Chapter 14

Alloy Design

14.1 INTRODUCTION

We have examined at some length the development of a theoretical basis for understanding and predicting the outcomes of high-temperature alloy corrosion reactions. On the one hand, thermodynamic analysis is aimed at predicting the identity of reaction products. On the other, diffusion analysis seeks to predict the rates of mass transfer in reaction product scales and the substrate alloy, thereby enabling calculation of overall corrosion rates and material lifetimes. In addition to exploring the intrinsically interesting nature of this complex problem, the theory aims to provide a rational basis for material selection and design. In situations where measured data are lacking, the theory provides guidance for exploring the experimental space: the relationships between corrosion rate and alloy composition, oxidant activity, temperature, cycle frequency, and so on. It is appropriate now to review the degree of success realised. A principal purpose of this examination is the identification of areas of inadequacy, where more work is required.

14.2 ALLOY DESIGN FOR RESISTANCE TO OXYGEN

Provided that exposure conditions are isothermal, the basic theory works rather well for steady-state conditions. Thermodynamic prediction of reaction product sequences is successful, even for complex multilayer scales and multiple internal oxidation zones. The Wagner theory for diffusion-controlled scale growth provides accurate predictive capability when the following conditions are met:

1. the scale layers are single-phase;
2. diffusion is via the oxide lattice;
3. the scale behaves as a parallel sided slab of structurally homogeneous material and develops no pores, cracks or voids;
4. the integrity of the scale-alloy interface is maintained;
5. mass-transfer processes in the substrate alloy and ambient gas are both rapid, and interfacial processes are close to equilibrium.

These conditions are met in the oxidation of the common base metals, iron, cobalt and nickel, and for alloys which are mixtures of these metals.

Quantitative success in predicting oxidation rates for these metals, and the effects thereon of oxygen partial pressure and temperature, rests on rather old research. Parabolic kinetics were reported by Tamman [1] in 1920 for steel, and by Pilling and Bedworth [2,3] in 1922 and 1923 for heater alloys. The theory of point defects in crystal lattices was developed by Frenkel [4] and Schottky [5] in the 1920s, and Wagner's model [6] for oxide scale growth supported by the diffusion of lattice defects dates from 1933. Despite that early success, a vast body of research into high-temperature oxidation has accumulated since that era. This reflects the unfortunate reality that Wagner's theory does not apply to scales grown by alloys of practical interest.

Oxides of iron, cobalt and nickel grow too fast for them to be acceptable as protective scales. Alloys must be designed to form other slow-growing oxides, most commonly Cr_2O_3 or Al_2O_3. The assumptions underlying Wagner's model do not apply to chromia or alumina scales. Instead, it is transport of reactants along grain boundaries (and perhaps other microstructural defects) which controls their growth rates. If scale microstructures were always the same, it would be possible to modify the Wagner equations simply by using an appropriately adjusted 'effective' diffusion coefficient. Of course, any such attempt is futile: grain size and shape, together with grain boundary segregation, vary with temperature, reaction time, surface preparation and both alloy and gas composition. The wide ranges of reported chromia (Fig. 3.20) and alumina (Figs 7.6 and 7.27) scale growth rates are therefore understandable.

Although the range of oxidation rates shown on the logarithmic scales of these figures is indeed large, it is in one sense unimportant. The ranges represent differences between very slow rates and even slower ones. The corresponding rates of alloy consumption are so slow as to be seldom of any concern. Accordingly, our inability to predict the scaling rate is unimportant, provided that we are able to design alloys in ways which ensure the rapid formation of the desired slow-growing scale, and its continued stability. Here Wagner's theories of alloy oxidation [7−9] are helpful in estimating the minimum alloy levels of chromium or aluminium, $N_{B,min}$, necessary to sustain exclusive chromia or alumina growth and prevent internal oxidation.

The difficulty of predicting scaling rate is avoided in Wagner's treatment of the alloy diffusion process which delivers chromium or aluminium to the growing scale. Instead, a measured rate of metal consumption is compared with the alloy diffusion coefficient, and the ratio $\left(k_c/\widetilde{D}\right)$ is formed. Although the theory is reasonably successful in predicting $N_{B,min}$ values for binary alloys, it turns out that avoiding internal oxidation often requires higher values. Wagner's treatment of this situation is based on a comparison of inward oxygen diffusion with outward metal diffusion and generally succeeds in predicting $N_{B,min}$ for binary alloys. This success derives from the usual validity of the assumption that both oxygen and metal diffuse via the alloy lattice. The methodology can fail in cases where diffusion is accelerated by the existence of favourable pathways such as internal surfaces.

Difficulties arise for alloys more complex than simple binaries, for which the necessary information on oxygen permeability and even metal diffusion coefficients is sparse. Because thermodynamic interactions between solute oxygen and oxide-forming metals are strong, deviations from ideal solution behaviour are large, and approximate calculations based on binary alloy data are of limited use.

A very clear example is provided by the so-called 'third element effect' in which alloying with a third metal promotes formation of the primary protective oxide scale. Examples are chromium in Fe-Cr-Al and zinc in Cu-Zn-Al. Wagner's theory [10] of secondary gettering is based on the supposition of transient oxidation of the third element to form a scale (of Cr_2O_3 or ZnO) which lowers the oxygen potential at the scale-alloy interface, thereby reducing greatly the alloy oxygen permeability. Outward diffusion of the aluminium is then favoured, and a scale of alumina develops beneath the other oxide. However, the theory is not quantitatively successful and can fail completely for other systems such as Ni-Si-Al. In the absence of adequate data for oxygen solubility and diffusivity in ternary alloys, it is difficult to assess the value of Wagner's gettering theory. The practical result is that our predictive capacity for the oxidation behaviour of the important M-Cr-Al alloys is very limited. Alloy design depends upon empirical knowledge gained by experimentation.

