

工業環境中高溫腐蝕問題與對策之探討

賴英典

INDUSTRIAL HIGH TEMPERATURE CORROSION PROBLEMS: CHALLENGES AND SOLUTIONS

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摘 要

本文針對有關化學、石化、石油精煉、燃煤、渦輪引擎葉片及焚化爐等工業應用環境上，遭遇之高溫腐蝕問題作一回顧。文中討論的重點是集中在製程環境，不同合金材料之行爲及材料選擇等方面，就各相關製程及系統上不同之腐蝕模式詳敘並分類說明，以便瞭解相關的腐蝕問題與防治之道。

關鍵詞：高溫腐蝕，腐蝕模式

ABSTRACT

High temperature corrosion problems are reviewed for chemical, petrochemical, petroleum refining, fossil energy, gas turbine and waste incineration industries. Corrosion modes for major processes and systems are identified, with discussions focusing on the process environment, the behavior of various alloys and materials selection guidance for solving high temperature corrosion problems.

Key words: High Temperature Corrosion, Corrosion Modes

INTRODUCTION

Proper management of corrosion problems associated with plant equipment is essential for reliable, efficient, and safe operation of an industrial plant. The most effective way to control corrosion problems is to make proper materials selections during both plant design and maintenance service. The materials selected should exhibit adequate and, hopefully, predictable service lives. To achieve this objective, the materials engineer must have not only a good understanding of the environment and the corrosion mode involved, but also an adequate corrosion database.

Many industrial processes require reactions at elevated temperatures. The equipment constructed to han-

dle these high temperature reactions can be degraded by reacting with the corrosive environment, resulting in high temperature corrosion. The type of environment depends upon the specific process involved. In general, high temperature corrosion encountered in various industrial processes can be categorized into eight different modes: oxidation, carburization and metal dusting, nitridation, sulfidation, salt-deposit corrosion, halogen corrosion, molten-salt corrosion, and molten-metal corrosion. Erosion/corrosion also plays an important role in high temperature degradation of structural components for some industrial processes.

The Pacific Rim region has been undergoing enormous economic and industrial expansion during the last decade or two. Chemical, petrochemical and petroleum refining have already become important industries

in the region. With continuing strong economic and industrial expansion, there is an increasing demand for more electric power, as well as a growing need for more waste incinerators for disposal of increasing amounts of both household/municipal and industrial/hazardous wastes. The present paper focuses on the high temperature corrosion problems commonly encountered in chemical, petrochemical, petroleum refining, fossil energy, gas turbine and waste incineration industries that are becoming more and more important to the Pacific Rim region.

ROLE OF OXIDATION IN HIGH TEMPERATURE CORROSION

Oxidation plays the most important role in high temperature corrosion. In many cases, it participates with other corrosion modes to cause equipment failures. For example, oxidation often accompanies sulfidation in coal gasification environments. In this case, sulfidation is the major mode of corrosion attack. Although oxidation here is not responsible for the alloy's corrosion failure, it plays a significant role in the sulfidation resistance of the alloy. In most sulfidizing environments, high temperature alloys rely on the oxidation reactions to form a protective oxide scale against sulfidation attack. Once the protective oxide scales are broken down, accelerated corrosion is initiated, which is commonly referred to as "breakaway corrosion". Under this condition, the alloy is attacked by sulfidation with the formation of sulfides in the corrosion front, which is followed by the formation of non-protective oxides, resulting in metal wastage and thinning of the metal cross-section. Once the major corrosion mode is determined, the remedy is to select an alloy that is more resistant to this type of corrosion mode. In this case, one should look for an alloy with better sulfidation resistance instead of the one with better resistance to oxidation.

OXIDATION IN AIR AND CLEAN COMBUSTION ATMOSPHERES

The oxidation attack discussed in this section involves mainly "clean" environments, where few or no corrosive impurities are present, such as air, pure O_2 and combustion atmospheres fired with natural gas or num-

ber one or number two fuel oil. These fuels generally contain low levels of contaminants - for example, sulfur, chlorine, alkali metals and vanadium. The oxidation covered in this section includes applications in a variety of industries except gas turbine where the gas velocity is extremely high and the oxidation which will be covered in the gas turbine section becomes much more severe.

A large oxidation database on commercial alloys, such as carbon steels, low alloy steels, Cr-Mo steels, ferritic stainless steels, austenitic stainless steels, Fe-Ni-Cr alloys, and superalloys, has been very well reviewed and documented.^[1-5] The database in general is reasonably adequate for making materials selection for heat exchangers, boilers, furnaces, retorts, calciners, kilns and other equipment for services up to about 1000°C. More importantly, extensive field experience has been accumulated by plant operators and designers for many commercial alloys up to 1000 °C.

