that is pretreated through processes such as demineralization or softening for its subsequent use for steam generation.

7.1.2 Condensate Water

In a typical thermal power plant, low-pressure steam (which is slightly above its boiling point) leaves the turbine and enters the condenser or heat exchanger, where it is condensed back to water. This water is termed condensate or condensate water. The condensate forms the main bulk of the feedwater to the boiler. High-purity DM water serves only as make-up water to manage losses due to leakages and blowdown. The amount of make-up water added to feedwater is typically less than 1.5%, though it is normally 5% per design. Hence, the quality of condensate is of vital importance for plant performance. If the condenser is leaky, the circulating cooling water, which is natural water, becomes entrapped in condensate, spoiling its quality. Therefore, it needs further treatment before being used in the boiler.

7.1.3 Feedwater

Water that enters the boiler is known as BFW. Condensate water and pretreated make-up water together constitute the BFW.

7.1.4 Boiler Water

Boiler water is water that is heated inside the boiler for the purpose of producing steam. Feedwater becomes boiler water after it is chemically treated by internal treatments.

7.1.5 Blowdown Water

The impurity level of boiler water increases when the steam is driven off the boiler drum. The impurity concentration also increases with compensation of evaporated water by make-up water. Eventually, the level of impurities in boiler water exceeds acceptable limits. A stage comes when some of the boiler or cycle water must be drained or blown out to maintain the concentration of impurities in the boiler water. This process is known as blowdown, and the water drained out is called blowdown water.

7.2 Impurities in Water and the Role of Water Chemistry

Impurities present in water are categorized as suspended, insoluble, and dissolved. Suspended impurities include clay, dirt, dust, sand, and silt particles, which are inorganic in nature. Suspended impurities in water make water turbid. Organic materials in the form of microorganisms such as algae, fungi, and bacteria, as well as natural organic matter from the decay of dead plants and animals in the form of fulvic and humic acids, are also types of suspended impurities in water. Organics from decayed vegetation and organic wastes impart color to natural water.

Additionally, there are soluble or dissolved impurities in water. Alkaline salts of calcium, sodium, and magnesium (mainly their bicarbonates) and the neutral salts of these elements such as chlorides and sulfates are found as soluble impurities in water. Mineral salts found in natural water include:

Calcium bicarbonate	$\text{Ca}(\text{HCO}_3)_2$	Calcium chloride	CaCl_2
Magnesium bicarbonate	$\text{Mg}(\text{HCO}_3)_2$	Magnesium chloride	MgCl_2
Sodium bicarbonate	NaHCO_3	Sodium chloride	NaCl
		Calcium sulfate	CaSO_4
		Magnesium sulfate	MgSO_4
		Sodium sulfate	Na_2SO_4

These minerals, when present in water, dissociate into their ionic form (Na^+ , Ca^{+2} , Mg^{+2} , Cl^- , SO_4^{-2} , etc). Salts of iron and manganese are also found in small amounts in water.

Natural water also contains gases such as oxygen, carbon dioxide, and hydrogen sulfide in dissolved form.

For trouble-free operation and longer life of the tubes and other high-pressure parts, there are certain parameters of water chemistry that must be controlled. Following is a brief summary of the role played by different impurities and feedwater parameters in governing the water chemistry and in turn the resultant damage to various high-pressure parts in a boiler (Ref 7.2–7.4).

7.2.1 *Suspended Solids*

Suspended solids are insoluble in nature and their content in water is expressed as the total suspended solids. They lead to carryover and choking of boiler tubes. The amount of total suspended solids in water is expressed as the nephelometric turbidity unit.

7.2.2 *Total Dissolved Solids*

Raw water contains dissolved salts. All dissolved solids together provide the total dissolved solids (TDS) content of water. Measures of dissolved solids in water are its conductivity, expressed as micromhos/cm, and the TDS in ppm. The TDS of water depends on its source and pretreatment. The higher the TDS value, the higher the conductivity of water and hence the higher the tendency for corrosion and scaling.

7.2.3 *Iron*

Suspended or dissolved iron from feedwater is deposited on boiler tube surfaces and can lead to tube failure. Rusted boiler tubes and condensate return (i.e., condensate water) are the main source for contamination of iron. Metallic iron remains in particle form because it does not dissolve in water. Iron particles account for erosion-related problems.

7.2.4 *Silica*

Silica is usually not present in very large quantities in water. However, even in small concentrations, it can form a hard scale. Silica has low thermal conductivity and forms a dense porcelain-like scale that cannot be removed even with acids. Silica combines with a wide variety of elements to form silicates. Silica can form a scale at pressures exceeding 4 MPa (600 psi). The presence of silica in BFW in excess of 20 ppb and above 4 MPa pressure is harmful because silica evaporates along with steam, in addition to mechanical carryover, and forms hard deposits on the turbine blades. With increasing operating pressure and temperature, the maximum allowable limit of silica decreases. The level of silica in boiler water should be such that the amount of silica in steam leaving the drum is less than 20 ppb.

7.2.5 *Scale Deposits*

Calcium and magnesium form a variety of compounds, namely sulfates, bicarbonates, carbonates, chlorides, and nitrates. They are responsible for problems such as hardness and alkalinity of water. During the process of steam production, water cycling through the boiler evaporates, resulting in adherence of some of these compounds to the walls of the boiler

tubes in the form of a scale. Scales are poor conductors of heat, reducing heat transfer across the walls of the boiler tubes, and causing failure of the tubes due to overheating.

7.2.6 Sodium

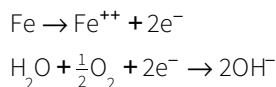
Sodium exists in water in its ionic form as Na^+ ions. Sodium ions combine with hydroxide ions to form sodium hydroxide (i.e., caustic soda). Sodium hydroxide attacks the highly stressed areas of boiler tubes and steam turbines, leading to stress-corrosion cracking failure.

Sodium undergoes a distinct cycle during hydrolysis. During this process, sodium carbonate is transformed to sodium hydroxide, which then attacks iron in the boiler to form sodium ferroate, which undergoes hydrolysis and regenerates into sodium hydroxide. Repeated caustic attack increases the risk of leakage and cracking of tube bends and joints in highly stressed areas.

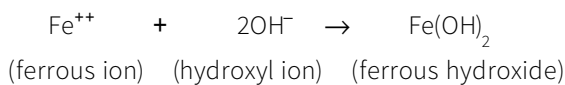
7.2.7 Dissolved Oxygen

Oxygen promotes corrosion of both iron and copper. Dissolved oxygen is a major cause of corrosion in steam power plants. Dissolved oxygen, if it exceeds 7 ppb, leads to pitting corrosion of the tubes and corrosion in the preboiler section. Therefore, the concentration of dissolved oxygen at the economizer inlet should not exceed 7 ppb. It should be less than 20 ppb in the hot well. These figures are based on the deaeration capability of modern plants with hydrazine as an oxygen scavenger. During operation, typically about 10 to 30 mg/L (an average of 20 mg/L) of residual hydrazine is able to keep oxygen within the specified limits. This controls the corrosion of iron, copper, and nickel in the preboiler system.

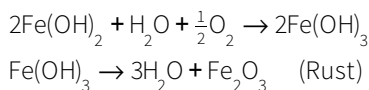
Oxygen in feedwater reacts with iron to form ferrous hydroxide initially, and then ferric hydroxide (Ref 7.5). Oxygen in combination with water attacks iron, resulting in corrosion.



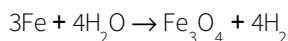
Fe^{++} and OH^- react to produce ferrous hydroxide:



In turn, the ferrous hydroxide combines with water and oxygen to produce ferric hydroxide, which further decomposes to form rust.

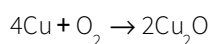


At high temperatures (above 400 °C, or 750 °F), in the absence of oxygen, iron combines with water to produce magnetite.

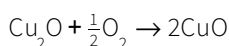


The magnetite coating provides protection against corrosion, forming a passive film.

Likewise, oxygen reacts with copper to produce its oxides (Ref 7.6). If oxygen is less than 20 ppb, it produces cuprous oxide (Cu_2O) and protects the metal from further corrosion.



However, uncontrolled oxygen reacts with Cu_2O (cuprous oxide) to produce CuO (cupric oxide). Cupric oxide does not protect copper metal from further corrosion. The copper release rate under this condition is about three times higher than that under reducing conditions.



Cupric oxide is nonprotective in nature and permits corrosion of the underlying copper.

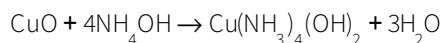
During shutdowns, when the temperature is reduced from 95 °C (200 °F) to about 25 °C (75 °F), the protective oxide layer (Cu_2O) on the surface quickly starts to change from cuprous oxide to cupric oxide within about 10 hours, with a marked increase in surface roughness. Due to thermal shock during start-ups, metal oxides ($\text{Cu}_2\text{O}/\text{CuO}$) exfoliate from the preboiler surfaces and make their way to the boiler as carryover. Copper being less active than iron, copper ions are reduced to copper metal in the boiler section and deposited on the surface. Thermal shock also promotes the corrosion of iron due to the formation of galvanic cells.

7.2.8 Dissolved Carbon Dioxide

The source of carbon dioxide is mainly condenser air leakage or alkalinity in the feed water in the form of an HCO_3^- radical. The decomposition of bicarbonate, carbonate alkalinities, and organic matter liberates carbon dioxide. Carbon dioxide reacts with water to form carbonic acid (H_2CO_3), which is highly corrosive in nature.

7.2.9 Ammonia

For plants that contain copper alloys in the condensate or feedwater system, it is essential to monitor ammonia to minimize ammonia attacks of copper alloys (particularly when oxygen is present). Ammonia in the presence of oxygen promotes corrosion of most copper alloys due to the formation of a metal complex. It reacts with cupric oxide to form a soluble copper complex.



To minimize the corrosion of copper-base alloys, oxygen should be kept below 7 ppb and ammonia kept up to 0.5 mg/kg in the preboiler section. The concentration of ammonia should be consistent with the pH range.

7.2.10 Organic Matter

Natural water contains organic matter in the form of long-chain compounds. These compounds block the functional groups of ion exchange resins in demineralization plants. The absorption of such long-chain compounds is an irreversible process that leads to reduction in the ion exchange capacity and deterioration in the quality of treated water.

Organic species, when they enter the boiler along with feedwater, decompose into acidic products and affect not only the boiler water pH but also increase the tendency toward foaming, thereby attacking the turbine.

7.2.11 Oil and Grease

Oil and grease form an emulsion with water that leads to foaming. The oil acts as a binder to form a scale. It is not present in boiler water but is a contaminant from the lubricant used for rotating or reciprocating equipment of the plant.

7.2.12 pH

The pH is defined as the negative logarithm of H^+ ions. The pH of any solution ranges from 0 to 14. When the pH is less than 7, the water is acidic, whereas when it is greater than 7, the water is basic or alkaline. Neutral water has a pH equal to 7. The pH of water determines its acidity or alkalinity and has a direct influence on corrosiveness. Feedwater with a low pH (below 8.5) is corrosive, but a high pH value (greater than 11) causes deposition and scaling on the inner walls of the tubes. A moderately high pH is conducive to longer tube life as it helps to promote the formation of a protective film of magnetite, which acts as a barrier between boiler water and the steel contacting surface. The corrosion reaction stops once

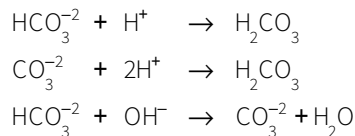
a uniform magnetite layer is formed. However, due to disturbances in pH, acidic or highly alkaline conditions are created, which destroy the protective magnetite film, resulting in corrosion of the underlying metal.

The corrosion rate of carbon steel reaches a minimal value at a pH of 9.0 to 9.6. Systems that have mixed metallurgy cannot minimize the corrosion rate of carbon steels and copper alloys simultaneously without increasing the corrosion rate of any one of them. Consequently, such plants have to compromise and maintain the condensate or feedwater pH between 8.8 and 9.2; for ferrous systems this range is 9.0 to 9.6.

7.2.13 Alkalinity

Alkalinity is the ability of natural water to neutralize acid. Alkalinity in raw water is mainly due to bicarbonates and to some extent carbonates. M-alkalinity, or total alkalinity, is defined as the sum total of carbonates, bicarbonates, and hydroxides in water (Ref 7.2). Thus, alkalinity is a measure of HCO_3^- , CO_3^{2-} , and OH^- ions in water. These ions are present as sodium compounds. Water with high alkalinity upon heating leads to the decomposition of carbonates and bicarbonates and liberates carbon dioxide. The liberated carbon dioxide reacts with water to form carbonic acid, resulting in corrosion.

Interaction of free H^+ and OH^- ions in water with HCO_3^- and CO_3^{2-} may be expressed by the following reactions:

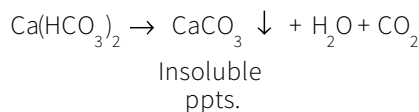


The carbonic acid so formed causes corrosion of the contacting surfaces.

7.2.14 Hardness

Hardness of boiler water is attributed to Ca^{+2} and Mg^{+2} minerals. Water hardness is responsible for scale formation. Carbonates and bicarbonates of calcium and magnesium lead to temporary hardness and form soft scales. When water is subjected to boiling, these compounds dissociate to form carbon dioxide and soft scales.

As shown in the following reaction, when water is boiled, the bicarbonates decompose and are precipitated, thereby eliminating temporary hardness:



On the other hand, noncarbonate salts such as sulfates, nitrates, and chlorides impart permanent hardness and form a hard scale, which is difficult to remove. Permanent hardness of water cannot be eliminated merely by the boiling of water and needs chemical treatment.

