# The Engineering Science of High Temperature Corrosion.

A Presentation to the University of Surrey Short Corrosion Course

Fred Starr : Modified 2011

## 1. Introduction

This paper adopts an "engineering science" approach to the corrosion of materials of high temperature. It seeks to show that, although the knowledge of the subject was once highly empirical, rational methods of tackling high temperature corrosion are now in prospect. High temperature corrosion is also put into an industrial context, and shows how it now limits advance in a number of key technologies.

The use of the term "engineering science" does imply the production of data and hardware which can be used with confidence in the design and operation of an "engineering system", for example, a generating plant, a refinery or hypersonic aircraft.

The subject of engineering science and design is exhaustively treated in a book by W.G. Vincenti, entitled "What Engineers Know and How they Know It" <sup>1</sup>. A major theme of the book is that engineering science can differ quite markedly from natural science. In engineering science, workable concepts need to be devised, not always based on scientific theories, which permit better design, better operating practices, and in our case, better materials to be formulated. Natural science has the aim of producing a genuine description of the mechanisms which govern, for example, the progress of ionic species through an oxide scale. There needs to be no commercial application of this work, simply the intellectual satisfaction of finding the truth is sufficient enough.

As natural science evolves we expect its theories to come into ever closer correspondence with what actually happens. This does not necessarily occur in engineering science. What we do expect is that our predictions allow us to get better at making money or, at least, to stop wasting it. Engineering has in fact been described as "doing for five bob (25 pence in modern money) what somebody else would do for a pound ".

The study of corrosion at high temperature, as both an engineering and scientific discipline, is quite recent. Accordingly, it is not surprising that some of the ideas involving quantitative predictions are not as fully worked out as one might wish. Alloy design is one example. Nevertheless, real progress has been made during the 1980's, much of it stemming from the growth of computational techniques in gas phase thermodynamics.

Among the main insights into the philosophy of engineering science and design in his book, Vincenti highlights the need to formulate, if rational progress is to be made "**the operational principle**" of a successful device. In the case of an aircraft, the operational principle is that the movement of air over the wings produces a lifting force; with a bridge, it is that the deck resists deflection in accordance with beam theory.

With respect to a material resistant to high temperature attack, the operational principle is that an oxide film, or scale, forms on the surface and protects the underlying material from attack. To do this, the oxide must:

- Be solid
- Be impervious to the penetration of molecular species
- Be adherent at all temperatures at and below the operating temperature
- Have a stochiometry that is extremely close to the ideal, to prevent the rapid diffusion of ionic species
- Have a melting or decomposition point that is well above the operating temperature

Most metals, in their raw condition, corrode at an almost unbelievable rate at quite modest temperatures. Hence, the tendency of metal powders, wire and turnings, to burn if gently heated. It is, therefore, only the presence of protective scales which permits us to use metals, alloys and certain ceramics at high temperature. The concern of the high temperature corrosion engineer is to deal with the breakdown of protective behaviour, whether from the contamination of the scale by other oxidants, deleterious elements in the base alloy or, simply, due to exposure at too high a temperature.

This paper falls into two halves that can be read independently of one another. The first half offers up a plain mans guide to the principle tenets of high temperature corrosion theory and practice. These principles are usually taken for granted by those fully experienced in the subject. However it is essential that the design engineer and operator of high temperature plant have some knowledge of the rules, especially when equipment is being pushed to the limit.

Furthermore because high temperature corrosion has influenced and is influencing the development of technology to an ever greater extent, the first half of the paper also gives a brief review of its historical impact. The examples given, it is hoped, will serve as a convenient peg on which to attach the principles that underlie the subject. The second half of this paper attempts to cover some of the more modern advances in high temperature corrosion and shows how our most recent work is much less empirical.

## 2. High Temperature Corrosion : A brief history

The first true corrosion-resistant materials, the nickel chromium alloys, were developed at the turn of the century and, in some respects, have hardly been bettered. However, the early use of these alloys was confined to the resistance heating field and had very little impact on Industry.

The need for oxidation and high temperature corrosion resistance in engineering applications dates from the 1920's. Before then corrosion at high temperature was of little concern to the practical engineer. From twenties onwards, however, the issue came to have an increasing dominance on technical development. But it is instructive to look briefly at prehistory and history of the applications of materials in high temperature corrosion environments, and see how modern theory explains some of the successes and failures of technology at various times.

## **2.1 The Industrial Revolution**

The Industrial Revolution was founded upon the availability of cast and wrought iron at an economic cost, and, later on, mild steel. These had the same impact on Victorian Industry as aluminium, stainless steel and the super-alloys have had in our own times. However, none of these nineteenth century "irons"

had much resistance to oxidation in air, or steam, even discounting more complex environments like the atmospheres in coal fired furnaces or coke retorts. Indeed the only technique the Victorians had for welding sheets and bars of wrought iron together, relies on the fact that the oxide scale which forms on the iron, at welding temperature, is fluxed away by the slag-like constituents of the wrought iron.

Experimental data shows that, with unalloyed iron, the oxidation rate reaches unacceptable levels in clean, dry air or uncontaminated combustion gases above about 550 -  $600^{\circ}$ C. Sulphur dioxide, a contaminant in most industrial atmospheres, would tend to increase the rate of attack somewhat. Figure 1 shows the weight change data for a variety of carbon and stainless steels, subjected to oxidation between 500° and 850° C for 10000 hours in air.

It will be seen that over a relatively small temperature range, the increase in oxidation rate can become quite unacceptable. In the case of carbon and low alloy steels the reason for this sudden increase is the formation of wustite, FeO. This is a non-stochiometric oxide which gives very poor protection, compared to haematite (Fe<sub>2</sub>O<sub>3</sub>), or magnetite (Fe<sub>2</sub>O<sub>4</sub>). During the Industrial Revolution, this temperature limit of about 550°C was, not a major constraint. The steam engines of the time ran at pressures of 15 bar and below, and metal temperatures could not have been much more than  $250^{\circ}$ C.

One rival to steam was the Stirling Cycle Engine, and the effort to develop this failed because of the inadequacies of wrought and cast-iron. This type of engine ran with a hot-air "boiler" which was under very little stress as internal pressures were low. But to give a useful output, the boiler, or heater as it is more properly called, needs to run at metal temperatures well over 600°C, quite beyond the temperature capability of the materials of the time. Indeed, the first recorded of the word oxidation, in the sense of metallic corrosion at high temperature, was used by the inventor of the Stirling engine, when he bewailed the shortcomings of the materials which were then available.

The same kind of oxidation problems would have affected the operations of the Neilson Hot Blast Stove, which revolutionised iron smelting in the middle of the nineteenth century. This was a tubular air preheater, constructed of wrought and cast iron, in which air was heated by burning coal for supply to blast furnaces. Air preheats of around 315° C were eventually attained, implying metal temperatures in excess of 500° C. Even with clean environments there would not have been much scope for an increase.

Modern work on power station boilers would suggest that, as well as suffering from straight air oxidation and sulphur dioxide, if the tubes in a Neilson Stove became blanketed with soot, chlorine-assisted corrosion might well have been a problem. See Fig. 2. The chlorine, in the form of HCl, tends to produce volatile metal chlorides which prevent good scale adherence, and reduces safe operating conditions in high CO environments by over 150°C. To-day, there are a host of materials which can overcome this form of attack, usually based on chromium steels; the main consideration is of specifying an alloy which will give the lowest cost solution.

Chromium steels, were, of course not available in the nineteenth century and the Neilson Stove was superseded by the Cowper Stove. This was a regenerative type of preheater, using refractory bricks. Air preheats increased immediately to 620°C.Even to-day, if one was heating air by burning coal or heavy oil, with the attendant problems of sulphur oxides and ash corrosion, such temperatures would

not be a simple requirement. Metallic recuperators operating on clean air, or the combustion products of natural gas, have a much easier time and can be good for temperatures up to 1000°C

What, lessons can be learnt from the prehistory of high temperature corrosion which are pertinent to engineering science and practice. These are:

- For every material, there is a fairly narrow range of temperatures, above which the rate of attack becomes unacceptable.
- The onset of rapid corrosion is associated with the appearance, or formation, of a non-protective oxide scale.
- Minor oxidants can reduce safe limiting temperatures, quite dramatically.

## 2.2 The Early Twentieth Century

The early twentieth century, which is the pre Second World War period, was on the heavy-engineering side, characterised by developments in oil refining and power station technology. The need to use materials at higher temperatures, and in more difficult environments, meant corrosion became a major concern. Nevertheless, the main preoccupation was, at the time, high temperature strength, rather than corrosion resistance.

The development of thermal cracking of heavy oil is illustrative of these trends. Cracking is essentially an elevated temperature treatment, which breaks up the heavier fractions of oil into lighter molecules that have good "knock resistance". Reaction temperatures were in the range 370° to 600°C, but metal temperatures were much higher than this. Internal pressures were also high, at around 70 bar.

With sweet feedstocks and good furnace design, a good life could be obtained from carbon steel cracking tubes. With sour, that is, high sulphur oils, it was necessary to use 5% chromium or the early "18/8 "austenitic stainless steels.

It is now known that if sulphur is present, especially when the conditions are highly reducing, the limiting temperatures for both carbon and stainless steels are hundreds of degrees below that in the clean air case. There are a number of reasons for this, including the bulky character of many sulphide scales, compared to the original metal. This gives rise to growth stresses. More fundamental reasons are related to the non-stochiometry of the sulphide scales, which form on iron, chromium, nickel and cobalt alloys. The absence of stochiometry, combined with the low melting point of these scales, tends to give very high growth rates, compared to oxides.

A good deal of practical knowledge was accumulated on the steels to be used with sour feeds. In the nineteen thirties a slightly different problem emerged with the development of catalytic cracking. Here corrosion was from  $H_2S$  in a hydrogen rich environment rather than from complex organic sulphides.

Backensto et al investigated  $H_2S$  attack during the nineteen fifties and concluded that the rate of attack could peak at a given temperature, the peak shifting to higher temperatures and increasing in size with  $H_2S$  concentration. The decline in attack at higher temperature was ascribed to a "thermodynamic cut off", when iron sulphide becomes unstable at low  $H_2S/H_2$  ratios. See Fig.3.