The oxidation resistance of steels increases with the addition and/or increase of such alloying elements as Cr, Ni, Si and Al. Austenitic stainless steels can handle higher temperatures than 9Cr, 12Cr and 17Cr steels. Temperatures greater than 870 °C may require stainless steels with more chromium and nickel, such as 22Cr-12Ni (i.e., Type 309 SS) and 25Cr-20Ni (Type 310 SS), or Fe-Cr alloy with 27Cr (Type 446). Also available for applications at temperatures in excess of 870 °C is a large selection of oxidation resistant alloys with much higher creep-rupture strengths, which include Fe-Ni-Cr alloys (e.g., 800H/800HT, Fe-32Ni-20Cr-Al-Ti), or newer HR-120 alloy (Fe-25Cr-37Ni-Nb-N), Ni-base alloys, such as, HASTELLOY X (Ni-22Cr-18Fe-9Mo), HAYNES 230 (Ni-22Cr-14W-2Mo-La), INCONEL 601 (Ni-23Cr-14Fe-1.4Al) and 617 (Ni-22Cr-12.5Co-9Mo-Al), RA 333 (Ni-25Cr-18Fe-3Mo-3W), and Co-base alloys, such as HAYNES 188 (Co-22Cr-22Ni-14W-La) and 25 (Ni-20Cr-10Ni-15W). Only fabricable wrought alloys were mentioned here.

Once the service temperature exceeds 1000 °C, the number of alloys that are capable of resisting oxidation attack becomes somewhat limited. Above 1000 °C, many alloys based on Cr_2O_3 scales begin to suffer much higher oxidation growth rates. The volatilization of Cr_2O_3 by converting to CrO_3 may become significant, thus diminishing the alloy's protective capability against

oxidation attack^[6,7]. Thus, selecting an appropriate alloy for application at temperatures above 1000 °C is no easy matter. This is particularly true for cases involving advanced technologies employing high temperature heat exchangers, catalytic combustion, fuel cells or other systems using thin sheet or foil (10 mils or less in thickness) construction. The field database for service in this very high temperature region is inadequate.

It is well known that, at very high temperatures, alumina formers (alloys forming aluminum oxides) are much more resistant to oxidation than chromia formers (i.e., alloys forming chromium oxides). These alloys develop a very protective, Al_2O_3 oxide scale which is also very resistant to thermal cycling. Three well known wrought alloys belonging to this category are HAYNES 214 alloy (Ni-16Cr-3Fe-4.5Al-Y), ALPHA IV (Fe-20Cr-5Al-Ce) and INCOLOY MA 956 (oxide-dispersion strengthened alloy, Fe-20Cr-4.5Al-0.5Y₂O₃). In dynamic oxidation tests under a high velocity combustion gas stream (0.3 mach velocity) at 1150 °C for 200 hours with very severe thermal cycling involving cooling the samples by fan cooling to less than 260 °C for two minutes before returning the samples to the test chamber, two alumina-formers, 214 and MA 956 alloys were found to be significantly better than Ni-base chromia-formers, such as alloys 230, X and 617.

HIGH TEMPERATURE CORROSION IN GAS TURBINES

In a gas turbine, air is first compressed and then fed into the combustor where fuel is burned to generate high temperature and high pressure gas streams which are guided by the transition piece (in a land-based gas turbine) into the turbine. The hot section components for the gas turbine include combustors, transition piece (for land-based gas turbines), turbine guide vanes (stationary airfoil) and rotor blades (rotating airfoil), and afterburners (for military aircraft turbine engines). The high temperature corrosion modes that are of importance to these hot section components are oxidation and hot corrosion.

Gas turbines not only have continued to dominate aircraft engines since their inception half a century ago, but also have been playing an increasingly important role in electric power generation in recent years. The nature of the high temperature corrosion remains quite

similar for aircraft, marine and land-based gas turbines. In the case of air foils, for example, severe oxidation and moderate hot corrosion are experienced by aircraft gas turbines, while moderate oxidation and severe hot corrosion are experienced by both marine and land-based gas turbines.^[8] The present review discusses only the nature of high temperature corrosion with no differentiation among the gas turbine types.

Oxidation in the Combustion Section

With firing temperatures in excess of 1200 °C, the combustion liners, even with cooling air, are exposed to the temperatures high enough to cause concern for oxidation of Ni- and Co-base sheet superalloys, such as alloys X, 188, 230, 617 and 263, major combustion liner and transition piece alloys. Oxidation is certainly the major high temperature corrosion mode for these components. With high velocity gas streams, oxidation is particularly severe. Recent studies have shown that the combustor alloys can also suffer nitridation under this high velocity condition.^[9,10] Extensive aluminum nitrides were found to form in an alloy 617 transition piece of a land-based gas turbine.^[9]