7.3 Water Chemistry–Related Problems in Power Plants

There are three water chemistry–related problems in boilers (Ref 7.2–7.4), namely,

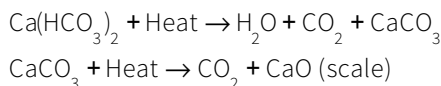
- Deposition and scaling
- Corrosion
- Carryover

7.3.1 Deposition and Scaling

Impurities carried along with feedwater are a potential source of deposition and scaling in various parts of the boiler, including boiler tubes' high heat zones. Their source is make-up water that contains mineral salts, condensate that contains process contaminants, corrosion products, or chemicals used for internal water treatment.

Water-borne impurities such as calcium, magnesium, and silica are found in most water supplies. Scaling and deposition on boiler tubes occur whenever there is a change or disturbance in the equilibrium conditions in the water that contacts the tube surface due to heat. The solubility of scale-forming salts is a function of their concentration and water temperature. Certain minerals such as carbonates and bicarbonates of calcium and magnesium have inverse solubility in water, whereby the higher the temperature, the lower the solubility. A scale forms when the solubility of the scale-forming salts in water decreases and the temperature and concentration increase. Under operating conditions, when the feedwater temperature rises to the boiler water temperature, the solubility of scale-forming salts decreases, and a solid scale begins to form on the heat transfer surfaces of the boiler.

As the evaporation of water in the boiler progresses, the concentration of dissolved impurities in the boiler water increases to the point where they precipitate out, forming a scale on the heat transfer surfaces of the boiler. Dissolved bicarbonates of calcium and magnesium dissociate under heat to give off carbon dioxide and form insoluble carbonates per the following reaction. These carbonates may precipitate directly on the metallic surfaces of the boiler or form sludge in the boiler water that may be deposited as an oxide on boiler surfaces.



Apart from oxides of calcium and magnesium, deposits or scales found in the boiler may also include calcium phosphate, silica, and magnesium silicate, oxides of iron and copper, and metallic copper. If the boiler water is subjected to phosphate treatment, calcium will preferentially precipitate as calcium phosphate, rather than as a carbonate.

Scales or deposits act as an insulator; they have poor thermal conductivity and reduce heat transfer across the tube, causing a drop in boiler efficiency and a rise in fuel consumption. Scale deposits also cause overheating or corrosion of the metal underneath the deposits, finally resulting in the failure of boiler tubes.

7.3.2 Corrosion

Corrosion is the destructive attack of metal by a chemical or electrochemical reaction with its environment. Corrosion results in metal loss, either by dissolution resulting in thinning or by formation of an insoluble product (oxide). It can be uniform over the metal surface or localized in the form of pitting. Corrosion leads to reduced heat transfer across the boiler tube surfaces and hence results in overheating failures. Corrosion also accounts for contamination of boiler water and an increase in operation and maintenance costs. Corrosion is a complex phenomenon, and many factors including physical, chemical, and biological ones influence it.

As far as corrosion in boilers and thermal power plants is concerned, water chemistry plays a major role. The corrosiveness of water depends on the amount and type of impurities present in it. For instance, dissolved gases such as oxygen, carbon dioxide, and ammonia, and dissolved solids in BFW corrode various metals and alloys used in boiler applications. Low-pH and high-pH conditions also lead to corrosion of boiler components at high temperatures. At a low pH, acid corrosion takes place, while at an excessively high pH, caustic corrosion occurs.

Four major areas of thermal power plants where corrosion damage is experienced are:

- Boiler feedwater system: The main reasons for corrosion in this area are dissolved gases such as oxygen and carbon dioxide, and low pH.
- Steam or condensate system: Corrosion is due to dissolved oxygen, carbon dioxide, or carbonic acid.
- During operation: Corrosion is mainly attributed to factors such as dissolved gases, scales and deposits, or excessively high or low boiler water alkalinity. High temperatures and stresses accelerate the damage.

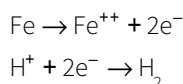
- When the boiler is in standby mode: Corrosion occurs when water containing oxygen comes in contact with a metal surface during idle periods. Such corrosion mainly occurs by oxygen pitting.

Corrosion of steam lines and condensate return lines occurs because of a low pH. The chief source of acid in steam is carbon dioxide. High temperature and pressure decompose alkalinity to carbon dioxide, some of which dissolves in steam. This lowers the condensate pH and leads to corrosion of return lines. Gases such as ammonia, hydrogen sulfide, and sulfur dioxide can also lead to corrosion of condensate lines.

Though various corrosion-related damage mechanisms for boiler tubes have been discussed in detail in Chapter 6, “Damage Mechanisms with Case Studies,” in this book, a quick review of some of the forms of corrosion is given below for clarity.

7.3.2.1 Acid Corrosion Boiler tubes have a tightly adherent natural protective layer of magnetite that protects the underlying metal from corrosion. However, acid or water with low pH is capable of destroying this layer. Hence, the water chemistry must be maintained so that the protective layer is not disrupted.

At a pH below 8.5, iron undergoes corrosion. Electrons moving freely in metal combine with hydrogen ions in an acid solution (with low pH) to produce hydrogen gas per the following reactions:



The net effect is corrosion as a result of removal of iron from the boiler tube surface, initially leading to thinning and finally failure due to rupture of the tube.

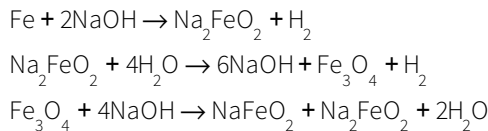
7.3.2.2 Oxygen Pitting Oxygen pitting damage occurs in the water supply system, preboiler systems, boilers, condensate return lines, and virtually any portion of the steam cycle where oxygen is present. It occurs at steam-blanketed surfaces where restricted boiler water flow causes overheating. Oxygen attack is accelerated by high temperature and low pH. Pitting corrosion is caused mainly by dissolved oxygen and results in premature replacement of feedwater lines, boiler, tubes, and condensate return lines. Oxygen pitting occurs during idle periods as well as when the boiler is in operation. During idle periods, it is more prevalent. Oxygen causes pitting of condensate lines due to occasional malfunctioning of deaerators. High velocity and low pH result in extremely severe corrosive conditions. The best way to minimize this is to keep the pH above 9.

7.3.2.3 Caustic Corrosion A less prevalent type of corrosion is alkali attack, which occurs in high-pressure boilers where caustic elements

concentrate in local areas of steam bubble formation because of the presence of porous deposits. It is known as caustic attack or caustic gauging.

Iron corrodes above pH 12 because of stripping of the protective magnetite film. Boiler feedwater is generally maintained at an alkaline pH. However, excess alkali dissolves the magnetite film, forming sodium ferrite (NaFeO_2) and sodium ferroate (Na_2FeO_2), both of which are soluble in hot concentrated caustic solution.

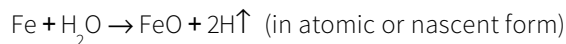
Caustic elements react with iron to form a soluble iron salt known as sodium ferroate, which in turn reacts with water to produce iron oxide per the following reactions:



Irregular wastage of the tube metal occurs beneath a porous deposit. The damage progresses to the extent that the tube wall thins to a point where it fails locally by stress rupture.

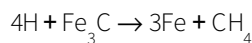
Free caustic elements are present in drum water at a high pH. This is the area where water changes its phase, and due to wick boiling conditions, caustic and other salts accumulate on the internal surface of the boiler tube. This high local concentration of caustic elements results in severe corrosion even if the free caustic elements in bulk water are at the ppm level. (The corrosion rate in such conditions is several hundred thousand times higher.)

7.3.2.4 Hydrogen Damage An electrochemical reaction between iron and water or steam under high-pressure and high-temperature conditions leads to liberation of atomic or nascent hydrogen under heavy deposits per the following reaction:



The liberated atomic hydrogen migrates into the steel and is accumulated at preferred locations such as voids or inclusions and results in the formation of microcracks or fissures.

Additionally, the nascent hydrogen resulting from the corrosion penetrates into the steel and reacts with the cementite in steel to produce methane:



Trapped methane molecules exert pressure at the grain boundaries and weaken the steel.

7.3.3 Carryover

Carryover is defined as the contamination of steam with droplets of boiler water. It occurs in the form of entrapped water droplets (containing impurities in the form of dissolved solids) in high-pressure and high-temperature steam. Boiler water carryover results in poor-quality steam. As a result of carryover, dissolved solids enter the steam or condensate system and form deposits. The deposits reduce heat transfer and also lead to corrosion in the system.

Carryover is a mechanical problem. It depends on the design of steam turbo separators. Normally it is about 2%. However, it can also be due to the properties of certain salts such as silica in boiler water that are vaporized and incorporated into the steam. A small amount of carryover is beneficial as it retards the corrosion of turbine components by forming a thin layer on them.

Priming and foaming are two terms used in conjunction with carryover. Priming is a sudden surge of boiler water drawn into the steam line and is usually caused by a high water level in boilers, a sudden change in steam demand, or operating the boiler above its rated capacity. Priming is thus due to mechanical factors.

Foaming is the formation of stable bubbles or froth on the boiler water surface, which is subsequently carried forward along with the steam. High TDS and high levels of suspended solids, alkalinity, and contaminants such as oil, fats, and grease contribute to foaming. Foaming is thus due to chemical factors.

In short, both mechanical as well as chemical factors contribute to carryover.

7.4 Water Treatment Programs

The uninterrupted and efficient functioning of any power plant largely depends on its water treatment program. The water used in boiler applications must be of good quality in order to produce quality steam and minimize problems such as deposition and scaling that lead to forced outages. Therefore, to attain required quality standards, the raw water is subjected to pretreatment.

Water treatment programs are grouped into two types: external and internal water treatment programs (Ref 7.7). External treatment is applied to make-up water, feedwater, or condensate water before it enters the boiler in order to minimize or completely eliminate impurities such as silica, hardness, and dissolved gases. Internal treatment is applied either to feedwater, boiler water, steam, or condensate using various chemicals.

The purpose of water treatment is not only to produce a stringent quality of steam such that there will not be any forced outage of the machine

due to improper water chemistry but also to ensure that minimum levels of contaminants and corrosion products enter the boiler.

7.4.1 External Treatment or Pretreatment (Ref 7.4, 7.5, 7.8)

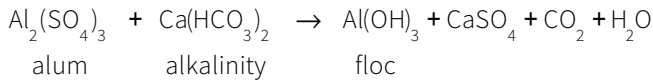
External water treatment includes the following steps: filtration, chlorination, clarification, softening, precipitation, ion exchange, dealkalization, demineralization, deaeration, and reverse osmosis (RO).

7.4.1.1 Filtration Filtration removes or minimizes such impurities as coarse suspended matter, silt, clay, and some organic materials. It also removes floc or sludge produced by coagulation or softening. Filtration is a mechanical process and therefore does not remove dissolved solids. Undissolved solid particles in water are removed by using either gravity filters or pressure filters. Filtration also removes the rust particles formed due to corrosion in the boiler and steam piping or tubing. Coarse suspended matter in water is removed by using gravity or pressure filters. However, when the suspended solids are very fine, clarification of the solution using a coagulation and flocculation step is mandatory to ensure effective filtration.

7.4.1.2 Clarification The objective of clarification is to remove suspended matter and color from water. The term *clarification* is used in connection with the turbidity in water. High-purity water is colorless and completely transparent. However, raw water used in boilers is not normally high purity and has several suspended impurities in it, which makes it turbid. Lack of clarity in water is referred to as turbidity. The suspended particles range from a few microns in diameter to the submicron and nano levels with a high surface area. They usually have a net negative charge on their surface, which keeps them in suspension in a medium such as water (as the like charges on the neighboring particles' surfaces repel them from each other). Clarification is a process of removal of such insoluble suspended impurities from water and consists of steps including coagulation and flocculation.

Coagulation Because ultra-fine-sized suspended solid particles are present in raw water, cartridge filters are at times unable to filter them. In such a situation, the water is treated before filtration with chemicals known as coagulants, and the treatment is known as coagulation. It is a process of neutralization of the negative charges from the surface of the fine particles, which makes them unite to one another by providing a nucleus to form masses or agglomerates that can be filtered. Chemicals such as alum (aluminum sulfate), sodium aluminate, ferric sulfate, ferric chloride, activated silica, and high-molecular-weight polyelectrolytes are often used as coagulants. They cause impurities that are otherwise present as fine suspensions in the solution to settle. Hard and high-TDS water is treated more easily than soft and low-TDS water.

A typical coagulation reaction is:



Flocculation Stable agglomerates of small particles are converted into large flocs by a process called flocculation. This is done by stirring or gentle agitation of a coagulated solution. Flocs, by virtue of their higher specific gravity, tend to settle at the bottom. The clear water is then separated from the flocs by decantation.

7.4.1.3 Deaeration As discussed earlier, the boiler water must be free from dissolved or entrained gases such as oxygen and carbon dioxide to combat corrosion of boiler tubes. Their concentration must be lowered to such levels that their corrosive potential with regard to steels used as boiler tubes is almost negligible. This is ensured by deaeration of feedwater in a deaerator. In order to remove dissolved gases from feedwater, the feedwater is heated with air above 100 °C (210 °F) in a deaerator. The solubility of oxygen in water decreases as the water temperature increases and the partial pressure of dissolved gas decreases. The most important variables of the process are deaeration temperature and time as well as the surface area of the water droplets sprayed into the deaerator. In water at about 21 °C (70 °F) and atmospheric pressure, there is 7000 ppb of dissolved oxygen. The removal of dissolved oxygen down to 7 ppb is possible by mechanical deaeration. Remaining traces of oxygen and carbon dioxide are removed by chemical treatment using oxygen scavengers. Likewise, mechanical deaeration can lower all free CO₂ to a nondetectable level.

Mechanical scrubbers and atomizers are also developed as deaerators. Here, the deaeration is accomplished by disintegration of preheated feedwater into small droplets by mixing it with the incoming steam flow. The incoming steam flow atomizes the feedwater into small droplets, thus increasing the surface area for scrubbing action by the steam and thereby improving the process efficiency.

