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High Temperature Corrosion Issues in Energy-Related Systems

*John Stringer**

EPRI, Palo Alto, California, USA

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The large majority of electric power that is generated world-wide involves heat engines of one kind or another. The significant exceptions are hydroelectric generation; wind; and photovoltaics. The thermal sources for the heat engines include: fossil fuels, nuclear fission, biomass, geothermal sources, and solar radiation. There has been a progressive move to higher overall cycle efficiencies for at least one hundred years, and in the case of fossil fuels this has accelerated recently in part because of concerns about greenhouse gas emissions, notably CO_2. For a heat engine, the overall efficiency is closely related to the difference between the highest temperature in the cycle and the lowest temperature. In most cases, this has resulted in an increase in the high temperature, and this in turn has led to increasing demands on the materials of construction used in the high temperature end of the systems. One of the issues is the chemical degradation because of reactions between the materials of construction and the environments to which they are exposed: this is high temperature corrosion. This paper will describe the issues for a range of current heat engines.

Keywords: *High temperature corrosion, energy relatet systems, materials issues*

1. Introduction

High Temperature Systems

This paper will principally be concerned with the generation of electricity. Obviously, ground transportation, marine, and air transport also use heat engines, and are large users of fossil fuels. They suffer from similar corrosion problems to those in engines used in electric power generation systems, but they will not be discussed here. High temperatures are encountered in a number of industrial processes: these applications have been drivers for materials developments, and the high temperature materials that have resulted have also been applied to heat engines. Again, for the purposes of this paper, those applications will not be expressly considered.

The steps involved in the use of a thermal source to generate electricity generally involve a heat engine, which converts thermal energy to mechanical energy. For small to moderate sized systems, reciprocating engines are commonly used: there are some high-temperature corrosion issues involved with these, but they will not be discussed in this paper, because these systems make a relatively small contribution to the generation of electricity, at least at the moment. The larger units all use turbines, in which hot compressed gases are expanded, generally through an axial flow turbine, to rotate a shaft. This shaft in turn rotates a generator: we will not discuss the generator here because it operates at low temperatures.

The hot gases are referred to as the ‘working fluid’, and the working fluid may be the combustion gases themselves, in which case we refer to this as a direct-fired system; or there may be a heat exchanger in which the hot combustion gases heat another working fluid, in which case it is called an indirect fired system.

The two major systems that are used for heat engines in electricity generation are:

- An indirectly-fired system in which the working fluid is steam; and
- A directly fired system in which the working fluid is the combustion gas itself.

In a system using a turbine, the working fluid is not only hot; it must also be pressurized. The fluid then expands through the turbine, and the work done on the successive turbine stages results in a fall in both the pressure and the temperature of the fluid. The work done by the compressor is a potential thermodynamic loss (because of the inherent irreversibilities) and thus optimizing the compression step is important.

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*e-mail: jstringe@epri.com

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In a system using steam as the working fluid, the pressurizing is done by water pumps, which are very efficient, prior to boiling the water. The water is converted to steam in a boiler, which in essence is a heat exchanger; the heat source may be a combustible fuel, or a nuclear reactor, or a geothermal source, or sunlight. For some systems the term ‘steam generator’ is used instead of ‘boiler’, but there is no functional difference between these. The heated and compressed steam is then expanded through a steam turbine; both the pressure and the temperature of the steam decrease as it passes through the turbine. At the low-pressure end of the turbine, the steam is condensed to water in a condenser; the coolant is usually water from a nearby source, which may be a river, lake, or the sea. The condensate is then returned to the boiler through the water pumps.

This cycle is called the Rankine cycle. As with all heat engines, the efficiency of the cycle is calculated relative to that of an ideal reversible cycle, which is called the Carnot cycle. The efficiency, μ, of this is defined in terms of the maximum temperature of the working fluid, T_{max}, and the minimum temperature, T_{min}; both of these temperatures are absolute.

$$\mu = (T_{max} - T_{min})/ T_{max} \qquad (1)$$

Notice that the pressure of the working fluid does not appear in this expression.

The actual efficiency of a cycle will be less than that of the ideal cycle, of course; the irreversibilities which are associated with the finite heat flux is one of the causes for this, but there are a number of other losses. These can be reduced by careful design, but the real efficiency will always be significantly lower than the Carnot efficiency.

For a Rankine system, T_{min} is defined by the temperature of the cooling water in the condenser; plus whatever the temperature difference between the inside and the outside of the condenser is; this is related to the flow rates, and this in turn is related to the size of the condenser. A large condenser has lower flow rates and the temperature difference is less, but the cost is of course higher.