A high velocity dynamic burner rig is commonly used to simulate this type of dynamic conditions. Dynamic burner rig tests at 980 °C for 1000 hours, with and without severe thermal cycling once every 30 minutes to less than 500 °C for two minutes, promoted not only oxidation but also nitridation attack. Alloys, such as alloys 617 and 263, containing small amounts of Al or Ti are very susceptible to nitridation attack by forming aluminum nitrides or titanium nitrides. The nitrogen content was increased from the initial value of 0.03% (wt) to 0.52% for alloy 617 as a result of the testing at 980 °C for 1000h with the thermal cycling; and from the 0.004% to 0.42% for alloy 263. Alloys with little or no Al or Ti are also susceptible to nitridation attack by forming chromium nitrides. Alloys containing more Fe were found to suffer more nitridation attack. Alloy 230 suffered the least nitridation attack among the four Ni-base combustor alloys tested. The extensive aluminum nitrides observed in the alloy 617 sample tested in the dynamic oxidation burner rig are quite similar to those observed in the alloy 617 transition piece of a land-based gas turbine. Thermodynamically, it is feasible to form

nitrides of chromium, aluminum and titanium in an Fe-, Ni- or Co-base alloy exposed to a combustion atmosphere. Alumina-formers, such as alloy 214 and MA 956, which formed a protective aluminum oxide scale, showed no evidence of nitridation attack under the same test condition.

Oxidation and Hot Corrosion in the Turbine Section

The combustion gas stream enters into the turbine section after leaving the combustor/transition piece. With the turbine entry temperatures (TET) for the gas stream reaching 1200 °C or higher, turbine blades and vanes may suffer oxidation attack, but, hot corrosion presents a more serious problem. The combustion gas stream often contains sulfate vapors which tend to deposit on the surface of the internally cooled blades and vanes, resulting in accelerated sulfidation attack, commonly known as "hot corrosion". Sulfur from the fuel reacts with sodium chloride from the ingested air (seawater is a major source of sodium chloride) during combustion to form sodium sulfate vapor. Seawater is also a source of sodium sulfate. This sodium sulfate becomes liquid in a temperature range of about 800 to 950 °C, resulting in accelerated sulfidation attack by fluxing away the oxide scales. This was later referred to as Type I hot corrosion to differentiate it from the low temperature Type II hot corrosion, which occurs in a temperature range of 700 - 800 °C involving generally Na_2SO_4 and CoSO_4 . The topic of hot corrosion has been covered extensively in the literature.^[11-16]

Hot corrosion data from burner rig tests have been generated for commercial Ni- and Co-base alloys as well as experimental alloys.^[16-19] Chromium is the most important alloying element in resisting hot corrosion attack. Co-base alloys are generally used by U.S. manufacturers for turbine vanes. The vane alloys, such as X-45, FSX-414 and ECY-768, typically contain high Cr contents, varying from 21% to 30% for these three alloys. Thus, hot corrosion is generally not a problem for turbine vanes. For turbine blades, Ni-base superalloys strengthened primarily by coherent, γ' - $\text{Ni}_3(\text{Al,Ti})$ precipitates and refractory elements are typically used. To increase the alloy's creep-rupture strength, the volume fraction in the alloy is increased by increasing Al and Ti and at the same time decreasing Cr content.^[20] As a result, the al-

loys used for turbine blades over the years have been progressively lowered in Cr content, with the following sequence of blade alloys: NIMONIC 80A (20Cr), U 500 (19Cr), U 700 (15Cr), IN 738 (16Cr) and GTD-111 (14Cr).^[21] The latest blade alloys contain much lower Cr contents, such as Rene N4 (9Cr) and PWA 1480 (10Cr).^[20] Consequently, turbine blades rely more and more on coatings for protection against hot corrosion.

Coatings are quite effective in resisting hot corrosion attack. Significant coating technology improvements have been made for gas turbine airfoils. The technology has evolved from the initial nickel aluminized coatings to the currently, widely used platinum aluminide coatings, such as Chromalloy's RT-22, and to electron beam-physical vapor deposition (EB-PVD) overlay coatings of NiCoCrAlY, and the latest vacuum plasma sprayed (VPS) or low pressure plasma sprayed (LPPS) overlay coatings of NiCoCrAlY as well as the thermal barrier coatings (TBC), such as yttria stabilized ZrO_2 coating. Review of the coating technology and the high temperature corrosion of these coatings is available in the literature.^[8,21,22,23]

HIGH TEMPERATURE CORROSION IN FOSSIL ENERGY SYSTEMS

Current fossil fuel power generation technologies that are of importance include fossil fuel-fired boilers, fluidized-bed combustors (FBC), and coal gasification combined cycle systems.