7.4.1.4 Softening Processes Surface water contains calcium and magnesium, referred to as hardness, in addition to other impurities such as iron, copper, and manganese. As part of the water chemistry, they give rise to scaling, and to corrosion or contamination if used in boilers without any pretreatment. However, if calcium and magnesium are removed, they improve heat transfer across the boiler tubes and piping, increase their life, and lower the operation and maintenance cost of the plant as a whole.

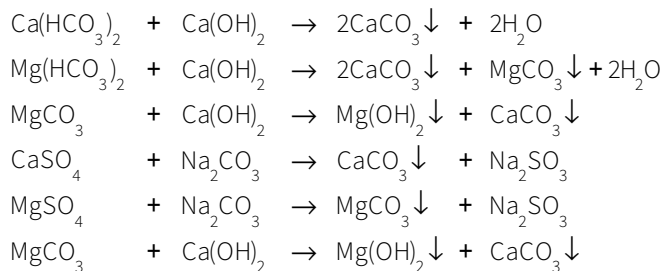
There are several methods available for softening water so as to remove calcium, magnesium, silica, and silt. They may be grouped into those based on precipitation principles and those based on ion exchange principles.

Precipitation methods reduce hardness, alkalinity, and in some cases, silica. Dissolved salts in the boiler water that form precipitates of a loose and slimy nature and are suspended in the boiler water are called *sludge*. The most common example of chemical precipitation in water treatment is lime-soda softening.

Lime-Soda Softening Treatment The lime-soda process is used for reducing water hardness that is mainly due to calcium and magnesium salts dissolved in water (Ref 7.4). The process involves addition of a calculated amount of lime (i.e., $\text{Ca}(\text{OH})_2$) and soda ash (Na_2CO_3) to the BFW. Calcium hydroxide (hydrated lime) reacts with soluble calcium and magnesium bicarbonates to form insoluble precipitates, which are removed by settling and filtration.

Similarly, lime reacts with magnesium sulfate and chloride and precipitates magnesium hydroxide, but in this process soluble calcium sulfate and chlorides are formed. Hence, lime is not effective in removing calcium sulfates and chlorides (permanent hardness). Therefore, instead of lime, soda ash is used to reduce nonbicarbonate hardness (permanent hardness).

Using the lime-soda method, both temporary and permanent hardness are removed. Some representative reactions are:



The process involves the addition of a calculated quantity of chemicals to the water along with a small amount of coagulants such as alum. The chemicals are thoroughly mixed with water and the precipitates formed are allowed to settle and are then removed by filtration. After the lime-soda process, the residual hardness will be around 25 ppm. The main advantage of lime-soda softening is that in reducing hardness, alkalinity, total dissolved solids, and silica are also reduced.

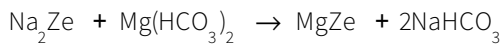
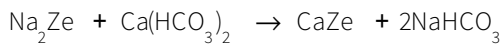
Phosphate Softening Boiler feedwater is subjected to phosphate treatment for hardness removal. In this treatment, calcium and magnesium are converted to tricalcium phosphate and magnesium hydroxide, respectively, by addition of phosphate (Ref 7.7). The reaction takes place above 100 °C (210 °F) and reduces the hardness of water to nearly zero. The precipitates formed are conditioned with polymers and subsequently removed from the boiler during blowdown.

7.4.1.5 Ion Exchange Processes

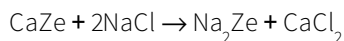
Dealkalization Dealkalization is one type of ion exchange process used for improving the quality of BFW with high alkalinity. It is recommended when the BFW has a high level of bicarbonate alkalinity and sulfates. In this process, softened water is passed through a tank containing an anion resin, such as chloride. This anion resin removes undesirable anions such as sulfate, nitrate, carbonate, and bicarbonate, and they are replaced by chloride. The treatment keeps boiler parts free from scale formation and corrosion.

Zeolite Softening Zeolite is hydrated sodium aluminosilicate ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), capable of exchanging reversibly its sodium ions with calcium and magnesium ions present in hard water. Zeolite used for softening of water can be natural or synthetic (Ref 7.2)

For softening of water by the zeolite process, hard water is passed through a bed of zeolite at a specified rate. The hardness-causing ions (mainly Ca^{+2} and Mg^{+2}) are retained by the zeolite as CaZe and MgZe (where Ze stands for zeolite), while the outgoing treated water contains sodium salts. Reactions taking place during the softening process are expressed as:



The used or inactivated zeolite is regenerated to Na_2Ze by passing a sodium chloride (salt) solution through the bed of inactivated zeolite. For example:



The hardness of water is reduced to about 10 ppm using zeolite treatment.

Demineralization Demineralizers are used to remove ionized mineral salts. They also work on the ion exchange principle. If there are tight restrictions on the quality of water to be used in a boiler, the demineralization route is adopted. Almost all dissolved solids can be removed by this method. In a demineralizer, positively charged ions (i.e., cations) such as calcium, magnesium, sodium, and iron are exchanged for hydrogen ions using sulfonic, carboxylic, and phenolic hydroxyl compounds. Likewise, negatively charged ions (i.e., anions), such as bicarbonate, sulfate, and chloride, and silica are exchanged by hydroxide ions with the help of amino or quaternary nitrogen. Cations are regenerated with hydrochloric or sulfuric acid, whereas anions are regenerated using sodium hydroxide.

Ion Exchange Process Minerals dissolved in water are present in the form of ions. For example, magnesium bicarbonate when dissolved in water forms positively charged magnesium ions and negatively charged bicarbonate ions. Positively charged ions are known as cations and negatively charged ions are called anions. Natural water typically contains ions such as:

Cations		Anions			
Sodium	Na ⁺	Chloride	Cl ⁻	Carbonate	CO ₃ ⁻²
Potassium	K ⁺	Nitrate	NO ₃ ⁻	Phosphate	PO ₄ ⁻³
Calcium	Ca ⁺²	Sulfate	SO ₄ ⁻²	Silicate	HSiO ₃ ⁻
Magnesium	Mg ⁺²	Bicarbonate	HCO ₃ ⁻	or amorphous silica	

The overall charge of the solution is neutral (no charge), because the positive charges of cations exactly counterbalance the negative charges of the anions.

The ion exchange process is used to remove the hardness of water to be used in boilers for steam generation (Ref 7.6). Some natural and synthetic materials have the ability of removing the cations and anions of minerals from water in exchange for other ions. The process involves a reversible exchange of ions between an external liquid phase (such as the BFW) and an ionic solid phase (i.e., the resin). The anions (for example HCO₃⁻, Cl⁻, and SO₄⁻²) in water are exchanged with anions (OH⁻) present in the anion exchange column, and the cations (for example Ca⁺², Mg⁺²) in water are exchanged with cations (H⁺) present in the cation exchange column of the ion exchange unit. For instance, bicarbonate ions from sodium bicarbonate in water can be exchanged with OH⁻ anions using an anionic exchange resin such as styrene-divinylbenzene with a quaternary ammonium group.

The resins used in ion exchange plants consist of cross-linked long-chain organic polymers with microporous structures. They are not soluble in water but are permeable to it. The structure of the resin includes fixed or immobile charged functional groups and mobile counterions (ions with opposite charge). During softening of water by the ion exchange process, these counterions are exchanged by the ions of dissolved minerals present in water. Cation exchange resins react only with positively charged ions such as Ca⁺² and Mg⁺², whereas anion exchange resins will react only with negatively charged ions such as bicarbonate (HCO₃⁻) and sulfate (SO₄⁻²).

The cation exchange resins usually operate on either a sodium or a hydrogen cycle. A sodium cycle exchanger replaces cations with sodium ions as in the case of a softener, whereas a hydrogen cycle exchanger replaces cations with hydrogen ions as in the case of a demineralization plant.

Two types of ion exchange resins are used in a demineralization plant. They are broadly classified as cation or cationic exchange resins and anion

or anionic exchange resins. Cation exchange resins are further classified as strong acid cation resins and weak acid cation resins. Similarly, anion exchange resins are classified as strong base anion resins and weak base anion resins. Resins containing acidic functional groups are capable of exchanging their H^+ ions with other cations, while those containing basic functional groups are capable of exchanging their anions with OH^- ions, which come in to contact with them.

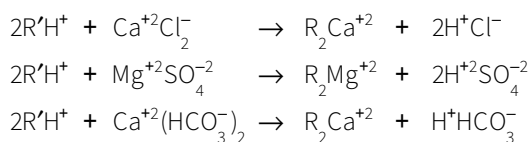
A strong acid cation resin comprises styrene divinylbenzene copolymer with a sulfonic acid functional group. It is effective over a wide pH range. This resin can neutralize strong bases and convert neutral salts into their corresponding acids.

A weak acid cation resin generally consists of a cross-linked acrylic polymer with a carboxylic acid functional group. This resin is only effective in alkaline conditions and has the ability to neutralize strong bases. The cations associated with alkalinity of HCO_3^- and CO_3^{2-} can be removed. A strong base anion resin comprises styrene or acrylic divinylbenzene copolymers with a quaternary ammonium functional group. It is effective over a wide pH range. These resins can neutralize strong acids and convert neutral salts into their corresponding bases. They can reduce silica and carbon dioxide as well.

Likewise, a weak base anion exchange resin is of a similar polymeric matrix but contains weaker amine functional groups. They are only effective in acidic solutions and can exchange only such ions as chloride, nitrate, and sulfate, and not silica or bicarbonates.

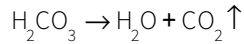
Ion exchange resins are available either as gel or a macroporous type. Gel-type resins have porosity with pore volumes typically up to 15 Å, whereas macroporous resins have a pore size of several hundred angstroms throughout the bead. Therefore, macroporous resins have more exchange surface area compared with gel resins. The typical bead size of ion exchange resins ranges from 0.3 to 1.2 mm (0.01 to 0.05 in.).

The ion exchange unit or the softener comprises anion and cation resins that fill two different columns. The water subjected to softening is first passed through the cation exchange column, so as to remove the cations from it. As a result of the exchange reaction, an equivalent amount of H^+ ions are released from this column and enter into the water. The cation exchange reactions are:

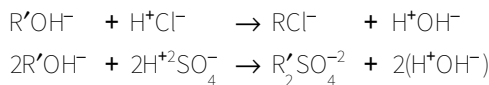


As a result, corresponding acids are formed. Carbonic acid so formed is a weak acid; it dissociates easily into carbon dioxide and water by a mechanical process. Hence, water is then passed through a degasser,

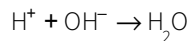
where it is sprayed with air blown in a direction from bottom to top. In this process, carbon dioxide is removed. This reduces the anionic load on the preceding unit; expenditure of the regenerant is reduced and so is the cost of DM water.



Water is then passed through the anion exchange column, which removes all the anions present in the water, and an equivalent amount of OH^- ions are released from this column to water per the following representative reactions:



Silica is absorbed by this resin. Finally, H^+ and OH^- ions unite to form a water molecule:



Subsequently, the water passes through a mixed bed unit. It contains both types of resin (cationic and anionic) together. It can remove traces of impurities that may have escaped from previous units to produce almost pure water with conductivity less than 1 micromhos/cm (typically 0.2 to 0.3 micromhos/cm) and a silica concentration less than 20 ppb.

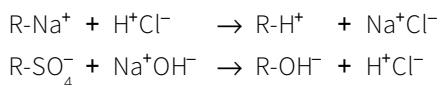
The water that emerges from the exchanger is free from hardness and is termed deionized water.

Some plants have a weak base anion unit. This type of resin has more efficiency. It can be regenerated with waste regenerant with a strong base anion unit. Because it is capable of removing strong acids, it reduces the anionic load on a strong base anion unit. Thus, it reduces the cost of DM water.

A combination of an RO plant with a mixed bed unit is also used to produce DM water.

Regeneration of Resin Similar to zeolites, ion exchange resins also become inactive or become exhausted after some specified use. In this situation, the cation and anion exchangers lose their ability to exchange H^+ and OH^- ions with corresponding ions from an aqueous solution. Consequently, the ion exchange unit will not generate the desired quality of water. The resins are brought to their original condition by subjecting them to regeneration. For regeneration, the ion exchange unit is taken off the line and replenished with corresponding ions. The cation exchanger

is replenished by treating it with dilute sodium chloride (NaCl) or dilute hydrochloric (HCl) or sulfuric acid (H₂SO₄). Likewise, the anion exchanger is regenerated using dilute caustic soda (NaOH) or dilute ammonium hydroxide (NH₄OH) solution, as demonstrated by the following reactions:

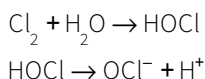


Here, R-Na⁺ represents exhausted resin, while R-H⁺ stands for regenerated resin; R-SO₄⁻ represents exhausted resin, whereas R-OH⁻ indicates regenerated resin.

Reverse Osmosis Osmosis is defined as the process in which a liquid moves from an area of low solute concentration to an area of high solute concentration, through a semipermeable membrane. In reverse osmosis, the exact opposite occurs.

Reverse osmosis is the process of demineralization of water by forcing it through a semipermeable membrane. Typically, polyamide thin films are used as the membrane. Here, the liquid flows from an area of high solute concentration to low solute concentration, or in other words, from high impurity to low impurity, leaving the concentrated impurity behind (i.e., on the feed side of the membrane). Pressure is required to reverse the natural process of osmosis by overcoming the osmotic pressure. Therefore, in reverse osmosis, an applied pressure is used to overcome osmotic pressure. Reverse osmosis removes solid particles, colloids, organic matter, pyrogens, up to 99% of dissolved salts, and bacteria from water. From a boiler application point of view, RO of the feedwater reduces the frequency of ion exchanger regeneration and thus reduces the consumption of chemicals. It also helps to reduce the TDS content of water and reduces the amount of blowdown.