An important function of any protective scale is preventing outward diffusion of alloy solvent metal, and formation of surface spinel layers. Existing knowledge of oxide phase equilibria, including intersolubility levels, would be sufficient for the construction of diffusion paths if adequate diffusion data were available. Apart from the work of Lobnig et al. [11] on chromia, data are lacking. Again, alloy design or selection is based on empirical knowledge, often in the form of oxide maps.

Despite the lack of important basic data for multicomponent diffusion and oxygen solubility, alloy designs for resisting attack by oxygen at high temperatures are rather successful. Oxidation resistance at intermediate temperatures can be more difficult to achieve using the lower chromium levels favoured for such service. The reason is the slow alloy lattice diffusion in effect at lower temperatures. The solution is cold working of the alloy to introduce subsurface deformation and multiple pathways for accelerated diffusion. More detailed information on the nucleation and growth of surface oxides during the transient stages of reaction would be desirable.

There are practical limits to the applicability of the alloy design approach we have discussed. An example is provided by nickel-base superalloys. Chromium additions to these alloys are deleterious to their creep strength at the levels required to ensure chromia scale formation and good hot corrosion resistance. The engineering solution is to provide a corrosion-resistant coating on an alloy with a composition optimised for strength. Another example is found in alumina-forming austenitic alloys. The relatively slow alloy diffusion process means that aluminia scale formation can be achieved for reasonable

N_{Al} levels only at very high temperatures. For some of these alloys, a pre-oxidation anneal is required to establish alumina scales before they are placed in service. The need to perform this operation after fabrication limits the size of components in which these alloys can be used.

Both examples, and there are many others, reflect the reality that alloy design has multiple purposes. Alloys must provide adequate mechanical properties at high temperature as well as being capable of survival in the service environment. Additional requirements, such as weldability, thermal conductivity, etc., will arise for particular applications. The idea of separating the mechanical and oxidation resistance functions of a component, thereby resolving the conflicting property requirements, is not new. A suitable substrate alloy provides mechanical functionality, and a coating or other surface modification provides oxidation resistance.

A different sort of design limitation can arise when developing alloys to resist internal oxidation. An interesting example is provided by the unsuccessful attempt to develop niobium-based alloys for very high temperature applications. Although niobium has a very high melting point (2467°C), it is unusable at high temperatures because it oxidises rapidly and is embrittled by dissolution of oxygen and nitrogen. The strategy of alloying with aluminium has been investigated a number of times (see for example [12−16]) in an attempt to develop ultrahigh temperature alloys. Forming alumina as a protective scale rather than internal precipitates is difficult because niobium has such a high permeability for oxygen. Solid solution alloys have a maximum aluminium content of about 12 atom % at 1400°C and consequently oxidise internally. The intermetallic $NbAl_3$ does form alumina scales. However, because it is closely stoichiometric, the intermetallic is transformed by aluminium depletion to Nb_2Al. Because the diffusivity of the latter phase is low, it cannot sustain alumina scale growth for long, and the alloy fails. Further work aimed at improving the oxidation resistance of $NbAl_3$ by adding chromium has led to multiphase alloys. An alternative approach based on titanium additions to increase the solubility and diffusivity of aluminium, and additions of chromium and vanadium to decrease the oxygen permeability, led to an optimised alloy composition of 25.4Nb−29.1Ti−2.8Cr−3.5V−39.2Al, in weight percent. In each case, the problem was solved only by making niobium a minor component. The goal of an oxidation resistant niobium-based alloy was not achieved.

A similar problem arises in the case of internal carburisation. As seen in Section 9.4, it is not possible to achieve exclusive external carbide formation by adjusting N_{Cr} in austenitic alloys. The main reason is the exceptionally high carbon permeability in these materials.

To summarise, our ability to design alloys to resist attack by oxygen is good, although the complexities of multiphase alloy oxidation need further attention [17,18]. Where compositional limits are set by the need to achieve mechanical or other properties, they can be outflanked by the use of a suitable

coating. However, formation of a protective oxide scale is a necessary but not a sufficient condition for design success. In addition the design must prevent or cope with mechanical failure of the scale.

14.3 DESIGN AGAINST OXIDE SCALE SPALLATION

The provision of surplus chromium or aluminium in an alloy can give it the ability to regrow the desired oxide scale when spallation exposes the partially depleted substrate to hot gas. Given knowledge of the spallation rate and accurate information on alloy diffusion, we can predict the number of regularly spaced spallation events required to exhaust an alloy's capacity for rehealing [19,20]. The problem here is lack of reliable $\left(k_c/\widetilde{D}\right)$ data for the multicomponent alloys of practical interest. In consequence, alloys are assessed for their ability to resist spallation by subjecting them to cyclic oxidation and the stress cycles resulting from the difference in coefficient of thermal expansion between alloy and oxide [21].