Fossil Fuel-Fired Boilers

The fossil fuel-fired boiler is typically constructed using carbon steel furnace tubes to form an enclosure where natural gas, oil or coal is burned to generate combustion gas in excess of 1200 °C. Water is circulated in these furnace tubes (also known as waterwall tubes) and is converted to steam by the radiant heat from the combustion. The steam is then superheated in superheater tubes before exiting into the steam turbine, which drives the generator. The alloys for furnace tubes and superheater tubes are governed by ASME Boiler Codes. Furnace tubes are made of carbon steel (SA-192) and superheater tubes are made of Cr-Mo steels, such as 2-1/4Cr-1Mo (SA-213, T-22), or austenitic stainless steels, such as, T304H, T321H, or Fe-Ni-Cr alloys, such as 800H.

Furnace tubes and superheater tubes can suffer high temperature corrosion on the fireside of the tubes (known as fireside corrosion). Because of impurities, such as Na, K, V, S and Cl, in the fuel, the combustion atmosphere most often contains salt vapors and ashes, which then deposit on cooler component surfaces, such as those of furnace tubes and superheater tubes. These deposits, in most cases, involve some type of salts and tend to accelerate high temperature corrosion, particularly when they become liquid.

The gas-fired boiler seldom suffers fireside corrosion on its furnace tubes or superheater tubes. This is because natural gas contains essentially no alkali metals and very little sulfur. Coal, however, contains Na, K, S and Cl. In coal-fired boilers, carbon steel furnace tubes typically suffer metal wastage on the front radiant face (facing the combustion radiant heat) in a temperature range of 260 to 450 °C with metal temperatures generally kept below 450 °C. Corrosion rates of less than 0.3 mm per year are quite typical, although 2-3 mm per year of corrosion rates have been reported.^[24] When the wastage rates on the furnace tubes become too excessive, a possible solution is the use of coextruded tubes with high Cr alloy cladding such as Type 310 SS.^[25,26] It is generally agreed that the accelerated corrosion attack is caused by localized reducing conditions. Although firing with excess air (e.g., about 4% excess oxygen) is normally employed, the combustion dynamics may create local areas with substoichiometric conditions (i.e., no "free" oxygen). As a result, sulfur takes the form of H₂S instead of SO₂ and / or SO₃. Thus, sulfidation of carbon steel furnace tubes becomes more aggressive. This furnace tube corrosion may become more severe for modern plants with new combustion systems to reduce NO_x (nitrogen oxides) emissions by using "staged combustion". This combustion scheme uses the substoichiometric conditions for initial combustion at the lower combustion zone, followed by the complete combustion at the upper zone with excess air in order to lower the temperature of the combustion, thus lowering the NO_x production. It is also believed that hydrogen chloride gas may play an important role in the furnace tube corrosion.^[25,27,28] However, Meadowcroft^[29] recently indicated that the substoichiometric combustion conditions were more important than the chlorine in coal.

The corrosion of the superheater has been very well characterized. The corrosion rate exhibits a bell-shaped curve with respect to temperature for austenitic stainless steels (common superheater alloys). The rate increases with temperature to a maximum and then decreases with increasing temperatures. The accelerated corrosion associated with this bell-shaped curve is related to the formation of molten alkali-metal iron trisulfate, (Na,K)₃Fe(SO₄)₃.^[30,31] The evaluation of coextruded tubes using high-Cr alloys (e.g., 310, INCONEL 671 and CR35A, 45Ni-35Cr-Fe) as an outer layer has been reported to be more resistant than the austenitic stainless steel superheater materials, such as T304H, T316H, T321H and T347H.^[32,33,34]

Fireside corrosion can be a severe problem in oil-fired boilers when low-grade fuel oils (e.g., Bunker C) with high S, V and Na are used for firing. Vanadium pentoxide and sodium sulfate are the principal constituents responsible for the type of corrosion, also known as oil-ash corrosion. Reactions between these two constituents result in the formation of low-melting-point vanadates. High Cr alloys, such as 50Ni-50Cr, generally performed much better than stainless steels such as 25Cr-12Ni (HH alloys) and 25Cr-20Ni (HK alloys) as hangers, tube supports and other uncooled components.^[35] A new high Cr, Ni-Co-Cr-Si alloy, HR-160 alloy (Ni-30Co-28Cr-2.75Si) may also be a good candidate. These high Cr alloys can also be used as outer cladding materials for coextruded tubes in superheater applications.

Fluidized-Bed Combustors

Coal can be burned efficiently in a fluidized bed combustor at temperatures somewhat lower than coal-fired boilers, thus, lowering NO_x emissions. Combustion is typically carried out at around 900 °C in a fluidized bed of particles maintained in a state of suspension by an upward flow of air. Limestone or dolomite is usually injected into the bed to capture sulfur as CaSO₄. Heat exchanger tubes both in bed and above bed are utilized in a steam raising system to convert water to steam which is superheated for electric power generation in a manner similar to coal-fired boilers. These heat exchanger tubes covered with CaSO₄ and CaO deposits are susceptible to sulfidation/oxidation at the temperatures

in excess of 600 °C. High nickel alloys are particularly susceptible to sulfidation attack. Minchener et al.^[36] postulated that the major factor contributing to the sulfidation attack was the deposits of CaSO_4 and CaO which resulted in low oxygen potentials and high sulfur potentials underneath the deposits..