7.4.1.6 Chlorination Chlorine is used to kill microorganisms such as bacteria, fungus, and algae that are present in untreated water. Chlorination of feedwater disinfects it from pathogenic bacteria, viruses, and germs. Chlorine reacts with water to form hypochlorous acid (HOCl) and hydrochloric acid (HCl), of which hypochlorous acid is effective as a biocide. Its stability is pH dependent; it is more effective at a low pH. At pH >9, its effectiveness is negligible.



Biofouling is controlled by chlorination. Residual chlorine is removed from water either by passing it through an activated carbon filter or adding sodium sulphite before it is subjected to ion exchange treatment.

7.4.2 Internal Treatment

Internal water treatment consists of the chemical treatment of water inside the boiler, irrespective of whether the amount of impurities is high or low, or whether the water has been subjected to external pretreatment or not (Ref 7.2, 7.4–7.9). The fact remains that for moderate- and high-pressure boilers, external pretreatment of the make-up water is mandatory for good results.

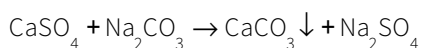
During internal water treatment, chemicals are added to the boiler water so that the scale that forms impurities is precipitated in the form of sludge, which is subsequently removed during the blowdown operation. Because impurities in dissolved conditions do not cause any harm to the boiler system, the impurities are converted to soluble compounds in some cases, preventing the formation of a scale. The main objectives of internal treatment are to prevent scale formation by precipitation of hardness in water, to eliminate oxygen from feedwater, and to provide adequate alkalinity to water to prevent corrosion.

Some of the commonly used internal water treatment methods and programs are:

- Colloidal conditioning
- Carbonate conditioning
- Calgon conditioning
- Sodium aluminate conditioning
- Caustic treatment
- Phosphate conditioning—includes conventional phosphate treatment, co-ordinated phosphate treatment, congruent phosphate treatment, and equilibrium phosphate treatment
- Chelant treatment
- Use of oxygen scavengers
- All volatile treatment (AVT)—AVT (R) and AVT (O)
- Oxygenated treatment (OT)—neutral water treatment and combined water treatment (CWT)

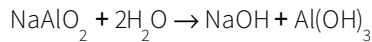
7.4.2.1 Colloidal Conditioning This treatment is mainly confined to low-pressure boilers. Organic materials such as kerosene or tannin are added. They form a coating over scale-forming precipitates, thereby yielding nonsticky, loosely adherent deposits that are easily removed during the blowdown operation.

7.4.2.2 Carbonate Conditioning This treatment is also restricted to low-pressure boilers. A scale that forms calcium sulfate is converted to calcium carbonate by the addition of sodium carbonate. The loose sludge of calcium carbonate is, in turn, removed by blowdown.

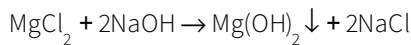


7.4.2.3 Calgon Conditioning In this method, the conversion of calcium sulfate to a water-soluble complex is ensured by addition of sodium hexa-meta phosphate (Na-HMP) as a water softener. (Calgon is the trade name for the softener with this chemical.)

7.4.2.4 Sodium Aluminate Conditioning Sodium aluminate is added to boiler water. Sodium aluminate (NaAlO_2) undergoes hydrolysis to form sodium hydroxide (NaOH) and aluminum hydroxide $\text{Al}(\text{OH})_3$ per the following reaction:



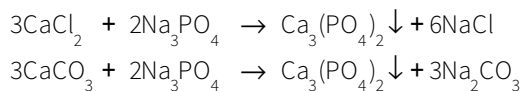
The sodium hydroxide in turn reacts with magnesium impurities such as magnesium chloride to form precipitates of magnesium hydroxide, $\text{Mg}(\text{OH})_2$.



The $\text{Mg}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$ together act as a flocculent and entrap the colloidal and fine suspended impurities such as silica in the boiler water and are finally removed by the blowdown operation.

7.4.2.5 Caustic Treatment Caustic soda is one form of alkali added to a boiler to maintain the boiler water pH within a range of 9.4 to 10.0. Approximately 1.0 to 1.5 ppm of NaOH is needed to maintain this pH level. However, there is a risk of corrosion-related damage such as caustic gouging or embrittlement if the NaOH concentration in water is not controlled properly. This treatment has proven to be a better option when there is a possibility of phosphate hideout during phosphate treatment.

7.4.2.6 Phosphate Conditioning Scale formation in high-pressure boilers can be prevented by adding sodium phosphate. It reacts with the hardness-forming impurities present in boiler or feedwater to form a soft sludge of calcium and magnesium phosphates, which are removed by the blowdown operation.

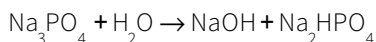


Phosphates are dosed either continuously or intermittently to meet phosphate requirements.

Phosphate Programs The underlying principle in any phosphate precipitation program is to neutralize the hardness of water by the reaction of phosphate with the alkalinity in boiler water to form tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$), an insoluble compound in the form of sludge that is removed

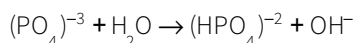
during the blowdown operation (Ref 7.6, 7.7, 7.9). During the process and in the presence of hydroxide alkalinity, magnesium and silica are also precipitated as magnesium hydroxide, magnesium silicate, or calcium silicate, and are subsequently removed as sludge.

However, when trisodium phosphate is used alone, it reacts with water at high temperature and raises the pH of boiler water by forming free sodium hydroxide per the following reaction:



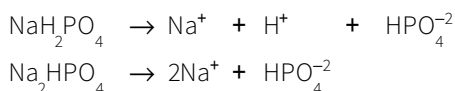
In order to prevent the formation of free NaOH, the pH and phosphate concentration in water, as in the case of high-pressure boilers, has to be controlled by keeping the Na to PO_4 ratio below 3.0. The treatment is named coordinated phosphate treatment.

Coordinated Phosphate Treatment The addition of trisodium phosphate alone in a conventional phosphate program produces OH^- ions due to hydrolysis per the following reaction:



This raises the pH of the water and leads to corrosion of boiler tubes.

On the other hand, the ionization of monosodium phosphate (NaH_2PO_4) and disodium phosphate (Na_2HPO_4) in water does not result in the liberation of free OH^- ions. On the contrary, monosodium phosphate ionizes to produce H^+ ions.



The recommended pH range for boiler water is 9.5 to 10.5. In this pH range the phosphate in boiler water is exclusively present as $(\text{HPO}_4)^{-2}$. Therefore, in a coordinated phosphate program, the trisodium phosphate is added along with monosodium phosphate and disodium phosphate in appropriate proportion. This helps to ensure an optimum pH without the presence of any free OH^- ions or free caustic alkali in water. When the pH fluctuates (as in the case of a condenser leakage), the ratio of these two phosphates is adjusted in order to bring the pH into the desired range. The absence of free caustic alkali ensures freedom from caustic attack by way of caustic embrittlement or gouging of boiler tubes.

The coordinated phosphate program is intended for drum-type high-pressure boilers because the potential for caustic attack increases with increasing pressure. A prerequisite of this program is that feedwater must be extremely pure and of consistent quality.

Because sodium orthophosphates precipitate incongruently under dry-out conditions, measures taken in coordinated phosphate programs are not sufficient to prevent the generation of free hydroxide.

Phosphate Hideout Normally, the solubility of any inorganic compound in water increases with increasing temperature. But trisodium phosphate exhibits a somewhat different behavior when added to feed or boiler water. Trisodium phosphate has retrograde solubility. The solubility of trisodium phosphate increases up to about 120 °C (250 °F) and reaches up to 94 g per 100 g of water. Then it decreases gradually up to about 200 °C (390 °F) (60 g per 100 g of water) and falls sharply with a further rise in temperature. At 230 °C (445 °F) the solubility is only 20 g per 100 g of water. Under high pressure conditions, the phosphate in boiler water prevails as HPO_4^{2-} ions and liberates OH^- ions in water. In turn, the boiler water pH increases, and detectable phosphate concentration decreases. On subsequent reduction of load or pressure, the phosphate again reappears and pH decreases. Thus, there is a variation in the phosphate level of water (i.e., increase or decrease) without any apparent reason. This variation in solubility of phosphate with temperature results in a problem known as phosphate hideout (Ref 7.7, 7.10). The phosphate is removed from the boiler water and hides out on surfaces in high-heat-transfer areas within the boiler. The severity of the attack increases when the tube surface is covered with iron oxide deposits. Sodium phosphates form a sodium-iron-phosphate complex with a magnetite layer. It is also an indication of the dirtiness of boiler steam generating tubes. The hideout problem occurs more in the case of boilers that are subjected to repeated start-ups and shutdowns as well as frequent variation in load and in cycling units. This in turn causes wide fluctuations in boiler water chemistry.

Phosphate hideout is thus viewed as the consequence of temperature-dependent interaction of sodium phosphate compounds with iron oxide, which creates a low-solubility reaction product. This compound precipitates in high-heat-flux areas or under high load conditions, and at lower loads and lower heat fluxes it redissolves.

Reduced solubility of phosphate causes phosphate deposition on tube walls, as shown in Fig. 7.1, and leads to acid phosphate corrosion. Deposition occurs even if the tube surface is clean.

Hideout or deposition of phosphates results in a rise in the boiler tube temperature and finally in tube failure. Periodic chemical cleaning of the boiler tubes is recommended to reduce hideout by minimizing the presence of porous magnetite deposits.

Congruent Phosphate Treatment In the congruent phosphate treatment process, monosodium, disodium, and trisodium phosphate are used, but the Na/PO_4 mole ratio is maintained between 2.4:1 and 2.8:1. The reaction of disodium and monosodium phosphate with free hydroxide generated by trisodium phosphate controls the alkalinity of boiler water. By adjusting the relative amounts of these two phosphates in the water, all free caustic

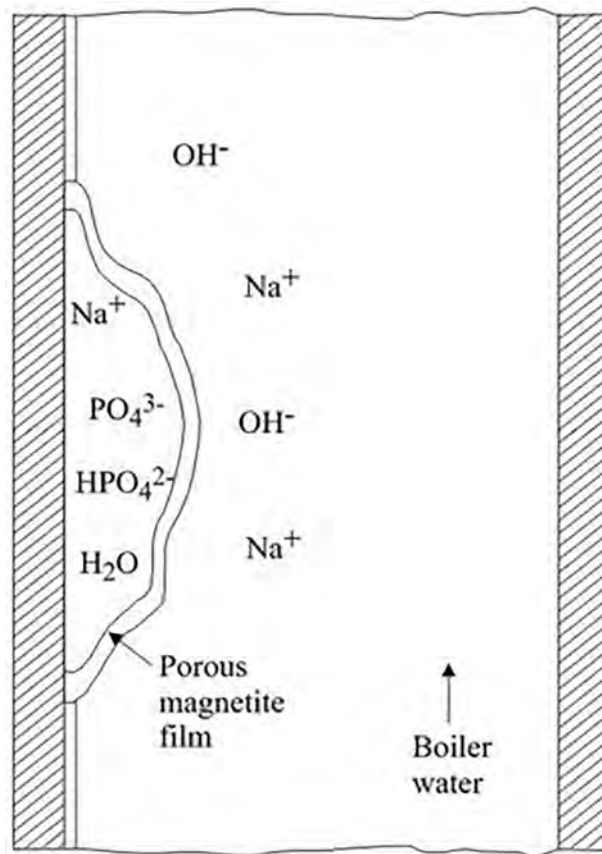


Fig. 7.1 Schematic expanded view of tube showing phosphate hideout on inner surface of the tube.

soda is reacted such that no free caustic soda is left in the boiler water. This ensures the prevention of a caustic buildup beneath the deposits. Monosodium phosphate also helps in lowering the pH of boiler water by generating hydrogen ions.

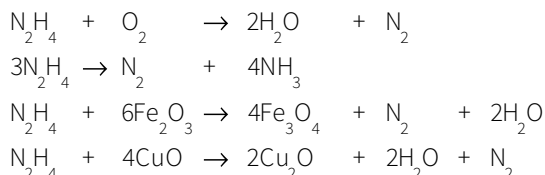
Equilibrium Phosphate Treatment Equilibrium phosphate treatment was developed mainly to minimize phosphate hideout and prevent acid phosphate corrosion. Equilibrium phosphate treatment is based on the use of low levels of phosphate along with a small amount of free caustic soda. In this treatment, the phosphate level is maintained below 2.5 ppm, caustic alkali below 1 ppm, and pH between 9.0 and 9.7. Equilibrium phosphate treatment offers many benefits to the system such as less hideout, low alkalinity, and less acid phosphate corrosion.

7.4.2.7 Chelant Program Chelants are low-molecular-weight compounds capable of forming water-soluble complexes. Ethylene diamine tetraacetic acid (EDTA) and nitrile triacetic acid (NTA) are widely used

chelating agents for the internal treatment of boiler water. The chelate ions react with calcium and magnesium, forming water-soluble complexes that can be removed during blowdown (Ref 7.7, 7.9). The concentration of the chelating agent has to be properly controlled because excess chelant reacts with the protective magnetite film. Once the protective magnetite film is damaged, direct contact of the feedwater with the underlying metal gives rise to corrosion.

7.4.2.8 Use of Oxygen Scavengers Feedwater must be kept in reducing condition at all times in order to prevent the corrosion of copper-based components in boiler systems that use copper alloys in their metallurgy. Most of the dissolved gases are removed from the feedwater mechanically in a deaerator. However, for removal of traces of gas such as oxygen, chemicals such as hydrazine, dimethyl hydroxylamine, and hydroquinone are dosed in feedwater to scavenge the dissolved oxygen (Ref 7.4, 7.7). These chemicals are known as oxygen scavengers.