Cyclic oxidation experiments appear to yield acceptably reproducible results and provide a means for ranking different alloys exposed to the same duty cycle. Difficulties can arise, however, in predicting the effects of changes in the key parameters, temperature and cycle length. These problems result from the empirical nature of the spallation models used in making these predictions. What is needed is a quantitative understanding of the ways in which temperature, scale thickness and gas composition change the mechanism of scale failure, its frequency and extent. Considerable research is being conducted into these questions, involving detailed consideration of the dynamic oxide-alloy interface, stress distribution and relaxation, the formation, interaction and growth of defects, etc. Whilst we await a successful outcome to this work, alloy design proceeds in a semiempirical way.

The discovery that sulphur is deleterious to scale adhesion (Section 7.5) has led to the production of superalloys with ultralow (less than 1 ppm) sulphur levels [22]. Whilst this approach is not economically viable for lower-cost heat-resisting alloys, the other major design strategy of alloying with reactive elements is, in principle, applicable to all chromia and alumina formers.

Our understanding of the several ways in which reactive elements contribute to spallation resistant scales seems reasonable, but it is qualitative. In designing an alloy or coating for spallation resistance, we need to know which reactive element (or combination of them) is best for a particular material, the minimum level required, and the optimal form (alloy solute or oxide dispersion) and distribution. Apart from thermodynamic information on solubility limits and the possible existence of reactive element intermetallics and mixed oxides, very little guidance is available. In this situation, designs are developed on the pragmatic basis of prior descriptive knowledge and new cyclic oxidation test programmes.

14.4 DESIGN FOR RESISTANCE TO OTHER CORRODENTS AND MIXED GASES

The classical theory of oxidation applies equally well to sulphidation, carburisation and nitridation. Thus the rapid growth of sulphide scales is predictable from the high diffusion coefficient values characteristic of many sulphides. Similarly, the extremely fast rates observed for internal carburisation and nitridation are accounted for by the high permeabilities of many alloys for carbon and nitrogen. When the Wagner model is extended [23−25] to take account of the low stability precipitates and the resulting incomplete reaction of alloy solute metals, excellent quantitative agreement is attained. Exploiting this success to design corrosion-resistant alloys is difficult in the case of sulphidation and apparently impossible in the case of carburisation.

Sulphidation-resistant alloy formulations have been developed to form stable, slow-growing sulphides. These materials contain large amounts of refractory metals in intermetallic phases and are not practical alloys. They might, however, constitute useful coatings for service in reducing sulphidising atmospheres.

As already noted, alloying to prevent internal carburisation in reducing environments appears not to be feasible. Furthermore, in reducing gases which are supersaturated with respect to carbon ($a_C > 1$), metal dusting attack on iron, nickel and cobalt-based alloys must be dealt with.

Elucidation of the different dusting mechanisms has been hampered by the development of metastable states: Fe_3C on ferritic alloys and carbon-supersaturated metal in the case of both ferritics and austenitics. The absence of diffusion and solubility data for the carbon supersaturated metal renders quantitative calculation impossible. However, it now appears that nucleation and growth of graphite could be important in controlling the overall reaction rate [26,27].

More work is required for a full understanding of the dusting reaction. However, a practical route to design resistance to carbon attack is through alloy compositions which will form protective oxides capable of excluding carbon. Thermodynamic analysis succeeds in predicting the conditions necessary to favour oxide rather than carbide. Almost all process gases are oxidising to alumina formers, and most are oxidising to chromia formers. Kinetic analysis methods to determine $N_{B,min}$ values necessary to support external oxide growth rather than internal carburisation have not yet been developed. However, design on the basis of preventing internal oxidation appears to succeed for initial isothermal exposure to carburising-oxidising gases.

The success of this approach is limited by the fact that oxide scales are not impermeable to species such as CO/CO_2. It also fails to deal with the competition between oxide scale rehealing and internal carburisation, which determines the outcome of temperature cycling during exposure to oxidising-carburising gases. Recent demonstrations that carbon penetrates chromia

scales via oxide grain boundaries may lead to a better understanding of the process, and perhaps to means of mitigation.

Oxide scale formation can also provide protection against corrosion by sulphur (Sections 8.6 and 8.9). In this case, however, the success of thermodynamic analysis in predicting conditions leading to oxide rather than sulphide scales is much less certain (Section 4.6). Sulphur adsorption and enrichment on the scale surface leads to a local environment which differs from the bulk gas and can stabilise chromium sulphide. To avoid this problem, it is necessary either to make the gas more oxidising or to change the alloy to an alumina former. The greater stability of Al_2O_3 relative to the sulphide underlies the superior performance of these alloys. However, the service temperatures involved may make Al_2O_3 formation difficult for many materials. High temperature preoxidation, or the use of aluminium-rich coatings or the selection of an FeCrAlY alloy, are then the available solutions.

Unfortunately, there is very little information available for the performance of engineering alloys under realistic, ie, temperature cycling, sulphidising-oxidising conditions. Long-term cyclic corrosion experiments under controlled gas atmospheres are required. Analogous cyclic carburisation-oxidation experiments have been carried out for a number of alloys, but far more information is desirable for a wider range of temperatures and gas compositions.

14.5 FUTURE RESEARCH

As has been said by a number of people, prediction is a difficult business, particularly when it concerns the future. In trying to identify possible future directions for research, it seems sensible to consider the factors motivating research groups and organisations as they make their choices. Closely related are the needs, choices and policies of the bodies which fund the research: private industry and government agencies.