T_{max} is related to the temperature of the heat source, and the heat flux across the heat exchanger wall. In fact, this is a much more difficult calculation than this simple statement would suggest. It is actually more meaningful to say that T_{max} is defined by the maximum temperature that can be attained with the material used for the heat exchanger which has to sustain the pressure difference between that required for the working fluid and that on the side of the heat source.

The large majority of electricity worldwide that is generated by heat engines comes from Rankine cycle units in which a fuel is combusted, typically in a large furnace. There are several different versions of this concept: in the simplest the fuel is gaseous, either natural gas, a byproduct gas from another process, or a gas generated by the gasification of a solid fuel. This last will be considered later. Liquid fuels, such as petroleum, are also used; and generally the furnace used for this purpose is essentially the same as that used for gaseous fuels. More commonly, a solid fuel is fired: in the majority of units worldwide this solid fuel is coal. However, byproduct solids from other processes can be used: examples are petroleum coke from oil refining; wood waste from forestry; and ‘municipal solid waste’. While waste from agricultural operations has been used in the past, there has been a move recently to provide biomass fuel as the principal product of farming.

There are number of different designs of solid fuel-fired furnaces. The choice depends to some extent on the form of the fuel provided, and also on the size of the unit. Smaller units burning relatively coarse fuels typically have grates, which may be stationary or moving. For larger units, the fuel is typically prepared, for example by grinding, before being fired. Most commonly, the fuel is transported pneumatically and blown into a large open furnace chamber through a number of burner nozzles, which may be openings in the furnace walls or the corners of the furnace chamber. The aim is to usually to establish a ‘fire-ball’ in the center of the furnace cross section. Typically, the fuel will contain some incombustible materials, and this forms an ‘ash’. The coarser ash particles fall to the bottom of the furnace, where they are removed; the finer particles become entrained in the combustion gas stream, and pass through the heat exchanger. This is called ‘fly-ash’ and generally environmental protection legislation requires that it is captured before it leaves the boiler. For various reasons, including overall combustion efficiency, the combustion air is a little in excess of the stoichiometric requirements to ensure as complete burn-out of the carbon as possible; typically the combustion gas will contain perhaps 3% oxygen. However, in recent years it has been the practice to add the air in two stages: the air in the primary combustion zone is slightly substoichiometric, and the balance is injected higher in the furnace. This is to control the formation of oxides of nitrogen in the combustion zone.

An alternative to this approach is the ‘fluidized bed combustor’ in which the fuel is injected into a bed of incombustible material, which is fluidized by air blown in through nozzles at the bottom of the chamber. Because of the excellent heat transfer and good mixing in such a bed, complete combustion can be achieved with a significantly lower combustion temperature, and this may be of benefit from an environmental point of view. There are a number of different designs of all these combustion methods, and they will not be discussed further in this paper.

The large electricity-generating boiler furnaces are usually of what is called ‘water-wall construction’. This means that the walls are formed from tubes joined to each other by relatively narrow membranes, and the working fluid passes through these tubes. In a typical boiler, the tubes are approximately 60 mm diameter, and the membranes are about 10 to 15 mm wide. In the lower section of the furnace, in the vicinity of the fire-ball, the transfer of heat to the fluid in the tubes is by radiation. As the gas loses temperature to the walls, the gas passage in the furnace turns horizontal, and there are a number of pendant tube bundles, which hang, essentially normal to the direction of gas flow. The final heating of the steam to its maximum temperature is achieved in these. Finally, the combustion gas cools to a temperature below that required for the steam heating, and the flow changes again to a downward stream. In this part of the path, there are tube bundles, which preheat the intake water before it enters the bottom of the water walls: this is called the economizer.

The steam is superheated, which means it is raised to a temperature above the water/steam equilibrium (the boiling point) at the chosen pressure. There are two different concepts for this. The water/steam equilibrium diagram as a function of temperature and pressure exhibits a critical point. Below this, water and steam may coexist as two distinct phases. Above it, there is no distinct phase change. These two regimes are called ‘subcritical’ and ‘supercritical’. The critical point is at a temperature of 647.29 K and 22.089 MPa (705.5 F; 3208.2 psia). World wide, the majority of units are currently subcritical. In the United States, the subcritical boilers operate at a pressure of 2400 psia (16.5 MPa). At this pressure, water boils at 623 K (662 F). This is the temperature of the water in the waterwall tubes when steam bubbles first appear. The phase rule then keeps the temperature constant as the volume fraction of steam increases. At the top of the boiler, the mixture passes into a large drum, called the stream drum, which separates the steam from the remaining water. The water then is returned to the bottom of the boiler; the now-dry steam enters the next series of heat exchangers, where its temperature is raised further. This is called superheating. Again in the United States, the finishing temperature is 811 K (1000 F). The current supercritical boilers operate at a pressure of 3500 psia (24.1 MPa); the water changes continuously to the vapor phase without the appearance of a two-phase steam water region, and the temperature thus increases continuously up the walls. However, the steam finishing temperature is essentially the same as in the subcritical units. In both cases, this steam is transferred to the steam turbine. The turbine may be in two (sometimes three) stages: the first part is referred to as the High Pressure (HP) turbine, and at the end of it the steam is returned to the boiler where it is reheated, usually to the same temperature, and returned to the next stage of the turbine, which is called the Intermediate Pressure (IP) turbine. The final stage of the turbine is called the Low Pressure (LP) turbine, and in supercritical units there may be a further reheat between the IP and LP turbines.