Couper-Gorman Curves for the Corrosion of Carbon and 18/8 Stainless Steels in a Hydrogen Sulphide Environment





Much more recently, this practical plant experience and early laboratory work has been put on a more solid footing. Improved correlations, based on the work of McConomy, for the corrosion of steels in sour feeds, have recently been published by Guzeit et al. Here, for sour feeds, two sets of curves are needed. See Figs.4 and 5. The first gives the rates of corrosion for various steels between 250° and 450° C, in a sour feed containing 0.6% sulphur. There are several classes of steel, carbon, 2Cr, 5Cr, 7Cr, 9Cr, 12Cr, and the 18/8 stainless types. Each upgrading of steel, roughly halves the corrosion rate, so that with austenitic stainless steel, corrosion is almost negligible. The second set of curves gives a corrosion rate multiplier, which allows for different sulphur levels in the feed. What is intriguing is that order of magnitude changes in sulphur content only change the corrosion rate by a factor of two.

Practical information is still being accumulated. It is thought that the drop off in corrosion above  $450^{\circ}$  C is due to coke formation, which protects the steel from direct contact with the feed. Presumably when the oil is heated the sulphur compound breaks down liberating H<sub>2</sub>S and other aggressive sulphur compounds which is in direct contact with the surface will cause sulphidation. The presence of small amounts of silicon in the low alloy steels can reduce corrosion to a very marked extent, in this by forming, presumably, a silica subscale which is not attacked by sulphur compounds.

Couper and Gorman have also compiled new data on corrosion in  $H_2S$  atmospheres. The thermodynamic cut off phenomenon is confirmed to be a real effect. The levels of corrosion at low temperatures are not dissimilar to those found with sour feeds. However, a distinctly smaller range of steels has been found to be useful. For example, the 2Cr steels show very little advantage over carbon steels.

The requirements of the prewar power generation industry were even more orientated towards creep, rather than corrosion resistance. Progress tended to be evolutionary, rather than revolutionary, with the large-scale use of stainless steel pipework lagging well behind the oil industry. This is a natural consequence in the development of the Rankine cycle. It is commonplace that, to achieve high thermal efficiency, an increase in cycle temperatures is a necessity. However, with the Rankine cycle, to take full advantage of any increase in steam temperature, pressures must also rise. Accordingly, at the start of our period, pressures were around 15 bar and temperatures around 230°C. By 1940, typical operating pressures were around 100 bar and temperatures were up to 450°C. It require the post war development of reheat in power stations to push temperatures higher.

This combination of pressures and temperatures led to the development of a range of low alloy steels, in which chromium was a key addition at the 1-3% level, in combination with molybdenum. Such small quantities of chromium have a modest but useful affect on oxidation resistance, since the chromium serves, in this case, to increase the stability of  $Fe_2O_3$  and  $Fe_3O_4$  to about 600°C... Levels of chromium above 9% give rise to true chromium-rich spinels which raise safe temperatures to at least 625°C. But above 16-20% chromium a true chromic oxide forms with the iron oxides being completely suppressed.

For most engineering purposes, a very small set of Type 400 ferritic and Type 300 austenitic stainless steels is now in use. Table 1 shows representative types and absolute maximum operating temperatures for relatively short term exposures of less than a year in clean atmospheres.

Type of Stainless	Description	Service Temperature °C
405	13Cr Ferritic	705
430	17Cr Ferritic	815
446	17Cr Ferritic	1095
321	18Cr 10Ni +Ti Austenitic	925
316	18Cr 10Ni +Mo Austenitic	925
347	18Cr 10Ni +Nb Austenitic	925
310	25Cr 20Ni +Si Austenitic	1100
HK	Cast 310 Equivalent	1095
HI	Cast Low Ni Sulphur Resistant	1120
HP	High Strength Cast Alloy	1100
HU	Cast Alloy with Good Cyclic Performance	1095

## Table 1: Maximum Medium Term Service Temperature for Resistance to Scaling

What are the main lessons that oxidation science can draw from the experience of this period?

- The most protective scales on normal engineering materials are oxides.
- For a very large range of engineering applications, the chromia-forming alloys are quite suitable.
- The presence of sulphur, especially under reducing conditions, has a very detrimental effect.
- Corrosion rates do not always increase with temperature and the thermodynamic of the system must be considered.

## 2.3 Mid-to-Late Twentieth Century

High temperature technology, since the Second World War, has been dominated by the Gas Turbine, Coal and Oil Fired Power Generation, and Nuclear Power. As we shall see, the problems of high temperature corrosion came to have a dominating effect on each of these.

#### 2.3.1 The Gas Turbine

The main requirement for the gas turbine are for HP stator and rotor blade alloys, which are able to combine exceptional creep strength with good oxidation resistance. Inlet temperature on early turbines were around 700°C at take off, today in the early nineties, they can reach 1400°C.

Metal temperatures have not increased anything like as much. Hard data is difficult to obtain, but there has been a relatively slow rate of advance from about 650°C in 1942, to about 1000°C to-day, in terms of peak, rather than bulk metal temperatures. There is now a very big discrepancy between the temperature of the combustion products, at the turbine inlet, and the blade temperature itself. This is due to the extensive use air of air-cooling of the blades on modern engines. Up to 10% of airflow is used for this purpose and this has a most detrimental effect on cycle efficiency.

How is it that there has been so little improvement in the capability of gas turbine blading materials? Why is it that the engine manufacturers continue to use, as a base for turbine blading, alloys based on nickel, and, for the stator blading, alloys based on cobalt? Neither has a very high melting point, the figures being, respectively, 1453° and 1492°C, the effect of alloying tending to depress these temperatures, rather than raise them.

There are a number of other elements, which, in principle, should have greater capability for turbine blading, these being titanium, molybdenum, niobium and tungsten. All of these, with the exception of titanium, have melting points well in excess of 2000°C. Even titanium is significantly better than nickel and cobalt with a melting point of 1660°C, and this ought to make a good alloy base, in view of its low density. However, no alloy based on these elements has come anywhere near use in a conventional gas turbine, simply because of their poor performance under oxidising conditions.

Molybdenum illustrates the problem. In air, the main oxide that forms is  $MoO_3$  which is, essentially, nonprotective. Even at 600°C, the loss in of metal is around one centimetre a year! Above the melting point of the trioxide, 795°C, the rate of attack increases by more than two orders of magnitude. See Fig 7. Clearly, liquid phases allow cationic and anionic transport to a much higher degree than solid scales. A further problem is that the trioxide is volatile and, in rapidly flowing air streams, material is removed by a process of ablation. Mass transfer techniques can be used to quantify the rate, which is helpful in the design of short-life equipment, for example, rocket nozzles.

Much effort was spent during the 1950s on alloy and coating development for molybdenum, without success. This story appears to be a closed book and of little relevance to modern industry. However, trioxide formation is always a potential problem in molybdenum containing Type 316 and 317 stainless steels. Under stagnant conditions, under lagging, in recesses in equipment, etc., selective oxidation of chromium will lead to a build-up in molybdenum. Eventually, a critical concentration is reached and the trioxide forms, which begins to flux protective scales. If low melting-point compounds are present, as in silicate-bearing insulating materials, the risk of localised catastrophic oxidation, with this type of molybdenum containing alloy is greatly increased.

During this programme on the refractory metals, a term which has some unfortunate overtones, work continued on the nickel and cobalt based alloys. Nickel based materials became the main focus for development as it was impossible to strengthen cobalt based alloys with a suitable intermetallic.

The aim was therefore to increase the concentration and stability of  $Ni_3$  (Al,Ti) in the nickel based alloys. To increase the solubility of aluminium and titanium during the heat treatment stage, chromium levels were progressively, reduced from around 20% in, for example, in Nimonic 80A, to about 13% as in IN713C. Table 1 on the oxidation of the low chromium stainless steels would suggest that the oxidation resistance of alloys with such low chromium contents would be somewhat marginal above 900 C. Figure 6 shows in fact that the oxidation resistance of the superalloys is inferior to the best stainless steels. The high level of aluminium helps, but the real problem for gas turbines is hot corrosion, from sulphur in the fuel and sea salt in the atmosphere. High levels of chromium are essential to give adequate resistance. In Section 5.5 a quantitative approach to alloy design is discussed, which covers this issue..



High levels of chromium are used in stator blade alloys, which are often cobalt based. Here temperatures of well over  $1000^{\circ}$  C can be encountered and chromium volatilisation is of some concern. The very high air velocities in gas turbines adds to the problems. Under these strongly oxidising conditions, the volatile species is CrO<sub>3</sub>. In reducing atmospheres, as in coal gasification plant CrO will also form. The need for compromise over chromium levels still dogs gas turbine blade development. The most modern alloys intended for military engines have chromium contents of under 10%, and it is essential to use protective coatings even though the environment is often quite clean and a relatively short life is acceptable.

The two main classes of coatings that are most often used both contain sufficient aluminium to form an alumina layer and hence their oxidation resistance is very good, for short periods, at least. Pack aluminising is the oldest of the coating processes. This is a diffusion treatment in which the final result is a surface layer largely composed of nickel aluminide. MCrAlY coatings are a later development in which an alloy containing cobalt or nickel, rich in aluminium and chromium, is sprayed on to the surface of the blading.

These coatings are not a complete solution even to straightforward oxidation. Back diffusion of aluminium is a particular shortcoming of the pack aluminide coatings. Both types of coating suffer from aluminium loss in another way. The alumina layer tends to flake off, under conditions of thermal cycling, once the oxide thickness is over a micron.

There are clearly several lessons which might be learnt from the gas turbine story. However for our purposes the main ones are:

- Oxides which melt or volatilise are of serious industrial concern
- Chromium, whilst of major importance, as a protective element has significant limitations

#### 2.3.2 Fossil Fuel Power Generation

It is only recently that anything other than coal or heavy oil have been considered as fuels for power generation. Neither is ideal from both the corrosion and environmental point of view. UK coals contain up 20% mineral matter and up to 1% sulphur and 0.5% chlorine. Most power station fuel oil has very high levels of sulphur, up to 4% in some cases. The cheaper grades of heavy oils come from Venezuela, and contain significant quantities of vanadium compounds. These combust to form low melting point ashes. Clearly this combination points towards serious corrosion problems. The evolution in power station design did nothing to help. By the start of the nineteen sixties, most new stations were operating at steam conditions of 530°-565°C, and at pressures of up to 200 bar. Metal temperatures, in superheater and reheater banks were up to 650°C. The austenitic stainless steels were the main materials of construction for these components.

There had also been in the post war period, a switch to pulverised fuel firing in coal burning stations, which had many advantages. One major drawback was the tendency of ash and partially combusted coal particles to accumulate on superheater tube banks. As the combustion product temperatures experienced in these sections are well over 900°C, the ash fuses and seriously adds to corrosion problems.