In this utilitarian age, research sponsors look to achieve value for their money rather than merely satisfying the curiosity of the researchers. Whilst it is not difficult to identify high-temperature corrosion research which is at once fundamentally interesting and also of potential practical value, it nonetheless behoves researchers to consider closely the meaning of 'value' to their sponsors. It is obviously associated with improving alloys and coatings so as to better provide the required mechanical performance at high temperatures in aggressive environments. The value of these improvements lies in the ability they confer on designers and operators to achieve desired process changes. This connection between materials technology and process design exists because so many processes already operate at or near the capability limits of the materials currently employed. Some desired process changes require significant advances in materials technology. An example is the desire to increase gas turbine inlet temperatures, thereby achieving greater fuel efficiency. Other changes can be accommodated by substituting already available, but more

expensive, materials for those in current service. The research opportunity in such instances is to develop cheaper materials with the required capabilities.

To proceed beyond these generalisations to the specification of particular research goals requires detailed analysis of each technology, and preferably some knowledge of the business plans of the organisations involved. Publicly available information of this sort is understandably scant. Nonetheless, it is possible to extrapolate from current research activities to the immediate future and to consider what other activities might arise out of current government and societal preoccupations. Finally, it is possible also to use the earlier parts of this chapter in an attempt to identify areas where advances in fundamental understanding might yield practical benefit.

14.5.1 Gas Turbines

An enormous research effort has been expended and continues still on the development of materials for service as hot stage components at ever higher inlet temperatures. Superalloy development is aimed at achieving high-temperature strength, and component design relies on coatings for corrosion resistance. Coating development aims at producing improved thermal barrier coatings, including their underlying bond coats. Current research preoccupations include improved resistance to erosion and impact damage and prevention of ceramic topcoat spallation.

Spallation results from the combination of bond coat oxidation and thermal cycling. Platinum-modified NiAl coatings progressively rumple, developing an undulating surface which ultimately induces cracks in the adjacent topcoat [28]. The cause of rumpling is the subject of dispute. In the case of MCrAlY bond coats, abrupt delamination occurs at the TGO-bond coat interface when imperfections penetrating the TGO form. The imperfection generation process is not fully understood.

Lifetime predictions for TBCs are based on a critical TGO thickness [29]. However, the time and temperature dependence of the resulting predictions are the same as those of other diffusion-controlled compositional and microstructural changes occurring in the TBC system. A detailed mechanistic description allowing lifetime prediction awaits completion.

14.5.2 Electric Power Generation

The total amount of electric power generated worldwide is increasing rapidly as Asia industrialises. This trend will presumably be continued in Africa. The majority of newly installed capacity so far has been thermal and largely coal-fired. An obvious consequence is a large increase in greenhouse gas emission, an issue considered in the next subsection. An additional consequence in some areas has been a rapid increase in air pollution by particulate matter. The more immediate nature of the latter threat to human health will

presumably produce more prompt regulatory change than global warming has to date. Technological change will result from the increasing use of super-critical and ultrasupercritical boilers throughout the world. The higher steam temperatures (600°C and even higher) mean that heat exchanger tubing operates at significantly higher temperatures than in conventional boilers, where the steam temperature is about 540°C. Improved corrosion resistance is being sought at a minimal increase in materials cost. Further progress to 'advanced ultrasupercritical' boilers will involve even higher temperatures (over 700°C) and necessitate a shift from austenitic steels to nickel-base alloys to achieve the necessary creep performance. Economic analysis of this tech-nology change should prove interesting, particularly the weight given to the 'externality' of reduction in carbon emissions.

Laboratory testing of candidate steels has been conducted in heated air. Unfortunately, the encouraging results produced in that work have since been shown to be misleading. The introduction of water vapour to the reaction gas causes much more rapid oxidation of the intermediate chromium level steels involved. Gases rich in CO_2 have proven to be similarly damaging. Clearly there is a need for testing under realistic conditions, including temperature cycling.

Alternative technologies for the more efficient production of electric power from coal are under consideration. Most involve gasification, com-bustion of the resulting H_2/CO mixture to drive a gas turbine and utilisation of the heat in raising steam which drives a conventional turbine. The effi-ciency of this 'integrated gasifier combined cycle' (IGCC) is attractive, as seen in Table 14.1, and can be achieved together with carbon capture. However, the technology presents some very significant materials challenges. These have contributed to the significant commissioning difficulties experi-enced with IGCC technologies (Fig. 14.1).

Gasifier designs vary and are affected by coal quality. In many cases, the gasifier itself is a refractory lined vessel. Problems arise in the handling of

TABLE 14.1 Thermal Efficiency (η) of Power Generation From Fossil Fuels[a] [30,31]