Coal Gasification

Coal can also be utilized to generate power in an integrated gasification combined cycle by first gasifying it to produce a synthetic gas, which is cooled by a gas cooler and a waste heat boiler, and then cleaned to remove sulfur and particulate matter before being fired in a gas turbine. Gasification processes typically produce environments with low oxygen potentials and high sulfur potentials. Environments are strongly sulfidizing with typical constituents of H_2 , H_2O , CO , CO_2 , H_2S , etc. A large engineering database on commercial alloys has been generated. The Metal Properties Council's coal gasification programs from 1972 to 1985 had been recently summarized by Howes.^[37] More than 80 commercial alloys and coatings were evaluated in the programs. Most commercial alloys are based on chromium oxide scales for protection, and in the coal gasification environments these alloys were found to develop oxide scales initially and then suffered breakaway sulfidation. Sulfidation attack is strongly temperature- dependent. Many commercial alloys can suffer severe sulfidation attack, particularly at high temperatures. The current consensus among designers and materials researchers in the coal gasification community is that the maximum temperature for metallic materials for long-term service as heat exchangers, such as gas coolers, would probably be 600-650 °C. Recent studies have focused on the alloy behavior at 650 °C and lower as well as some of the newer commercial alloys and alumina-formers. Iron-base alumina-formers, such as MA 956, were found to exhibit good sulfidation resistance.^[38] A newly developed HAYNES HR-160 (Ni-30Co-28Cr-2.75 Si), based on chromium and silicon oxides, was found to be very resistant to sulfidation attack.^[39] Norton, et al.^[40] tested the alloy at 600 °C in a simulated entrained slagging gasifier atmosphere and found the alloy to be better than MA 956. They attributed this to the formation of a SiO_2 -rich layer on the metal surface.

HIGH TEMPERATURE CORROSION IN WASTE INCINERATORS

Waste incineration has become an important means for disposal of waste ranging from household/municipal waste to industrial/hazardous waste. The heat generated in the incineration process is generally recovered to generate electric power, particularly for large incinerators such as municipal waste incinerators, also known as waste-to-energy plants. Some of the incineration types commonly used on a commercial scale include: (a) municipal waste incinerators-mass burning type where fuel is not sorted, (b) municipal waste incinerator-refuse derived fuel, where the fuel is sorted, (c) sewage sludge incinerators, (d) rotary kiln type for industrial/hazardous waste, and (e) fluidized-bed combustors for biomass and other waste. Chemical companies often use incineration process to dispose of chemical or hazardous waste on line or at on-site incinerators which are often referred to as "thermal oxidizers".

Waste such as municipal and industrial/hazardous waste generally contains corrosive impurities, such as Cl, S, Na, K, Zn, Pb, P, etc. Because of these impurities, many complex salts, particularly chlorides and sulfates, are formed in the combustion, and then deposited on component surfaces, promoting mainly chloride attack and/or sulfidation depending upon temperatures and type of waste. Many of the chlorides have very low melting points. Corrosion can become very severe when these chloride deposits become molten. Both mass burning and refuse-derived fuel types of municipal waste incinerators have adopted the coal-fired boiler technology for raising steam to generate electric power. Fireside corrosion of furnace tubes and superheater tubes has been found to be more serious than coal-fired boiler counterparts. Therefore, lowering the steam temperature, thus the tube metal temperature, is one effective way to reduce the fireside corrosion problems.^[41] For furnace tubes, the current effective approach is to apply a weld overlay of alloy 625 (Ni-21.5Cr-9Mo-3.6Cb) on the carbon steel furnace tube. Many municipal waste-to-energy plants have taken this approach to solve the fireside corrosion problems for the furnace tubes. Other Ni-Cr-Mo alloys, such as C-22 (Ni-22Cr-13Mo-3W), would also be good weld overlay alloys. For superheater tubes, one of

the common approaches is the use of tube shields made of Type 309 SS, 253 MA, RA 85H and HR-160 to protect portion of the superheater tubes that are subjected to more severe conditions. Due to higher metal temperatures, the superheater tubes can suffer both chloride attack and sulfidation. The use of higher Cr-Ni alloys such as alloy 825 (Ni-21.5Cr-30Fe-3Mo) for superheater tubes has also been found to be effective in some plants.^[41]

For rotary kiln type industrial/hazardous waste incinerators, internal components, such as afterburners, feedchutes and even kilns, are made of metallic materials and are exposed to temperatures up to 1200 °C. These uncooled components exposed to a wide temperature range from 600 to 1200 °C can suffer sulfidation/chloride attack/oxidation, depending on type of waste, component design and temperature, among other factors. The corrosion species can vary from HCl, chloride salt deposits at lower temperatures to chloride vapors and sulfate deposits at intermediate temperatures, to chloride vapors, SO₂ and oxidation at high temperatures. HR-160 alloy with good resistance to both chloride attack and sulfidation has been used in various incinerators.