FIGURE 9 Corrosion of Superheater Tubing by Coal and Oil Ash : Gas and Metal Temperature Dependence

			ASSI	MING	STOIC	HIOME	RED TRIC N	a : C1 R						011	L FIRE	0			
GAS TEMP.	MID-WALL METAL TEMP.	LOW ALLOY			HIGH ALLOY FERRITIC (UP TO 12% Cr)			AUSTENITIC (TYPES 347, 321, 316, ESSHETE 1250)			LOW ALLOY FERRITIC			HIGH ALLOY FERRITIC (UP TO 12% Cr)			AUSTENITIC (TYPES 347, 321, 316)		
°c	°c	HIGH > 0.30 %CI	MED. 0.30 0.15 %C1	LOW < 0.15 %C1	HIGH > 0.30 %C1	MED. 0.30' 0.15 %C1	LOW <0.15 %C1	HIGH >0.30 %C1	MED. 0.30 0.15 %C1	LOW <0.15 %C1	V: N2 > 3.0	V:Na 3.0+1.0	V:Na <1.0	V:Na >3.0	V:Na 3.0-1.0	V: Na <1.0	V Na > 3.0	V:Na 3.0-1.0	V Ha <1.0
	540																100		
	580															_			
975	620										Carlanda and Carlanda	Contraction of the	100 B						
	660																		
	700		5.99 F			17 m	191	3333333											
	540	1.	Γ									· ·							
	580																		
1050	620																******		
	669			41				11.1.1											
	700	104455	जिन्दि हाथ	1	<i>ा र<sub>े</sub>र्म्</i> व			de la como				-		- inclusion	inter a second			<u>et es e</u>	
	540			1			[	[											
	580			t s sign			1						1						
1150	620																		
	660		. A share															1	
<u>.</u>	700	1999 - A	- #i ***		fre Se	3 . T. T	the specific	40 M ()	the second		1.15	11.41	2.04		a the first		1.4.1.1.1		19.23
	< 25 nm/h			25-50	nm · h	1		50-100	nm h	E	******	100-200	nm · h	, E	>	200 nm	h		
ORMAL	TOLERABLE		SIGNIFI	CANT R	ATE OF	:	SERIOUS	RATE	DF	N c	ERY SE	RIOUS P	ATE	01	TASTRI	DPHIC I	RATE		

The actual mechanism of fuel ash corrosion involves both the molten ash and the sulphur dioxide in the combustion products. Examination of corroded sections of tubing show several layers to be present, starting with ash on the outside. Underneath this there is a deposit of haematite, then what has been a molten iron-chromium sulphate layer at operating temperature. Finally there are the oxide scales themselves, which consists of a mixture of iron-chromium nickel spinels underlaid by a layer of intergranular sulphidation. Coal ashes contain sodium and potassium which act as additional fluxing agents to the molten layer. Chlorine is also probably involved. See Fig.8.

The formation of the molten sulphate layer is a key phenomenon. It acts in two ways. As a molten layer it will tend to dissolve protective oxides. It also acts as a reservoir for sulphur. This diffuses down below the protective spinels and gives rise to the intergranular corrosion. As section 2.2 showed when sulphur is present there is always a marked increase in the rate of attack. The molten sulphate is an unexpected feature in the deposits. It only forms because of the presence of  $SO_2$  in the furnace atmosphere. When the  $SO_2$  partial pressure falls below 25 Pa the sulphate will dissociate.

The rate of attack increases with both metal and gas temperature and a great deal of work was done by the CEGB to produce corrosion rate data over a wide range of operating conditions. This is displayed in a tabular form in Figure 9. This diagram is of some complexity and deserves of careful study. It shows the resistance of different alloys, austenitic materials being best, although even these are not particularly good in high chlorine coals. As might be expected increasing metal temperature, within the range covered also increases attack rate. However Figure 9 also shows that high flue gas temperature also increases the attack rate.

Coal and oil ash corrosion have been a major impediment to the continued advance of power station technology, as it is difficult to formulate an alloy which has the appropriate combination of strength, corrosion resistance. Increasing the chromium and silicon content will reduce corrosion by reducing the fluxing qualities of the sulphate layer. Unfortunately, both of these elements tend to promote two-phase structures in austenitic stainless steels, with either ferrite or sigma phase being produced. A very serious reduction in strength and ductility then results.

To keep stainless steels austenitic, the nickel content must be increased. However, nickel rich alloys have poor resistance to corrosion by sulphur compounds, so that the chromium content must be increased to compensate for this affect. Accordingly, the most resistant alloys have over 40% chromium, with the iron being cut to a minimum. Alloys such as IN 671 and IN 657 are typical of this class. Unfortunately, these are not very strong, and are very expensive.

A vast amount of effort was spent during the period 1950 to 1985 on the fuel ash problem and it certainly was a major factor in preventing the advance of power station technology. However, the 1990s and beyond will see new forms of power generation based, namely, on natural-fuelled combined cycle, fluidised bed steam generation and, possibly, integrated coal gasification combined cycle. They should make coal and oil ash corrosion a thing of the past. From the environmental point of view, they will reduce the acid rain emissions from the power station sector. This will also operate at thermal efficiencies of between 40-55%, substantially better than the 35% of the technology of the fifties and sixties.

The main points worth remembering from the ash corrosion story are :

- Second and third order reactants can act synergistically, reducing limiting temperatures by hundreds of degrees.
- Industrial corrosion problems involving the deposition of ash, molten fluxes and carbonaceous deposits, especially where sulphur is involved, can be highly complex and difficult to eradicate.

## 2.3.3 Gas Cooled Reactors

The U.K. series of gas cooled reactors can, in principle, be traced back to the early days of nuclear power, when plutonium was produced from "atomic piles". These were built up from masses of air-cooled graphite blocks, interspersed with uranium rods.

The Magnox and AGR (Advanced Gas Cooled Reactors) were, basically, designed around this principle. Carbon dioxide, rather than air, was used as a cooling medium and this was pressurised to increase its effectiveness. The  $CO_2$  was circulated through the reactor and, then, into the boiler and superheater section of the reactor complex. One advantage of gas cooling is that the reactor pressure is independent of that of the steam plant. Hence, it was possible to foresee a gradual evolution in temperatures, efficiency and output of gas cooled reactors. Magnox ran at better steam conditions than Calder Hall, the first electricity producing reactor in the West, and the AGR ran better than Magnox. If gas-cooled systems had continued to evolve, we would now be seriously considering the High Temperature Reactor (HTGR), which would have a gas outlet temperature approaching 1000°C.

As is known, Magnox and the AGR have been abandoned, and work on the HTGR, basically a German programme, has slowed. It would be too much to claim that this was all the result of oxidation problems. However, virtually everyone, in the UK engineering profession, born before 1950, has heard of breakaway corrosion, and is aware of its impact on the nuclear industry.

Breakaway corrosion has now become a generic term in the oxidation field, meaning a rapid increase in the rate of attack, after a relatively extended period when the oxidation rate is acceptable. It should not be confused with an incubation period, when the basic corrosion process is establishing itself.

There can be many causes of breakaway corrosion, the most important of which include exhaustion of protective elements through over rapid scale growth or from spallation and fracturing of the scale. An additional cause of breakaway is the tie-up protective elements. This can result from subscale formation below the protective layer or from a process known as internal oxidation. Here certain elements such as carbon and nitrogen can diffuse into the alloy and have the capacity to react with chromium.

It is not always possible to demonstrate classical breakaway corrosion in the laboratory, but Figure 10 shows the weight increase with time of a Fe-0.29 Mn steel in a  $CO_2/CO$  mixture at 550°C and 13.8 bar pressure. Up to about 1000 hours, the corrosion rate is fairly low and parabolic, with a weight change of 2-3 mg.cm<sup>-2</sup>. After about 1500 hours, the rate begins to accelerate, so that, at 3000 hours, the weight gain is about 20 mg.cm<sup>-2</sup>.

Breakaway corrosion led to the well-known "rusty bolts" phenomenon, more prosaically termed, "oxide jacking", in which layers of oxide formed between the bolt-heads and the nuts, where were used to hold reactor components in place. The bolts would eventually break as the bolt was forced to get longer and longer. On the AGR breakaway corrosion could also lead to the disintegration and blocking of the finning on the fuel pins.

FIGURE 10 Breakaway Corrosion of Fe-Mn Steel in a CO2 / 5% CO / 400ppm H2O Atmosphere at 550 C and 13.8 bar pressure



FIGURE 11 Effect of Moisture Content and Weight Gain on Probability of Breakaway Corrosion of a 9% Cr Steel at 640 C



A great deal of work was done to contain breakaway corrosion, by prescribing plant operating procedures. In the Magnox reactors, where many components had gone into breakaway, before the significance of the phenomenon was fully recognised, the main consideration was to predict the post-breakaway rates of corrosion. Here, it was found that the key factors were the silicon content of the steel, the water content of the atmosphere and the metal temperatures.

However, as the following equations show, none of these factors affected corrosion in a simple way. For example, at lower temperatures, the rate of attack was proportional to the -0.49 power of the silicon content. Such obscure fits are typical of those found in engineering science.

In the Magnox reactors the rate of post-breakaway attack is the sum of two terms, so that the actual rate, R, is given by

$$\hat{\underline{1}} = \underline{1} + \underline{1}$$
  
R R R<sub>1</sub> R<sub>2</sub>

 $R_1$  is more important at low temperatures and governed by a temperature dependant function and the silicon content of the metal. It is given by the function :

$$R_1 = 0.07$$
 (Si)-0.49 exp (-43000  $T_b$ )

 $T_b$  is the temperature function which is given by

 $T_b = 0.5033 ( \_\_1\_ \_\_1\_ ] )$ Metal Temperature °C 633.16

 $R_2$  is more significant at higher temperatures and is influenced by the moisture content of the atmosphere as well as the silicon content of the metal and the temperature. The function is:

 $R_2 = 0.48 \text{ (Si)}^{-0.185} \cdot \text{(W)}^{0.9} \cdot \text{exp} (-13000 \text{ T})$ 

Where:

W = (gas pressure psi)\*(moisture content in v.ppm)\*  $5.122.10^{-5}$ 

It will be clear from the complexity of the equations that a very large number of specimens and tests were needed, the results of which required statistical analysis. This work resulted in a decision to cut back the operating temperatures in the later Magnox stations by about 30°C, apart from periods when the rest of the system could not meet the demands.

The risks of breakaway corrosion were known, however, before the AGR plants came on-stream, although Fe-9Cr steels were being used. Here, again, a statistical approach was used to delineate safe operating temperatures.