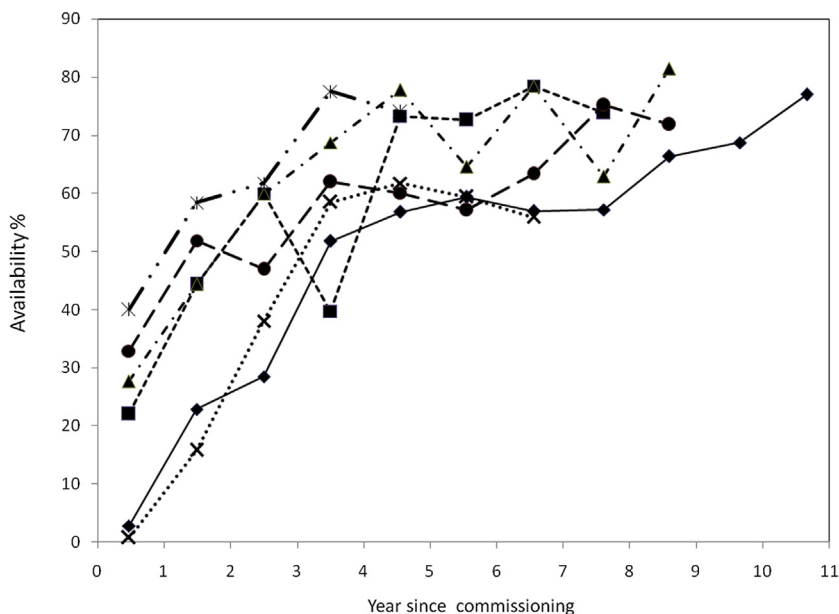| Technology	η/%
Conventional coal-fired	32−34
Supercritical coal-fired	39−42
Ultrasupercritical coal-fired	42−47
Combined cycle gas-fired	52−60
IGCC	40−43

[a]With no carbon capture.

FIGURE 14.1 Integrated gasifier combined cycle availability after commissioning (excluding operation on back-up fuel).

the product gas. This can contain sulphur impurities and will be laden with dust. Cleaning the gas before its supply to a gas turbine is essential. In addition, extraction of heat from the gas will involve the use of heat exchangers. Metallic components of the gas handling system must withstand reducing, strongly carburising and perhaps sulphidising gases. The performance of candidate alloys and coatings under realistically simulated conditions will need to be investigated experimentally.

The possibility of underground coal gasification is being investigated. The in situ gasification of coal has the attraction of replacing a coal mine and a gasification plant, both of which are capital-intensive. Clearly, the long-term reliability of process control systems is an important issue. Conveying the product synthesis gas (H_2 plus CO) from its underground source to surface facilities can be expected to involve a drop in temperature, and the risk of metal dusting.

Using turbines instead of coal-fired boilers for base load power generation reduces CO_2 generation, and is attractive when gas prices are low. However, the very long operating periods will require high-performance coatings, reliable life expectancy prediction and online monitoring capabilities. Slow alloy-coating interdiffusion processes can, in the long-term, degrade bond coat performance. The current research efforts on more stable coatings [32] and diffusion barrier coating layers [33] seem likely to continue and expand.

14.5.3 Petrochemical and Chemical Process Industries

A diversity of high-temperature processes is used to produce many widely used commodities, such as materials (metals, cement, plastics), fertilisers and fuels. Expanding markets, combined with limited resources, will presumably continue to drive the search for improved process efficiencies. Process changes can also result from altered feedstocks, the development of new catalysts and the desire for increased profitability. The higher process temperatures used to enhance efficiency will test materials capabilities. Indeed, an American process equipment planning exercise [34] identified the key need as 'fundamental models for corrosion behaviour of alloys'.

Very high-temperature processes are usually carried out in refractory-lined vessels. The refractory lining is commonly cast (in the same way as concrete) onto the steel shell of the vessel, to which it is held by a large number of metal anchors. A common arrangement is illustrated in Fig. 14.2. Because the refractory has some degree of porosity, the anchors are in contact with process gases. There is a large temperature drop across the refractory lining thickness. Consequently, the heat-resisting alloy chosen for the anchors must be able to resist corrosion over a range of temperatures up to a maximum somewhat below that of the refractory hot face. Increases in process temperatures can often be accommodated by the refractory but are limited by the temperature capability and corrosion resistance of the anchors.

14.5.4 Greenhouse Gas Emission Control

Greenhouse gas abatement strategies based on emissions trading schemes or tax and regulation schemes are intended to provide powerful economic incentives for the introduction of technological change. The rate at which they are introduced and spread internationally are difficult to predict. The first of
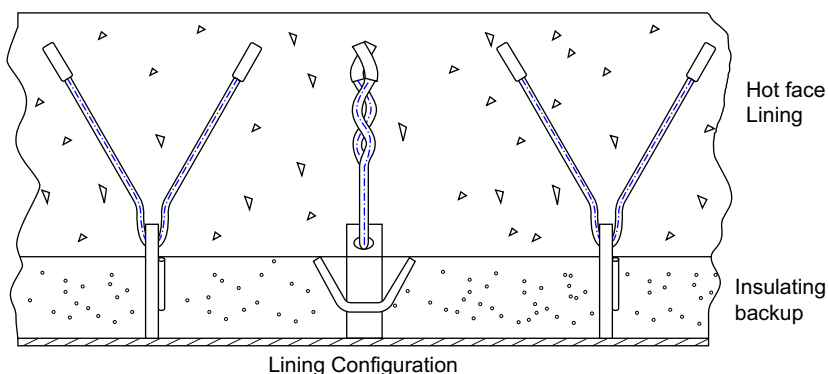

Hot face
Lining

Insulating
backup

Lining Configuration

FIGURE 14.2   Alloy anchors holding two-layered refractory lining. *Courtesy of Antec Engineering Pty. Ltd.*

these, the European Union emissions trading scheme, commenced in 2005 with a three-year trial. The second phase, from 2008 to 2013, was intended to introduce more realistic emission caps, but political will was lacking. Other countries have introduced or are at least considering similar schemes.

These schemes are aimed at reducing emissions of CO_2, the principal greenhouse gas in industrialised economies. Technological changes which result are of two sorts: avoidance of CO_2 production and modification of existing technologies to allow the capture and storage (sequestration) of CO_2 emissions. The avoidance strategy replaces existing technologies; for example, wind power turbines replace coal-fired steam power turbines to generate electric power, nuclear or solar replace thermal power, solar energy is used to heat water and hydrogen fuel cells generate power.