The Carnot efficiency, μ_{Car}, for these conditions, assuming that the condenser temperature is 290 K, would be 0.64; however, the actual efficiency of the Rankine cycle, μ_{Ran}, is closer to 0.39.

There has been a long history of attempting to raise T_{max} to improve the cycle efficiency. In the US, the highest temperature achieved was in the Eddystone plant, at 1200 F (922 K); the design main steam pressure was 5000 psia (34.4 MPa). The Carnot efficiency for these conditions (assuming the same condenser temperature) is 0.68; the unit achieved 0.41 when it was new, in 1956. For various operational reasons, both the main steam temperature and pressure were reduced somewhat, quite early in the plant life, but it was retired only recently.

Both the US Department of Energy and EPRI conducted a number of studies of possible high temperature and pressure Rankine cycles in the 1980s, but the real developments have only occurred recently; the driver appears not to be efficiency as such, but the desire to reduce CO_2 emissions. Recent calculations of efficiencies for different proposals, converted to US practice, show that the most recent proposals are looking at main steam temperatures of 973 K (1292 F) and pressures of as high as 37.8 MPa (5500 psia), with a calculated efficiency of 0.48. Recent installed plant have achieved 0.42 (ELSAM Nordiylland 3), fairly similar to the Eddystone result nearly 50 years ago.

The fireside temperatures for superheater tubes that generate this steam can be calculated from the heat flux through the tube wall: there are eight terms in the calculation, going from the inside out: (1) the steam temperature; (2) the temperature drop across the wall gaseous boundary layer on the inside of the tube; (3) the temperature drop through oxide layer on the inside tube wall; (4) the temperature drop through the tube wall itself; (5) the temperature drop through the thermal oxide layer on the fireside of the tube; (6) the temperature drop through the ash/deposit layer on the fireside of the tube; (7) the temperature drop through the gaseous boundary layer on the outside of the tube; and (8) the temperature of the combustion gases in the vicinity of the tube. In fact, if the thermal flux is well-enough known (and a global value for this can be determined from the boiler performance), the temperature of the metal at the outer metal/oxide interface can be calculated relatively simply so long as one can measure the thickness of the internal oxide layer. For discussion purposes, a value in the range 50 – 75 K higher than the main steam temperature is typical.

The other large heat engine used for electric power generation is the combustion turbine (generally called gas turbine in aviation applications). This is called the Brayton cycle. For this cycle, the working fluid is the combustion gas itself, with some additions. The intake air is compressed using either a radial or an axial compressor: the first has some benefits for small units; virtually all utility scale electricity generating units use axial compressors. Fuel is injected via a number of nozzles into combustion chambers: it is uncommon for there to be a single combustion chamber, but some large units have just two large combustion chambers. A more common geometry now is to have a number of combustion chambers arranged round the engine, often manifolded into a single circumferential chamber from which the now-heated gas is directed into a turbine. In essentially all units, this is an axial flow turbine; the first row of airfoils is stationary: these airfoils are called the inlet guide vanes; this row is followed by a row, which rotates, the first stage rotor blades. The combination of the stator and the rotor is called a stage, and the turbine has a number of stages. The first stage experiences the most severe conditions: the temperature at the inlet guide vanes is the highest in the turbine, but the stresses are greater in the rotor blades. The first few turbine stages drive the compressor; the later stages provide the output power. This is called the Brayton cycle. After the pressure has fallen to a little over atmospheric, the combustion gas is exhausted to the atmosphere. The temperature of the exhaust is still relatively high, and the gas is generally cooled before exhausting. The maximum temperature in the cycle is the temperature of the gas entering the turbine, and this set by the capabilities of the materials of the first stage. The combustion gas is cooled to this temperature; in the simplest systems this is done with air from the compressor, so the gas entering the turbine has a significant oxygen partial pressure, in contrast to the combustion gas in the Rankine cycle system described above. However, again the excess air is introduced after the primary combustion zone: it serves to keep the walls of the combustor relatively cool, and is also ducted in a way which stabilizes the flame. There are other ways of controlling the Turbine Entry Temperature (TET): in some cases the exhaust gas can be recycled; and in other designs water or steam is injected in the combustor. This 'Humid Air Turbine' (HAT) concept is capable of improving the specific power output of the engine, and there are a number of variants on this approach, which will not be discussed here.