Because breakaway corrosion is a localised phenomenon, Monte Carlo methods are used to predict the probability of breakaway nucleation, when the overall rate of attack reaches a critical level. For example,

at a moisture content of 270 rpm at 640°C, if the pre-breakaway weight change is less than 20 mg.cm<sup>-2</sup>, it is unlikely that the steel will go into breakaway. However, at above 40 mg.cm<sup>-2</sup>, there is a 100% probability that breakaway will occur. As Figure 11 shows, the critical weight for breakaway falls with increasing moisture content, as does the actual post-breakaway oxidation rate.

From the point of view of the engineering science of high temperature corrosion, the gas cooled reactor saga brings out the following points.

- Breakaway corrosion is always a risk in long-life plant, where the medium term oxidation rate is relatively high, but, nevertheless, appears to be acceptable.
- Trace quantities of alloying elements, or gaseous components, can have a dramatic effect on breakaway corrosion.
- To obtain predictive data, a large test programme may be necessary and the results may need to be subject to refined statistical analysis.

## 2.4. Comment

The intention of the foregoing was to not only outline something of the industrial history of high temperature corrosion, but to illustrate by means of examples its key aspects. Some of these will be considered further, in Section 5, when we review modern developments in high temperature corrosion.

The examples show how, from being a mild inconvenience to the engineering profession, high temperature corrosion has become a serious impediment to advance. Given the range of metallic materials which are on offer, if we could ignore the effects of high temperature corrosion, steam plant would be operating at 700°C and gas turbines at 1500 to 2000°C; the latter, without blade cooling. This would lead to fuel savings of around 10% in power stations and perhaps as much as 50%, in the case of aeroengines. When it is considered that the fuel load on Concorde is 100 tonnes and the payload a mere 15 tonnes, the implications for advanced aircraft design are clear.

## **3.** Corrosion Allowance Criteria

Where high temperature corrosion is a threat, the designer of engineering equipment can use one of two criteria to circumvent the problem. He or she can specify the material and operating temperatures so that, even after very extended periods of operation, the loss in thickness, due to corrosion, will be negligible. The alternative is to design for a known rate of corrosion and accept that, if the equipment performs to specification, it will need replacing after a set time.

Operation below a limiting temperature is the one most favoured by designers. The approach seems to be to design to at least 50°C, below the temperature at which corrosion is known to become rapid in medium-term tests. This can lead to over-conservative design and can give a false sense of security. After long periods of service, equipment can fail, due to breakaway corrosion. Nevertheless, many designers prefer this approach and sometimes, this is mandatory, as the following examples show:

- Loss of section critical: Inlet and exhaust valves on internal combustion engines
- Clearance critical: As above, plus control and block valves on steam turbine and petrochemical plant

#### Retention of surface geometry: Cooling passages in gas shape and character in turbine blading

However, in many engineering systems, a greater or lesser degree of corrosion must be tolerated, and we will briefly examine some of these below.

For both petrochemical plant heat exchangers and for the external surfaces of steam boiler and superheater tubing, acceptable corrosion rates can be up to 0.5 mm/annum, and the designer needs to build in an appropriate corrosion allowance for the plant life. The nominal design life for power stations is about 100,000 hours and this would give a corrosion allowance of 6 mm on thick-walled tubing. The replacement period in refinery practice can be much shorter - three to five years. For thick-walled components, given the usual corrosion allowances, even higher rates of corrosion may be deemed acceptable. In practice, it has been found that if the corrosion rate exceeds 0.5 mm, there is a real risk that scales will exfoliate and block downstream valves and heat exchange tubing. Exfoliating scales are also a real hazard in steam turbine plant, causing erosion of the turbine blades.

For gas turbine blading, Stringer suggests that the acceptable rate of corrosion, is around 0.5 mm in 10,000 hours. Much, of course, depends on the size and shape of the blade, whether it is air-cooled, and the location of corrosion. In practice, corrosion rates can be several times higher than this for industrial engines, but the 0.5 mm standard is a good criteria for design purposes, when the blades are uncoated. Because turbine blades are exposed to an aerodynamically favourable pressure gradient, it would appear that they can tolerate quite amazing losses of material at the leading and trailing edges, without a noticeable loss of performance.

The increasing use of thermal barrier coatings is, however, imposing much stricter limitations on acceptable corrosion rates. Thermal barrier coatings consist of a low conductivity, porous ceramic, which is sprayed on to a turbine blade. The thermal stress through the ceramic is very severe, yet there is only a mechanical key between the coating and the blade material. Practical experience has shown that the coating will exfoliate if the blade material oxidises by more than  $3-5 \,\mu\text{m}$ .

A major difficulty which the designer has, in using corrosion data, is the multiplicity of units and parameters used to denote rates of attack. Furthermore, experimental results are usually quoted in terms of weight gain; occasionally, as oxide thickness, and very rarely as metal loss, plus internally oxidised material. The prime reason for the lack of direct measurements of metal loss is, that at the rates of corrosion, 0.5 mm per annum or less, which are of interest to the designer, it is extremely difficult to do such measurements in experiments lasting less than 1,000 hours. It is more convenient to measure weight changes, but even here very small changes can be critical. A corrosion rate of between 1 - 10 mg.cm<sup>-2</sup> per 1000 hours weight gain is, in most situations, reaching the tolerable limits.

A major assumption is that in general, oxides are protective and hence grow so that the growth rate is inversely proportional to the thickness. It follows from this that the scale growth follows a parabolic law, that is that to reach twice the thickness will require four times the time. It is also assumed that corrosion rates are usually activation energy controlled; hence it is common to plot the "parabolic rate constant" kp against the reciprocal of the absolute temperature. The units employed are  $(wt)^2$  (area)<sup>-4</sup> (time)<sup>-1</sup>. These are not "transparent" so that Table 2 gives approximate conversions for chromia formers. It will be seen that kp rates in excess of  $10^{-11}$  to  $10^{-10}g^{-2}cm^{-4}.s^{-1}$  would be intolerable for most purposes.

Kp	1000h Wt Change	One-Year Wt Change	One-Year Metal Loss Microng
g .cm .s	ing.cm	ing.cm	whereis
<b>10.E-13</b>	0.6	1.8	10
10.E-12	1.9	5.6	30
<b>10.E-11</b>	6.0	17.8	90
10.E-10	19.0	56	280
10.E-9	60	180	890 ( c.1 mm)
10.E-8	190	560	2800 (c.3 mm)

## Table 2: Parabolic Rate Constant Conversion Table

## Where the rate constant is given in milligrams, multiply by 10<sup>-6</sup>.

For alumina formers which operate at high temperatures, Quadakkers has pointed out that aluminium exhaustion could be the main consideration. Here, aluminium is gradually lost through scale growth and spalling. When the aluminium content in the component falls below a critical level, a form of breakaway corrosion starts. The time to failure therefore depends on the growth rate of alumina, the rate of spalling, the aluminium content of the alloy and the thickness of the component. Figure 12 shows that, for metallic foils, failure can occur in just a few hours at 1200°C. This is important in thin sheet material intended for use in catalytic combustor supports, for example.

## 4. Changes in Emphasis in High Temperature Corrosion 1975 - 1990

## 4.1 Preamble

From the mid-seventies onwards, a vast amount of effort was put into the challenge of high temperature corrosion. Much of the activity stemmed from a variety of new processes designed to turn coal and heavy oil into gas, petrol (gasoline) substitutes or electrical energy. The new processes differed in one important respect from that of the old coal and oil burning systems, in that, in general, molten species were not present. This greatly helped the understanding of the corrosion mechanisms, even though there were at least two, and sometimes four, corrosive gases present at the same time. Work on molten fluxing mechanisms still continued in the gas turbine field, with the increasing use of such equipment in the industrial and marine environments being a major drive, to improve blade materials and coatings.

However, an objective view would suggest that the expectations for the survival of materials of construction in these new environments, in particular in some forms of Fluidised Bed Combustors and Advanced Coal Gasification Plant, were over optimistic. This was, in part, due to the perception that these new processes would have to be built very quickly, using off-the-shelf materials. Once this view had been discarded, work was started on a number of advanced alloys and coatings; many of these have great promise, and we will refer to these in Section 5.

However, the fuel of the 1990s appears to be natural gas, which is essentially sulphur-free and, as a result, largely removes one of the principal sources of high temperature corrosion. The word "largely" is a necessary qualification; sulphur and other contaminants are present in sea spray, and in polluted furnace atmospheres. Nevertheless, natural gas does give tremendous opportunities to raising of temperatures, both in the energy conversion and process fields, so that resistant materials will still be needed.

## 4.2 Instrumentation and Predictive Techniques

High temperature corrosion could never be put on a properly scientific basis until it became possible to analyse the composition of scales and the metallic materials underlying them. This became possible through the invention of the electron probe/scanning electron microscope, which is as important to the understanding of high temperature corrosion as is the potentiostat in aqueous corrosion. Other techniques have also helped, including X-ray diffraction, which can be used to identify the <u>crystalline</u> compounds which make up much of the scales but the technique does mean prising off layers of material. The results from both of these techniques can be misleading and there is a particular problem with the electron probe, especially the older models, with the analysis for the light elements, carbon, oxygen and nitrogen.

More advanced techniques are available, including ESCA, Auger and Raman Spectroscopy. None of these is widely available, although such services can be hired at reasonable cost. So far, the main contribution of ESCA and Auger techniques is for very sophisticated element analysis, either at or close to surfaces. Raman spectroscopy is still under development, but if its current limitations could be overcome, it could be used as an in-situ X-ray diffraction method. It has already been used to study the development of iron oxides on a chromium steel.

The main advance in predictive techniques has stemmed from thermodynamics. This permits the calculation of so-called phase stability fields, so that it is possible to state which compounds, either solid, liquid or gaseous, are thermodynamically stable in a given gas environment. Again, there are shortcomings, in that it is not clear whether one could use the equilibrated or the real gas atmosphere in the calculations. The actual partial pressures of the reactants, rather than the partial pressures of pS<sub>2</sub>, pO<sub>2</sub>, pCl<sub>2</sub> or the carbon activity, that they give rise to at real or pseudo-equilibrium, also need careful consideration. Here pseudo-equilibrium is defined as the pO<sub>2</sub> for example, which is calculated from ratio of two components. In a practical situation the pO<sub>2</sub> calculated using the H<sub>2</sub>/H<sub>2</sub>O ratio is likely to be different to that using the CO/CO<sub>2</sub> ratio. If the environment were at equilibrium the pO<sub>2</sub> would be the same in both cases. Nevertheless, despite these problems, these thermodynamic techniques are a real guide to the choice of elements in alloy design and in the control of atmospheres to prevent corrosion.