Biomass combustion to raise steam and fermentation to produce ethanol are in a similar category. The concept is that the biomass would otherwise decompose, releasing at least some of its carbon content into the atmosphere anyway. Harnessing that carbon produces energy, at what is sometimes claimed to be no net carbon cost. To the extent that the biomass is existing waste, and to the degree that its decomposition products would enter the atmosphere rather than being retained in soil, this is correct. However, the effort involved in biomass collection and handling prior to combustion can vitiate the carbon economics of the operation. An exception is provided by bagasse, the waste remaining after sugar has been extracted from crushed cane. The combustion of bagasse to raise steam is a traditional practice.

Raising crops for the express purpose of providing biomass is also carbon neutral: CO_2 removed from the atmosphere by photosynthesis is returned to it by combustion. Counting the carbon costs of fertilising, raising, harvesting and transporting the crops, and allowing for the social costs of likely adverse effects on food crop prices, makes for an interesting exercise.

The significance of biomass combustion from the corrosion point of view lies in the very different ash chemistries which result. Alkali metal contents can be high, and the possibility of molten deposits is increased (Chapter 12). To date, operating temperatures are kept low, so as to limit corrosion rates. Cost-effective materials or coatings which would permit higher temperatures would be highly desirable.

Modifications to coal- or gas-fired power generating technologies range from those which increase efficiency (producing less CO_2 per unit of power) to those which capture the CO_2. The latter approach is made more feasible in the oxyfuel process by burning the coal with oxygen rather than air, thereby avoiding the need to subsequently separate CO_2 from nitrogen. Alternatively, coal is gasified to produce synthesis gas which is subsequently burnt. In both cases, the exhaust gas is CO_2 plus water vapour. The need to handle this mixture at high temperatures could drive research into suitable materials, as recently published results (Chapter 10) show adverse effects on the resulting corrosion.

14.6 FUNDAMENTAL RESEARCH

The fundamentals of high-temperature corrosion science continue to provide a fertile area for research. One reason for this is undoubtedly the existence of technological needs, some of which are examined in Section 14.5. In addition, scientific research in this area is prompted by much the same factors as in any other field: new and puzzling observations, new techniques and new theories.

Although no completely new theories of high-temperature oxidation have emerged, theories and models from other areas have been applied. The methods of fracture mechanics [35−37] have yielded a much improved understanding of scale spallation and cracking. The development of quantitative methods for predicting the probability of scale failure as a function simultaneously of scale thickness and oxide microstructure, cycle frequency, heating and cooling rates and system chemistry, including gas phase composition, remains to be achieved.

The physical nature of the scale-metal interface is obviously important. Pieraggi and Rapp [38] have modelled the interface in terms of misfit dislocations. Further investigation, experimentally by TEM and atom probe microscopy, and theoretically via ab initio calculation, seems warranted. These approaches might improve our understanding of the interactions between sulphur, reactive elements and the metal-oxide interface.

New characterisation techniques have been applied to the dissection of oxidation mechanisms with considerable success. When electron probe microanalysis was used to define metal distributions in alloy scales, the results assisted greatly in deducing mechanisms. Similar information on oxygen diffusion was obtained by using secondary ion mass spectrometry to probe isotope profiles. Subsequently developed techniques are providing information on the nanoscale necessary to understand grain boundary and other interface processes. The widespread adaption of focused ion beam (FIB) milling to produce TEM foil samples is likely to prove important. The ability to rapidly produce these foils from precisely located positions in reaction zones means that interfaces are easily captured for examination. The new atom probes are providing atomic resolution images for both conducting and nonconducting materials. Volumes of 10^6-10^7 atoms can be analysed in reasonable times. Application of this technique to the study of interfacial interactions among reactive element metals, alloy solvent metal, scale constituents and species derived from the gas phase would obviously be of interest. Work in this area has just commenced [39−41].

Electron back scattered diffraction now provides a rapid method for identifying the orientations of grains intersected by a polished surface. It is therefore suitable for application to traditional metallographic cross-sections, where it can identify preferred growth directions of corrosion products and any orientation relationships they may have with the parent alloy phases.

14.6.1 Grain Boundaries in Oxide Scales

As has been demonstrated conclusively, transport in chromia and alumina is predominantly a grain boundary process (Sections 7.2 and 7.3). What is now needed is a modelling capability, presumably based on an atomic level description of the movement of individual species within the boundary. Because the boundaries are surfaces, they will be surrounded by narrow space-charge regions. Because transport occurs within the same narrow zones, space charge effects cannot be ignored. Experimental measurement of grain boundary diffusion parameters has been applied by Atkinson [42] to the growth of NiO scales.

Application to Cr_2O_3 and Al_2O_3 is more difficult because of the importance of impurity effects. As seen in Chapters 4, 7, 9−11, alloy solvent metal, reactive element metals and gas phase constituents all segregate to grain boundaries. Interactions between these various species and with the oxide constituents need also to be modelled. The application of high-resolution microscopy techniques, including atom probe tomography, to grain boundaries dosed with different mixtures of segregant species seems likely to be rewarding.