Hydrazine (N_2H_4) removes traces of dissolved oxygen in boiler feedwater by forming nitrogen and water. Hydrazine not only removes the oxygen, but it also dissociates to liberate ammonia if it is in excess quantity, which helps in maintaining pH. Additionally, it reduces ferric ions to ferrous ions and cupric ions to cuprous ions to reduce the corrosion of iron and copper.



The amount of ammonia has to be controlled as it leads to corrosion of copper.

A typical dosage of hydrazine is 3 parts of hydrazine to 1 part of dissolved oxygen. The maximum permissible amount of dissolved oxygen in water is not more than 5 ppb.

7.4.2.9 All Volatile Treatment All volatile treatment (AVT) was developed mainly for once-through boilers. It is a water treatment program where ammonia is used with or without hydrazine as an oxygen scavenger (deoxidant) (Ref 7.6, 7.7). It is called AVT because it uses volatile chemicals such as hydrazine and ammonium hydroxide to control the pH and the oxygen level of water. Due to their volatilization, the chemicals are carried through the boiler into the steam and are condensed on turbine and condenser surfaces, thus providing protection. All volatile treatment also combats corrosion by keeping the dissolved oxygen in feed and boiler water close to zero and keeping the pH under control by maintaining weak alkalinity. The recommended pH range is 9.3 to 9.6, and the ammonia levels are from 1 to 2 ppm with less than 2 ppm dissolved solids.

There are two types of all volatile treatments—AVT (R) and AVT (O). If the metallurgy of the boiler involves copper alloys (i.e., if it is a mixed metallurgy), then AVT (R) is recommended. In this treatment, an oxygen scavenger such as hydrazine is added to BFW in addition to ammonia. Hydrazine treatment, which is reducing in nature, is called AVT (R). All volatile treatment (R) results in formation of a protective layer of magnetite (Fe_3O_4). However, if the boiler has an all ferrous metallurgy (i.e., no copper or copper-base alloys are used) then the treatment preferred is AVT (O). In AVT (O), no reducing agent is added. All volatile treatment (O) allows a layer of hematite to form on the top of the magnetite. Condensate polishing is a must for once-through boilers operating under AVT alone, even if fresh water is used as cooling water.

Irrespective of whether the treatment is AVT(R) or AVT(O), the BFW must be of high purity at all times.

The advantage of AVT is that it does not involve any precipitation reaction and hence there is no question of sludge removal by blowdown. Also, there is no carryover of solids. The main drawback of AVT is its lack of buffering capacity. For instance, if a condenser tube leaks or there is some other contamination of a similar nature, the alkalinity or pH of water drops quickly, promoting corrosion. In other words, AVT does not provide any protection against contamination. In such circumstances, coordinated phosphate treatment is more effective.

7.4.2.10 Oxygenated Treatment In the case of OT, oxygen is deliberately injected into the feedwater to keep the oxygen level between 30 and 50 ppb. The traces of oxygen help to protect the underlying metal from corrosion by forming an additional protective layer. Here, a protective layer of hematite (Fe_2O_3) forms over the preexisting magnetite (Fe_3O_4) layer.

There are two types of oxygen treatments, neutral water treatment (NWT), in which dissolved oxygen is allowed to coexist in neutral water with pH 7 to 8, and CWT, wherein the pH of feedwater is maintained at 8.0 to 9.0 by ammonia addition along with a controlled dose level of dissolved oxygen (Ref 7.6, 7.7).

The solubility of hematite, the layer formed in CWT, is lower than that of the magnetite generated during AVT and thus ensures complete protection of the underlying metal from corrosion.

The prerequisite for OT is pure feedwater. As a result, the condensate water must be subjected to polishing before use. Secondly, no copper-base alloys can be used in the feedwater and condensate system of the boiler.

Thus, water chemistry plays a very important role in uninterrupted running of a power plant with a maximum plant load factor. The following tables list representative data on typical quality levels of water for use in boilers as feedwater and boiler water (Tables 7.1 and 7.2). The data shown is just for reference, and the actual values may vary from plant to plant depending on the original equipment manufacturer guidelines.

Table 7.1 Typical quality levels for feedwater

Quality parameter	Boiler drum operating pressure, MPa (psi)						Once-through boiler
	0.0–2.0 (0–300)	2.0–4.1 (300–600)	4.1–6.2 (600–900)	6.2–6.9 (900–1000)	10.3–13.8 (1500–2000)	16.5–20.0 (2400–3000)	
Type of treatment	...	...	...	...	...	Phosphate and AVT	AVT
Iron, ppm	0.1	0.03–0.05	0.020–0.025	0.02	0.01	0.005	0.005
Copper, ppm	0.05	0.020–0.025	0.015–0.020	0.015	0.01	0.005	0.003
Total hardness, ppm	0.300	0.200–0.300	0.100–0.200	0.00	0.00	0.003	nil
Oxygen before scavenging, ppm	0.05	0.02	0.01	0.007	0.007	0.007	0.007
Silica, ppm	0.02	0.02	0.02	0.02	0.02	0.02	0.01
pH at 25 °C (75 °F)	8.3–9.5	8.3–9.5	8.3–9.5	8.8–9.6	8.8–9.6	8.8–9.2 (Cu alloys) 9.0–9.4 (Non-Cu alloys)	8.8–9.2 (Cu alloys) 9.0–9.4 (Non-Cu alloys)

Table 7.2 Typical quality levels for boiler water

Quality parameters	Boiler drum operating pressure, MPa (psi)					Once through boiler
	0.0–2.0 (0–300)	2.0–4.1 (300–600)	4.1–6.2 (600–900)	6.2–6.9 (900–1000)	10.3–13.8 (1500–2000)	
TDS, ppm	3500	2500–3000	750–1000	600	50–100	0.05
TSS, ppm	15	8–10	2–3	1	...	...
Silica, ppm	150	40–90	20–30	8	1	0.02
Total alkalinity, ppm	700	500–600	300	150–200	150	...
pH	11–12	11–12	10.5–11	9.5–10.5	9.1–9.6	> 8.5

REFERENCES

- 7.1 P. Cohen, *The ASME Handbook on Water Technology for Thermal Power Systems*, American Society of Mechanical Engineers, 1989
- 7.2 A. Bhatia, “Boiler Water—Problems & Solutions,” PDH Course M165, p 1–44, <https://www.pdhonline.com/courses/m165/m165.htm>
- 7.3 K. Nagar, “Boiler Water Problems and Its Causes,” Baron Chemicals & Systems Pvt. Ltd., last modified Dec 2017, www.baronchemicals.com/BoilerWater.pdf
- 7.4 M. Natarajan, *Practical Boiler Water Treatment Handbook*, Chemical Publishing Company, 2011
- 7.5 Vogt Power International Inc., “Importance of Good Boiler Feedwater Treatment,” Technical Bulletin, Jan 2001, <https://www.babcockpower.com/pdf/VPI-SI-0006.pdf>
- 7.6 B. Buecker, *Power Plant Water Chemistry—A Practical Guide*, Pennwell Publishing Company, 1997

- 7.7 I.J. Cotton et al., “Boiler Systems,” Association of Water Technologies, Technical Manual, 2003, p 58–95
- 7.8 Syntech Fibres, “Boiler Feedwater Treatment (Part II): Water Treatment Fundamentals,” 2011, www.sedifilt.com/technical_library/boiler_feedwater_treatment_part_ii_water_treatment_fundamentals.html
- 7.9 I.M. Baghni and A.I. Zwebek, Using of Congruent Phosphate as Equilibrium Phosphate Boilers Water Treatment, *WIT Transactions on The Built Environment*, Vol 110, 2009, p 159–169
- 7.10 Babcock & Wilcox Power Generation Group, “Boiler Water Phosphate Chemistry,” last modified Dec 2016, <http://www.babcock.com/resources/-/media/a56169eabd20469e89856e8196e437ab.ashx>

CHAPTER 8

Remaining Life Assessment of Boiler Tubes

8.1 Introduction

A large number of coal-fired power plants are currently in operation world-wide and some are older than 30 years. One of the global problems faced by the power sector is the aging of its power plants, including aging of high-pressure parts such as turbines, boiler drums, headers, and boiler tubes. The efficiency and reliability of coal-fired power plants decreases with age.

The designed life of a boiler and its components in a thermal power plant is about 20 to 30 years (i.e., approximately 200,000 to 300,000 hours). The question is whether, after a certain stage, the equipment can be put into further service, and if it can, how long. The answer to this question is vital not only from a safety and reliability point of view but also from an economic viewpoint, especially when managing plants on limited budgets.

In view of the ever-increasing demand for power for sustainable growth in all countries, it is essential to have a guaranteed uninterrupted supply of power from existing plants in addition to increasing the generation capacity. Increases in power production by installation of new plants is capital intensive and cannot be looked upon as the only solution to power shortages. Instead, uninterrupted functioning of existing power plants at a high plant load factor should also be thought of as a viable solution to overcoming a power crisis, at least in part. This makes it mandatory to know how long a particular existing power plant or piece of equipment, including boiler tubes, can be operated safely and cost-effectively, even after their designed life. The answer to this important question regarding

the operational capability of existing plants lies in remaining life assessment (RLA) (Ref 8.1).

In general, aging of any plant and equipment leads to frequent failures, and in the case of thermal power plants, it is mainly the failure of boiler tubes. As discussed in Chapter 6, “Damage Mechanisms with Case Studies,” in this book, failure of boiler tubes may be attributed to reasons including overheating, creep, various forms of corrosion, erosion, fatigue, manufacturing, and operational issues. Any such failure ultimately affects the performance of the plant due to unscheduled forced shutdowns. Therefore, the condition of the tubes needs to be checked periodically by RLA tests. Remaining life assessment evaluates the present condition of the tubes and predicts their potential remaining life span. Remaining life assessment of boiler tubes is necessary because the tubes undergo in-service structural and microstructural damage due to mechanical and thermal stresses, and the tubes interact chemically with the environment. Thus, RLA evaluates boiler tubes to determine their health. Remaining life assessment takes into account only those damage mechanisms that are dependent on temperature and time.

8.2 Objectives of Remaining Life Assessment

There are certain phenomena that occur during operation of a thermal power plant that are inevitable and that lead to damage to the pressure parts of the boiler. For example, exposure of the outer surfaces of a boiler tube to hot gas results in corrosion or erosion. Despite water chemistry control, the inner surface of the tubes experiences scaling and corrosion because of contact with the water used for steam generation. High-pressure parts such as superheater and reheater tubes are prone to creep damage because of acting or residual stresses at elevated temperatures. The starting and stopping of the boiler results in cyclic stresses and failure due to fatigue. All of these factors individually or collectively lead to material degradations of different magnitudes, resulting in failure of the tubes and forced outages. Remaining life assessment aims to minimize such failures and forced outages.

The main objectives of RLA of boiler tubes are (Ref 8.2):

- To prevent the catastrophic failures of tubes
- To increase safe operational reliability for extended life
- To prevent forced outages and repairs
- To predict the probable root cause or causes of forced outages and also to suggest remedial action to prevent the recurrence of similar failures in the future
- To avoid premature scrapping of the tubes
- To ensure cost reduction and lessen downtime

- To assist in setting up proper inspection schedules as well as maintenance and operating procedures
- To estimate the remaining life of tubes

8.3 Remaining Life Assessment Methodology

An RLA program for boiler tubes includes a metallurgical examination and theoretical calculations based on fracture mechanics. The remaining life of a tube is estimated by assessing the microstructural deterioration or damage that it has undergone, using a fundamental knowledge of the material properties and the stress distribution. For example, long-term overheating of waterwall tubes below Ac_1 leads to changes in microstructure such as degradation of pearlite to form ferrite and carbides. Similarly, long-term service of superheater and reheater tubes at elevated temperatures results in the precipitation and coagulation of alloy carbides along the grain boundaries, leading to creep. In components such as headers and pipes, which are subject to high pressure and high temperature, creep occurs, which manifests itself in the form of cavities in the microstructure. These microstructural changes lead to changes in mechanical properties as well, including a drop in tensile strength, stress-rupture strength, hardness, and impact toughness. Remaining life assessment establishes correlations of the microstructural changes with time and temperature. It can also be used to determine changes in the properties of materials such as strength and hardness with time and temperature and the extrapolate the observed behavior in order to predict the remaining life of the tubes. Dimensional measurements taken to evaluate the extent of thinning and measurement of oxide scale thickness also are part of RLA.

The remaining life of boiler tubes is normally estimated using a three-level approach (Ref 8.3). Level I RLA begins with an assessment based on collected background data and plant records such as design stresses and temperatures, material properties from the original equipment manufacturer, interaction with plant personnel, and collected details of operational history. Level II involves visual examination of the tube (either on-site or in a laboratory) and measurement of dimensions, followed by simplified stress calculations, in conjunction with the data on minimum material properties per the original equipment manufacturer. Level III involves in-depth inspection and generation of material data from the samples removed from the component (destructive testing).

A wide range of destructive and nondestructive tests are performed during RLA. The various tests include ultrasonic testing for thickness and oxide scales, radiography, magnetic particle inspection, dye penetrant testing, in situ replication and metallography, eddy current testing, fibroscopy, acoustic emission, positive material identification, hardness and

microhardness measurement, flattening testing, microstructural evaluation, and accelerated creep tests.

The results of these tests are systematically analyzed and based on the findings and calculations, the remaining life of the tubes is calculated.

8.4 Remaining Life Assessment Testing Practice

During RLA, a wide range of destructive and nondestructive tests are carried out for health assessment of the tubes. Nondestructive testing (NDT) techniques are used to compare the current condition of a tube with its original condition to evaluate the amount of deterioration it has undergone and to assess its structural integrity. Prediction of remaining life simply on the basis of the results of NDT can be difficult because of scatter in the results of material properties. It is therefore necessary to determine the mechanical properties using test samples drawn from the actual tube. Tube samples from various locations, as stipulated in American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessel Code—2017, are collected for destructive tests such as tensile and impact tests, creep rupture tests, flattening tests, and chemical analysis. The following are brief descriptions on the scope of some of the tests carried out in an RLA of boiler tubes (Ref 8.2, 8.4, 8.5). Detailed discussion on individual tests is beyond the scope of this book.