Other advances in thermodynamics include the production of multicomponent equilibrium diagrams for both molten salts and metallic systems. If such techniques can be combined with the ability to identify and analyse the composition of the compounds formed during high temperature corrosion, a great advance in understanding will be made.

Much of the following account stems from the use of these new analytical techniques and thermodynamic models. Hopefully, within another fifteen years, similar advances will be made with respect to the kinetic aspects of scale formation. This will allow the subject to be put on a truly predictive basis.

## 5. Modern High Temperature Corrosion Challenges and Materials of Construction

## **5.1 New Commercial High Temperature Alloys**

Until a comparatively short time ago the only alloys for high temperature use were the so-called chromia formers. These fall into three main classes: the ferritic stainless steels, the austenitic stainless steels and the nickel- and cobalt-based superalloys. There is an intermediate class of alloys which lie between the true austenitics and the true superalloys. These contain quite large amounts of nickel and cobalt, with varying amounts of carbon, which by forming carbides will give reasonable long-term strength between  $900^{\circ}$  and  $1050^{\circ}$ C.





FIGURE 15 Ternary Alloy Oxidation Map for Ni-Cr-Al Alloys



As indicated earlier some of the stated temperature limits for long-term exposure of the chromia formers, except for very thick section parts, should be treated with caution. For example, Type 310 (Fe-25Cr-20Ni) stainless steel is reckoned by the ASM to be able to withstand continuous service at 1135°C However, Edwards and Nicolson, after an investigation of Types 302, 304, 316 and 310 stainless steels, at test times up to 10,000 hours, commented that because of the irregular nature of the corrosion on Type 310, "the question of limiting temperatures for this alloy are debatable". Vyklicky and Mericka showed that, whilst for short-term exposures Type 310 is acceptable, after 2000 hours at 1100°C, breakaway corrosion occurs, leading to a loss of thickness of almost 1 mm after 7000 hours. See Fig.13. For long-life structural applications, even the best simple chromia formers are limited to around 1000°C. Alloys which do better than this usually contain small amounts of silicon.

These relatively low temperature limits result from high growth rate of chromic oxide at temperature. At  $1000^{\circ}$ C, the kp varies from  $10^{-12}$  to  $10^{-10}$  g<sup>2</sup>.cm<sup>-4</sup>.s. See Fig.14. However, there is also a loss of chromium through CrO<sub>3</sub> volatilisation. Even in relatively short-term exposures at 1000°C, chromia volatisation is significant, halving the probable weight change. Furthermore, the loss of chromium, unlike that which results from scale formation, does not decrease with time. It is also strongly temperature dependent. For high temperature use, development of new chromia forming alloys has virtually ceased. The new materials which are on offer, such as Haynes 230 and 556, have high levels of chromium, but are intended to operate in contaminated environments below 900°C.

Figure 14 shows that the parabolic rate constants of the alumina formers are between one and two orders of magnitude lower than that of the chromium-rich alloys. Accordingly, the potential limit for the alumina formers is over 1200°C, even for long-term operation. Aluminium, on its own, is not very good at giving protection, even in clean environments. Very large amounts are needed. For example, 30% atomic (circa. 15%) weight of aluminium in binary nickel alloys is required to give complete protection. Such large amounts are detrimental to mechanical properties.

All commercial alumina formers contain much smaller amounts of aluminium, usually between 3 and 6% but to make up the deficiency, contain between 13 and 25% chromium. A whole range of alloys has now been built up on this basis and it is best rationalised using a ternary alloy oxidation map, as shown in Figure 15 for Ni-Cr-Al. This shows areas in which the main oxides that form are NiO,  $Cr_2O_3$  and  $Al_2O_3$ . It should be emphasised that these areas are determined empirically, and shift about with temperature and time. However, they do help with the rational design of materials.

Aluminium is not very effective on its own, since alumina is such a slow-growing oxide. In binary alloys, the oxides of the base elements, for example NiO or  $Fe_2O_3$ , grow very much more quickly and swamp the slowly growing alumina. When chromium is present, as well as aluminium. a chromia-rich scale forms initially, suppressing the formation of the more harmful oxides. At a later stage, the alumina begins to establish itself and overgrows the chromia.

The situation for nickel-based alloys is shown schematically in Figure 16, which is a Time-Temperature-Oxidation diagram for IN-100. Note that NiO and TiO are the first oxides form below 1800°F (982°C). Later on a protective scale forms. The diagram also shows that, after a sufficiently long period, breakaway results, with the formation of nickel-rich spinels and, in air, internal nitridation.



The fact that a completely different oxide will form during the initial stages of oxidation, and can affect the subsequent performance of an alloy, is not always appreciated. If a sulphidising or carburising gas comes into contact with an aluminium-containing alloy, before a protective scale of alumina forms, the alloy will sulphidise or carburise. See Fig.17. Hence the results from both laboratory experiments and practical plant experience can be greatly affected by the start-up conditions. Where possible, it is therefore advisable to try to pre-oxidise alumina formers, whenever possible. It is beneficial to start-up plant in air, steam or steam-hydrogen.

Providing a preoxidised film of alumina is present, this can form a very effective barrier at intermediate temperatures. Figure 18 shows that the log time to failure is proportional to the reciprocal of the absolute temperature and that the lifetime of a preoxidised film can be up to 16 years at 700° C.

Besides the difficulties associated with the formation of the alumina films, these materials suffer another problem: spallation, which occurs when the oxide reaches more than a few microns thick. Spalling usually occurs during cooling to room temperature and is associated with the mismatch in expansion coefficients between the alloy and oxide. Improvements have resulted from the incorporation of "active elements", such as yttrium, hafnium, zirconium and lanthanum, into the alloys in the elemental form, or as oxides in the so-called mechanically alloyed materials. The levels of the active elements range between 0.05 and 1.0%, but it is not certain just how they act.

Most modern superalloys, are alumina-formers. For industrial applications, where strength is not a necessity, aluminium-chromium ferritics can be used up to 1200°C. Typical commercial alloys are Fecralloy, Gilphal and Kanthal. These ferritic alloys are brittle at room temperature because of their basic BCC ferritic structure and large grain size. Where greater tolerance to embrittlement is desired, Cabot 214 is available. This is an FCC nickel-based alloy containing 16% Cr and 4% Al. The high level of nickel means that the alloy is, however, unsuitable for high sulphur environments.

The most interesting of this new range of oxidation resistant materials are the ODS (oxide dispersion strengthened) alloys. Here, yttria ( $Yt_2O_3$ ) is incorporated into the alloy, using a process called mechanical alloying, in the form of a very fine dispersion, about 20 nµ in diameter. At this level, the yttria improves scale adherence but it also gives extremely good long-term high temperature strength, at 1100°C and above. Accordingly, these materials are of industrial interest for heat recovery.

At the time of writing, that is 1992, British Gas is leading a programme of work to investigate the potential of the iron-based ODS alloys. Very long term tests are under way at British Gas, Harwell and KFA Jülich, and have now reached test times in excess of 8000 hours.

Up to 1150°C, the growth rates of these alloys are extremely slow and are very much better than the best chromia forming alloys IN617 and IN 671. See Fig.19. One interesting conclusion from KFA Jülich is that the growth rate of the alumina formers is slower than predicted, from short-term measurements of the parabolic growth rate constant. It is believed that the rate-determining step of alumina (and chromia) scales involves transport along grain boundaries in the oxide. During long-term service, grain growth occurs in the outer layers of the alumina, reducing the number of short circuit paths for either metal ions or more likely oxygen gas. This explanation accords with the known facts that the Wagner theory of defective oxides cannot be used to predict rates of growth of alumina or chromia. In these oxides, transport through the lattice is insignificant.



Chromic oxide forming alloys lose weight

**IN MA956** 

Alloy name

---- IN 671

IN 617

## **5.2 Non-Oxide Ceramics**

A number of non-oxide ceramics, including silicon carbide, silicon nitride, Sialon and molybdenum disilicide, all rely on the formation of a silica film for protection at temperature. Silicon carbide and molybdenum disilicide can be used for resistance heating, but the carbide is proving a very strong competitor to metals in high temperature heat exchange. Furthermore repeated attempts have been, and continue to be made, to use silicon nitride and Sialon for turbine blades and poppet valves.

The rates of attack on single crystals of these materials can be very low, even at high temperatures. However, on bulk materials, there is some risk in reliance on weight changes or visual examination. The non-oxide ceramics consist of grains that are sintered, or held together with glassy phases, or metallic silicon. Oxidation can, therefore, take place within the bulk of the material, resulting in a loss of toughness and strength.

An unusual feature of these silicon containing ceramics is that protective oxide has a glass-like structure, with no definite lattice. It is currently held that corrosion results from oxygen transport through the glass as molecules, rather than ions. Because silica is a glass, bonding is greatly affected by additions of other elements and by the external environment. Water vapour has a particularly adverse effect, from the formation of O-H bonds in the glass. The rate of oxidation may then increase by an order of magnitude, or more, at high steam pressures, as experienced in coal gasification processes.

## **5.3 Mixed Gas Corrosion Theory**

Following the 1973 oil crisis, and the increasing concern for the environment, a great deal of effort was put into "clean coal technology". One of the most promising of these technologies was high pressure coal gasification. Here, pulverised coal is reacted with steam and oxygen, or hydrogen-rich gas, to produce a gas which can be "upgraded" to a substitute natural gas. The basic reactions for the two processes are:

$$C + H_2O + O_2 = CH_4 + CO + CO_2 + (unreacted H_2O)$$

 $C + H_2 + H_2O + CO + CO_2 = CH_4 + (unreacted H_2 + H_2O + CO + CO_2)$ 

Neither of these two equations give a complete story but, in the form given, do show that in both cases oxidising components are present in the product gases and why they are present. The actual oxygen potential can be derived, quite simply, from the  $CO/CO_2$  and  $H_2/H_2O$  nomograms, otherwise known as Richardson/Ellingham diagrams. See Fig.20.

At fixed CO/CO<sub>2</sub> and H<sub>2</sub>/H<sub>2</sub>O ratios, the oxygen potential increases with temperature. For example, at a CO/CO<sub>2</sub>ratio of 1/1, typical of the Hygas process at 600°C, the pO<sub>2</sub> will be  $10^{-25}$ atm; whereas, at 1000°C, it will rise to  $10^{-14}$  atm. In practice, if there is excess elemental carbon in the environment, no additional CO would be formed and the rise in oxygen potential will not be so great. It is important to realise that this rise in the oxygen potential with temperature will not necessarily make a gas more oxidising; the Richardson/Ellingham diagrams also show that metal oxides become less stable as temperature increases. At most practical CO/CO<sub>2</sub> and H<sub>2</sub>/H<sub>2</sub>O ratios one can conclude that if a gas oxidises an alloy at a low temperature, it will do so at a higher one.