During the past decade, there has been an increasing number of incinerators burning sawdust, hog fuel, construction wood waste, wooden pallets and spools, orchard, vineyard waste or other agricultural residues. This type of incinerator is referred to as a biomass incinerator which commonly utilizes the fluidized-bed combustion design for electric power generation. Currently there are 46 power plants in central and northern California using wood wastes and/or agricultural residues.^[42] In general, these wastes contain significantly less corrosive impurities than municipal and industrial/hazardous waste. Fire-side corrosion of furnace tubes and superheater tubes is generally less severe than that of municipal waste incinerators. Incidences of higher wastage rates on superheater tubes have occasionally occurred, but they are not believed to be an industry wide problem.

HIGH TEMPERATURE CORROSION IN CHEMICAL PLANTS

Process environments are different for different chemical plants depending on the specific product and

manufacturing process involved. Many processes and products are proprietary in nature. Discussion of all the corrosion modes involved in the chemical process industry is beyond the scope of this paper. This section covers only two corrosion modes that are of importance in the chemical processing. Chlorination is an important corrosion mode for a number of chemical processes and will be reviewed here. Metal dusting is becoming an important corrosion mode for steam reformers in modern hydrogen, ammonia, and nitric acid plants, and will also be discussed here. Sulfidation is also important in several chemical processes such as carbon black manufacturing. Recuperators made of metallic materials are commonly used in carbon black plants to preheat the combustion air. The process gas stream is typically reducing and sulfidizing, with oxygen and sulfur potentials similar to those of coal gasification environments. Thus, the materials selection guidelines for this type of environment can basically rely on the database generated for coal gasification processes, which were covered in an earlier section.

Chlorination

Manufacturing processes involving ethylene dichloride cracking and production of TiO₂ pigment, SiO₂, and some other proprietary products produce chlorine-bearing environments. Alloys behave differently in Cl₂ or HCl environments than in O₂ atmospheres. In an O₂ environment, alloys form condensed phases of oxides when heated to elevated temperatures. For Cl₂ or HCl environments, they form either volatile or liquid corrosion products of metal chlorides. In an environment involving both oxygen and chlorine gases, corrosion involves a combination of condensed oxides and volatile (or liquid) chlorides.

Daniel and Rapp^[43] discussed in detail the behavior of iron and Fe-base alloys in Cl₂ environments. Adding chromium and/or nickel to iron improves the alloy's resistance to chlorination attack. Austenitic stainless steels are more resistant to chlorination than ferritic stainless steels, which in turn are more resistant than cast iron and carbon steel. Nickel and Ni-base alloys are widely used in chlorine-bearing environments. Kane investigated many commercial Fe-base and Ni-base alloys in Ar-30% Cl₂ at 704 °C and found that increasing the al-

loy's nickel content increases the chlorination resistance.^[44] Additional tests at 400, 500 and 600 °C in the same environment revealed the same trend. The above data are related to corrosion attack in Cl₂ environments containing no measurable O₂. Corrosion by gaseous HCl also showed that nickel and Ni-base alloys are more resistant to chlorination attack than Fe-base alloys. Molybdenum appears to be beneficial in improving the alloy's resistance to chlorination attack in reducing environments containing HCl. Hossain et al.^[45] found that Mo-containing Ni-Cr alloys, such as INCONEL 625 and HASTELLOY C-4, were the best performers among various Ni-base alloys including nickel.

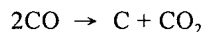
In oxidizing environments, however, molybdenum, particularly at high concentrations, is detrimental to the chlorination resistance.^[46] Oh et al.^[46] attributed this to the formation of molybdenum oxychlorides which have very high vapor pressures. For example, in a test environment of Ar-20% O₂-2% Cl₂ at 900 °C, the partial pressure of MoO₂Cl₂ in equilibrium with the oxide (MoO₃) was 2.1 atm. The poor resistance of high Mo, Ni-Cr-Mo alloys to chlorination attack in oxidizing atmospheres at temperatures above 600 °C has been confirmed by service experience in chemical waste incinerators. At lower temperatures, the Ni-Cr-Mo alloys were found to perform well. The maximum service temperature for high Mo-containing Ni-Cr-Mo alloys, such as C-276, is probably around 500-600 °C in oxidizing environments. It is not recommended to use high Mo-containing Ni-base alloys in excess of 500-600 °C in oxidizing environments. For reducing atmospheres, no such limitation is required because no molybdenum oxychlorides are likely to form. The advantage of using high Mo-containing Ni-base alloys such as C-276 and C-22 for applications at less than 500-600 °C is that these alloys also have been widely used to resist HCl dew point corrosion. For chlorine-bearing flue gas streams, HCl dew point corrosion presents a real corrosion problem for downstream equipment; and C-276 and C-22 are among the best alloys resistant to HCl dew point corrosion.