The permeability of oxide scales to gaseous species such as CO, SO_2, HCl and H_2O is an important but poorly understood phenomenon. The nature of the transporting species (ionic or molecular) has not been determined, and reasons for their slower penetration of alumina are not well understood. High-temperature adsorption experiments in mixed-gas atmospheres might contribute to an understanding of the complex interaction effects reported. It is generally agreed that alumina scales are much better barriers to secondary oxidants than is chromia, but the observation is unexplained. An improved understanding of the detailed structure of the grain boundaries in the two oxides is required. It is likely that progress will result from both improved characterisation and atomistic modelling.

14.6.2 Water Vapour Effects

The multiple ways in which water vapour interacts with oxides have made an understanding of the overall situation elusive. The different behaviour of alloys in pure steam and in air-steam mixtures has further complicated the set of observations.

Part of the difficulty in arriving at an understanding is the sensitivity of the oxidation result to small differences in exposure conditions. A review [43] of a comparative testing exercise, in which P92 alloy samples were exposed at 600 and 650°C for 1000 h in different laboratories revealed variations in scale thickness of 40−240 μm at 650°C. Some of the reasons were obvious, such as whether the steam was aerated or not. Additional changes were associated with steam pressure, flow rate, diluent argon levels and cooling procedures after the experiment.

When chromia scales are formed, the presence of water vapour improves scale-alloy adhesion. In the case of alumina scales, spallation is promoted by the presence of water vapour. In addition, the presence of water vapour alters the rates at which transient alumina phases grow and are transformed, thereby modifying the oxidation rate [44−46]. A systematic investigation of the interactive effects of water vapour and reactive element additions on the cyclic oxidation of different chromia and alumina formers is desirable.

14.6.3 Nucleation and Growth Phenomena

The classical theories based on Wagner's diffusion analyses all assume steady-state behaviour and provide little guidance on how to achieve that desirable state. As already noted, forming the desired scale at intermediate temperatures can be difficult. Whilst we know that increasing $\tilde{D}$ speeds formation of an oxide scale of the diffusing metal, we lack information on the surface nucleation and growth phenomena which must also be involved.

Electron microscopy has been used to observe the initial formation of oxide islands on pure metal surfaces. Differential pumping of the microscope allows a small pressure of oxygen to be maintained around the specimen, whilst a high vacuum in the remainder of the column maintains a stable electron beam. Extension of the technique to alloys exposed to mixed gases is experimentally challenging, but might prove rewarding.

The importance of nucleation and growth in the formation of internally precipitated oxide was first recognised and analysed by Bohm and Kahlweit [47]. Whilst that treatment was applicable only to very high stability precipitates, it showed clearly the difficulty of performing calculations in the absence of information on precipitate-matrix surface free energies and on oxidant activity coefficients. It now appears that the presence of secondary interstitial solutes (H, C, etc.) can affect the competition between nucleation and growth [48−50]. The same difficulties arise in treating the nucleation and growth of graphite, the essential feature of metal-dusting reactions.

Currently, we have no ability to predict the rates of dusting reactions. There are qualitative indications that graphite nucleation, its growth and the diffusion of carbon to the nucleation or growth sites are all important, but a quantitative assessment of the contributions of these processes to overall rate control is lacking. Perhaps more importantly, we are unable to predict the onset of dusting in the case of protective scale-forming alloys.

14.7 CONCLUSION

The deficiencies of the classical theory of oxidation have long been known and indeed were recognised by the original authors. In deliberately excluding from consideration the complexities of oxide microstructure and mixed-gas environments, Wagner was able to solve an otherwise intractable problem.

Given that not even calculators, let alone computers, were available at the time, the decision to consider simple cases is eminently understandable. Moreover, it yielded considerable insight into the oxidation problem, one which continues to be of value.

Modern approaches to alloy microstructure control through the modelling of phase transformation and grain growth kinetics are of interest in this context. Their application to the evolution of scale microstructure with time and temperature, and perhaps to initial transient oxidation, will surely be explored.

The complexities of corrosion in mixed gases are in need of resolution. After all, the gases encountered in practice are almost all of mixed composition. Work done to date has taught us how to avoid a number of deficiencies in experimental design. It has also shown us the necessity for using realistic reaction conditions and for being cautious in applying accelerated corrosion testing. Importantly, it has identified points of focus for future research.

Mechanical scale failure continues to be an issue of great importance. Empirical research on optimising the reactive element effect for particular alloys and coatings is complemented by theoretical and experimental research based on adhesion theory and a fracture mechanics approach.

Research into high-temperature oxidation dates from 1920. Many quite difficult problems have been solved, but others await resolution. As in other fields of science and technology, past research provides a basis for future investigations; technological relevance provides motivation for their pursuit.