As before, improvements in efficiency require an increase in T_{max}, which for this cycle is TET, or a decrease in T_{min}; which here is the exit temperature from the final turbine stage. Unlike the Rankine cycle, there are opportunities to decrease this temperature, which will be discussed later. The history of the development of the combustion turbine over the years has been, to a large extent, the drive to higher TET. This has involved four approaches:

1. A progressive improvement in the high-temperature strength of the alloys used for the turbine airfoils, specifically those used for the inlet stage vanes and blades.
2. The development of methods of cooling the vanes and blades, initially by injecting air from the compressor into cooling passages within the airfoils, and most recently by using steam for the same purpose.
3. The use of protective coatings: this is in part because the paths which lead to strength improvement in the alloys used for the airfoils also diminish the high temperature corrosion resistance; and in part because the increases in the gas temperatures increase the corrosivity.
4. The use of Thermal Barrier Coatings, which are coatings with low thermal conductivity; coupled with airfoil cooling, these increase the temperature difference between the hot gas and the airfoil.

All four of these approaches are continuing; later papers will describe these in more detail.

Generally, the approach to reducing T_{min} is to recover the thermal energy in the turbine exhaust by the use of what is called a 'bottoming cycle'. In the Rankine cycle, considerable use is made of preheating as a heat recovery approach to reduce heat otherwise lost in the overall process, but this is generally more difficult in the Brayton cycle. For utility electricity generating systems, the most common bottoming cycle is a Rankine cycle: the relatively hot combustion gases from the combustion turbine enter a heat exchanger that is essentially a boiler. In the jargon of the business, this is called a 'Heat Recovery Steam Generator' (HRSG). The steam then passes to a steam turbine, with its own electric generator. The resulting system is referred to as a 'combined cycle'.

Within the last few years, there have been some remarkable developments in advanced combined cycles. A program was initiated by the U.S. Department of Energy, called the Advanced Turbine Systems (ATS) Program, one of whose objectives was to develop a large combined cycle electricity generating system capable of achieving an efficiency pf 0.60. The efficiency of the simple Brayton cycle is not, in fact, very different from that of the Rankine cycle: a figure of 0.39 is typical for a modern machine: the ability to combine these two to achieve a much higher figure lies in the Rankine cycle's ability to attain a very low T_{min}, and the Brayton cycle's ability to attain a very high T_{max}. The ATS program involved the major US combustion turbine manufacturers, and all are now offering combined cycle machines which are very close to the 0.60 goal; it is believed that engines now being delivered and in test will achieve it.

Given the complexity apparent in the Rankine cycle system, and their very large size, compared with the simplicity and small size of a Brayton cycle system, it will come as no surprise that the cost of the latter is one half (or even less) that of the former, for the same output. While the advanced combine cycle units have relatively large Rankine bottomers, the overall cost is still very competitive. Furthermore, the construction times are much shorter for the Brayton units, and the 'footprint' is much smaller. One might ask, therefore, why the Rankine cycle systems are still used. The answer is the cost of the fuel. Although over the years there have been many attempts to fire coal and other solid fuels directly into a combustion turbine, they have all failed. The net effect is that the cost of electricity generated is generally less for a Rankine system; systems using a Brayton cycle not only require high-cost fuel, but the variability in the fuel cost is significantly greater: in the US, at least, electricity generation is virtually the only market for coal, whereas natural gas and liquid fuels have a number of market places.

A second question is: if combined cycles are so good, why are simple cycle combustion turbines used at all? The answer to this relates to the way electricity is used. There are variations in demand: some are seasonal variations; some are weekly; some are diurnal; and some are of quite short duration – the broadcast of a popular TV show, for example. In addition, there is no real way to store electricity. This means that the generation pattern has to match the demand. For the short-term fluctuations – 'peaks' – a simple cycle gas turbine generator is uniquely qualified; and the high cost of the fuel is largely irrelevant. The combined cycle units have a much slower response, and the advanced units are particularly sluggish, for reasons that are somewhat beyond the scope of this meeting.

The issue of directly firing coal in a combustion turbine has arisen several times over the last fifty years, and the essentially insurmountable problems associated with this have also been demonstrated several times. I really hope that nobody else tries this again without reading the prior literature very carefully indeed! In my opinion, the same issues will arise in any effort to fire a solid fuel; or (come to that) any liquid or gaseous fuel with a significant amount of solid particles in the combustion product. One technique which has been the subject of much study over the past several years ahs been the Pressurized Fluidized Bed Combustion (PFBC) of coal or other solid fuels. The combustion process is followed by a Hot Gas Clean-Up (HGCU) system, which essentially is an inertial separation system such as a cyclone (or series of cyclones) followed by a positive filtration system. This last is typically a porous filter: the major efforts have looked at porous ceramics. This is followed by a turbine designed to have as much tolerance as possible: this is often called a 'ruggedized turbine'. At present, I think it would be fair to say that there has been a significant level of success under well-controlled steady-state operation; but the penalties of any deviation are very significant.