Metal Dusting

Steam reforming is an important process in a number of chemical plants, such as hydrogen, ammonia, ni-

tric acid, and syngas plants.

The process gas stream is typically enriched in H₂ and CO. The metallic components can suffer metal dusting, when exposed to this type of gas composition at temperatures of 480 to 850 °C, with maximum attack being at approximately 650 °C, depending on the alloy. Generally, the corrosion products consist of carbon soot and powders of oxides, metals and carbides. Alloys typically are corroded by pitting, and the underlying metal may or may not show carburization. Although the reformer gas typically consists of H₂, CO, H₂O and CO₂, sometimes with some CH₄, it is believed that these gaseous components do not reach a thermodynamic equilibrium, because of relatively low reaction temperatures. The corrosion is likely governed by one of or both of the following chemical reactions:



For both reactions, the carbon activity decreases with increasing temperature. Once the activity reaches the values less than one, metal dusting is not likely. Thus, neither reactions are favored thermodynamically to induce metal dusting at higher temperatures. As the temperature decreases, the carbon activity increases, thus favoring the metal dusting reactions thermodynamically. Kinetics, however, favor high temperatures, but not low temperatures. As a result, metal dusting is predicted by both chemical reactions to follow a bell-shaped curve with diminishing corrosion rates at both high and low temperatures.

Grabke et al.^[47] recently suggested that the protective chromium oxide scale is effective in delaying the metal dusting reaction. However, all the alloys will eventually suffer metal dusting. For Fe-base alloys, it is caused by oversaturation of carbon in the alloy matrix and the formation of unstable carbides, M₃C (M=Fe, Ni), followed by decomposition of these carbides. For Ni-base alloys (more than 80% Ni), they proposed that an oversaturated solid solution of carbon in the alloy matrix disintegrates into graphite and metal particles. A number of metal dusting instances involving alloy 800H failures have been known to occur recently in modern steam reformers. No other alloys have been tried and proved to be definitely better in this particular process.

HIGH TEMPERATURE CORROSION IN PETROCHEMICAL PROCESSING

The discussion for petrochemical processing is limited only to ethylene production. Carburization of pyrolysis furnace tubes is a major issue in ethylene manufacturing. Ethylene is formed by cracking ethane and naphtha with steam at temperatures as high as 1150 °C, with a strong carburizing process stream generated inside the pyrolysis tubes. Because of high service temperatures for these tubes, creep-rupture strength is as important as the resistance to carburization for the alloy. Most designs have used centrifugally cast tubes made of mainly HK-40 alloy (Fe-25Cr-20Ni), which have been recently replaced by HP-type alloys (modifications of HK-40) for improvement of both creep-rupture strength and carburization resistance. Initial HP modified composition involved an increase in Ni from 20 to about 35% for increasing the stability of the austenitic structure and a minor addition of Nb for creep-rupture strength improvement. Later modifications involved increases in Cr along with minor additions of other strengthening elements such as W, Mo, and Ta, with increases in Si as well. These HP modified alloys exhibit better creep-rupture strengths and carburization resistance. Both Ni and Si are beneficial in improving the alloy's carburization resistance.^[48] Some of these HP alloys include APV Paralloy H39W (25Cr-35 Ni-0.4C-1.3Si-1.2Nb-Fe), S-22H alloy (28Cr-48Ni-0.5C-1.75 max Si-5W-3.6Co-Fe), and Kobelco HV (28Cr-48Ni-0.5C-1.5 max Si-5W-Fe). Higher Cr and Ni also resulted in better oxidation resistance which is also important during decoking of the furnace tube with steam/air.

HIGH TEMPERATURE CORROSION IN PETROLEUM REFINING

High temperature petroleum refining processes involve crude distillation, hydroprocessing (e.g., hydrocracking and hydrotreating), and thermal cracking (e.g., fluid coking, Flexicoking, fluid catalytic cracking). These processes operate at various temperatures with many processes up to 450 °C, and some processes such as regeneration of catalysts up to 750 °C, and gasification of coke up to 1000 °C. Sulfur is a major corrosive

impurity in the feeds for various high temperature refining processes; and sulfidation is, thus, a common high temperature corrosion problem.^[49,50] This review discusses mainly the sulfidation issue, although there are other high temperature corrosion modes involved in refining processes. For heaters and boilers burning high sulfur fuel oil contaminated with vanadium, oil ash corrosion can be a problem for the support structure and other internal components. The oil ash corrosion was discussed earlier in the Fossil Energy Section.