8.4.1 Visual Examination

Visual examination assesses the condition of the tube's surface appearance. Features developed due to exposure to high temperature, oxidation, corrosion or rusting, scaling, erosion, or erosion-corrosion are analyzed during visual examination. Examination of physical deviations in critical components such as distortion and bowing of superheater and reheater coils is also one of the objectives of visual examination during RLA.

8.4.2 Ultrasonic Testing

Tubes are subjected to ultrasonic testing using high-frequency sound waves to detect surface and subsurface flaws, if any. Discontinuities such as cracks, fissures, flakes, laminations, shrinkage cavities, and pores can be detected using ultrasonic testing. This technique is also used for measuring the oxide scale thickness of high-temperature tubes. Advanced techniques such as time-of-flight diffraction and phased arrays have been developed for this purpose.

8.4.3 Dimensional Measurement

Any bulging or swelling of the tube that arises out of heat effects or thinning due to flue gas erosion is usually detected by subjecting it to an outside

diameter measurement. The outside diameter of the tube is measured at several locations along the length of the tube.

8.4.4 Tube Thickness Measurement

Boiler tubes are subjected to thickness measurement at strategic locations using an ultrasonic thickness gauge. Tubes undergo thinning over a period of time due to erosion and corrosion. If the thickness is reduced below a certain limit, the tube cannot sustain operating pressures at the prevailing metal temperature and this leads to failure. A certain minimum remaining thickness of a tube is a must to sustain the maximum permissible stress under actual operating conditions of pressure and temperature.

A technique known as the internal rotary inspection system is employed for measuring the thickness of the entire tube. It uses ultrasonic waves to detect the loss of wall thickness. In this technique, the probe is inserted into a tube filled with water and the probe scans the entire circumference of the tube while it is withdrawn slowly. The probe detects metal loss from the inside and outside of the tube wall, and the results are displayed on a cathode ray tube screen and recorded.

8.4.5 Oxide Scale Thickness Measurement

Formation of oxide scales on tube walls results in a local temperature rise due to the insulating nature of the scale. This results in the operation of tube walls at temperatures increasingly higher than the nominal or designed temperature, ultimately shortening the tube life. The thickness of the oxide scale therefore plays a vital role in RLA. Measurement of oxide scale thickness is an indirect method of evaluating the status of creep damage.

Oxide scale thickness can be determined destructively or nondestructively. A destructive method of scale thickness measurement is based on the deposit weight density approach, in which the change in the weight of the tube divided by the water-touched area from where the deposit was removed is calculated. The scale thickness can also be measured nondestructively, using an ultrasonic method, and the remaining life is computed using software. The tube and deposit layer thicknesses are measured by assessing the change in waveforms through the material. It is possible to measure the oxide scale to 0.1 mm in thickness.

8.4.6 Fibroscopic Inspection

Similar to endoscopy in medical diagnosis, fibroscopy is used for assessment of the internal surfaces of headers and tubes. The technique makes use of a flexible fiber-optic bundle mounted inside a flexible tube with an eyepiece on one end and a lens on the other. Information about the condition of the internal surface of the tubes is obtained by illuminating

the surface with a laser beam and inspecting the surface. The fibroscope works on the principle of total internal reflection of light.

8.4.7 Dye Penetrant Inspection

In dye penetrant inspection, a dye or liquid penetrant is applied to the surface to be examined and allowed to penetrate into the discontinuities. The excess penetrant is then removed, the surface is dried, and the developer applied. The developer serves both as a blotter to absorb the excess penetrant and as a contrasting background to enhance the visibility of the indication. This method, however, can only be used for detecting those cracks and weld defects that open to the surface.

8.4.8 Magnetic Particle Inspection

Magnetic particle inspection is limited to ferromagnetic materials (i.e., only those materials that can be magnetized). Surface and subsurface defects such as grinding cracks, quenching cracks, in-service fatigue cracks, seams, and laps are detected. Resolution is further improved by use of a wet fluorescent magnetic particle inspection approach.

8.4.9 Hardness Measurements

Hardness measurements yield the metallurgical status and condition of the tube. There are standard correlations available between the hardness and the tensile properties of a material. A portable hardness tester is used for in situ hardness measurement, whereas Brinell, Rockwell, or Vickers hardness testers are used for laboratory samples. For tubes that have undergone carburization or decarburization, obtaining a microhardness profile using a microhardness tester is recommended.

8.4.10 Flattening Test

According to ASME Boiler and Pressure Vessel Code—2017, boiler tubes are subjected to flattening tests by applying compressive loads between two parallel plates. A tube should not develop any cracks or breaks until the distance between the plates is less than a certain specified value per the standard.

8.4.11 Evaluation of Chemical Deposits

Boiler tubes are vulnerable to the formation of iron oxide scale deposits, alkali-earth scales, and copper and silicate scales. Analysis of chemical deposits on the internal surface of the tubes and of external deposits is important to establish the trend of aging due to corrosion and to identify its source. Energy dispersive spectroscopy in conjunction with scanning electron microscopy (SEM) has proven to be an effective method for

qualitative analysis of chemical and scale deposits. Conventional chemical methods, atomic absorption spectrometry, and x-ray fluorescence spectroscopy are also used to evaluate chemical deposits.

8.4.12 Replication and Metallography

Irrespective of knowledge about the operational history of the plant, replication or in situ metallography and examination of replicas or metallographic samples in the laboratory provide useful information about the microstructural degradation that the tube has undergone over a period of time due to its exposure to high-pressure, high-temperature conditions and corrosive environments. Microstructural changes such as the spheroidization of carbides in pearlite, bainite breakup, precipitation and coarsening of carbides at grain boundaries, decarburization, and scale formation are evaluated using metallography.

8.4.13 Accelerated Creep Rupture Test

Superheater and reheater tubes are exposed to temperature ranges of 600 to 700 °C (1110 to 1290 °F) during service and are prone to creep failure. Creep is a time-dependent deformation of the material at constant load below its yield strength. The conventional creep test is cumbersome and time consuming and therefore an accelerated creep test is performed to evaluate the behavior of the material under controlled laboratory conditions. The accelerated creep rupture test is conducted at a temperature and stress higher than that to which the tube is normally exposed, and the remaining creep life is obtained using software based on the Larson-Miller parameter (LMP). The performance of the material under such aggravated conditions of temperature and pressure is converted and correlated with its behavior under normal operating conditions using empirical relations and software programs.

The results of the microstructural examination and the accelerated creep rupture test are used to assess the remaining life of boiler tubes.

8.5 Remaining Life Assessment Methods (Ref 8.6–8.8)

8.5.1 Hardness-Based Approach

Low-alloy steels, such as those used in waterwall tubes, experience changes in strength (which are reflected in terms of corresponding changes in hardness) due to changes in their microstructure, depending on the service temperature and exposure time. The strength or hardness of the tube material under any given set of conditions is a measure of its mean operating temperature. A correlation exists between the hardness, H , and the LMP, P .

The LMP is derived experimentally by aging material with a given initial hardness at temperature T and measuring the change in hardness as a function of time, t . A typical softening curve for 9Cr-1Mo steel is given in Fig. 8.1.

Remaining life is assessed by carefully analyzing the data on hardness and strength versus time for tubes subjected to long-term service. The method is especially useful when the change in the strength of the material is due to coarsening of carbides.

8.5.2 Method Based on Allowable Reduction of Tube Wall Thickness

Boiler tubes undergo thinning due to exposure to high temperature under stress within the creep range. There is a minimum value of thickness below which a tube will experience stress-rupture failure if subjected to continued service at a given stress level. Therefore, maximum allowable reduction in tube wall thickness can be used as a criterion for RLA. Design stress in the creep range is a function of exposure time and temperature. At a given operating temperature, the longer the exposure time, the less is the maximum permissible design stress. Also, the minimum value of required wall thickness of the tube will be greater, thereby permitting less reduction in the thickness.

Based on the allowable working stress, the minimum value of the allowable thickness for a tube of a certain diameter at a given operating pressure is calculated.

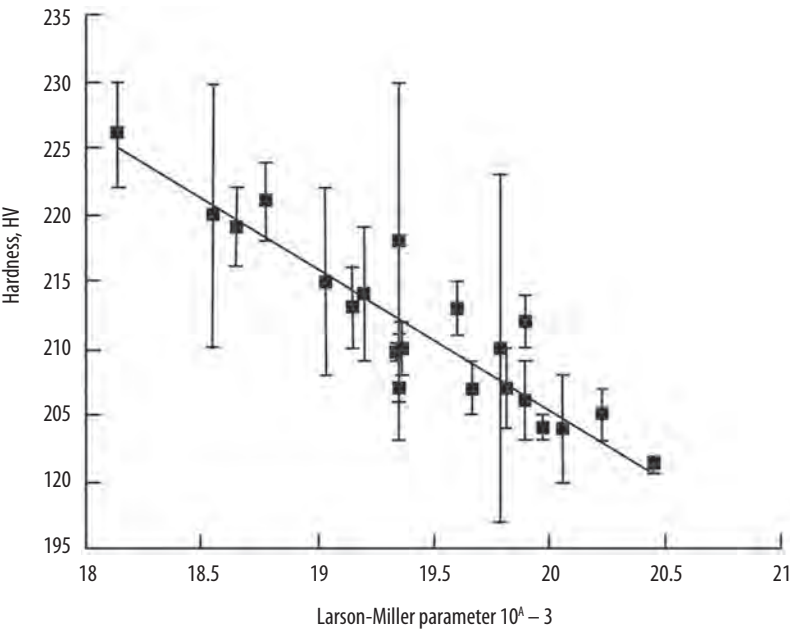


Fig. 8.1 Plot of hardness against the Larson-Miller parameter for 9Cr-1Mo steel tested at different stresses and temperatures. Source: Ref 8.9

8.5.3 Oxide Scale Thickness Method

Estimation of remaining life based on the oxide scale thickness is relatively simple and an easier approach than the accelerated creep rupture test. The thickness of the oxide scale formed on superheater and reheater tubes is measured microscopically or by NDT.

Studies reveal that the thickness of steam-side oxide scales is linearly proportional to the temperature and time of exposure and follows specific rate laws (Fig. 8.2).

This correlation between scale thickness and temperature is used to arrive at the tube metal temperature. Once the tube metal temperature is estimated, the remaining life is computed using the LMP as given by:

$$\log x = 0.00022P - 7.5$$

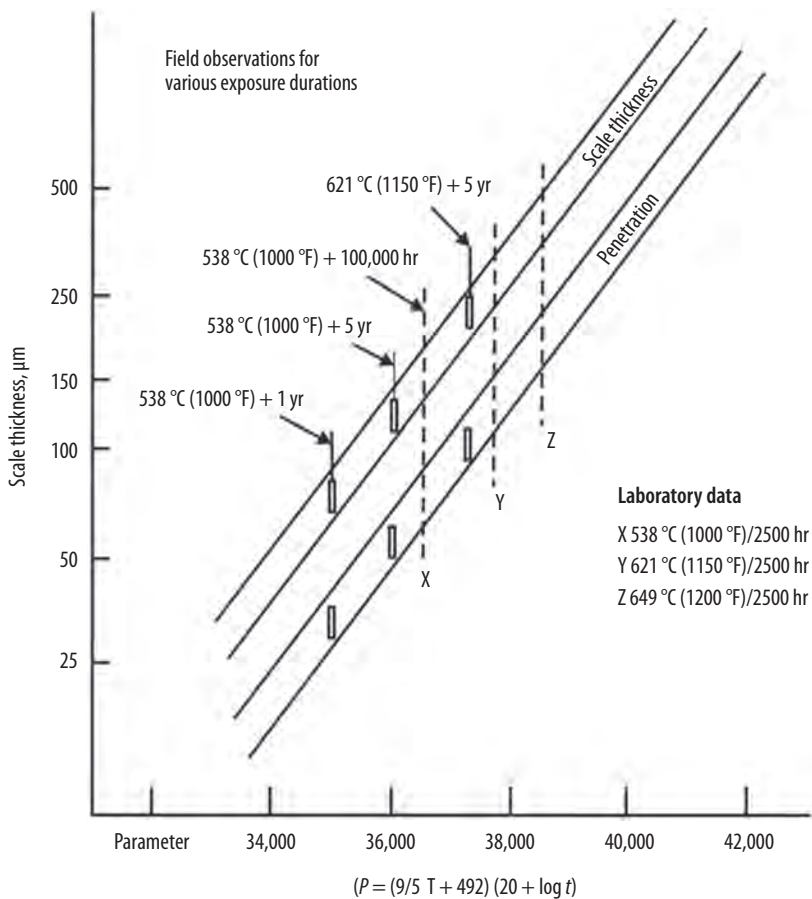


Fig. 8.2 Steam-side scale formation for 1–3% chromium ferritic steels correlated with the Larson–Miller parameter. Source: Ref 8.10

where

$$P = T(20 + \log t)$$

x = thickness of oxide scale in mils (1 mil = 25.4 μm)

T = maximum temperature that the metal has been exposed to
in degrees Kelvin

t = time to rupture

This empirical relation takes into account only the steam-side (i.e., ID surface) scale and does not consider the effect of fire-side deposition (if any) on the tube wall temperature. Any deposits on the fire side will introduce errors in estimated temperature by this method and in turn in the estimated life of the tube.

8.5.4 Metallographic Analysis Method

Creep is the predominant damage mechanism for high-pressure, high-temperature parts of a boiler. Creep is manifested by the formation of cavities known as creep cavities along the grain boundaries of the steel. The evolution of the morphology of creep cavities and coarsening of carbides during creep is used to assess the creep life of boiler tubes (Ref 8.11).