REFERENCES

[1]   G. Tamman, Z. Anorg. Chem. 111 (1920) 78.
[2]   N.B. Pilling, R.E. Bedworth, Chem. Met. Eng. 27 (1922) 72.
[3]   N.B. Pilling, R.E. Bedworth, J. Inst. Met. 29 (1923) 529.
[4]   J. Frenkel, Z. Phys. 35 (1926) 652.
[5]   W. Schottky, C. Wagner, Z. Phys. Chem. 11B (1930) 163.
[6]   C. Wagner, Z. Phys.Chem. B 21 (1933) 25.
[7]   C. Wagner, J. Electrochem. Soc. 99 (1952) 369.
[8]   C. Wagner, Z. Elektrochem. 63 (1959) 772.
[9]   C. Wagner, Corros. Sci. 8 (1968) 889.
[10] C. Wagner, Corros. Sci. 5 (1965) 751.
[11] R.E. Lobnig, H.P. Schmidt, K. Henneson, H.J. Grabke, Oxid. Met. 37 (1992) 81.
[12] R.C. Svedberg, in: Z.A. Foroulis, F.S. Pettit (Eds.), Properties of High Temperature Alloys, The Electrochemical Society, Pennington, NJ, 1967, p. 331.
[13] R.A. Perkins, K. T Chiang, G.H. Meier, Scripta Met. 22 (1988) 419.
[14] J. Doychak, M.G. Hebsur, Oxid. Met. 36 (1991) 113.
[15] V. Gauthier, C. Josse, J.P. Larpin, M. Vilasi, Oxid. Met. 54 (2000) 27.
[16] S. Taniguchi, H. Tanaka, T. Maeda, Mater. Sci. Forum 522−523 (2006) 625.
[17] M.P. Brady, B. Gleeson, I.G. Wright, JOM (January 2000) 16.
[18] D.J. Young, B.G. Gleeson, Corros. Sci. 44 (2002) 2345.
[19] D.P. Whittle, Oxid. Met. 4 (1972) 171.

[20] J.A. Nesbitt, J. Electrochem. Soc. 136 (1989) 1518.

[21] J.L. Smialek, C.A. Barrett, in: ASM Metals Handbook, Materials Selection and Design, Vol. 20, ASM International, Materials Park, OH, 1997, p. 589.

[22] R.C. Reed, The Superalloys: Fundamentals and Applications, Cambridge University Press, Cambridge, 2006.

[23] J.S. Kirkaldy, Canad. Met. Q. 8 (1969) 35.

[24] E.K. Ohriner, J.F. Morral, Scripta Met. 13 (1979) 7.

[25] M. Udyavar, D.J. Young, Corros. Sci. 42 (2000) 861.

[26] J. Zhang, D.J. Young, ECS Trans. 3 (2007) 27.

[27] D.J. Young, Mater. Sci. Forum 522−523 (2006) 15.

[28] A.G. Evans, D.R. Munn, J.W. Hutchinson, G.H. Meier, F.S. Pettit, Prog. Mater. Res. 46 (2001) 505.

[29] R.A. Miller, J. Amer. Ceram. Soc. 67 (1984) 517.

[30] C. Henderson, International Energy Agency. http://www.iea.org/Textbase/publications/free_new_Desc.asp?PUBS_ID=1978.

[31] E. Ikeda, A. Lowe, C. Spero, J. Stubington, Technical performance of electric power generation systems, Cooperative Research Centre for coal in Sustainable Development, Pullenvale, Queensland, 2007.

[32] T. Izumi, N. Mu, L. Zhang, B. Gleeson, Surf. Coat. Technol. 202 (2007) 628.

[33] T. Narita, K.Z. Thosin, L. Fengqun, S. Hayashi, H. Murakami, B. Gleeson, D.J. Young, Mater. Corros. 56 (2005) 923−929.

[34] Roadmap for Process Equipment Materials Technology, 2003. https://www1.eere.energy.gov/manufacturing/industries_technologies/imf/pdfs/mtiroadmap.pdf.

[35] H.E. Evans, Int. Mater. Rev. 40 (1995) 1.

[36] M. Schütze, Protective Oxide Scales and Their Breakdown, Institute of Corrosion and Wiley, Chichester, 1997.

[37] J.A. Nychka, T. Xu, D.R. Clarke, A.G. Evans, Acta Mat. 52 (2004) 256.

[38] B. Pieraggi, R.A. Rapp, J. Electrochem. Soc. 140 (1993) 2844.

[39] D.J. Young, T.D. Nguyen, P. Felfer, J. Zhang, J.M. Cairney, Scripta Mater. 77 (2014) 29.

[40] A. La Fontaine, B. Gault, A. Breen, L. Stephenson, A.V. Ceguerra, L. Yang, T.D. Nguyen, J. Zhang, D.J. Young, J.M. Cairney, Interpreting atom probe data from chromium oxide scales, Ultramicroscopy 159 (2015) 354.

[41] F. Liu, M. Halvarsson, K. Hellstrom, J.-E. Svensson, L.-G. Johansson, Oxid. Met. 83 (2015) 441.

[42] A. Atkinson, Phil. Mag. B 55 (1987) 637; Solid State Ionics, 28 (1988) 1377.

[43] S. Osgerby, T. Fry, Measurement Good Practice Guide No. 74, National Physical Laboratory, Teddington, 2005.

[44] D. Naumenko, W.J. Quadakkers, A. Galerie, Y. Wouters, S. Jourdain, Mater. High Temp. 20 (2003) 287.

[45] H. Goetlind, F. Liu, J.-E. Svensson, M. Hakvorsson, L.-G. Johansson, Oxid. Met. 67 (2007) 251.

[46] D.J. Young, D. Naumenko, E. Wessel, l. Singheiser, W.J. Quadakkers, Mater. Corros. 61 (2010) 838.

[47] G. Bohm, M. Kahlweit, Acta Met. 12 (1964) 641.

[48] A.R. Setiawan, M.H.B. Ani, M. Ueda, K. Kawamura, T. Maruyama, ISIJ Int. 50 (2010) 259.

[49] P. Guo, J. Zhang, D.J. Young, C.H. Konrad, Oxid. Met. 83 (2015) 223.

[50] W. Zhao, B. Gleeson, Oxid. Met. 83 (2015) 607.