The route generally accepted to provide the best opportunity for using solid fuels and other difficult fuels is gasification, again followed by appropriate clean-up, to provide an essentially clean gaseous fuel to fire in the turbine. There is a variety of approaches that have been developed; I do not propose to discuss them here, although I am sure that other papers in this meeting will discuss them. A favored route is entrained gasification, which has a very high temperature within the gasification vessel. The off-gas temperature is moderated by the use of a heat exchanger within the vessel itself; this is typically part of a steam circuit for a bottoming Rankine cycle. The conditions for the materials of this heat exchanger are very demanding; I shall discuss them briefly, but again I expect other papers in this meeting to deal with the issues in more detail. The system in which a gasifier is integrated with a combined-cycle power unit is called an IGCC, where the meaning of the initials is obvious.

A final group of high-temperature electricity generation systems are not 'heat engines' at all in the sense used here. They are fuel cells, in which the oxidation process, which in electrochemical terms is the removal of electrons, is done in an electrochemical cell. This can be done cold or hot, but there are some benefits in using high temperature processes. The differences are in the electrolytes: the low-temperature fuel cells have phosphoric acid or PEMs (alternatively translated as Proton Exchange Membranes or Polymer Electrolyte Membranes); the high-temperature fuel cells use solid oxide electrolytes (the most common example is yttria-stabilized zirconia) or molten carbonate electrolytes. The latter two systems do have problems with high temperature corrosion.

The Corrosive Environments

From the discussion above, it is apparent that the corrosive environments vary over a wide range. I will list them here, and discuss some aspects in more detail later.

1. Oxygen
2. Air
3. Moist Air
4. Low-Oxygen Activity Steam
5. 'Oxygenated' Steam
6. Hyperstoichiometric Combustion Gas
7. Near-stoichiometric Combustion Gas
8. Hypostoichiometric Combustion Gas
9. Ash Deposits

10. Molten Alkali Sulfate – Containing Salt Deposits
11. Molten Vanadium Compound – Containing Deposits
12. Molten Salts
13. High Carbon Activity Gases
14. High Nitrogen Activity Gases
15. Chlorine, HCl, Containing Gases
16. 'Mixed – Oxidant' Gases

This is a relatively simple-minded list. There are all sorts of other factors which affect (usually adversely!) the corrosiveness of the environment, such as the effects of thermal cycling; fluctuations in the environment chemistry; the effect of periodic shedding of deposits; the effect of an erosive component in the environment; the rate at which the gas approaches equilibrium as it passes through regions of varying temperature; to mention just a few.

In addition, it must be recognized that the damage in a particular situation may involve a number of these factors. For example, in a coal-fired boiler, the fireside corrosion of the water-walls may involve a sulfur-rich deposit on the walls; this may become more severe if a high-chlorine coal is burnt. If, in addition, low NOx combustion methods are used, the lower portion of the water-walls will experience a substoichiometric environment. The combination of these factors can result in an enhanced attack. Finally, if one was to look at the same situation for an advanced supercritical boiler, the corrosion rate might be further enhanced. However, because of the way a large system like this operates, one might find that the high corrosion rates are localized: the majority of the boiler surface may behave in an entirely acceptable way. This makes instrumentation to detect corrosion and to assess remaining life particularly difficult.

2. Materials Issues

Materials Selection Criteria

Selection of materials for high-temperature applications presents some significant problems. The principal factors are:

- Properties suitable for the application
- Initial Cost
- Lifetime
- Failure impacts
- Predictability
- Fabricability
- Repairability

The corrosive impact on these factors is significant in most situations, and may be critical in some.

In general, for structural materials, corrosion resistance is not the primary criterion for selection. In most cases, for the applications described above, the mechanical properties are the major needs. Obviously, this usually means strength (rupture strength, creep strength, toughness) at the required service temperature. Since in all cases the systems have to be fabricated at ambient temperature, and in normal operation will need to be cooled to ambient temperature several times during their service lives, there will also be some mechanical property requirements for low temperatures: the usual minimum requirement is adequate fracture toughness. The selected materials must be fabricable to the extent required to manufacture the system; but there is often a further requirement in the fabricability of the materials since it is likely that during service repairs and replacements may be necessary. In most of the systems, the high-temperature-capable materials will have to be joined; the usual method is welding by one means or another; this is often an issue in repairability also.