The phenomenon of creep is governed by factors such as stress, temperature, time, and the material properties. For a given material subjected to constant stress and temperature, the extent of creep damage is proportional to time. Since the morphology (i.e., shape and orientation) of cavities changes with time, it is used to judge the status of the component in terms of its remaining life. Microstructural studies indicate that during creep, creep voids or cavities formed at the grain boundaries have a tendency to coalesce during prolonged exposure to high temperature, finally forming micro- or macrocracks. These cracks grow in an intercrystalline manner, which leads to failure. Based on a metallographic investigation, Neubauer and Wedel (Ref 8.12) developed a correlation between the consumed creep life of power plant components, including boiler tubes, and the cavity classification.

Replicas of crack-sensitive areas on the tube surface are taken and examined under SEM to study the morphology of the cavities formed. Neubauer and Wedel classified the cavities into four types, namely,

- Isolated cavities (stage I)
- Oriented cavities (stage II)
- Formation of microcracks (i.e., linking of cavities, stage III)
- Formation of macrocracks (stage IV)

Figure 8.3 shows the change in cavity morphology with respect to time on the creep curve. Also established are the approximate time intervals between the two consecutive stages of creep cavities (Fig. 8.3 and Table 8.1).

Shammas (Ref 8.13) correlated the cavity classification with expended creep life fractions. Accordingly, the damage condition as designated by

stages 1, 2, 3, 4, and 5 corresponds to the expended life fraction equal to *undamaged*, 0.46, 0.50, 0.84, and 1.0, respectively (Fig. 8.4).

Table 8.1 reproduces the graphical data given in Fig. 8.3 and 8.4 and displays the expended life fraction of the tube for the corresponding stage of creep damage.

Once the expended life fraction for a particular damage classification is known, the remaining life of the tube is calculated using the relationship:

$$t_{\text{rem}} = t_{\text{exp}} \left[\left(\frac{t_r}{t_{\text{exp}}} \right) - 1 \right]$$

where

t_{rem} = remaining life of the tube

t_r = rupture life of the tube

t_{exp} = expended life of the tube

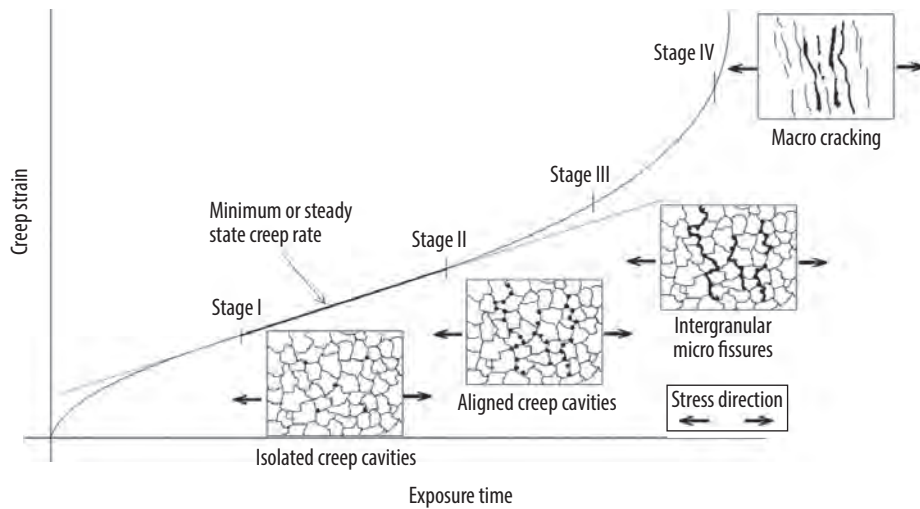


Fig. 8.3 Stagewise progress in cavity morphology with respect to creep curve

Table 8.1 Data on damage classification and expended life fraction of creep damage for boiler components

Stage of damage	Microstructure	Expended life fraction
Stage 1 (service rendered without damage)	Ferrite and pearlite (free from cavities and cracks)	0.12
Stage 2	Isolated creep cavities	0.46
Stage 3	Aligned creep cavities	0.50
Stage 4	Formation of microcracks	0.84
Stage 5	Linked, macrocracks	1.00

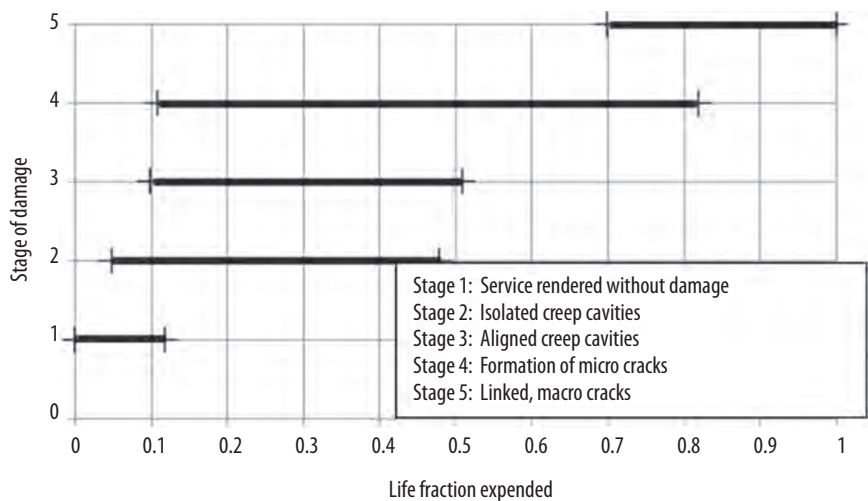


Fig. 8.4 Correlation between the damage classification and expended fraction of creep life. Source: Ref 8.13

8.5.5 Accelerated Creep Test Method

The most reliable results on the creep life of any material are obtained by subjecting it to classical long-term stress-rupture tests at stresses and temperatures actually encountered during service. However, such tests are time consuming and cumbersome and are not preferred for RLA. Instead, the accelerated creep test is a viable option. Under accelerated test conditions, the rupture time is reduced significantly. This is ensured by either increasing the stress above the actual service conditions or increasing the temperature, or both. Using the accelerated creep test, results are made available in a shorter time.

The remaining life of a tube is estimated by the uniaxial creep test. A test sample from the service-exposed tube is subjected to rupture under accelerated conditions in the laboratory. The test is performed either by keeping the stress constant and raising the temperature (i.e., in iso-stress mode) or by keeping the temperature constant and increasing the level of stress (i.e., in isothermal mode). The iso-stress accelerated creep rupture test is conducted at the chosen higher temperature (usually above 540 °C, or 1005 °F) for the number of hours determined during precalculation. If the material passes this test duration without rupture, the extension of life for the tube is recommended for the calculated years.

A plot of the LMP verses stress on a logarithmic scale for time to rupture (Fig. 8.5) is obtained, and by using the following equation, the life of a boiler tube is obtained:

The value of *P* (LMP) is calculated by using the following equation:

$$P = T(20 + \log t) \times 10^{-3}$$

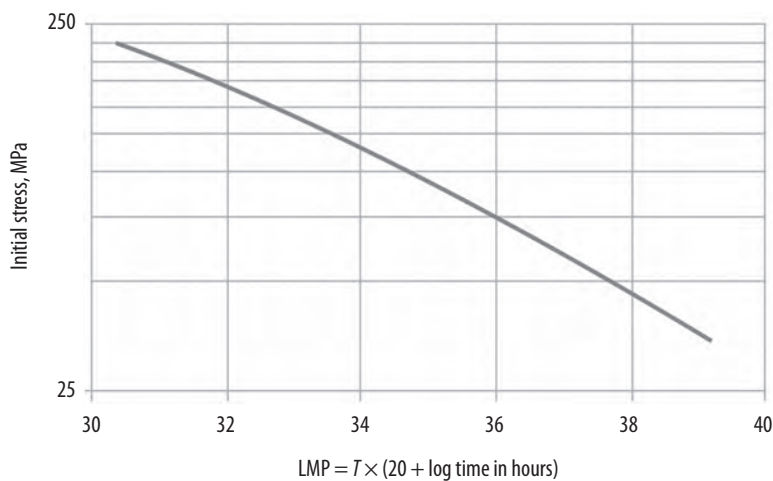


Fig. 8.5 Plot of stress versus Larson-Miller parameter for annealed 2.25Cr-1 Mo steel

where

T = Temperature in degrees Kelvin

t = Expected time to rupture in hours

The LMP describes the equivalence of time at temperature for a steel under the thermally activated creep process of stress rupture. In other words, it enables the calculation of the equivalent times necessary for stress rupture to occur at different temperatures. For a given stress, the LMP for the material can be obtained and the time to rupture can be predicted for any temperature.

8.5.6 Remaining Life Assessment Based on the A Parameter

The scientist Cane (Ref 8.14) proposed a model for RLA known as the *constrained cavity growth model*. In this model, an attempt was made to establish a correlation between the number fraction of boundaries with a cavity or cavities (known as the *A parameter*) and the expended life fraction of a boiler tube. The A parameter is the ratio of the number of grain boundaries that are damaged by cavitation or cracks to the total number of grain boundaries when microstructural measurements for cavities are made on a transverse plane parallel to the direction of maximum principal stress. This number is then correlated to a life fraction.

8.6 Case Study—Residual Life Assessment of Secondary Superheater Tube

8.6.1 Background Details

A superheater tube in a corner-fired boiler was considered for detailed assessment of its condition and potential for continued service. The tube

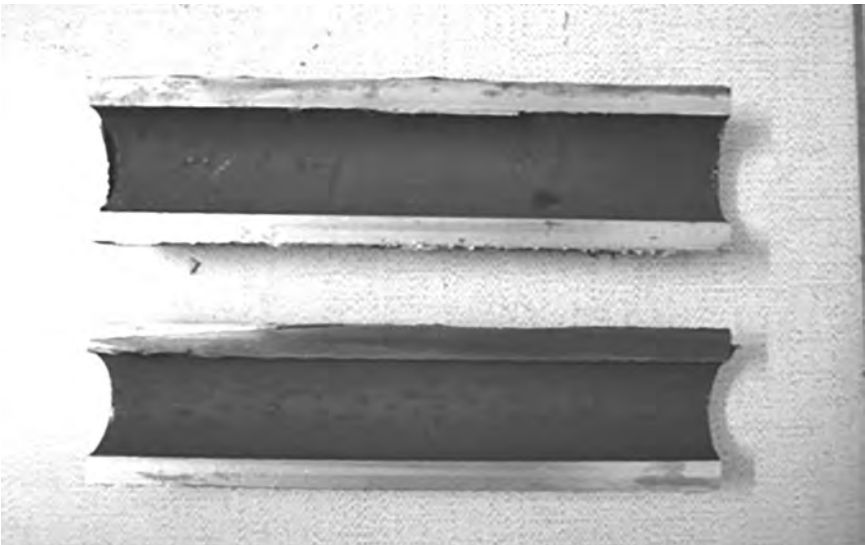
had a service life of 225,000 hours. Natural gas, crude oil, gas oil, and heavy fuel oil were used as the fuel. The boiler was operated at 15 MPa (2 ksi) and 470 °C (880 °F) and was in service for more than 20 years. The material of construction of the tube was SA 213 Grade T22 Ø 1¼” Sch 160 (i.e., 42.16 mm, or 1.66 in., diameter and 6.35 mm, or 0.25 in., thickness)

8.6.2 Investigation and Findings

Visual examination of the tube revealed the presence of a greenish yellow scale on the external surface and an adherent blackish scale on the inner surface of the tube, as shown in Fig. 8.6 (a) and (b).



(a)



(b)

Fig. 8.6 Photographs showing (a) outer and (b) inner surface of the tube with greenish yellow and blackish scales, respectively (a) 1000x, (b) 2000x

Dimensional measurements on the tube indicated an average outside diameter equal to 42.08 mm (1.65 in.) and an average tube thickness of 5.9 mm (0.2 in.). Chemical analysis of the tube confirmed that the tube material met the specifications for SA 213 Grade T22. The tube satisfactorily passed tensile, hardness, and flattening tests.

Energy dispersive spectroscopy analysis on the inner surface showed the presence of oxygen, chromium, and manganese. Energy dispersive spectroscopy analysis on the outer surface showed the presence of oxygen, manganese, sodium, magnesium, silicon, sulfur, calcium, and vanadium.

Microstructural analysis showed a ferrite and bainite structure with in situ degradation of bainite to form ferrite and carbides (Fig. 8.7). Scanning electron microscopy analysis after metallography showed the onset of creep damage, as indicated by the presence of isolated creep voids.

Both the inner and outer surfaces were covered with an adherent scale. The average scale thickness on the inner surface on the flue gas side was 220.0 μm and on the far side it was 175.5 μm . The average scale thickness on the outer surfaces, on the flue gas side was 372.3 μm , and on the far side it was 290.9 μm .

8.6.3 Steps in Remaining Life Computation

8.6.3.1 Corrosion Rate Measurement Ultrasonic thickness mapping at various locations of the tube indicated maximum wall thinning by 0.45 mm (the original wall was 6.35 mm) after about 225,000 hours of operation. The rate of thinning (corrosion) was derived as:

Operation time :	225,000 hours
Original thickness :	6.35 mm (0.25 in.)
Total thinning :	0.45 mm (0.018 in.)
Rate of thinning per hour :	2.0×10^{-6} mm/hour (0.45/225,000)
	~ 0.69 mils per year (0.017 mm per year)

This indicated a corrosion rate of 0.69 mils per year (MPY), considering a uniform rate of corrosion throughout its service life.