## FIGURE 20

Richardson - Ellingham Diagram for Oxide Formers Showing Increase in Oxygen Potential at Fixed CO / CO2 Ratios at Increasing Temperature



All coals contain significant amounts of sulphur, as pyrites, which reacts to form H<sub>2</sub>S. As with the oxygen potential, the sulphur potential can be estimated from the H<sub>2</sub>/H<sub>2</sub>S ratio. For the synthane process, the H<sub>2</sub>/H<sub>2</sub>S ratio is 17.2/1, which corresponds to a sulphur potential of  $10^{-8}$  atm at 600°C, and  $10^{-5}$  atm at 1000°C, which is quite sulphiding. In this case, this rise does not necessarily mean that a gas will become more aggressive with increasing temperature. The sulphides, like the oxides, become less stable as the temperature rises. In an extreme case sulphidation may cease above a certain temperature. This is the underlying cause of the "thermodynamic cut off" noted in Section 2.2. For an objective assessment of the corrosivity of a gas, it is vital that the following be considered:

- The CO/CO<sub>2</sub>, H<sub>2</sub>/H<sub>2</sub>O and H<sub>2</sub>/H<sub>2</sub>S ratios.
- The fraction of protective species i.e. H<sub>2</sub>O, CO<sub>2</sub>.
- The fraction of destructive species i.e. H<sub>2</sub>S, CO, CH<sub>4</sub>.
- The gas and metal temperatures.
- The equilibrium pS<sub>2</sub> and pO<sub>2</sub> values at the gas and metal temperatures.

There is a deplorable tendency in the literature, to quote  $pS_2$  and  $pO_2$  values, without giving more information. This can be extremely misleading, if apparently comparable values are used, where experiments are done at quite different temperatures. Furthermore, as noted, in practice gases can be far from equilibrium.

Sulphidation and oxidation reactions compete. For conventional alloys, as we have seen, sulphidation is detrimental whereas oxidation is protective. The basic competitive reactions can be shown with the following example:

 $FeO + H_2S = FeS + H_2O$ 

Whether FeO or FeS is the most stable phase, at any given temperature, depends on the  $H_2S/H_2$  ratio which, in turn, relates to the pO<sub>2</sub> and pS<sub>2</sub>. Instead of laboriously working this out for all the possible compounds which may occur, thermochemical stability diagrams can be plotted, using elaborate computer programs, such as MTDATA originally developed by the National Physical Laboratory UK. These show areas over which, for example, iron metal, FeO, FeS, etc., are stable. In these diagrams, pS<sub>2</sub> is normally plotted on the vertical axis, and pO<sub>2</sub> on the horizontal. See Fig.21.

Thermochemical stability diagrams have been of considerable predictive value in the coal gasification field, since the oxidising components (H<sub>2</sub>O, CO<sub>2</sub> and CO) in the environment are distinct from the sulphidising ones (H<sub>2</sub>S) It is then possible to consider the individual  $pO_2$  and  $pS_2$  values quite separately, and plot the appropriate point on the diagram. The phase which is indicated, it should be emphasised, is that which is in actual contact with the gaseous environment. That is the outermost scale. In most situations, where fairly normal alloys are being used, this outermost scale will be chromia or alumina.

The implication here is that the  $H_2S$  plays no part in the surface reactions. However deeper down in the scale, according to the Wagner rules, the pO<sub>2</sub> falls until, at the oxide scale metal interface, the pO<sub>2</sub> corresponds to that given by the Cr<sub>2</sub>O<sub>3</sub>/Cr or Al<sub>2</sub>O<sub>3</sub>/Al stability boundary. Over time, H<sub>2</sub>S and H<sub>2</sub> (plus all the other non-reacting gases in the environment) will diffuse down to the scale/metal interface. In most cases, chromium rich sulphides may be expected to form. Once these are present in quantity, the rate of attack will begin to increase rapidly as they will prevent the reformation of the protective scale if defects were too occur.





If the  $pS_2$  is sufficiently high, the base metals in the alloy, for example, iron, nickel or cobalt, will eventually form sulphides, despite the fact that the initial oxide was protective and the corrosion rate being reasonable. The parabolic rate constants for sulphide formation of these metals are about two orders of magnitude higher than for chromium. Once these appear, the rates of attack will become catastrophic.

In practice, coal gasification atmospheres are carburising and, as a result, carburisation can take place underneath the oxide and sulphide films. Work at Leeds University would appear to show that carburisation, under these conditions, is governed by the same principles which control sub-scale sulphidation. That is, if the surface oxide is not quite protective enough, carburising gases accumulate at the base of the oxide layer and begin to react with chromium. Hence, a sequence of layers is found, starting with oxides at the top, sulphides underneath, and carbides at the base. In effect, a so-called "reaction path" can be drawn from the oxide, down to the unattacked alloy. The same analysis is helpful when diagnosing combined oxidation/nitridation in air at very high temperatures.

The above briefly describes the simplest of mixed oxidant cases and as we shall see later, this information is useful in assisting with alloy design and helping the process designer to decide on how much treatment of the feedstock needs to be done to minimise the risk of corrosion. The diagrams are of rather less assistance, both theoretically and practically, when the attack is a corrosive species which contains both protective and non protective elements. Examples of such include COS,  $CO_2$  and  $SO_3$  for example. Here, the combination of  $SO_3$  with the metal involves both oxidation and sulphidation. If corrosion takes place at the scale/gas interface, the effects will be much less serious than if it occurs deeper in the metal.

## 5.4 Corrosion by the Formation of Volatile Species

As we have seen, high temperature corrosion of molybdenum, tungsten and chromia-forming alloys can involve the formation of volatile species. Less well-known forms of volatilisation corrosion involve iron and nickel carbonyls, gaseous silica-based compounds, and silicon sulphide. Fortunately, the stability ranges of these is limited to peculiar situations, involving high temperatures, pressures or reducing conditions, etc.

When they do occur, they can be very difficult to deal with. In this brief account, we will concentrate on volatilisation attack by chlorine compounds, under reducing atmospheres. This is important in coal gasification and fluidised bed combustion. The vapour pressure of iron, nickel and cobalt chloride is around one atmosphere at temperatures between 800 and 1000°C, so the attack mechanism can be serious.

Volatilisation attack does not get the attention it merits because, in many industrial situations, the corroding species leaves no direct evidence of its presence. For example sodium chloride is known to have a very dramatic effect on hot corrosion in gas turbines, but chloride-containing species are rarely detected. When volatilisation experiments are done in the laboratory, the flow of corroding gases is very slow and, in consequence, the volatile species can build up and suppress further reaction.

Thermochemical stability diagrams can help clarify the situation. However, it is best to start with a typical volatilisation reaction where, at temperature, the products of the reaction are gaseous.

$$Fe + 2HCl = FeCl_2 + H_2$$

Note how the reaction will be driven to the right if the fugacity, or vapour pressure, of the FeCl<sub>2</sub> falls and or if vapour pressure of the corrosive species, HCl rises.

In terms of thermochemical stability diagrams, this complicates the situation, as a number of diagrams are needed when volatile species are present. Separate diagrams must be produced for each vapour pressure, if a reliable estimate of the likelihood of attack are to be made. Figures 22a and b exemplify the situation. It will be seen that as the vapour pressure of the volatile species falls, the stability area of the solid phases is greatly reduced. This makes it clear why, apparently, innocuous amounts of chlorine containing gases can be so harmful.

This, briefly, covers the thermodynamics of chloridation, but it will be noticed that, from considerations of the reaction,  $H_2 + Cl_2 = 2HCl$ , increasing pressure drives the reaction to the left, that is increasing the pCl<sub>2</sub>. In consequence, materials in high pressure coal gasification processes, especially where the hydrogen content is low, would be expected to suffer from volatilisation corrosion.



Turning now to kinetics and morphology of chlorine corrosion, as might be expected, owing to the absence of protective films, the rate of attack can be very rapid. A peculiar feature of chloridation is that grain boundaries are often selectively attacked. This involves a selective leaching out of those elements which form the most stable chlorides. This grain boundary channel can, in some situations, lead to the complete removal of one or more of the elements. Of the standard commercially available alloys, if chlorine is the main species of concern, nickel-based materials are best, cobalt is intermediate and the iron-based alloys, in general, would be by far the worst. The presence of aluminium and chromium in most high temperature alloys, gives some protection against chloridation, as their oxides have a high stability under normal conditions.

## 5.5 Hot Corrosion in Gar Turbines: Modern Developments

It seems likely that from the 1990s onwards, industrial gas turbines for power generation will become a very important component of the energy scenario. With the progressive rise in turbine inlet temperatures from  $1200^{\circ}$  to  $1300^{\circ}$ C, even simple cycle machines can offer thermal efficiencies of up to 42% (net). When used in combined cycle mode, efficiencies of up to 53% are claimed. These figures compare with just over 40% for the most advanced, coal-fuelled, steam cycle plants.

However, for the reasons referred to in Section 2.3.1, blade temperatures are in the range  $700^{\circ}$  -  $1000^{\circ}$ C, depending on the type of equipment and how conservative is the design philosophy. However, it should be realised that, because of the extensive use of air cooling, there will be very marked temperature gradients along the blading. Temperatures near the blade root will be substantially different to those near the tip. On the RB211 engine, the blade-to-tip variation is at least 150°C. Furthermore, stator and rotor blade temperatures will fall along the engine as the pressure drops and more work is extracted from the gas flow. Whereas, parts of the first row of stator blades, immediately after the combustion chamber, might be running at just over 1000°C; the temperature on parts of the LP stages could be down to the 500°-600°C.

It is important to recognise that there is this wide range of metal temperatures in gas turbines as, in terms of hot corrosion, it is believed that there are two distinct forms of attack. Type I occurs in the range  $800^{\circ}$  -950°C; and Type II, at a somewhat lower temperature range of  $700^{\circ}$  to  $800^{\circ}$ C. Both forms of hot corrosion occur, as a result of airborne salt having been deposited on the turbine blades, which then fluxes the protective oxides. Sodium sulphate in sea-salt can decompose and react with the metal to form a sulphidation front underneath porous oxides and molten species.

The indications, at present, are that Type II hot corrosion is restricted to situations where the combustion gases contain high levels of  $SO_3$ , for example, when fuel oil is being used in marine gas turbines. Here, the  $SO_3$  helps stabilise the mixture of sodium sulphate and the sulphate of the base metal oxide. The morphology of attack is quite different to that of Type I. In Type II, pitting can occur and sulphidation is not normally present. Where there is doubt about the reaction temperature, the underlying microstructure may give some indications from the coarsening of Ni<sub>3</sub>Al precipitates. Above a gas temperature of 1000°C, hot corrosion will not normally occur since the temperature is too great to permit condensation of sodium salts.