The lifetime of the materials in service is an issue. For a large electricity-generating unit, the unit as a whole will be required to have a minimum lifetime of the order of 20 years, but in practice considerably longer service lifetimes are achieved. However, the required lifetime for the high temperature components may well be less than this, and they may be replaced or at least refurbished a number of times during the plant lifetime. However, in practice the minimum desired time between the planned outages which would allow such actions is three years (25,000 operating hours for a base-loaded unit); and most operators are now requiring five years between major outages. Obviously, the required lifetime depends on the component. It would be expected that the water-wall tubes in a large fossil-fuel fired boiler would last the lifetime of the plant; the superheater panels might be replaced, but generally a ten-year lifetime would be expected. Combustion turbine inlet stages and combustors might be replaceable on a shorter time scale, but since the very large advanced turbines in modern combined cycles may be base-loaded (at least for the first ten years or so) the opportunities for replacements will be limited.

From an operator's point of view, lifetime means minimum lifetime: major outages have to be planned a considerable time ahead, and thus a high degree of reproducibility and thus predictability in the materials properties are essential.

The nature of the possible failure is also a matter of concern. Catastrophic failures, such as an 'unzipping' of a main steam line, are to be avoided: the cost penalties in an outage of this sort are truly enormous. The term "leak before break" is often used in steam plant, and this assumes that the leak can be detected to allow an orderly shutdown to allow a repair. A similar term is used for aviation gas turbines: we talk of a "fly home capability".

High temperature corrosion must be considered in this context. The following effects may be a consequence of corrosion:

- Loss of section due to removal of useful material as a result of the formation of a corrosion product.
- Loss of useful section due to removal of strengthening alloy elements, or the inward diffusion of embrittling impurities.
- Changes in the heat transfer properties of materials in heat exchanger duties due to the build-up of a low thermal conductivity surface layer.
- Effects such as a progressive increase in the ductile-to-brittle transition temperature reducing the ability of the component to accommodate a cooling to ambient temperature.

Materials for use at high temperatures in the systems described above may need to resist corrosion in two very different environments. For example, a water wall tube in a subcritical pulverized coal-fired boiler will see an environment on the fire side which consists of combustion gases, quite possibly substoichiometric, and a deposit on the tube walls with a significant temperature gradient across the deposit; on the water side, it will see high temperature very high purity water, perhaps with very low oxygen potential. The mass flow rates will be high. Further up on the boiler wall this will be further complicated by the onset of boiling. Corrosion issues are significant for all of these environments!

It is important to remember that for many situations the steady-state corrosion rate of materials is largely irrelevant. Of course materials are selected to have adequate corrosion lifetimes under these conditions! As a consequence, what we have to worry about is the response of the materials to the real conditions they will experience in service. It should be clear from the list above that information derived from exposure times of (say) 1,000 h will have only limited value. One of the methods used to attempt to get useful information from relatively brief tests is to increase the severity of the conditions: thus, if the expected service temperature is 750 °C, tests will be run a 1,000 °C. This is exceedingly dangerous, because there may well be significant mechanistic differences which make the results meaningless at best, and positively misleading at worst.

Methods for Improving High-Temperature Corrosion Resistance

First, remember that a very large part of these heat engines, including much of the elevated temperature sections, are made of alloys, which have not been optimized at all for oxidation or high temperature corrosion resistance. All the plain carbon and low alloy steels are oxidizing at what one might call their ‘natural’ rate. Without exception, they are oxidizing at temperatures below that at which wustite, FeO, is stable: for plain carbon steels this is 570 °C. The oxide formed in air has an inner layer of magnetite, Fe_3O_4; and an outer layer of hematite, Fe_2O_3. Generally, the thickness of the magnetite layer is considerably larger than that of the hematite. On the steam side of the boiler tubes, if the water treatment is low in oxygen, the oxide is entirely magnetite; hematite is generally absent. With oxygenated water treatment, the oxide has a significant amount of hematite, and the overall scale thickness is significantly less; this has the effect of reducing the metal temperature for a given water/steam temperature. Improving the strength of these ferritic steels has involved the addition of relatively small amounts of chromium and molybdenum: a widely-used ferritic tube steel is designated T22 in the US; essentially it is Fe-2.25%Cr-1%Mo. The presence of the chromium raises the stability temperature for FeO, so the oxidation limit temperature is a little higher. The difference, however, is not great. The maximum use temperature for T22 is 600 °C.

For superheater temperatures, a ferritic steel whose composition is approximately Fe-9%Cr-1%Mo, whose designation is T91 may be used; the maximum use temperature is usually given as 649 °C. At this level, the oxide is often written as M_2O_3, where ‘M’ is a combination of Cr and Fe. A magnetite-like phase may also be formed.