8.6.3.2 Remaining Life Based on the Thinning Rate The thinning rate was 0.69 MPY. If all other parameters of the operation remain unchanged, it was assumed that thinning of the tube would continue during further operation at the same rate of thinning. The time until the thickness decreases to the minimum permissible thickness gives the estimate on the remaining life. Minimum permissible thickness is given as:

$$t = (P \times D) / 2(SE + PY)$$

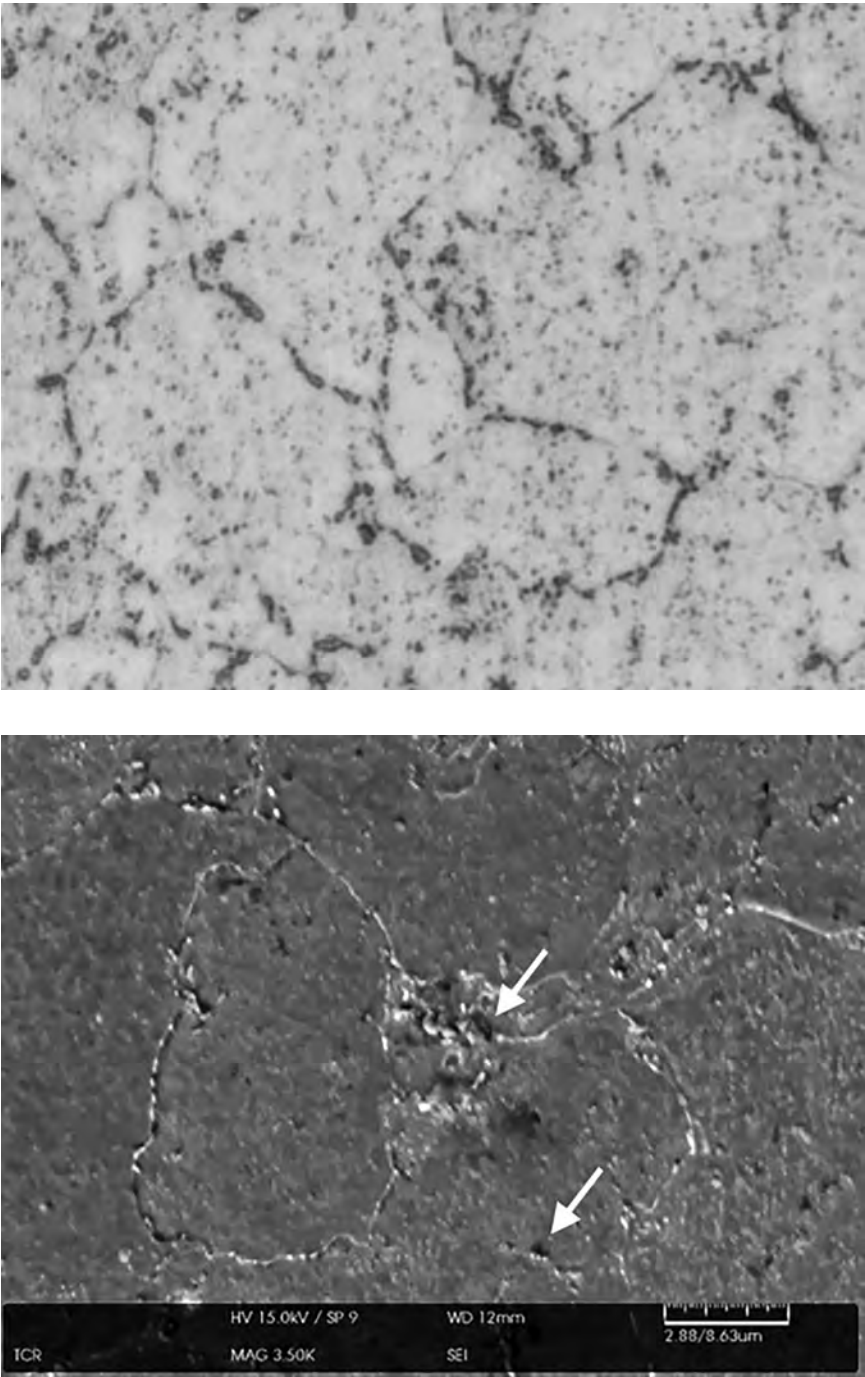


Fig. 8.7 (a) Microstructure of tube sample showing degradation of bainite into ferrite and carbide and (b) SEM micrograph showing onset of creep damage, as indicated by isolated creep cavities

where

t = minimum permissible thickness (mm)

P = internal working pressure = 15.0 MPa

D = measured average outer diameter = 42.08 mm

S = allowable working stress at operating temperature as per ASME Sec II-D = 102.80 MPa

E = quality factor = 1.0 for seamless tubes

Y = coefficient from Table 304.1.1 of ASME B31.3 = 0.4 for ferritic steels

Substituting these values into the formula yields

$$t = 2.90 \text{ mm}$$

The measured minimum thickness was 5.90 mm (0.23 in.). The allowable reduction until the wall thickness reached 2.90 mm (0.11 in.) was $5.90 - 2.90 = 3.00$ mm (0.12 in.).

At the thinning rate of 0.69 MPY (0.017 mm per year), it would take more than 5 years for the tube thickness to decrease to 2.90 mm.

8.6.3.3 Calculation of Theoretical Remaining Life Based on Neubauer and Wedel Classification According to an SEM examination (Fig. 8.7), the microstructure showed the onset of creep damage, as evidenced by isolated creep cavities, and indicated Class 1 damage per the Neubauer and Wedel classification. Table 8.2 describes the theoretical remaining life with respect to the microstructural observation on creep damage for each class defined by Neubauer and Wedel (Ref 8.13). Based on the measurements made and the plant data, the theoretical remaining life of the tube was calculated as per Table 8.2, for a Class 1 damage range of $t_{\text{exp}}/t_{\text{rup}} = 0$ to 12% (i.e., remaining life, $t_{\text{rem}} = 227,520 \times (1 - 0.12)/0.12 = 1,668,480$ hours).

According to the values determined from Table 8.2, the minimum theoretical life of the tube from microstructural observations was up to 1,668,480 hours. Therefore, it was judged that the microstructural condition indicated a remaining life of more than 5 years.

8.6.3.4 Remaining Life Based on Scale Thickness The remaining life of the tube was also estimated based on the steam-side scale

Table 8.2 Calculated theoretical remaining life for each damage class

Damage class	Range of life fraction, $t_{\text{EXP}}/t_{\text{RUP}}$	Range of life spent, %	Residual life, h
1	0 to 0.12	0 to 12%	∞ to 1,668,480
2	0.05 to 0.48	5 to 48%	4,322,880–246,480
3	0.1 to 0.51	10 to 51%	2,047,680–218,597
4	0.11 to 0.82	11 to 82%	1,840,844–49,943
5	0.7 to 1	70 to 100%	97,508–0

thickness. The average skin temperature estimation was based on the present steam-side scale thickness of 220 μm (8.65 mils), and the remaining life was assessed for future operation at this temperature.

The estimated temperature based on the present steam-side scale thickness was estimated from Fig. 8.8.

The LMP is:

$$LMP = T(^{\circ}R) \times [13.62 + \log(t)] / 1000$$

The LMP from the graph was determined to be 27.46.

For a service life t of 225,000 hours, the average skin temperature estimate is 1447 °R (531 °C). As the scale thickness increases during subsequent operation, the skin temperature also increases. Determination of theoretical remaining life was therefore performed assuming a 50 °C rise in future operation, that is., 581 °C (1537 °R). Life is estimated through the equation:

$$LMP = T[20 + \log(t)] / 1000 \text{ as given in Fig. 8.5}$$

where

T = temperature of operation in °R (1537),

t = remaining life in hours

LMP = 38.00 at hoops stress induced due to internal pressure

Substituting the values in to the above equation yields

$$38.00 \times 1000 = 1537 \times [20 + \text{Log}_{10} t]$$

Accordingly, the theoretical remaining life is 52,903 hours.

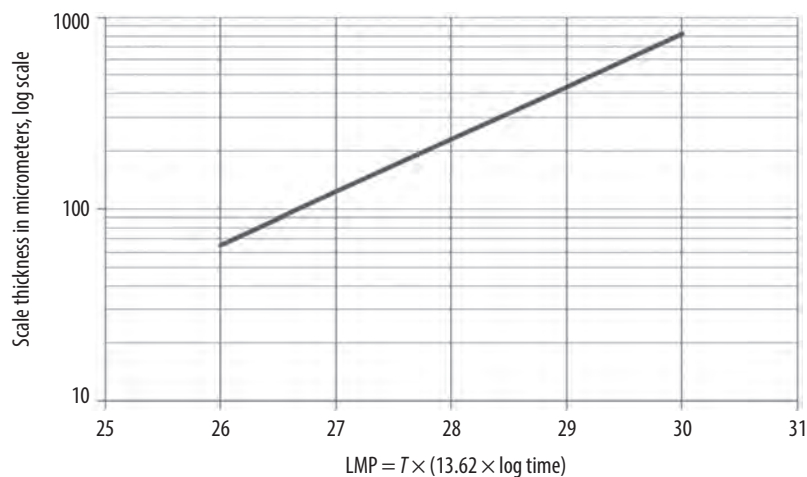


Fig. 8.8 Plot of oxide scale thickness versus Larson-Miller parameter

8.6.3.5 Discussion The metallurgical integrity of the tube in terms of chemical and physical properties appeared acceptable and met the requirements per specifications of SA 213 Grade T22. The microstructure at all locations was ferrite and degraded bainite in terms of carbides, which indicated normal aging. The scale on the inner surface of the tube resulted in a lowering of the heat transfer rate and an increase in the tube (skin) metal temperature. This resulted in a lowering of the remaining tube life. Outer surface scale containing vanadium along with sodium and sulfur pointed toward the possibility of formation of low melting glassy scale that could penetrate if the tube skin temperature exceeded 590 °C (1094 °F) or above to cause hot corrosion damage; although, at present the tube thickness was not showing any significant damage. Optical microscopy and SEM indicated the onset of creep damage in terms of isolated cavities as detected under the SEM. The condition of the tube with respect to the Neubauer and Wedel classification caused it to be rated as Class 1 damage with service exposed material and the presence of isolated creep voids.

8.6.3.6 Conclusion The remaining life was estimated to be more than 5 years.

Recommendations

- The steam-side oxide scale (ID side) thickness of all the tubes needs to be checked with NDT.
- The higher ID side scale requires chemical cleaning of the tubes.
- In situ metallography must be conducted after 2 years to monitor the condition of the microstructure from a creep damage point of view.

REFERENCES

- 8.1 R. Viswanathan, S.R. Paterson, H. Grunloh, and S. Gehl, Life Assessment of Superheater/Reheater Tubes in Fossil Boilers, *Journal of Pressure Vessel Technology*, Vol 116 (No. 1), 1994, p 1–16
- 8.2 P.R. Dongre and V.B. Rakhunde, Residual Life Assessment in High Temperature Zones of Power Plant Components, *International Journal of Mechanical and Production Engineering*, Vol 1 (No. 2), 2013
- 8.3 C. Laire and M. Eyckmans, “Evaluating the Condition and Remaining Life of Older Power Plants,” VGB PowerTech, Oct 2001, p 98–101
- 8.4 M. Nakashiro, H. Yoshizawa, K. Murakami, S. Kihara, T. Tanoue, and H. Umaki, Methods of Residual Life Assessment and Creep Damage Evaluation for Heat Transfer Tubes in Aged Power Boiler, Materials Ageing and Component Life Extension, *Proceedings of an International Symposium on Materials Ageing and Component Life Extension*, Oct 1995 (Milan), p 1337–1346
- 8.5 R. Viswanathan and R. Tilley, Creep Damage—Industry Needs and Future Research and Development, *Creep Resistant Steels*, F. Abe,

- T.-U. Kern, and R. Viswanathan, Eds., Woodhead Publishing Limited, 2008, p 637–666
- 8.6 K. Sankhala, Z. Gauri, P. Sharma, and D.K. Jain, Study of Microstructure Degradation of Boiler Tubes Due to Creep for Remaining Life Analysis, *International Journal of Engineering Research and Application*, Vol 4 (No. 7, Version 2), 2014, p 93–99
- 8.7 I. Klevtsov, H. Tallermo, T. Bojarinova, and A. Dedov, Assessment of Remaining Life of Superheater Austenitic Steel Tubes in Oil Shell of PF Boilers, *Oil Shale*, Vol 23 (No. 3), 2006, p 267–274
- 8.8 P.U. Pathy, Condition Assessment of Boiler and Its Components, *3rd MENDT—Middle East Nondestructive Testing Conference & Exhibition*, 27–30 Nov 2005 (Bahrain)
- 8.9 H.C. Furtado, L.H. de Almeida, and I. Le May, Damage and Remaining Life Estimation in High Temperature Plant with Variable Operating Conditions, *OMMI*, Vol 5 (No. 1), 2008
- 8.10 I.M. Rehn, W.R. Apblett Jr., and J. Stringer, Controlling Steamside Oxide Exfoliation in Utility Boiler Superheaters and Reheaters, *Materials Performance*, Vol 20 (No. 6), 1981, p 27–31
- 8.11 R. Viswanathan, *Damage Mechanisms and Life Assessment of High Temperature Components*, ASM International, 1989, p 218
- 8.12 B. Neubaur, U. Wedel, D.A. Woodford, and J.R. Whitehead, Eds., Restlife Estimation of Creeping Components by Means of Replicas, *Advances in Life Prediction Methods*, American Society for Mechanical Engineers, 1983, p 307–314
- 8.13 M. Shammass et al., “Remaining Life of Boiler Pressure Parts, HAZ Models,” Final Report RP 2253-1, Vol 2, Electric Power Research Institute, 1988
- 8.14 N.G. Needham and B.J. Cane, Creep Strain and Rupture Prediction by Cavitation Assessment in 2¼Cr-1Mo Steel Weldments, *Advances in Life Prediction Methods*, D.A. Woodford, Ed., ASME, 1983, p 65–73

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