Attempts have been made to correlate alloy composition with resistance to hot corrosion. Because of the practical difficulties in testing in real engines, most work is based on crucible or burner rig tests. A number of authors attempt to use a "chromium equivalent" figure to rank alloys. A comparison of the various equations is shown below; they are:

## • Lewis and Smith:

Donachie et al:.

 $Cr_D = \% Cr + 3.8 (\% Al - 5) + 2. \% W - 12.5. \% C - 1.4 (\% Mo - 1)$ 

• Stetson and Moore:

$$Cr_{SM} = \% Cr + 0.5. \% Al - \% Mo$$

• Finally, Felix use an entirely different type of relationship in which the corrosion resistance is given by:

$$RF = (\% Cr) * 0.5 (\% Ti) /(\% Al)$$

There is not too much agreement between the various authors about the benefits of the various elements, except that chromium is beneficial and molybdenum is detrimental. However, some of the ideas are intriguing. The Donachie equation attempts to allow for the tie-up of chromium and molybdenum as carbides. Also, both Lewis and Smith, and Felix regard titanium as increasing resistance whereas, in normal oxidation processes, this element is regarded as being harmful. Aluminium is regarded, by Felix, as undermining the effect of chromium, but Donachie feels that its absence can have a catastrophic effect on resistance.

Table 3 compares a number of turbine alloys. The first three, IN 939, IN 738 and GTD-111 are modern alloys, designed to combine acceptable strength with corrosion resistance. The next two, Nimonic 105 and In 713, were alloys designed with strength in mind, and would no longer be used where there was a risk of hot corrosion. Nimonic 80A is included, for comparison, as it was the first reliable blade material.

Although the agreement is not tremendous, IN 939 ranks best, with all the correlations. Also, Nimonic 105 and IN 713C are bottom of almost every list.

In practice, none of the modern alloys are used without some form of coating. Here, high levels of chromium and aluminium will have the result of slowing-up back diffusion. It is also noteworthy that all of the modern alloys contain only relatively small amounts of molybdenum.

Superalloy	Crls	Cro	Сгр	RF
IN 939	27.7	14.2	23.5	9.2
IN 738	22.0	12.0	16.0	4.0
GTD-111	21.2	12.0	14.0	6.1
NIM 105	19.55	7.6	12.35	0.98
IN 713C	17.3	12.9	11.4	0.5
NIM 80A	23.0	12.7	20.2	8.2

## 5.6 The Gettering Theory of Alloy Design : The Current Situation

When alumina or chromia alloys are used in complex oxidising atmospheres, quite marked improvements in performance can be made, if gettering elements are added to these alloys. These elements react with the secondary oxidant in the environment, for example, gases containing sulphur, nitrogen and carbon, which have penetrated an otherwise protective alumina or chromia scale.

A considerable amount of work at Newcastle Polytechnic, Leeds University and UMIST was carried out in the early 1980's, with the aim of making the gettering theory more predictive. Most of the work was carried out in  $H_2/H_2O/H_2S$ , mixtures, but the principles are applicable to all situations where the atmosphere contains two or more oxidants which give rise to solid phases. These U.K.studies were initiated by Strafford of Newcastle Polytechnic and Starr of British Gas, who independently suggested that slow-growing sulphides would make ideal gettering elements. Some early work by British Gas, reported at the 1980 Isle of Man Conference on Environmental Degradation of High Temperature Materials, appeared to confirm this view.

Figure 23 shows a variety of materials exposed to a sulphiding gas of very low oxygen potential around  $10^{-23}$  atm at 750°C. This shows that molybdenum and its alloys, compared to a number of heat-resistant stainless steels and nickel-based alloys, corroded extremely slowly. Furthermore, it is also apparent that cobalt and iron-based alloys were, in general, more resistant than their nickel-based analogues.

The fact that Hasteloy X and AiResist 213c did so well (both containing significant amounts of molybdenum or tungsten), also seemed encouraging from the point of view of the gettering theory. One apparent anomaly was the very high rate of corrosion of Hasteloy B2, which is a Ni-28 Mo containing, only a small amount of chromium.

Work at Newcastle Polytechnic showed that the intrinsic resistance of molybdenum was also shared by a number of other refractory elements, including vanadium and niobium. At 750°C, the kp values here were up to four orders of magnitude, less than that for the formation of chromium sulphide. See Fig 24.

Studies at Leeds University confirmed these general trends, and also suggested the cause of the very high rate of attack of Hasteloy B2. Although the Leeds work was on iron-based alloys, they showed that, whereas in the case of pure molybdenum, a protective scale of  $MoS_2$  forms, if a few per cent or more of iron is present, an (Fe,Mo)S scale results. This is non-protective. It seems likely that a similar non-protective scale forms on Hasteloy B2.

The investigations at Newcastle Polytechnic were then extended to the incorporation of gettering elements in a range of model cobalt and iron-based alloys which contained aluminium and chromium. Cobalt is the choice base, as its sulphides are less stable than those of either iron or nickel. This permits the gettering element to work to greater effect. Good results were obtained from the cobalt alloys, when  $H_2S$  levels were high. See Fig.25.

Cobalt-based alloys are expensive and a new series of alloys, based on iron, were formulated. The use of iron restricted the range of gettering elements which can be used, and the most successful alloy contained relatively large amounts of niobium and hafnium. Tantalum had similar properties but because of its higher atomic weight, compared to niobium, was added in roughly double the quantity. The tests on the iron based alloys were only short- to medium-term, but were in very aggressive conditions. The principal test temperature was 900°C, with the gas containing 2.8% H<sub>2</sub>S/4.7% H <sub>2</sub>O/balance H<sub>2</sub>.

Earlier work at UMIST had revealed the importance of preoxidation in steam/hydrogen atmospheres for alumina forming alloys. See Fig 26. When this treatment was applied to the Newcastle niobium containing alloy, even after 400 hours exposure to the test conditions, only negligible attack occurred. In contrast, the weight changes on preoxidised Fecralloy reached about 35 mg.cm<sup>-2</sup>. See Fig.27.





FIG 26 Corrosion of Experimental Iron Based Alloys Containing Gettering Elements in a H2S / H2O / H2 Atmosphere at 900 C







These are :

- The stability of the gettering element sulphide should be significantly higher than that of the base alloy, the difference being at least 20 kJ.
- The rate of growth of the gettering element sulphide should be slow. The kp should be less 10<sup>-10</sup> g<sup>2</sup>.cm<sup>-4</sup>.s<sup>-1</sup>.
- The concentration of the gettering element in the alloy should be in excess of 4% atomic..
- The diffusion rate of the gettering element should be high.
- If the gettering element forms intermetallics with other constituents (especially chromium or aluminium), these should be relatively unstable at temperature.

If the alloy is an alumina former, the basic composition should be resistant to oxidation at well above the proposed operating temperature. This implies having an appropriate aluminium and chromium content.

It is also advisable to preoxidise in an atmosphere of low oxygen potential, to suppress the formation of non-protective refractory metal oxides.

## 6. Conclusions

This text has had three basic aims; these are :

- To show that high temperature corrosion has a much greater impact on technological advance than is commonly supposed.
- To state explicitly the factors which need to be considered when using materials in high temperature corrosive environments.
- To indicate some of the latest advances in predictive techniques and how they can be used to "life" components and assist with materials design.

As befits an "engineering science" approach, there has been an emphasis in the text on quantitative prediction, rather than a review of corrosion mechanisms and failure investigations. This, however, is the way that the subject will evolve. Even in more fundamental and basic work, there will be an increasing effort to put quantitative factors into mechanistic explanations of high temperature corrosion. This inevitably will lead to the use of such mechanisms, by design engineers, to predict how materials will behave.

It seems inevitable, however, in the medium term that we will need to continue with long-term exposure tests of materials, both in plant and laboratory. To get the best out of these, we will need to resort, more and more, to statistical analysis. The work on breakaway corrosion in gas cooled reactors shows that only a statistical approach could properly reveal the significance of gas pressure, humidity levels and the silicon content of the steels. Fortunately, desk-top computing should greatly help the investigator in this respect.

The correct practice of Engineering Science requires the identification of the "Operational Principle". As stated in the Introduction, the operational principle is that the oxide scale must protect the underlying metal. This implies that in future, there will need to be a greater emphasis on the scale itself, rather than on the make-up of the alloy, especially where the attack does not involve fluxing mechanisms. It is now beginning to be recognised that the Wagner rules do not directly control the growth of protective oxide scales, such as chromia, alumina and silica. The rate of formation seems to depend on the presence of non-electronic defects, such as grain boundaries, dislocation pipes, etc. Here, mathematical modelling of transport processes and recrystallisation behaviour of the oxide scale should be extremely fruitful areas of investigation.

#### References

1.Vincenti G.W: What Engineers Know and How They Know It. John Hopkins Mem. Press.: 1990

**2.Ibid**, pp.208-11.

3.Colombier. L. and Hochmann. : J. Stainless and Heat-Resistant Steels. p. 378, : E. Arnold. 1965

4.Steels for High Temperature Service : United Steel Companies Ltd. 1968

- **5.Truman. J.E. and Pirt K:** Resistance of Alloy Steels to Oxidation at Elevated Temperatures : Br. Corr.J.Vol 11. April 1976
- 6. Yuganova. S.A. and Sorokina. Yv.G. "Metalloved Tern Obra Met. 6", pp.279-283
- 7. Walker : Stirling Engines
- 8. Singer. C. et al : A History of Technology, Vol. 4, p.109. Oxford Press.1979
- **9. Brooks. S. and Meadowcroft. D.B.**:The Influence of Chlorine on the Corrosion of Mild and Low Alloy Steels in Sub-Stoichiometric Combustion Gas: Corrosion-Resistant Materials for Coal Conversion Systems.Ed. Meadowcroft D.B. and Manning M.I.: Applied Science, 1983
- **10. Dixon S.D.** Needs of the Oil Industry for Metals at High Temperature on Metals :ASTM and ASME. 1931
- **11.Backensto. E.B. et al.** High Temperature Hydrogen Sulphide Corrosion: Corrosion, 12, pp.213-234. 1956
- **12.Gutzeck. J.** High Temperature Sulfide Corrosion of Steels in Conf. on Process Industries Corrosion -The Theory and Practice : NACE. 1986
- 13.Mrowec. S. and Weber. J : The Gas Corrosion of Metals, p.219. NBS. 1978