Distillation Units and Associated Heater Tubes and Transfer Lines

The organic sulfur compounds in the crude and its fractions are responsible for the sulfidation attack for the metallic reactor and piping in contact with these liquid hydrocarbon streams with no hydrogen present. It is generally agreed among the refinery community that the corrosion behavior of the common refinery alloys can be reasonably described by the modified McConomy curves.^[51] The curves are applicable only to the liquid hydrocarbon streams with 0.6% (wt) sulfur. For process streams with sulfur content more than 0.6 %, it is necessary to apply correction factors for the corrosion rates.^[51] The corrosion rates in general increase with increasing temperature. Carbon steel can suffer excess scaling at temperatures in excess of around 290° C. The addition of Cr to iron significantly improves its sulfidation resistance. The 12 Cr steel exhibits essentially negligible corrosion rates up to 430 °C, and the 18-8 austenitic stainless steels (higher Cr) are much more resistant than the 12 Cr steel.

Carbon steel basically relies on the formation of iron sulfide scales for protection against sulfidation in this type of environment. Low Cr steels (i.e., up to 9 % Cr) continue the formation of iron sulfides with probably some Cr participation, making the scales more protective. For 12 Cr and 18-8 austenitic stainless steels, the scales may consist of iron sulfides and iron chromium sulfide spinel (FeCr_2S_4) or chromium sulfide. Because of the sulfide scales providing the protection against sulfidation attack for alloys, any conditions that are conducive to cause scale disruption or spallation so as to expose the fresh metal surface to the environment are likely to result in accelerated corrosion. These in-

clude regions with high flow rates and turbulent flow, such as return bends, piping elbows, etc.

Hydrocrackers, Hydrotreaters and Other Hydroprocessing Units

These high temperature processes are used to convert the feed to lighter fractions or to remove sulfur by using high pressure and high temperature hydrogen. Sulfur in the process streams is, thus, converted to H_2S , and the sulfidation in these systems is dictated by H_2H/H_2S . The corrosion of the common refinery alloys is adequately described by the Couper-Gorman curves.^[52] These iso-corrosion curves are plotted as a function of H_2S content and temperature for various alloys, from low Cr to 18-8 austenitic stainless steels.^[52] Chromium, again, is an effective alloying element in improving the sulfidation resistance. Nevertheless, the addition of at least 5% Cr to iron is needed to improve the alloy's sulfidation resistance. Again, the alloy relies on the formation of sulfides for protection against sulfidation. However, at low H_2S concentrations, iron sulfides become thermodynamically unstable, thus no interactions with the environment and, consequently, no corrosion for carbon steel. With about 18 % Cr, 18-8 austenitic stainless steels exhibit negligible corrosion rates even up to 540 °C. Mrowec^[53] studied sulfidation of Fe-12 Cr and Fe-20 Cr and attributed the increasing sulfidation resistance to the formation of FeS and either $FeCr_2S_4$ or Cr_2S_3 .

Catalyst Regeneration and Coke Gasification

Regeneration of catalysts is carried out at higher temperatures (up to 750 °C for some catalysts). Sulfur may be present as SO_2 and/or SO_3 with some excess O_2 in the flue gas. Alloys can suffer oxidation/sulfidation. Gasification of resid or coke to produce syngas is carried out at much higher temperatures (up to 1000 °C). The combustion environments produced generally consist of H_2 , CO, CO_2 , H_2O and H_2S , with low O_2 potentials and high S_2 potentials, similar to those generated by coal gasification. If carbon steel, Cr steels and austenitic stainless steels suffer excessive sulfidation attack, consideration should then be given to high Cr alloys, such as Fe-25Cr-20Ni (Type 310 SS) or Ni-30Co-28Cr-2.75Si (HR-160)

Sulfur Plant

Hydrogen sulfide collected from various refinery units is converted to sulfur in the Claus process. The process involves partial combustion of H_2S in a reactor furnace, typically refractory-lined, to form S, SO_2 and H_2O . This process gas stream is then cooled in a waste heat boiler, typically made of carbon steel, and then passed over catalyst bed to react SO_2 to additional H_2S to form S and H_2O . Sulfur is condensed from the effluent. If carbon steel, Cr steels and austenitic stainless steels are not adequate, consideration should then be given to high Cr alloys, such as Type 310 or even HR-160 alloy.

SUMMARY

High temperature corrosion problems in chemical, petrochemical, petroleum refining, gas turbine, fossil energy and waste incineration industries are reviewed. Corrosion modes in major industrial processes and systems are identified. The behavior of commercial alloys in different industrial environments is discussed with a particular focus on the materials selection guidance for solving these industrial high temperature corrosion problems.

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