The temperature quoted here is the midsection temperature for strength criteria; the fireside surface temperature for an oxidation criterion. These temperatures are of the order of 25 and 40 °C higher than the steam temperature, so that the attainment of a 650 °C steam temperature which is a typical ultrasupercritical main steam temperature will require a different steel. In the past, it was not uncommon to specify austenitic steels for the finishing superheaters, and a typical alloy would be Type 347, which is approximately Fe-18%Cr-11%Ni-Nb; the recommended maximum use temperature is 760 °C. For this alloy, the oxide would be essentially a single-phase Cr_2O_3.

The materials for the components outside of the combustion path are at essentially the main steam temperature, and this is true of the main steam control valve and the turbine inlet stages.

The high temperature corrosion issues in this area are as follows:

- Accelerated corrosion of the fireside waterwall tubes in the lower part of the furnace because of deposits containing (a) uncombusted carbon; (b) uncombusted iron sulfides; (c) chlorine-containing species.
- Accelerated fireside corrosion of the superheaters, particularly the leading tubes of the pendant finishing superheaters, because of deposits containing complex iron-alkali sulfates. A key issue here is the local SO_3 partial pressure in the gas.
- Spallation of the steamside oxide, primarily from the reheater circuit, although the effect is also seen in

superheaters. This can either (a) collect in the bottom of pendant tubes; reducing the steam flow leading to overheating; or (b) be transported with the steam to the inlet valve and the turbine inlet stages, producing erosion.

- Waterside hydrogen damage of the waterwall tubes, resulting from the formation of iron oxide from reaction with the water.

Now, for higher temperature applications, it is necessary to produce alloys with higher intrinsic oxidation resistance. Developments along these lines had begun for quite different reasons in the late 1920s, when a series of alloys were developed, primarily for electric resistance heater applications, which relied on the growth of a protective Cr_2O_3 'chromia' scale. These alloys were nickel or cobalt based, and when the first gas turbines were developed for aviation purposes these were selected for the hot components. The history of this development is beyond the scope of this paper, but these alloys – the 'superalloys' – were of enormous historical significance. As time went by, it became clear that chromia scales were insufficient: the primary reason was that above about 850 C in high-velocity gas streams the scale was lost as a result of the further oxidation of the chromia to form the volatile species CrO_3. The answer to this was to develop superalloys with a sufficient Al content to form a protective Al_2O_3 'alumina' scale. However, the development of superalloys for higher strength eventually prejudiced the ability of the alloy to form a protective alumina scale.

The solution to this was to use what is called a 'system' approach, in which the strengthening aspects of the alloy design and the oxidation resistance aspects were separated. This was done by developing coatings that were capable of producing an outer alumina protective scale, while maintaining good adhesion to the high-strength substrate. It is outside the scope of this paper to discuss this development in detail, but there is a considerable literature describing the history.

These coated superalloys, now largely nickel-base, have been the materials of choice for the first stages in advanced combustion turbines. For reasons beyond the scope of this paper, the investment-cast components went through fabrication developments, first to produce aligned grains by directional solidification, and then to produce single crystal components. The materials developments to make this possible have had significant impacts on the intrinsic oxidation and corrosion resistance of the alloys, but they are essentially always coated.

A further parallel development was to cool the hot components using air from the compressor: this presented significant fabrication problems, which have received much attention over the last thirty years.

The most recent development has been to use a low thermal conductivity coating (a 'Thermal Barrier Coating" (TBC)) on the outside of the airfoil: this is exactly the same general principle that was used something like one hundred years ago to protect the outer metallic casings of blast furnaces. However, the thermal protection had to be achieved on the turbine airfoils with very thin layers having excellent adhesion to the airfoil substrate; the material of choice is yttria-stabilized zirconia, and the adhesion is generated by using an inner alumina-forming coating. Again, the details of this process are outside the scope of this paper.

The issues of first cost, lifetime, and repairability are of great importance for the components resulting from these developments, and as yet not all of these potential problems have been solved. Furthermore, there is as yet insufficient field experience to identify what the important issues are, and whether any of these relate to high-temperature oxidation and corrosion. It is obvious that the growth of the oxide on what is called the 'bond coat' – this oxide is referred to in this field as the 'Thermally Grown Oxide' (TGO) – is matter of importance, and the adherence between this and the oxide TBC is also an interesting issue. The TBC is generally porous, and there are good reasons for this: in fact, at elevated temperatures the TBC may sinter, and this can have adverse effects on the thermal cycling resistance. An issue of interest to this audience is that there have been questions as to whether the corrodent species responsible for hot corrosion could 'wick down' to the bond coat, and compromise the TGO.

Given that the oxidation issue in the high oxygen activity of the combustion turbine exhaust has been solved by the use of alumina-forming coatings, the remaining problems are:

- High temperature, or Type I hot corrosion: molten alkali salt deposit induced accelerated attack.
- Lower temperature, or Type II hot corrosion: molten complex transition metal/alkali sulfate deposit induced accelerated corrosion: this requires a significant local SO_3 partial pressure, or some related chemistry modification.