14.Ibid. pp.334-367

- 15.Sedriks J.A : Corrosion of Stainless Steels, p.241: J. Wiley & Sons. 1979
- **16.Schulenburg. T**: Specific Problems in Advanced Stationary Gas Turbine Design : High Temperature Materials for Power Engineering. 1990 : Ed. Bachelet E., et al. Kluwer. 1990
- 17.Northcott. L : Chapter 8 in Molybdenum (Metallurgy of the Rarer Metals Series. Butterworth. 1956
- 18.Kofstad. P: High Temperature Corrosion. pp.379-382.:Elseview. 1988
- 19.Betteridge W. and Heslop. J : The Nimonic Alloys. Chapter 5. Edward Arnold. 1974
- **20.Fleetwood D.P. and Whittle J.E:** The Cyclic Oxidation of Nickel-Based Alloys and Heat-Resistant Steels. Br. Corr. J., Vol.5. May. 1970

- **21.Wasielewski. G.E. and Rapp. R.A.**High Temperature Oxidation : The Superalloys. :Ed. Sims C.T. and Hagel W.C. Wiley. 1972
- 22. The Control of High Temperature Fireside Corrosion : CERL, Leatherhead. 1974

**23.Stringer. J.** :High Temperature Corrosion in Fossil Energy Systems : High Temperature Corrosion in Energy Systems : Ed. M.F. Rothman Metallurgical Soc. of AIME. 1985

- **24.Harris R.J. and Menzies J.A:** Variability in CO2 Oxidation Resistance of 2.25Cr-1Mo and 1Cr-0.5Mo Steels. Br. Corr. J., Vol.3, January 1968
- **25.Meadowcroft D.B:** Corrosion Control in Power Plants : Surface Stability.:Ed. Rhys-Jones, Inst. of Metals. 1989
- **26.Gardiner D.J. and Littleton C.J.** Identification of Oxide and Sulphide Corrosion Products using Raman Spectroscopy : High Temperature Alloys Their Exploitable Potential. Ed. Marriot J.B., et al.Elsevier. 1987
- **27.Bennett M.J., et al.** The Laser Raman Microprobe A New Technique for the Identification of Corrosion Scale Constituents : Ibid.
- **28.Neuman W., et al:** High Temperature Corrosion of Internal Combustion Engine Valves : High Temperature Corrosion of Energy Systems.Ed, Rothman M.F. Met. Soc. of AIME
- **29.Nicholls J.R. and Saunders S.R.J.:** The Influence of Fuel and Alloy Composition on the Lives of Current Diesel Engine Exhaust Valve Materials: High Temperature Materials for Power Engineering :Ed. Bachelet E., et al. Kluwer. 1990
- 30.Cutlet A.J.B., et al. CEGB Research, pp.13-26. October 1978
- 31.Cooper C.M. Hydrocarbon Processing, pp.123-126. May 1972
- **32.Stringer J.:** Corrosion and Erosion in Complex High Temperature Environments : Behaviour of High Temperature Alloys in Aggressive EnvironmentsEd. Kirman I., et al. The Metals Soc. 1980

33.Quadakkers W.J. COST 501 Round 2 WP4 Report. 1991

34. ?????

- **35.Edwards A.M. and Nicholson A :** Some Effects of Reheating Stainless Steels : Stainless Steels: Iron and Steel Inst. 1969
- **36.Vyklicky M. and Mericka M:** Oxidation of Heat-Resistant Chromium Steels and Chromium-Nickel Steels. Br. Corr. J. Vol.5. May 1970
- 37.Kofstad P: High Temperature Corrosion, p.401. Elsevier. 1988
- 38. Haynes 230 and 556 : Haynes International Literature : Data Summaries. 1987 and 1988
- **39.Lai G.Y:** A New Sulphidation -Resistant Ni-Co-Cr-Si Alloy : High Temperature Materials for Power Engineering.Ed. Bachelet et al. Kluwer. 1990

- **40.Meir G.H** :Fundamentals of the Oxidation of High Temperature Intermetallics:Ed. Grobstein T. and Doychak J., Minerals, Metals and Materials Soc. 1988
- **41.Wood G.C. and Stott F.H:**The Development and Growth a-Al2O3 Scales on Alloys: High Temperature Corrosion.Ed. Rapp R.A. NACE. 1983
- **42.Stott F.H. and Chong M.F:** The Influence of Pre-Oxidation on the Degradation of Alloys in Sulphurcontaining Gases at High Temperature: Corrosion-resistant Materials for Coal Conversion Systems Ed. Meadowcroft D.B. and Manning M.I. Applied Science. 1983
- **43.El Majid Z. and Lambertin** M.High Temperature Sulphidation of Aluminised Alloys: High Temperature Alloys Their Exploitable Potential. Ed. Marriott J.B., et al. Elsevier. 1987
- 44.Froes F.H. and de Barbadillo J.J: Structural Applications of Mechanical Alloying: ASM International.1990
- **45.Meadowcroft D.B**. Materials for Heat Exchangers The COST 501 Programme, Inst. of Metals Conference on Materials for Combined Cycle Plant : 10 12 June 1991
- **46.Nickel H. and Quadakkers W.J:** Growth Mechanisms and Protective Properties of Chromia and Alumina Scales on Oxide Dispersion Strengthened Alloys. First Int. Conf. on Heat-Resistant Materials.Ed. Natesan K. and Tillack D.J. ASM International. 1991
- 47.Kofstad P: High Temperature Corrosion. pp.189-192; pp.272-273. Elsevier. 1988
- **48.Fitzer F. and Schlichting J**: Coatings containing Chromium, Aluminium and Silicon for High Temperature Alloys : High Temperature Corrosion. Ed. Rapp R.A. NACE. 1983

**49.Gray J.A. and Starr F:** Coal Conversion (Combustion and Gasification): Behaviour of High Temperature Alloys in Aggressive Environments.Ed. Kirman I., et al. The Metals Soc. 1980

- **50.Nagarajan V., et al.:** The Rôle of Chromium in the Corrosion Resistance of Alumina-forming Alloys in Coal Gasification Atmospheres. J. Electrochem. Soc. April 1982
- **51.Strafford K.N., et al:** On the Design of Coatings to Resist High Temperature Chloridation : Surface Engineering Practice. Ed. Strafford K.N., et al. 1990
- **52.Starr F., et al.** Investigation of Hot Salt Corrosion at a Land-based Gas Turbine Installation. Inst. of Met. Conf. on Materials for Combined Cycle Power Plant. 1991
- 53.Deposition and Corrosion in Gas Turbines.Ed. Hart A.B. and Cutler J.B. Applied Science. 1973
- **54.Shatynski S.R:** Oxidation and Hot Corrosion : Materials and Processes, pp.164-195. Editors, Young F. and Shane R.S. Marcel Dekker 1985
- **55.Starr F. and Denner S.G:** High Temperature Corrosion Aspects of Thermal Hydrogenation Processes: Environmental Degradation of High Temperature Materials. Inst. of Metals. 1980
- **56.Stafford K.N., et al:** The Influence of Refractory Elements on the Sulphidation Behaviour of Cobaltbased Alloys. Corrosion Science, Vol.29, No. 6, 1989

**57.Stafford K.N., et al:** Composition of Coating Materials to Inhibit Breakaway Corrosion in Complex Gas Atmospheres at High Temperatures : Surface Engineering Practice.Ed. Strafford K.N. et al. Horwood. 1990





Oxidation in Synthetic Flue Gas Containing HCl at 500 C



#### FIGURE 1

Temperature Dependence of Long Term Oxidation Rates Using 10000 Hour Isothermal Weight Change Data



#### FIGURE 5

Couper-Gorman Curves for the Corrosion of Carbon and 18/8 Stainless Steels in a Hydrogen Sulphide Environment







#### FIGURE 8 Schematic of Deposition and Corrosion on Power Station Superheaters





	MID-WALL METAL TEMP. °C		ASSI	JMING	A STOIC	HIOME	TRICIN	a : C1 R	ATIO	OIL FIRED									
GAS TEMP.		LOW ALLOY FERRITIC			HIGH ALLOY FERRITIC (UP TO 12% Cr)			AUSTENITIC (TYPES 347, 321, 316. ESSHETE 1250)			LOW ALLOY FERRITIC			HIGH ALLOY FERRITIC (UP TO 12% Cr)			AUSTENITIC (TYPES 347, 321, 316)		
		HIGH > 0.30 %C1	MED. 0.30 0.15 %C1	LOW < 0.15 %C1	HIGH > 0.30 %C1	MED. 0.30' 0.15 %C1	LOW <0.15 %C1	HIGH >0.30 %C1	MED. 0.30 0.15 %C1	LOW <0.15 %C1	V : Na > 3.0	V:Na 3.0+1.0	V:Na <1.0	V:Na >3.0	V : Na 3.0+1.0	V: Na <1.0	V Na > 3.0	V:Na 3.0+1.0	V N KIO
	540	-			10000														
975	580		Ang sha																
	620					Construction of the				1		and a second second	1. S. F. G.						
	660	tex								1									
	700		and a	S. 199	1.1	17 W						1. <b>1</b> . 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1.		•					
	540			T	1		1		l							[	1		
	580				1.800.5													1	
050	620					1			1.00						1.4.5				
	669		i ya i									NY CONT							
	700	1 Salla		1.00	ार्ट्स्			digelity.				1			and the second		de seg	4.25	
	540			1	1		<b></b>	1		1		1			<u> </u>	<u> </u>		1	
	580			1.000	1996	1.00	100 a		1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1				0.495		1.10	and in		1997	
150	620	1. Section		1	[			Į –											
	660	P.T.	1	-														. /	
	700		24.84		pre 35	1.114	i arig	1.1.1			18 A.	10.89		1 1 4	Sec. 10			. 3.2.7	(S-3)
	< 25 nm/h		<u></u>	25-50	nm·h	•		50-100	nm h	E		100-200	nm · h		>	200 nm	h		
RMAL TE OF			CORRO	CANT R	ATE OF	:	SERIOUS	RATE	DF	v	ERY SE	RIOUS P	ATE	01	TASTR	OPHIC I	RATE		







Effect of Moisture Content and Weight Gain on Probability of Breakaway Corrosion of a 9% Cr Steel at 640 C















FIGURE 21 Thremochemical Stability Diagrams for Iron - Oxygen and Sulphur at 982 C



## FIGURE 23 Corrosion of Various Alloys in a Laboratory GRH Test Atmosphere Containing 1% H<sub>2</sub>S at 750 C