It was shown when this issue of 'hot corrosion' was first discovered, that the presence of significant chromium in the alloy or coating was of great benefit, even for an alumina-forming substrate. However, the alloy developments and coating developments required for the advanced engines has reduced the chromium levels below those that we would have thought appropriate a few years ago. This situation will have to be watched with care.

Again, it is beyond the scope of this paper to review superalloy and coating hot corrosion: there are still a number of controversies concerning the mechanisms and the appropriate remedies.

The corrosion of heat exchangers in gasifiers is in many ways similar to that of waterwall corrosion in low NOx boilers. Again, the metal temperatures are relatively low; the gas has very low oxygen activity, but high carbon and sulfur activities. If anything, the environment is less severe, because the deposits on the metal surface are usually less aggressive.

For these situations, given that the tube material of choice is low alloy ferritic steels, the concept of relatively low-cost coatings has often been proposed: flame spray high aluminum coatings are generally preferred.

The issues of graphitization and metal dusting have not been mentioned here, because the conditions for these processes are seldom encountered in electricity generating systems. However, the development of fuel cells will probably require a hydrogen fuel, and this will be produced from natural gas by reforming. The reformer itself may suffer from carbon-related damage, but I will not discuss this here.

3. Overall Approaches to High Temperature Oxidation and Corrosion Issues in Energy-Related Systems

From the discussion above, it can be seen that there are perhaps three different issues here. In most cases, the materials of construction are selected on the basis of criteria in which oxidation and corrosion resistance are not of the first importance. However, recent developments, largely driven by a desire to improve thermal efficiency, have increased operating temperatures to a point where the oxidation lifetime is a matter of concern.

The approaches to these problems have been:

- Alloy development.
- Systems approaches, primarily coating or cladding the strong material with an oxidation- or corrosion-resistant layer.
- Reducing the component temperature by cooling, or by the use of thermally-insulating layers (obviously this is not appropriate for heat exchangers!).

A second area is the impact of operation outside the design envelope. When service failures are examined, we often see evidence that the failed component has been subject to higher temperatures than the material is capable of sustaining. For example, we see wustite formation on low alloy steels, ‘gamma-prime’ coarsening in nickel-base superalloys, and so forth. This may arise because the system has been overdriven to satisfy an immediate need; but more commonly it is because overall inhomogeneities in these very large systems: progressive misalignment of burners in pulverized coal-fired boilers, unequal flow distribution in manifolded heat exchangers, or excessive ‘pattern factors’ in combustion turbine combustors and inlet volutes. The methods of solving these problems are increasing the inspection of the plant, and remedying the inhomogeneities as they develop; improved diagnostic instrumentation is the key to this.

The third area is the influence of impurities. These may be fuel-borne, or brought in with the combustion air. Perhaps the most common issue is the incorrect location of air intakes, particularly combustion turbines. Often this is coupled with inadequate air filtration or poor maintenance of the filters themselves.

The desire for flexibility in fuel is also a matter of concern in this context. For example, coals vary in chemistry very considerably, even in the same coal field. In the Illinois coal basin, the majority of coals have been very low in chlorine, but at the periphery of the basin, or in deep mines, the chlorine content is higher, and over the life of a mine the chlorine content of the mined coal may progressively increase over time. In the US, mined coal is transferred to the customer in rail cars, and particularly in the winter a significant amount of superficial chlorine-containing material derived from road de-icing can contaminate the coal during its journey. Similar effects are seen with marine oil tankers: in this case the salt is sometimes introduced as a result of sea-water washing of tanks. Biomass, particularly municipal solid waste and agricultural wastes, has a very variable chemistry. For very high-performance equipment, such as aviation gas turbines, very tight fuel specifications coupled with continuous monitoring is used as a method to combat this problem; coal-burning plant also attempt to sample the incoming fuel where they are in the custom of using coal from a single source. However, the desire for finding the lowest-cost fuel, and taking advantage of what are called ‘opportunity fuels’ can cause significant problems – not only high temperature corrosion, but also impacts on combustion efficiency, unburnt carbon, fly ash, and fouling of heat exchanger surfaces.

Many of the high-temperature corrosion (as opposed to oxidation!) issues that have interested us over the years are ultimately related to impurity effects. We should all remember that step one should be attempting to eliminate or at least limit the harmful impurity!

Overall, the area of high temperature oxidation and corrosion in energy-related systems is of considerable importance. Failure to ‘get it right’ can have major influences on the cost of the product, and on the reliability of supply. However, it is also important to remember that this is a component of a larger system, involving engineering, operation, and economics; and all researchers in the field should develop an understanding of their place in the total system needs.